Characterisation of Bio-Oil and Bio-Char from Slow-Pyrolysed Nigerian Yellow and White Corn Cobs

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Abstract: Cobs from yellow and white corn were slow pyrolysed at 450°C in a laboratory-scaled fixed bed reactor. Product distribution obtained was: 42.6% and 44.8% condensate, 33.3% and 33.5% bio-char, and 24.1% and 21.7% non-condensable gas for white and yellow corn cobs respectively. 13.6% bio-oil was recovered from white cob condensate and 10.12% for yellow cob. The resulting bio-oil with pH of around 5 and density of ~1.1 g/cm^3 was found to be stable on storage over a period of 10 months. Ash level and viscosity at 50°C were (0.12% and 0.10%) and (41.2 cSt and 20.8 cSt) in bio-oils from the cobs of yellow and white corn respectively. Characterisation with gas chromatography revealed that the bio-oil contained cellulose and lignin-derived compounds. Bio-chars from these residues have higher heating value of ~30.00 MJ/kg, pH of ~8, bulk density of ~0.220 g/cm^3 and ash level of ~1.7%. Scanning Electron Microscopy (SEM) coupled with Energy Dispersive X-ray Spectrometry (EDS) was used to examine the morphology and elemental composition of these bio-chars. The bio-char produced is capable of contributing 83.6 billion MJ to energy demand in Nigeria and preventing about 6.8 million tonnes of CO_2 emission into the environment.

Keywords: Bio-oil, bio-char, pyrolysis, corn cob, fixed bed reactor, agricultural wastes.

1. Introduction

The use of biomass materials as renewable energy sources has continued to attract global attention over the last two decades and is much more pronounced in countries where agricultural activities are abundant [1]. This is because products obtained from them (of which bio-oil is the most important) have numerous prospects for a low carbon economy.

Maize, also known as corn, is the most important cereal crop in sub-Saharan Africa and an important staple food for more than 1.2 billion people in this region and Latin America. More maize is produced annually than any other grain. Worldwide production of maize is 785 million tons, the largest African producer being Nigeria with nearly 8 million tons, followed by South Africa [2].

When harvested, corn wastes namely corn cobs and stovers are either left to dry on the farm after which they are burnt off or found littering the streets of market places. This practice does not help in building an eco-friendly economy. A better approach to this is to convert them to more useful energy products by the use of thermochemical technologies. The products obtained have higher energy values than the biomass and because of their abundance; they can continue to serve as feedstock for the production of bio-oil and bio-char in Nigeria. More so converting biomass to bio-oil enhances their storage, transportation and handling than the solid biomass [3].

The potentials of bio-oil and biochar from corn wastes have been investigated recently. Boateng *et al*. [4], using a pilot scale fluidized-bed fast pyrolysis reactor, already characterised bio-oil and bio-char from the cobs and stover of corn. The physical and chemical properties of bio-oils from microwave pyrolysis of corn stover have also been investigated [5]. Biochar's potential as a low-cost adsorbent for environmental pollutants has been reported [4,6]. A lot of experimental results have indicated that bio-char applications can improve soil properties [7-9], increase crop yield [10-11] and sequester carbon [12].

Of the thermochemical technologies known, fast pyrolysis has received the most attention because it gives very high bio-oil product of above 70 percent [13-15] and has been assessed as a promising biofuel alternative [16]. However, fast pyrolysis is very expensive and requires a high level of engineering technology which has limited its utilisation for biomass conversion especially in this part of the world. Alternatively, slow pyrolysis is relatively cheaper and has been found to suitably convert biomass in good yields to give about 35% of bio-oil and 35-40% bio-char despite its long residence time [13].

In this study, a modified slow pyrolysis technique has been applied to suitably convert Nigerian yellow and white corn cobs to bio-oil and bio-char using a laboratory scale fixed bed reactor and the products have been characterised for physical, chemical and structural compositions and their energy values.

2. Experimental

2.1 Feedstock Preparation

Yellow and white corn cobs were obtained from the University Agricultural Farm in Akure, Ondo State. Samples were dried, ground with both mechanical and electrical blenders, and sieved to a fine size of less than 2 mm, precisely 1.14 mm using a BS mesh. The samples were then stored in sacks and labelled until the time of analysis.

2.2 Chemical Analysis on Feedstocks

Alcohol-Benzene Soluble Matter and ash content of the biomass feedstock were determined in accordance with ASTM D1107-56 and D1102-56 respectively [17-18]. Lignin was determined as Klason lignin following TAPPI T222 OM-98 [19] and cellulose by the Kurschner-Hoffer cellulose method [20]. Higher heating value (HHV) and pH of the biomass feedstock were also determined.

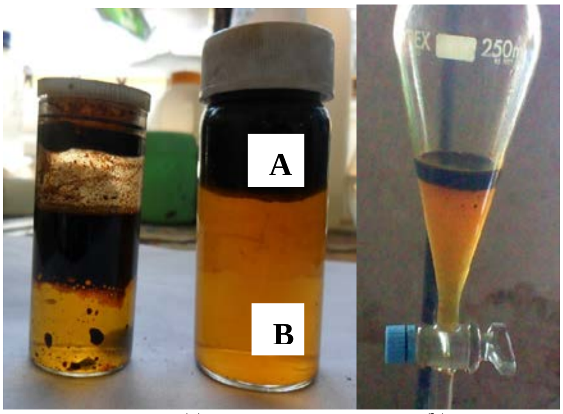
2.3 Slow Pyrolysis of Feedstock

Samples already sieved to a size of 1.14 mm were first oven dried at 120°C in a specially fabricated metal box after which a known weight was taken and transferred into a 2-litre flat bottom Pyrex glass reactor. The glass reactor was then put inside a muffle furnace and adjusted to set exactly under the exhaust orifice of the furnace through which a glass pipe already connected to a reflux condenser is fitted into it (Figure 1). A free board was created in the glass reactor by not filling it up totally in order to allow for easy passage of product gas. The temperature of the furnace was set at 450°C and as the temperature rose to around 260°C, part of the feedstock cellulose started to volatilise which was followed by condensation of the product gas in the reflux condenser and collected inside a polyethylene bottle (as suggested by Oasmaa et al. [21] and Czernik [22]) while bio-char was collected as a solid product inside the reactor. The reaction was assumed to have reached completion after one hour of reaching reaction temperature (450°C) since there was no more product gas evolving from the reactor. The set up was then allowed to cool down and thereafter dismantled, washed, cleaned and dried for another experiment. The experiment was repeated three times.

(a) (b)

Figure 1. Modified slow pyrolysis set up showing (a) pyrex glass reactor in the muffle furnace (b) glass tubes conveying product gas to the reflux condenser.

The condensate collected in the polyethylene bottle separated into two distinct phases: hydrophobic viscous dark brown liquid at the top named viscous bio-oil and polar liquid at the bottom called aqueous bio-oil (Figure 2). The phases were separated using a separating funnel. Bio-char was obtained as a solid product inside the reactor and was collected after allowing the reactor to cool down and dismantled. It was stored inside a polyethylene bag.



(a) (b)

Figure 2. (a) Pyrolysis condensate separating into two distinct layers: portion labelled A is the viscous phase and B is the aqueous phase. (b) Separation of the phases using a separating funnel.

2.4 Characterisation of Pyrolysis Products

2.4.1 Chemical Composition of Bio-oil

To identify the chemical composition of the bio-oil, GC analysis was performed on a GC/MS-Q P2010 plus Shimadzu model equipped with a Mass Spectrometer detector (National Research Institute for Chemical Technology, Zaria, Nigeria). The column used was RTX-1-Integral and contained 100% dimethyl polysiloxane (DMPS). The column dimension was 30 m × 0.25 mm and the oven was programmed at 70°C to hold at 0 min, ramped at 10°C/min up to 280°C at 5 min. The injection temperature was 250°C, the flow rate of the helium gas was 1.80 mL/min and the film thickness was 0.25 µm. Compounds were identified by means of the NIST 05 library.

2.4.2 pH and Viscosity of Bio-oil

pH of aqueous bio-oil was taken by dipping the electrode directly into the bio-oil using a Jenway 3015 pH meter at room temperature. For the viscous bio-oil, 0.5 g of it was dissolved in 50 ml ethanol in a conical flask and covered with foil for about 30 hours while stirring occasionally. For the viscosity measurement, the temperature of the bio-oil was first raised to 50°C and then filled into a viscometer of known constant (which was immersed in water bath maintained at the operating temperature) and then allowed to fall under gravity. Time of flow through the capillary was taken in seconds. Kinematic viscosity was calculated as the product of the measured flow time and the calibration constant of the viscometer. The viscosity was taken twice at an interval of 10 months after production (viscous bio-oil was stored in tightly capped bottles and covered up in a container) to determine the level of polymerisation as the bio-oil ages.

2.4.3 pH of Bio-char

pH of bio-char was taken using a Jenway 3015 pH meter at room temperature. 0.5 g of bio-char was dissolved in 50 ml de-ionized water in a conical flask and covered with foil for about 30 hours while stirring occasionally [4].

2.4.4 SEM/EDS Analysis

The morphology of the various kinds of bio-char from the individual biomass feedstock was examined by scanning electron microscopy (SEM). Images and analyses of elements of the bio-char were obtained using Carl Zeiss Scanning Electron Microscope-EVO/MA 10 model coupled with Energy Dispersive X-ray Spectrometer (EDS) at Sheda Scientific and Technology Complex (SHESTCO), Abuja, Nigeria. Samples already screened to a size of 125 µm were attached to multi-stub sample holder with the use of double sided conductive carbon tape after which it was mounted onto the specimen chamber. The specimen chamber and column were kept under vacuum. After reaching the vacuum target, the electron gun was switched on and accelerating voltage of 20 kV, probe current of 227 pA and working distance of 8.5 mm were maintained.

2.4.5 Higher Heating Value (HHV) Analysis

Determination of higher heating value for bio-char was performed using e2k Bomb Calorimeter at the National Institute of Science and Laboratory Technology (NISLT), Ibadan, Nigeria by burning 0.5 g of bio-char in the calorimeter with oxygen level regulated to 3000 Kpa. The instrument was thereafter operated to display the HHV of the bio-char.

3. Results and Discussion

3.1 Analysis on Feedstock

Ash and moisture contents were 9.80% and 3.81% for yellow corn cob and 9.77% and 6.43% for white corn cob respectively. Chemical composition analysis of the feedstock showed that both corn cobs have very close values for cellulose but different in lignin composition (Table 1). The extractive, determined as alcohol-benzene soluble matter, was 1.06% higher in yellow corn cob than in white corn cob. pH values obtained for both biomass showed that they are slightly acidic (Table 8). The higher heating value of the corn cobs was almost the same, with yellow corn cob having 16.15 MJ/kg and white corn cob at 16.54 MJ/kg (Table 2).

3.2 Products distribution

Three products were obtained from slow pyrolysis of the biomass feedstock: condensate containing bio-oil and polar liquid, bio-char and the non-condensable gas (NCG). Temperature of 450°C and feedstock size particle of 1.14 mm were chosen for pyrolysis to optimise product distribution in favour of the

Table 1. Physico-Chemical Analysis of Yellow Corn Cobs (YCC) and White Corn Cobs (WCC).

	Moisture	Ash	Lignin	Cellulose	Extractives*
YCC	3.81±0.09	9.80 ±0.07	13.40 ±0.33	33.19 ±2.39	2.61 ±0.07
WCC	6.43 ±0.08	9.77 ±0.04	18.32 ±0.74	33.57 ±0.21	1.55 ±0.03

*The extractives here refer to the Alcohol-Benzene Soluble Matter

condensate and obtain composition comparable to fast pyrolysis. The distribution of the products (Tables 3 and 4) showed that of the 44.8% condensate obtained from yellow corn cob pyrolysis, only 10.1% of the pyrolysed feedstock was recovered as bio-oil while 13.6% was obtained from the 42.6% condensate of white corn cob. A possible reason for higher viscous bio-oil content in white corn cob may be due to the fact that it has higher lignin content value than yellow corn cob. Yellow corn cob has higher aqueous bio-oil converted (34.68%) than white corn cob (29.0%). It was observed that both lignin and cellulose content determine pyrolysis product distribution (apart from temperature and particle size). It is clear from the result that biomass with higher lignin content gave higher bio-char yield (which is in agreement with other authors [23-25]) and lower condensate.

Table 2. Higher Heating Value (HHV) Analysis of Yellow Corn Cobs (YCC), White Corn Cobs (WCC) and their bio-chars using Bomb Calorimeter (MJ/kg).

	YCC	YCC char	WCC	WCC char
HHV (MJ/kg)	16.15	32.03	16.54	30.60

Table 3. Distribution of condensate, bio-char and non-condensable gas obtainable from Yellow Corn Cobs (YCC) and White Corn Cobs (WCC) feedstock after pyrolysis. (%)

	Total Condensate	Bio-char	Non-Condensable Gas*
YCC	44.8±0.12	33.5±0.49	21.7±0.24
WCC	42.6±0.81	33.3±1.61	24.1±1.04

* Non-condensable gas was obtained by difference

Table 4. Percentage by mass of bio-oil and polar liquid recovered from the feedstock.

	Bio-oil	Polar liquid
YCC	10.12%	34.68%
WCC	13.60%	29.00%

The quantity of bio-char obtained from yellow and white corn cobs is almost the same in value: 33.3% and 33.5% respectively. Considering the products distribution, the biomass will be more appropriate for producing liquid and solid fuels. It must, however, be said that gas product resulting from pyrolysis was not analysed in this work. Physicochemical analyses and heating value of viscous bio-oil, aqueous bio-oil and bio-char from the residues are shown in Table 5.

3.3 Bio-oil Characterisation

GC-MS analysis revealed the chemical composition of the bio-oils from the feedstock. While some peaks obtained from the spectra were tentatively assigned, a few were, however, unidentified. The most abundant compound found in the viscous bio-oils of yellow and white corn cobs was 4-ethyl phenol (29.33% and 25.53% respectively). There was similarity in the chemical composition of viscous bio-oil of these residues as indicated by the presence of compounds like 2-Methyl-2-cyclo pentenone, 3-Methyl-1, 2-cyclopentanedione, phenol, 4-Ethyl phenol, guaiacol, 2, 6-Dimethoxy phenol, and 2-Methoxy-4-ethyl phenol in bio-oils from both corn residues (Tables 6 and 7). This agrees with what was already reported for chemical compounds found in bio-oils from fast pyrolysis of corn cobs [4]. Bio-oil from white corn cob was higher in lignin-derived compounds than that from yellow corn cob. This is expected since the former was richer in lignin than the latter.

Table 5. Physicochemical analyses and Heating value of viscous bio-oil, aqueous bio-oil and bio-char from Yellow Corn Cobs (YCC) and White Corn Cobs (WCC).*

Parameter	YCC	WCC
pH		
Viscous Bio-oil	5.30	5.20
Aqueous Bio-oil	2.97	2.98
Bio-char	7.80	8.20
Density (g/cm^3)		
Viscous Bio-oil	1.110	1.162
Bio-char (Tapped)	0.220	0.263
Bio-char (Freely settled)	0.174	0.202
Viscosity @ 50^0C (cSt)		
At production	41.20	20.80
After 10 months	44.03	21.85
Ash (%)		
Viscous Bio-oil	0.120	0.100
Bio-char	1.719	1.650
HHV (MJ/kg)		
Bio-char	32.03	30.60

*Determination of some parameters stated here is not discussed in the paper [26].

Table 6. GC/MS Quantification and Characterisation of ***Yellow Corn Cobs*** *bio-oil*.

t_R (min)	Tentative Assignment	Peak Area (%)
3.188	2-Methyl-2-cyclopentenone	2.89
4.051	Phenol	16.57
4.431	3-Methyl-1, 2-cyclopentanedione	5.37
4.562	2, 3-Dimethyl-2-cyclopenten-1-one	3.21
5.253	o-Guaiacol	7.03
5.596	4-Ethyl cyclohexanone	2.35
6.366	4-Ethyl phenol	29.33
7.180	2, 3-Dihydro benzofuran	1.01
7.795	4-ethyl -2-Methoxy- phenol	7.92
8.244	4-ethenyl-2-methoxy-phenol	5.21
8.607	2, 6-Dimethoxy phenol (Syringol)	3.00
10.861	3, 5-Di-tert-butyl phenol	2.74
11.577	x	1.78
12.897	Methoxy eugenol	1.19
15.776	x	2.22

x Unidentified

Table 7. GC/MS Quantification and Characterisation of ***White Corn Cobs*** *bio-oil*.

t_R(min)	Tentative Assignment	Peak Area (%)
3.188	2-Methyl-2-cyclopentenone	3.55
4.050	Phenol	15.25
4.430	3-Methyl-1, 2-cyclopentanedione	5.19
4.907	o-Cresol	4.66
5.253	o-Guaiacol	11.37
5.596	4-Ethyl cyclohexanone	3.20
6.365	4-Ethyl phenol	25.53
6.635	2-Methoxy-4-methyl phenol	2.45
7.179	2, 3-Dihydro benzofuran	1.00
7.795	4-Ethyl-2-methoxy phenol	11.07
8.244	2-Methoxy-4-ethenyl phenol	4.08
8.606	2, 6-Dimethoxy phenol (Syringol)	3.08
10.860	3, 5-Di-tert-butyl phenol	2.07
12.896	Methoxy eugenol	0.90
17.050	10-Octadecenoic acid methyl ester	0.81
17.425	1, 15- Pentadecanediol	5.84

It should be mentioned that pyrolysis condensate separated into polar liquid and the viscous bio-oil. Most of the cellulose decomposed to form compounds expected to be acetic acid, acetol, furfuryl alcohol and levoglucosan contained in the aqueous bio-oil. This is the reason why most of the chemical compounds revealed by GC-MS analysis are lignin-derived. For this reason the pH of both polar liquid and viscous bio-oil were reported in this study (Table 8). The pH values of viscous bio-oils from yellow and white corn cobs are slightly acidic. The values obtained for aqueous bio-oils from yellow and white corn cobs are in the range of pH values for a typical bio-oil [27].

Table 8. pH of Feedstock, Bio-char and Bio-oil.

	Feedstock	Bio-char	Bio-oil (aq.)	Bio-oil (visc.)
YCC	5.50	7.80	2.97	5.30
WCC	5.70	8.20	2.98	5.20

It is expected that the ageing of the bio-oil will be slower compared with other bio-oils since compounds like 2-oxo-propanal, 2-butanone, hydroxy-propanal, propanone and dihydro-methyl-furanone (that have been reported to be responsible for ageing of bio-oil [28]) are not readily present in the result obtained. The compounds may either be in the aqueous fraction of the oil or the pyrolysis method employed has not favoured their formation.

Ash content of bio-oils is very vital in determining their use as renewable energy sources to fire plants and combustion engines. Ash contents determination (Table 5) revealed that bio-oils from yellow and white corn cobs have low ash content values: 0.12% and 0.10% respectively. Although the values are very low, they should preferably be less than 0.1 wt.% for use in engines [29]. Thus the bio-oil will still need to be upgraded before being used in order to avoid erosion, corrosion and kicking problems in the engines and the valves.

Bio-oils from both corn residues have very close values in density with yellow corn cob having 1.1102 g/cm^3 and white corn cob at 1.1615 g/cm^3 and are comparable to what was obtained from the fast pyrolysis of the same material [4].

The viscosities obtained at 50°C at production were 41.2 cSt and 20.8 cSt for bio-oils from yellow and white corn cobs respectively. This may be due to the slight difference in their chemical composition (as revealed by GC-MS analysis) and moisture content. Viscosities increased fairly to 44.03 cSt and 21.85 cSt for yellow and white corn cobs respectively after 10 months of production indicating a slow rate of ageing. This is expected because the compounds that may catalyse polymerisation reaction have been separated from the viscous bio-oil. Low ash content of the bio-oils, a reflection of their low inorganic matter, could also be another reason for slow ageing observed.

3.4 Bio-char Characterisation

Owing to their high suitability as potential renewable energy sources, the higher heating value (HHV) of bio-chars obtained was determined. Yellow corn cob bio-char has higher energy value (32.03 MJ/kg) than white corn cob bio-char (30.60 MJ/kg) as shown in Table 2. This may be due to lower value of moisture content recorded in yellow corn cob bio-char despite higher ash content. It was also observed that pyrolysis increased the energy potential of yellow corn cob and white corn cob by 98.3% and 85.0% respectively. Thus they will be good sources of solid fuels for local cooking and heating. Assuming all the 8 million tonnes of maize produced annually in Nigeria to be pyrolysed, about 83.6 billion MJ will be accrued to the energy supply which is equivalent to burning about 2.9 million tonnes of coal.

pH values of bio-chars from the biomasses showed that they are slightly alkaline (Table 8) and are almost the same with those already reported for corn cob bio-char by other researchers [4]. Ash and bulk density for the bio-char were (1.719% and 1.650%) and (0.220 and 0.263 g/cm^3) in yellow and white corn cobs respectively.

Quantitative results of elemental composition of bio-chars (obtained from EDS coupled with SEM) are presented in Figure 3. About 3 elements essential for plant growth were identified in the biomasses bio-char. There were marked variations between the elemental composition of yellow and white corn cob bio-chars despite the fact that they have the same origin. K was obtained as a plant macro-nutrient in white corn cob bio-chars only. While Ca content was 0.13% in yellow corn cob bio-char, it was not detected in white corn cob bio-char. Again, bio-char from yellow corn cob has higher silicon content (17.21%) compared to that of white corn cob (0.18%). The differences observed may be due to some environmental factors. With the availability of these essential plant nutrients, the bio-chars may thus be used as soil improvers and amenders especially on acid soils as already established for many other bio-chars [7-11].

The EDS analysis revealed that carbon contents are 72.93% and 67.02% in white and yellow corn cobs bio-chars respectively. Chlorine levels in bio-chars are also essential to maintaining environmental sustainability when being used as solid fuels. Cl was detected in white and yellow corn cob bio-chars with levels ranging between 0.14% and 0.25%. The information is very vital for predicting HCl emissions from combustion of bio-chars.

Micrographs from SEM, which were taken to determine the morphology of bio-chars from the feedstock, revealed that bio-chars from yellow and white corn cobs contain diffuse-structured (like a forming cloud) and amorphous flakes of 1-20 µm in size as shown in Figures 4 and 5. The large structural surface and amorphous nature of these bio-chars suggest their suitability for adsorption purposes- subject to further surface tests using BET technique.

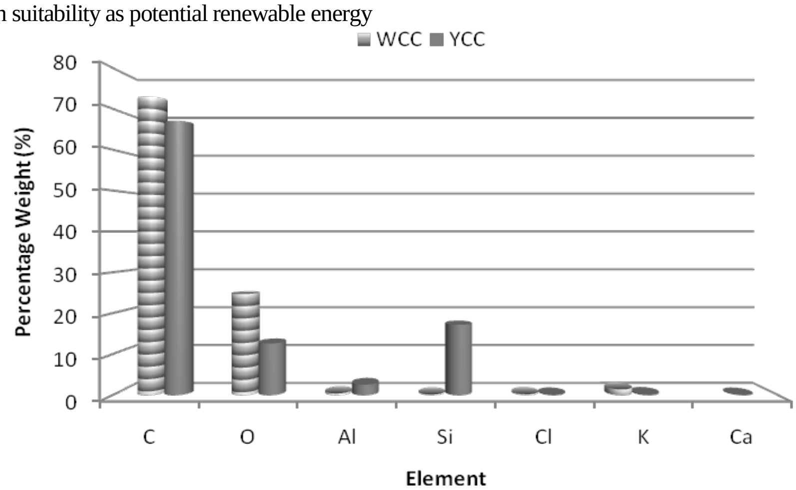


Figure 3. Elemental Composition of Bio-chars of White Corn Cob (WCC) and Yellow Corn Cob (YCC).

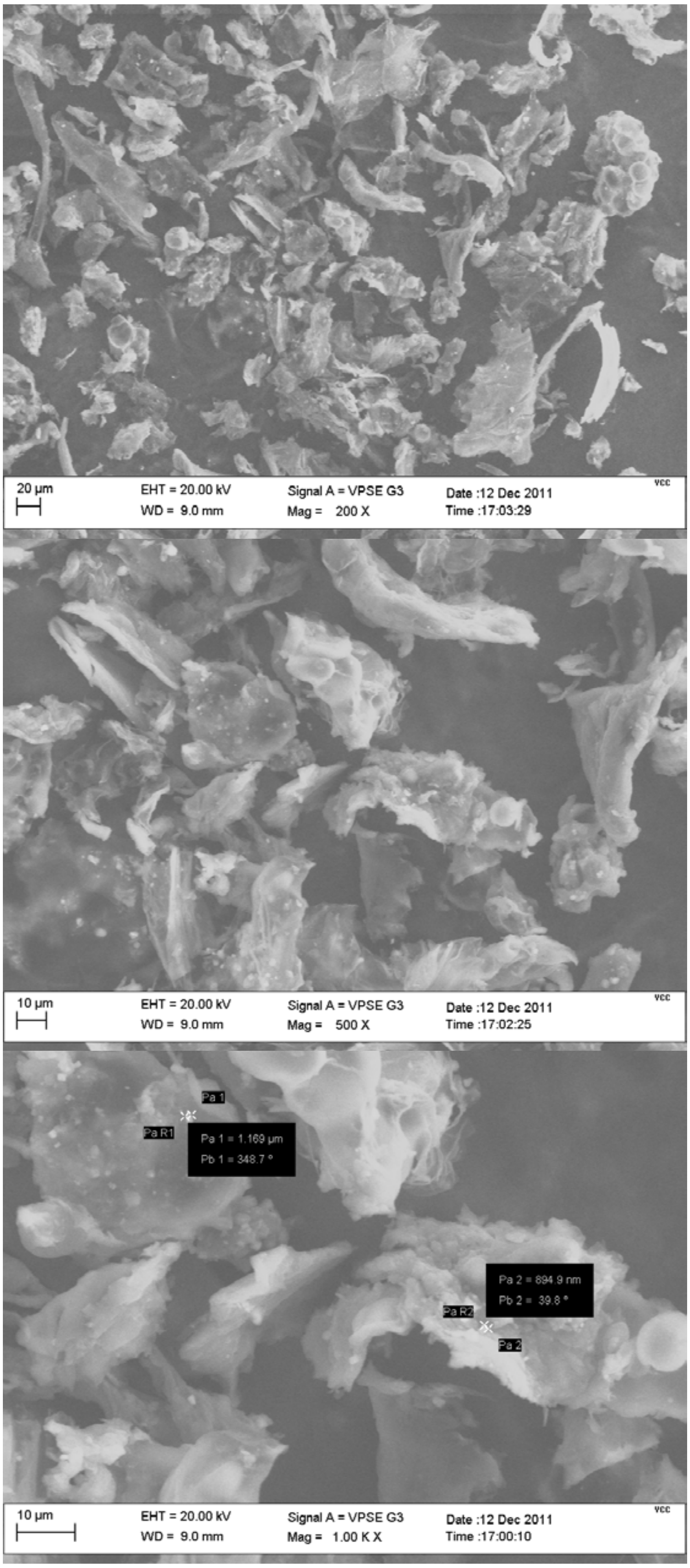


Figure 4. Scanning electron micrographs of bio-char of Yellow corn cob at 200X, 500X and 1000X.

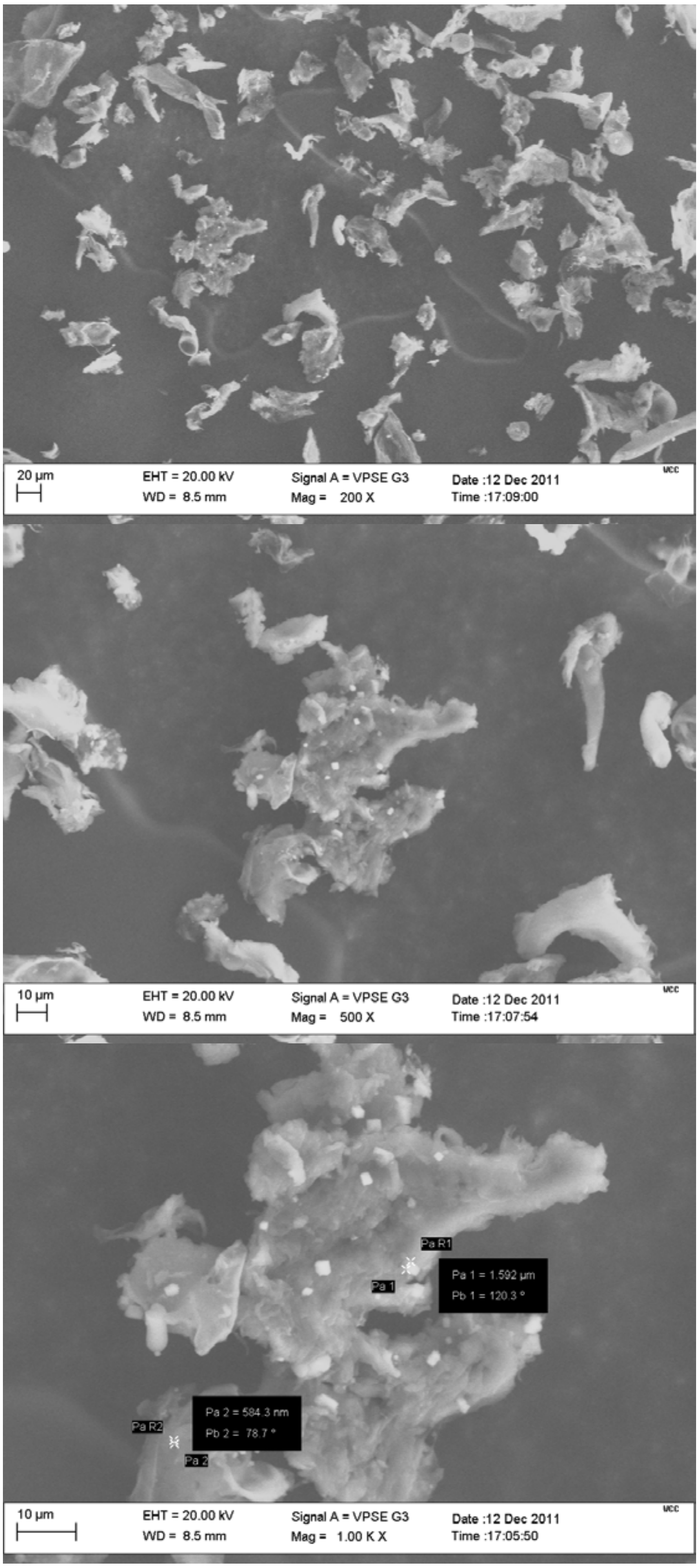


Figure 5. Scanning electron micrographs of bio-char of White corn cob at 200X, 500X and 1000X.

4. Conclusion

Corn cobs from Nigeria have been pyrolysed using a modified slow pyrolysis technique to give bio-oil and bio-char as major products. Chemical composition of bio-oils from the residues shows that they contain lignocellulosic compounds which could serve as raw materials for local industries when fast pyrolysis is employed. The Aqueous bio-oil obtained could be used as food flavours and also to treat vulnerable furniture. Upgrading of bio-oils by separation into aqueous and viscous phases could enhance storage of bio-oils for a longer period as reflected in the viscosity determination, reduce bio-oil acidity and also inhibit ageing.

Bio-chars from yellow and white corn cobs have nearly twice as much as the energy potentials of their corresponding biomass feedstock and can be used as solid fuels in the form of briquettes for local cooking and heating in bakeries, especially in the rural areas of the country. Elemental composition obtained from EDS analysis of the bio-chars also reveals that they are environmentally friendly when used as solid fuels since they do not contain sulphur and have low chlorine concentration. More so with annual contribution of 83.6 billion MJ to energy demand, about 6.8 million tonnes of CO_2 emission will be saved from the environment when bio-char from these residues are used as energy sources. Bio-chars from white and yellow corn cobs also contain appreciable amount of essential plant nutrients that makes them suitable as potential soil amenders and improvers for agricultural purposes especially in places where the soil is deficient of some specific mineral present in the bio-chars. Besides improving soil properties and fertility, the bio-chars could also serve as sink for carbon when applied to soil, thus encouraging the development of a sustainable environment. Micrographs from SEM analysis showed the porous structural nature of these bio-chars and hence their tendency for application in adsorption studies.

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