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

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24 **Abstract**

25 This study provides first report on thermochemical conversion of residue from one of the
26 underutilized crops, Bambara groundnut. Shells from two Bambara groundnut landraces KARO
27 and EX-SOKOTO were used. Pyrolysis was conducted in a vertical fixed bed reactor at 500,
28 550, 600 and 650 °C; 50 °C/min heating rate and 5 L/min nitrogen flow rate. The report gives
29 experimental results on characteristic of the feedstock, impact of temperature on the pyrolysis
30 product distribution (bio-oil, bio-char and non-condensable gas). It evaluates the chemical and
31 physicochemical properties of bio-oil, characteristics of bio-char and composition of the non-
32 condensable gas using standard analytical techniques. KARO shell produced more bio-oil and
33 was maximum at 600 °C (37.21 wt%) compared to EX-SOKOTO with the highest bio-oil yield
34 of 32.79 wt% under the same condition. Two-phase bio-oil (organic and aqueous) was collected

35 and analyzed. The organic phase from both feedstocks was made up of benzene derivatives
36 which can be used as a precursor for quality biofuel production while the aqueous from KARO
37 consisted sugars and other valuable chemicals compared to the aqueous phase from EX-
38 SOKOTO which comprised of acids, ketones, aldehydes and phenols. Characteristics of bio-char
39 and composition of the non-condensable were also determined. The results show that bio-char is
40 rich in carbon and some minerals which can be utilized either as a solid fuel or source of bio-
41 fertilizer. The non-condensable gas was made up of methane, hydrogen, carbon monoxide and
42 carbon dioxide, which can be recycled to the reactor as a carrier gas. This study demonstrated
43 recovery of high quality fuel precursor and other valuable materials from Bambara groundnut
44 shell.

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

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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

48
49

50 **1. Introduction**

51 Bambara groundnut (*Vigna subterranea* (L.) Verdc), is an underutilized pulse legume cultivated
52 primarily for its seeds, which are consumed in various forms of dishes, rich in protein (16-25 %),
53 carbohydrate (42-60 %), lipid (5-6 %) ([Brough and Azam-Ali, 1992](#)), fibre (4.8 %) and ash (3.4
54 %) ([Brink et al., 2006](#)). The fresh pods containing the seeds are boiled and eaten as snacks
55 whereas the haulm, is used as livestock feed in most of the drier parts of Africa ([Heller et al.,](#)
56 [1997](#)). Legume such as Bambara groundnut with the ability to meet greater % of their N
57 requirement as a result of atmospheric N fixation have been identified as potential alternative
58 crops for mitigating climate change ([Jensen et al., 2012](#)) and offer an important alternative to the
59 use of inorganic N fertilizers that are costly and unavailable to resource-poor farmers. The crop
60 is predominantly grown by subsistence farmers over much of semi-arid Africa and is reported to
61 spread into new production areas such as Indonesia, Malaysia and Thailand in the Asian
62 continent and is increasingly becoming popular due to its ability to thrive under conditions which
63 are too poor for other tropical legumes such as cowpea and groundnut ([Mohale et al., 2014](#)).
64 Bambara groundnut shell constitutes the weight of the pod wall after the grain is removed and is
65 highly variable depending on the pod yield and shelling percentage and sometimes could reach

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

81 Pyrolysis is currently one of the most promising thermochemical processes for converting
82 biomass materials to products with high energy potentials. Typical pyrolysis products are bio-oil,
83 bio-char and non-condensable gas ([Alburquerque et al., 2016](#); [Gómez et al., 2016](#)). Distribution
84 of pyrolysis products depends heavily on the process parameters such as pyrolysis temperature,
85 heating rate and vapor residence time in the reactor. There are different types of pyrolysis
86 namely; slow, intermediate and fast pyrolysis. Slow pyrolysis is also referred to as
87 carbonization. It is carried out at a temperature up to 400 °C, solid residence time of 1 h to
88 several hours, with product distribution of about 35 % bio-char, 30% bio-oil, and 35% non-

89 condensable gas. Fast pyrolysis can produce up to 80 % bio-oil, 12 % bio-char, and 13 % non-
90 condensable gas at temperature around 500 °C, high heating rate, a short vapor residence time of
91 about 1 s, and rapid cooling of volatile ([Bridgwater, 2012](#); [Mohammed et al., 2015a](#)). For
92 intermediate pyrolysis, 500-650 °C pyrolysis temperature and vapor residence time of
93 approximately 10 to 30 s are typical operating conditions. About 40-60% of the total product
94 yield is usually bio-oil, 15-25% bio-char and 20-30% non-condensable gas. Intermediate
95 pyrolysis produce bio-oil with less reactive tar which can be used directly as fuel in engines and
96 boilers, and dry char suitable for both agricultural and energy applications ([Tripathi et al., 2016](#)).
97 To the best of our knowledge, thermochemical conversion of Bambara groundnut shells has not
98 been reported in the literature. In this study, intermediate pyrolysis of Bambara shell was
99 investigated in a fixed bed reactor and pyrolysis products were characterized.

100 **2. Materials and methods**

101 Shells from two Bambara groundnut landraces, Karo (RKO) and EX-Sokoto (SKT) were
102 collected from Crops for the Future (CFF) field research Centre Semenyih, Selangor, Malaysia.
103 The material was dried at 105 °C in electrical oven. The dried materials were then shredded in a
104 Retsch[®] rotor beater mill (SM100, Retsch GmbH, Germany) to particle sizes between 0.2 mm
105 and 2.5 mm and stored in airtight plastic bags for further analysis. Volatile matter and ash
106 content on dry basis were determined. Fixed carbon was computed from the remaining bone dry
107 sample mass. The biomass ash elemental composition was analyzed with energy dispersive X-
108 ray EDX (X-Max 20 mm², Oxford Instruments, UK). Higher heating value (HHV) was
109 determined using an oxygen bomb calorimeter (Parr 6100, Parr Instruments, Molin, USA).
110 Elemental compositions were determined using CHNS/O analyzer (2400 Series II CHNS/O
111 analyzer, Perkin Elmer Sdn Bhd, Selangor, Malaysia). The nature of chemical functional groups

112 were evaluated with Fourier transform infrared spectroscopy (Spectrum RXI, PerkinElmer,
113 Selangor, Malaysia) using the potassium bromide (KBr) method. Potassium bromide (KBr) disc
114 (13 mm diameter translucent) was made from a homogenized 2 mg sample in 100 mg KBr using
115 a bench press (Carver 43500, Carver Inc.,USA) by applying 5.5 tonnes load for 5 min. Spectra
116 were recorded with Spectrum V5.3.1 software within wave number range of 400 to 4000 cm^{-1} at
117 32 scans and a resolution of 4 cm^{-1} . Thermogravimetric study was carried out using
118 thermogravimetric simultaneous thermal analyzer (TGA) (STA 6000, Perkin Elmer Sdn Bhd,
119 Selangor, Malaysia) in nitrogen atmosphere, flow rate 20 mL/min at temperatures between 30-
120 950 $^{\circ}\text{C}$ and heating rate of 20 $^{\circ}\text{C}/\text{min}$. About 10 mg (particle size of 0.2 mm) of sample was used.

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

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

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

136 Yield (wt%)_{non - condensable gas} = 100 - (Eq(1) + Eq (2))----- (3)

137

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

148 The composition of non-condensable pyrolysis product was monitored offline. The gas sample
149 was collected in a gas sample bag (Tedlar, SKC Inc., USA) and its composition analyzed using a
150 gas chromatography equipped with stainless steel column (Porapak R 80/100) and thermal
151 conductivity detector (TCD). Helium was used as a carrier gas and the GC was programed at 60
152 °C, 80 °C and 200 °C for oven, injector and TCD temperature respectively. Bio-char ultimate
153 analysis and inorganic composition were carried out following the procedure outlined for the
154 feedstock characterization. Crystallographic structure in the produced bio-char was examined
155 between 2θ angle of 10°–70° at 25 mA, 45 kV, step size of 0.025°and 1.0 s scan rate. Surface

156 and structural characteristics of the bio-char were also determined .

157 **3. Results and Discussion**

158 *3.1 Characterization of feedstock*

159 Characteristic of the feedstock is summarized in Table 2. Moisture content of SKT and RKO (as
160 received) was 4.67 and 7.12 wt%. Higher volatile matter (76.24 wt%) and lower ash content
161 (8.98 wt%) was recorded for the RKO compared to 73.83 wt% volatile matter and 10.10 wt%
162 ash content in the SKT. Similarly, the ultimate analysis revealed that RKO has carbon and
163 oxygen content of 37.36 wt% and 49.11 wt%, while 34.63 wt% carbon and 51.93 wt% oxygen
164 was recorded for the SKT. RKO has higher heating value (HHV) of 20.46 MJ/kg relative to
165 19.19 MJ/kg recorded for SKT. The higher energy content recorded for the RKO could be
166 attributed to its lower ash and oxygen contents. These physiochemical characteristics are similar
167 to properties of peanut shell reported by [Zhang et al. \(2011\)](#). The authors recorded high volatile
168 matter and heating value of 71.5 wt% and 18.1 MJ/kg respectively. Their ultimate analysis result
169 showed higher carbon (47 wt%), and lower oxygen (34 wt%) and hydrogen (6 wt%) contents
170 compared to that of the Bamabara shells. EDX analysis of the ash showed that the inorganic
171 element in the RKO and SKT is in the following order potassium (K)>silica (Si)>Aluminum
172 (Al)>phosphorus (P)>Chlorine (Cl)>iron (Fe)>calcium (Ca)>magnesium (Mg) and
173 K>Cl>Si>Al>P>Mg respectively. The proportion of metallic elements in the RKO is similar to
174 that of peanut reported by [Kuprianov and Arromdee \(2013\)](#). The authors also reported
175 distribution of minerals in tamarin shell which is comparable to that of SKT except for the Si,
176 which is higher in SKT. The result of thermogravimetric analysis (TGA) analysis is shown in
177 Figure 2. The thermogravimetric (TG) and derivative thermogravimetric (DTG) profiles of both
178 samples exhibited similar decomposition characteristics. The residual weight at the end of the

179 decomposition process was found to be 23 and 29 wt% for RKO and SKT respectively. From the
180 DTG curves, two main peaks from ambient to 100 °C and from 240 to 420 °C, which is attributed
181 to evaporation of moisture and decomposition of holocellulose (hemicellulose and cellulose)
182 component of the biomass. Hemicellulose which normally decomposes around 250 °C in a
183 lignocellulosic material was not observed in this study. It means that Bambara shells have less or
184 infinitesimal amount of hemicellulose. A noticeable peak around 200 °C was also observed,
185 which is ascribed to the decomposition of extractives. The pattern observed at the temperature
186 above 420 °C is attributed to the decomposition of lignin. This region exhibited unsteady thermal
187 degradation, which is ascribed to the presence of different oxygen functional groups in the lignin
188 ([Mohammed et al., 2015b](#)). TGA analysis of almond shell by [Grioui et al. \(2014\)](#) showed a
189 residual weight fraction of 27.5 wt%. The DTG curve exhibited main peak at temperature
190 between 220 and 400 °C, which was attributed to the decomposition of cellulose and
191 hemicellulose. The decomposition temperature values observed in this study are also similar to
192 those of other lignocellulosic biomass in the literature ([Mohammed et al., 2015c](#)).

193 3.2 *Pyrolysis product distribution and physicochemical properties of the bio-oil*

194 Product distribution from the pyrolysis of RKO and SKT at temperature between 500 and 650
195 °C, 5 L/min nitrogen flow and heating rate 50 °C/min is shown in Fig. 3. From Figure 3(a), total
196 bio-oil yield from RKO increased from 33.26 to 37.21 wt% as the temperature increased from
197 500 to 600 °C. This observation could be attributed to the decomposition of more lignin at such a
198 high temperature. At 650 °C, the oil yield dropped to 27.69 wt%, which is due to secondary
199 reactions of pyrolysis vapor at the elevated temperature ([Mohammed et al., 2015a](#)). The bio-oil
200 collected consist of organic phase and an aqueous phase. The yield of organic phase increased
201 from 9.8 wt% to 15.0 wt% at the temperature between 500 and 600 °C and latter declined to 9.3

202 wt% at 650 °C. On the other hand, a continuous decrease in the aqueous phase from 24.3 to 18.4
203 wt% was recorded. Generally, the aqueous phase bio-oil is a product of holocellulose
204 decomposition whose yield and composition is greatly affected by the inorganic minerals in the
205 source biomass. The significant reduction in the bio-oil aqueous phase and increased non-
206 condensable yield observed could be attributed to the synergistic effect of the most abundant
207 minerals in the biomass ash, which are Al and K (Table 2) since Si is an inert material and may
208 not possess any catalytic activity ([Mohammed et al., 2016a](#)). The yield of non-condensable gas
209 was 32.43 and 32.57 wt% at 500 and 550 °C but increased rapidly to 33.28 and 43.11 wt% at
210 600 and 650 °C. The corresponding bio-char yield was 32.96, 32.26, 29.51 and 29.20 wt%. The
211 high yield of non-condensable gas observed above could be mainly due to the secondary
212 reactions of pyrolysis vapor at the elevated temperature ([Mohammed et al., 2015a](#)) since there
213 was no substantial reduction in the biochar yield. Figure 3b shows pyrolysis product distribution
214 from the SKT. The total bio-oil yield was 26.17, 32.18, 32.78 and 27.58 wt% at 500, 550, 600
215 and 650 °C respectively. Similar to RKO, two phase bio-oil was collected from the pyrolysis of
216 SKT and the corresponding organic and aqueous phases recorded were 5.90, 10.84, 11.17, 5.77
217 wt% and 20.27, 21.34, 21.61, 21.81 wt%. The bio-char yield decreased from 39.91 wt% at 500
218 °C to 28.56 wt% at 650 °C while the corresponding yield of non-condensable gas increased from
219 33.92 to 43.86 wt%. The high yield of non-condensable gas could be a resultant effect of a
220 secondary reaction of pyrolysis vapor and devolatilization of the bio-char at high temperature.
221 Comparing the product distribution between RKO and SKT, the highest total bio-oil yield of
222 37.21 wt% was recorded at 600 °C from RKO compared to 32.78 wt% from SKT. A substantial
223 decrease in the biochar yield (11.35 %) with increasing temperature (500-650 °C) was observed
224 from SKT compared to 4.06 % recorded from the RKO. Higher non-condensable gas yield was

225 also recorded with SKT at all temperatures relative to that obtained from RKO. These
 226 observations can be attributed to the differences in the characteristics of the
 227 feedstocks([Mohammed et al., 2016b](#)), as summerized in Table 2. Comparing the pyrolysis
 228 product distribution with products yield from other shells, [Zhang et al. \(2011\)](#) reported a total
 229 pyrolysis oil of 60 wt% from peanut shell at 500 °C with corresponding 19 wt% char and 15
 230 wt% non-condensable gas. [Grioui et al. \(2014\)](#) reported pyrolysis products distribution of 40
 231 wt% bio-oil , 47 wt% gas and 13 wt% solid. Pyrolysis oil yield from other biomass species have
 232 been reported by [Lim et al. \(2015\)](#) and [\(2016\)](#). They recorded bio-oil yield of 41.91-57.21 wt%
 233 and 37.98-43.66 wt% from Napier grass and sago waste respectively at 600 °C pyrolysis
 234 temperature. The variation in the products distribution can be linked to physicochemical and
 235 structural characteristics of the respective feedstock. Physicochemical properties of Bamabara
 236 shell bio-oil are summarized in Table 3. The pH value of organic phase from RKO and SKT was
 237 4.4 and 3.3, which indicate that the oils are less acidic relative to the almond bio-oil (pH = 3.1)
 238 reported by [Grioui et al. \(2014\)](#) (Table 3). Similarly, density of the bio-oils are relatively lower
 239 than the values reported in the literature for almond and peanut bio-oil. Ultimate analysis result
 240 (dry basis) calculated from the wet basis results using Eq (4), (5), (6) ([de Miguel Mercader et al.,](#)
 241 [2010](#); [Mohammed et al., 2016c](#)) and (7) ([Mohammed et al., 2015d](#)) indicated that C, H, O and
 242 HHV of the organic phase bio-oil from both Bambara shells are comparable to the elemental
 243 composition of peanut and almond shell bio-oil.

244

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

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

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

$$\text{HHV}_{\text{dry}} = \frac{(\text{LHV}_{\text{wet}}) + \left(1 - \left(\frac{\eta_{H_2O}}{100} \right) \right) \times \text{LH}_w}{\left(1 - \left(\frac{\eta_{H_2O}}{100} \right) \right)} \quad \text{--- (7)}$$

C, H and O is carbon, hydrogen and oxygen content in wt %; η_{H_2O} 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)

251

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 (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 C–H stretching vibration, which indicate the presence of saturated hydrocarbon in the organic phase while the

258 peak between 2041 and 2132 cm^{-1} common to all the samples is ascribed to the $\text{C}\equiv\text{N}$
259 functional group ([Guo et al., 2015](#)). Vibrations observed between 1625 cm^{-1} and 1707 cm^{-1} in all
260 the oil phases are attributed to $\text{C}=\text{O}$, which signifies the presence of aldehydes, ketones or
261 carboxylic acids. The vibration at a frequency of 1515 cm^{-1} in both organic phases is ascribed to
262 $\text{C}=\text{C}$ bond while the band around 1454 cm^{-1} in all the samples is ascribed to $\text{C}-\text{H}$ bending,
263 suggesting the presence of alkenes/aromatic hydrocarbons. The vibrations observed at 1364,
264 1230 and 1273 cm^{-1} signify $\text{C}-\text{N}$ stretching ([Yorgun and Yıldız, 2015](#)). The sharp band
265 around 1112, 1093, 1050 and 1025 cm^{-1} are due to $\text{C}-\text{O}$ vibration indicating the presence of
266 alcohol and esters. The fingerprint at 755 cm^{-1} is ascribed to aromatic $\text{C}-\text{H}$ bending vibrations
267 while the fingerprint between 655 and 531 cm^{-1} is ascribed to alkyl halide ([Yorgun and Yıldız,](#)
268 [2015](#)).

269 3.4 GC-MS analysis of the bio-oil samples

270 Identification of detail chemical compounds in the bio-oil samples collected at 600°C was carried
271 out by GC-MS. The chromatograms (Figure 5) show twenty (20) most abundant compounds in
272 the bio-oils. The analysis revealed that the organic phase from both RKO and SKT consist of
273 similar compounds such as alkenes, benzene derivatives, nitrogenated compounds, esters,
274 aldehydes, ketones and acids in different proportions. A trace of sugar (L-Galactose) was also
275 detected in the oil from RKO while none was observed in the oil from SKT. The aqueous phase
276 from RKO consists predominant sugars and fine chemicals while that from SKT consist mainly
277 acids, ketones, aldehyde and phenolics. In order to elucidate the variation of these compounds in
278 the oil samples, the compounds were further grouped to hydrocarbon(HC), esters (ES), phenolics
279 (PH), sugars (SGR), value added chemicals (VAC) and acid, aldehyde, ketones (AAK). From
280 Figure 6, based on the GC-MS peak area (%), 7.09 % HC and 52.17 % PH was recorded in the

281 organic phase RKO while 66.06 %PH was observed in the SKT with 2.31 % HC. The high
282 content of SGR (30.69 %) and low content of AAK (7.04 %) in the aqueous phase from the RKO
283 compared to low SGR (4.42 %) and high AAK (36.95 %) in the SKT is attributed to the
284 catalytic effect of the respective biomass ash. Studies have shown that alkaline metals tend to
285 catalyze pyrolysis reactions which usually lead to degradation and polymerization of pyrolysis
286 product intermediate ([Deshmukh et al., 2015](#); [Bordoloi et al., 2015](#)). Potassium (K) has been
287 identified to have impacts on both the pyrolysis product distribution and the composition of bio-
288 oil. Studies by [Shimada et al. \(2008\)](#); [Nowakowski et al. \(2008\)](#); [Mohammed et al. \(2016a\)](#) have
289 demonstrated that potassium strongly promoted the formation of low molecular weight
290 compounds and inhibited the formation of sugar during biomass pyrolysis. Similar observations
291 have also been reported by [Wang et al. \(2010\)](#) and [Trendewicz et al. \(2015\)](#) during the pyrolysis
292 of pine wood and cellulose respectively. They also reported greater phenol yield with K as a
293 catalyst during the pyrolysis. Therefore, the high proportion of PH, AAK and lower content of
294 SGR in the oil from the SKT relative to RKO is ascribed to the higher K content in the SKT
295 (72.57 wt%) relative to 44.96 wt% in the RKO (Table 2). Compositions of bio-oil from almond
296 shell bio-oil were mainly HC (alkanes and oleifins) as reported by [Grioui et al. \(2014\)](#) while
297 peanut shell bio-oil constitutes about 59 % PH and 31 % AAK ([Zhang et al., 2011](#)). [Lim et al.](#)
298 [\(2016\)](#) reported that bio-oil from Napier grass and sago waste constitute mainly PH and AAK
299 and PH, AAK and trace of HC respectively. The authors linked the difference in the chemical
300 composition to the presence of different mineral elements in the respective biomass.

301 3.5 GC analysis of the non-condensable gas sample

302 Composition the non-condensable gas collected at 600 °C is summarized in Table 4. The gas
303 constitutes a high percentage of methane (CH₄), hydrogen (H₂), carbon monoxide (CO) and

304 carbon dioxide (CO₂). The high composition of CH₄ signifies thermal cracking mechanisms that
305 produce small organic molecules during the pyrolysis. The proportion of CH₄ recorded in the
306 gas from RKO (9.43 vol%) was higher than that obtained from the SKT (7.42 vol%). This
307 suggests that there is interaction between the minerals Al (19.61 wt%) and K (44.96 wt%) since
308 Si is an inert material, (Table 2) in the biomass ash promoted the conversion of CH₄ precursors
309 to form hydrocarbons. This observation is in good agreement with the higher percentage of total
310 hydrocarbons recorded in the bio-oil from RKO (18.28 % in both phases) relative to SKT (2.31
311 %). On the other hand, higher composition of H₂, CO and CO₂ in the gas from SKT was recorded
312 compared to RKO and could be linked to the higher percentage of K in the SKT ash. Study by
313 [Wang et al. \(2010\)](#) has shown that K promotes production of H₂, CO and CO₂ during pyrolysis
314 of lignocellulosic biomass.

315 3.5 Characteristics of produced bio-char

316 The properties of bio-char collected at 600 °C (Table 5) shows that both RKO and SKT produced
317 bio-char rich in carbon. The atomic ratio, H/C and O/C were 0.03 and 0.14 in RKO-char while
318 0.01 and 0.13 were recorded in SKT-char. The relative lower ratios observed in the SKT-char
319 indicates that SKT produced higher carbonized char which connotes a greater degree of
320 aromaticity. Comparing this characteristic with the individual biomass feedstock, H/C, O/C of
321 RKO and SKT biomass was 0.3, 1.3 and 0.33, 1.5 (Table 2). The decrease in the ratio,
322 particularly, the O/C in the produced bio-char was due to dehydration reaction during the
323 pyrolysis ([Al-Wabel et al., 2013](#)).

324 FTIR of the produced bio-char was compared with the source biomass as shown in Figure 7. The
325 averaged spectra showed similar characteristic peaks for both RKO and SKT biomass. Similarly,
326 common characteristic peaks were observed for the produced biochars. The peaks detected

327 between 3723 and 3505 cm^{-1} in the feedstocks are assigned to different hydroxyl groups (O–H),
328 principally from the cellulose component of the biomass. The peak at 3334 cm^{-1} is ascribed to
329 N–H functional group, indicating the presence of nitrogenous group in the feedstock while the
330 peak observed at 3165, 3111 and 2960 cm^{-1} are due to C–H stretching vibrations of cellulose,
331 hemicellulose and lignin in the biomass samples ([Usman et al., 2015](#)). These peaks disappeared
332 in the produced bio-chars, confirming the decomposition of structural component of the biomass
333 feedstock ([Mimmo et al., 2014](#)) while that observed around 3700 cm^{-1} due to O–H could be
334 attributed to moisture adsorbed during sample preparations ([Chen et al., 2016](#)). The vibration at
335 1658 and 1588 cm^{-1} in the feedstock and produced bio-char is due to C=C stretching while the
336 band at around 1417 cm^{-1} in all the samples is ascribed to C–H bending. The band observed in
337 the feedstock at 1246 and 1033 is ascribed to C–O–C and C–O stretching vibrations of
338 polysaccharides while the fingerprint at 545 and 462 cm^{-1} is due to alkyl halides ([Mohammed et](#)
339 [al., 2015b](#)). These peaks completely disappeared in the produced bio-char confirming the
340 degradation of polysaccharides and alkyl halides during pyrolysis.

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

346 XRD analysis of the feedstocks and the produced bio-char is presented in Figure 9. The
347 diffractogram showed main characteristic peak for both RKO and SKT biomass at 22.23° and
348 22.09° respectively, which represent the crystalline component in the biomass, mainly cellulose
349 ([Timpano et al., 2015](#)). This peak completely disappeared in the produced bio-char,

350 confirming complete decomposition of cellulose during the pyrolysis. New sets of peaks were
351 identified in the produced bio-chars around 26, 28, 30, 31, 40 and 50°. XRD search and
352 match reveal that the bio-char constituted predominantly sylvite mineral represented by the
353 peaks in both chars around 28.63°, 40.65° and 50.43° ([Usman et al., 2015](#)). The peak observed
354 around 26.83° and 30°, 31° indicate the presence of quartz and calcite ([Yuan et al., 2011](#)).
355 Thermogravimetric analysis (Figure 10a) of the produced bio-char showed a total residual weight
356 of 85.38 wt% and 86.49 wt% at 600 °C for SKT-bio-char and RKO-bio-char respectively
357 compared to the individual feedstock with 37.67 wt% and 32.47 wt%. This result indicates that
358 almost all the volatile matters in the biomass were completely volatilized during the pyrolysis.
359 This observation is also confirmed in the DTG plot (Figure 10b) as all the peaks in the feedstock
360 completely disappeared at 600 °C and above. The weight loss recorded at 600 °C in the bio-char
361 (13.51 wt%-RKO-char, 14.62 wt%-SKT-char) is due to combustion of the remaining organic
362 material in the bio-char. At higher temperature (900 °C), the total weight loss was 78.77 wt% in
363 RKO-char and 76.76 wt% in SKT-char, which correspond to about 7.72 wt% and 8.62 wt%
364 weight loss between 600 and 900 °C . This observation could be attributed to the decomposition
365 of inorganic materials in the biochar at higher temperature ([Azargohar et al., 2014](#)).

366 **4. Conclusion**

367 Pyrolysis of Bambara groundnut shell was carried out in a fixed bed reactor. This study evaluates
368 impact of temperature on the pyrolysis product distribution (bio-oil, bio-char and non-
369 condensable gas). It assesses the chemical and physicochemical properties of bio-oil,
370 characteristics of bio-char and composition of the non-condensable gas. The bio-oil collected
371 was a two-phase liquid, organic and aqueous phase. The organic phase from both shells have
372 high energy content (25-29 MJ/kg) and could be used directly as a fuel in boilers or a precursor

373 for quality biofuel production. The aqueous phase particularly from RKO was predominantly
374 made up of sugars and other value-added chemicals, which can be used as a raw material for
375 production of consumer products and fine chemicals. Bio-char was a porous material rich in
376 carbon, which may well be used as a solid fuel. The bio-char also consist of macronutrient and
377 may be applied as a source of nutrient for plant growth. Non-condensable gas consists of
378 methane, hydrogen, carbon monoxide and carbon dioxide which can be recycled to the reactor as
379 an energy supplement for the endothermic pyrolysis reaction or as a carrier gas. Using Bambara
380 shells as feedstock for bioenergy production will encourage more production of the groundnut,
381 which will bring about food security, particularly in challenging environments where major
382 crops are severely limited by adverse climatic conditions in addition to income generation.

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