

## Biochar Production Technology for Conversion of Cotton Stalk Bioresidue into Biochar and its Characterization for Soil Amendment Qualities

G. Venkatesh<sup>1</sup>, B. Venkateswarlu<sup>1</sup>, K.A. Gopinath<sup>1</sup>, Ch. Srinivasrao<sup>1</sup>, G.R. Korwar<sup>1</sup>, B. Sanjeeva Reddy<sup>1</sup>, J.N.V.S. Prasad<sup>1</sup>, M. Grover<sup>1</sup>, B.M.K. Raju<sup>1</sup>, Ch. Sasikala<sup>2</sup> and K. Venkanna<sup>1</sup>

<sup>1</sup>Central Research Institute for Dryland Agriculture, Hyderabad-500 059, Andhra Pradesh

<sup>2</sup>Center for Environment, Jawaharlal Nehru Technological University Hyderabad, Hyderabad-500 085, Andhra Pradesh

Email : g.venkatesh@crida.in

**ABSTRACT:** Production and application of biochar from small-scale units on farm level may solve several environmental problems. The aim of the study was to develop a low cost portable kiln and to investigate the relationship between the production parameters with biochar characteristics. On-farm usable portable kiln unit (approx. cost per kiln was ₹ 1200) was developed on a single barrel design of vertical structure with perforated base and design function with direct up-draft principle. Cotton stalk bioresidues were subjected to thermo-chemical conversion at different loading rates and holding time. Holding time for each loading rate was correlated with internal kiln temperature. Grey gas colour was correlated with to 350-400°C and blue gas colour to 450-500°C kiln temperature range. Volatile matter content decreased, whereas fixed carbon and ash content increased with increase in temperature in each load. Biochar yield decreased with increasing temperature in each load types. Total C and N content of the biochars ranged between 592.4 to 719.3 g/kg and between 10.3 to 17.4 g/kg, respectively. The amount of total C and N recovered in the biochar ranged from 26 to 38% and 16 to 34%, respectively. Total P, K, Ca, Mg, Fe, Cu, Mn and Zn contents were higher in biochar compared to raw cotton stalk. The CEC of the biochar samples ranged from 11.7 to 51.3 cmol/kg. Highest maximum water holding capacity (3.9 g/g of dry biochar) and available water capacity (0.89 g/g of dry biochar) was exhibited at highest at 450-500°C. Therefore, cotton stalk biochar produced at 450-500°C showed the greatest potential for use as soil amendment to improve the fertility of rainfed soils as well as to sequester carbon.

**Key words:** Biochar production, bioresidue, portable kiln, soil amendment

The role of agriculture in mitigating climate change through options such as by carbon sequestration via conversion of bioresidues (short-term biodegradable carbon) into a more recalcitrant form of C (biochar) appears to be one of the most promising strategies to sustainably sequester atmospheric CO<sub>2</sub> (Stavi and Lal, 2013). In India, the agricultural bioresidues are becoming an issue of importance due to lack of bio residue management practices. The Ministry of New and Renewable Energy (MNRE, 2009), Govt. of India has estimated that about 500 Mt of bioresidues are generated every year. Cotton crop generates a maximum (53 Mt) with 11% of total bioresidues. Until recently the majority of cotton stalks have not been utilized fully, a part of these is consumed as household needs. Estimated total amount of surplus cotton bioresidues in India (MNRE, 2009) is 11.8 Mt. The surplus residues, when left unattended, often disrupt land preparation, crop establishment and early crop growth, and are typically burnt on farm

causing environment and public health problems and substantial nutrient losses.

A novel opportunity to reutilize the bioresidues is by thermo-chemical conversion (slow pyrolysis) of bioresidues to become biochar. Biochar is capable to increase the rate of soil carbon sequestration through shift from short-term bio-atmospheric carbon cycle to the long-term geological carbon cycle (Forbes *et al.*, 2006) and improves the soil fertility and crop yield (Stavi and Lal, 2013). Biochar production from a variety of high-molecular lignocellulosic bioresidue resource is a carbon-neutral process. Woolf *et al.* (2010) estimated that the mitigation potentials of biochar was as high as 12% of current anthropogenic CO<sub>2</sub> emissions (net emissions of GHGs could be reduced by 1.8 Gt CO<sub>2</sub>-C equivalent per year). Slow pyrolysis is a direct thermo-chemical decomposition (exothermic) process that can be used to transform

low-density bioresidue matrix into a biochar at a temperature ranging usually from 450-550°C under low-oxic or anoxic conditions (Roberts *et al.*, 2010). Biochar obtained by slow pyrolysis is a porous, high-carbon-density, fine-grained solid material rich in paramagnetic centers having both organic and inorganic nature, possessing oxygen functional groups and aromatic surfaces (Amonette and Joseph, 2009). In contrast to charcoal, which is produced for various industrial purposes, whereas bioresidue derived biochar is produced specifically as a soil amendment (Lehmann and Joseph, 2009). The beneficial effects of biochar on soil properties have been reported by many and includes chemical (Yamato *et al.*, 2006), physical (Vaccari *et al.*, 2011), and biological changes in soil (Rondon *et al.*, 2007).

To the best of our knowledge, biochar production protocols in India are yet to be standardized. Biochar can be produced at scales ranging from large industrial facilities down to the individual farm. One of the key features of the portable pyrolysis units is simple and can be designed at smaller scales, to take the conversion unit to the bioresidue source to avoid bioresidue transport for onsite reapplication at farm level. The rate and extent of decomposition of each of these components depends on the thermo-chemical process parameters such as holding time, biomass type and loading rate (Venkatesh *et al.*, 2010).

Currently, however, very little biochar is being utilized in modern Indian agriculture. Use of bioresidues for producing biochar for improving soil quality as well as crop productivity in the dryland farming systems may be ecologically promising. The present work was undertaken to examine the feasibility of development of low cost portable kiln for production of biochar on-farm at different loading rates and holding time so as to determine their correlation with internal kiln temperature and to characterize the carbonaceous materials produced for its soil amendment qualities.

## Materials and Methods

### Biomass pre-configuration and seasoning

Freshly harvested stalks of cotton were used to produce biochar. Cotton stalk biomasses were manually comminuted to appropriate size (average 19 cm in length and 0.9 cm in diameter) with an axe for uniform heat transfer within and between bioresidues during thermal decomposition process. The pre-configured

fresh samples were securely stored and left to sundry naturally to moisture content below 10% (9% was the moisture content of the cotton stalk). Dry bioresidues are prerequisite to hasten satisfactory and quicker conversion. Representative biomass samples were taken for content analysis.

### Description of kiln system

In this study, on-farm usable portable kiln unit was developed to match the needs of the small farmers. Kiln was designed for low initial investment, simple to handle, and portable to minimize fuel emissions for transport of bioresidues to conversion point and with no operational power input. The cost of one unit of the kiln was ₹ 1200 (approx.) including cost of metal drum, vent making charges and side fittings.

Kiln design functions with direct up-draft principle with bottom ignition. The cylindrical metal drum kiln of about 212 L capacity was based on a single barrel design of vertical structure with perforated base (Fig1). Cabinet was circular in cross section and consisted of an intact bottom and top section. The kiln was about 28 cm in radius and 86 cm tall with one square shaped hole of 16 cm x 16 cm cut at the kiln top for loading bioresidues that can be closed at the end of conversion by a metal lid (about 26 cm in length and 26 cm in width) with a handle (110 cm). The gross volume of the kiln was about 0.21 m<sup>3</sup>. For making of vents, three concentric circles at equidistant interval of approximately 9 cm were marked from the center of kiln base to border of the kiln. Total of 40 circular vents (each about 2 cm in radius) was cut in such a way that 16, 16 and 08 vents were in first, second and third circle from the rim. Staggered arrangement was maintained by alternating the vents in all the three circles to avoid row arrangement. In addition, a central vent of about 2.5 cm radius was made in the center of the kiln base to hold wooden pole of about 110 cm height and 2.0 cm radius. Under open atmospheric conditions, the central and concentric staggered vents at the kiln base hasten hot gas movement through the bioresidues for uniform heat transfer by primary air movement while the kiln's top hole vents out the released water vapors and hot gasses. A strip of metal was continuously welded around at 3/4<sup>th</sup> height of kiln, to which two metal rods of about 1.3 cm in radius and 17 cm in length were welded on opposite sides to serve as lifting jack.

## Thermo-chemical conversion of bioresidues to biochar

Prior to loading, a wooden pole (110 cm height and 2.0 cm radius ) was inserted through top hole and fixed to central bottom vent of the kiln to create a central vent through the packed bioresidues. Pre-configured and Sun dried bioresidues were loaded through kiln top vent into the combustion chamber. Depending upon the loading rates, stalk fragments were manually packed and arranged parallel to bottom in as many voids as possible in the kiln chamber by gentle shaking. Empty drum and loaded drum weights were measured before being moved to conversion site. The loaded kiln was lifted and placed over hearth of three flat stones (minimum of about 20 cm height) on level surface to facilitate primary air flow through the bottom vents. A schematic diagram of the operation is shown in Fig 2. depicting the various processes. Before initiating the conversion process, the wooden pole was carefully removed leaving a central vent through the loaded biomass to ensure efficient flow of hot gases from bottom to top for continuous heat transfer through the bioresidues. Sufficient quantities of locally available dry twigs were used as combustible source at firing point of the kiln base vents to raise the temperature for spontaneous ignition under open atmospheric conditions. The concept of “carbon neutral” bioresidues was followed for ignition throughout the conversion process with complete elimination of hydrocarbon fuels. Exposed bioresidues at concentric base vents were flamed for 3–4 minutes for partial direct combustion to develop sufficient exothermic temperature to trigger thermal biocarbonization in the remaining residues. Primary airflow through the concentric staggered base ports were used as carrier medium for rapid heat development through partial oxidation and flow of hot volatiles toward cooler fragments for uniform thermal exchange in kiln chamber and subsequently for upward thermal buoyancy of the released water vapor and volatiles. The target end stage of biocarbonization was indicated by distinctive thin grey and blue gases for each temperature range from top vent with puff of flame. At this stage, the kiln was ready to be sealed with clay and sand sealing mixture to restrict the flow of carrier medium through the kiln for significant yield realization. The metal lid was placed over the top vent to block the hot gases; the pressure of the hot gases slows down the partial combustion. Later, the kiln was transferred to a leveled surface to ensure that no significant primary air ingress occurs in order to cutoff totally the partial combustion process. Sealing mixture of clay was used to seal the circumferential edges

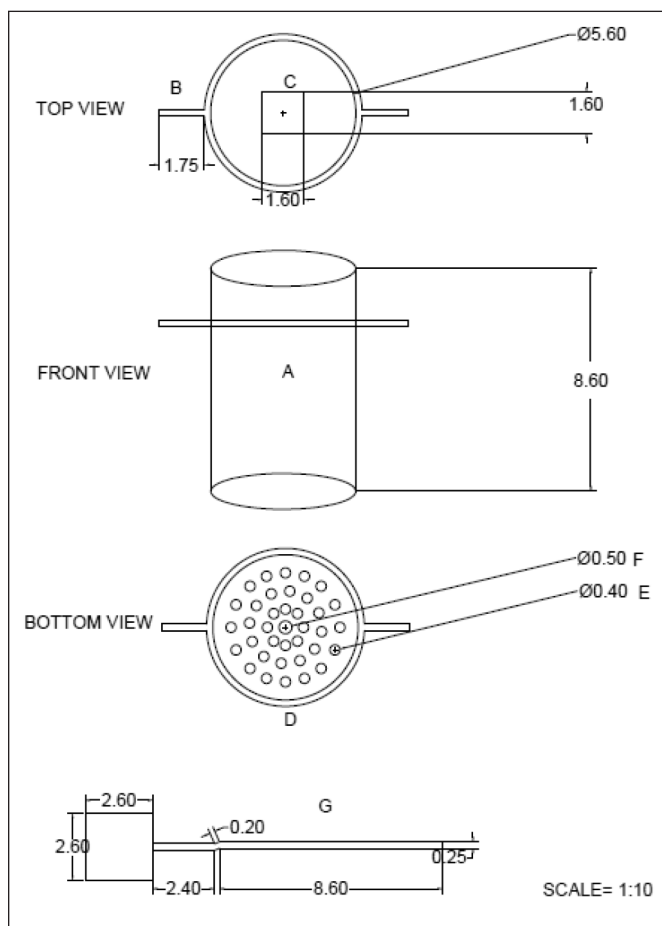
of the drum and also along the edges of the metal lid used for covering the top hole for development of gas pressure in the enclosed space of kiln. During the cooling cycle, it was ensured that no volatiles were escaping from the kiln, by sealing all possible air-entry points. Biochar samples in the kiln were left for cooling for three to four hours by heat loss through natural convection and radiation. After cooling, the sealed mixture was removed thoroughly and the biochar was taken out from the kiln in each run and weighed on mass basis. Biochar samples were tightly packed in air tight container for further analysis.

To identify the appropriate holding time for different quantities of bioresidues, we conducted three groups of load experiments and four independent replicates were run for each of the two colour phase development. Time required for development of respective colour phase (holding time) was recorded for each load category. Holding time is the time period required by the biomass to attain the requisite thermal conditions with first appearance of requisite exhaust colour phase for biocarbonization under open atmospheric conditions. Varying holding times for appearance of gray and blue gases with puff of flame were due to the variable quantities of the bioresidue materials.

## Biochar analysis

The dry biochar from each batch was homogenized thoroughly, manually ground to pass through a 2 mm sieve, and sampled prior to analyses. The biochar samples were oven dried at 105°C for 24 h. The pH of the biochar was measured by adding 1 g of biochar in 20 ml of deionized water (1:20 w/v) and was measured using a pH meter (Systronics pH system 362). The Electrical conductivity (EC) of biochars was measured at room temperature after suspending biochar in deionised water for 24 h in a (1:10 ratio biochar: deionised water) using a EC meter (Systronics conductivity meter 306). Cation exchange capacity of the biochar samples was determined by saturating the biochar exchange complex with 1N sodium acetate solution (pH 8.2). One g of biochar sample was leached with sodium acetate solution (pH 8.2) for replacement of exchangeable cations by Na<sup>+</sup> ions. The excess salts was washed down by ethanol and the adsorbed Na<sup>+</sup> ions were released by NH<sub>4</sub><sup>+</sup> ions, using 1N ammonium acetate (pH 7.0) solution. The Na<sup>+</sup> ions so released from the exchange spots were measured by using flame photometer (Rhoades, 1982).

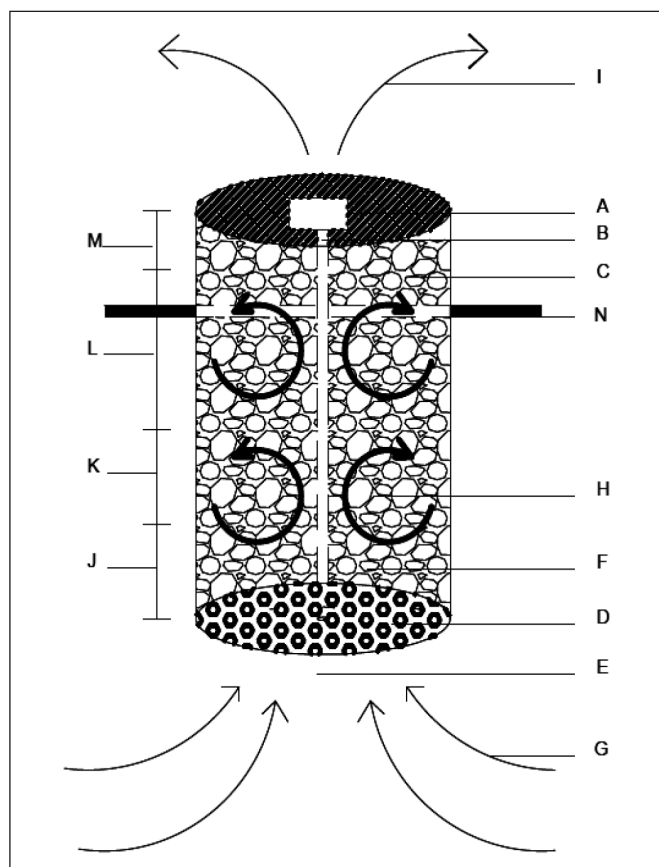
Total Carbon (C) and Nitrogen (N) abundances in the biochar and raw/ original feedstuffs were determined



**Fig 1 : Schematic structures of the biochar kiln**

A. cylindrical chamber, B. metal handle, C. top feed and exhaust vent, D. bottom vents in three concentric rings at equidistant from the rim, E. staggered vents in three concentric circles, F. central vent and G. metal lid

directly by dry combustion on CHN analyzer (Vario El Cube, Elementar) via high temperature catalyzed complete combustion of biochar C and N followed by detection of the resulting combustion products  $\text{CO}_2$  and N oxides, respectively by thermal conductivity detector. Concentrations of total P, K, Ca, Mg, Fe, Cu, Zn and Mn were determined by digesting 0.5 g of each biochar samples in a di-acid mixture ( $\text{HNO}_3:\text{HClO}_3$  in 3:1 ratio) (Miller, 1998). Maximum water holding capacity (MWHC) of the biochar samples was determined using the Hilgard or Keen Rackzowski box method (Baruah and Barthakur, 1997). Biochar water retention characteristics at both field capacity and permanent wilting point was measured using pressure plate apparatus (Soil Moisture Inc, U.S.A.) at 0.033 MPa and 1.5 MPa, respectively (Klute, 1986).



**Fig 2 : Schematic diagram of the kiln operational process**

A. top feed and exhaust vent, B. central continuous vent from bottom to top, C. sun dried bioresidues, D. bottom vents for air flow, E. initial firing point, F. ignited bioresidues, G. primary air flow, H. heat transfer process between hot gases and bioresidues, I. hot gas exhaust, J. combustion zone, K. drying zone, L. reduction and M. biocarbonization zone

The yields (burn-off levels) of the resulting carbonized products were calculated based on their difference between the masses before and after conversion using the following equation: Biochar yield (%) =  $(m_{\text{biochar}} / m_{\text{straw}}) \times 100$ , where  $m_{\text{biochar}}$  was the mass of biochar obtained after conversion and  $m_{\text{straw}}$  was the dry mass of the original bioresidue loaded into the kiln (Antal and Groni, 2003). Proximate analyses were conducted for each biochar to estimate the percentage fixed C, volatile matter (VM), ash content, on an oven dry-weight basis. The percentages of VM, ash and fixed C were estimated by measurement of weight loss / mass balance from a sequential muffle procedure. The VM content of the biochar was determined by heating the biochar in a covered ceramic crucible to  $700^\circ\text{C}$  ignition for 10 min using laboratory muffle furnace. The samples were

withdrawn and weighed and measured weight loss was defined to be volatile matter (VM), and the residual solid was carbonized biochar. Ash content was determined by heating the carbonized biochar residue of the VM determination in an open crucible via combusting at 700°C for 2 h. The percentage fixed carbon, volatile matter (VM) and ash content of the biochars was calculated using the following equation (Antal and Groni, 2003 ).

Volatile matter (%) =  $(m_{\text{biochar}} - m_{\text{cc}}) / m_{\text{biochar}} \times 100$ , where  $m_{\text{biochar}}$  was the initial dry mass of biochar,  $m_{\text{cc}}$  was dry mass of the carbonized biochar that remained after heating. Ash content (%) =  $(m_{\text{ash}} / m_{\text{biochar}}) \times 100$ , where  $m_{\text{ash}}$  was the dry mass of ash remains following combustion of the carbonized biochar,  $m_{\text{biochar}}$  was the initial dry mass of biochar. The fixed carbon content was calculated as, Fixed carbon (%) =  $100 - \text{VM} (\%) - \text{Ash} (\%)$ , where VM was the volatile matter content of biochar. All statistical analyses were conducted using SAS Institute Enterprise Guide v.9.2. for Anova with Tukey's adjustment for multiple means comparison to determine significance at  $P \leq 0.05$ .

## Results and Discussion

### Gas colour correlation with the kiln temperature

Changes in colour of the exhaust were considered for approximation of kiln temperature required for slow pyrolysis. Grey and blue colour phases were observed during slow pyrolysis in the study. We used the correlation given in USAID (1984) and Tillman *et al.* (1981) to arrive at an internal kiln temperature range of about 350-400°C for the grey, and an internal kiln temperature range of 450-500°C for the blue gas colour. Holding time as explained earlier, was assigned with the above temperature range. In the present study, each load category had two holding time in accordance

with hot gas colour. Holding time was higher for blue compared to grey colour which corresponds to increase in kiln temperature. However, this holding time will be referred to as temperature range throughout the text to facilitate inference (Table 1). Quantity of biomass loaded significantly influenced the holding time.

### Cotton stalk biochar yield and proximate analysis

Biochar yield distribution was dependant on the load and temperature range (Table 2). Yield of the cotton stalk biochar decreased with increasing temperature range from 20.4 to 16.7%, 23.5 to 21.4% and 22.6 to 20.3%, for 11, 20 and 27 kg/kiln load, respectively for grey and blue colour phase. Volatile matter content decreased with increased temperature range in each load. Proximate analysis indicated that fixed carbon and ash content generally increased with temperature range in each load. Variation in yield and other proximate parameters with increasing temperature range are consistent with Wu *et al.* (2012). Present results reveal that biomass load influences temperature range which significantly affected the yield, volatile matter, ash and fixed carbon.

### Ultimate analysis of cotton stalk and its biochar

The raw cotton stalk used in this study contained 411.7 g/kg total C, 11.2 g/kg total N, 3.7 g/kg total P, 1.0 g/kg total K, 17.9 mg/kg Mg, 66.7 mg/kg Ca, 3.1 mg/kg Na, 3.1 mg/kg Fe, 0.4 mg/kg Mn, 0.02 mg/kg Cu and 0.2 mg/kg Zn with C/N ratio of 36.9 (Table 3). The chemical and nutrient concentrations in the bioresidue and kiln temperature range can strongly influence the chemical composition of the biochar. We observed a compositional relationship between cotton stalk bioresidue and biochar at varying temperature range. These results are consistent with earlier findings of Gaskin *et al.* (2008). Compared with its cotton stalk,

**Table 1 : Colour phase correlation with temperature range for different cotton stalk bioresidue load and holding time during thermo-chemical conversion process**

Load (kg/kiln)	Holding time (min.)	Colour phase development	Corresponding temperature range (°C)
11	12	Grey	350-400
11	15	Blue	450-500
20	18	Grey	350-400
20	20	Blue	450-500
27	25	Grey	350-400
27	29	Blue	450-500

**Table 2 : Yield and proximate analysis of cotton-stalk derived biochars**

Load (kg/kiln)	Holding time (min.)	Temp. range (°C)	Biochar yield (%)	Ash <sup>a</sup> (%)	VM <sup>a</sup> (%)	Fixed carbon <sup>a</sup> (%)
11	12	350-400	20.4 ± 0.8c	29.1 ± 0.4a	12.2 ± 0.4b	58.7 ± 1.1e
11	15	450-500	16.7 ± 0.1d	30.2 ± 0.2a	11.0 ± 0.2bd	58.8 ± 0.6e
20	18	350-400	23.5 ± 0.4a	18.1 ± 0.4c	15.3 ± 0.4a	66.6 ± 1.6d
20	20	450-500	21.4 ± 0.6bc	21.2 ± 0.6b	10.1 ± 0.6cd	68.7 ± 1.4b
27	25	350-400	22.6 ± 0.6ab	20.6 ± 1.1b	11.8 ± 1.1bc	67.6 ± 1.6c
27	29	450-500	20.3 ± 0.5c	21.2 ± 0.3b	7.9 ± 0.3e	71.0 ± 1.2a

The data followed by different letters within a column are significantly different ( $P < 0.05$ ;  $n = 4$ ; ANOVA; Tukey's HSD test);  
<sup>a</sup> Ash content, volatile matter (VM) and fixed carbon expressed on dry weight basis.

**Table 3 : Chemical properties of cotton-stalk derived biochars**

Load (kg/kiln)	Holding time (min.)	Temp. range (°C)	pH <sup>a</sup>	EC <sup>a</sup> (dS/m)	CEC (cmol / kg)	Total concentration (g/kg)				C/N Ratio
						N	P	K	C	
11	12	350-400	9.2	0.05	46.3 ± 0.2b	10.3 ± 0.1c	4.6 ± 0.1c	4.1 ± 0.5a	592.4 ± 2.0e	57.8
11	15	450-500	9.3	0.08	11.7 ± 0.7e	10.5 ± 0.4c	3.4 ± 0.3de	4.0 ± 0.2a	651.1 ± 2.5d	61.9
20	18	350-400	8.9	0.08	51.3 ± 0.2a	15.9 ± 0.7b	3.8 ± 0.7ce	4.7 ± 0.6a	668.3 ± 1.4c	42.0
20	20	450-500	9.0	0.10	32.9 ± 0.7c	16.0 ± 0.8b	4.2 ± 0.2cd	4.0 ± 0.01a	685.0 ± 1.6c	41.8
27	25	350-400	9.0	0.09	49.5 ± 0.4a	16.7 ± 0.6ab	11.0 ± 0.4b	4.0 ± 0.7a	679.1 ± 3.3b	40.8
27	29	450-500	9.0	0.11	22.7 ± 1.6d	17.4 ± 0.3a	12.2 ± 0.2a	4.0 ± 0.8a	719.3 ± 0.6a	41.3

<sup>a</sup> Single determination; The data followed by different letters within a column are significantly different ( $P < 0.05$ ;  $n = 4$ ; ANOVA; Tukey's HSD test)

the biochars had higher contents of total C (592.4 to 719.3 g/kg) and total N (10.3 to 17.4 g/kg). Elemental analysis indicated that conversion led to increase in total C and total N concentration and increasing temperature range tended to further increase the total C concentration in the biochar, and the results are consistent with the findings of Wu *et al.* (2012).

The biochars C/N ratios ranged from 40.8 to 61.9. The magnitude of the changes in concentration of total C and total N in the biochars varied under increasing production temperature indicating a preferential volatilization of nitrogen over carbon resulting in wider C/N ratios with increasing temperature range (Hass *et al.*, 2011). The contents of total P in the biochar were higher compared with its cotton stalk bioresidue suggesting that the associated chemical components were concentrated in

the biochar during thermal conversion of cotton stalk, leading to higher total P contents (Yuan *et al.*, 2011). On the basis of the elemental concentration in the biochar, significant increase in total P contents could be attributed to increase in production temperature within each load (Peng *et al.*, 2011). Total K concentrations in the biochars were 4 times higher than in the raw feedstock. Potassium vaporizes at temperature relatively above 760°C (Knicker, 2007) whereas the higher limit adopted in the present study was 450-500°C, which might have contributed to reduced volatilization and effective concentration of relevant chemical components during the conversion process.

Biochar pH values ranged from 8.9 to 9.0. Biochar produced at 450-500°C temperature range had a higher pH. The trend of increased pH values with a concomitant

increase in temperature range within each load was observed, a characteristic that was found associated with increase in kiln temperature (Fuertes *et al.*, 2010). Biochar pH correlated well with the ash content ( $r^2 = 0.948$ ) and the sum of K, Ca, Mg and Na ( $r^2 = 0.949$ ), which is in accordance with Enders *et al.* (2012). Higher temperature during the conversion process had the strongest influence on the biochar pH suggesting that higher temperature may have attributed to higher degree of volatilization, decomposition of surface oxygen groups and dehydroxylation contributing to increased ash residue portion in the biochar (Hass *et al.*, 2012). The salinity of all biochars had low EC values ranging from 0.05 to 0.11 dS/m. The highest EC values were found for biochar produced at 450-500°C. Within each load group, higher temperature range would have contributed to increase in biochar EC values. This is in agreement with Kloss *et al.* (2011), who reported similar trend for biochar produced from wheat straw at 400 and 460°C.

CEC of the biochar samples ranged from 11.7 to 51.3 cmol/kg and it significantly decreased with increase in temperature range within each load. Decrease in surface acidic functional groups such as carboxyls and phenolic hydroxyls, with increase in production temperature range (Guo and Rockstraw, 2007) may have contributed to the lower CEC values associated with the biochar in the present study. The concentrations of elements (Ca, Mg, Fe, Z, Cu, Mn and Na) of biochar were higher compared

to its feed stock concentration suggesting that production temperature may have resulted in concentration (Table 4). There was significant interaction between temperature and load for trace elements concentration. Trace elements concentration tended to significantly increase with increasing temperature from 350-400°C to 450-500°C which was in accordance with findings of Gaskin *et al.* (2008).

### Recovery of total C and N in the cotton stalk biochar

The amount of C conserved in the biochar ranged from 26.4 to 39% and was inversely proportional to the ash content of the corresponding biochars in varying temperature range within each load. Loss of C with increase in production temperature range during conversion might have attributed to volatilization of carbon elements bonded with volatile chemicals constituents compared to less volatile elements that concentrated during carbonization (Kloss *et al.*, 2011). The recovery of total N in the biochar ranged from 16 to 35% and was inversely proportional to increase in production temperature range within each load. Novak *et al.* (2009) suggested that the decrease in N during higher production temperature can be attributed to aromatization (Almendros *et al.*, 2003) and condensation of N-containing structures in the biochar into recalcitrant heterocyclic N rather than the more bioavailable amine N (Table 5).

**Table 4 : Total concentrations (mg/kg) of different nutrients in cotton-stalk derived biochars**

Load (kg/kiln)	Holding time (min.)	Temp. range (°C)	Fe	Cu	Zn	Mn	Na	Ca	Mg
11	12	350-400	1409.0 ± 8.5 f	22.2 ± 0.1d	9.2 ± 0.1d	87.4 ± 0.8e	6282.8 ± 1.9d	41412 ± 26.6b	8223.0 ± 22.9f
11	15	450-500	2101.0 ± 0.7e	27.2 ± 0.2c	18.0 ± 0.2b	105.0 ± 2.7d	7556.2 ± 1.0a	45010.0 ± 19.8a	8528.0 ± 5.7d
20	18	350-400	2502.0 ± 9.6d	18.2 ± 0.3e	1.2 ± 0.16e	90.0 ± 0.1e	4630.2 ± 0.2f	41381.0 ± 15.5f	8406.0 ± 7.3e
20	20	450-500	2784.0 ± 13.1c	20.0 ± 0.8c	1.0 ± 0.01e	123.0 ± 1.6c	5097.6 ± 0.3e	44269.8 ± 13.7c	9146.0 ± 3.3c
27	25	350-400	2821.0 ± 17 b	38.2 ± 1.0b	12.0 ± 0.4c	132.0 ± 1.8b	6300.2 ± 0.2c	41549.0 ± 0.8e	11077.7 ± 8.4b
27	29	450-500	4332.0 ± 2.9a	47.2 ± 0.7a	27.2 ± 0.8a	161.4 ± 1.1a	6392.0 ± 1.6b	43349.0 ± 8.2d	11251.3 ± 7.1a

The data followed by different letters within a column are significantly different ( $P < 0.05$ ;  $n = 4$ ; ANOVA; Tukey's HSD test)

**Table 5 : Changes in C and N levels during conversion to biochar**

Load (kg/kiln)	Holding time (min.)	Temp. range (°C)	Biochar yield (kg)	Total C in cotton stalk (kg)	Total C in biochar (kg)	C recovery in biochar (%)	Total N in cotton stalk (kg)	Total N in biochar (kg)	N recovery in biochar (%)
11	12	350-400	2.24	4.53	1.33	29	0.12	0.02	19
11	15	450-500	1.84	4.53	1.19	26	0.12	0.02	16
20	18	350-400	4.7	8.23	3.14	38	0.22	0.07	33
20	20	450-500	4.27	8.23	2.93	35	0.22	0.07	31
27	25	350-400	6.09	11.11	4.14	37	0.30	0.10	34
27	29	450-500	5.47	11.11	3.94	35	0.30	0.10	31

### Moisture retention properties of cotton stalk biochar

Increasing temperature in each of the loading rate had improved the maximum water holding capacity and available water capacity (AWC) of the biochar with highest maximum water holding capacity (3.9 g/g) and available water capacity (0.89 g/g) of dry biochar was exhibited at highest order of loading rate at 450-500°C relative to other lower order levels adopted for conversion. Hydrologically desirable biochar would have a high field capacity and a wilting point, effectively increasing the plant-available biochar-soil water content. Biochar water potential will almost certainly be a function of pore structure connectivity and size, with smaller pores and narrow pore throats leading to increased biochar water potential values (Kinney *et al.*, 2012). The AWC of biochar is to be increased, the magnitude of increase in FC should be greater than that PWP, otherwise the net effect will be no change or even a decrease in AWC. This was clearly observed in this study, which indicated that there was a considerable effect due to the hydrophilic groups on AWC, recording 123% higher AWC over

the biochar produced at lowest loading and lowest temperature (Table 6).

The chemical components were concentrated in the cotton stalk biochar during pyrolysis, leading to higher contents of these chemical components in biochar compared to the feedstock. The CEC of cotton stalk biochar was higher, which can enhance the adsorption ability to retain cationic nutrients to improve soil fertility. Moisture retention characteristics were well exhibited and indicated the potential of cotton stalk biochar to retain moisture in rainfed soils to overcome the moisture stress during sensitive stages of crop growth period. Overall, cotton stalk biochar produced at 450-500°C showed the greatest potential for use as soil amendment to improve the fertility of rainfed soils as well as to sequester carbon. The most effective approach to predicting amendment performance of biochar is to first define the predominant limiting factors of a particular soil-crop-climate situation. However, some properties of biochars may be positive or negative in all soils. For example, greater biochar stability is not only useful from a climate mitigation point of view, but also for maintaining possible positive agronomic effects over longer periods of time. On the

**Table 6 : Moisture retention characteristics of cotton-stalk derived biochars**

Load (kg/kiln)	Holding time (min.)	Temp. range (°C)	MWHC	FC (at 0.3 bar)	PWP (at 15 bar)	AWC (FC-PWP)
11	12	350-400	3.1	1.33	0.92	0.40
11	15	450-500	3.2	1.46	1.06	0.40
20	18	350-400	3.4	1.43	1.05	0.38
20	20	450-500	3.5	1.62	1.03	0.59
27	25	350-400	3.7	1.65	0.96	0.68
27	29	450-500	3.9	1.70	0.81	0.89

MWHC, maximum water holding capacity; FC, field capacity; PWP, permanent wilting point; AWC, available water capacity, all are expressed as g H<sub>2</sub>O/g of dry biochar

other hand, phytotoxicity of certain elements such as Na is likely detrimental across different soils and crops.

## Conclusion

The conversion of cotton stalk bioresidue to biochar offers small farmers an attractive option for minimizing waste product disposal instead of on field burning. The influence of loading rate and holding time (correlated to kiln temperature) on the degree of carbonization and other biochar properties was evidenced. Bioresidue characteristics had the greatest influence on key biochar properties. With increase in pyrolysis temperature, the char yield decreased in each of the load rates whereas nutrients got concentrated in biochar compared to parent bioresidue. Charring temperature greatly enhanced the moisture retention characteristics of the cotton stalk biochar. The cotton stalk biochar is potentially a valuable soil amendment because it contains most of the stalk derived nutrients. Further studies are necessary to fully document how the enhanced biochar production conditions influence its quality? How much biochar can the soil sustain? How much will the farmers benefit? and How can supply be sustainably maintained? These issues need to be addressed in the near future while transferring technology experiments from laboratory to field.

## References

- Almendros G, Knicker H and Gonzalez Vila FJ. 2003. Rearrangement of carbon and nitrogen forms in peat after thermal oxidation as determined by solid state  $^{13}\text{C}$  and  $^{15}\text{N}$  NMR spectroscopy. *Organic Geochemistry*, 34(11): 1559-1568.
- Amonette J and Joseph S. 2009. Characteristics of biochar: Microchemical properties. In: *Biochar for environmental management: Science and technology* (J Lehmann and S Joseph, Eds.), Earth scan, London. pp 33-52.
- Antal MJ and Gronli M. 2003. The art, science, and technology of charcoal production. *Industrial and Engineering Chemistry Research*, 42: 1619-1640.
- Baruah TC and Barthakur HP. 1997. Determination of single value soil constants by Hilgard apparatus or Keen-Rackzowski box. In: *A text book of soil analysis*, Vikas Publishing House Pvt. Ltd., New Delhi. pp 28-31.
- Enders A, Hanley K, Whitman T, Joseph S and Lehmann J. 2012. Characterization of biochars to evaluate recalcitrance and agronomic performance. *Bioresource Technology*, 114: 644-653.
- Forbes, MS, Raison RJ and Skjemstad JO. 2006. Formation, transformation and transport of black carbon (charcoal) in terrestrial and aquatic ecosystems. *Science of the Total Environment*, 370: 190-206.
- Fuertes AB, Camps Arbestain M, Sevilla M, Macia-Agullo JA, Fiol S, Lopez R, Smernik RJ, Aitkenhead WP, Arce F and Macias F. 2010. Chemical and structural properties of carbonaceous products obtained by pyrolysis and hydrothermal carbonization of corn stover. *Australian Journal of Soil Research*, 48: 618-626.
- Gaskin JW, Steiner C, Harris K, Das KC and Bibens B. 2008. Effect of low temperature pyrolysis conditions on biochar for agricultural use. *Transactions of the ASABE*, 51: 2061-2069.
- Guo Y and Rockshaw AD. 2007. Activated carbons prepared from rice hull by one-step phosphoric acid activation. *Microporous Mesoporous Materials*, 100: 12-19.
- Hass A, Gonzalez JM, Lima IM, Godwin HW, Halvorson JJ and Boyer DG. 2012. Chicken Manure Biochar as Liming and Nutrient Source for Acid Appalachian Soil. *Journal of Environmental Quality*, 51(4): 1096-1106.
- Kinney TJ, Masiello CA, Dugan B, Hockaday WC, Dean MR, Zygourakis K and Barnes RT. 2012. Hydrologic properties of biochars produced at different temperatures. *Biomass and Bioenergy*, 41: 34-43.
- Kloss S, Zehetner F, Dellantonio A, Hamid R, Ottner F, Liedtke V, Schwanninger M, Gerzabek MH and Gerhard Soja, G. 2011. Characterization of Slow Pyrolysis Effects of Feedstocks and Pyrolysis Temperature on Biochar Properties. *Journal of Environmental Quality*, 41: 990-1000.
- Klute A. 1986. Water retention: laboratory methods. In: *Methods of soil analysis* (A Klute, Ed.), Part 1, 2<sup>nd</sup> edn. Agron. Monogr. 9. ASA and SSSA, Madison, WI. pp 635-662.
- Knicker H. 2007. How does fire affect the nature and stability of soil organic nitrogen and carbon? A review. *Biogeochemistry*, 85(1): 91-118.
- Lehmann J and Joseph S. 2009. Biochar systems. In: *Biochar for Environmental Management: Science and Technology* (J Lehmann and S Joseph, Eds.), Earth scan Books Ltd, London. pp 147-168.
- Miller R. 1998. Nitric-perchloric acid wet digestion in an open vessel. In: *Hand book of reference methods for plant analysis* (YP Kalra, Ed.), CRC press, New York. pp 57- 61.
- MNRE (Ministry of New and Renewable Energy Resources). 2009. Govt. of India, New Delhi. [www.mnre.gov.in/biomasssources](http://www.mnre.gov.in/biomasssources).
- Novak JM, Busscher WJ, Laird DL, Ahmedna M, Watts DW and Niandou M A S. 2009. Impact of biochar amendment on fertility of a southeastern coastal plain soil. *Soil Science*, 174(2): 105 - 112.
- Peng X, Ye LL, Wang CH, Zhou H and Sun B. 2011. Temperature- and duration-dependent rice straw-derived biochar: Characteristics and its effects on soil properties of an Ultisol in southern China. *Soil and Tillage Research*, 112: 159-166.
- Rhoades JD. 1982. Cation exchange capacity. In: *Methods of soil analysis* (Miller *et al.*, Eds.) Part 2. Agron. Monogr. 9, Am. Soc. Agron., Madison, WI. pp 149-157.
- Roberts KG, Gloy BA, Joseph S, Scott NR and Lehmann J. 2010. Life cycle assessment of biochar systems: Estimating the energetic, economic and climate change potential. *Environment Science and Technology*, 44 (2): 827-833.

- Rondon M, Lehmann J, Ramirez J and Hurtado M. 2007. Biological nitrogen fixation by common beans (*Phaseolus vulgaris* L.) increases with biochar additions. *Biology and Fertility of Soils*, 43: 699-708.
- Stavi I and Lal R. 2013. Agroforestry and biochar to offset climate change: a review. *Agronomy for Sustainable Development*, 33: 81-96.
- Tillman DA, Rossi AJ and Kitto William D. 1981. *Wood combustion: Principles, Processes, and Economics*. Academic Press, New York. 208 p.
- USAID. 1984. Charcoal production improvement for rural development in Thailand. Renewable Nonconventional Energy Project, Royal Thai Government, Report submitted to the National Energy Administration Ministry of Science, Technology and Energy. 163 p.
- Vaccari PF, Baronti S, Lugatoa E, Genesio L, Castaldi S, Fornasier F and Miglietta F. 2011. Biochar as a strategy to sequester carbon and increase yield in durum wheat. *European Journal of Agronomy*, 34(4): 231-238.
- Venkatesh G, Korwar GR, Venkateswarlu B, Gopinath KA, Sanjeeva Reddy B, Mandal UK, Srinivasarao Ch and Grover MT. 2010. Preliminary Studies on Conversion of Maize Stalks into Biochar for Terrestrial Sequestration of Carbon in Rainfed Agriculture In: *Extended Summaries, National Symposium on Climate Change and Rainfed Agriculture*, 18-20 February, 2010, Indian Society of Dryland Agriculture and Central Research Institute for Dryland Agriculture, Hyderabad, India. pp 388-391.
- Woolf D, Amonette JE, Street-Perrott FA, Lehmann J and Joseph S. 2010. Sustainable biochar to mitigate global climate change. *Nature Communications*, 1(5): 1-9.
- Wu W, Yang M, Feng Q, McGrouther K, Wang H, Lu H and Chen Y. 2012. Chemical characterization of rice straw-derived biochar for soil amendment. *Biomass and Bioenergy*, 47: 268-276.
- Yamato M, Okimori Y, Wibowo IF, Anshiori S and Ogawa M. 2006. Effects of application of charred bark of *Acacia mangium* on the yield of maize, cowpea and peanut, and soil chemical properties in South Sumatra, Indonesia. *Soil Science & Plant Nutrition*, 52: 489-495.
- Yuan JH, Xu RK and Zhang H. 2011. The forms of alkalis in the biochar produced from crop residues at different temperatures. *Bioresource Technology*, 102: 3488-3497.

---

Received : May 2013; Accepted : June 2013