Valorization of Bambara groundnut shell via intermediate pyrolysis: Products distribution and characterization

MOHAMMED, Isah Yakub, ABAKR, Yousif Abdalla, MUSA, Mukhtar, YUSUP, Suzana, SINGH, Ajit and KABIR, Feroz <http://orcid.org/0000-0002-3121-9086>

This document is the Accepted Version [AM]

Citation:

MOHAMMED, Isah Yakub, ABAKR, Yousif Abdalla, MUSA, Mukhtar, YUSUP, Suzana, SINGH, Ajit and KABIR, Feroz (2016). Valorization of Bambara groundnut shell via intermediate pyrolysis: Products distribution and characterization. Journal of Cleaner Production, 139, 717-728. [Article]

Valorization of Bambara Groundnut Shell *via* Intermediate Pyrolysis : Products Distribution and Characterization

Isah Yakub Mohammed[a,f,*], Yousif Abdalla Abakr[b], Mukhtar Musa[c,f], Suzana Yusup[d], Ajit Singh[c] and Feroz Kabir Kazi[e]

[a]Department of Chemical and Environmental Engineering, the University of Nottingham Malaysia Campus, Jalan Broga, Semenyih 43500, Selangor Darul Eshan, Malaysia

[b]Department of Mechanical, Manufacturing and Material Engineering, the University of Nottingham Malaysia Campus, Jalan Broga, Semenyih 43500, Selangor Darul Eshan, Malaysia

[c]School of Biosciences, the University of Nottingham, Malaysia Campus, Jalan Broga, 43500 Semenyih, Selangor, Malaysia

[d]Department of Chemical Engineering, Universiti Teknologi PETRONAS, Bandar Seri Iskandar, 31750, Tronoh, Malaysia

[e]Department of Engineering and Mathematics, Sheffield Hallam University, City Campus, Howard Street, Sheffield S1 1WB, UK

[f]Crops for the Future (CFF), the University of Nottingham Malaysia Campus, Jalan Broga, Semenyih 43500, Selangor Darul Eshan, Malaysia

---

Abstract

This study provides first report on thermochemical conversion of residue from one of the underutilized crops, Bambara groundnut. Shells from two Bambara groundnut landraces KARO and EX-SOKOTO were used. Pyrolysis was conducted in a vertical fixed bed reactor at 500, 550, 600 and 650 ^{o}C; 50 ^{o}C/min heating rate and 5 L/min nitrogen flow rate. The report gives experimental results on characteristic of the feedstock, impact of temperature on the pyrolysis product distribution (bio-oil, bio-char and non-condensable gas). It evaluates the chemical and physicochemical properties of bio-oil, characteristics of bio-char and composition of the non-condensable gas using standard analytical techniques. KARO shell produced more bio-oil and was maximum at 600 ^{o}C (37.21 wt%) compared to EX-SOKOTO with the highest bio-oil yield of 32.79 wt% under the same condition. Two-phase bio-oil (organic and aqueous) was collected and analyzed. The organic phase from both feedstocks was made up of benzene derivatives which can be used as a precursor for quality biofuel production while the aqueous from KARO consisted sugars and other valuable chemicals compared to the aqueous phase from EX-SOKOTO which comprised of acids, ketones, aldehydes and phenols. Characteristics of bio-char and composition of the non-condensable were also determined. The results show that bio-char is rich in carbon and some minerals which can be utilized either as a solid fuel or source of bio-fertilizer. The non-condensable gas was made up of methane, hydrogen, carbon monoxide and carbon dioxide, which can be recycled to the reactor as a carrier gas. This study demonstrated recovery of high quality fuel precursor and other valuable materials from Bambara groundnut shell.

Keywords: Bambara groundnut shell; Pyrolysis; Bio-oil; Bio-char; Non-condensable gas; Characterization

---

***Corresponding author: Isah Yakub Mohammed (kebx3iye@nottingham.edu.my)**

Abbreviations

AAK	Acid, aldehyde, ketones
AMH	Atomic mass of hydrogen
AMO	Atomic mass of oxygen
C	Carbon
CFF	Crops for the future
DTG	Derivative thermogravimetric
EDX	Energy dispersive x-ray
ES	Esters
FTIR	Fourier transform infrared
GC	Gas chromatograph
GC-MS	Gas chromatograph-mass spectrometer
H	Hydrogen
HC	Hydrocarbon
HHV	Higher heating value
KBr	Potassium bromide
LHV	Lower heating value
LH_w	Latent heat of vaporization of water

N	Nitrogen
O	Oxygen
PH	Phenolics
RKO	Karo Bambara shell
S	Sulfur
SGR	Sugars
SKT	EX-SOKOTO Bambara shell
TCD	Thermal conductivity detector
TG	Thermogravimetric
TGA	Thermogravimetric analyzer
VAC	Value added chemicals
XRD	X-ray diffraction

1. Introduction

Bambara groundnut (*Vigna subterranea* (L.) Verdc), is an underutilized pulse legume cultivated primarily for its seeds, which are consumed in various forms of dishes, rich in protein (16-25 %), carbohydrate (42-60 %), lipid (5-6 %) (Brough and Azam-Ali, 1992), fibre (4.8 %) and ash (3.4 %) (Brink et al., 2006). The fresh pods containing the seeds are boiled and eaten as snacks whereas the haulm, is used as livestock feed in most of the drier parts of Africa (Heller et al., 1997). Legume such as Bambara groundnut with the ability to meet greater % of their N requirement as a result of atmospheric N fixation have been identified as potential alternative crops for mitigating climate change (Jensen et al., 2012) and offer an important alternative to the use of inorganic N fertilizers that are costly and unavailable to resource-poor farmers. The crop is predominantly grown by subsistence farmers over much of semi-arid Africa and is reported to spread into new production areas such as Indonesia, Malaysia and Thailand in the Asian continent and is increasingly becoming popular due to its ability to thrive under conditions which are too poor for other tropical legumes such as cowpea and groundnut (Mohale et al., 2014).

Bambara groundnut shell constitutes the weight of the pod wall after the grain is removed and is highly variable depending on the pod yield and shelling percentage and sometimes could reach up to 1000 kg ha^{-1}. Musa et al. (2016) reported 374-896 kg ha^{-1} of shell weight which corresponds to about 28.6-34.2 % of the total pod weight. Kishinevsky et al. (1996) reported a shelling percentage of 59-76 %, which translates to about 648-1107 kg ha^{-1} (24-41 % of the pod weight) considering the average pod yield of 2700 kg ha^{-1} reported by Collinson et al. (1999). Mwale et al. (2007) reported pod yield of 2980 kg ha^{-1} and a shelling percentage of 80 %, which corresponds to a shell weight of 596 kg ha^{-1} (20 % of the total pod weight). Despite the high weight of the crop's shells, information on the utilization of this potential is limited and is seldom reported as a yield component due to lack of a specific value (Mwale et al., 2007). There is need to explore alternative ways to promote the utilization of this product which could address the problem of crop waste disposal and promote the integration of the crop into new production areas. Crop residue disposal in the sub-humid tropical regions such as Malaysia and Indonesia has been attracting a major global concern due to inappropriate methods adopted by the resource poor farmers, particularly in Indonesia, where farmers resort to the use of open burning as a cheap way of clearing crop residues from the farm and thereby causing air pollution (haze) to the neighboring countries and the entire region (Varkkey, 2013; Forsyth, 2014).

Pyrolysis is currently one of the most promising thermochemical processes for converting biomass materials to products with high energy potentials. Typical pyrolysis products are bio-oil, bio-char and non-condensable gas (Alburquerque et al., 2016; Gómez et al., 2016). Distribution of pyrolysis products depends heavily on the process parameters such as pyrolysis temperature, heating rate and vapor residence time in the reactor. There are different types of pyrolysis namely; slow, intermediate and fast pyrolysis. Slow pyrolysis is also referred to as carbonization. It is carried out at a temperature up to 400 °C, solid residence time of 1 h to several hours, with product distribution of about 35 % bio-char, 30% bio-oil, and 35% non-condensable gas. Fast pyrolysis can produce up to 80 % bio-oil, 12 % bio-char, and 13 % non-condensable gas at temperature around 500 °C, high heating rate, a short vapor residence time of about 1 s, and rapid cooling of volatile (Bridgwater, 2012; Mohammed et al., 2015a). For intermediate pyrolysis, 500-650 ^{o}C pyrolysis temperature and vapor residence time of approximately 10 to 30 s are typical operating conditions. About 40-60% of the total product yield is usually bio-oil, 15-25% bio-char and 20-30% non-condensable gas. Intermediate pyrolysis produce bio-oil with less reactive tar which can be used directly as fuel in engines and boilers, and dry char suitable for both agricultural and energy applications (Tripathi et al., 2016). To the best of our knowledge, thermochemical conversion of Bambara groundnut shells has not been reported in the literature. In this study, intermediate pyrolysis of Bambara shell was investigated in a fixed bed reactor and pyrolysis products were characterized.

2. Materials and methods

Shells from two Bambara groundnut landraces, Karo (RKO) and EX-Sokoto (SKT) were collected from Crops for the Future (CFF) field research Centre Semenyih, Selangor, Malaysia. The material was dried at 105 °C in electrical oven. The dried materials were then shredded in a Retsch® rotor beater mill (SM100, Retsch GmbH, Germany) to particle sizes between 0.2 mm and 2.5 mm and stored in airtight plastic bags for further analysis. Volatile matter and ash content on dry basis were determined. Fixed carbon was computed from the remaining bone dry sample mass. The biomass ash elemental composition was analyzed with energy dispersive X-ray EDX (X-Max 20 mm^{2}, Oxford Instruments, UK). Higher heating value (HHV) was determined using an oxygen bomb calorimeter (Parr 6100, Parr Instruments, Molin, USA). Elemental compositions were determined using CHNS/O analyzer (2400 Series II CHNS/O analyzer, Perkin Elmer Sdn Bhd, Selangor, Malaysia). The nature of chemical functional groups were evaluated with Fourier transform infrared spectroscopy (Spectrum RXI, PerkinElmer, Selangor, Malaysia) using the potassium bromide (KBr) method. Potassium bromide (KBr) disc (13 mm diameter translucent) was made from a homogenized 2 mg sample in 100 mg KBr using a bench press (Carver 43500, Carver Inc.,USA) by applying 5.5 tonnes load for 5 min. Spectra were recorded with Spectrum V5.3.1 software within wave number range of 400 to 4000 cm^{-1} at 32 scans and a resolution of 4 cm^{-1}. Thermogravimetric study was carried out using thermogravimetric simultaneous thermal analyzer (TGA) (STA 6000, Perkin Elmer Sdn Bhd, Selangor, Malaysia) in nitrogen atmosphere, flow rate 20 mL/min at temperatures between 30-950 ^{o}C and heating rate of 20 ^{o}C/min. About 10 mg (particle size of 0.2 mm) of sample was used.

Intermediate pyrolysis study was conducted at 500, 550, 600 and 650 ^{o}C in a vertical fixed bed pyrolysis system as shown in Figure 1. The system consists of a fixed bed reactor made of stainless steel (115 cm long, 6 cm inner diameter), a distribution plate with 1.5 mm hole diameter which sit at 25 cm from the bottom of the tube, two nitrogen preheating sections, a cyclone, oil collector, gas scrubbers and water chiller operating at 3 ^{o}C attached to a coil condenser. 200 g of shell (bone dried, 2.5mm particle size) was placed on a gas distribution plate inside the reactor tube. The setup was heated in a vertical furnance at 50 ^{o}C/min under 5 L/min nitrogen flow. The reaction temperature was monitored with a thermocouple (K-type, NTT Heating, Sdn Bhd, Selangor, Malaysia). The reaction time was kept at 60 min after the temperature attained the set-value. Pyrolysis vapor was condensed by passing through a condenser attached to the water chiller and condensate (bio-oil) was collected in a container. Bio-oil, bio-char and non-condensable gas yields were calculated using Eq (1), (2) and (3). The experiment was repeated in triplicates and stanadard deviations were computed.

$$\text{Yield (wt\%)}_{\text{bio-oil}} = \left[\frac{\text{weight of the bio-oil collected}}{\text{weight of biomass feed}} \times 100\right] \text{--------} (1)$$

$$\text{Yield (wt\%)}_{\text{bio-char}} = \left[\frac{\text{weight of the bio-char collected}}{\text{weight of biomass feed}} \times 100\right] \text{------} (2)$$

$$\text{Yield (wt\%)}_{\text{non-condensable gas}} = 100 - \left(\text{Eq(1)} + \text{Eq (2)}\right) \text{----} \quad (3)$$

Characterization of bio-oil, bio-char and non-condensable gas were carried out accordingly using analytical instruments as summerized in Table 1. FTIR of bio-oil was determined using a pair of circular demountable KBr cell windows (25 mm diameter and 4 mm thickness). Detail chemical composition of the bio-oil was determined using a gas chromatograph-mass spectrometer (GC-MS) system equipped with a quadruple detector and column (30m x 0.25mm x 0.25µm). The oven was programmed at an initial temperature of 40 °C, ramp at 5 °C /min to 280 °C and held there for 20 min. The injection temperature, volume, and split ratio were 250 °C, 1 µL, and 50:1 respectively. Helium was used as carrier gas at a flow rate of 1 mL/min. The peaks of the chromatogram were identified by comparing with standard spectra of compounds in the National Institute of Standards and Technology library (NIST, Gaithersburg, USA).

The composition of non-condensable pyrolysis product was monitored offline. The gas sample was collected in a gas sample bag (Tedlar, SKC Inc., USA) and its composition analyzed using a gas chromatography equipped with stainless steel column (Porapak R 80/100) and thermal conductivity detector (TCD). Helium was used as a carrier gas and the GC was programed at 60 ^{o}C, 80 ^{o}C and 200 ^{o}C for oven, injector and TCD temperature respectively. Bio-char ultimate analysis and inorganic composition were carried out following the procedure outlined for the feedstock characterization. Crystallographic structure in the produced bio-char was examined between 2ϴ angle of 10°–70° at 25 mA, 45 kV, step size of 0.025°and 1.0 s scan rate. Surface and structural characteristics of the bio-char were also determined .

3. Results and Discussion

3.1 Characterization of feedstock

Characteristic of the feedstock is summarized in Table 2. Moisture content of SKT and RKO (as received) was 4.67 and 7.12 wt%. Higher volatile matter (76.24 wt%) and lower ash content (8.98 wt%) was recorded for the RKO compared to 73.83 wt% volatile matter and 10.10 wt% ash content in the SKT. Similarly, the ultimate analysis revealed that RKO has carbon and oxygen content of 37.36 wt% and 49.11 wt%, while 34.63 wt% carbon and 51.93 wt% oxygen was recorded for the SKT. RKO has higher heating value (HHV) of 20.46 MJ/kg relative to 19.19 MJ/kg recorded for SKT. The higher energy content recorded for the RKO could be attributed to its lower ash and oxygen contents. These physiocchemical characteristics are similar to properties of peanut shell reported by Zhang et al. (2011). The authors recorded high volatile matter and heating value of 71.5 wt% and 18.1 MJ/kg respectively. Their ultimate analysis result showed higher carbon (47 wt%), and lower oxygen (34 wt%) and hydrogen (6 wt%) contents compared to that of the Bamabara shells. EDX analysis of the ash showed that the inorganic element in the RKO and SKT is in the following order potassium (K)>silica (Si)>Aluminum (Al)>phosphorus (P)>Chlorine (Cl)>iron (Fe)>calcium (Ca)>magnesium (Mg) and K>Cl>Si>Al>P>Mg respectively. The proportion of metallic elements in the RKO is similar to that of peanut reported by Kuprianov and Arromdee (2013). The authors also reported distribution of minerals in tamarin shell which is comparable to that of SKT except for the Si, which is higher in SKT. The result of thermogravimetric analysis (TGA) analysis is shown in Figure 2. The thermogravimetric (TG) and derivative thermogravimetric (DTG) profiles of both samples exhibited similar decomposition characteristics. The residual weight at the end of the decomposition process was found to be 23 and 29 wt% for RKO and SKT respectively. From the DTG curves, two main peaks from ambient to 100 °C and from 240 to 420 °C, which is attributed to evaporation of moisture and decomposition of holocellulose (hemicellulose and cellulose) component of the biomass. Hemicellulose which normally decomposes around 250 °C in a lignocellulosic material was not observed in this study. It means that Bambara shells have less or infinitesimal amount of hemicellulose. A noticeable peak around 200 °C was also observed, which is ascribed to the decomposition of extractives. The pattern observed at the temperature above 420 °C is attributed to the decomposition of lignin.This region exhibited unsteady thermal degradation, which is ascribed to the presence of different oxygen functional groups in the lignin (Mohammed et al., 2015b). TGA analysis of almond shell by Grioui et al. (2014) showed a residual weight fraction of 27.5 wt%. The DTG curve exhibited main peak at temperature between 220 and 400 °C, which was attributed to the decomposition of cellulose and hemicellulose. The decomposition temperature values observed in this study are aslo similar to those of other lignocellulosic biomass in the literature (Mohammed et al., 2015c).

3.2 Pyrolysis product distribution and physicochemical properties of the bio-oil

Product distribution from the pyrolysis of RKO and SKT at temperature between 500 and 650 °C, 5 L/min nitrogen flow and heating rate 50 °C/min is shown in Fig. 3. From Figure 3(a), total bio-oil yield from RKO increased from 33.26 to 37.21 wt% as the temperature increased from 500 to 600 °C. This observation could be attributed to the decomposition of more lignin at such a high temperature. At 650 °C, the oil yield dropped to 27.69 wt%, which is due to secondary reactions of pyrolysis vapor at the elevated temperature (Mohammed et al., 2015a). The bio-oil collected consist of organic phase and an aqueous phase. The yield of organic phase increased from 9.8 wt% to 15.0 wt% at the temperature between 500 and 600 °C and latter declined to 9.3

wt% at 650 °C. On the other hand, a continuous decrease in the aqueous phase from 24.3 to 18.4 wt% was recorded. Generally, the aqueous phase bio-oil is a product of holocellulose decomposition whose yield and composition is greatly affected by the inorganic minerals in the source biomass. The significant reduction in the bio-oil aqueous phase and increased non-condensable yield observed could be attributed to the synergistic effect of the most abundant minerals in the biomass ash, which are Al and K (Table 2) since Si is an inert material and may not possess any catalytic activity (Mohammed et al., 2016a). The yield of non-condensable gas was 32.43 and 32.57 wt% at 500 and 550 °C but increased rapidity to 33.28 and 43.11 wt% at 600 and 650 °C. The corresponding bio-char yield was 32.96, 32.26, 29.51 and 29.20 wt%. The high yield of non-condensable gas observed above could be mainly due to the secondary reactions of pyrolysis vapor at the elevated temperature (Mohammed et al., 2015a) since there was no substantial reduction in the biochar yield. Figure 3b shows pyrolysis product distribution from the SKT. The total bio-oil yield was 26.17, 32.18, 32.78 and 27.58 wt% at 500, 550, 600 and 650 °C respectively. Similar to RKO, two phase bio-oil was collected from the pyrolysis of SKT and the corresponding organic and aqueous phases recorded were 5.90, 10.84, 11.17, 5.77 wt% and 20.27, 21.34, 21.61, 21.81 wt%. The bio-char yield decreased from 39.91 wt% at 500 °C to 28.56 wt% at 650 °C while the corresponding yield of non-condensable gas increased from 33.92 to 43.86 wt%. The high yield of non-condensable gas could be a resultant effect of a secondary reaction of pyrolysis vapor and devolatilization of the bio-char at high temperature. Comparing the product distribution between RKO and SKT, the highest total bio-oil yield of 37.21 wt% was recorded at 600 °C from RKO compared to 32.78 wt% from SKT. A substantial decrease in the biochar yield (11.35 %) with increasing temperature (500-650 °C) was observed from SKT compared to 4.06 % recorded from the RKO. Higher non-condensable gas yield was also recorded with SKT at all temperatures relative to that obtained from RKO. These observations can be attributed to the differences in the characteristics of the feedstocks(Mohammed et al., 2016b), as summerized in Table 2. Comparing the pyrolysis product distribution with products yield from other shells, Zhang et al. (2011) reported a total pyrolysis oil of 60 wt% from peanut shell at 500 ^{o}C with corresponding 19 wt% char and 15 wt% non-condensable gas. Grioui et al. (2014) reported pyrolysis products distribution of 40 wt% bio-oil , 47 wt% gas and 13 wt% solid. Pyrolysis oil yield from other biomass species have been reported by Lim et al. (2015) and (2016). They recorded bio-oil yield of 41.91-57.21 wt% and 37.98-43.66 wt% from Napier grass and sago waste respectively at 600 ^{o}C pyrolysis temperature. The variation in the products distribution can be linked to physicochemical and structural characteristics of the respective feedstock. Physicochemical properties of Bamabara shell bio-oil are summarized in Table 3. The pH value of organic phase from RKO and SKT was 4.4 and 3.3, which indicate that the oils are less acidic relative to the almond bio-oil (pH = 3.1) reported by Grioui et al. (2014) (Table 3). Similarly, density of the bio-oils are relatively lower than the values reported in the literature for almond and peanut bio-oil. Ultimate analysis result (dry basis) calculated from the wet basis results using Eq (4), (5), (6) (de Miguel Mercader et al., 2010; Mohammed et al., 2016c) and (7) (Mohammed et al., 2015d) indicated that C, H, O and HHV of the organic phase bio-oil from both Bambara shells are comparable to the elemental composition of peanut and almond shell bio-oil.

$$\mathrm{C_{dry}} = \frac{\mathrm{C_{wet}}}{\left(1-\left(\frac{\eta_{H_2O}}{100}\right)\right)} -------------(4)$$

$$\mathrm{H}_{\mathrm{dry}}=\frac{\left(\mathrm{H}_{\mathrm{wet}}\right)-\left[\eta_{H_2O}\times\left(\dfrac{2\times\mathrm{AMH}}{\left(2\times\mathrm{AMH}+\mathrm{AMO}\right)}\right)\right]}{\left(1-\left(\dfrac{\eta_{H_2O}}{100}\right)\right)}\text{--------------}(5)$$

$$\mathrm{O}_{\mathrm{dry}}=\frac{\left(\mathrm{O}_{\mathrm{wet}}\right)-\left[\eta_{H_2O}\times\left(\dfrac{\mathrm{AMO}}{\left(2\times\mathrm{AMH}+\mathrm{AMO}\right)}\right)\right]}{\left(1-\left(\dfrac{\eta_{H_2O}}{100}\right)\right)}\text{--------------}(6)$$

$$\mathrm{HHV}_{\mathrm{dry}}=\frac{\left(\mathrm{LHV}_{\mathrm{wet}}\right)+\left(1-\left(\dfrac{\eta_{H_2O}}{100}\right)\right)\times LH_{w}}{\left(1-\left(\dfrac{\eta_{H_2O}}{100}\right)\right)}\text{--------------------}(7)$$

C, H and O is carbon, hydrogen and oxygen content in wt %; η_{H2O} is the amount of water in the oil (wt %); AMH and AMO is atomic mass of hydrogen and oxygen; LH_w is the latent heat of vaporization of water (2.2MJ/kg)

3.3 Fourier-Transform Infra-Red (FTIR)

FTIR spectra of chemical species in the bio-oil are shown in Figure 4. The common broad peak around 3439 cm^{-1} implies that the samples contain chemical compounds with hydroxyl group ($\mathrm{O-H}$) such as water, alcohols and phenol (Bordoloi et al., 2015). The peaks between 2838 and 2948 cm^{-1} common to the organic phase bio-oils (Figure 4a and 4b) is $\mathrm{C-H}$ stretching vibration, which indicate the presence of saturated hydrocarbon in the organic phase while the peak between 2041 and 2132 cm^{-1} common to all the samples is ascribed to the $C \equiv N$ functional group (Guo et al., 2015). Vibrations observed between 1625 cm^{-1} and 1707 cm^{-1} in all the oil phases are attributed to $C = O$, which signifies the presence of aldehydes, ketones or carboxylic acids. The vibration at a frequency of 1515 cm^{-1} in both organic phases is ascribed to $C = C$ bond while the band around 1454 cm^{-1} in all the samples is ascribed to $C - H$ bending, suggesting the presence of alkenes/aromatic hydrocarbons. The vibrations observed at 1364, 1230 and 1273 cm^{-1} signify $C - N$ stretching (Yorgun and Yıldız, 2015). The sharp band around 1112, 1093, 1050 and 1025 cm^{-1} are due to $C - O$ vibration indicating the presence of alcohol and esters. The fingerprint at 755 cm^{-1} is ascribed to aromatic $C - H$ bending vibrations while the fingerprint between 655 and 531 cm^{-1} is ascribed to alkyl halide (Yorgun and Yıldız, 2015).

3.4 GC-MS analysis of the bio-oil samples

Identification of detail chemical compounds in the bio-oil samples collected at 600^{o}C was carried out by GC-MS. The chromatograms (Figure 5) show twenty (20) most abundant compounds in the bio-oils. The analysis revealed that the organic phase from both RKO and SKT consist of similar compounds such as alkenes, benzene derivatives, nitrogenated compounds, esters, aldehydes, ketones and acids in different proportions. A trace of sugar (L-Galactose) was also detected in the oil from RKO while none was observed in the oil from SKT. The aqueous phase from RKO consists predominant sugars and fine chemicals while that from SKT consist mainly acids, ketones, aldehyde and phenolics. In order to elucidate the variation of these compounds in the oil samples, the compounds were further grouped to hydrocarbon(HC), esters (ES), phenolics (PH), sugars (SGR), value added chemicals (VAC) and acid, aldehyde, ketones (AAK). From Figure 6, based on the GC-MS peak area (%), 7.09 % HC and 52.17 % PH was recorded in the organic phase RKO while 66.06 %PH was observed in the SKT with 2.31 % HC. The high content of SGR (30.69 %) and low content of AAK (7.04 %) in the aqueous phase from the RKO compared to low SGR (4.42 %) and high AAK (36.95 %) in the SKT is attributed to the catalytic effect of the respective biomass ash. Studies have shown that alkaline metals tend to catalyze pyrolysis reactions which usually lead to degradation and polymerization of pyrolysis product intermediate (Deshmukh et al., 2015; Bordoloi et al., 2015). Potassium (K) has been identified to have impacts on both the pyrolysis product distribution and the composition of bio-oil. Studies by Shimada et al. (2008); Nowakowski et al. (2008); Mohammed et al. (2016a) have demonstrated that potassium strongly promoted the formation of low molecular weight compounds and inhibited the formation of sugar during biomass pyrolysis. Similar observations have also been reported by Wang et al. (2010) and Trendewicz et al. (2015) during the pyrolysis of pine wood and cellulose respectively. They also reported greater phenol yield with K as a catalyst during the pyrolysis. Therefore, the high proportion of PH, AAK and lower content of SGR in the oil from the SKT relative to RKO is ascribed to the higher K content in the SKT (72.57 wt%) relative to 44.96 wt% in the RKO (Table 2). Compositions of bio-oil from almond shell bio-oil were mainly HC (alkanes and oleifins) as reported by Grioui et al. (2014) while peanut shell bio-oil constitutes about 59 % PH and 31 % AAK (Zhang et al., 2011). Lim et al. (2016) reported that bio-oil from Napier grass and sago waste consititute mainly PH and AAK and PH, AAK and trace of HC respectively. The authors linked the difference in the chemical composition to the presence of different mineral elements in the respective biomass.

3.5 GC analysis of the non-condensable gas sample

Composition the non-condensable gas collected at 600 ^{o}C is summarized in Table 4. The gas constitutes a high percentage of methane (CH_4), hydrogen (H_2), carbon monoxide (CO) and carbon dioxide (CO_2). The high composition of CH_4 signifies thermal cracking mechanisms that produce small organic molecules during the pyrolysis. The proportion of CH_4 recorded in the gas from RKO (9.43 vol%) was higher than that obtained from the SKT (7.42 vol%). This suggests that there is interaction between the minerals Al (19.61 wt%) and K (44.96 wt%) since Si is an inert material, (Table 2) in the biomass ash promoted the conversion of CH_4 precursors to form hydrocarbons. This observation is in good agreement with the higher percentage of total hydrocarbons recorded in the bio-oil from RKO (18.28 % in both phases) relative to SKT (2.31 %). On the other hand, higher composition of H_2, CO and CO_2 in the gas from SKT was recorded compared to RKO and could be linked to the higher percentage of K in the SKT ash. Study by Wang et al. (2010) has shown that K promotes production of H_2, CO and CO_2 during pyrolysis of lignocellulosic biomass.

3.5 Characteristics of produced bio-char

The properties of bio-char collected at 600 °C (Table 5) shows that both RKO and SKT produced bio-char rich in carbon. The atomic ratio, H/C and O/C were 0.03 and 0.14 in RKO-char while 0.01 and 0.13 were recorded in SKT-char. The relative lower ratios observed in the SKT-char indicates that SKT produced higher carbonized char which connotes a greater degree of aromaticity. Comparing this characteristic with the individual biomass feedstock, H/C, O/C of RKO and SKT biomass was 0.3, 1.3 and 0.33, 1.5 (Table 2). The decrease in the ratio, particularly, the O/C in the produced bio-char was due to dehydration reaction during the pyrolysis (Al-Wabel et al., 2013).

FTIR of the produced bio-char was compared with the source biomass as shown in Figure 7. The averaged spectra showed similar characteristic peaks for both RKO and SKT biomass. Similarly, common characteristic peaks were observed for the produced biochars. The peaks detected between 3723 and 3505 cm^{-1} in the feedstocks are assigned to different hydroxyl groups ($O-H$), principally from the cellulose component of the biomass. The peak at 3334 cm^{-1} is ascribed to $N-H$ functional group, indicating the presence of nitrogenous group in the feedstock while the peak observed at 3165, 3111 and 2960 cm^{-1} are due to $C-H$ stretching vibrations of cellulose, hemicellulose and lignin in the biomass samples (Usman et al., 2015). These peaks disappeared in the produced bio-chars, confirming the decomposition of structural component of the biomass feedstock (Mimmo et al., 2014) while that observed around 3700 cm^{-1} due to $O-H$ could be attributed to moisture adsorbed during sample preparations (Chen et al., 2016). The vibration at 1658 and 1588 cm^{-1} in the feedstock and produced bio-char is due to $C=C$ stretching while the band at around 1417 cm^{-1} in all the samples is ascribed to $C-H$ bending. The band observed in the feedstock at 1246 and 1033 is ascribed to $C-O-C$ and $C-O$ stretching vibrations of polysaccharides while the fingerprint at 545 and 462cm^{-1} is due to alkyl halides (Mohammed et al., 2015b). These peaks completely disappeared in the produced bio-char confirming the degradation of polysaccharides and alkyl halides during pyrolysis.

Physisorption analysis (Table 5) revealed that the produced bio-char is a porous material with a pore volume of 0.01 cm^3/g (RKO-char), 0.2 cm^3/g (SKT-char) with corresponding specific surface area (BET) of 1.2 and 1.72 m^2/g. This observation is also evident in the SEM micrograph (Figure 8) which showed cracked, uneven and visible porous structure in the bio-char due to the high degree of devolatilization at high temperature (600 ^{o}C) during the pyrolysis.

XRD analysis of the feedstocks and the produced bio-char is presented in Figure 9. The diffractogram showed main characteristic peak for both RKO and SKT biomass at 22.23^{o} and 22.09^{o} respectively, which represent the crystalline component in the biomass, mainly cellulose (Timpano et al., 2015). This peak completely disappeared in the produced bio-char, confirming complete decomposition of cellulose during the pyrolysis. New sets of peaks were identified in the produced bio-chars around 26, 28, 30, 31, 40 and 50°. XRD search and match reveal that the bio-char constituted predominantly sylvite mineral represented by the peaks in both chars around 28.63°, 40.65° and 50.43° (Usman et al., 2015). The peak observed around 26.83° and 30°, 31° indicate the presence of quartz and calcite (Yuan et al., 2011). Thermogravimetic analysis (Figure 10a) of the produced bio-char showed a total residual weight of 85.38 wt% and 86.49 wt% at 600 °C for SKT-bio-char and RKO-bio-char respectively compared to the individual feedstock with 37.67 wt% and 32.47 wt%. This result indicates that almost all the volatile matters in the biomass were completely volatilized during the pyrolysis. This observation is also confirmed in the DTG plot (Figure 10b) as all the peaks in the feedstock completely disappeared at 600 °C and above. The weight loss recorded at 600 °C in the bio-char (13.51 wt%-RKO-char, 14.62 wt%-SKT-char) is due to combustion of the remaining organic material in the bio-char. At higher temperature (900 °C), the total weight loss was 78.77 wt% in RKO-char and 76.76 wt% in SKT-char, which correspond to about 7.72 wt% and 8.62 wt% weigth loss between 600 and 900 °C . This observation could be attributed to the decomposition of inorganic materials in the biochar at higher temperature (Azargohar et al., 2014).

4. Conclusion

Pyrolysis of Bambara groundnut shell was carried out in a fixed bed reactor. This study evaluates impact of temperature on the pyrolysis product distribution (bio-oil, bio-char and non-condensable gas). It assesses the chemical and physicochemical properties of bio-oil, characteristics of bio-char and composition of the non-condensable gas. The bio-oil collected was a two-phase liquid, organic and aqueous phase. The organic phase from both shells have high energy content (25-29 MJ/kg) and could be used directly as a fuel in boilers or a precursor for quality biofuel production. The aqueous phase particularly from RKO was predominantly made up of sugars and other value-added chemicals, which can be used as a raw material for production of consumer products and fine chemicals. Bio-char was a porous material rich in carbon, which may well be used as a solid fuel. The bio-char also consist of macronutrient and may be applied as a source of nutrient for plant growth. Non-condensable gas consists of methane, hydrogen, carbon monoxide and carbon dioxide which can be recycled to the reactor as an energy supplement for the endothermic pyrolysis reaction or as a carrier gas. Using Bambara shells as feedstock for bioenergy production will encourage more production of the groundnut, which will bring about food security, particularly in challenging environments where major crops are severely limited by adverse climatic conditions in addition to income generation.

Acknowledgments

The project was supported by the Crops for the Future (CFF) and University of Nottingham under the grant BioP1-005.

References

Alburquerque, J. A., Sanchez, M. E., Mora, M., Barron, V., 2016. Slow pyrolysis of relevant biomasses in the Mediterranean basin. Part 2. Char characterization for carbon sequestration and agricultural uses. Journal of Cleaner Production 120, 191-197

Al-Wabel, M.I., Al-Omran, A., El-Naggar, A.H., Nadeem, M., Usman, A.R.A., 2013. Pyrolysis temperature induced changes in characteristics and chemical composition of biochar produced from conocarpus wastes. Bioresource Technology 131, 374-379

Azargohar, R., Nanda, S., Kozinski, J.A., Dalai, A. K., Sutarto, R., 2014. Effects of temperature on the physicochemical characteristics of fast pyrolysis bio-chars derived from Canadian waste biomass. Fuel 125, 90-100.

Bordoloi, N., Narzari, R., Chutia, R.S., Bhaskar, T., Kataki, R., 2015. Pyrolysis of Mesua ferrea and Pongamia glabra seed cover: Characterization of bio-oil and its sub-fractions. Bioresource Technology 178, 83–89

Bridgwater, A.V., 2012. Review of Fast Pyrolysis of biomass and product upgrading. Biomass and Bioenergy 38, 68-94.

Brink, M., Ramolemana, G.M., Sibuga, K.P., 2006. *Vigna subterranea* (L.) Verdc. In: Brink, M. & Belay, G. (Editors). PROTA 1: Cereals and pulses/Cereales et legumes secs. [CD-Rom]. Wageningen, Netherlands

Brough, S.H., Azam-Ali, S.N., 1992. The effect of soil moisture on the proximate composition of Bambara groundnut (*Vigna subterranea* (L) Verdc). Journal of the Science of Food and Agriculture 60(2), 97-203.

Chen, T., Liu, R., Scott, N.R., 2016. Characterization of energy carriers obtained from the pyrolysis of white ash, switchgrass and corn stover — Biochar, syngas and bio-oil. Fuel Processing Technology 142, 124-134

Collinson, S.T., Azam-Ali, S.N., Chavula, K.M., Hodson, D.A., 1999. Growth, development and yield of Bambara groundnut (*Vigna subterranea*) in response to soil moisture. Journal of Agricultural science (Cambridge) 126, 307-318.

Deshmukh, Y., Yadav, V., Nigam, N., Yadav, A., Khare, P., 2015. Quality of bio-oil by pyrolysis of distilled spent of Cymbopogon flexuosus. Journal of Analytical and Applied Pyrolysis 115, 43-50.

de Miguel Mercader, F., Groeneveld, M.J., Kersten, S.R.A., Venderbosch, R.H., Hogendoorn, J.A., 2010. Pyrolysis oil upgrading by high pressure thermal treatment. Fuel 89, 2829–2837

Forsyth, T., 2014. Public concerns about transboundary haze: a comparison of Indonesia, Singapore, and Malaysia. Global Environmental Change 25, 76-86

Gómez, N., Rosas, J.G., Cara, J., Martínez, O., Alburquerque, J. A., Sánchez, M.E., 2016. Slow pyrolysis of relevant biomasses in the Mediterranean basin. Part 1. Effect of temperature on process performance on a pilot scale. Journal of Cleaner Production 120, 181-190

Grioui, N., Halouani, K., Agblevor, F.A., 2014. Bio-oil from pyrolysis of Tunisian almond shell: Comparative study and investigation of aging effect during long storage. Energy for Sustainable Development 21, 100-112

Guo, Y., Song, W., Lu, J., Ma, Q., Xu, D., 2015. Wang S. Hydrothermal liquefaction of Cyanophyta: Evaluation of potential bio-crude oil production and component analysis. Algal Research 11, 242–247.

Heller, J., Begemann, F., Mushonga, J., 1997. Bambara groundnut (*Vigna subterranea* (L.) Verdc.). Promoting the conservation and use of underutilized and neglected crops. Proceedings of the workshop on Conservation and Improvement of Bambara Groundnut (*Vigna subterranea* (L.) Verdc.), 14–16 November, Harare, Zimbabwe.

Jensen, E.S., Peoples, M.B., Boddey, R.M., Gresshoff, P.M., Hauggaard-Nielsen, H., Alves, B.J., Morrison, M.J., 2012. Legumes for mitigation of climate change and the provision of feedstock for biofuels and biorefineries. A review. Agronomy for Sustainable Development 32(2), 329-364.

Kishinevsky, B.D., Zur, M., Friedman, Y., Meromi, G., Ben-Moshe, E., Nemas, C., 1996. Variation in nitrogen fixation and yield in landraces of Bambara groundnut (*Vigna subterranea* L.). Field Crops Research 48(1), 57-64.

Kuprianov, V. I., Arromdee, P., 2013. Combustion of peanut and tamarind shells in a conical fluidized-bedcombustor: A comparative study. Bioresource Technology 140, 199–210

Lim, C.H., Mohammed, I.Y., Abakr, Y.A., Kazi, F.K., Yusup, S. and Lam, H.L., 2016. Novel input-output prediction approach for biomass pyrolysis. Journal of Cleaner Production 30, 1-11.

Lim, C.H., Mohammed, I.Y., Abakr, Y.A., Kazi, F.K., Yusup, S. and Lam, H.L., 2015. Element characteristic tolerance for semi-batch fixed bed biomass pyrolysis. *Chemical Engineering 45*, 1285-1290

Mimmo, T., Panzacchi, P., Baratieri, M., Davies, C. A., Tonon, G., 2014. Effect of pyrolysis temperature on Miscanthus (Miscanthus x giganteus) biochar physical, chemical and functional properties. Biomass and Bioenergy 62, 149-157.

Mohale, K.C., Belane, A.K., Dakora, F.D., 2014. Symbiotic N nutrition, C assimilation, and plant water use efficiency in Bambara groundnut (*Vigna subterranea* L. Verdc) grown in farmers' fields in South Africa, measured using 15N and 13C natural abundance. Biology and Fertility of Soils 50, 307-319

Mohammed, I.Y., Abakr, Y.A., Kazi, F. K., Yusuf, S., Alshareef, I., Soh, A.C., 2015a. Pyrolysis of Napier Grass in a Fixed Bed Reactor: Effect of Operating Conditions on Product Yields and Characteristics. BioResources 10 (4), 6457-6478.

Mohammed, I.Y., Abakr, Y.A., Kazi, F.K., Yusup, S., Alshareef, I., Soh, A.C., 2015b Comprehensive characterization of Napier grass as a feedstock for thermochemical conversion. Energies 8(5), 3403-3417.

Mohammed, I.Y., Abakr, Y.A., Kabir, F., Yusuf, S., 2015c. Effect of aqueous pretreatment on pyrolysis characteristics of Napier grass. Journal of Engineering Science and Technology 10(11), 1487-1496.

Mohammed, I.Y., Kazi, F.K., Abakr, Y.A., Yusuf, S., Razzaque, M.A., 2015d. Novel method for the determination of water content and higher heating value of pyrolysis oil. BioResources 10(2), 2681-2690.

Mohammed, I.Y., Lim, C.H., Kazi, F.K., Yusup, S., Lam, H.L. and Abakr, Y.A., 2016a. Co-pyrolysis of Rice Husk with Underutilized Biomass Species: A Sustainable Route for Production of Precursors for Fuels and Valuable Chemicals. Waste and Biomass Valorization, 1-11.

Mohammed, I.Y., Abakr, Y.A., Kazi, F.K. and Yusuf, S., 2016b. Effects of pretreatments of Napier grass with deionized water, sulfuric acid and sodium hydroxide on pyrolysis oil characteristics. Waste and Biomass Valorization, 1-19.

Mohammed, I.Y., Kazi, F.K., Yusup, S., Alaba, P.A., Sani, Y.M., Abakr, Y.A., 2016c. Catalytic Intermediate Pyrolysis of Napier Grass in a Fixed Bed Reactor with ZSM-5, HZSM-5 and Zinc-Exchanged Zeolite-A as the Catalyst. Energies 9 (4), 246.

Murty, T.S., Scott, D., Baird, W., 2000. The 1997 El Nino, Indonesian forest fires and the Malaysian smoke problem: A deadly combination of natural and man-made hazard. Natural Hazards 21(2-3), 131-144.

Musa, M., Massawe, F., Mayes, S., Alshareef, I., Singh, A., 2016. Nitrogen fixation and N-balance studies on Bambara groundnut (*Vigna subterranea* L. Verdc) landraces grown on tropical acidic soils of Malaysia. Communications in Soil Science and Plant Analysis 47(4), 533-542.

Mwale, S.S., Azam-Ali, S.N., Massawe, F.J., 2007. Growth and development of Bambara groundnut (Vigna subterranea) in response to soil moisture: 1. Dry matter and yield. European Journal of Agronomy 26(4), 345-353.

Nowakowski, D.J., Jones, J.M., 2008. Uncatalysed and potassium-catalysed pyrolysis of the cell-wall constituents of biomass and their model compounds. Journal of Analytical and Applied Pyrolysis 83, 12–25.

Shimada, N., Kawamoto, H., Saka, S., 2008. Different action of alkali/alkaline earth metal chlorides on cellulose pyrolysis. Journal of Analytical and Applied Pyrolysis 81, 80–87.

Timpano, H., Sibout, R., Devaux, M.-F., Alvarado, C., Looten, R., Pontoire, B., Martin, M., Legée, F., Cézard, L., Lapierre, C., 2015. Brachypodium cell wall mutant with enhanced saccharification potential despite increased lignin content. Bioenergy Research 8(1), 53-67.

Trendewicz, A., Evans, R., Dutta, A., Sykes, R., Carpenter, D., Braun, R., 2015. Evaluating the effect of potassium on cellulose pyrolysis reaction kinetics. Biomass and bioenergy 74, 15-25

Tripathi, M., Sahu, J.N., Ganesan, P., 2016. Effect of process parameters on production of biochar from biomass waste through pyrolysis: A review. Renewable and Sustainable Energy Reviews 55, 467–481

Usman, A.R.A., Abduljabbar, A., Vithanage, M., Ok, Y.S., Ahmad, M., Ahmad, M., Elfaki, J., Abdulazeem, S.S., Al-Wabel, M.I., 2015. Biochar production from date palm waste: Charring temperature induced changes in composition and surface chemistry. Journal of Analytical and Applied Pyrolysis 115, 392-400

Varkkey, H., 2013. Patronage politics, plantation fires and transboundary haze. Environmental Hazards 12(3-4), 200-217.

Wang, Z., Wang, F., Cao, J., Wang, J., 2010. Pyrolysis of pine wood in a slowly heating fixed-bed reactor: Potassium carbonate versus calcium hydroxide as a catalyst. Fuel Processing Technology 91, 942–950

Yorgun, S., Yıldız, D., 2015. Slow pyrolysis of paulownia wood: Effects of pyrolysis parameters on product yields and bio-oil characterization. Journal of Analytical and Applied Pyrolysis 114, 68-78.

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), 3488-3497.

Zhang, C., Zhang, R., Li, X., Li, Y., Shi, W., Ren, X., Xu, X., 2011. Bench-scale fluidized-bed fast pyrolysis of peanut shell for bio-oil production. Environmental Progress and Sustainable Energy 30, 11–18.