PREPARATION AND CHARACTERIZATION OF BIOCHAR FROM BAW-ZA-GAING (*Leucaena leucocephela* (LAM.) DE WIT)

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Abstract

The aim of this research is to study the preparation and characterization of biochar which made from Baw-za-gaing (*Leucaena leucocephela* (Lam.) De Wit). Firstly, ash content (1.2 %), moisture content (2.65 %) and bulk density (0.85 g mL^{-1}) were determined in the plant material. The biochar (17.64%) obtained was characterized by EDXRF, SEM, UV and FT IR. By EDXRF analysis, K, Ca, S, Fe, Cu, Zn, Rb, and Sr were detected in wood chips of Baw-za-gaing but Ca, P, Cl, K, S, Fe, Sr, Cu, Mn, Zn were detected in its biochar. EDXRF analysis showed Ca and K as the most abundant elements in both biochar and wood chips. Besides, Mn, Fe, S, Sr, Zn and Cu were found to be present in both biochar and wood chips samples, except P which was detected only in biochar. The porous structures of wood chips of selected plant materials (samples) and its biochars were studied by SEM spectroscopic techniques.Some organic functional groups such as aromatic ring, C=C, C–H, C–O, $–CH_2–$ and $–CH_3$ groups, *etc.* , were studied by UV and FT IR spectrosopic techniques. The plant nutrients such as nitrogen and phosphorous were determined by chemical methods and that of potassium by AAS spectroscopic technique. The nitrogen content (3.10 %), potassium content (5.25%) and phosphorus contents (0.03%) were practically determined for biochar obtained from the plant sample. Elemental analysis of biochars was carried out by AAS (Atomic Absorption Spectroscopic Technique). These were found that Ca, K, Fe, Cu, Zn, Mn and Sr in biochar.

Keywords: Biochar, Plant nutrients (N, P, K) contents, Baw-za-gaing, Wood chips, Spectroscopic techniques

Introduction

Biochar is a subject of current debate. It is commonly defined as the product of thermal decomposition (300-1000 ºC) of organic matter (biomass feedstock), under limited oxygen conditions, also known as pyrolysis (IBI, 2011). As a material, biochar is charcoal, since charcoal is the term generally used for 'charred organic matter'. However, from both soil science and environmental quality perspectives, a distinction needs to be made between

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the two, as recommended by Verheijen *et al.*, (2010). It is the view of these authors that this distinction should be based on their function. While charcoal is mostly used as a fuel (*e.g*. heating), biochar is meant for application to soils and thus, caution needs to be taken for preventing any deleterious impact on the quality of soil and ground and surface waters (Verheijen *et al*., 2010). Charcoal is a product of incomplete combustion of organic material (mostly wood and vegetation), from events such as wildfires, and is therefore naturally present in soils around the world (Preston and Schmidt, 2006). Large deposits of charcoal in soils were specifically found in the Amazon region, commonly known as 'Terra Preta' (or Dark Earths). 'Terra Preta' are highly fertile soils, but this charcoal does not have a natural origin, rather it was concentrated there alongside a mixture of other residues, including animal and fish bones, animal shells and pieces of pottery (Sohi *et al*., 2009). However, it is the link between the presence of charcoal and their fertility that is the base for today's concept of biochar. Biochar application to soils is thus expected to improve soil properties, processes and functions (Lehmann and Rondon, 2006; Jeffery *et al*., 2011) and in that way, help to meet current agricultural challenges, including food security (Collison *et al*., 2009). On a different scale, biochar is also being suggested as a means of sequestering carbon (C) in soils, particularly when used in combination with other strategies for a balanced way to combate climate change (Verheijen *et al*., 2010). The main reason behind biochar's capability to be a C sink in soils is its environmental recalcitrance, with long mean residence times in soil estimated (for wood biochar) to be in the range of hundreds to thousands of years, compared to that of natural organic matter (NOM) or other common organic soil amendments, which are rapidly mineralised to carbon dioxide (CO_2). The debate on 'biochar' is being further extended to other domains (e.g. remediation of environmental pollutants, renewable energies, waste management), where it is also expected to provide a solution to some of the current problems (Collison *et al*., 2009; Verheijen *et al*., 2010)

Materials and Methods

Collection and Preparation of Sample

The sample, Baw-za-gaing was collected from an area of 20-Quarter, Shwepyithar Township, Yangon Region. It was cut into many pieces of nearly

equal size, which was 1.5 cm in length and 0.4 cm in width. And then, they were kept in air to dry at room temperature for a few weeks and dried in an oven at 99 ºC for 4 h because of its moisture content.

Determination of some Parameters of Plant Materials

Determination of Bulk Density of Samples

A clean dry 10 mL graduated cylinder was weighed. It was then filled with the dry sample to the 10 mL mark and reweighed. The graduated cylinder was placed in a tapping box and the cylinder was gently tapped until there was no more reduction in volume. The minimum volume was recorded and the bulk density was calculated (Antal and Gronli, 2003). The results are illustrated in Table 1.

Determination of Moisture Content (Oven Drying Method)

Into a flat–bottom metallic dish, finely divided asbestos were spread in a thin layer. It was firstly dried at 110 ºC for 1 h and the dish was covered, cooled and weighed. 20 g of sample was uniformly spread over the asbestos layer. It was weighed as quickly as possible to avoid loss of moisture. The cover was removed and dried in a hot air oven at atmospheric pressure. A temperature of 100 ºC was maintained in the case of plant tissue. The duration of heating will vary with the type of tissues; 16 – 18 h is sufficient for most tissues. After drying, the lid was replaced, the sample was cooled in a desiccator, and it was reweighed. The sample was reheated, if necessary, until the consecutive weighing do not vary by more than 3 – 5 mg. Tissues which contain volatile organic constituents or high percentage of sugars cannot be brought to a constant weight. In such cases, a compromise procedure must be adopted. A standard technique should be employed. Drying at 55 ºC for four days is generally suitable. The sample after determination of moisture content–could be used for ashing and estimation of minerals. The results were shown in Table 1.

Determination of Ash Contents of Plant Materials

Accurately weighed about 10 g of some plant material: Baw-za-gaing was placed in tared porcelain crucible and the organic matter was dried and burnt off without flaming and finally heated in a muffle furnace at 823 K (550 ºC). Heating was continued until the resultant ash was turned into white

in color and free from particles of unburnt carbon and fused. Then, the crucible containing the residue was cooled to room temperature in a desiccator and weighed. Heating, cooling and weighing were repeated until a constant weight was obtained. The ash content was then calculated. The result is shown in Table 1.

Preparation of Biochar from Baw-za-gaing

Accurately weighed 600 g wood chips of prepared sample (Baw-za-gaing) was put into top-lit up draft (TLUD) Furnace. Three nails, which were triangle in position, were placed under a TLUD can. One–third of sample was mixed with fuel such as absolute ethyl alcohol (25 mL) and it was put into a TLUD-can as a top-layer. Then, they were started to burn with a candle flame. As burning continues, the crown was set up at the top of TLUD – can and then chimney, two feet height, was kept over the crown. After complete burning, a blue coloured smoke came out and it was stopped to prevent-ventilation because air entered from bottom to top during burning which rose in temperature 252 ºC by using two feet chimney height for 26 min and it was allowed for cooling. And then, the weight of biochar was calculated (Antal and Gronli, 2003).The result was shown in Table 2.

Characterization of Biochars by Modern Spectroscopic Techniques

FT IR Analysis

Biochar sample (using KBr) was first inserted (biochar sample including KBr) in the sample holder (cassette). Then using air as reference, FT IR spectrum of the pellet was recorded. FT IR spectrum of the sample described in Figure 1 shows the characteristic feature of FT IR spectrum of the sample. Table 4 shows the spectral assignment for the Baw-za-gaing biochar.

UV Analysis

Biochar sample which dissolved in methanol was first inserted in the sample holder (cassette). Then using air as reference, UV measured in solution were also recorded. The characteristic feature of UV- spectra of samples shows the spectral assignment for biochar samples.

SEM Analysis

The wood chip of Baw-za-gaing and the prepared biochar samples were analysed by using Scanning Electron Microscopy. The photographs are shown in Figures 2(a) and 2 (b).

EDXRF Analysis

Materials used for the EDXRF analysis were the wood chip and the prepared biochar of Baw-za-gaing sample. EDXRF model is Rigaku X-ray Diffractometer, RINT 2000/PC software, Cat. No. 9240 J101, Japan. Copper tube with nickel filter was used for the analysis. The EDXRF spectra of samples are shown in Figures 3 (a) and 3 (b).

Determination of Plant Nutrients in Biochar

Determination of Nitrogen Contents in Biochar (Micro Kjeldahl Method)

(a) Digestion

0.1 g of finely ground biochar was transferred to a Kjeldahl flask. 1mL of salicylic acid sulphuric acid mixture was added and thoroughly mixed. After 20 min, approximately 0.3 g sodium thiosulphate was added and gently heated until fumes are evolved. The mixture was cooled and 0.06 g of catalyst and 0.75 mL nitrogen free H_2SO_4 were added. The mixture was heated on a digestion rack (electric) over a small flame for about an hour until the solution became apple green in colour. The digested sample was cooled and diluted with about 10 – 15 mL of distilled water to dissolve the sample.

(b) Distillation

The digest was transferred to the flask of the distillation unit through the side tube. The digestion flask was repeatedly washed with 2 – 3 mL of distilled water so that no digest was left in the flask. Excess of 40 % NaOH was added to the flask and the distillation process was continued. A conical flask was placed below the condenser containing 5 mL of 2 % boric acid solution. The distillation process was continued until20 mL of distillate collects in the receiving flask.

(c) Titration

Two drops of Conway's indicator was added to the conical flask containing boric acid and it was titrated against 0.01 N HCl until a faint pink

colour is obtained. Blank determination (without sample) using all the reagents as in the case of sample (Burzarbarua, 2000). The result is shown in Table 3.

Determination of Phosphorus Content in Biochar (Colorimetric Method)

2 mL of digested sample extract was transferred into 25 mL volumetric flask. A few drops of 2, 4-dinitrophenol indicator was added and the contents was neutralized with 4 N ammonia solution. Any excess of ammonia was neutralized with 2 N H_2SO_4 and the volume to about two third of the flask was made with water. 1 mL of sulphomolybdate solution was dispensed into it. The neck of the volumetric flask was washed with distilled water, and 0.5 mL of freshly prepared stannous chloride solution was added. The contents were thoroughly mixed and the volume was made to 25 mL. Then, within 4 to 20 mins the absorbance was recorded at 660 nm using a spectrophotometer. Following the above procedure a standard curve containing 0.2 – 1.0 ppm phosphorus was prepared. The amount of phosphorus in the sample was found out from the standard curve and the results were expressed as mg /100 g dry weight of the sample after taking into account the dilution factors. The result is shown in Table 3.

Determination of Potassium Content in Biochars

The atomic absorption spectrophotometer was switched 'ON' and the instrument was allowed to warm up as per the instruction in the user's manual. The appropriate combination of flame gases were used for a specific mineral to be assayed using appropriate gas pressure so as to get an optimum height of a non-luminous flame. The recommended hollow cathode tube was checked that pertaining to the mineral to be analyzed was fitted into the instrument. One by one different volumes of the standard solutions were introduced for preparation of a reference curve using the standard conditions for the mineral to be analyzed after compensation for the blanks. The sample mineral extract to be analysed was aspirated into the instrument and the observation was recorded after compensation for the blanks. Readings of the standard solutions were periodically taken in between the samples to ensure proper functioning and reproducibility of the instrument response. The result is shown in Table 3.

Results and Discussion

Collection and Preparation of Samples

Myanmar, our country, was covered with many forest areas where different types of trees are growing naturally. Some of them were also cultivated for uses. So, the plant materials, namely baw-za-gaing was collected to prepare biochar. The material is abundantly found in our environment. Biochar could come from just about any thermochemical processing of a carbonaceous material. Feedstocks could include agricultural wastes potential biochars could come from just about any thermochemical, forestry residues, used tires, old building materials, municipal solid wastes, *etc*. Those feedstocks and processes suitable for the production of biochar are, in reality, limited by feedstock material safety and availability, market conditions for biochar and its process co-products, local soil properties, and the combined environmental impacts. After collection of sample, it was firstly cut into small pieces of sample, dried to get moisture content less than 10 %, and then it was stored for the preparation of biochar.

Some Parameters of Baw-za-gaing

Bulk density

Bulk density is an important property of biomass that directly affects the costs of distribution and storage. The bulk density as the physical characteristic depends on material composition, shape and dimensions of particles, orientation of particles, their density and size distribution, moisture content, pressure, contamination degree, rate and kind of deposit formation. The bulk density of Baw-za-gaing was found to be 0.85 g mL^{-1} (Table 1).

Table1: Some Parameters of Baw-za-gaing for the Preparation of Biochars

Parameter	Bulk density (g mL^{-1})	Moisture content (%)	Ash content (%)
Baw-za-gaing	0.85	2.65	1.2

Moisture content

Moisture content of Baw-za-gaing determined by drying in an oven was observed to be 2.65 %. This method consists in measuring the weight loss by plant materials due to the evaporation of waters. Drying methods are generally used as they give accurate result was found to be 2.65 % as shown in Table 1.

Ash content

Ash content of plant materials represents inorganic residues remaining after destruction of organic matter. It may not necessarily be exactly equivalent to the mineral matter as some changes may occur due to volatilization or some interaction between constituents. High ash content and / or a low alkalinity of the ash may in some cases be suggestive of the presence of adulterants. The acid insoluble ash is a measure of sand and other siliceous matter present. Difficulty of effecting complete combustion in some sample, and the possible loss by volatilization on ignition may be overcome by moistening the substance to be ignited or the carbonaceous residue there from with concentrated sulphuric acid. The ash content in Baw-za-gaing was found to be 1.20 % as shown in Table 1.

Biochar from Baw-za-gaing

Biochar was firstly prepared from baw-za-gaing by using two feet height of chimney and the rise in temperature was recorded. Furthermore, biochar was prepared at different chimney heights (1.0 to 3.0 ft) and the rise in temperatures are recorded. In the preparation of biochar by changing the chimney height, the yield percent was the highest at 2.0 ft (17.64 %) and 1.5 ft (17.64 %) heights. The results are shown in Table 2.

Table 2: Biochar Prepared from Baw-za-gaing Wood at Different Chimney Heights

Sample No.	Chimney height (ft)	Sample wt (g)	Time taken (min)	Temperature (ºC)	Product wt (g)	Yield (%)
I	1.0	400	18	280	50	12.50
II	1.5	400	18	289	75	17.64
III	2.0	400	18	300	75	17.64
IV	2.5	400	20	320	50	12.50
V	3.0	400	17	300	50	12.50

Plant Nutrients in Biochars

Nitrogen content in biochars

Nitrogen content is estimated by the micro Kjeldahl method which is based on the determination of the amount of reduced nitrogen (NH_2 and NH) present in the sample (char). The various nitrogen compounds are converted into ammonium sulphate by boiling with concentrated H_2SO_4. The ammonium sulphate formed is decomposed with an alkali (NaOH), and the ammonia liberated is absorbed in excess of neutral boric acid solution and then titrated with standard acid. The result (3.10 % nitrogen content in biochar) is shown in Table 3.

Table 3: Plant Nutrients in Biochars

Sample	Nitrogen content (%)	Phosphorus content (%)	Potassium content (%)
Baw-za-gaing	3.10	0.03	0.18

Phosphorus content in biochars

For the determination of total phosphorus, the sample in which organic matter has been destroyed by tri-acid mixture is used. The phosphate containing solution is treated with sulphomolybdic acid to produce phosphomolybdic acid. This is then reduced by stannous chloride giving a blue coloured complex whose colour intensity is proportional to the amount of phosphate in the preparation. The phosphorus content of biochar was found to be 0.03 % (Table 3).

Potassium content in biochars

The atomic absorption spectrophotometry may be used for the determination of potassium content. The plant tissue must first be properly processed before its introduction into the atomic absorption spectrophotometer (AAS). Dry ashing can effectively be used for determination of potassium in plant tissue. Baw-za-gaing biochar was observed to contain 0.18 % of potassium.

Characterization of Biochars by Modern Spectroscopic Techniques

FT IR analysis of biochars

Fourier transform infrared spectroscopy (FT IR) is frequently used to identify and qualitatively track changes in functional groups in biochar. Since, biochars are opaque solids, an FT IR analysis requires special sample preparation and/or detection method. Some common methods include conventional transmission FT IR using potassium bromide (KBr) pressed pellets. A char sample set of FT IR spectrum is shown in Figure1. Important peaks in the biochar spectrum are the O-H stretch (3400 cm^{-1}), the aliphatic C-H stretch (3000-2860 cm^{-1}), the aromatic C-H stretch (3060 cm^{-1}), the carboxyl (C=O) stretch (1700 cm^{-1}) and the various aromatic ring modes at 1590 and 1515 cm^{-1}. As the pyrolysis reaction progresses, certain peaks (O-H stretch and carboxyl C=O stretch) disappeared, the CH peaks shifted from being more aliphatic to more aromatic (and eventually disappear altogether), and peaks representing aromatic carbon compounds begin to appear. FT IR spectrum indicates peak changes and helps identification of functional groups. Observed prominent peaks and its associated functional groups are given in Table 4.

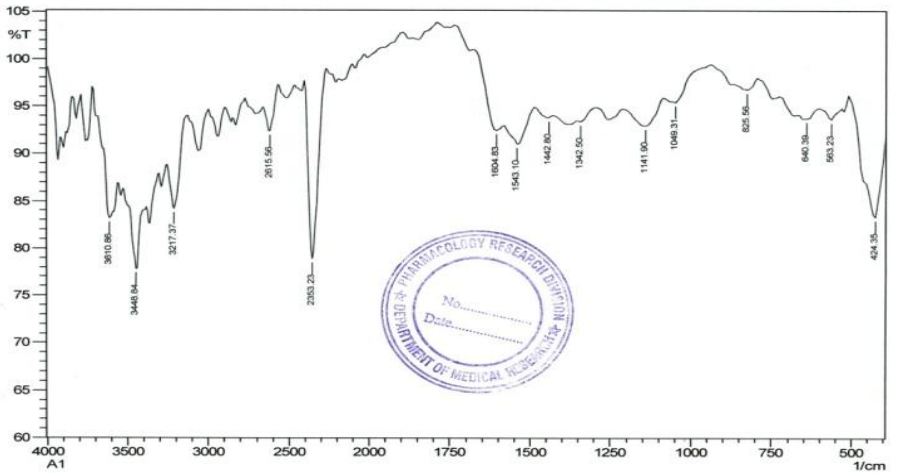


Figure 1: FT IR spectrum of biochar (Baw-za-gaing)

Table 4: Infrared Spectral Assignment of Biochar

Observed band (cm^{-1})	Mode of Vibration
3448	ν_{O-H}
3217	ν_{C-H} (arC–H gp)
3050	ν_{C-H} (arC–H gp)
1604	$\nu_{C=C}$ (aromatic)
1543	$\nu_{C=C}$ (aromatic)
1442	$\nu_{C=C}$ (aromatic)
1342	δ_{C-H} (alkane gp)
1141	ν_{C-O} (C-O-C gp)
825	δ_{C-H} (aromatic)

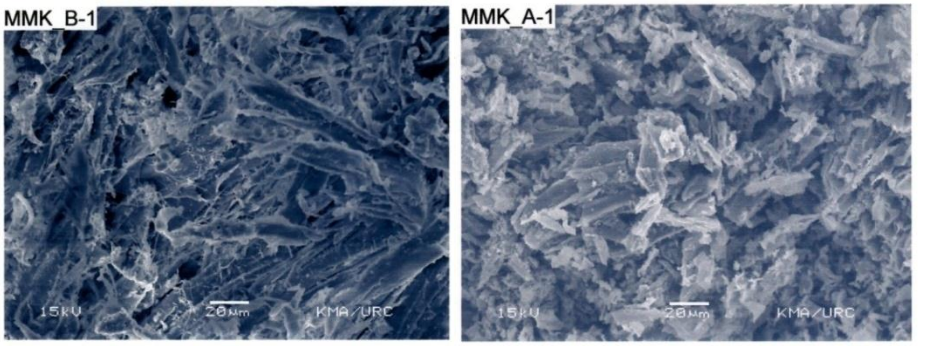
UV analysis of biochars

In analysis of UV for biochars prepared from Baw-za-gaing, the interaction of UV and visible radiation with matter could provide qualitative identification of molecules and polyatomic species, including ions and

complexes. The shape and intensity of UV/VIS absorption bands related to the electronic structure of the absorbing species. This would focus on the relationship of the absorption to the structure of simple organic molecules. Strong bands around 215 and 245 nm suggest a phenolic structure.

SEM analysis of biochars

SEM images indicate structural changes between raw Baw-za-gaing plant sample and biochar. Surface area increase was observed in biochar. Fragmentation of structure favoured increased adsorptive properties for biochar with increased porosity due to slow pyrolysis. SEM study of Baw-za-gaing clearly showed the microporous and microtubular structures for the cross-sectional and longitudinal sections of the prepared biochar. SEM images of raw sample of plant material (Baw-za-gaing wood chips) and biochar produced are shown in Figures 2(a) and 2(b).

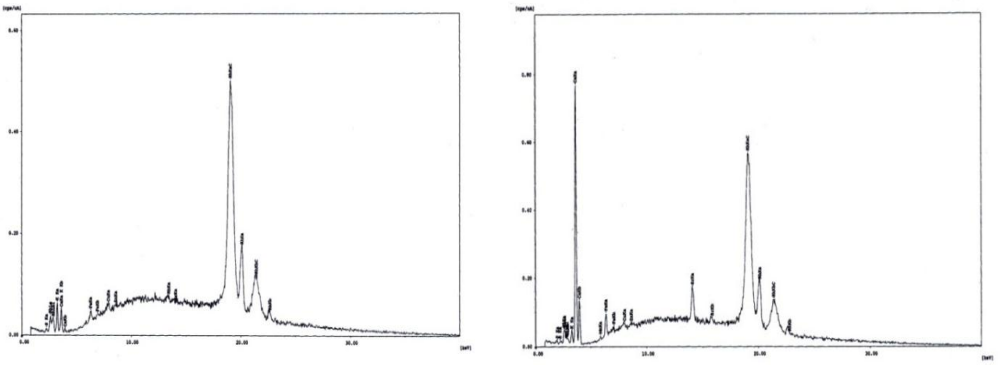


(a) (b)

Figure 2: (a) SEM microphotograph of woodchips (Baw-za-gaing)
(b) SEM microphotograph of biochar (Baw-za-gaing)

EDXRF analysis of biochars

The elemental analysis and the ash composition of the baw-za-gaing wood chip and its biochar were determined by EDXRF. Due to the nature of the samples and the calibration method, the relative concentrations of the elements are accurate, but the overall mineral content in the char is overestimated.



(a) (b)

Figure 3: (a) EDXRF spectrum of woodchips (Baw-za-gaing)
(b) EDXRF spectrum of biochar (Baw-za-gaing)

Table 5: EDXRF Data of Wood Chips and Biochar from Baw-za-gaing

Wood chips (Baw-za-gaing)		Biochar (Baw-za-gaing)	
Analyte	Relative abundance (%)	Analyte	Relative abundance (%)
K	38.449	Ca	67.816
Ca	32.980	P	11.121
S	15.226	Cl	6.815
Fe	5.321	K	5.257
Cu	3.241	S	3.044
Zn	2.058	Fe	2.907
Rb	1.552	Sr	1.138
Sr	1.172	Cu	0.765
		Mn	0.571
		Zn	0.567

In EDXRF analysis of biochar and woodchips from Baw-za-gaing, the EDXRF spectra as shown in Figures 3(a and b)showed the relative abundant elements such as Ca, K, S, Fe, Cu, Sr, P, Cl, Mn, Rb and Zn. But, it did not show Mn and Cl in woodchip. The content of element, K, was found to be the highest in woodchips and that of Ca was the highest in biochar and Sr was the least in woodchips but Zn was the least in biochar. The results are shown in Table 5.

Conclusion

In the preparation of biochar, it could be concluded that the prepared biochar was obtained in 17.64 % yields from Baw-za-gaing wood chips. Bulk density of Baw-zagaing 0.85 g mL^{-1} were determined. Moisture content was found out to be 2.65 % and ash content was found to be 1.20 % in Baw-za-gaing. By EDXRF analysis, K, Ca, S, Fe, Cu, Zn, Rb, and Sr were detected in wood chips of Baw-za-gaing but Ca, P, Cl, K, S, Fe, Sr ,Cu, Mn, Zn were detected in its biochar. SEM study clearly shows the microporous and microtubular structures for the cross sectional and longitudinal sections of the prepared biochar. Some characteristics of organic functional groups such as aromatic, C=C, C–H, C–O, $–CH_2–$, $–CH_3$, *etc.*, in the biochar was studied by UV and FT IR spectroscopic techniques. The plant nutrients such as nitrogen, phosphorus, and potassium contents in biochars were also determined. The nitrogen content of biochar from Baw-za-gaing was determined to be 3.10 %. The phosphorus content of biochar from Baw-za-gaing were 0.03 %. The potassium content in biochar Baw-za-gaing was also determined as 0.18 %. The biochars produced by the present method should be useful as soil amendment in agriculture.

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