

Pyrolytic transformation of indigenous biomass wastes into biochar: an insight into char structure and physicochemical characteristics

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Abstract

Biochar, the product obtained by the pyrolysis of organic materials with little or no available air, acts as a long-term recalcitrant source of organic carbon when applied to soil. In the present study an in-farm method has been standardized for the pyrolytic conversion of four indigenous biomass resources into biochar. The biomass feedstocks viz. bovine bone (BB), coconut shell (CS), rubberwood (RW) and water hyacinth (WH) were dried and subjected to proximate, ultimate, biochemical analysis and were subjected to slow pyrolysis (563 °C). The biomass feedstocks showed an ash content ranging from 1.04-61.23 %, moisture content of 8.46-20.83 %, volatile matter of 27.92-74.92 % and fixed carbon of 1.17-18.75 %. The biochar yield was maximum for BB (56.65 %). Scanning electron microscope analysis of the biochar samples showed aligned honeycomb like groups with the greatest porosity (3.90-8.43 μm) in WH biochar. X-ray spectroscopy (EDX) analysis showed highest number of elements in WH biochar. The electrical conductivity, bulk density and water holding capacity of the biochars ranged from 102.56-7569.03 $\mu\text{s cm}^{-1}$, 16.83-72.58 g cm^{-3} and 57.89-431.17 %, respectively. The Fourier Transform Infrared spectrometer (FTIR) analysis of biochar samples showed several functional groups which help them to act as a good soil conditioner. Characteristics of the biochar produced from these biomass wastes revealed its potential as good soil conditioners in crop production systems.

Keywords: bovine bone, coconut shell, EDX, FTIR, pyrolysis, rubberwood, SEM, water hyacinth

1 Introduction

Climate change has now become a global concern owing to elevated levels of greenhouse gases (GHGs) in the atmosphere (Maucieri *et al.*, 2017). Since 1970, CO₂ emissions have increased by about 90 %, with emissions from the combustion of fossil fuel and industrial processes contributing about 78 % of the total GHG emissions increase from 1970 to 2011 (Boden *et al.*, 2017). Agriculture, deforestation, and other land-use changes have been the second-largest contributors (IPCC, 2014). Mitigation of CO₂ emission through C sequestration proved to be a viable solution and is being tried successfully in many developing countries (Lehmann *et al.*, 2006). Use of biochar as a soil amendment for sequestering C is considered to be a robust choice to offset the C emissions (Brassard *et al.*, 2019).

Biochar is a fine grained, black solid carbon-rich (70-80 %) porous substance produced from pyrolysis of biological materials in the absence of oxygen at relatively low temperature (Lehmann *et al.*, 2002). Physicochemical characteristics of biochar such as high porosity, change capacity, high content of plant available nutrients and sometimes high pH makes it a preferred soil additive in degraded soils of the tropics (Major *et al.*, 2010) as well as more fertile soils in the temperate regions (Novak *et al.*, 2009; Laird *et al.*, 2010).

Biochar when applied in soil can act as a recalcitrant source of organic carbon which remains for long time (Sun *et al.*, 2020). Biochar application to the soil has been reported to boost soil fertility and improve soil quality resulting in better crop yields (Hussain *et al.*, 2016). Soil benefits include improving soil structure and retention of soil moisture, decreasing soil acidity (Spokas *et al.*, 2012), improving cation exchange capacity (CEC), retaining nutrients, changing biological community composition, and stimulat-

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ing soil microbial populations and functions (Pietikäinen *et al.*, 2000).

Biochar application has shown to have positive effects on beneficial soil microorganisms e.g. increased levels of biological N₂ fixation by rhizobia in legumes and improved activity of plant growth promoting organisms in the rhizosphere and high levels of mycorrhizal colonization (Hammer *et al.*, 2015; Egamberdieva *et al.*, 2016).

Biochar can be produced from a wide range of biomass wastes such as wood chips (James *et al.*, 2017), rice straw (Wu *et al.*, 2009), hazelnut shells (Olgun *et al.*, 2011), meat bone meal (Vassilev *et al.*, 2010), municipal solid waste (Ramzan *et al.*, 2011) and aquatic biomass such as microalgae (Roberts *et al.*, 2015). But the composition and quality of the biochar as a soil amendment depends upon the type of feedstock used and the condition under which it is produced (McLaughlin *et al.*, 2009).

In rural villages of Kerala, India, the accumulation of biomass resources such as bovine bone, coconut shell, rubberwood cuttings and water hyacinth poses perennial waste burden to the environment. Kerala generates approximately 38,100 tonnes of slaughter wastes per annum from its units which hardly have any waste disposal facilities (Envis Centre, 2022). Yet another concern is the invasive water hyacinth which adversely affects the aquatic environment of this region (Vaidyanathan & Induchoodan, 2017). Further, coconut shell, rubberwood etc form bulk waste in Kerala (KSWNP, 2020) which often crosses the manageable limit. Therefore, an appropriate strategy with a minimal investment to transform these wastes into useful products is the need of the time.

The present study aims to 1) devise an in-farm method for the pyrolytic conversion of indigenous biomass resources into biochar which otherwise would have been waste burden to the environment, 2) characterisation of four different feedstocks used in the study, 3) characterisation of the four different biochars produced through pyrolysis for its structure and properties with an aim to use it as an additive in crop production systems.

2 Materials and methods

2.1 Collection, processing and characterisation of feedstock

The feedstocks bovine bone (BB), coconut shell (CS), rubberwood (RW) and water hyacinth (WH) for biochar production were collected from Ernakulam (9°53'56.79" N and 76°22'5.05" E) District, Kerala, India. BB collected from local slaughter houses were buried in pits of 90 × 90 × 90 cm

size for a month till the adherent tissues were completely disintegrated. The bones were then dug out, dried and chopped for biochar production. CS collected from a coconut processing unit was broken into small pieces in order to accommodate a large quantity in the drum used for pyrolysis. RW was collected from 25 years old plants that stopped its latex yield, chopped into 10–20 cm pieces. WH feedstock was prepared by collecting water hyacinth (*Eichhornia crassipes*) from local water bodies and sun-dried for one month to eliminate the water content completely. A sub-sample from each dried and pulverised feedstock was subjected to proximate analysis for the determination of ash content (AC), moisture content (MC), volatile matter (VM) and fixed carbon (FC). Analysis of AC, MC and VM were done as replicates following ASTM E830-87, ASTM E871-82 and ASTM E872-82 respectively (ASTM E830-87, 1996; ASTM E871-82, 2006; ASTM E872-82, 2019). The FC was calculated from the formula:

$$FC \text{ (wt. \%)} = 100 [VM + AC] \text{ (wt. \%)} \quad (1)$$

Ultimate analysis was performed to determine the elemental composition of carbon (C), hydrogen (H), nitrogen (N) and oxygen (O) in feedstocks. For this, powdered feedstocks were analysed using Elementar Vario EL III elemental analyser. The percentage of O was obtained from (Schmidt *et al.*, 2016):

$$O \text{ (wt. \%)} = 100 - [Ash + C + H + N + S] \text{ (wt. \%)} \quad (2)$$

Calorific values of the feedstocks were determined using a bomb calorimetric method according to JIS M8814 (Japanese Industrial Standard, 2003).

The percentage of cellulose, hemicelluloses and lignin were determined as described by Goering & Van Soest (1970). The extractives of alcohol-benzene, hot and cold-water solubility were determined from ASTM D1110-84 and ASTM D1107-96, respectively (ASTM D1110-84, 2013; ASTM D1107-96, 2013).

2.2 Production of biochar

A simple in-farm improvised method replacing a reactor (Venkatesh *et al.*, 2010) making use of slow pyrolysis (400–500 °C) technique was setup with certain modifications. Discarded cylindrical oil drums (91 × 56 cm; 200 L capacity) with upper and lower sides intact were procured from local market and modified for the use as a charring kiln. A single square shaped opening (20 × 20 cm) was made at the centre on topside of the drum for loading the feedstocks. On the

bottom side of the oil drum 35 holes measuring 4 cm² were made with a 5 cm² hole at the centre covering about 20 % of the bottom side of the drum. The kilns were loaded with each feedstock separately. The feedstocks placed at the extreme bottom of the kiln were slightly sprayed with diesel to facilitate initial ignition. The fully loaded kilns were kept over cement bricks of 15 cm height placed in circular pits (96 cm dia; 30 cm depth) taken in ground having a soil slant at one end (30 cm width) for feeding the firewood during ignition. The bottom and space around the kiln was packed with firewood and coconut husk and ignited for 35–40 min at approximately 563 °C and the temperature was measured using a dual laser IR thermometer. After the reduction of the thick smoke, a metal sheet (30 × 30 cm) was placed partially over the top hole of the kiln to control flow of air into the drum so that the feedstocks are not burned to ashes. At the end of the burning process, the top hole was closed completely and sealed with soil-clay (1:1 v/v) slurry and kept overnight. The drums when cooled down were taken out and harvested for biochar. Three batches of biochar per feedstock were prepared. For the characterisation of each biochar, all the three batches were pooled together and sub-samples were taken from it. The harvested sub-samples of biochar were taken to the laboratory for further analysis.

The yield of biochar (Y_1) was determined as the ratio of the produced biochar weight to the weight of pyrolysis feedstocks and was calculated using the formula:

$$Y_1 (\%) = \frac{m_1}{m_2} \times 100 \quad (3)$$

where m_1 is the weight of biochar, and m_2 is the weight of feedstock samples.

2.3 Physical and chemical characterisation of biochar

Micromorphology of the biochar samples were examined using a scanning electron microscope (SEM, Make: JEOL JSM-6390LA, Japan) equipped with an energy dispersion X-ray spectroscopy (EDX). Elemental analysis of the biochar samples were performed using EDX and the elemental weight (%) was recorded.

The pH and EC were measured in a suspension of biochar in deionized water (1:10 w/v) using a multimeter (Eutech PC2700, Eutech Instruments, Singapore). The EC was presented in $\mu\text{S cm}^{-1}$. For bulk density, a glass cylinder (25 ml) was filled to specified volume with biochar powder (40 mesh), dried in a hot air oven at 80 °C overnight. The cylinder was tapped for 2 min to compact the biochar and the bulk density was calculated as the ratio between the weight (g) of the dried biochar and volume (ml) of the biochar and expressed as g cm^{-3} (Ahmedna *et al.*, 1997). For the de-

termination of water holding capacity, 20 g of dried biochar sample was taken in a plastic container and placed in a dish of water. This was allowed to saturate for 6 h. The plastic container was then taken out from the water and covered with a thin polythene cover to prevent loss of water by evaporation. It was then hanged on a stand overnight to allow drainage. All samples were allowed to drain for the same amount of time. The biochar was carefully transferred from the plastic container to a pre-weighed container (M1) and the total weight of moist biochar with container (M2) was taken. The samples were then dried in an oven at 105 °C till constant weight (M3) is recorded. The water holding capacity was calculated following the formula (Dugan *et al.*, 2010).

$$\text{Water holding capacity} (\%) = \frac{M_2 - M_3}{M_3 - M_1} \times 100 \quad (4)$$

The chemical functional groups present in the biochar samples were investigated by Fourier transform infrared spectroscopy (FTIR) (Avatar 370 Thermo Nicolet Corporation, USA) in the range of 4000–400 cm^{-1} at a resolution of 4 cm^{-1} with an interferogram of 32 scans (Gomez-Serrano *et al.*, 1999). FTIR analysis gives an idea about the chemical composition of the biochar.

2.4 Statistical Analysis

The data was analysed by analysis of variance (ANOVA) in order to find the significant variation among different properties of feedstocks and biochar. The means were separated using Tukey's Honestly Significant Difference (HSD) test with a significant level $P < 0.05$, $n = 3$ using SYSTAT 9.

3 Results

3.1 Proximate, ultimate and biochemical analysis of biomass feedstocks used for biochar production.

The results of proximate, ultimate, biochemical analysis and HHV values of the feedstocks used for biochar production are presented in Table 1. The results of proximate analysis showed that the ash percentage ranged between 1.0 and 61.2 % whereas, moisture, volatile matter and fixed carbon ranged between 8.5–20.8 %, 27.9–74.9 % and 1.2–18.7 % respectively.

The results of ultimate analysis revealed that the carbon percentage ranged between 23.50 and 46.50 % whereas, hydrogen ranged between 0.31–3.43 % and nitrogen and oxygen ranged between 4.53–7.07 and 7.31–52.18 % respectively. Among the biomass feedstocks, CS had a higher C while BB had the least. Conversely, BB recorded the highest

Table 1: Proximate, ultimate and biochemical analysis of biomass feedstocks used for biochar production.

Parameters	BB	CS	RW	WH
<i>Proximate analysis</i>				
Ash (%)	61.2 ± 0.02 ^a	22.2 ± 0.02 ^b	1.0 ± 0.01 ^d	17.6 ± 0.02 ^c
Moisture (%)	9.7 ± 0.01 ^b	9.1 ± 0.01 ^c	8.5 ± 0.02 ^d	20.8 ± 0.03 ^a
Volatile matter (%)	27.9 ± 0.02 ^d	52.7 ± 0.03 ^b	74.9 ± 0.01 ^a	42.8 ± 0.03 ^c
Fixed carbon (%)	1.2 ± 0.01 ^d	16 ± 0.01 ^b	15.6 ± 0.01 ^c	18.8 ± 0.02 ^a
<i>Ultimate (elemental) analysis*</i>				
Carbon (%)	23.50	46.50	38.46	32.53
Hydrogen (%)	3.43	0.31	1.25	1.90
Nitrogen (%)	4.53	5.88	7.07	5.84
Oxygen (%)	7.31	25.07	52.18	42.10
Sulphur (%)	ND	ND	ND	ND
O/C	0.31	0.54	1.36	1.29
H/C	0.15	0.01	0.03	0.06
Calorific value (MJ kg ⁻¹)				
HHV	7.89	23.69	20.66	18.64
<i>Biochemical analysis</i>				
Cellulose (%)	ND	35.2 ± 0.43 ^b	35.4 ± 0.41 ^b	57.9 ± 0.45 ^a
Hemicellulose (%)	ND	26 ± 0.38 ^a	25.5 ± 0.35 ^a	25.6 ± 0.28 ^a
Lignin (%)	ND	36.7 ± 0.35 ^b	39.9 ± 0.45 ^a	2.1 ± 0.21 ^c
Extractives (%)	ND	2.5 ± 0.06 ^b	0.5 ± 0.04 ^c	14.5 ± 0.35 ^a

Values are mean ± standard deviation of three replicates. Mean in each line with different letters are significantly different ($P < 0.05$) by Tukey's HSD. ND, not detected

* Results based on one time analysis.

BB-Bovine Bone, CS- Coconut Shell, RW-Rubberwood, WH- Water hyacinth

H and CS the least. RW and WH showed the highest N and O respectively while BB the least.

The calorific value (HHV) of the feedstocks ranged between 7.89 and 23.69 MJ kg⁻¹ with highest in CS and lowest in BB.

The feedstocks analysed in the present study had the cellulose, hemicelluloses and lignin ranging between 35.20-57.97, 25.47-26.00 and 2.07-39.97 % respectively. The percentage of extractives differed with biomass feedstocks that ranged between 0.53-14.53 % which was highest in WH.

3.2 Biochar production and characterisation

The char yield from feedstocks ranged between 26.55-56.65 %. Maximum values were obtained for BB (56.65±2.92 %) followed by WH (35.44±4.70 %), CS (32.84±3.36 %) and RW (26.55±2.89) under the present pyrolytic condition (Fig. 1).

The SEM images of the biochar samples are shown in Fig. 2. Pore size was measured using an image processing software ImageJ. The biochar porous structure showed various proportion and shapes. Biochar derived from WH showed the greater porosity with pore size measuring from

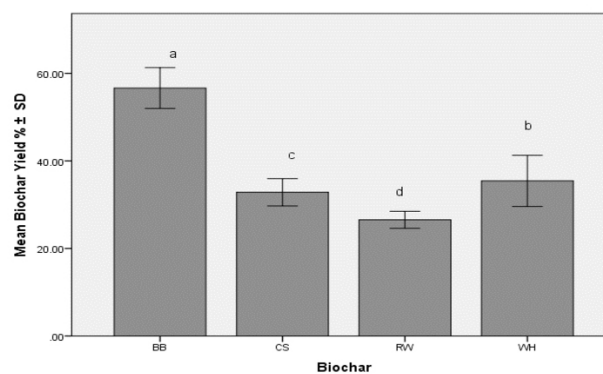


Fig. 1: Biochar yield from four feedstocks. (A) Bovine Bone (BB), (B) Coconut Shell (CS), (C) Rubberwood (RW), (D) Water Hyacinth (WH). Mean with different letters are significantly different ($P < 0.05$) by Tukey's HSD.

3.90-8.43 μm with uniform distribution of pores. The CS and RW biochars had a pore size ranging from 3.77-7.52 μm and 2-4.45 μm respectively. From the external aspect, the pores of CS have some large pores interconnected with small pores. Whereas RW has a smooth surface and the pores are few in number and are not found to be cross-linked.

Biochar produced from BB had the least porosity with pore size around 333.20-995.09 nm.

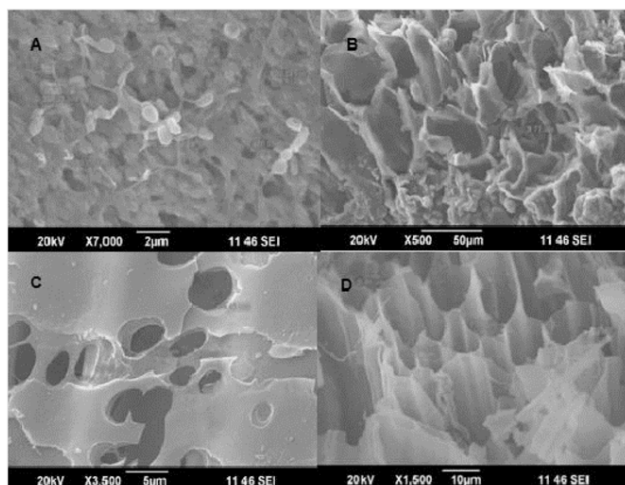


Fig. 2: Scanning electron micrographs (SEM) of different biochar samples. (A) Bovine Bone (BB) at 7KX, (B) Coconut Shell (CS) at 0.5KX, (C) Rubberwood (RW) at 3.5KX, (D) Water Hyacinth (WH) at 1.5KX magnifications.

The EDX of the biochars detected 9 elements in BB, 11 elements in CS, 10 elements in RW and 16 elements in WH (Table 2). The elements such as P, Ca and Na showed a relatively high weight percentage in BB. The elemental weight of Fe was more in CS while K and Mg was high in RW. Si and Al had a higher value in WH. Further, S, Cu, Cl and Ti were detected only in WH.

The properties of biochar derived from waste biomass such as pH, EC, bulk density and water holding capacity is shown in Table 3. The pH of most biochars (CS, RW, and WH) varied from neutral to alkaline range while the biochar derived from BB had an acidic pH. Electrical conductivity (EC) is an indicator of salts and is responsible for exchange of ions. The EC of biochars in the present study ranged between 102.56-7569.03 $\mu\text{s cm}^{-1}$. In the present study, bulk density is highest in BB and lowest in WH suggesting increased char porosity in WH compared to other biochars examined. Water holding capacity is highest in WH and lowest in CS.

FTIR analysis provides the chemical composition. The BB and CS biochars showed 1 prominent peak, 12 peaks with RW and 6 peaks with WH. The surface functional groups, according to the FTIR reports of the four biochar samples, were represented in Table 4. The OH, peroxide and nitrogen containing functional groups was present in all four types of biochar. These groups help in sorption of water, ion exchange, ageing, adsorption and energy storage. The carbonate group which helps in ion exchange and immobilization of heavy metals was present in three biochars except

Table 2: Major elemental composition of the biochars in this study.

Element (wt. %)	BB	CS	RW	WH
C	10.13	66.25	72.73	41.3
H	0.05	1.43	1.41	0.12
N	1.54	1.32	1.15	1.86
O	34.24	21.27	9.31	37.41
P	11.51	0.15	0.46	0.12
K	0.12	0.53	4.2	1.65
Ca	24.31	0.23	4.33	1.55
Mg	0.52	0.21	0.96	0.41
S	BDL	BDL	BDL	0.09
Fe	BDL	1.27	BDL	0.87
Cu	BDL	BDL	BDL	0.29
Cl	BDL	BDL	BDL	1.31
Na	0.51	BDL	BDL	0.36
Si	BDL	1.83	0.34	3.03
Al	BDL	2.25	0.33	3.26
Ti	BDL	BDL	BDL	0.14

Values are based on one time analysis
BDL, below instrument detection limit
BB-Bovine Bone, CS- Coconut Shell,
RW-Rubberwood, WH- Water hyacinth

CS. But CS and RW contains organic phosphate group that aid in CEC and immobilization of heavy metals. Methylene and methoxy ether were present in BB and CS which is an indication of carbon sequestration. Aryl thio ether (CS) and aromatic CH (BB, WH) is a positive signal for persistence of the biochar.

4 Discussion

Mineral matter (ash), moisture, volatile matter and fixed carbon are generally regarded as major constituents that determine the suitability of feedstocks for biochar production (Antal & Gronli, 2003). The biochar produced from feedstocks can be used as a fertiliser and can be used for carbon sequestration. When feedstocks are classified based on ash content as low (<5%), medium (5-10%) and high (>10%) (Iyer *et al.*, 2002), the rubberwood alone was low while bovine bone, coconut shell and water hyacinth could be classified as high. Suliman *et al.* (2016) reported that the ash content of the feedstock is closely related to biochar yield which was evident in the present study. Keeping the moisture content of the feedstock up to 10% (by weight) appears to be ideal (Collison *et al.*, 2009) as higher moisture contents increase the cost of biochar production. In the present study, WH recorded higher moisture (20.8%) which was above this limit while BB, CS and RW had moisture content within this limit. The volatile matter is naturally high in most feedstocks

Table 3: Properties of biochar derived from waste biomass.

Parameters	BB	CS	RW	WH
pH	6.3± 0.01 ^d	7.6± 0.01 ^c	8.2± 0.01 ^b	8.3± 0.01 ^a
Electrical conductivity ($\mu\text{s cm}^{-1}$)	160.8± 0.15 ^c	102.6± 0.15 ^d	558.9± 0.12 ^b	7569± 0.15 ^a
Bulk density (g cm^{-3})	72.6± 0.02 ^a	45.7± 1.32 ^b	18.8± 0.03 ^c	16.8± 0.07 ^d
Water holding capacity (%)	100.6± 1.4 ^c	57.9± 1.57 ^d	321.1± 1.33 ^b	431.2± 2.4 ^a

Values are mean± standard deviation of three replicates. Mean in each line with different letters are significantly different ($P < 0.05$) by Tukey's HSD.

BB-Bovine Bone, CS- Coconut Shell, RW-Rubberwood, WH- Water hyacinth

which make it easy to ignite (Ciolkosz, 2010). Among the feedstocks volatile matter was high in RW (74.92 %) followed by CS (52.65 %) indicating its easy decomposition by heat (Lam *et al.*, 2016). The fixed carbon content was high in WH (18.75 %) followed by CS (16.02 %) and RW (15.56 %) while BB had the least (1.17 %). Feedstocks with high fixed carbon are able to produce high percentage of biochar during pyrolysis process (Lee *et al.*, 2013).

C, H, N and O values in the present study are similar to those already described for similar feedstocks from different geographical locations (Moreira *et al.*, 2016; Tripathi *et al.*, 2016). The elemental ratios of H/C and O/C explain the degree of aromaticity and bonding arrangement of the feedstocks. In general, the H/C and O/C ratios seemed to be low in the feedstocks particularly in CS which were 0.01 and 0.54 respectively indicating that C in these materials is predominantly unsaturated (Ghani *et al.*, 2013).

The calorific value was highest in CS and lowest in BB. The elements C, H, O are known to improve the calorific value of feedstock (Channiwala & Parikh, 2002).

Cellulose, hemicelluloses and lignin in plant based feedstocks (CS, RW and WH) varied while these components were not detected in BB. Cellulose and lignin form components of biomass and lignocellulosic materials often occur as a mixture of 40-80 wt % of cellulose, 15-30 wt % of hemicellulose and 0-25 wt % of lignin (Carrier *et al.*, 2011). High cellulose content was obtained in WH which increased up to 64 % compared to other feedstocks. Hemicellulose content of these feedstocks was more or less on par. Lignin content showed normal (CS) to higher (RW) levels however too low in WH. These values fall within the broad range of values obtained with other biomass materials in earlier studies (Abnisa *et al.*, 2013; Mary *et al.*, 2016; Shariff *et al.*, 2016). More extractives in biomass feedstocks contribute to liquid and gas products either through simple volatilization or decomposition (Shariff *et al.*, 2016).

Earlier reports indicate that the relative amount of cellulose, hemicelluloses and lignin could significantly influence char yield (Abnisa *et al.*, 2013). Lee *et al.* (2013) reported that feedstock with high hemicelluloses and cellulose content could produce higher char yield during pyrolysis process. According to Mokrzycki *et al.* (2020) high cellulose content in the feedstock often lead to the formation of volatile products and high char yield. If that is the case, the increased char yield obtained in WH is quite normal because the WH feedstock showed a high value for cellulose and extractives. Conversely, BB, which had no detectable quantities of these components exhibited higher char yield in the present study remains as a fact which is surprising and warrants special attention. In this context, it is worth mentioning the finding of Domingues *et al.* (2017) and Tomczyk *et al.* (2020) that inorganic compound such as P, K, Ca and Mg results in high ash and biochar yield. This finding holds good in our study because a high value of P and Ca was detected in BB and it can have lead to the high char yield.

Biochar production and characterisation

The SEM images of biochar revealed the presence of aligned honeycomb like groups of pores which are thought to have evolved consequent to the removal of condensed volatiles and other decomposition products that block porosity (Demirbas, 2006) during pyrolysis. All the biochars showed porous structure with different size. The four types of biochars holds microporous structure with varying shape. WH has the greatest porosity of around 9 μm followed by CS and RW with porosity around 8 and 5 μm which help them to carry bacteria and mycorrhiza (Mangrich *et al.*, 2015). The microporous nature of biochar helps to retain water thus increasing water holding capacity (Quilliam *et al.*, 2013), allows the movement of roots through the soil (Downie *et al.*, 2009), and serve as a safe nest for various microorganisms to survive and proliferate (Pietikäinen *et al.*, 2000; Quilliam *et al.*, 2013). So, WH and CS biochars can act as a suitable

Table 4: Functional groups and components in biochars.

Wave number (cm ⁻¹)	Functional group assignment	Role of functional groups	Reference	Detected Biochar
3431.83, 3427.05, 3394.60, 3342.52	OH stretch	Sorption of water; ion exchange	(Yang <i>et al.</i> , 2019)	BB, CS, RW, WH
3037.26	Terminal (vinyl) C-H stretch	Mineralization	(Singh <i>et al.</i> , 2016)	RW
3035.54	Ammoniumion	Adsorption of pollutants, catalysis, energy storage immobilization and release of nutrients	(Godwin <i>et al.</i> , 2019; Leng <i>et al.</i> , 2020)	CS
2925.43, 2847.67	Methylene C-H asymmetric/symmetric stretch	Carbon sequestration; mitigate climate change	(Shareef & Zhao, 2017)	BB
2900.02	Methylene C-H stretch	Carbon sequestration; mitigate climate change	(Shareef & Zhao, 2017)	CS
2835.2	Methoxy methyl ether O-CH stretch	Carbon sequestration; mitigate climate change	(Shareef & Zhao, 2017)	CS
1651.21	Alkenyl C=C stretching	Adsorption	(Abd-Elhamid <i>et al.</i> , 2020)	BB
1613.62	Aromatic ring structure	Persistence of charcoal	(Glaser <i>et al.</i> , 2001)	WH
1578.44, 1571.87, 1556.41	Secondary amine NH stretch	Adsorption of pollutants, catalysis, energy storage immobilization and release of nutrients	(Godwin <i>et al.</i> , 2019; Leng <i>et al.</i> , 2020)	CS, RW, WH
1455.74, 1430.27, 1429.19	Carbonateion	Ion exchange; promote adsorption and immobilization of heavy metals	(Leng <i>et al.</i> , 2020; Yang <i>et al.</i> , 2019)	BB, RW, WH
1417.32, 1411.69	Carboxylate	Ionised and influence soil charges- sorption, increase CEC, heavy metal stabilization	(Leng <i>et al.</i> , 2020; Uchimiya <i>et al.</i> , 2012)	BB, CS
1362.28	Phenol or tertiary alcohol, O-H bend	Sorption of water and other hydrous materials; ion exchange	(Yang <i>et al.</i> , 2019)	CS
1259.52, 1258.12	Organic phosphate, P=O stretch	Nutrient element, precipitator for heavy metals, mineralization, immobilization and release of nutrients	(Xiao <i>et al.</i> , 2018)	CS, RW
1102.84	Sulfate ion	Promote adsorption and immobilization of heavy metals	(Yang <i>et al.</i> , 2019)	WH
1035.71, 959.85	Aromatic C-H in plane bend	Persistence of charcoal	(Glaser <i>et al.</i> , 2001)	BB
1030.32	Aliphatic phosphate P-O-C stretch	Nutrient element, precipitator for heavy metals, mineralization, immobilization and release of nutrients	(Xiao <i>et al.</i> , 2018)	BB
874.57, 874.22, 873.89, 871.57	Peroxides, C-O-C stretch	Degree of aging or oxidation	(Nguyen & Lehmann, 2009)	BB, CS, RW, WH
819.03	Nitrate ion	Adsorption of pollutants, catalysis, energy storage, immobilization and release of nutrients	(Godwin <i>et al.</i> , 2019; Leng <i>et al.</i> , 2020)	RW
810.64	Epoxy and oxirane rings	Degree of aging or oxidation	(Chen <i>et al.</i> , 2019; Leng <i>et al.</i> , 2020)	CS
754.43	Aryl thioethers, (C-S stretch)	Persistence of charcoal	(Glaser <i>et al.</i> , 2001)	RW
748.39	Methylene-rocking	Carbon sequestration; mitigate climate change	(Shareef & Zhao, 2017)	CS
713.07	Alcohol, OH out of plane	Sorption of water and other hydrous materials; ion exchange	(Yang <i>et al.</i> , 2019)	RW
603.17, 602.85, 565.35, 562.65	Disulfides (S-S stretch)	Promote adsorption and immobilization of heavy metals	(Chen <i>et al.</i> , 2019)	BB, RW

BB- Bovine Bone, CS-Coconut Shell, RW-Rubberwood, WH-Water hyacinth

habitat for microorganisms, decrease water stress, and will enhance the movement of roots.

The elemental weight of C, H, N and O were high in plant derived biochars which is in congruence with earlier findings (Ramzan *et al.*, 2011; Tillman, 2000). The presence of considerable amounts of alkaline metals in the biochar suggests its potential as soil amendments for enhancing soil fertility, increasing soil organic carbon, and reducing soil acidity. O/C and H/C ratios are indicators of carbonization process during pyrolysis (Weber & Quicker, 2018). It also explains the longevity of biochars in the environment. Biochars with O/C ratios < 0.2 are regarded as most stable (>100 years), between 0.2 and 0.6 are moderately stable (100 to 1000 years), < 0.6 are unstable (<100 years) (Spokas, 2010). In this regard RW is most stable and CS is moderately stable. H/C ratio less than 0.7 indicates fused aromatic ring structure of biochar (Ippolito *et al.*, 2020). The H/C ratio < 0.3 of biochar defines its N₂O mitigation property (Cayuela *et al.*, 2015). So, all the biochars in our study have N₂O mitigation property and have fused aromatic ring structure.

The pH of biochar is in accordance with the findings of Jiang *et al.* (2012) and Machado *et al.* (2018) that most biochars have a pH value within the alkaline range. Previous reports showed that, high pH of biochar leads to increase in ash content (Qayyum *et al.*, 2015). The increase in electrical conductivity was manifold in WH compared to other biochars. High C content is suggested to be a reason for the high EC of biochars (Gabhi *et al.*, 2017). The electrical conductivity of biochar also depends on the type of feedstock and the pyrolysis temperature. At higher temperatures the ash content increases by the loss of volatile components (Cantrell *et al.*, 2012). Low bulk density is considered as a desirable characteristic of biochars and it appears to be mostly due to high porosity which facilitates greater movement of roots, water and ion exchange (Downie *et al.*, 2009). Further the increased porosity might have facilitated the accommodation of more water in its spaces resulting in the highest water holding capacity of WH biochar.

The chemical interaction between biochar and environment is governed by its surface chemistry (Ghani *et al.*, 2013). The surface functional groups of the four biochar samples were hydroxyl, alkane, alkenyl methyl, carboxyl, carbonate, nitrate, phosphate, thioester and peroxide suggesting that these biochars could be used as soil amendment for improving sorption of water, ion exchange, release of nutrients, adsorption of pollutants, immobilisation of heavy metals and C sequestration.

Implications for soil amendment

The chemical and physical characteristics of the four biochars under study showed that they can be used as a soil

amendment to improve the water retention, carbon sequestration, soil structure and fertility. The porosity, water holding capacity and bulk density of all the four biochar types were almost similar or higher than found in previous studies using the same biomass resources (Hariz *et al.*, 2015; Piash *et al.*, 2016; Devens *et al.*, 2018). So, these biochars can be used to improve soil physical characteristics. Biochars also contain qualitative minerals in high percentage (Piash *et al.*, 2016; Bao *et al.*, 2021; Hussain *et al.*, 2021). So, it also helps to improve the chemical properties of the soil such as carbon sequestration, mineral cycling, microbial diversity and soil fertility.

5 Conclusion

The results showed that pyrolytic conversion of the four indigenous biomass resources into biochar is possible using the standardized in-farm method. The ash content, moisture content, volatile matter, fixed carbon, C, H, N, O percentage, calorific value, cellulose, hemicelluloses and lignin content of feedstocks affected char yield and elemental composition of biochars. Physiochemical analysis and biochar structure analysis revealed different elemental and functional group composition, porosity and water holding capacity and EC for each biochar. Properties of the biochar produced from these biomass resources showed their potential as good soil conditioners. Though the char yield was more in BB (animal derived biochar), the plant derived biochars (RW, CS, WH) had higher value for carbon. High pH, low bulk density, high porosity, high water holding capacity and high elemental composition of the WH biochar makes it unique as a liming agent, soil conditioner and source of nutrients compared to other plant based and animal based biochars studied. By pyrolytic conversion of WH into useful biochar, an efficient disposal of this weed which is a menace to the environment is also achieved.

Conflict of interest

The authors declare that they have no conflict of interest.

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