Comparative Analysis of Biochar Derived from Rice straw and Soybean straw

ABSTRACT

Aim: Recycling agricultural postharvest waste and re-introducing it again into farmland is one of the tangible ways to address zero waste dream, soil infertility and climate change. Pyrolysis of crop leftovers into biochar remains the most acceptable alternative for proper management of crop waste. The possibility of sustainable biochar production practices and multi-functionality features makes it promising to fufill an increasing demand for soil amendment, agricultural sustainability, environmental protection, cutting-edge materials and mitigation of climate change.

Methodology: Same amount (14450 g) in feedstock of rice straw (RS) and soybean straw (SS) undergo slow pyrolysis separately to produce biochar. Physical (percentage yield, moisture, ash, volatile matter, bulk density, pH ,electrical conductivity), chemical characterization (Microwave Plasma Atomic Emission Spectroscopy (MP-AES), Scanning Electron Microscope Energy Dispersive X-ray (SEM-EDX), Fourier Transformed Infrared (FTIR) and Thermogravimetric Analysis and Derivative Thermogravimetry (TGA and DTA)) and evaluation of bochar was determined. Lower char yield of 25.6% in soybean straw biochar (SSB) was observed when rice straw biochar

Results: (RSB) recorded a higher char yield of 42.1% . Both lignocellulosic biochars were black and porous with a higher silica (10.6%) content in RSB and higher carbon (82.2%) content in SSB as was revealed by SEM-EDX. Higher ash 27.1%, volatile matter (VM) 31.3% and moisture 29.4% content was seen in RSB compared to SSB because of feedstock composition. Rice straw biochar show higher peaks of macro and micro mineral elements K(14561.21mg/kg), Ca(2401.28 mg/kg), and Na(1735.27 mg/kg) than soybean straw biochar. FTIR was used to identify functional groups that might act as cation adsorbents. As the temperature increased, the TGA and DTG graphs showed mass loss and sample breakdown.

Conclusion: Rice and soybean crop wastes were converted into biochar, a nutrient-rich material that maybe utilized to balance acidic soils promoting healthy plant growth and also protecting the environment.

Keywords: Recycling; postharvest waste; pyrolysis; biochar; climate change.

1.0 INTRODUCTION

Postharvest leftovers make up a sizeable portion of agricultural biomass. Straw, husks, peels, leaves, and other plant parts that are usually thrown away during processing or left behind in the field to waste [1,2]. Plant postharvest waste needs to be managed and used effectively for agricultural and environment sustenance.The production of biochar, a highly porous and stable form of carbon, involves a thermochemical process that breaks down organic material at high temperatures under limited oxygen. Biochar, bio-oil, and syngas are the three main products that are produced from feedstock through this method. The primary focus is on biochar, the solid residue, because of its numerous advantages for agriculture and the environment [3]. Scientists first became interested in biochar in the late 20th century when they discovered how well it could trap carbon and improve soil fertility. The discovery of Terra Preta prompted studies into the application of biochar to simulate these rich environments elsewhere in the world [4]. The application of biochar to soils can improve soil structure, increase water retention, and enhance nutrient availability, hence promoting plant growth and crop yield [5,6]. Furthermore, it has been demonstrated that biochar sequesters carbon, lowering greenhouse gas emissions from soils and assisting in the mitigation of climate change [7,8]. Biochar, which immobilises organic pollutants and heavy metals to promote soil health and crop productivity in contaminated areas, can be added to agricultural soils to reduce emissions of methane and nitrous oxide, two potent greenhouse gases associated to agricultural operations [9-12]. Difference in biochar characteristics result from varying feedstocks, pyrolysis temperatures, and durations, which makes cross-study comparisons difficult [3]. Not every study thoroughly describes the chemical and physical characteristics of the biochar that was produced. Comparing data and drawing broad generalizations regarding the usefulness of biochar is challenging due to this inconsistent reporting [13]. This discrepancy makes evaluating the comparative efficacy of biochar more difficult [14]. Comparisons between studies could be deceptive if these characteristics are ignored [15]. According to Sohi *et al.*, [16] the comparability of study findings was hampered by the absence of consistent measurements. To properly evaluate research findings, biochar must be thoroughly and consistently characterized. Thorough understanding of the characteristics of biochar can aid in pin-pointing the particular circumstances in which biochar functions best [13]. This research seeks to produce biochar from rice straw and soybean straw characterize the physico-chemical properties and compare the biochars.

2.0 MATERIALS AND METHODS

Mortar, pestle, sample container, kiln, desiccator, crucible, pH meter, measuring cylinder, beaker, stirring rod, oven, analytical weighting balance, furnace, conductivity meter, distilled water, sieve, polyethylene bag and spreading mat. Microwave Plasma Atomic Emission Spectroscopy (MP-AES), Scanning Electron Microscope (SEM), Fourier Transform Infrared Spectroscopy (FTIR) and Thermogravimetric Analysis (TGA and TGA) are the instrumental techniques used in this study.

2.1 Sample Collection and Preparation

Sack bags were used to collect rice straw and soybean straw from Air Force Base Farm in Makurdi Local Government Area of Benue State. The samples were transported to Ministry of Agriculture, Benue State Government in Makurdi for identification. Spreading mat was used to sun-dry the biomass and sorting was carried to remove impurities. After sun-drying for 10 days to get rid of excess moisture. The biomass was cut 8-10 cm for length reduction.

2.2 Methods

2.2.1 Biochar production.

Separately, same amount (14450 g) of rice straw and soybean straw was fed into the pyrolysis drum with a height of 587 mm and 585 mm in diameter with a perforated base of 20 mm. The bass drum was fitted with an air tight adaptor (height 310 mm; diameter 585 mm) incorporated with a chimney (height 700 mm; diameter 140 mm). Separately the heating was started using a match box, after pyrolysis for 30 minutes the yield of RSB and SSB were collected. The biochar was allowed to cool down to room temperature, and the sample was examined for their physical and chemical characteristics.

2.2.2 Physicochemical properties of biochar

Percentage yield (%) was determined as the absolute weight of the biochar formed during pyrolysis divide by the total weight of the feedstock consumed.

Percentage yield (%) = $\frac{\text{mass of biochar}}{\text{mass of feedstock}} \times 100$

The moisture, ash and volatile matter content was determined using standard procedure [17].

% Moisture content = $\frac{ws - (w2 - w1)}{ws} \times 100$

Where: W_1 = Constant weight of a crucible

W_s = Weight of the crucible with its content100

W_2 = Weight of the crucible with its content when cooled in a desiccator

Ash content (%) = $\frac{\text{Ash weight} - \text{crucible weight}}{\text{biochar weight}} \times 100$

Volatile Matter (%) = $\frac{W2 - W3}{W2 - W1} \times 100$

Where: W_1 = Weight of pre-heated crucible

W_2 = Weight of pre-heated crucible with the sample

W_3 = Weight of the crucible with the sample after being heated

Percentage % fixed carbon = 100 – weight % moisture + weight % volatile matter + weight % ash

The bulk density was determined as the dry weight of the sample divided by its volume. A known weight of the sample was put into an empty measuring cylinder. It was gently tapped for two minutes until it was compact and evenly packed. Then, the volume of the sample in the measuring cylinder was measured.

$$\textbf{Density} = \frac{\textit{mass of sample}}{\textit{volume occupied}}$$

The standard procedure was used to determine the pH. and EC using pH meter (HANNA) and electrical conductivity meter (ROS)

2.2.3 Mineral elemental analysis

The Angilent 4210 MP-AES [18] was used for mineral element determination in biochar.

2.2.4 Scanning electron microscope (SEM)

The morphological characterization was achieved using SEM instrument (Make: PhenomProXQ150R Netherlands) at an accelerating voltage of 20.00kv [18].

2.2.5 Fourier transform infrared pectroscopy (FTIR)

The infrared spectrum was obtained using Agilent Technology Cary 630 FT-IR spectrometer over the infrared region of 4000 – 1000 cm^{-1} and a resolution of 4 cm^{-1}. The sample was compacted into KBr pellets before scanning. The spectrum of the pure Kbr was measured before the sample measurement.

2.2.6 Thermogravimetric analysis and derived thermogravimetry (TGA and DTG)

The thermogravimetric analysis was performed under the flow of nitrogen at a max heat-up rate of 20ºC and maximum operating temperature of 1200ºC while monitoring the weight loss and thermal behaviour of the biochar on a PerkinElmer TGA 4000, made in the Netherlands, analyzer. The analysis enabled the observed changes in physical and chemical properties of materials (breakdown of the poultry litter biochar) as a function of increasing temperature.

3.0 Results and discussion

Table 1. Shows the percentage yield of biochar

Feedstock	Feedstock concentration (g)	Biochar concentration (g)	Percentage (%) yield
Rice straw	14450	6083	42.1
Soybean straw	14450	3700	25.6

Rice straw biochar exhibited a higher charring yield of 42.1% while soybean straw biochar had a lower yield of 25.6% because silica and other inorganic components in rice straw biochar do not volatilize during pyrolysis which contribute to a higher yield of biochar [19]. Also at elevated temperatures during pyrolysis the high organic matter content in soybean straw volatilizes leaving behind small percentage yield of soybean straw biochar. The yield of rice straw biochar at 400 ºC does not fall within the range of 45-50% reported by Purakayathsa et al., [20] for rice straw biochar but higher than the 29.7% and 32% yield observed by Kamara et al., [21] and Um-e-Laila et al., [22].

Physical characterization of biochar

Table 2. Represents the proximate composition of biochars

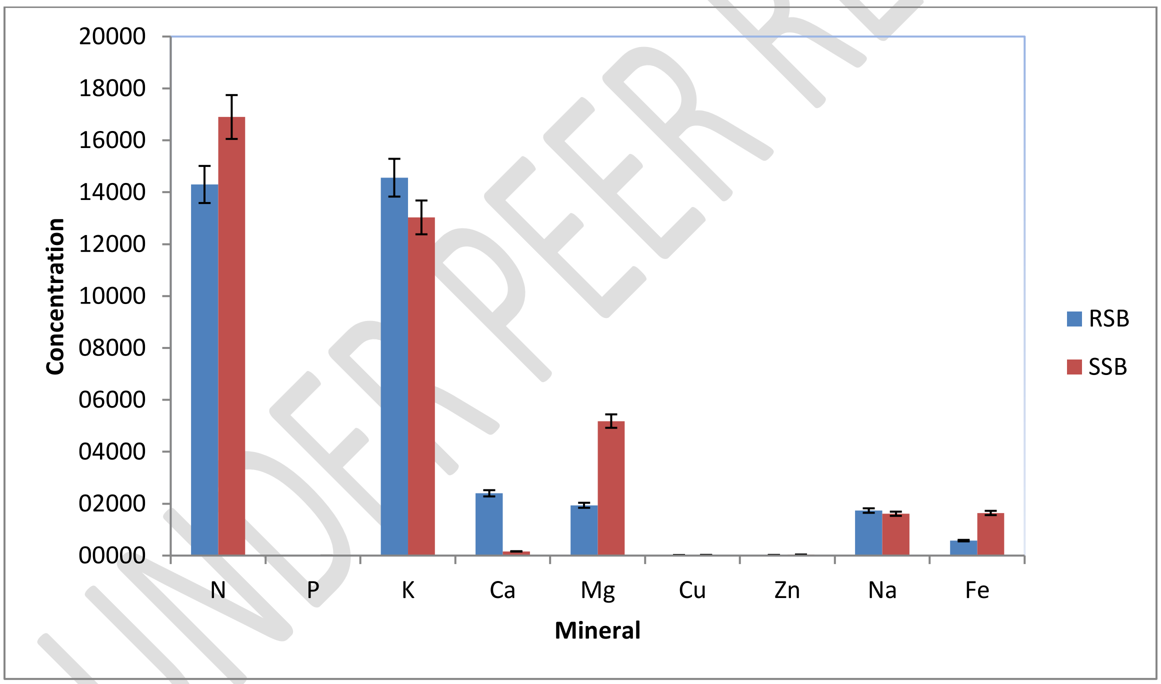
Biochar	% Moisture	%Ash	%Volatile matter	%Fixed carbon	Bulk density g/mL	pH	Electrical conductivity dS/m

RSB	29.4±3.77	27.1±8.16	31.3±4.08	12.1	0.199±0.0191	11.9±1.3	0.542±0.0576
SSB	17.6±0.834	21.9±0.663	25.4±8.97	34.9	0.25±0.0171	12.5±0.808	0.695±0.36

In table 2. Rice straw biochar show high amount of moisture (29.4%), ash (27.1%) and volatile matter (31.3%) when compared to soybean straw biochar with higher fixed carbon 34.9% content. This implies that rice straw biochar has high mineral concentration than soybean straw biochar. The ash 21.9% content of SSB observed in this study was higher than the 10.19% ash value reported by Wu et al.,[23] for SSB. The RSB ash content in this research does not agree with the 34.2% ash value reported by Kamara et al.,[21] but similar to the 28.8% ash content presented by Wu et al., [24]. Soybean straw biochar present a high pH of 12.5 and a high ash content of 21.9% when compared to the relative low pH 9.46 and ash content 10.19% as reported by Sarfaraz et al., [25] and Wu et al., [23] . Both biochars are highly alkaline and aligns with the work of Sarfaraz et al., [25] with high alkaline values for crop residue when compared to the slightly alkaline values of crop residue as reported by Garba et al., [26]. Electrical conductivity is the concentration of all soluble salt present in solution. Soybean straw biochar's high pH and electrical conductivity can be useful for delivering nutrients and reducing soil acidity [27]. On the other hand, there could be negative effects such as elevated soil salinity and probable nutrient imbalances, which call for cautious handling to guarantee ideal plant development and soil well-being [28].

Mineral analysis

Fig.1. Mineral element characterization of rice straw biochar (RSB) and soybean straw biochar (SSB)



Macro elements like N (14300 mg/kg), P (-4.75 mg/kg), K (14561.21 mg/kg), Ca (2401.28 mg/kg), and Mg (1937.88 mg/kg) are found in rice straw biochar, whose micro elements include Cu (20.46 mg/kg), Zn (24.81 mg/kg), Na (1735.27 mg/kg), and Fe (576.51 mg/kg). The macro-minerals in soybean straw biochar are (N 16900 mg/kg, P 3.00 mg/kg, K 13031.97 mg/kg, Ca 162.32 mg/kg, Mg 5118.91 mg/kg), whose micro elements (Cu 25.24 mg/kg, Zn 34.09 mg/kg, Na 1612.25 mg/kg, Fe 1642.80 mg/kg). Soybean straw biochar had the lowest P (3.00 mg/kg) and highest N (16900 mg/kg) mineral element composition than rice straw biochar. For plants to flourish, nitrogen is crucial because it is a major component of amino acids and chlorophyll [29]. Studies according to Um-e-Laila et al., [22] reported macro nutrient (N, K, Ca, and Mg) values for RSB which were lower in concentration compared to the ones reported in this investigation. But the micro elements (Cu and Zn) in RSB identified Um-e-Laila et al., [22] were higher than those observed in this work. Um-e-Laila et al.,[22] reported 38 mg/kg of phosphorus in rice straw biochar but phosphorus was not found in rice straw biochar in this investigation.

Scanning Electron Microscope and Energy Dispersive X-ray (SEM-EDX)

Figures 2a and b shows the changes in the surface morphology of rice straw biochar and soybean straw biochar

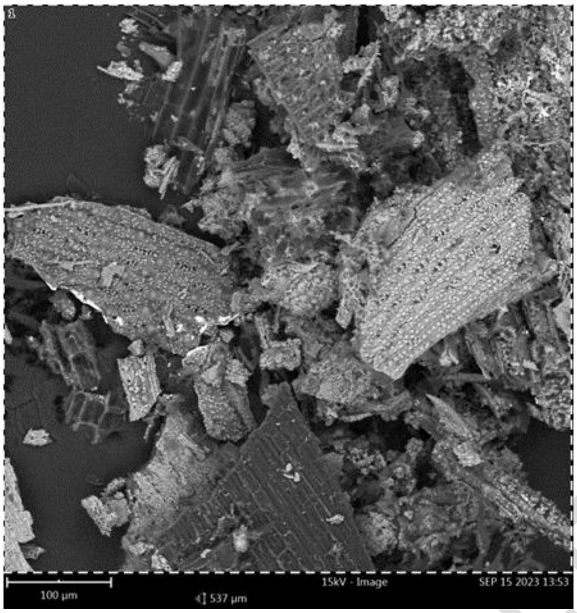


Fig.2a SEM of rice straw biochar

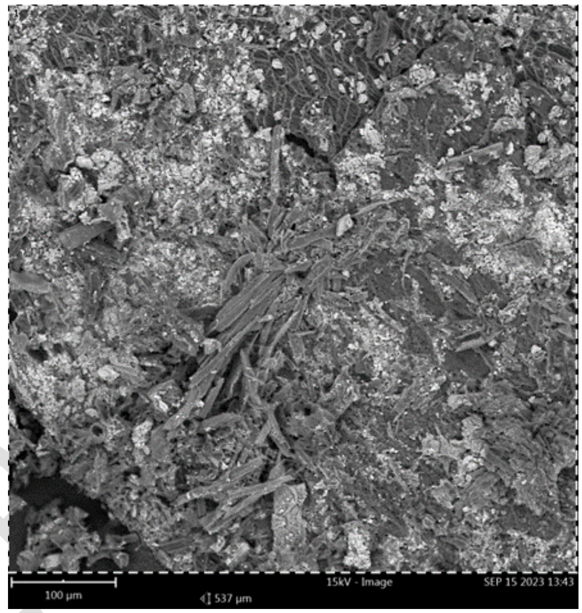


Fig.2b SEM of soybean straw biochar

Both varieties of lignocellulosic biochar have embedded organic and inorganic components and are porous and black due to carbonisation. In rice straw biochar, a porous structure with a high level of microporosity was typically observed. A rough surface roughness and a linked network of pores are revealed in Fig. 2a, which was often visible on the SEM images. As shown in fig. 2b, the porosity structure of soybean straw biochar is more variable and uneven than that of rice straw biochar. The surface could appear smoother if there are fewer, larger pores. The pores in soy straw biochar are often less visible and more uneven in shape. EDX spectral lines of rice straw biochar show high silica content (10.68%) and low carbon content (79.9%) which both contribute to the structure's rigidity and brittleness. EDX peaks of soybean straw biochar reveal a higher carbon content (82.24%) and a lower silica concentration (1.03%), which leads to a less brittle structure. The variation in mineral composition attributes to the differences in feedstock composition [18]. By breaking down the organic matter and producing ash that is rich in minerals, the pyrolysis process concentrates these minerals even more in the biochar [30].

Fourier transformed infrared (FTIR)

Table 3. shows the FTIR analysis of rice straw biochar and soybean straw biochar

Frequency cm^{-1} RSB	SSB	Intensity	Functional group	References
3305.1		Broad	O-H$_{(stretch)}$	[31,32,33]
	3265.1	Broad	O-H$_{(stretch)}$	[18,34,23,35]
2113.4		strong	C≡C$_{(stretch)}$	[36,37,33]

	2109.7	strong	$C \equiv C_{(stretch)}$ or $C \equiv N_{(stretch)}$	[38,39,]
	1900.9	strong	C=O	[40]
1871.1		medium	$C=C=O_{(stretch)}$	[41,42]
1625.1	1625.1	medium	$C=C_{(stretch)}$	[36,43,44,45,46]
1379.1		Weak	$C\text{-}H_{(bend)}$	[37,32,43,47]
	1375.4	narrow	$C\text{-}H_{(bend)}$	[47]
	1043.7	Weak	$C\text{-}O_{(stretch)}$ or Si-O-Si	[48]
1028.7		narrow	$C\text{-}O_{(stretch)}$ or $Si\text{-}O_{(stetch)}$	[41,36,43]
872.2	872.2	Weak	$C\text{-}H_{(bend)}$	[37,32,47,49]

Table 3. displays seven peaks for each type of biochar. Broadly intensified bands with wavenumbers 3305.1 cm^{-1} and 3265.1 cm^{-1} were linked to $O\text{-}H_{(stretch)}$ [33,23] vibrations of hydroxyl groups in rice and soybean straw biochars. Do and Nguyen [31] and Zhao *et al.*, [32] reported bands at 3322 cm^{-1} and 3426 cm^{-1} for hydroxyl group in rice straw biochar which were higher than the OH band in this study. Soybean straw biochar vibrational broad band at 3265.1cm^{-1} fits within the range of 3500-3200cm^{-1} as was described by Chen et al., [34]. The two types of biochar differ in their structural makeup and chemical composition, which accounts for the little variation in wavenumbers. Soybean straw biochar and rice straw biochar had wavenumbers at 2109.7 cm^{-1} and 2113.4 cm^{-1}, suggesting C≡N or C≡C stretching vibrations [38,37,33,36,39]. These vibrations may be from nitriles or alkynes. The frequency at 1871.1cm^{-1} and 1900.9 cm^{-1} indicate carbonyl stretching vibrations. The absorption bands at 1871.1 cm^{-1} is often associated with carbonyl compounds such as ketenes (C=C=O) in rice straw biochar. Similar band around 1870cm^{-1} was observed by Chen *et al.*, [41] in which both bands fall within the range of 1850-1900 cm^{-1} in rice straw biochar according to [42]. The frequency 1900.9cm^{-1} was attributed to C=O in soybean straw biochar but however, this band was not reported in other studies by Gaskin *et al.*, [46], Cantrell *et al.*, [50] and Qian *et al.*, [51] which typically observe C=O within the range of 1650-1750 cm^{-1}. The biochar from rice and soybean straws had a common band at 1625.1 cm^{-1}, representing aromatic C=C stretching vibrations [44,46]. This implies that both kinds of biochar have about the same level of aromaticity. The band found in the rice straw biochar examined in this study corresponds to a comparable band in rice straw biochar that was located between 1600 - 1630 cm^{-1} [36,43]. The wavenumbers for rice straw biochar (1379.1 cm^{-1}) and soybean straw biochar (1375.4 cm^{-1}) are similar, suggesting that the two have medium-intensity C-H bending vibrations [36,43,44,47]. The variations in C-O stretching vibrations suggested by the difference between 1028.7 cm^{-1} and 1043.7 cm^{-1} [41,36,43,52] indicate narrow peaks in rice straw biochar an`dd weak peaks in soybean straw biochar from alcohols, esters, ethers, or residual polysaccharides. Various kinds of functional groups containing oxygen could be the cause of this. Indicating comparable out-of-plane C-H bending vibrations in aromatic compounds, rice straw and soybean straw biochar both exhibit a weak peak at the same frequency of 872.2 cm^{-1} [37,32,47,49].

Thermogravimetry and derivative thermogravimetric analysis

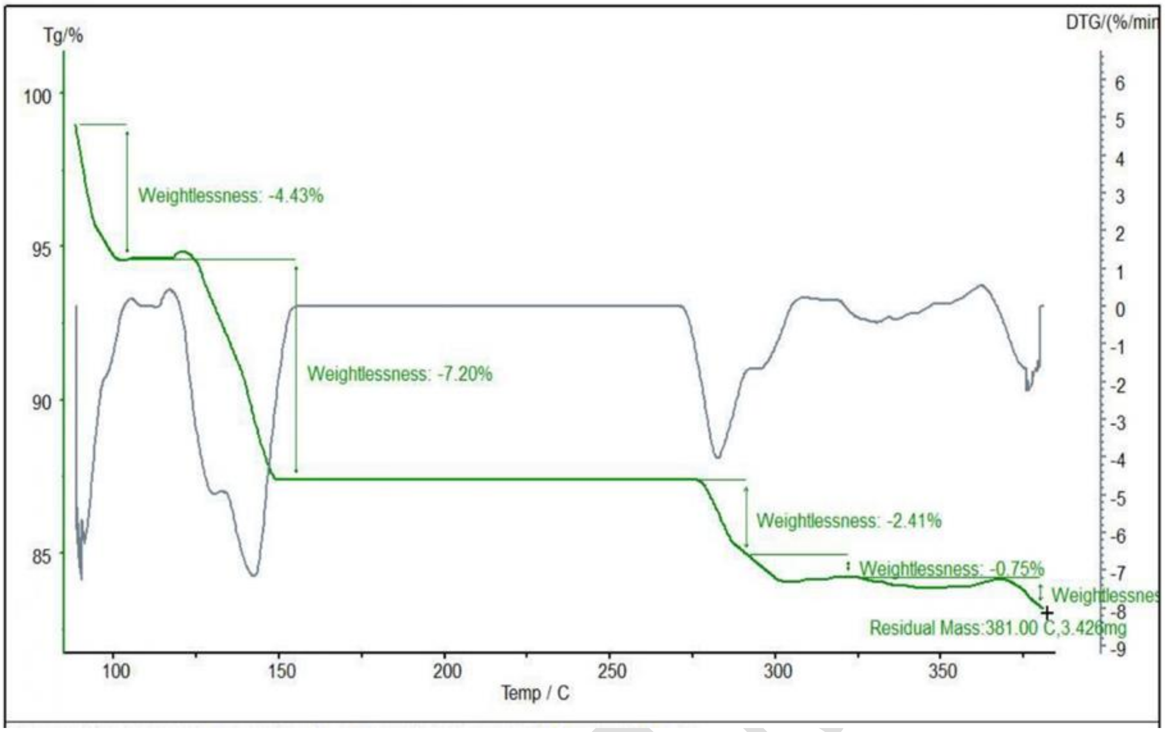


Fig.3a. Rice straw biochar thermogravimetry and derivative thermogravimetric analysis

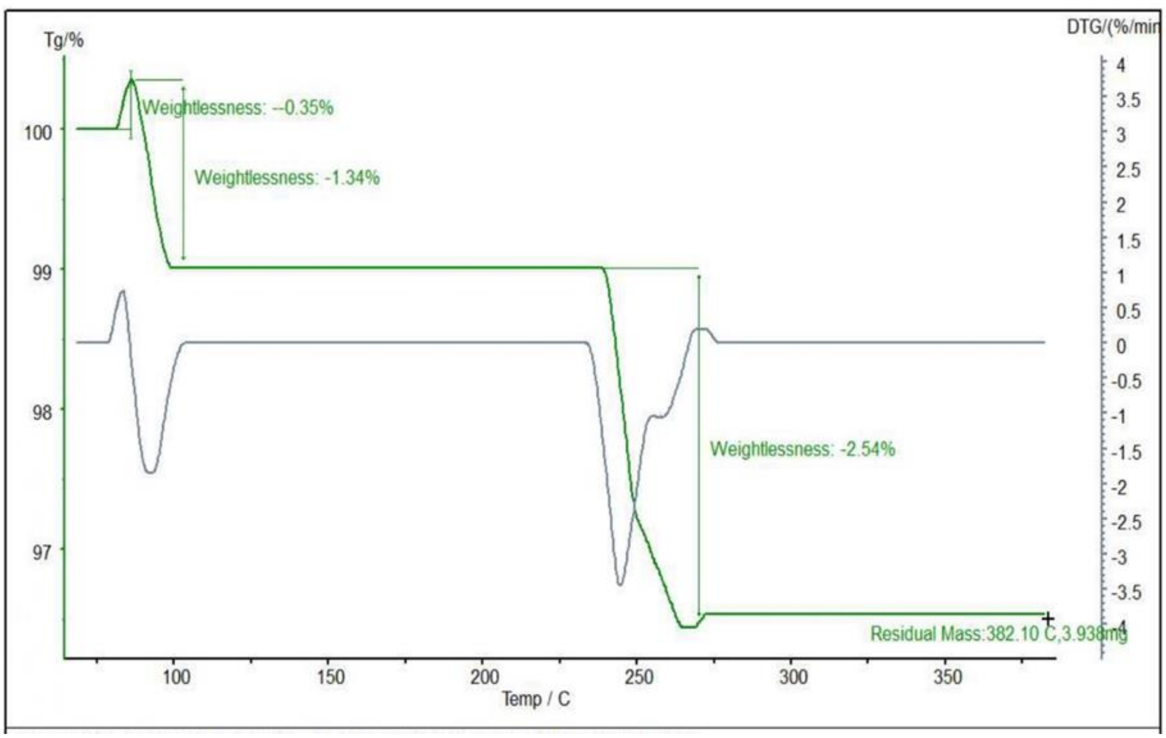


Fig. 3b. Soybean straw biochar thermogravimetry and derivative thermogravimetric analysis

The thermal properties of rice straw biochar and soybean straw biochar can be analyzed using TGA and DTG. In an inert nitrogen environment, volatile chemicals can thermally decompose up to 1200°C at a maximum rate of 20°C min^{-1}. In figures 3a and b the result of the TGA analysis for rice straw biochar had four (4) stages [36,41,] of mass loss when compared to the three (3) stages [53,54,55] of mass loss displayed by soybean straw biochar. Rice straw biochar initial stage I(155.4-104°C) exhibit a higher weight loss of -4.43% corresponding to moisture [56] and light volatiles [36] occurring on the DTG shoulder at 116.8°C within a temperature range of 125-104°C while soybean straw biochar's initial stage I(102.8-36.8°C) had the lowest mass loss of -0.35% that was attributed to moisture loss [57] positioned on the dip temperature of 42.0°C on the DTG curve within a limit of (102.8-36.8°C). In the second stage II(291.2-155.4°C), rice straw biochar exhibits the highest weight loss of -7.20% attributed to continuous degradation of hemicellulose and cellulose [41] at a peak temperature of 276.2°C on the DTG curve within a temperature limit of 285-270°C. This second stage is usually marked by significant weight loss ranging from 30-50% [58]. Contrastingly, the soybean straw biochars second stage II(270.5-102.8°C) show a lower weight loss of -1.34% which indicates a steady and continuous degradation of hemicellulose and cellulose [59] with an obvious dip on the DTG curve and a shoulder positioned at 269.9°C within a temperature region of 275-250°C. Soybean straw biochar's third stage III(382.1-270.5°C) was associated with a higher weight loss of -2.54% which represents a constant thermal degradation of cellulose, lignin [60] and de-volatilization of biochar. The DTG curve hump positioned at 270.5°C followed by a constant decomposition showing a residual mass of 3.938mg at a temperature of 382.1°C in the thermogram. Comparably, rice straw biochar third stage III(322.2-291.6°C) weightlessness of -2.41% attributed to lignin [35] was lower as reflected on the DTG curve positioned on 308.1°C within a temperature limit of 322.2-300°C. The fourth stage IV(381.8-322.2°C) of the TGA curve exhibit a mass loss of -0.75% which represents minor degradation of decaying organic matter and possible formation of stable aromatic structures [61] as shown by the narrow peak position on 370°C on the DTG curve within a temperature range of 375-350°C. Residual mass (3.426mg) consist primarily of ash and stable carbon structures indicating a substantial amount of inorganic material and recalcitrant carbon remaining after pyrolysis.

4.0 Conclusion

The same amount of postharvest crop leftovers was used to produce biochars using a local reactor. Rice straw biochar exhibited higher percentage yield, ash and mineral element (K, Ca, Na) concentration except in the case of N and Fe when compared to soybean straw biochar. Furthermore, rice straw biochar was higher in Si and lower in C composition than soybean straw biochar. The pH and EC of soybean straw biochar produced at 400°C was higher which implies that such biochar neutralize acidic soils when placed in it. Hydroxyl and carbonyl functional groups common between the biochars enable adsorption of organic and inorganic soil pollutants. Cellulose and hemicellulose was decomposed into soluble fractions while lignin was partially decomposed in the biochar.

DISCLAIMER(ARTIFICIAL INTELLIGENCE)

Authors hereby declare that no generative AI technologies such as Large Language Models (ChatGPT, COPILOT, etc) text to image generators have been used during writing or editing of manuscripts.

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