YIELD AND NUTRIENT COMPOSITION OF BIOCHAR PRODUCED FROM DIFFERENT FEEDSTOCKS AT VARYING PYROLYTIC TEMPERATURES

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Variation in pyrolytic temperatures and feedstocks affects the yield and nutrient composition of biochar. Selection of suitable feedstock and optimum pyrolytic temperature is crucial before using it for agricultural purposes. We compared biochars produced from two feedstocks (wheat straw and rice) at three temperatures (300, 400 and 500°C). Biochar yield decreased significantly (p<0.05) with increasing pyrolysis temperature, while ash contents were increased. The cation exchange capacity was significantly higher (119 cmol, kg⁻¹) at temperature 400°C. The pH, electrical conductivity (EC) and carbon content of biochars increased significantly with increasing temperature and maximum pH (10.4) and EC (3.35 dS m⁻¹) were observed in rice straw biochar (WSB) at 500°C and carbon content (662 g kg⁻¹) in wheat straw biochar (RSB) at 500°C. Concentration of phosphorus (P) and potassium (K) increased significantly with increasing temperature, while nitrogen (N) decreased. Overall, the maximum N (13.8 g kg⁻¹ at 300°C) and P (3.4 g kg⁻¹ at 500°C) concentrations were observed in WSB while, maximum K (48 g kg⁻¹ at 500°C) in RSB. High pyrolysis temperature reduced AB-DTPA extractable nutrients (expect Mn). The highest AB-DTPA extractable nutrients such as P (113 mg kg⁻¹) and Ca (1.07 g kg⁻¹) were observed in WSB at 300°C while, K (18 g kg⁻¹) and magnesium (Mg) (1.55 g kg⁻¹) in RSB at 300°C. Selected feedstock and use of low pyrolysis temperature may produce nutrient-rich biochar, with high CEC and low pH and these could have positive effects on calcareous soils.

Keywords: Feedstock, pyrolytic temperature, nutrient contents, biochar

INTRODUCTION

The removal of crop residue for energy production has negative effect on soil organic carbon (SOC) accumulation and negatively impacts on soil fertility (Lal, 2004). Biochar may help to maintain or increase stable SOC pools and cycle nutrients back into agricultural fields (Gaskin et al., 2008). Biochar is recalculated against decomposition that is a byproduct of pyrolysis (thermo conversion of biomass under anaerobic conditions). Pyrolytic biochar is described as an effective soil conditioner, as it improves the soil chemical properties (Oguntunde et al., 2004; Liang et al., 2006), nutrient availability (Gaskin et al., 2008) and carbon sequestration in soils (Peng et al., 2011). In addition, its higher nutrient retention capacity increases efficiency of added inorganic fertilizers reducing the fertilizer requirements and environmental hazards. Hence, biochar may be a potential solution for many agricultural and environmental problems.

However, the physical and chemical characteristic of biochar is influenced by the properties of the feedstock and pyrolysis conditions, such as temperature and furnace residence time (Gaskin et al., 2008). During pyrolysis, biomass undergoes a variety of physical, chemical and molecular changes. Volatilization during pyrolysis causes significant loss in mass and therefore volume reduction and shrinking without causing much change to the original structure of the feedstock (Laine et al., 1991). In addition, pyrolysis affects cation exchange capacity (CEC), pH and carbon content of biochar (Wu et al., 2012). For example, high pyrolysis temperature (700°C) compared to low temperature (300°C) decreases the CEC and increases pH of biochar (Wu et al., 2012).

Moreover, pyrolysis alters the nutrient content in the resulting biochar, which affects nutrient uptake by plants. The increase in nutrient content with thermal degradation can be explained by loss of volatile compounds (C, H, and O) of the original material (Chan and Xu 2009) and relatively small losses of alkali nutrients in the gaseous phase. Some of the alkali nutrients can be lost through volatilization (Kuhlbusch et al., 1991). However, potassium (K) and phosphorus (P) vaporize at temperatures above 760°C, and Magnesium (Mg) and Calcium (Ca) are lost only at temperatures above 1107°C and 1240°C, respectively (Knicker, 2007).

In contrast to nutrients conserved in biochar, the availability of nutrients for plants, and the effect of pyrolysis conditions on these characteristics are unclear. For biochar to be used in agriculture, especially alkaline calcareous soils of Pakistan, a better understanding of its properties and how it affects nutrient availability must be explored. The main objective of present study was to optimize pyrolytic temperature and
selection of feedstock for production of biochar and effect of feedstock and temperature on properties of biochar in order to increase the immediate benefits of biochar application in agriculture.

MATERIAL AND METHODS

**Feedstock collection and preparation:** Wheat and rice straws were collected directly from farmer’s fields. The samples were air-dried and then oven dried at 50 °C in a forced air oven (Eyela WFO-600ND, Tokyo Rikakikai, Tokyo, Japan). The dried samples were crushed to a particle size of 2–3 mm and stored in air tight plastic bags.

**Biochar production:** 150 g ground samples were pyrolysed in a laboratory setup as described by Sanchez et al. (2009). The pyrolysis was done in Pyrex flask of 2 litres along with a U- shaped tube, an outlet for gases which was placed in a muffle furnace. U-shaped tube having 2.5 feet basal length while one feet vertical length. The angle between these axes was 60°. For removal of gas from working area, an outlet composed of glass cone and a plastic pipe was used. The experiment was performed at three peak temperature 300°C, 400°C and 500°C. The feedstocks were pyrolysed at 7-10°C min⁻¹ heating rate and 20 min residence time at peak temperature.

**Biochar Yield:** Conversion efficiency of biochar was calculated using the following equation:

\[ \text{Conversion efficiency (\%)} = \frac{\text{Weight of biochar}}{\text{Weight of feedstock used}} \times 100 \]

The ash content of the biochar was measured in a muffle furnace (Slattery et al., 1991) and calculated by using the following equation:

\[ \text{Ash content (\%)} = \frac{\text{Weight of ash}}{\text{Weight of biochar}} \times 100 \]

Carbon was determined by loss-on-ignition method (Nelson and Sommers 1982), the loss-on-ignitions of biochar were calculated as:

\[ \text{Carbon (\%)} = \frac{\text{Weight}_{105} - \text{Weight}_{400}}{\text{Weight}_{105}} \times 100 \]

**Chemical Analysis:** The pH and electrical conductivity (EC) of biochars were measured using 1:20 solid: solution ratio after shaking for 90 min in deionized water on mechanical shaker. The CEC of the biochars was measured by a modified NH₄⁺-acetate compulsory displacement method (Gaskin et al., 2008).

Nutrients (P, K, Ca, Mg, Zn, Fe and Mn) were extracted from biochar samples by digestion in hydrogen peroxide (H₂O₂) and sulphuric acid (H₂SO₄) (Wolf, 1982). An AB-DTPA extraction (1 M NH₄HCO₃ + 0.005 M DTPA) (Soltanpour and workman 1979) was used to assess the potentially plant-available nutrients index of biochar samples. Calcium, Mg, Zn, Fe and Mn concentrations in biochar digest were determined on an atomic absorption spectrophotometer (AAanalyist 100, Perkin-Elmer, Norwalk, USA) while K and Na were determined on a flame photometer (PFP7, Jenway, Essex, UK). Phosphorus (P) concentration was measured on a UV–visible spectrophotometer (UV-1201, Shimadzu, Tokyo, Japan) after developing yellow colour by vanadate-molybdate method (Chapman and Pratt, 1961).

**Statistical analysis:** Statistical analysis and data computations were made on Microsoft Excel 2010® (Microsoft Corporation, Redmond, WA, USA) and Statistix 8.1® (Analytical Software, Tallahassee, USA). Significantly different treatment means were separated using least significant difference (LSD) test (Steel et al., 1997).

RESULTS

**Biochar yield:** The biochar yield ranged between 32–48% and there was a decreasing trend with increasing temperature (p<0.05) (Table 1). Maximum biochar yield (48%) was obtained from wheat straw (WB) followed by rice straw (RS). On average basis, significant reduction (43%) in biochar yield was observed at highest temperature (500°C) compared to 300°C. The rate of yield loss was the rapid at 200 to 300°C, which is the temperature of torrefaction (Bergman and Kiel, 2005), losing approximately 67% of the initial mass.

**Physico-chemical properties:** There was significant (p<0.05) effect of feedstock and temperature on agronomic properties of biochar. The biochar ash content ranged between 25-52% and ash content significantly (p<0.05) increased with increasing temperature (Table 1). The maximum ash content (52%) was observed in rice straw biochar (RSB) at 500°C while minimum (25%) in wheat straw biochar (WSB) at 300°C. Similarly to ash content, carbon increased with increasing temperature and maximum carbon was observed in WSB (662 g kg⁻¹) at 500°C. The pH and CEC of the biochars were also significantly (p<0.05) influenced by feedstock and temperature (Table 1). The pH of biochars ranged from 7.7 to 10.4 (Table 1). The pH of the all biochars increased with increasing temperature and highest pH (10.4) was observed in RSB at 500°C. The CEC of the biochar samples varied from 77 to 119 cmol,
Soluble base cations are sum of soluble Ca$^{2+}$, Mg$^{2+}$, K$^+$ and Na$^+$. Exchangeable base cations are sum of exchangeable Ca$^{2+}$, Mg$^{2+}$ and K$^+$. *LSD at P≤0.05, respectively for feedstock, temperature and feedstock x temperature

**Table 2. Nutrient concentration of wheat and rice straw biochar produced at three pyrolytic temperatures (300, 400 and 500°C). Values are mean of three replicates ± standard deviation**

<table>
<thead>
<tr>
<th>Nutrients</th>
<th>Wheat straw biochar</th>
<th>Rice straw biochar</th>
<th>*LSD&lt;sub&gt;0.05&lt;/sub&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>300°C</td>
<td>400°C</td>
<td>500°C</td>
</tr>
<tr>
<td>N (kg kg$^{-1}$)</td>
<td>13.8 ± 0.62</td>
<td>9.4 ± 0.60</td>
<td>8.5 ± 0.50</td>
</tr>
<tr>
<td>P (kg kg$^{-1}$)</td>
<td>2.6 ± 0.06</td>
<td>3.0 ± 0.07</td>
<td>3.4 ± 0.10</td>
</tr>
<tr>
<td>K (kg kg$^{-1}$)</td>
<td>30 ± 1.47</td>
<td>32 ± 2.20</td>
<td>36 ± 1.67</td>
</tr>
<tr>
<td>Ca (g kg$^{-1}$)</td>
<td>6.3 ± 0.16</td>
<td>8.3 ± 0.13</td>
<td>8.7 ± 0.27</td>
</tr>
<tr>
<td>Mg (g kg$^{-1}$)</td>
<td>4.5 ± 0.11</td>
<td>5.6 ± 0.15</td>
<td>6.9 ± 0.11</td>
</tr>
<tr>
<td>Zn (mg kg$^{-1}$)</td>
<td>47 ± 2.16</td>
<td>59 ± 3.74</td>
<td>70 ± 4.08</td>
</tr>
<tr>
<td>Fe (mg kg$^{-1}$)</td>
<td>158 ± 11.9</td>
<td>259 ± 10.7</td>
<td>422 ± 13.3</td>
</tr>
<tr>
<td>Mn (mg kg$^{-1}$)</td>
<td>106 ± 9.7</td>
<td>117 ± 6.3</td>
<td>163 ± 9.7</td>
</tr>
</tbody>
</table>

*LSD at P≤0.05, respectively for feedstock, temperature and feedstock x temperature

**Table 3. AB-DTPA extractable nutrient concentration of wheat and rice straw biochar produced at three pyrolytic temperatures (300, 400 and 500°C). Values are mean of three replicates ± standard deviation**

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Wheat straw biochar</th>
<th>Rice straw biochar</th>
<th>*LSD&lt;sub&gt;0.05&lt;/sub&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>300°C</td>
<td>400°C</td>
<td>500°C</td>
</tr>
<tr>
<td>P (mg kg$^{-1}$)</td>
<td>113 ± 0.01</td>
<td>102 ± 0.00</td>
<td>66 ± 0.00</td>
</tr>
<tr>
<td>CaO (kg kg$^{-1}$)</td>
<td>13 ± 1.25</td>
<td>12 ± 0.05</td>
<td>10 ± 0.06</td>
</tr>
<tr>
<td>Ca (g kg$^{-1}$)</td>
<td>1.07 ± 0.04</td>
<td>1.07 ± 0.05</td>
<td>0.76 ± 0.05</td>
</tr>
<tr>
<td>Mg (g kg$^{-1}$)</td>
<td>0.30 ± 0.04</td>
<td>0.25 ± 0.05</td>
<td>0.22 ± 0.03</td>
</tr>
<tr>
<td>Zn (mg kg$^{-1}$)</td>
<td>6.7 ± 0.51</td>
<td>4.1 ± 0.51</td>
<td>3.0 ± 0.25</td>
</tr>
<tr>
<td>Fe (mg kg$^{-1}$)</td>
<td>73.0 ± 3.06</td>
<td>60.9 ± 2.06</td>
<td>56.8 ± 2.03</td>
</tr>
<tr>
<td>Mn (mg kg$^{-1}$)</td>
<td>1.4 ± 0.50</td>
<td>1.5 ± 0.33</td>
<td>4.3 ± 0.82</td>
</tr>
</tbody>
</table>

*LSD at P≤0.05, respectively for feedstock, temperature and feedstock x temperature

kg$^{-1}$ soil (Table 1). Pyrolysis temperature decreases the CEC and highest CEC was observed in WSB at 400°C and lowest in RSB at 500°C.

**Nutrients composition**: There were significant (p<0.05) main effects of feedstock and temperature on soluble and exchangeable cations while interactive effect was non-significant (Table 1). Exchangeable cation increased from 55 to 84 cmol. kg$^{-1}$ and soluble cation increased from 110 to 325 cmol. kg$^{-1}$ in biochars when temperature was increased from 300 to 500°C. The maximum soluble and exchangeable cations were observed in RSB at 500°C (Table 1).

Pyrolysis significantly altered the nutrient contents (N, P, K, Ca, Mg, Zn and Mn) of feedstock and nutrients concentration in the biochar were significantly different (Table 2). The concentration of all nutrients were higher in the biochar produced at 500°C expect N (Table 3) which decreased as temperature increased. Overall, the maximum N (13.8 g kg$^{-1}$) was observed in WSB at 300°C while, minimum (8.5 g kg$^{-1}$) in RSB at 500°C. The amount of N
conserved ranged from 18% (in RSB at 500°C) to 41% (in WSB at 300°C) (Fig. 1b). With increasing temperature, conserved N in biochar significantly decreased by 2.5 times from 300 to 500°C.

The P concentration in biochars increased, when the temperature was increased from 300 to 500°C indicating P is associated with the inorganic fraction of the crop residues (Table 2). The maximum P was 3.4 g kg\(^{-1}\) in WSB at 500°C, while minimum 1.1 g kg\(^{-1}\) at 300°C in RSB. Conserved P in biochar at different temperature was different and with increasing temperature conserved P in WSB and RSB significantly decreased. The maximum conserved P in WSB was 110% at 300°C while, minimum 69% in RSB at 500°C (Fig. 1c).

An increase in K concentration was observed with increasing temperature and maximum K was (48 g kg\(^{-1}\)) was present in RSB at 500°C and minimum (30 g kg\(^{-1}\)) in WSB at 300°C (Table 2). Conserved K in biochars has opposite

Figure 1. Percentage of conserved nutrients in wheat and rice straw biochars produced at three pyrolysis temperatures (300, 400 and 500°C). (Error bars are standard deviation of the mean)
trend as compared to P (with increasing temperature conserved K in biochar decreased) (Fig. 1b). The maximum conserved K (59%) in biochar was observed at temperature 300°C, whereas an increase temperature decreased conserved K in WSB biochar to 48% at 500°C (Fig. 1, d). There was significant effect of temperature and feedstock on Ca and Mg concentrations in biochars. The total concentration of Ca, and Mg significantly (p<0.05) increased with increasing volatization losses of C, H, O, and N (Table 3). In case of Ca and Mg concentration varies significantly for biochars produced at 300, 400 and 500°C (Table 2). The highest Ca (13.3 g kg\(^{-1}\)) and Mg (11.3 g kg\(^{-1}\)) concentrations were observed in RSB at 500°C. The conserved Ca and Mg in biochar were significantly different with temperature and feedstocks. The maximum conserved Ca (84%) was observed in WSB at 400°C while, maximum conserved Mg (59%) in RSB at 500°C (Fig. 1e,f).

The maximum Zn, Fe and Mn concentration were observed in RSB (Table 2). The concentration of these micronutrients significantly increased with increasing pyrolysis temperature and highest Zn (98 mg kg\(^{-1}\)), Fe (521 mg kg\(^{-1}\)) and Mn (649 mg kg\(^{-1}\)) were observed in RSB at 500°C.

**AB-DTPA extractable nutrients:** There was a significant (p<0.05) interaction between temperature and feedstock for Ammonium bicarbonate-diethylene triamine penta acetic acid (AB-DTPA) extractable concentrations of these elements. The pattern of AB-DTPA extractable nutrient concentrations (expect Mn) was different to that of the total nutrient concentrations (Table 3). Ammonium bicarbonate-diethylene triamine pentaacetic acid extraction method is a technique used to estimate the readily available concentration of elements for plant uptake (Soltanpour and workman 1979). In this work, the availability of some nutrients (P, K, Ca, Mg, Zn, Fe and Mn) in biochars was compared for different feedstocks and pyrolytic temperatures using this method (Table 3). There was significant difference in AB-DTPA extractable nutrients with temperature and it significantly decreased with increasing temperature (expect Mn). Among the AB-DTPA extractable macronutrient, the highest K (18 g kg\(^{-1}\)) and Mg (1.6 g kg\(^{-1}\)) was observed in RSB at 300°C, while P (113 mg kg\(^{-1}\)) and Ca (1.2 g kg\(^{-1}\)) in WSB at 300°C. Maximum Zn (13.8 mg kg\(^{-1}\) at 300°C) and Mn (126.4 mg kg\(^{-1}\) at 500°C) were observed in RSB while, maximum Fe (73 mg kg\(^{-1}\) in
WSB at 300°C. There was significant difference in percentage conserved AB-DTPA extractable nutrients with temperature and feedstock and it significantly decreased with increasing temperature (Fig. 2). The maximum percentage of AB-DTPA extractable P (4.3%) and Ca (17%) were observed in WSB at 300°C and K (50%) and Mg (20%) in RSB at 300°C (Fig. 1a,b,c,d). The results of the AB-DTPA test suggest that high pyrolysis temperature reduces bioavailability of nutrients as already reported by Yuan et al. (2011).

DISCUSSION

Pyrolysis of crop residue altered the nutrient contents and the availability of nutrients in the organic amendments. The increase in nutrient content with thermal degradation can be explained by loss of volatile compounds (C, H and O) of the original material (Chan and Xu, 2009) and relatively small losses of alkali nutrients in the gas phase. Some of the alkali nutrients can be lost through volatilization (Kuhlbusch et al., 1991). Potassium and P vaporize at temperatures above 760°C, and Mg and Ca are lost only at temperatures above 1107°C and 1240°C, respectively (Knicker, 2007). In this study the process of pyrolysis for Wheat and rice straw ranged between 300-500°C, well below the temperatures necessary for vaporization losses to occur.

Increasing temperature resulted in reduction in yield of biochar and this reduction may be due to rapid reduction of oxygen (O), hydrogen (H) and volatiles content at high temperature 500°C (Peng et al., 2011). The biochars’ ash contents increased with pyrolysis temperature (Table 1) due to volatilization accompanied by the relative enrichment of various inorganic components (Table 2). The highest ash content of biochars was found at 500°C (Table 1), most of which is due to high metal cation K (e.g. 31-48 g kg⁻¹) (Peng et al., 2011). The EC of biochar increased with increasing temperature and highest EC value of biochar produced at 500°C may be due to an increase of high soluble and exchangeable base cations (Table 1). Singh et al. (2010) also reported that EC values increased with increasing pyrolysis temperature.

The significant increase in pH of biochars at higher temperature can be attributed to the higher ash contents at higher temperature (Table 1), and furthermore to the hydrolysis of salts of Ca, K and Mg (Gaskin et al., 2008). In this study, low temperature biochar had both the lowest total concentrations of cations (Ca, K and Mg) and the lowest pH. Increasing temperature has been found to decrease acidity and increase basicity of the biochar (Mukherjee et al., 2011; Yuan et al., 2011).

Cation exchange capacity is indicative of the capacity of soil to retain key nutrient cations in plant available form. Oxidized functional group on biochar particles could lead to high CEC and charge density to retain cations (Liang et al., 2006). Higher CEC of WSB at 400°C temperature may be due to high oxygen-containing functional groups (Table 1) (Wu et al., 2012).

The higher content of base cations in biochar suggested that the relevant chemical components were concentrated in biochars during the pyrolysis of crop residues (Yaun et al., 2011). The decrease in N concentration in biochar with increasing temperature may be due to the volatilization of N during pyrolysis (Gaskin et al., 2008; Wu et al., 2012; Rajkovich, 2012). Nitrogen is removed through loss of the NH₄-N and NO₃-N fraction as well as the loss of volatile matter containing N groups at temperature of 200-250°C, but with increased temperature (>600°C) it is gradually transformed into pyridine like structure (Bagreev et al., 2001). Although N is usually lost in the form of gas through the process of thermal degradation, some biochar’s have been reported to become enriched in N (Knicker, 2007), through the formation of heterocyclic N compounds. Our study indicated that a relatively high proportion of the feedstock N was conserved at low pyrolysis temperatures, and as expected more N was retained in the biochar at 300°C compared to 400 and 500°C (Fig. 1. b). Field trials of wheat straw biochar as a soil amendment with rape indicated that WSB produced at temperature 200°C increased the total soil N than WSB produced at 500°C, when compared to control soil (Zhang et al., 2011).

The concentration of P, K, Ca and Mg in biochars increased with increasing pyrolytic temperatures and this increment may be due to their high vaporization temperature (760 -1240°C) (Knicker, 2007; Olsson et al., 1997). The concentration of P in plant tissues is relatively small compared to C, and a significant portion of plant P is incorporated within organic molecules through ester or pyrophosphate bonds (Stevenson and Cole, 1999). This organic P in dead plant tissues is not available for plant uptake without microbial cleavage of these bonds. When plant tissue is heated, organic C begins to volatilize at approximately 100°C, whereas P does not volatilize until approximately 700°C (Knoppep et al., 2005). Combustion or charring of organic materials can greatly enhance P availability from plant tissue by disproportionately volatilizing C and by cleaving organic P bonds, resulting in a residue with high soluble P salts associated with the charred material. Therefore, when biomass is subjected to pyrolysis and combustion, these metals are released from the complex matrix of the biomass and left in an available form for plants use.

The variability of the micronutrients with temperature is due to their volatility and effect of pyrolysis temperature on both composition and chemical structure of the biochar (Chan and Xu, 2009). In biochars, AB-DTPA extractable macro and micronutrients (expect Mn) tended to decrease with increasing temperature.
Biochar produced from different feedstocks

significantly. Considering the concentration of these nutrients is enriched in the biochar (Table 3), results of the AB-DTPA test suggest that high pyrolysis temperature reduces bioavailability of nutrients as already reported by Yuan et al. (2011).

**Conclusion:** It is concluded that pyrolysis temperature and feedstock have significant effect on the chemical properties of the biochar, in this study with important implication regarding their suitability as soil amendment. The yield of biochar decreased while, ash content increased with increasing pyrolysis temperature. The pH of all biochar was found to increase with increasing temperature while CEC decreased. The concentration of N decreased with increasing temperature and a high proportion of the feedstock N was conserved in the biochar at lowest temperature. On the other hand, the process of pyrolysis concentrated nutrients in the biochar and concentrations of all macro and micronutrients were found to increase with increasing pyrolysis temperature. However, AB-DTPA extractable concentrations of some elements such as P, K, Mg and Ca were found to decrease with increasing pyrolysis temperature and therefore this indicates a tendency of these elements to become less available to plants at highest temperature. Selected feedstock (wheat straw) and use of low pyrolysis temperature may produce nutrient-rich biochar, with high CEC and low pH and these could have positive effects on our soils generally low in organic matter.

**REFERENCES**


