Catalytic effect of Kaolin on the pyrolysis of Sawdust and Poultry wastes to produce Biochar for CO_2 Sequestration

Mohammed A.[1]; Bello A.[2]; Habibu U.[3]; Mohammed U.G.[4]; Abubakar G.I.[5] and Aisha F.[6]

[1,3-6]Chemical Engineering Department, Federal University of Technology, Minna, Nigeria.
[2]Entrepreneurship Development Centre, Kwara State Polytechnic, Ilorin, Nigeria.
Email: moh.alhass@futminna.edu.ng

Abstract

There is an increasing realisation that biomass and organic waste are valuable feedstock for pyrolysis process that produces biochar, bio-oil and biogas. The Oxides such as aluminium oxide (Al_2O) and calcium oxide (CaO) could have catalytic effect on biochar production from biomass. To study the catalytic effect of Kaolin, the raw kaolin was calcinated, acid modified and characterised. Saw dust (SD) and Poultry waste (PW) biomass were impregnated with the modified Kaolin at different ratio (25wt%, 50wt%, and 75wt%)and subjected to pyrolysis at temperature between 300°C and 600°C.The biochar produced were analysed, characterised and the carbon sequestration potential was evaluated hypothetically. The result showed that co-pyrolysis of SD impregnated with 25wt% of Kaolin (SDK25) increased the biochar yield by 25wt% and carbon sequestration potential by 10wt% as compared to PW impregnated with 25wt% Kaolin (PWK25) which increased the biochar yield by 15wt% and carbon sequestration potentials by 5wt%. Fourier Infrared spectroscopy (FT-IR) spectra displayed that all biochars at 500°C contain C-H alkyl group and aromatic band at $1571cm^{-1}$ which may impact positively on nutrient and water retention. Scanning Electron Microscope (SEM)and X-ray diffraction (XRD) analysis showed the development of well define pores for biochar produced at 500°C, while the Brunauer–Emmett–Teller (BET) analysis showed that the biochar produced from the two biomass has a good surface structure and characteristics (surface area: $410 m^2.g^{-1}$ and $276.3 m^2.g^{-1}$) and could be employed as adsorbent in CO_2 adsorption.

Introduction

Biomass is made of organic compounds originally produced by absorbing atmospheric CO_2 during the process of plant photosynthesis. As an energy source, biomass can either be used directly via combustion to produce heat, or indirectly after converting it to various forms of biofuels. One of the most convenient methods to utilize biomass is by conversion to hydrophobic solid with a high energy density called biochar. What is needed is a method and system for conversion of biomass to biochar that lead to higher biochar yield. It is to the provision of this need among others that the present invention (pyrolysis) is primarily directed.

The potential to convert lignocelluloses materials into biochar and bio-oil is generating renewed interest in pyrolysis (Bridgewater *et al.*, 2000; Huber, 2008; Antal, 2003). Biochar has the capacity to increase soil fertility and sequester carbon (Granatsetein *et al.*, 2009; Lehman *et al.*, 2006). Interest has been increasing in using biochar as a soil amendment to sequester carbon (C), improve soil quality and also to minimise the potential negative impacts of bioenergy production (Laird *et al.*, 2007). Biochar is thought to be recalcitrant (Kuzyako *et al.*, 2009; Lehmann and Joseph, 2009) and thus is a stable source of carbon. Biochar has effects on other soil characteristics, including pH and fertility

(Lehmann *et al.*, 2003). However, these effects depend on the biochar feedstock and pyrolysis conditions (Chan *et al.*, 2009; Gaskin *et al.*, 2008) as well as on the soil itself (Lehmann and Joseph, 2009).

Biochar is being recognized as a promising tool for long term carbon sequestration and biochar with high carbon retention and strong stability is supposed to be explored for that purpose. Stability is an important property that determines the suitability of biochar for carbon sequestration, but currently in literature there are no standard methods to assess stability in biochar. Wang, (2013) investigated the catalytic gasification of biomass and pointed out that with the use of catalyst, conversion efficiency can be increased by 10wt%. However, a considerable amount of tar generated during gasification and the energy in the tar consumed up to 5-15wt% of the total energy. Impregnation of biomass with catalyst was reported to enhance product yields (Sutton *et al.*, 2001; Wu-Jun *et al.*, 2015; Lehmann *et al.*, 2015). The use of supported catalyst is gaining more attention due to its potential to enhance performance and yield of pyrolysis products. Utilisation of locally available clay will reduce the cost of producing supported catalyst. This study therefore uses kaolin clay to impregnate biomass catalytically after conventional pyrolysis of bare sawdust and poultry waste in order to improve yield, carbon retention and stability in biochar.

Materials and Method

Sawdust and poultry waste are representative of the woody and agricultural waste biomass. Poultry waste was obtained at Amasco Poultry Farm in Ilorin, while Sawdust was procured at Belad Furniture workshop in Ilorin, Kwara State. Kaolin was sourced from abundant kaolin area at Kutigi, in Lavun Local Government Area of Niger State. About 10 kg each of the biomass procured were prepared as followed: The samples were air-dried as received prior to division and utilization in the experiment. Parts of the samples were dried in Gallenkhamp muffle furnace operated at 105°C. The weight of the samples was periodically measured using a standard scout pro weighing balance (Ohaus) until constant weight was achieved. A local grinding mill was used to crush the biomass while mortar and pestle were used to crush the kaolin lumps prior to drying. A laboratory sieve stalk model BS410-1:20 was used to obtain a uniform particle size fractions in the range between 1 – 2mm according to the ASTME828 method of determination of particle size distribution. Samples of the saw dust and poultry waste without the addition of kaolin were called (SD) and (PW) respectively, while the ones impregnated with kaolin were denoted as SDK and PWK respectively. Prior to the impregnation of SD and PW with kaolin, the Kaolin was activated using a convectional activation approach where the Kaolin was contacted with 1M H_2SO_4 solution and then calcined at 500°C using liquid to solid ratio of 10ml.1g^{-1}. Detail of these procedures can be found in Panda *et al.* (2010) and Alhassan *et al.*, (2016). A fixed bed reactor of 50cm length and 15cm diameter was inserted into a Carbonate furnace with serial number 21-301418. About 20g of sample with particle sizes in the range 1-2mm were placed inside the crucible and inserted into the pyrolyser. The system was closed and degassed with nitrogen for five minutes prior to the carbonation. The operating temperature which ranged from 300°C–

Mohammed A.[1]; Bello A.[2]; Habibu U.[3]; Mohammed U.G.[4]; Abubakar G.I.[5] and Aisha F.[6]

650°C was set. The furnace was switched on, heated at the rate of 20°Cmin⁻¹ and maintained at the set temperature for 1hr. The flue gases were condensed through the attached condenser. These experimental conditions are believed to favour biochar production in slow pyrolysis as temperature being a major driving force in pyrolysis was varied within the range of 300°C – 650°C to ascertained maximum yields. It was at the range of maximum yield temperatures that different percentages of Kaolin were impregnated into biomass and pyrolysed to enhance carbon retention and stability in biochar. After the reaction had cooled down, the sample crucible was removed through the reactor exit. The biochar yield was measured with the aid of weighing balance and kept in a well labelled sample bag for further analysis. The same method was used for bio-oil yield while biogas yield was determined by mass difference. The biochars were analysed using Elementary analyser (EA), X-ray diffraction (XRD), Scanning Electron Microscope (SEM) and BET analyser. The percentage weight yield and weight conversion in Equation (1) and (2) were determined according to methods proposed in Alhassan and Andresen (2013).

$$Percentage\ weight\ yield = \frac{mass\ of\ biochar}{mass\ of\ Biomass} \times 100\% \tag{1}$$

$$Percentage\ weight\ conversion = \frac{mass\ of\ biomass - mass\ of\ biochar}{mass\ of\ Biomass} \times 100\% \tag{2}$$

Carbon sequestration potentials of the biochar produced were assessed using method suggested in Alhassan (2013)

where carbon sequestration potentials of biochar was calculated using equation (3-5).

$$Total\ carbon\ sequestration\ potentials = carbon\ content\ of\ the\ biochar \tag{3}$$
$$Amount\ biochar\ produced = Amount\ of\ biomass\ produced \times \%\ conversion \tag{4}$$
$$Carbon\ sequestration\ potential\ interms\ of\ assumed\ 80\%\ stability$$
$$= amount\ CO_2\ reduction \tag{5}$$

Thermal analysis was performed on both the raw biomass and the biochar produced using Thermogravemetric analysis equipment with model number C5300 mega series, where proximate compositions such as moisture, ash, volatile matter and fixed carbon content of both the biomass and the biochar were obtained. These properties of the sample were obtained following the British Standard Test methods CEN/S15403:2006 (CENT/TS, 2006). Principle adopted for the determination of these properties according to Alhassan (2013) is as follows: Weight loss observed when the sample was heated from 30°C to 105°C was attributed to its moisture content. Weight loss observed between 105°C and 800°C was attributed to the volatile matter content of the sample. When the sweeping gas was switched from nitrogen to oxygen at 800°C, the weight loss observed was attributed to fixed carbon content of the sample and residues remaining after cooling represent the ash content. Elemental analysis was performed using LebigPregle method (BSI, 2004) where the percentage Carbon (C), Hydrogen (H), Nitrogen (N) and sulphur

were determined. Oxygen was determining by difference. The surface morphology of the biochar produced at optimum experimental conditions was carried out using Scanning Electron Microscope (SEM) with model number 44465, while the micro structure and mineral content of the biochar produced were analysed using X-ray Diffraction machine operated at a scan range of $2\theta = 50°$ to $650°$ at a rate of 20 $°min^{-1}$. The presence of mineral compounds were identified using Diffraction Technology trace V.3 software with a data base of diffraction spectra which was developed by the Joint Committee on Powder Diffraction Standard International Center for Diffraction Data (JCPDS-ICDD). Fourier Transformed Infra Red (FT-IR) analysis was carried out to identified presence of functional groups in the biochar produced so as asses its suitability in carbon sequestration using FT-IR machine with model number 8400S, while the surface area of the biohars were analysed using a BET machine NOVA4200e.

Results and Discussions

This section presents the results as well as the discussions of results. It reveals both the physical and chemical properties of biomass and the biochar produced which were determined using standard methods of analysis. These analyses include proximate and ultimate analysis, FTIR, SEM, BET and XRD and calculation of carbon sequestration potentials of biochar.

Table 1: Proximate and ultimate analysis of biomass and the biochar produced

Properties* (wt%)	SD	PW	SBC	SKBCBC	PBC	PKBC
Moisture Content	3.56	1.4	-	-	-	-
Ash Content	1.49	15.0	-	-	-	-
Volatile Matter	66.63	32.0	-	-	-	-
Fixed Carbon	28.32	60.0	-	-	-	-
Carbon	72.32	64.72	76.32	78.1	70.01	68.3
Hydrogen	14.36	13.82	10.68	11.73	12.96	13.836
Nitrogen	3.19	4.82	0.02	0.21	0.27	0.34
Oxygen	9.94	16.43	10.14	8.55	13.48	12.81
Sulphur	0.19	0.21	2.84	1.41	3.28	2.714
H/C	-	-	1.68	1.80	2.22	2.22
O/C	-	-	0.03	0.02	0.04	0.04

a. as determined; -., Not determined

The proximate analysis of the sawdust and poultry waste in Table 1 shows that saw dust contain 3.56wt% moisture, 66.63wt% volatiles matters, 14.36wt% hydrogen and 9.94wt% Oxygen, while poultry waste contains 1.4 wt% moisture, 32 wt% volatiles, 64.72wt% carbon, and 13.82wt% of hydrogen. These values suggest that both biomass can generate appreciable amount of bio oil during pyrolysis and since the target was to produced biochar, efforts was geared towards repolymerisation of the volatiles formed into biochar during pyrolysis by employing a low heating rate, and low swept gas flow rate. The differences observed in the proximate analysis values between the present research and the reported values in Wang *et al.* (2010), could be attributed to the origin of the feedstock and the pretreatment method adopted by the authors. The fixed carbon content of SW and PW were 28.32wt% and 60.6wt% respectively which is an indication that stable char can be produced from the biomass. The values of sulphur and nitrogen are small from both biomass and thus can be accepted to be the future source of sustainable green energy (Tsai *et al.*, 2006; Criado and Ortega, 1986). Sulphur is a major contributing factor to ash formation as they facilitate the mobility of inorganic compounds from the fuel to surfaces where they form the corrosive compounds (Wilson, 2010). The

Mohammed A.[1]; Bello A.[2]; Habibu U.[3]; Mohammed U.G.[4]; Abubakar G.I.[5] and Aisha F.[6]

ash content of sawdust (woody biomass) as might be expected is significantly lower than that of poultry waste (15.0wt%) which is also consistent with prior study (Gaskin et al., 2008). From the Table 1 it can be observed from the biochars produced that the SKBC has higher carbon content of 78.1wt%, followed by SBC (76.32wt%), PKBC (72.95wt%) and PBC (70.1 wt%) respectively. This indicates that the PBC which has least wt% of carbon has the highest H/C ratio of 2.22 and O/C of 0.04. The molar H/C and O/C are indicators of the degree of carbonisation and therefore of the biochar stability (Mattias, 2013). H/C and O/C of SBC are (1.68, 0.03), SKBC (1.80, 0.01) and PKBC (2.13, 0.03) respectively.

XRF analysis of kaolin

The chemical analysis of the Kutigi kaolin as shown in Table 2 indicates that it contains alumina, silica, iron and calcium in major quantities and other elements in minor quantities. Result as presented shows that percentage of SiO_2 was 27.67wt%, Fe_2O_3 is 1.93wt% while that of Al_2O_3 was 40.0wt%. The sum of SiO_2, Fe_2O_3 and Al_2O_3 was 70.72wt% which suggests the kaolin to be a good pozzolanic material since it has met the 70wt% minimum requirement recommended by ASTM C618 and can improve the pore size distribution and permeability of the char produced for carbon sequestration applications. Also it is expected that the presence of Al_2O_3 and Cao in kaolin could aid char formation by serving as heat shield during char formation and good source of Al^{2+} to promote char formation. CaO according to Alhassan and Andresen, (2013) can promote dehydration and decarbonxylation at the expense of bio oil and gas formation. The metal oxide compositions of Kutigi kaolin as presented

is close to the reported literature values in Mohammed et al. (2013). The little variation could be attributed to differences in geographical and geological formation of in kaolin. The authors reported that kaolin has approximately 45wt% SiO_2, 37wt% Al_2O_3, 0.29wt% Fe_2O_3, 0.17wt%CaO, 0.96wt% Na_2O, 0.50wt% K_2O, and 0.95wt%MgO.

Table 2: XRF of Kutigi kaolin

Compounds	Values (wt%)
SiO_2	27.90
Al_2O_3	40.9
Fe_2O_3	1.925
CaO	6.075
Mn_2O_3	0.004
TiO_2	3.141
LSF	4.783
$CaCO_3$	10.843
L.O.I	4.57

Thermogravemetric Analysis of Biomass

Thermogravemetric profile of sawdust and poultry waste samples were carried out in order to access the thermal properties of the samples. Fig. 1 shows the normalised weight loss for the sawdust and poultry waste as a function of temperature. The weight loss started from 29°C to 887°C. The first mass loss ($29 < T \leq 100$°C) is due to moisture and some extractive compound evaporation. The second weight loss ($100 < T \leq 400$°C) is mainly related to hemicelluloses and cellulose thermal degradation. Lignin is a more stable component presenting a large range of thermal degradation (from 250°C to 500°C or even higher temperature depending on the biomass) and in this way the third degradation step ($400 < T 600$°C) is attributed to lignin degradation (Brebu and Vasile, 2010; Imam and Capareda, 2011). Also, according to Alhassan and Andresen (2013), composition such as moisture,

volatile, fixed carbon and ash content of the biomass can be approximated from the TGA profile, for example weight loss between points A-B, B-C, C-D and D represent moisture, volatile matter, fixed carbon and ash content respectively.
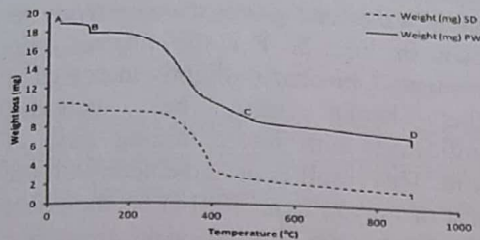

Fig. 1: TGA of Sawdust and Poultry Waste.

Catalytic biomass pyrolysis

Effect of Temperature on the Pyrolysis Product Distribution

The effect of temperature on the yields of pyrolysis products of sawdust and poultry waste at temperature range of 300°C-650°C, heating rate of 20°Cmin^{-1}, a holding time of 1hr and nitrogen flow rate of 60ml/min in a horizontal tube pyrolyser was investigated and the result is graphically represented in Figure 2. It was observed that the yield of biochar initially increased with increase in temperature from 300°C-500°Cwhich correspond to 28.1wt%-34.8wt% with maximum yield of 34.8wt% at 500°C. However, above 500°C the yield decreased till the final pyrolysis temperature of 650°C corresponding to 22.7wt%. The initial increment of biochar could be due to the minimization of the losses of carbon in the form of gases and liquids. Glaser *et al.* (2002) reported that biochar produced at temperature range of 250°C– 400°C have higher yield recoveries. Since the heating rate employ for this study is low (20°Cmin^{-1}), one can say slow pyrolysis is simulated Wright and Brown, (2011). The reduction in biochar yield

above 500°C could be attributed to the primary decomposition of the feedstock at higher temperature or secondary decomposition of biochar (Alhassan and Andresen, 2013). The trend of the weight loss observed from this study is consistent with that of the other researchers (Brebu and Vasile, 2010; Imam and Capareda, 2011). For example, biochar yield from switchgrass pyrolysis conducted by Imam and Capareda, (2011) decreased from 48wt% to 43wt% from sample pyrolysed at 400°C and 500°C respectively and more pronounced between sample pyrolysed between 500°C and 600°C giving 43wt% to 23wt% decreased. Likewise for poultry waste, result reveals maximum biochar yield at 450°C corresponding to 41wt%biochar, 24wt% bio-oil and 35wt% syngas.
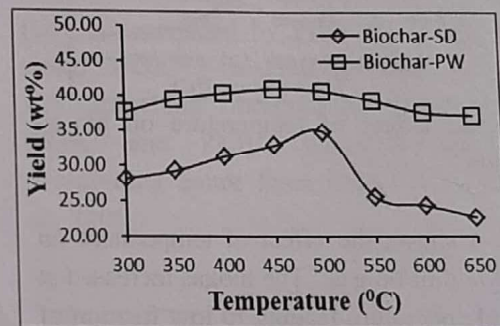

Fig. 2: Effect of temperature on biochar yield

Fig. 3 shows the effect of temperature on bio-oil yield, it can be observed from the figure that the bio-oil increase gradual till 500°C and thereby starts diminishing up till 650°C. Lin *et al.*, (2015) reported that bio-oil yields are higher with increased pyrolysis temperature up to 600°C, although depending on other pyrolysis conditions and equipment utilised. Above this temperature, secondary reaction causing vapour decomposition to prevailed

Mohammed A.[1]; Bello A.[2]; Habibu U.[3]; Mohammed U.G.[4]; Abubakar G.I.[5] and Aisha F.[6]

and the condensed bio-oil yields are reduced, favouring more production of syngas and carbon content in biochar. Also, the condensable fraction obtained at low temperature 300°C-400°C was less viscous when compared to that obtained at 500°C. Demirbas, (2001) reported a peak liquid yields of 28wt%-41wt% at temperature between 337°C and 577°C, depending on the feedstock when using a laboratory slow pyrolysis technique, while in this study the bio-oil yield was 31wt%-33wt% (at 400°C-550°C) for sawdust and 24wt%-27wt% (at 350°C-500°C) for poultry waste. The difference in value may be attributed to feedstock compositions and characteristics.
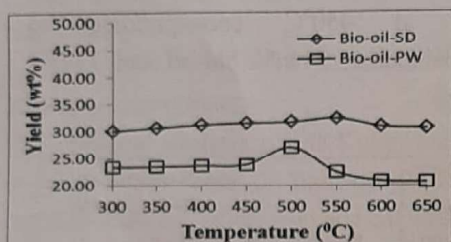

Fig. 3: Effect of temperature on bio-oil yields.

Fig. 4 shows the effect of temperature on the yield of biogas. The biogas increased at high temperature leading to low fraction of biochar and bio-oil. At high temperature, the secondary cracking of volatiles and the char formed into biogas increases, leading to high biogas production from both biomasses.
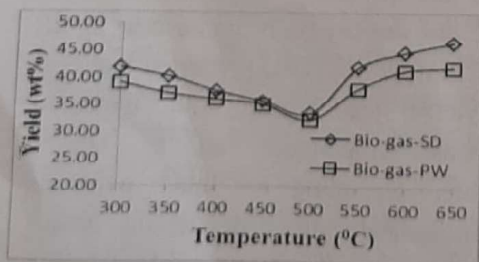

Fig. 4: Effect of temperature on bio-gas yields

Effect of Kaolin on Pyrolysis Product Yield

The effect of kaolin and its mixing ratio (75-25wt%, 50wt%-50wt% and 25wt%-75wt%) on the pyrolysis of sawdust and poultry waste was studied in a horizontal tube pyrolyser operating at optimum temperatures of 450°C and 500°C for poultry waste and sawdust respectively as shown in Fig. 5. For the mixing ratio investigated, biochar is slightly increased at higher kaolin ratio but increased significantly with lower mixing ratio of kaolin. This result is in agreement with the report of Feiyue *et al.* (2014) on the effect of kaolin on the biochar yield from rice straw.
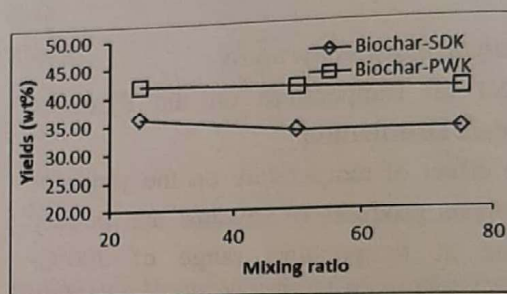

Fig. 5: Effect of mixing ratio on biochar yield at 500°C.

The bio-oil yields for both sawdust and poultry waste mixed with kaolin is shown in Fig. 6. It was observed that bio-oil yield was enhanced at low mixing ratio and decreased as the mixing ratio increased (Onay, 2014). This indicates that the changes observed in char yield from Fig. 5 might be related to the delay devolatilization observed as the mixing ration increases from Fig. 6. Bardalai and Mahanta, (2013) reported that when sawdust was mixed with catalyst (Al_2O_3), there was no such drastic change in weight, so the rate of volatilisation was slow up to the temperature of 600°C.
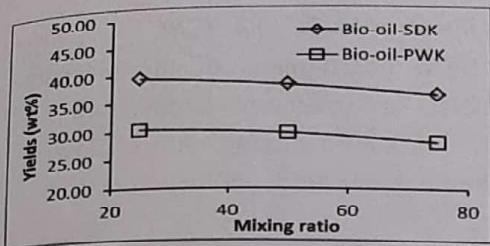
Fig. 6: Effect of mixing ration on bio-oil yield at 500°C.

Fig. 7 shows biogas yields from sawdust and poultry waste impregnated with kaolin. It was noticed that biogas production increased with increase in kaolin addition. These suggest the ability of kaolin to promote secondary reaction at higher mixing ratio which favoured biogas production.
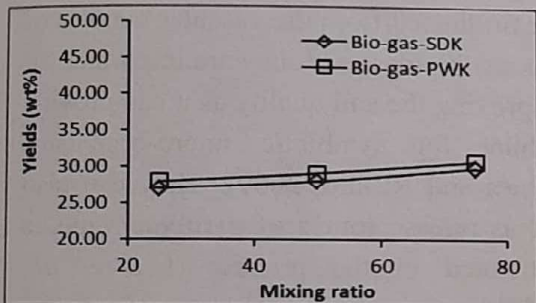

Fig. 7: Effect of mixing ratio on bio-gas yield at 500°C

FT-IR Analysis of Biochars

FT-IR analysis of samples of biochar from SBC, SKBC, PBC and PKBC for the detection of functional groups, impurities and water is shown in Fig. 8. These parameters are known to alter the sequestration ability of biochar (Allyson, 2011). Some of the differences in the spectra are as a result of organic matter combustion and the concentration of the mineral components that were changed when heated (Cao and Harris, 2010). FTIR data graphs revealed number of similarities amongst the functional groups present for the four biochars. The broad peak in the spectrum at the range $630cm^{-1}$-$880cm^{-1}$ can be assigned to the existence of C-H alkyl stretch in all biochars at different areas. Aliphatic amines (NH) stretch amines are common stretch of SBC and SKBC at band $3380cm^{-1}$-$3415cm^{-1}$ while hydroxyl groups (OH) are revealed by PBC and PKBC at peak$3381cm^{-1}$ and$3400cm^{-1}$respectively. C=C stretching vibrations are common in SKBC and PKBC which might be contributing factor from kaolin (Cheng *et al.*, 2006).
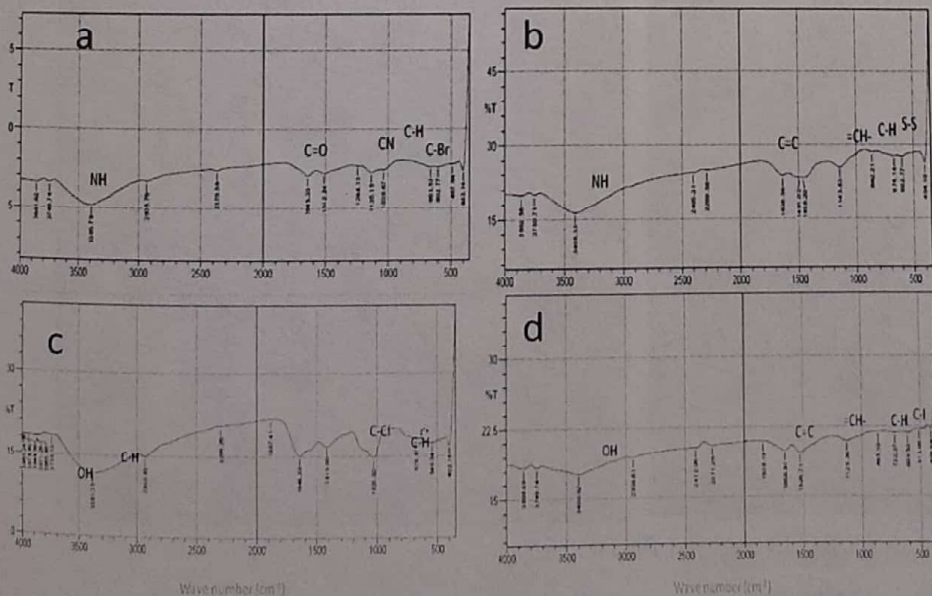

Fig. 8: FTIR Spectra of (a) SKBC; (b) SKBC25; (c) PBC; (d) PKBC25

125

BET Analysis of Biochars

Table 3 shows the pore volume and BET surface area of SBC and PBC pyrolysed at 500°C. Surface areas were high enough, corresponding to 410 $m^2.g^{-1}$ for (SBC) and 276.3 $m^2.g^{-1}$ for (PBC) respectively. Having a high surface area is important to the placement of the biochar underground. Adsorption and nutrient retention can be enhanced for plant growth (Yao *et al.,* 2012). Erosion impact on the soil is reduced with high biochar surface area per gram of the sample and more ability to capture any particulates that may pass through the sink or in to the biochar fertilised soil (Allyson, 2011). Therefore, the longevity is enhanced and carbon capturing can take place over a longer period of time.

Table 3: Surface Area and Pore Volume

Biochar	Surface Area ($m^2.g^{-1}$)	Pore Volume ($cm^3.g^{-1}$)	Pore Size (Å)
SBC	410	0.1185	13.24
PBC	276.3	0.07403	13.24

SEM Result of SKBC and PKBC

The SEM micrographs of the biochars produced at optimum temperature of 500°C and kaolin mixing ratio of 25wt% are shown in Fig. 9 (a) and (b).

Increased porosity due to the escape of volatiles during pyrolysis process can be observed from Fig. 10a. The particle size decrease observed in the process is believed to be caused by rapid devolatilization creating very porous (mesoporous) and fragmented chars (Scala *et al.,* 2006). The PKBC developed high porosity, presenting longitudinal pores with size ranging from micro to macro pores (20 to 200µm) while that of SKBC ranges from 30 to 200 µm. The large pores are originated from the vascular bundles of the raw biomass and they are important for improving the soil quality as it can provide habitat for symbiotic micro-organisms (Thies and Rilling, 2009). They can also act as release routes of pyrolytic vapours generated in the process (Lee *et al.,* 2013b).
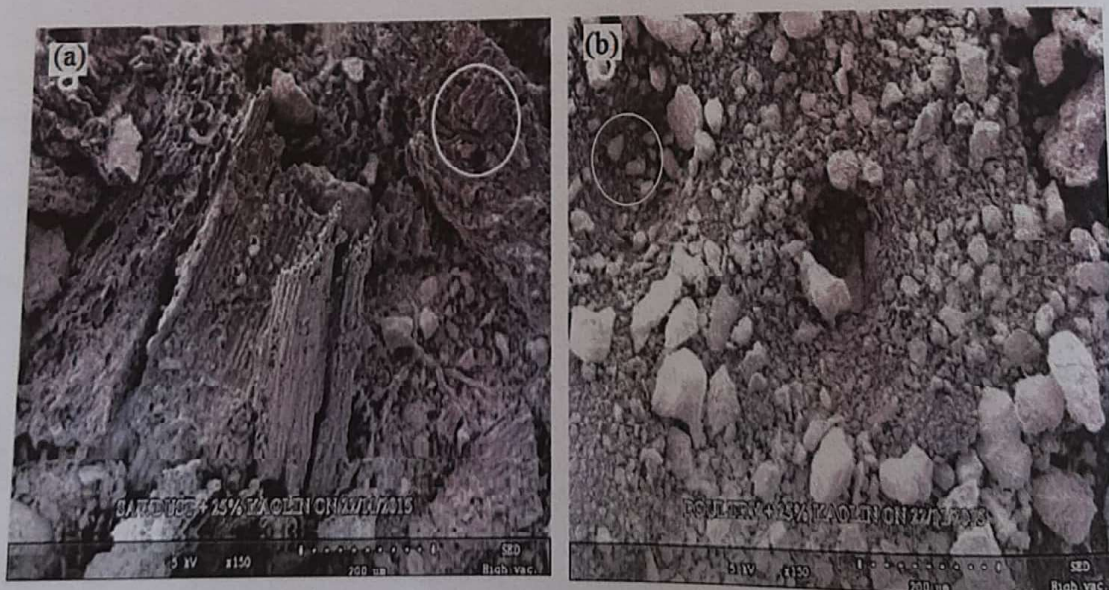

Fig. 9: SEM Image of (a) SKBC25 and (b) PKBC25

XRD Results of Biochars

X-ray diffraction analysis of the biochar from the PWBC and SDBC showed similar trend and indicates the presence of kaolinite, quartz and muscovite which is commonly associated with poultry waste derived biochar. Fig. 10 displays the diffractogram of SKBC25 and PKBC25 at 500°C. Quartz (SiO_2) with highest peaks corresponded to $2\square = 26.6°$, followed by kaolinite $2\square = 20.5°$ and muscovite $2\square = 35°$. Similar diffractogram was reported by Wang *et al.*, (2008) for pine wood sawdust. The obtained sharp peaks indicate the transformation from amorphous to crystalline structure (Mohammed *et al*, 2013; Alhassan and Andresen, 2013).
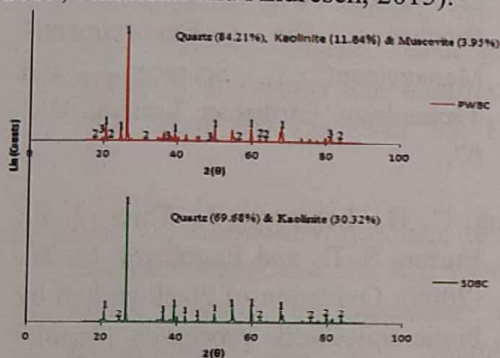

Fig.10: XRD patterns of Biochars.

Potential of Biochar as Carbon Sequester

The potential of biochar as a carbon sequestration agent depends upon both the amount and the rate that carbon dioxide could be removed from the atmosphere and stored as carbonaceous solid in soils (Catherine, 2012). In calculating the carbon sequestration potential of biochar, it is important to make valid assumptions as used in the literature and utilisation of equations 3-5 as proposed in Alhassan (2013). Some of the assumptions include: 80wt% Carbon contain in biochar is stable and can be sequestered.

Table 4 shows the data used for calculation of carbon sequestration potentials. Thus, for every tonnes of SDK25 pyrolysed at 500°C, approximately 66.5wt% of it is converted to biochar. Similarly, 65.2wt%, 59.3wt% and 59.0wt% were obtained for pyrolysis of SD, PW, SDK25 and PWK25 respectively. The Table also shows the amount of Carbon dioxide that can be sequestered if the sawdust and poultry waste were impregnated with 25wt% kaolin and thermo-catalytically pyrolysed. Catalytic conversion of sawdust with kaolin at 25wt% mixing ratio yields the highest carbon sequestration potential carbon and thus the higher amount of carbon dioxide captured (41.6wt%). This is followed by SD (39.8wt%), PWK25 (34.4wt%) and PW (33.2wt%).

Table 4: Amount of Carbon dioxide Removed through Biochar production system

Biomass*	Biochar Produced (kg)	Carbon Content (wt%)	Sequestration Potential of Biochar (kg)	CO_2 Removed (kg)
SD	65.2	76.32	49.76	39.81
SDK25	66.5	78.10	51.94	41.55
PW	59.3	70.01	41.52	33.22
PWK25	59.0	72.95	43.04	34.43

*Basis: 100 kilograms of biomass

Conclusion

Kaolin clay was functionalized via calcinations and acid modification. The functionalized kaolin was used in slow pyrolysis of Sawdust and Poultry waste to produce char which was subsequently used for the study of carbon sequestration

Mohammed A.[1]; Bello A.[2]; Habibu U.[3]; Mohammed U.G.[4]; Abubakar G.I.[5] and Aisha F.[6]

potential. SKBC has the highest wt% Carbon present in biochar and subsequently the highest potential CO_2 sequestration. SBC has the highest surface area when compared to PBC and thus a potential to increase soil cation exchange capacity and surface sorption capacity.

References

Alhassan, M.; Auta, M., Sabo; J. K., Umaru, M. And Kovo, A. S. (2016): CO_2 Capture Using Amine-impregnated Activated Carbon from Jatropha Curcas Shell. *British Journal of Applied Science & Technology*, Vol. 14 No.4, 1-11.available at:www.sciencedomain.org

Alhassan, M. (2013): Biochar for Combined Carbon Sequestration and Bio-oil Generation from Co-pyrolysis of Biomass with Bone Matter. PhD Thesis submitted to the *University of Nottingham, UK*. 10-150.

Alhassan, M. and Andresen, J. (2013): Effect of Bone Matter during Fixed Bed Pyrolysis of Pistachio nut shell. *International Journal of Science and Engineering Investigations*, Vol. 2, Issue 12, 37-48. Available at: www.IJSEI.com

Allyson, S. (2011): Biochar Production for Carbon Sequestration" B.Sc Project in Chemical Engineering, Worcester polytechnic Institute. Shanghai Jiqo Tong University.

Antal, M. J. and Grønli, M. (2003): The art, science and technology of charcoal production. *Industrial and Engineering Chemistry Research*. 42, (8), 1619-1640.

Bridgewater A.V. and Peacock, G.V. C. (2000): Fast Pyrolysis Process for Biomass Renewable and Sustainable Energy. *Reviews*, 4, 1-73

Catherine, E. B. (2012): Biochar Characterization and Engineering. PhD Thesis in Chemical engineering, *Iowa State University*, Ames, Iowa.

CENT/TS. (2006): Solid fuels-Method for the determination of the volatile content.

Chan, K.Y. and Xu Z. H. (2009): Biochar - Nutrient Properties and their Enhancement (Chapter 5), in: Lehmann, J. and Joseph, S. (Eds.): Biochar for Environmental Management": Science and Technology, Earthscan, London, UK. 67.

Cheng, C. H., Lehmann, J., Thies, J. E., Burton, S. D. and Engelhard, M. H., (2006): Oxidation of black carbon by biotic and abiotic processes. *Organic Geochemistry*, 37, (11), 1477-1488.

Criado, J. M. and Ortega, A. (1986): Non-isothermal transformation kinetics", Remarks on Kissinger's method. *Journal of Non-crystalline Solid*, Vol. 87, 302-311.

Demirbas, A. (2001): Recent advances in biomass conversion technologies. *Energy Educ. Sci. Technol*. 2000, Vol. 6, 77-83

Gaskin J. W.; Steiner K.; Harris K.; Das, K. C. and Bibens, B. (2008): Effect of Low Temperature Pyrolysis conditions on Biochar for agricultural Use. *Trans ASABE* 52:2061-2069

Granatstsein, D.; Kruger, C.; Collins, H.; Garcia-Perez, M. and Yoder, J. (2009): Use of Biochar from the pyrolysis of Waste Organic Material as a Soil amendment. Final Project of Interagency Agreement C0800248, July 2009

Huber, G.W. (2008). Breaking the Chemical and Engineering Barriers to Lignocellulosic Bio-fuels"Next Generation Hydrocarbon Biorefineries. http//www/ecs.umass.edu/biofuels/image/roadmap.

Imam, T. and Capareda, S. (2012): Characterization of bio-oil, syn-gas and bio-char from switchgrass pyrolysis at various temperatures. *J. Anal. Appl. Pyrolysis* Vol. 93, 170–177.

Kuzyakov, Y., Subbotina, I., Chen, H. Q., Bogomolova, I. And Xu, X.L. (2009): Black Carbon decomposition and Incorporation into Soil Microbial Biomass Estimated by C-14 Labelling" Soil Biology Biochem. 41, 210-219.

Laird, D. A. (2008): The Charcoal Vision: A Win-Win-Win Scenario for Simultaneously Producing Bioenergy, Permanently Sequestered Carbon, while Improving Soil and Water Quality. *Agronomy Journal* 100:178-181.

Lehmann, J.; DA Silva, J. P.; Steiner, C.; Nehls, T.; Zech, W. and Glaser, B. (2003): Nutrient availability and leaching in an archaeological Anthrosol and a Ferralsol of the Central Amazon basin: fertilizer, manure and charcoal amendments. *Plant and Soil*, 249, 343-357.

Lehmann, J. and Joseph, S. (2009): Biochar for Environmental Management: Science and Technology. Earthscan; London, UK.

Lee, K. H.; Kang, B. S.; Park, Y. K. and Kim, J. S. (2005): Influence of reaction temperature, pretreatment, and a char removal system on the production of bio-oil from rice straw by fast pyrolysis using a fluidized bed. *Energy Fuels*, Vol. 19, No. 5, 2179-2184.

Mathias, G. (2013): Pyrolysis for Heat Production Biochar- the primary by-product. Masters' Thesis in Energy System. University of Gavle.

Mohammed, A.; Abdulrasoul, A.; Ahmed, H. E.; Mahmoud, N. and Adel, R.A. (2013): Pyrolysis Temperature Induced Changes in Characteristics and Chemical Composition of Biochar Produced from Canocarpous Waste. *Bioresources Technology*, Vol. 131, 374-379.

Onay, O. (2014): Effects of catalyst on pyrolysis of Laure seed in a Fixed Bed Tubular Reactor. *Chemical Engineering Transaction*. Vol 37, published by AIDIC.

Panda, A. K.; Mishra, B. G.; Mishra D. K. and Sin, R. K. (2010): Effect of sulphuric acid treatment on the physico-chemical characteristics of kaolin clay.*Colloids Surfaces* A, Vol. 363, 98 – 104, doi:10.1016/j.colsurfa.2010. 04.022

Mohammed A.[1]; Bello A.[2]; Habibu U.[3]; Mohammed U.G.[4]; Abubakar G.I.[5] and Aisha F.[6]

Scala, F.; Chirone, R. and Salatino, P. (2006): Combustion and Attrition of Biomass Chars in a Fluidized Bed. *Energy & Fuels*, Vol. 20, No. 1, 91-102.

Sutton, D., Kelleher, B. and Julian, R. H. (2001): Review of literature on catalysts for biomass gasification, Fuel Processing Technology 73 2001 155–173.

Tsai, W.T., Lee, M. K., and Chang, Y. M. (2006): Fast pyrolysis of rice straw, sugarcane Bagasse and coconut shell in an induction- heating reactor". Journal of Applied Pyrolysis. Vol. 76 230-237.

Thies, J. E., Rilling, M. C., (2009): Characteristics of biochar, Biological properties, Biochar for environment management Science and technology" Earthscan, London, UK, 85.

Wang, D., Yuan, W., and Ji, W. (2010): Use of biomass hydrothermal conversion car as the Ni catalyst support in benzene and gasification tar removal, *Trans. ASABE*, Vol. 53, No. 3, 795-800.

Wang, D. (2013): Study of Ni/car Catalyst for biomass gasification in an Updraft gasification: Influence of catalyst granular size on catalytic performance. *Bioresources*, Vol. 893, 3479-3489.

Wang, G.; Li, W.; Li, B. and Chen, H. (2008): TG study on pyrolysis of biomass and its three components under syngas. *Fuel* 87, 552-558.

Wilson, L. (2010). Biomass Energy Systems and Resources in Tropical Tanzania. Licentiate *Thesis in Furnace Technology* Sweden, ISBN 97891-7415-732-1

HCao X., Harris W. (2010): Properties of dairy-manure-derived biochar pertinent to its potential use in remediation. *Bioresource Technology*, 5222-5228.

Yao, Y., Gao, B., Zhang, M., Inyang, M., Zimmerman, A. R. (2012): Effect of biochar amendment on sorption and leaching of nitrate, ammonium, and phosphate in a sandy soil. *Chemosphere* Vol. 89, 1467–1471.

BSI (Bureau of Indian standard). (2004): Solid Mineral Fuels Sectional Committee, PCD7. ManakBhavan, 9Bahadur Shah Zafar Marg. New Delhi, 1-20.

Feiyue, L.; Wang, F., YueXie, J., He, L, Li, X, (2014): Effects of Mineral Additives on Biochar Formation: Carbon Retention, Stability and Properties. *Environmental science and technology* Vol. 48, No. 19, 11211 - 11217

Brebu, M. and Vasile, C. (2010): Thermal Degradation of Lignin – A Review. *Cellulose Chem. Technol.* Vol. 44, No. 9, 353-36.

Wu-Jun L., Hong J., and Han-Qing Y. (2015) Development of Biochar-Based Functional Materials: Toward a Sustainable Platform Carbon Material, Chemical Review, Vol. 21, 718.