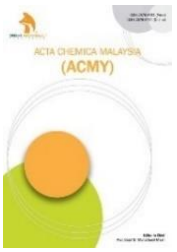
ZIBELINE INTERNATIONAL™ PUBLISHING

ISSN: 2576-6724 (Print)
ISSN: 2576-6732 (Online)
CODEN: ACMCCG

Acta Chemica Malaysia (ACMY)

DOI: http://doi.org/10.26480/acmy.02.2025.122.130



RESEARCH ARTICLE

EVOLUTION OF FUNCTIONALITIES AND STRUCTURE OF BIOCHAR IN PYROLYSIS OF COCONUT SHELL AT DIFFERENT TEMPERATURES

Chima Maximus Ejimadu*, James M. Okuo, and Felix Ebhodaghe Okieimen

[a] DUniversity of Benin, Department of Chemistry, Centre for Biomaterials Research, Benincity City, Nigeria
**Corresponding Author Email: ejimaduchima@gmail.com*

ARTICLE DETAILS

Article History:

Received 17 April 2025
Revised 25 May 2025
Accepted 27 June 2025
Available online 09 July 2025

ABSTRACT

The aim of this study was to investigate the effect of pyrolysis temperature on the physicochemical properties and structures of coconut shell biochar. Biochar was produced by slow pyrolysis of coconut shell at different heat treatment temperatures (350, 400, 400, 500, 600 and 700°C) and were designated BC350, BC400, BC500, BC600 and BC700 respectively for heat treatment duration of 30mins. The biochar samples obtained were characterized in terms of physicochemical properties; quantitative surface oxygen groups, surface morphology/elemental composition (SEM/EDX), Brunauer-Emnett-Teller (BET) surface area and ultimate composition (%) C,O,H,N, and S. The physicochemical properties of the biochar sample; yield (wt %), bulk density ($g.cm^{-3}$) decreased by about 40% with increase in heat treatment temperature, while the pH, cation exchange capacity ($cmol.kg^{-1}$) and electrical conductivity ($mS.cm^{-1}$) increased with heat treatment temperature and tended to attain maximum values at about heat treatment temperature 400 - 500° C. The total oxygen containing groups in the biochar samples decreased with increase in heat treatment temperature by up to 56%, from 4.94 $mmol.g^{-1}$ for BC350 to 2.17 $mmol.g^{-1}$ for BC700. Scanning electron micrograph of the biochar samples revealed largely mesoporous surface structures, that varied somewhat with the heat treatment temperature, while the energy dispersive X-ray (EDX) showed that the elemental content of the biochar samples decreased markedly with increase in heat treatment temperature and that carbon was the predominant element, contributing more than 60% of the total elements in the samples. The evolution of surface area of the biochar samples followed two patterns: an initial increase in surface area with heat treatment temperature from 282 $m^2.g^{-1}$ for BC350 to 712 $m^2.g^{-1}$ for BC450 followed by gradual decrease from 618 m2.g^{-1} for BC 500 and then to 220.7 m^2.g-1 for BC 700. The changes in the pore volume ($cm^3.g^{-1}$) of the biochar samples with heat treatment temperature were found to be synchronous with the observed changes in BET surface area. The pore volume of the biochar samples increased almost two-fold with increase in heat treatment temperature, varying from 2.8nm for BC350 to 4.9nm for BC700 indicating that the biochar samples were mesoporous. These results suggest a range of potential benefits; agronomic, environmental, including carbon sequestration in soil remediation and wastewater treatment using coconut shell biochar.

KEYWORDS

coconut husk, biochar, pyrolysis temperature, physicochemical properties, ultimate composition, hydrogen - carbon ratio, oxygen - carbon ratio

1. INTRODUCTION

Coconut shell and coconut husk biochar generated by the coconut industry world wide exceeds 124 million tons annually (Agien et al., 2023). The biomass of coconut waste is generally prodigiously disposed into the environment or by open-air burning causing considerable

environmental and public health concerns (Jain et al., 2014). Pyrolysis as an aspect of thermochemical technology that includes combustion and gasification, has received considerable attention as a flexible and simple process to convert biomass into fuel and chemicals (Kim et al., 2012). Depending on the heat treatment temperature (HTT), heat treatment duration (HTD) and heat ramp rate (HRR) pyrolysis can typical be divided into three types; slow, fast and flash pyrolysis, results in marked difference in the type and proportional of end products ; solid (biochar), oil (biochar) or gas (kan et al., 2016). Biochar is the main product of slow pyrolysis of biomass to yield 30 to 40 wt% biochar, 25 to 30 wt% bio-oil and 22 - 35 wt% biogas (Dhyani and Bhaskar, 2019). Physicochemical properties, structure and porosity of biochar can be affected by processing factors of which temperature is considered the most important (Dong et al., 2023; Lian et al., 2023). During pyrolysis, biomass undergoes a series of reaction with increase in temperature that includes degradation, decarboxylation and decarbonylation leading to distinct char phases and physical states, and including marked changes in the structure of biochar from transitional through amorphous and composite chars to turbostic char (Keiluweit et al., 2010). This changes are accompanied with changes in the physicochemical properties, surface roughs, micromorphology and porous structure of biochar (Gupta et al., 2019). On account of the potential for multifunctional application of biochar, for agronomic, environmental (including carbon sequestration and wastewater treatment etc.) and industrial (e.g as catalyst) (Wang et al., 2024; Weber and Quicker, 2018; Zhang et al., 2020; Cao et al., 2004); studies in the pyrolysis of biomass materials; wood residue, crop residues, animals wastes, etc. for the production of biochar has retained interest (Jindo et al., 2014; Obonukut et al., 2022; Ma et al., 2017; Prahan et al., 2020; Demirbas,

Quick Response Code	Access this article online	
	Website: www.actachemicamalaysia.com	**DOI:** 10.26480/acmy.02.2025.122.130

Cite the Article: Chima Maximus Ejimadu, James M. Okuo, and Felix Ebhodaghe Okieimen (2025). Evolution of Functionalities and Structure of Biochar in Pyrolysis of Coconut Shell at Different Temperatures. *Acta Chemica Malaysia, 9(2): 122-130.*

2004; Cao et al., 2004). There are several reports on the pyrolysis of coconut shell biomass. The activation of coconut shell carbon by either chemical or physical methods appear to be a dominant route for the utilization of low-cost coconut biomass, particularly for removing impurities in purification and related industries. They carried out a competitive study on the chemical and physical activation of coconut shell and reported variations in the pore structure of the biochar: physical activation by CO_2 resulting in biochar with narrow pore size distribution, while chemical activation with H_3PO_4 and $ZnCl_2$ produced largely, high bulk densities, mesoporous biochar and mechanical resistance (Praiacher and Rodriguez-Reinoso, 2012). They described a modified pyrolysis reactor for improving the quality, with particular reference to specific surface area of coconut derived biochar (Sari et al., 2020). They reported on a one-step self sustained low temperature carbonization process for improving the specific surface area of coconut shell derived biochar (Samsudin et al., 2019). Specific surface area is an important property of biochar relevant in many applications. They reported on the effect of pyrolysis temperature on the properties; pH, functional groups, surface area, proximate and ultimate composition of coconut husks (Suman and Gautman, 2017). Increase in pyrolysis temperature was reportedly associated with decrease in volatile matter, C:H ratios and to an increase in pH, surface area of the resultant biochar samples. They described the application of coconut shell derived activated biochar and its MnO_2 nanocomposites for capacitive deionization (CDI) applications (Adorma et al., 2020). Capacity deionization is an emerging desalination process based on ion electrosorption in which saline water is passed through a porous, usually carbon-based electrodes. The effect of pyrolysis temperature on the yield, physicochemical properties, proximate and ultimate composition, together with the high heating value, and BET surface area of biochar of coconut husks was reported by (Noor et al., 2019). The report indicated that higher pyrolysis temperature was associated with reduction in yield of biochar, increase in fixed carbon content and decrease in volatile matter within the range of pyrolysis temperature (350 to 700° C) studied. The BET surface area of the biochar sample was reported to increase several folds within the studied temperature range. Coconut waste biomass, shell, husks, trunk, fronds, differ markedly in their chemical composition and would be expected to yield biochars which may differ in physicochemical properties, elemental composition, morphology and surface properties. The effect of heat treatment temperature on the properties of biochars from coconut shell pertinent to their application to soil for agronomic and environmental benefits, including, carbon capture and climate change adaptation have received relatively less attention. In this study the effect of heat treatment temperature (350 to 700°C) at constant heat treatment duration (30 mins) on the physicochemical properties, surface functional groups, surface morphology and ultimate composition of coconut shell biochar samples relevant for their multifunctional application is reported.

2. Materials and Methods

2.1 Materials

Coconut shells were collected from a local market in Benin City. They were washed repeatedly with tap water and rinsed with distilled water to remove physical impurities, then air-dried at room temperature for seven days. The dried coconut shells were crushed to a particle size of 2 mm before being converted into biochar through pyrolysis at different temperatures (350, 400, 450, 500, 600, and 700 °C) and held at the highest heating temperature for 30 mins. The resulting biochars were further crushed and sieved through a 250 µm sieve. The sieved coconut shell biochars (CSB) were then stored in a plastic container and labeled BC350, BC400, BC450, BC500, BC600 and BC700 respectively. All chemicals used in this study were of analytical grade and were utilized without further purification.

2.2 Physicochemical Characterization

2.2.1 Determination of pH and Electrical Conductivity

The pH was measured in deionized water using 1:5 ratio. Samples were thoroughly mixed and allowed to stand for 1hr. The pH was measured with a precalibrated digital pH meter (Jenway 3020, DUNMOW ESSEX, JENWAY LTD., England).

The electrical conductivity (EC) of the biochar slurry was determined following the method described by (Singh et al., 2017). A mixture of biochar and deionized water in a 1:10 ratio was agitated for 1 hr. Afterward, the samples were allowed to stand for 30 minutes, and the EC of the suspension was measured using a precalibrated conductivity meter (DDS-307, SearchTech Instrument, No. X619070942).

2.2.2 Bulk Density

Bulk density was determined using the tapping method as described by (Ahmedna et al., 1997). 10 ml tubes were filled with dry biochar and capped. The tubes were tamped to a constant (minimum) volume by the tapping on a table, and weighed. The bulk density of the biochar's were calculated by:

$$\text{Bulk density (g.cm}^{-3}) = \frac{\text{Weight of dry sample (g)}}{\text{Volume of packed dry material (cm3)}}$$

2.2.3 Cation Exchange Capacity (CEC):

The CEC was determined using the modified ammonium acetate displacement method as described by Othugile et al. (2022). Samples (0.2g each) were leached five times with 20 mL deionized water to reduce interference from soluble salts. The samples were then leached five times with 20 mL of 1M sodium acetate (pH 7), to remove or extract exchangeable cations. The samples were later washed with 20ml of ethanol five times to remove the excess sodium ion (Na+). The Na^+ on the exchangeable sites of the material was then displaced five times using 100ml of 1M ammonium acetate (pH 7). The CEC was calculated from the Na^+ displaced by NH_4^+, measured using a flame photometer.

2.2.3 Surface morphology and elemental composition

The Scanning Electron Microscope (SEM, Hitachi SU 3500 scanning microscope, Tokyo) and an Energy Dispersive X-ray Spectrometer (EDX) were used in combination to analyze the surface morphology of the produced samples and determine their elemental composition.

2.2.4 Determination of surface area

The surface area of the samples were analyzed using the nitrogen adsorption-desorption method based on the Brunauer–Emmett–Teller (BET) theory. 0.3 g of each of the sample was placed in a BET glass tube and weighed before and after loading. The samples were degassed at 473 K for 3 hours using a Micromeritics FlowPrep 060 system under a flow of nitrogen gas to remove physically adsorbed moisture and gases. After degassing, the samples were reweighed and the analysis was carried out in micromeritics Tristar 3000 V4.02 under liquid nitrogen temperature where BET surface area and pore volume/size of the samples were automatically calculated by the instrument using Nitrogen adsorption-desorption isotherms and the results were recorded on the computer attached to the instrument (Aimikhe et al., 2022 Shoaib et al., 2020).

2.3 Ultimate analysis

The percentages of C, H, S, and N in biochars were determined with an elemental analyzer (Elemental Vario EL III, Germany), and the O content was calculated by subtracting C, H, N, S, and ash contents from the total (Gazulla et al., 2016).

3. Results and Discussion

3.1 Physicochemical properties

The effect of heat treatment temperature on the physicochemical properties of the coconut shell biochar is given in Table 1.

Table 1: Variation of the physicochemical properties of coconut shell biochar with pyrolysis temperature.

Parameters	Pyrolysis Temperature (°C)					
	350°C	400°C	450°C	500°C	600°C	700°C
Yield (%)	67.700 ± 0.50	53.300 ± 0.35	46.500 ± 0.10	41.670 ± 0.55	39.440 ± 0.64	35.760 ± 0.42
pH	7.900 ± 0.90	8.250 ± 1.20	9.730 ±1.11	10.010 ± 0.50	10.250 ± 0.36	10.700 ± 0.77
Electrical conductivity ($ms.cm^{-1}$)	5.12 ± 1.50	7.58 ± 1.22	12.18 ± 1.07	15.34 ± 1.00	18.54 ± 0.95	25.60 ± 1.11
Bulk density ($g.cm^{-3}$)	1.12 ± 0.22	0.97 ± 0.09	0.91 ± 0.18	0.75 ± 0.30	0.70 ± 0.11	0.59 ± 0.15

Table 1 (cont): Variation of the physicochemical properties of coconut shell biochar with pyrolysis temperature.						
Cation exchange Capacity ($cmol.kg^{-1}$)	11.472 ± 2.43	23.061 ± 2.59	28.031 ± 2.00	19.660 ± 2.26	19.012 ± 1.95	14.110 ± 2. 50

The yield of biochar as given in Table 1 depended on the pyrolysis temperature, decreasing with increase in pyrolysis temperature. The yield decreased by about 47.17% from 67.70% at 350° C to 35.76% at 700° C. The decrease in biochar yield with increase in heat treatment temperature could be attributed to the decomposition of the biomass at higher temperatures (Mimmo et al., 2014) and to secondary decomposition of biochar residue that involved the charring and devolatilization reactions at higher heat treatment temperature (Claoston et al., 2014). The results are consistent with the reports by previous workers (Chen et al., 2014, Noor et al., 2019).

The results in Table 1 show that the pH of the coconut shell biochar samples increased by about 2.8 pH units within the range of heat treatment temperatures (350 - 700°C) used in this study. The increase in pH of biochar samples with heat treatment temperature may be related to the observed high degree of carbonization and accumulation of inorganic salts (carbonates) in the biochar samples (Yuan et al., 2011). High pH is generally considered to have ameliorative effect on the soil properties relevant to agronomic benefits. Cation exchange capacity (CEC $cmol.kg^{-1}$) is the amount of exchangeable cation such as Na^+, K^+, NH_4^+, Ca^{2+} and Mg^{2+} that a material is capable of holding. It is a result of negative surface charges attracting cations and it is used as an indicator of soil fertility (Roberston et al., 1999). Therefore CEC depends directly on this surface structure with functional groups providing surface charges and surface area making surface charges accessible (Liang et al., 2006). Therefore higher values of CEC are found for biochar produced under relatively mild heat treatment temperature at which the surface functional groups remains in the structure to provide negative charges (Mukherjee et al., 2011). At a more than 100% increase in values of CEC ($cmol.kg^{-1}$) as highest heating temperature increased from 350° C to 450° C, followed by a decrease in the value of CEC (cmol.kg-1) from 28.03 to 14.11 as highest heating temperature increased to 700°C.

The bulk density ($g.cm^{-3}$) of the biochar samples (Table 1) decreased by about 47% within the heat treatment temperatures used in this study from 1.12 for sample obtained at 350° C to 0.59 for sample at 700° C. The variation in the values of bulk density ($g.cm^{-3}$) with heat treatment temperature from 1.12 at 350° C to 0.59 at 700° C representing a decrease of about 96% is as expected (Weber and Quicker, 2018). During pyrolysis and as gases are devolatilized from the biomass with increase in heat treatment temperature, the solid mass becomes porous. The higher the porosity, the ligher the mass becomes and the smaller the mass of the char per unit volume (bulk density).

3.2 Surface oxygen functional groups

The results of the quantitative determination of the surface oxygen functional groups on the coconut shell biochar samples are given in Table 2.

Table 2: Surface oxygen functional groups of coconut shell biochar prepared at different heat treatment temperatures.						
Functional Groups	**Biochar Samples**					
	BC350	BC400	BC450	BC500	BC600	BC700
Phenolic ($mmol.g^{-1}$)	1.65	1.58	1.27	1.81	1.27	0.50
Lactonic ($mmol.g^{-1}$)	1.51	1.30	0.39	1.15	0.80	0.43
Carboxylic ($mmol.g^{-1}$)	1.78	1.23	1.81	0.65	0.41	1.24
Total ($mmol.g^{-1}$)	4.94	4.11	3.47	3.61	2.48	2.17

There is no apparent pattern of variation of the level of the various functional groups phenolic, lactonic and carboxylic with heat treatment temperature but the total surface oxygen functional groups decreased from 4.94 mmol.g-1 for BC350 to 2.17 mmol.g-1 for BC700, a change of about 56%. The decrease in surface oxygen functional groups are considered to result from the volatilization of the surface groups during pyrolytic decomposition of biomass (Yang et al., 2004; Ogede et al., 2024). Surface oxygen functional groups in biochar are important to it sorptive capacities and biochar surface modification processes are aimed at enhancing the sorptive properties for environmental benefits.

3.3 Surface area

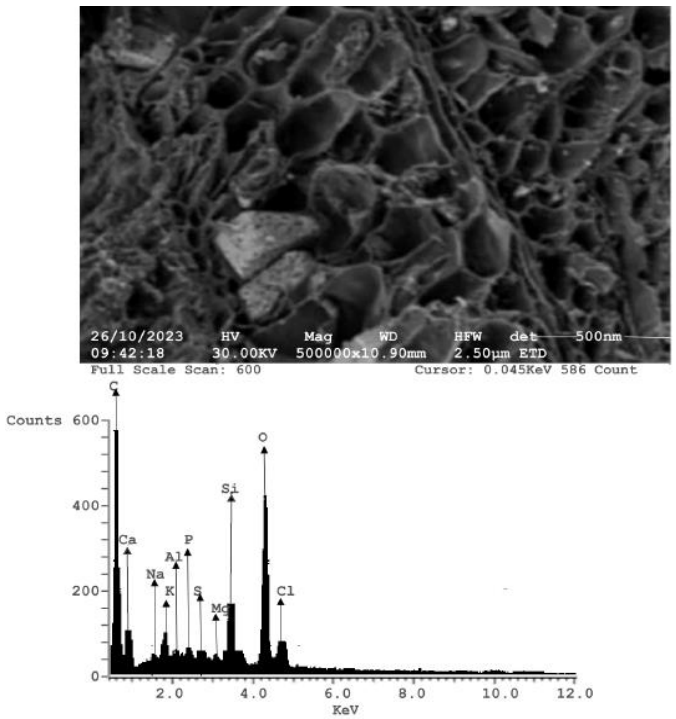
The BET surface area, porosity and pore volume of the coconut shell biochars prepared at different heat treatment temperatures are given in Table 3.

Table 3: Surface area, porosity and pore volume of coconut shell biochar samples prepared at different heat treatment temperatures.						
Properties	**Biochar Samples**					
	BC350	**BC 400**	**BC450**	**BC 500**	**BC600**	**BC 700**
S_{BET} ($m^2.g^{-1}$)	282.00	314.00	712.00	618.30	572.10	320.70
Pore diameter (nm)	2.80	2.13	2.11	3.51	3.94	4.85
Pore volume ($cm^3.g^{-1}$)	0.17	0.17	0.36	0.29	0.18	0.10

The specific surface area ($m^2.g^{-1}$) of the coconut shell biochars range from 282.00 for BC350 through 712.00 for BC450 to 320.70 for BC700 indicating an initial marked increase of about two and a half fold in specific surface area, followed by a decrease thenceforth to BC700 with specific surface area of 320.70. This trend is similar to the report of Brown et al. (2006) for biochar produced by the slow pyrolysis of wood. The reports on the effect of pyrolysis temperature on the evolution of porous structures on biochar derived from different biomass suggest that increase in specific surface area of biochar occurred by the release of volatiles from the biomass components and from the crack resulting from the fusion of benzene rings and possible graphic microcrystals in the biochar (Yang and Sheng, 2012; Yang et al., 2016). Increase in heat treatment temperature resulted in increase of about 1.7 fold, 72%, in the pore size (nm) of the biochar samples, and the values suggested that the biochar samples were largely mesoporous. The pore volume ($cm^3.g^{-1}$) of the biochar samples followed an opposite trend and decreased an order of 1.74 fold, and about 41%, with the range of heat treatment temperature used in this study. The porous structures of biochar are important in many applications; sorptive capacity (i) relevant for the removal of pollutants from wastewater ii) mitigating the dispersion of pollutant molecules in soil, and iii)in industrial applications relative to catalytic activity, etc.

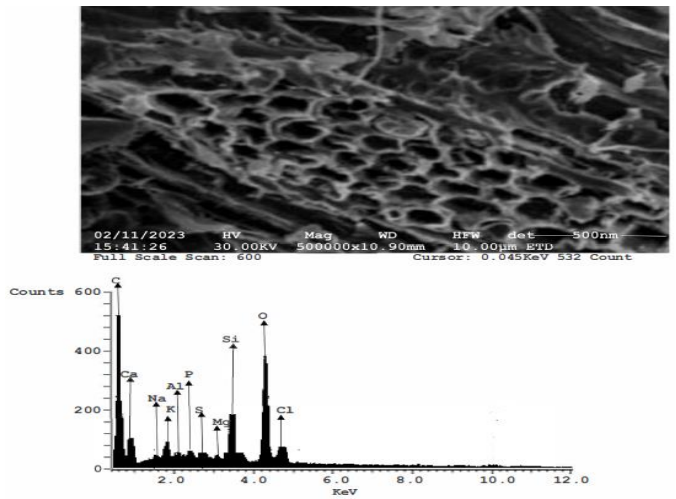
3.4 Surface Morphology

The scanning electron micrographs and surface elemental composition determined by energy dispersive x-ray (SEM/EDX) of the coconut shell biochar samples obtained at different heat treatment temperatures are given in Figures 1(a-f).



(a)

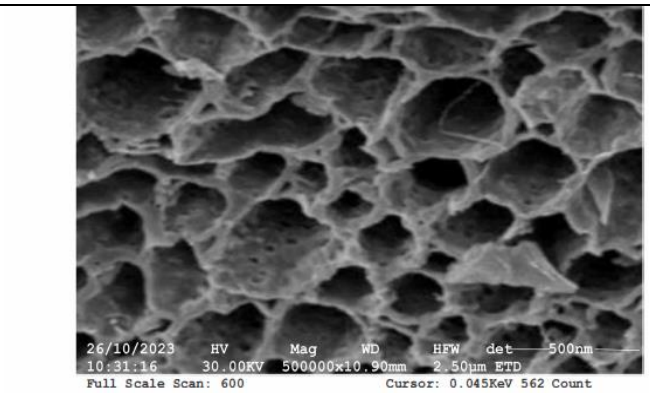
Elements	Composition (%)
C	60.50
O	29.72
Ca	1.15
Si	3.01
Al	0.20
K	1.76
Na	0.78
Mg	0.56
P	1.04
Cl	1.16
S	0.11

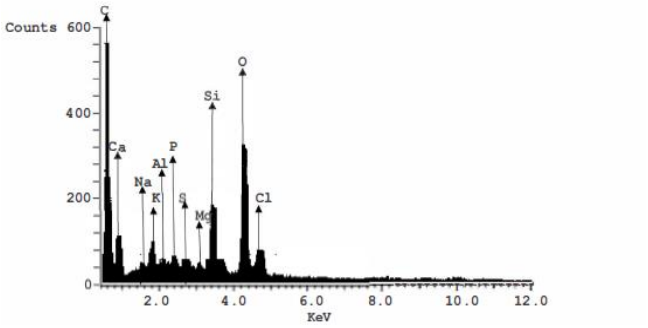


(b)

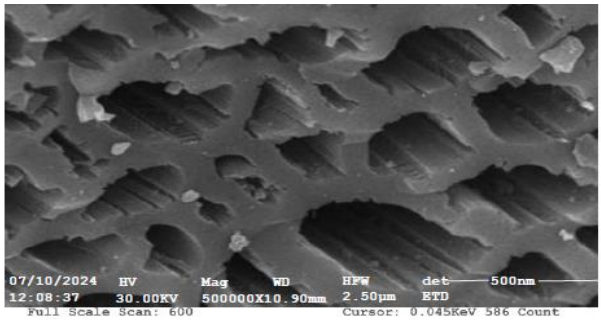
Elements	Composition (%)
C	63.11
O	24.07
Ca	1.87
Si	3.51
Al	0.49
K	2.06
Na	1.12
Mg	0.87
P	1.24
Cl	1.49
S	0.15

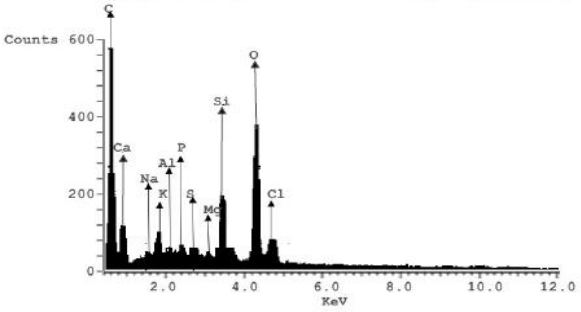
Elements	Composition (%)
C	66.03
O	18.40
Ca	2.02
Si	3.92
Al	0.91





(c)



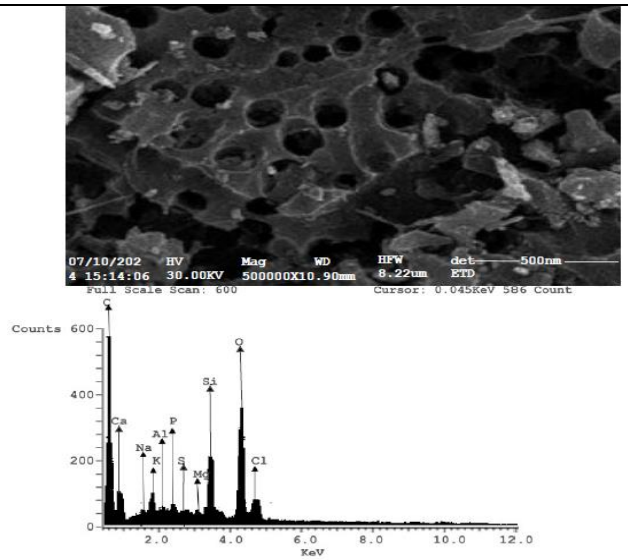


(d)

K	2.11
Na	1.55
Mg	1.50
P	1.34
Cl	2.09
S	0.12

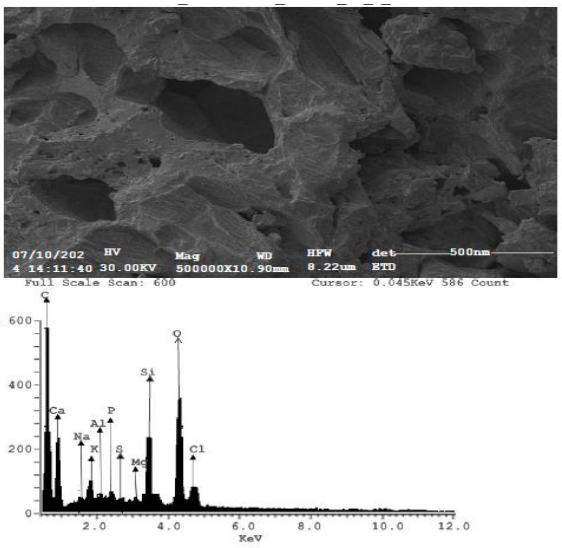
Elements	Composition (%)
C	65.15
O	17.13
Ca	1.47
Si	6.17
Al	1.11
K	2.31
Na	1.73
Mg	1.11
P	1.59
Cl	2.11
S	0.10

Elements	Composition (%)
C	67.07
O	18.81
Ca	1.04
Si	6.41
Al	0.23
K	2.71
Na	1.26
Mg	0.22
P	0.61
Cl	1.56
S	0.07



(e)

(f)



Elements	Composition (%)
C	64.66
O	15.92
Ca	1.70
Si	7.92
Al	1.50
K	2.54
Na	1.75
Mg	1.06
P	1.10
Cl	1.80
S	0.04

Figure 1: SEM/EDX of coconut shell biochars (a) BC350 (b) BC400 (c) BC450 (d) BC500 (e) BC600 (f) BC700

The results given in Figure 1 indicate that the coconut shell biochars obtained at the various heat treatment temperatures were large mesoporous as indicated from the porosity results. The surface elemental composition showed that the amounts of carbon and oxygen were the dominant elements in the biochar samples varied markedly from 60.53 to 64.66% and 24.07 to 15.92% respectively within the range of heat treatment temperatures used in this study. The results give a decrease in the O:C index from 0.49 for BC350 to 0.25 for BC700.

The EDX showed the level of mineral nutrients (Ca, Na, K, Mg and P) in the coconut shell biochar samples obtain at different heat treatment temperatures. A close examination of the results showed that the total level of the mineral nutrients (Ca2+ Na+ K+ Mg2+) decreased markedly by about 35% from 8.52% at heat treatment temperature of 350° C to 5.82% at 600°C heat treatment temperature. These results indicate that a higher proportion of the mineral nutrient present in the biomass may be retained in the biochar obtained at moderate heat treatment temperatures.

3.5 Ultimate composition of biochar samples

The results of the ultimate (C, H, S, N, and O) analysis of the biochar samples obtained from coconut shell at the different heat treatment temperature are given in table 4.

Table 4: Effect of heat treatment temperature of ultimate composition of coconut shell biochar.

Samples	Ultimate Composition (wt%)				
	C	H	O	N	S
CS	54.03 ± 0.00	3.22 ± 0.01	41.74 ± 0.07	0.60 ± 0.04	0.43 ± 0.01
CSB350	60.18 ± 0.02	3.03 ± 0.02	36.14 ± 0.03	0.41 ± 0.02	0.22 ± 0.02
CSB400	61.39 ± 0.02	2.99 ± 0.02	33.85 ±0.06	0.48 ± 0.00	0.24 ± 0.01
CSB450	62.92 ± 0.02	2.61 ± 0.02	33.76 ± 0.00	0.57 ± 0.02	0.14 ± 0.02
CSB500	63.95 ± 0.03	2.53 ± 0.03	33.75 ± 1.78	0.59 ± 0.00	0.40 ± 0.00
CSB600	65.01 ± 0.00	2.43 ± 0.02	33.37 ± 0.00	0.93 ± 0.01	0.083 ± 0.01
CSB700	68.63 ± 0.01	2.30 ± 0.02	27.36 ± 0.04	0.98 ± 0.03	0.037 ± 0.01

CS – unpyrolysed coconut shell

Compared to the unpyrolysed coconut shell (CS), the results in Table 4 show an increase of up to 21.3% in carbon content of coconut shell

biochar, while within the range of heat treatment temperature used in this study, the biochar carbon content increases by 12.3%. Coconut shells is a hard biomass with relatively high lignin 33% and cellulose 30% contents. The results from previous worker indicated that carbon content in biochars from nuts/ shell, lignin and cellulose rich materials showed remarkable increase at high pyrolysis temperatures (Novak et al., 2009; Masek et al., 2011).

The level of oxygen and hydrogen content in a biochar samples can be seen in Table 4 to decrease with increase in heat treatment temperature. The value of oxygen content varied from 41.74% for the unpyrolysed coconut shell through 36.14% for BC350 to 27.76% for BC700 representing an overall decrease of 40.61%. A corresponding overall decrease in hydrogen content of 28.57% within the temperature range used in this study can also be observed (Table 4). During heat treatment oxygen and hydrogen are released from biomass via low molecular weight degradation products such as H_2, CO_2, CH_4 etc. It will therefore be expected that relatively large qualities of these volatile molecules will be evolved at the highest heat treatment temperature, resulting to the reduced levels of oxygen and hydrogen in the biochar samples. Nitrogen is a important nutrient element for growing crops. The nitrogen concentrations in the samples were generally low below 1%, and varied from 0.60% in the unpyrolysed coconut shell, and 0.41% to 0.9% within the heat treatment temperatures used in this study. The low level of nitrogen in the coconut shell is consistent the values for some lignin-rich biomass, nuts and shells (Gashin et al., 2008). The more than two-fold increase in levels of nitrogen on the biochar samples associated with increase in heat treatment temperatures of coconut shell can be attributed to the presence of nitrogen complex structure within the high-lignin component of the biomass that requires higher decomposition temperatures that result in altered chemical structures and nitrogen (Gaskin et al., 2008). This high levels of nitrogen in biochar samples obtained at high heat treatment temperatures may account for the elevated pH levels of biochar samples obtained at high heat temperatures. Generally, biomass has low levels of sulfur, a large proportion of which is reportedly lost during pyrolysis (Chan and Xu, 2009). The sulphur content of coconut shell was 0.43% and decreased markedly with increase in heat treatment temperature to 0.037% at the highest heat treatment temperature of 700° C. The atomic mass ratios O/C, H/C, (O + N)/C and (O + N + S)/C in the coconut shell biochars prepared at different temperatures are given in Table 5.

Table 5: Atomic mass ratios in coconut shell biochar pyrolysed at different temperatures

Samples	O/C	H/C	(O + N)/C	(O + N + S)/C
CS	0.77	0.06	0.78	0.79
CSB350	0.60	0.05	0.60	0.61
CSB400	0.55	0.05	0.56	0.56
CSB450	0.54	0.04	0.54	0.55
CSB500	0.53	0.04	0.53	0.54
CSB600	0.51	0.04	0.52	0.53
CSB700	0.40	0.03	0.41	0.41

CS – unpyrolysed coconut shell

These atomic indices are useful in assessing the stability and recalcitrance of biochar to chemical and biological degradation. The H/C index is a particularly useful indicator of the degree of aromatization in the biochar samples. The O/C and H/C indices can be seen to decrease markedly from 0.77 and 0.06 respectively for the unpyrolysed coconut shell to 0.40 and 0.03 for BC700. This pattern of variation in the O/C and H/C atomic indices has been attributed to increasing carbonization within the biochar with increase in heat treatment temperature (Kim et al., 2012). Fig. 2 is the plot of H/C versus O/C of coconut shell biochar samples obtained at various heat treatment temperature (Van Krevelen plot).

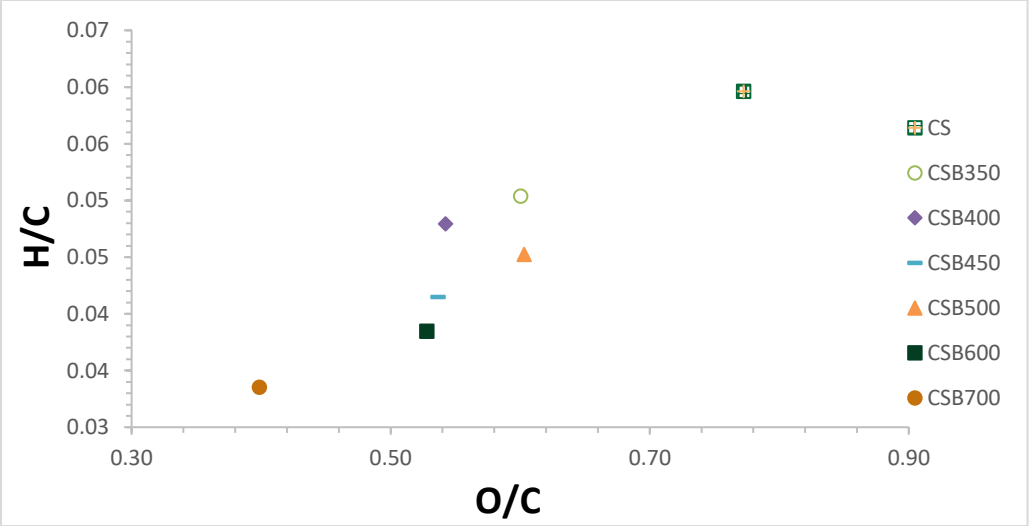


Figure 2: A plot of H/C versus O/C as a function of heat treatment temperature

The results show marked degrees in the H/C and O/C atomic ratios in the biochar samples compared with the unpyrolysed coconut shell. The general rule is that the lower these ratios, the greater the degree of aromatization and stability of the biochar. The values of (O + N)/C and (O + N + S)/C indices (Table 5) were highest (0.78 and 0.79) for the unpyrolysed coconut shell and decreased with increase in heat treatment temperature to 0.41 for BC350 and 0.41 for BC700 respectively. These indices reflect the variation in polarity of the biochar samples (Ahmad et al., 2012).

4. Conclusion

The effect of heat treatment temperature on the physicochemical properties, surface morphology, surface area, porosity and ultimate composition of coconut shell biochar was evident from this study. The present of high value of pH and cation exchange capacity, surface functional oxygen groups; carboxylic, phenolic and lactonic, large specific surface area, and microporosity of the biochar samples were related and relevant to the potential value of the biochar samples in soil amendment for agronomic and environmental benefits. The relative stability and the recalcitrance of the biochar samples deduced from their ultimate elemental composition and using the O/C and H/C ratio suggested that the coconut shell biochar may be useful in carbon sequestration application. The result indicated that biochar samples derived from low-cost coconut shell may find multifunctional applications for agronomic, water/ waste water treatment, soil remediation benefits and in carbon sequestration and indicate a potential for the application of coconut shell biochar obtained at temperatures higher than ≥ 600°C.

ACKNOWLEDGEMENT

The authors are sincerely grateful to the Department of Chemistry, University of Benin, Benin City, Nigeria for allowing us use some of their facilities.

REFERENCES

Adorna, J. Jr., Borines, M., Dang, V.D., and Doong, R.-A., 2020. Coconut shell derived activated biochar–manganese dioxide nanocomposites for high performance capacitive deionization. Desalination, 492: Pp. 114602. doi:10.1016/j.desal.2020.114602.

Ahmad, M., Lee, S. S., Dou, X., Mohan, D., Sung, J.-K., Yang, J. E., and Ok, Y. S., 2012. Effects of pyrolysis temperature on soybean stover- and peanut shell-derived biochar properties and TCE adsorption in water. Bioresource Technology, 118: Pp. 536–544. doi:10.1016/j.biortech.2012.05.042.

Ahmedna, M., Johns, M. M., Clarke, S. J., Marshall, W. E., and Rao, R. M., 1997. Potential of agricultural by-product-based activated carbons for use in raw sugar decolourisation. Journal of the Science of Food and Agriculture, 75(1): Pp. 117–124. doi:10.1002/(sici)1097-0010(199709)75:1<117::aid-jsfa850>3.0.co;2-m

Aimikhe, V. J., Anyebe, M. S., and Ibezim-Ezeani, M., 2022. Development of composite activated carbon from mango and almond seed shells for CO_2 capture. Biomass Conversion and Biorefinery, pp 1-15.

Ajien, A., Idris, J., Md-Sofwan, N., Husen, R., and Seli, H., 2022. Coconut shell and husk biochar: A review of production and activation technology, economic, financial aspect and application, Waste Management and Research, 41(1): Pp. 37–35. doi:10.1177/0734242X221127167.

Bakshi, S., Banik, C. and Laird, D.A., 2018. Quantification and characterization of chemically- and thermally-labile and recalcitrant biochar fractions. Chemosphere, 194: Pp. 247-255.

Brown, R.A., Kercher, A.K., Nguyen, T.H., Nagle, D.C. and Ball, W.P., 2006. Production and characterization of synthetic wood chars for use as surrogates for natural sorbents. Organic Geochemistry, 37(3): Pp. 321–333. doi:10.1016/j.orggeochem.2005.10.008.

Cao, Q., Xie, K.-C., Bao, W.-R., and Shen, S.-G., 2004. Pyrolytic behavior of waste corn cob', Bioresource Technology, 94(1):83–89. doi:10.1016/j.biortech.2003.10.031.

Chan, K.Y. and Xu, Z., 2009. Biochar: Nutrient properties and their enhancement. In: Lehmann, J. and Joseph, S. (Eds), Biochar for Environmental Management. Eastern Publications,London. Science and Technology. Pp. 67 - 84

Chen, D., Zhou, J., and Zhang, Q., 2014. Effects of heating rate on slow pyrolysis behavior, kinetic parameters and products properties of moso bamboo. Bioresource Technology, 169: Pp. 313–319. doi:10.1016/j.biortech.2014.07.009.

Claoston, N., Samsuri, A., Ahmad Husni, M., and Mohd Amran, M., 2014. Effects of pyrolysis temperature on the physicochemical properties of empty fruit bunch and rice husk biochars. Waste Management and Research, 32(4): Pp. 331–339. doi:10.1177/0734242x14525822.

Demirbaş, A., 2004. Effects of temperature and particle size on biochar yield from pyrolysis of agricultural residues. Journal of Analytical and Applied Pyrolysis, 72(2): Pp. 243–248. doi:10.1016/j.jaap.2004.07.003.

Dhyani, V and Bhaskar, T., 2019. Pyrolysis of Biomass In: Pandey, A., Larroche, C., Dussap, C.-G., Gnansounou, E., Khanal, S.K. and Ricke, S. (eds.). Biofuels: Alternative Feedstocks and Conversion Processes for the Production of Liquid and Gaseous Biofuels. 2nd edn. Amsterdam: Elsevier, pp. 217–248.

Dong, J., Jiang, P., Wang, H., Lu, R., Liu, Y., Li, Y., Gan, Y. and Bolan, N., 2023. Influence of biomass feedstocks on magnetic biochar preparation for efficient Pb(II) removal. Environmental Technology and Innovation, 32: Pp. 103363. doi:10.1016/j.eti.2023.103363.

Gaskin, J., Steiner, C., Harris, K., Bibens, B. and others., 2008. Effect of low-temperature pyrolysis conditions on biochar for agricultural use. Transactions of the ASABE, 51(6): Pp. 2061–2069. doi:10.13031/2013.25409.

Gazulla, M. F., Rodrigo, M., Orduña, M., and Ventura, M. J., 2016. Determination of organic oxygen in petroleum cokes and coals. Microchemical Journal, 126: Pp. 538–544. doi:10.1016/j.microc.2016.01.018

Gupta, S., Gupta, G.K. and Mondal, M.K., 2019. Slow pyrolysis of chemically treated walnut shell for valuable products: Effect of process parameters and in-depth product analysis. Energy, 181: Pp. 665–676. doi:10.1016/j.energy.2019.05.214.

Jain, N., Bhatia, A. and Pathak, H., 2014. Emission of Air Pollutants from Crop Residue Burning in India. Aerosol and Air Quality Research, 14: Pp. 422-430. https://doi.org/10.4209/aaqr.2013.01.0031

Jindo, K., Mizumoto, H., Sawada, Y., Sanchez-Monedero, M. A., and Sonoki, T., 2014. Physical and chemical characterization of biochars derived from different agricultural residues. Biogeosciences, 11(23): Pp. 6613–6621. doi:10.5194/bg-11-6613-2014

Kan, T., Strezov, V., and Evans, T. J., 2016. Lignocellulosic biomass pyrolysis: A review of product properties and effects of pyrolysis parameters. Renewable and Sustainable Energy Reviews, 57: Pp. 1126–1140. doi:10.1016/j.rser.2015.12.185

Keiluweit, M., Nico, P. S., Johnson, M. G., and Kleber, M., 2010. Dynamic Molecular Structure of Plant Biomass-Derived Black Carbon (Biochar). Environmental Science and Technology, 44(4), Pp. 1247–1253. doi:10.1021/es9031419

Kim, K.H., Cho, T.-S. and Choi, J.W., 2012. Influence of pyrolysis temperature on physicochemical properties of biochar obtained from the fast pyrolysis of pitch pine (Pinus rigida). Bioresource Technology, 118: Pp. 158–162. doi:10.1016/j.biortech.2012.04.094.

Lian, W., Shi, W., Tian, S., Gong, X., Yu, Q., Lu, H., Liu, Z., Zheng, J., Wang, Y., Bian, R., Li, L., and Pan, G., 2023. Preparation and application of biochar from co-pyrolysis of different feedstocks for immobilization of heavy metals in contaminated soil. Waste Management, 163: Pp. 12–21. doi:10.1016/j.wasman.2023.04.015.

Liang, B., Lehmann, J., Solomon, D., Kinyangi, J., Grossman, J., O'Neill, B., Skjemstad, J.O., Thies, J., Luizão, F.J., Petersen, J., and Neves, E.G., 2006. Black carbon increases cation exchange capacity in soils. Soil Sci. Soc. Am. J., 70: Pp. 1719 – 1730.

Ma, Z., Yang, Y., Ma, Q., Zhou, H., Luo, X., Liu, X., and Wang, S., 2017. Evolution of the chemical composition, functional group, pore structure and crystallographic structure of bio-char from palm kernel shell pyrolysis under different temperatures. Journal of Analytical and Applied Pyrolysis, 127: Pp. 350–359. doi:10.1016/j.jaap.2017.07.015.

Mašek, O., Brownsort, P., Cross, A. and Sohi, S., 2013. Influence of production conditions on the yield and environmental stability of biochar. Fuel, 103: Pp. 151–155. doi:10.1016/j.fuel.2011.08.044.

Mimmo, T., Panzacchi, P., Baratieri, M., Davies, C. A., and Tonon, G., 2014. Effect of pyrolysis temperature on miscanthus (Miscanthus × giganteus) biochar physical, chemical and functional properties. Biomass and Bioenergy, 62, Pp. 149–157. doi:10.1016/j.biombioe.2014.01.004

Mukherjee, A., Zimmerman, A. R., and Harris, W., 2011. Surface chemistry variations among a series of laboratory-produced biochars. Geoderma, 163(3-4): Pp. 247–255. doi:10.1016/j.geoderma.2011.04.021.

Noor, N.M., Shariff, A., Abdullah, N., and Aziz, S., 2019. Temperature effect on biochar properties from slow pyrolysis of coconut flesh waste. Malaysian Journal of Fundamental and Applied Sciences, 15(2): Pp. 153–158. doi:10.11113/mjfas.v15n2.1015.

Novak, J., Lima, I., Xing, B., Schomberg, H. and others., 2009. Characterization of designer biochar produced at different temperatures and their effects on a loamy sand. Annals of Environmental Science, 3: Pp. 195–206.

Obonukut, M., Alabi, S. and Jock, A., 2022. Biochar from cassava waste: A paradigm shift from waste to wealth. In: Biochar - Productive Technologies, Properties and Applications. DOI: 10.5772/intechopen.105965

Ogede, L.O., Ejimadu, C.M. and Okieimen, F.E., 2024. Chemical and textural properties of melon seed shell-derived biochar relevant to their application in the remediation of contaminated soil. Nigerian Research Journal of Engineering and Environmental Sciences, 9(2): Pp. 681–688.

Othugile, L. E., Lekgoba, T. and Ntuli, F., 2022. Sequestration of Heavy Metals From Coal Wash Water Using Biochar From Pyrolysis of Morula Shells. European Journal of Sustainable Development Research, 6(1), em0173. https://doi.org/10.21601/ejosdr/11377

Pradhan, S., Abdelaal, A. H., Mroue, K., Al-Ansari, T., Mackey, H. R., and McKay, G., 2020. Biochar from vegetable wastes: agro-environmental characterization. Biochar, 2: Pp. 439–453. https://doi.org/10.1007/s42773-020-00069-9.

Prauchner, M. J., and Rodríguez-Reinoso, F., 2012. Chemical versus physical activation of coconut shell: A comparative study. Microporous and Mesoporous Materials, 152: Pp. 163–171. doi:10.1016/j.micromeso.2011.11.040

Robertson, G.P., Sollins, P., Ellis, B.G., and Lajtha, K., 1999. Exchangeable ions, pH, and cation exchange capacity. In: Robertson, G. (eds.) Standard Soil Methods for Long-Term Ecological Research. New York: Oxford University Press, pp 106–114.

Samsudin, M. H., Hassan, M. A., Idris, J., Ramli, N., Mohd Yusoff, M. Z., Ibrahim, I., … Shirai, Y., 2019. A one-step self-sustained low temperature carbonization of coconut shell biomass produced a high specific surface area biochar-derived nano-adsorbent. Waste Management and Research, 0734242X1882395. doi:10.1177/0734242x18823953

Sari, R.M., Gea, S., Wirjosentono, B., Hendrana, S., and Hutapea, Y.A., 2020. Improving quality and yield production of coconut shell charcoal through a modified pyrolysis reactor with tar scrubber to reduce smoke pollution. Polish Journal of Environmental Studies, 29(2): pp. 1815–1824. DOI: 10.15244/pjoes/110582.

Shoaib, A. G., El-Sikaily, A., El Nemr, A., Mohamed, A. E. D. A., and Hassan, A. A., 2020. Preparation and characterization of highly surface area activated carbons followed type IV from marine red alga (Pterocladia capillacea) by zinc chloride activation. Biomass Conversion and Biorefinery, pp 1-13

Singh, B., Dolk, M.M., Shen, Q., Camps-Arbestain, M., 2017. Biochar pH, electrical conductivity and liming potential. Biochar: A Guide to Analytical Methods: pp 23–38.

Suman, S., and Gautam, S., 2017. Pyrolysis of coconut husk biomass: Analysis of its biochar properties. Energy Sources, Part A: Recovery, Utilization, and Environmental Effects, 39(8): Pp. 761–767. doi:10.1080/15567036.2016.12632

Wang, J., Li, Z., Li, Y., Wang, Z., Liu, X., Liu, Z. and Ma, J., 2024. Evolution and correlation of the physiochemical properties of bamboo char under successive pyrolysis process. Biochar, 6:33. https://doi.org/10.1007/s42773-024-00321-6.

Yang, F., Zhao, L., Gao, B., Xu, X., and Cao, X., 2016. The interfacial behavior between biochar and soil minerals and its effect on biochar stability. Environmental Science and Technology, 50(5): Pp. 2264–2271. doi:10.1021/acs.est.5b03656.

Yang, H., and Sheng, K., 2012. Characterization of Biochar Properties Affected by Different Pyrolysis Temperatures Using Visible-Near-Infrared Spectroscopy. ISRN Science Technology, 2012: Pp. 1–7. doi:10.5402/2012/712837.

Yang, H., Yan, R., Chin, T., Liang, D. T., Chen, H., and Zheng, C., 2004. Thermogravimetric Analysis–Fourier Transform Infrared Analysis of Palm Oil Waste Pyrolysis. Energy and Fuels, 18(6): Pp. 1814–1821. doi:10.1021/ef030193m.

Yuan, J.-H., Xu, R.-K., and Zhang, H., 2011. The forms of alkalis in the biochar produced from crop residues at different temperatures. Bioresource Technology, 102(3): Pp. 3488–3497. doi:10.1016/j.biortech.2010.11.018.

Zhang, C., Zhang, Z., Zhang, L., Li, Q., Li, C., Chen, G., Zhang, S., Liu, Q., and Hu, X., 2020. Evolution of the functionalities and structures of biochar in pyrolysis of poplar in a wide temperature range. Bioresource Technology, 304: Pp. 123002. doi:10.1016/j.biortech.2020.123002.