

Physicochemical characteristics of activated Biochar derived from different sources

ABSTRACT

An experiment was carried out to study the characteristics of biochar made from rice husk, rice straw, Toria stover and bamboo leaves. Biochar was produced by slow pyrolysis system (300 – 400°C). Locally available bio-wastes viz. rice husk, rice straw, toria stover and bamboo leaves were used as raw materials to produce chars. Two samples of feedstock each from 5 development blocks of Jorhat district of Assam were collected, dried and pyrolysed for production of char for their physicochemical properties. Per cent moisture and ash content, bulk density, particle density and porosity of biochars ranged from 3.26 to 4.91%, 3.70 to 24.97%, 0.178 to 0.729 g/cm³, 0.85 to 2.02 g/cm³ and 61.54 to 78.90%, respectively. Pore volume, particle size and specific surface area ranged from 0.83 to 1.15 ml, 310×147 to 350×209 µm² and 89.40 to 184.75 m²/g, whereas pH, EC, CEC, total Carbon varied from 7.74 to 9.46, 0.272 to 1.005 dsm⁻¹, 12.74 to 16.68 c mol (p⁺)/kg and 36.63 to 49.424%, respectively. Porosity maintained significant and positive correlation with pore volume (0.715**) and specific surface area (0.614**). CEC had significant positive correlations with total C (0.583**), total N (0.587**), total K (0.443**) and IAN (0.766**). Percent total N, P, K, and S had their value ranged from 47.27 to 60.07, 0.017 to 0.032, 0.237 to 0.453 and 0.083 to 0.099; while, Ca and Mg, Fe, Zn, Cu and Iodine adsorption number ranged from 1.11 to 5.23 and 0.148 to 1.326 c mol (p⁺)/kg, 16.65 to 2.91, 30 to 162, 8.6 to 43 mg/kg and 186.64 to 489.77 mg/g of biochar.

KEYWORDS: Biochar, Pyrolysis, Feedstock, Physico chemical properties, Carbon

INTRODUCTION

Biochars, a product of thermal decomposition or incomplete combustion of biomass or biowaste under limited oxygen supply, are fine-grained highly porous charcoal substances that are distinguished from other charcoals in its intended use as soil amendments (Berek and Hue, 2013). The most common management of the crop residue is in-situ burning in a field, which is considered as a convenient and economical method for the farmer to deal with them (Lu *et al.* 2010). But it leads to loss of carbon and other nutrients to the atmosphere causing GHGs emission. Hence, Pyrolysis of rice straw to create biochar for soil amendment appears to be a promising method to address concerns about improving soil fertility, increasing Carbon storage and decreasing Green House Gas emissions. (Singh, Y. *et al.*, 2004). Biochar can affect many physical and chemical properties in the soil, e.g. pH, water holding capacity, nutrient availability and soil structure. Since biochars are produced from a variety of feedstocks under different production process and conditions, they have different physical, chemical and biological properties and therefore have different effects when applied as the

soil amendment (Antal and Gronli, 2003). The understanding of its chemical and physical properties, which are firmly related to the type of the initial material used and pyrolysis conditions, is crucial to identify the most suitable application of biochar in soil. The type of feedstock material is another important factor that determines the final application of the biochar and its effect in the soil because its properties are affected by the nature of the original material. It is expected that addition of biochar can improve soil fertility, with an added option to mitigate climate change through carbon sequestration in agricultural soils (Lehman, 2007). Biochars, being alkaline might have enough potential in reducing the detrimental effect due to soil acidity and increasing the solubility of soil nutrients for growth and development of plants more particularly in acid soils. In Assam 51% of the total geographical area is acidic, and 98 per cent of the net sown area has the soil pH less than 6.7. Moreover, 2.33 million hectares of cultivable area is under firm soil acidity having soil pH less than 5.5. Although the effort has been to apply lime as the routine practice to correct soil acidity in most of the acid soil but due to the high cost of liming our poor and needy farmers could not afford to apply in their fields. Rice husk (RH) and rice straw (RS) were used as the starting materials because the global amount of residues from rice crops (*Oryza sativa* L.) is 0.9 Gt per year, i.e., 25 % of the total amount of the global agricultural residues (Knoblauch et al., 2011).

MATERIALS AND METHOD

The present investigation was conducted at Department of Soil Science, AAU, Jorhat with an aim to characterise physicochemical properties of biochars produce under slow pyrolysis system. Locally available bio-wastes viz. rice straw, rice husk, *toria* stover and bamboo leaves were used as raw materials to produce chars in slow pyrolysis process. The feedstocks were collected from five development blocks of Jorhat district viz., Ujani Majuli Development Block, Majuli Development Block, Central Jorhat Development Block, Eastern Jorhat Development Block and Titabar Development Block.

A biochar production unit, fabricated in AICRP on Irrigation Water Management Laboratory, AAU, Jorhat, for small-scale production of biochars from bio-wastes of an agricultural field was used in the present study on trial basis. The present design of biochars unit has the potential for easy handling with faster production rate.



Fig . Pyrolysis chamber

Moisture Content Determination

A 1.0 g of the activated carbon sample was collected and dried in an oven for four hours at 150° C, until the weight of the sample became constant. The moisture content was calculated from the relationship (Madu P. C. and Lajide L, 2013).

$$X_0 = \frac{W_1 - W_2}{W_1} \times 100$$

where,

X_0 = Moisture content on weight basis

W_1 = Initial weight of sample, (g)

W_2 = Final weight of sample after drying (g)

Ash content

Dry (Activated Carbon) sample (1.0g) was placed into a porcelain crucible and transferred into a preheated muffle furnace set at a temperature of 1000°C. The furnace was left on for one hour after which the crucible and its content was transferred to a desiccator and allowed to cool. The crucible and content were reweighed and the weight lost was recorded as the ash content of the sample (Madu P. C.1 and Lajide L, 2013). The per cent ash content (dry basis) was calculated from the equation

$$\text{Ash}(\%) = \frac{W_{\text{ash}}}{W_0} \times 100$$

Where,

W_{ash} = Weight of ash (grams).

95 W_0 = is the dry weight of carbon sample before ashing.

96 **Particle Size**

97 The particle size of the biochar was determined with the help of microscope ZEISS
98 (Stemi 2000c). For the particle size determination, 2-3 biochar particles in each biochar
99 samples were placed on the slide of the microscope and determined the particle size of
100 biochar in μm .

101 **Determination of Porosity and Bulk Density**

102 One gram sample was dispersed in 20 ml water in a graduated cylinder with the aid of
103 a shaker; this was further centrifuged for 10 minutes. The resulting volume of the water was
104 read as V_T and recorded. The equation below was used for the calculation of the porosity and
105 bulk density as the case may be (Madu P. C. and Lajide L, 2013).

$$\begin{aligned} \text{Porosity} &= V_w/V_T, \\ \text{Density} &= \rho / (1 - \alpha) \text{ while} \\ \rho &= M_a/V_w \end{aligned}$$

111 **Pore Volume**

112 The sample (1 g) was collected and transferred entirely into a 10 ml measuring
113 cylinder to get the total volume of the sample. The sample was then poured into a beaker
114 containing 20 ml of deionised water and boiled for 5 min. The content in the beaker was then
115 filtered, superficially dried, and weighed. The pore volume of the sample was determined by
116 dividing the increase in weight of the sample by the density of water (Aneke and Okafor,
117 2005).

118 **Specific surface area (m^2/gm)**

119 The specific surface areas of the samples were determined using the European Spot
120 Method as described by Santamarina *et al.* (2002) according to the following formula

$$121 \quad S_s = 1/319.87 \times 1/200 \times (0.5N) \times AV \times AMB \times 1/10$$

122 Where,

123 N = the number of Methylene Blue (MB) increments added to the soil suspension solution,

124 AV = Avogadro's number ($6.02 \times 10^{23}/\text{mol}$), and A_{MB} is the area covered by one MB molecule.

125 **Chemical properties**

126 **pH**

127 One gram of the sample was weighed and dissolved in 10 ml of de-ionized water. The
128 mixture was heated and stirred for 3 minutes to ensure proper dilution of the sample. The
129 solution was filtered and pH was determined using a digital pH meter.

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131 **EC**

132 One gram of the sample was weighed and dissolved in 10 ml of de-ionised water. The
133 mixture was heated and stirred for 3 minutes to ensure proper dilution of the sample. The
134 solution was filtered and its EC was determined using a digital EC meter

135 **Cation Exchange Capacity**

136 CEC was determined by leaching the biochars with neutral normal ammonium acetate
137 solution followed by distillation method (Blake, 1965).

138 **Total carbon (%)**

139 0.5 g of sample was weight and pre-digest with 5 ml Nitric acid (HNO₃) for 24 hour,
140 and complete digestion was performed after addition of 10 ml of diacid mixture in the digest.
141 Taking the total carbon (%) content was estimated by wet digestion method (Walkley and
142 Black, 1934) as described by Jackson (1973).

143 **Total N**

144 Total N was determined by the Kjeldahl method (Bremner, 1960).

145 **Total P**

146 Total P was determined by Vanadomolybdate method.

147 **Total S**

148 Total S was determined by Turbidimetric Method.

149 **Heavy Metals**

150 Calcium, Magnesium, Zinc, Iron, and Copper was determined by Atomic Absorption
151 Spectrophotometer using DTPA (diethylene triamine penta-acetic acid) method (Lindsay and
152 Norvell, 1978)

153

154 **Results and Discussion**

155 The results of the analysis on physical and chemical properties of biochar showed that
156 biochar made from toria stover has higher moisture percentage; high particle density, total K,
157 total P, total S and also higher total Fe then the other 3 chars. Rice straw showed the higher

alkaline properties with a pH of 9.46 then the other chars. Compared to rice husk, toria stover and bamboo leaf, rice straw biochar had a higher elemental Ca, Mg, Cu and Zn.

Physical Properties

Moisture Content

The highest mean gravimetric moisture content was found in rice husk biochar (4.91%) followed by biochars derived from *toria* stover (4.88%), rice straw (3.38%) and bamboo leaves (3.26%). Comparatively higher percentage of moisture content in biochar could be attributed to BD, porosity and particle size of chars (Table 1) which was evident from the result of significant negative correlations of moisture content with BD, porosity and particle size (Table 2). Biochar with low bulk density, an indication of highly porous and small particle size, has got the potential to hold moisture was earlier reported by several workers (Masulili *et al.*, 2010; Hernandez-Men *et al.*, 2014). The highest ash content, among all the biochar, in rice straw followed by rice husk, *toria* stover, and bamboo leaves could be attributed to their relative amount of total carbon which could also be evident from their positive significant correlations with BD, PD and negative significant correlations (Table 2) with porosity, pore volume and specific surface area. Weixiang *et al.* (2010) reported that rice straw derived biochar had the highest ash content than that obtained from grass (<20%) and woody feedstock (typically lies between 2 and 8%). The result was also in conformity with the findings of Peng *et al.* (2011) and Hernandez-Mena *et al.* (2014).

177 **Table:1 Physical properties of different biochars (mean values $\pm$ standard deviation)**

Biochar type	Moisture content (%)	Ash content (%)	Bulk Density (g/cm ³)	Particle Density (g/cm ³)	Porosity (%)	Particle size (μ m)		Pore volume (ml)	Specific surface area (m ² /g)
						length	breadth		
Rice husk	4.91 $\pm$ 0.60	13.17 $\pm$ 1.44	0.629 $\pm$ 0.064	1.92 $\pm$ 0.07	67.25 $\pm$ 3.57	350 $\pm$ 18.37	209 $\pm$ 8.38	1.05 $\pm$ 0.12	89.40 $\pm$ 5.09
Rice straw	3.38 $\pm$ 0.33	24.97 $\pm$ 3.05	0.729 $\pm$ 0.096	1.91 $\pm$ 0.11	61.54 $\pm$ 6.15	326 $\pm$ 26.95	153 $\pm$ 8.38	0.83 $\pm$ 0.09	121.48 $\pm$ 8.38
Toria stover	4.88 $\pm$ 0.49	5.63 $\pm$ 0.38	0.641 $\pm$ 0.063	2.02 $\pm$ 0.20	68.08 $\pm$ 3.95	331 $\pm$ 11.62	197 $\pm$ 12.17	0.96 $\pm$ 0.17	108.70 $\pm$ 5.98
Bamboo	3.26 $\pm$ 0.53	3.70 $\pm$ 0.30	0.178 $\pm$ 0.040	0.85 $\pm$ 0.04	78.90 $\pm$ 5.30	310 $\pm$ 8.27	147 $\pm$ 5.75	1.15 $\pm$ 0.11	184.75 $\pm$ 9.01

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181 **Table 2. Correlations among the biochar physical properties**

	Moisture content	Ash content	Bulk Density	Particle Density	Porosity	Pore volume	Specific Surface Area
Moisture content	1						
Ash content	-0.178	1					
Bulk Density	-0.405**	0.633**	1				
Particle Density	-0.231	0.468**	0.901**	1			
Porosity	0.537**	-0.652**	-0.892**	-0.625**	1		
Pore Volume	0.037	-0.513**	-0.670**	-0.489**	0.715**	1	
Specific Surface Area	-0.675**	-0.389*	-0.830**	-0.911**	0.614**	0.345*	1

182 ** Correlation is significant at the 0.01 level (2-tailed).

183 * Correlation is significant at the 0.05 level (2-tailed).

Bulk density of biochars followed a descending trend showing the highest in rice straw followed by *toria* stover, rice husk and bamboo leaves biochars (Table 1). Maximum mean PD in *toria* stover followed by rice husk, rice straw and bamboo leaves could be attributed to high mean specific surface area of the biochar. Similar results were reported earlier by Prima *et al.*, (2015), Kamara *et al.*, (2015) and Hernandez-Mena *et al.* (2014). Mean porosity of biochar was found to be highest in bamboo leaves followed by *toria* stover, rice husk and rice straw which could be supported by the lowest dimension of particle size and highest pore volume of bamboo leaves biochar. This could also be evident from the positive and significant correlation with pore volume and SSA. The highest mean pore volume in bamboo leaves biochar followed by rice husk, *toria* stover and rice straw biochar, respectively could be justified by the highest specific surface area along with significant and positive correlation with SSA. The aggregated fused-ring carbons are stacked to form small lamellar crystallites which were randomly orientated that left voids between them (Rutherford *et al.*, 2004). Particle size dimension was found to be the highest in rice husk biochar that was followed by rice straw, *toria* stover and bamboo leaves biochars. This could be discussed in the light of SSA which was recorded to be the lowest in rice husk biochar. The crystallite size of biochar particles was found to be accelerated by the increasing charring temperature as was earlier reported by Weixiang *et al.* (2010). Specific surface area (SSA) of biochars prepared from four different feed stocks revealed the highest value in bamboo leaves that was followed by rice straw, *toria* stover and rice husk biochars. This could be inferred from the highest carbonized content along with lowest particle size dimension. This was evident from the significant positive correlations of SSA with porosity and pore volume. Nevertheless, the exact structural and chemical composition, including surface area, is dependent on feedstock type and the pyrolysis conditions (mainly temperature) used as it was early reported by Brown *et al.* (2006)

Chemical properties

It is seen that all chars are alkaline in nature as the pH ranges from 7.74 to 9.46. Considering the very large heterogeneity of its properties, biochar pH values are relatively homogeneous, *i.e.*, they are largely neutral to basic Chan and Xu (2009) reviewed biochar pH values from a wide variety of feedstocks and found a mean of pH 8.1 in a total range of pH 6.2 – 9.6. Biochar from rice straw was highly alkaline followed by *toria* stover, bamboo leaves and rice husk. Highest pH recorded in rice straw biochar could be supported by high Ca and Mg content in the biochar. Weixiang (2012) reported that rice straw derived biochar

contain pH more than 9. The result could also be reaffirmed by the significant and positive correlations of pH with total Ca and Mg content of biocars. Highest EC in rice straw derived biochar followed by toria stover, rice husk and bamboo leaves biochars might be attributed to highest ash content and significant positive correlations with total K, Ca and Mg. Prima *et al.* (2015) also found electrical conductivity of biochar is largely determined by the total base content in the biochar which were varied according to the feedstock type and pyrolysis temperature. Biochar derived from bamboo leaves showed comparatively higher CEC which was followed by rice straw, *toria* stover and rice husk biochar. Relatively higher particle size and SSA might be another reason to increase the CEC of bamboo leaves biochar. Weixiang (2012) reported similarly that CEC of any biochars irrespective of its type and pyrolysis temperature was largely governed by particle size and SSA.

Total C, N, P, K and S

Bamboo leaves derived biochar contained the highest total carbon that was followed by rice straw, *toria* stover and rice husk biochars. The difference in carbon content could be explained on the basis of variation of ash content. The highest carbon content in biochar could be inferred for having a high amount of carbonaceous compound which is created when biomass is heated to temperatures between 300 to 1000°C under low (preferably zero) oxygen concentrations. The result was in consistent with the findings of Weixiang (2012). The same trend was also noticed for total N content of biochars. A high amount of total C also led to increasing the total N which could be seen from the significant and positive correlations of total C with total N.

The highest mean total P and K were recorded in biochar derived from *toria* stover. It can be discussed in the light that nature of feedstock, pyrolysis temperature etc. mainly influenced the variations of total nutrient content in biochars. It was earlier found by Kamara *et al.* (2015). Sulphur content was found to be low in almost all biochars, but may be high enough to serve as a secondary nutrient for plants. Biochar derived from rice husk showed comparatively higher total S followed by bamboo leaves, rice straw and *Toria* stover. The contents significantly varied from one biochar to another, and therefore it was the quality of source materials from which biochar was developed. Similar results were earlier reported by many scientists (Hernandez-Mena *et al.*, 2014).

248 **Table:3 Chemical properties of different biochars (mean values $\pm$ standard deviation)**

Biochar type	pH	EC(dS m ⁻¹)	Total C (%)	CEC cmole (p ⁺)kg ⁻¹	Total N (%)	Total P (%)	Total K (%)
Rice husk	7.74 $\pm$ 0.188	0.457 $\pm$ 0.041	36.63 $\pm$ 1.88	12.74 $\pm$ 1.30	0.473 $\pm$ 0.017	0.0237 $\pm$ 0.0025	0.237 $\pm$ 0.014
Rice straw	9.46 $\pm$ 0.332	1.005 $\pm$ 0.070	41.16 $\pm$ 4.54	15.67 $\pm$ 0.86	0.526 $\pm$ 0.046	0.0185 $\pm$ 0.0037	0.420 $\pm$ 0.028
Toria stover	8.68 $\pm$ 0.154	1.001 $\pm$ 0.098	39.26 $\pm$ 0.38	14.72 $\pm$ 0.69	0.0499 $\pm$ 0.005	0.0324 $\pm$ 0.0020	0.453 $\pm$ 0.057
Bamboo	7.96 $\pm$ 0.050	0.272 $\pm$ 0.093	49.424 $\pm$ 0.26	16.68 $\pm$ 1.15	0.601 $\pm$ 0.0039	0.0173 $\pm$ 0.0022	0.337 $\pm$ 0.041

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250 **Table:4 Secondary nutrients and heavy metal content of different biochars (mean values $\pm$ standard deviation)**

Biochar type	Total Ca (%)	Total Mg (%)	Total S (%)	Total Cu (%)	Total Zn (%)	Total Fe (%)
Rice husk	2.191 $\pm$ 0.139	0.822 $\pm$ 0.092	0.099 $\pm$ 0.017	17.3 $\pm$ 2.91	66 $\pm$ 3.50	2.918 $\pm$ 0.213
Rice straw	5.234 $\pm$ 0.377	1.326 $\pm$ 0.118	0.059 $\pm$ 0.013	43 $\pm$ 4.35	162.6 $\pm$ 6.80	5.49 $\pm$ 0.500
Toria stover	3.767 $\pm$ 0.154	1.062 $\pm$ 0.074	0.0183 $\pm$ 0.005	8.6 $\pm$ 2.01	54.6 $\pm$ 4.40	16.655 $\pm$ 0.399
Bamboo	1.111 $\pm$ 0.073	0.148 $\pm$ 0.047	0.065 $\pm$ 0.008	11.6 $\pm$ 2.27	30 $\pm$ 5.73	4.644 $\pm$ 0.246

Heavy metals

Heavy metals content viz. Ca, Mg, Cu, Zn and Fe of biochars derived from four different feedstocks revealed that baring Fe all were found to be high in rice straw biochars whereas *toria* stover acquired biochar had the highest level of Fe. Rice straw biochar, therefore, was considered to be highly alkaline based on the higher content of bases showing significant positive correlations with EC. Several workers reported earlier that the primary constituents of biochars could not be inferred universally and their heterogeneity in respect of physical as well as chemical characteristics are largely governed by types and quality of source materials from where biochars are prepared along with the pyrolysis temperature (Lehmann and Joseph, 2009).

CONCLUSIONS

Pyrolytic biochar has the potential to be used in agricultural production to sequester carbon and serve as a fertiliser. Although pyrolysis conditions are known to affect the chemical and physical characteristics of biochar, at the relatively low pyrolysis temperatures used in this study, feedstock characteristics had the most significant influence on key agricultural characteristics. The primary constituents of biochars could not be inferred universally and their heterogeneity in respect of physical as well as chemical characteristics are largely governed by types and quality of source materials from where biochars are prepared along with the pyrolysis temperature

Ethical approval and consent: NA

Table: 5 Correlations among the chemical properties of biochars

	pH	EC	CEC	Tot C	Tot N	Tot P	Tot K	Tot S	Ca	Mg	Cu	Zn	Fe
pH	1												
EC	0.800**	1											
CEC	0.29	0.005	1										
Tot C	-0.081	-0.428**	0.583**	1									
Tot N	-0.07	-0.422**	0.587**	0.998**	1								
Tot P	-0.043	0.446**	-0.309	-0.499**	-0.499**	1							
Tot K	0.748**	0.707**	0.443**	0.126	0.133	0.264	1						
Tot S	-0.457**	-0.605**	-0.348**	-0.021	-0.025	-0.520**	-0.803**	1					
Ca	0.911**	0.910**	0.009	-0.414**	-0.403**	0.155	0.628**	-0.389**	1				
Mg	0.702**	0.870**	-0.298	-0.633**	-0.624**	0.340**	0.403**	-0.248	0.909**	1			
Cu	0.656**	0.443**	0.127	-0.133	-0.118	-0.439**	0.184	0.187	0.691**	0.598**	1		
Zn	0.788**	0.624**	0.020	-0.260	-0.246	-0.263	0.304	0.035	0.846**	0.768**	0.939**	1	
Fe	0.214	0.613**	0.048	-0.180	-0.179	0.772**	0.690**	-0.860**	0.344**	0.319**	-0.379**	-0.177	1

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