

Effect of Bone during Fixed Bed Pyrolysis of Pistachio Nut Shell

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Abstract- Biomass will constitute a major part of the renewable energy matrix in the future. The large scale utilization of biomass, however, is constrained by its wide geophysical spread, low energy density and poor fuel quality. Pyrolysis-based bio-char and bio-oil production is a promising way to simultaneously achieve solid carbon sequestration and co-produced bio-oil with increased energy density and improved fuel quality. This paper provides new data on co-pyrolysis of 10wt% bone meal blended with pistachio nut shell and its effects on the yields of bio-char, bio-oil and non-condensable gases. In particular the bio-char was found to be suitable for soil amendment. A fixed bed pyrolysis reactor was used to investigate the effect of the addition of 10 wt% bone meal (BM) to pistachio nut shell (PS) to produced bio-chars and bio-oils up to 600°C. At 350°C the char yield was 53.3wt% for PSBM10 (sample containing 90wt% of PS and 10 wt% of BM) compared to only 30.9wt% for the PS alone. This was linked with the ability of the PSBM10 to retain condensable compounds at this temperature. The formation of condensable liquids from the PSBM10 reached 48 wt% at 550°C compared to only 20 wt% for the PS alone. The H/C atomic ratio for this PS bio-oil was 1.01 which increased to 1.11 for the PSBM10 bio-oil indicating an improvement in the bio-oil quality for the co-pyrolysis with bone, where the calorific value increased from 18.5 MJ/kg for the PS bio-oil to 19.9 for the PSBM10 bio-oil. The bio-char stability in terms of the ratio of volatile matter (VM) to that of fixed carbon (FC) content confirmed that at 300°C the PSBM10 char retained more condensable compounds with a VM/FC ratio of 1.60 compared to 1.10 for the PS char. At 400°C the VM/FC ratio decreased rapidly down to 0.15 for the PSBM10 compared with 0.25 for the PS alone reflecting the release of condensable liquids from the PSBM10. The PSBM10 bio-char at 550°C contained 0.45 wt% nitrogen compared with 0.18 wt% for the PS char which suggest increase in nitrogen availability in the char from co-pyrolysis with bone at this temperature. From E.A, SEM-EDS and XRD analysis, the reaction mechanisms between bone mater and PS involved dehydration and decarboxylation which is promoted by CaO

from the bone matter. Also, the inhibition of the depolymerization stage of pyrolysis of biomass by Ca²⁺ lead to high char yield at the expense of volatile release. These results indicate that a combination of bone and biomass could yield bio-chars suitable for soil amendment, and possibly carbon sequestration, while improving the production of bio-liquids for renewable energy.

Keywords- Bio-char, pistachio nut shell, bone meal, bio-oil, stability, carbon sequestration.

I. INTRODUCTION

Bio-char from biomass pyrolysis offers a geotechnical solution to the major global issues of climate change, soil degradation and food shortage [1]. Trapping CO₂ from the atmosphere into bio-char through pyrolysis and its application to soil can not only result in a safe carbon sequestration option but can also improve soil fertility and crop production [2]. The bio-oil co-generated during the process can further be used to substitute crude oil where bio-char production integrates carbon sequestration, soil fertility and bio-energy production. However, bio-char generation suffers draw back due to high production temperature typically above 500°C and low char yield that has hindered its application beyond solid fuels [2,3]. There are some evidence that co-pyrolysis with bone can offset some of these issues where the nutrients from the biomass minerals and nitrogen from the bone addition can be used as a soil amender along side with the bio-oil for energy generation [4-8]. Although bio-char and oil production from biomass alone has extensively been carried out, the role of bone in biomass pyrolysis to promote char yield and the assessment of the suitability of bio-char for carbon sequestration has received less attention [9-11]. This has been the focus of this study with respect to co-pyrolysis of bone with pistachio nut shell.

Pistachio nut shell (PS) has a high cellulose content of about 70 wt% and a resultant high weight loss during heating

of 75 to 80 wt%, which facilitates its use for the investigation on the effect of bone addition during biomass pyrolysis [12,13]. The world pistachio nut production was 0.21Mt in 1999, where Turkey alone produces between 0.03 to 0.09Mt of pistachio nut annually [14]. Apaydin-Varol *et al.*, studied slow pyrolysis of pistachio nut shell between 300°C and 700°C and observed a maximum liquid yield of 20.5% obtained between 500°C and 550°C, while a maximum char yield of 28% was obtained at 300°C [15]. Rapid and slow pyrolysis of pistachio nut shell was studied by Putun *et al.*, (2007), in a tubular reactor where a maximum bio-oil yield of 27.7% was obtained at 500°C and a bio-char yield of 29.5% was obtained at 300°C [12]. The use of bone meal (BM) as a fertilizer is well established due to its high N, P and Ca content where some of these elements are believed to exhibit catalytic effect during co-pyrolysis with biomass [16]. The alkali salts may favor dehydration, which leads to increased char formation at lower temperatures. This indicates that the bio-chars properties can be tailored based on the physio-chemical properties of the different feed stocks during co-pyrolysis and synergies during their conversion [17-21].

Tailored bio-char structures, such as terra-preta, is known for their fertility and long term carbon sequestration capability [22-25]. The replication of terra-preta bio-chars to amend highly weathered and infertile tropical soils have had variable results [25,26]. Although synergistic relationship has been suggested from the combination of bio-char and N-fertilizer, the co-pyrolysis of bone and biomass is still not well understood [27-26]. It is therefore a need to further understand the co-pyrolysis system to optimize the bio-char nitrogen content for plant availability and at the same time retain carbon for storage. Application of char with high volatile matter of 23%w/w at 10-20% w/w to tropical soil supplemented with N₂ fertilizer was found to decline the NH₄-N content of the soil, while that with low volatile matter of 6.3% at the same rate shows positive effect [1]. The negative effect was attributed to the stimulation of microbial growth and immobilization of plants available nitrogen by phenolic and other compounds contained in the high volatile char. A laboratory produced bio-char from pine and Douglas Fir was observed to have a negative effect on plant growth upon application whereas the same bio-char produced from wildfires promoted plant growth [29]. This effect was attributed to the fact that low temperature charring methods adopted in the laboratory may be responsible for the accumulation of toxic compounds in the char due to retaining volatile matter. Bone addition may prevent this while adding additional nutrient to the char. Hence, there is a need to develop a more stable carbonized bio-char with low volatile matter that still has high nutritional content [25,30]. Accordingly, this study focuses on co-pyrolysis of bone meal and pistachio nut shell at low temperature to produce char with increased nutrient availability suitable for soil amendment while retaining high percentage of carbon for sequestration and produce bio-oil of high quality.

II. EXPERIMENTAL

Pistachio nut shells from Turkey and cattle bone waste from local source in Nottingham, U.K were procured. The bone waste was disinfected using a virkon disinfectant. The biomass was dried in a Gallenkamp oven operated at 105°C until constant weight was achieved. A Retsch SM 2000/750UPM cutting mill was used to crush the biomass and the bone material. A sieve stack mounted on an Inclyno sieve shaker model 2 by Capco Test Equipment Ltd. Fractionation was used to obtain a uniform particle size fraction between 0.85mm -1mm according to the ASTM E828 method of determination of particle size distribution. The sample without bone added was called PS while the one with 10% bone added was referred to as PSBM10. Thermal analysis was performed on the raw samples and the bio-char produced from the prototype reactor using a TGA HRG C5300 mega series fitted with a Carlomega 5300 auto sampler. Elemental analysis was performed using a Thermo Flash EA 1112 series fitted with a MAS 200R auto sampler controlled with Eager 300 software according to the following standard test methods for Carbon and hydrogen (ASTM E 777), nitrogen (ASTM E 778) and sulfur (ASTM E775). The gross calorific value (GCV) of the samples was determined using the Dulong's formula [31]. The chemical analyses of the samples were carried out according to standard test methods (ASTM D1103-80 and ASTM D1104-56). The standard test methods adopted for proximate analysis included moisture content determination (ASTM E871) ash (ASTM D1102), volatile matter (ASTM E 872), and ash elemental analysis (ASTMD3682, ASTM D2795, ASTM D4278, AOAC 14.7). The Brunker 8D advanced X-ray powder diffraction was used to record the X-ray diffraction pattern of the ash from PS and BM using Cu K α radiation of wavelength at 0.154. The weight of products from the reactor were expressed in weight % while the elemental components of the char and oil were expressed on a dry and ash-free basis (daf), and the average yields from three experimental runs were presented within an acceptable error level. A fixed bed reactor was used during the pyrolysis experiments. The reactor consisted of a 45.0 cm stainless tube with an internal diameter of 10.1 cm inserted into a horizontal clamp type Elite furnace. A known weight of biomass with particle size in the range of 0.85mm-1mm was placed into a stainless steel boat and inserted into the middle of the reactor. Nitrogen was used as sweep gas at a flow rate of 60ml/min. The system was degassed at room temperature for five minutes prior to pyrolysis. The furnace was then heated at 47°C/min to reach the desired temperature between 150°C-600°C and maintained at that temperature for 1hr. This was to simulate a conventional way of bio-char production. The condensable volatiles were collected in a train of two tar trap bottles of 250 mL and 100 mL and their weight measured. The liquid was removed physically using a pipette. The uncondensed gases were released to a vent. The amount of uncondensed gas was measured by difference. After the experiment the furnace was cooled to room temperature under constant nitrogen sweep. The boat containing the char was removed and its weight was obtained and the char was collected for analysis. The actual

%wt of bio-char obtained was calculated according to Equation 1 while the calculated wt% was obtained according to equation 2.

$$MC_{PSBM10 \text{ actual}} = (M_{PSBM10} / M_{Biomass}) * 100 \quad (1)$$

$$MC_{PSBM10 \text{ calculated}} = 0.9 \times MC_{PS} + 0.1 \times MC_{BM} \quad (2)$$

Where;

$M_{Biomass}$ = Weight of biomass before pyrolysis.

M_{PSBM10} = Weight of solid remaining after pyrolysis.

MC_{PS} = Weight of char remaining from PS (wt %).

MC_{BM} = Weight of char remaining from BM (wt %).

$MC_{PSBM10 \text{ actual}}$ = Weight of char (solid) remaining from PSBM10 (wt %).

$MC_{PSBM10 \text{ calculated}}$ = Weight of char calculated from PSBM10 (wt %).

$PSBM10_{\text{adjusted}}$ = Weight of char remaining from PSBM10 less the contribution from BM (wt %).

III. RESULTS AND DISCUSSION

A. Analysis of biomass and bone

The proximate and elemental analysis of the pistachio nut shell (PS) and bone meal (BM) are listed in Table 1 and compared with similar results from literature. The ash content of the PS and BM was 1.2wt% and 62.9wt%, and their moisture contents were 5.3wt%, and 2.2wt%, respectively. This indicates that when added to the bio-mass the bone meal can add a significant amount of minerals to the resulting char. The volatile matter for the PS and BM was 75.6wt% and 31.9wt%, respectively, suggesting that both samples will contribute to the makeup of the bio-oil generated. This was further supported by the calorific values of 16 MJ/kg for PS and 12 MJ/kg for the BM, suggesting that the non-ash part of the BM can significantly contribute to the bio-oil. However, the BM had a fixed carbon content of only 3.0% compared to 18.0wt% for PS indicating that the carbon in the resulting char from co-pyrolysis will mainly come from the biomass. For both samples, the sulphur content was below 0.1wt% indicating that the resulting bio- chars and oils will be virtually sulphur free. However, the nitrogen content of the BM was 4.2wt% and significantly higher than that of the PS of 0.1wt%. These results are similar to what was reported by authors [12, 32]. This suggests that co-pyrolysis with BM can add nitrogen contents to the PS bio-chars and make them more suitable as a soil amender [3]. Elemental analysis of the ash produced at 600°C from pistachio (PS) and bone matter (BM) are presented in Table 1. The major elements in the ash from both pistachio and bone matter were calcium (Ca), and phosphorous (P). The ash from the BM had higher Ca and P contents of 19wt% and 9wt% respectively, while for the PS ash, the Ca, and P contents were only 0.4wt%, and 0.2wt% respectively. These results suggest that addition of BM to PS

will make Calcium highly available, which may exhibit catalytic effect during biomass pyrolysis and CaO that may interact with PS to promote dehydration and decarboxylation of PS to increase char formation at the expense of bio-oil and gas formation. Additionally, the less abundant elements, such as K, Mg and Na, from bone matter could improve the beneficial effect of bone addition on the char produced for soil amendment purposes.

TABLE I. PROXIMATE AND ULTIMATE ANALYSIS OF PISTACHIO NUT SHELL (PS) AND BONE MATTER (BM).

Properties ^a	Pistachio shell (PS)	Bone matter (BM)
Moisture	5.3	2.2
Volatiles	75.6	31.9
Fixed carbon	18.0	3.0
Nitrogen	0.1	4.2
Carbon	45.5	22.0
Hydrogen ^b	5.4	3.5
Oxygen ^b	42.5	4.2
Sulphur ^a	<0.1	<0.1
GCV (MJ/kg) ^a	17.0	33
H/C atomic ratio	1.42	1.91
O/C atomic ratio	0.70	0.14
Ash Elements		
Ca	0.4	18.6
P	0.2	8.7
O	0.5	30.2
Na	<0.1	0.4
C	0.1	4.4
Mg	<0.1	0.2
K	<0.1	0.2
S	0	0
Cl	<0.1	0.1
Al	<0.1	0.1
Si	<0.1	<0.1
Fe	<0.1	<0.1
Total ash elements	1.2	62.9

a. as determined, b. excluding the amount from ash and moisture

In addition, Figure 1 shows that the XRD diffratograms of ash from PS and BM confirmed the presence of CaCO₃ and Ca(PO₃)₂ from the PS ash and CaCO₃, Ca(PO₃)₂ and Ca₅(PO₄)OH from the BM ash. The high peak observed for Ca₅(PO₄)₃OH from BM is an indication of a good phosphate source for soil amendment, and a good source of Ca⁺ to promote char formation. Other crystalline phases were present but in minute quantity. The presence of these mineral in the ash of the study biomass signifies their suitability for soil improvement.

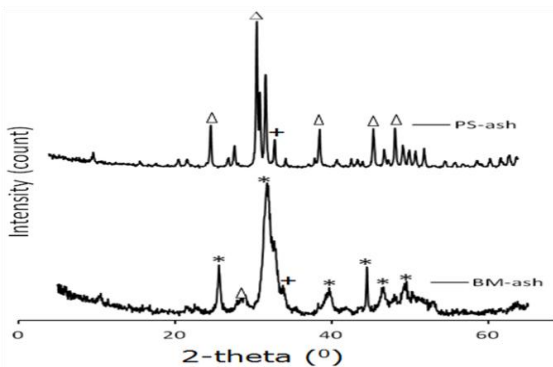


Figure 1. XRD patterns of ash from PS and PSBM10

Compounds identified; Δ = CaCO_3 ; += $\text{Ca}(\text{PO}_3)_2$ and *= $\text{Ca}_5(\text{PO}_4)_3\text{OH}$.

Figure 2 shows the XRD traces of the samples of PS, BM and PSBM10. It showed that the samples exhibit similar pattern of diffraction. Numerous and sharp peaks identified were quantified and presented in Table 2. The % peak area of compounds identified from the XRD traces of PS, BM and PSBM10 in Figure 2 are presented in Table 2. It can be observed from the Table that at $2\theta = 47^\circ$, the % peak area of the $\text{Ca}_5(\text{PO}_4)_3\text{OH}$ increase with BM addition similar to that of the $\text{C}_2(\text{PO}_3)_2$ at $2\theta = 14^\circ$ which was as expected since high percentage of these compound are contained in BM. However, the high peak of this mineral in PS was not expected and this could be error from the machine or the handling processes. The peak representing CaCO_3 which was identified at $2\theta = 32^\circ$ also increased with BM addition. These support the observation which was linked to the increased interaction of CaO and CO_2 during solid-vapour interactions with the formation of CaCO_3 . At $2\theta = 26^\circ$, it can be observed that the peak representing $\text{C}_2\text{CaO}_4\text{H}_2\text{O}$ decrease when BM was added to PS. The decrease in the % peak area of the amorphous carbon base structure at $2\theta = 22$ of the char formed can be said to be a transformation from amorphous to graphite like structure [33].

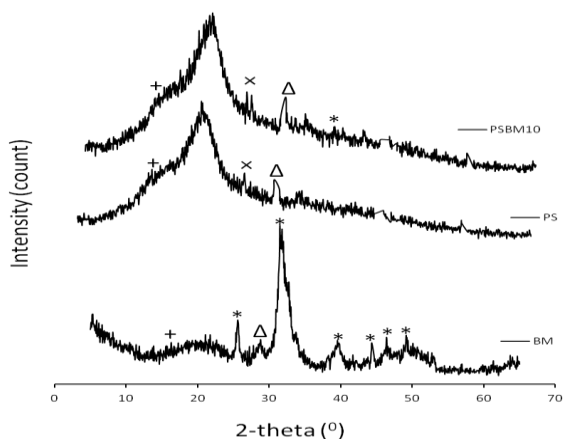


Figure 2. XRD patterns of sample of biomass from PS and PSBM10

Compounds identified; Δ = CaCO_3 ; += $\text{Ca}(\text{PO}_3)_2$ *= $\text{Ca}_5(\text{PO}_4)_3\text{OH}$ and x= $\text{C}_2\text{CaO}_4\text{H}_2\text{O}$.

TABLE II. PERCENTAGE PEAK AREA OF COMPOUNDS IDENTIFIED FROM THE XRD TRACES OF CHAR PRODUCED AT 300°C FROM PS AND PSBM10.

2θ ($^\circ$)	Compounds	PS	PSBM10
14	$\text{C}_2(\text{PO}_3)_2$	19.2	21.0
22	\wedge	32.2	20.7
26	$\text{C}_2\text{CaO}_4\text{H}_2\text{O}$	18.5	18.0
32	CaCO_3	12.0	18.1
47	$\text{Ca}_5(\text{PO}_4)_3\text{OH}$	8.1	11.2

\wedge , amorphous carbon base structure; 2θ ($^\circ$) = peak angle.

B. Bio-char generation

Figure 3 compares the weight of solid remaining from the fixed bed reactor from 150°C to 600°C for the bone matter (BM) on its own, the pistachio nut shell (PS) on its own and the co-pyrolysis of pistachio nut shell mixed with 10 wt% bone meal (PSBM10 actual and calculated). The weight loss of the PS on its own started rapidly after 200°C and slowed down after 400°C . The weight remaining at 600°C was 19wt% and 66wt% for PS and BM respectively, which was very similar to the 19 wt% (sum of fixed carbon and ash) for PS from proximate analysis in Table 1. The BM on its own started its main weight loss after 250°C that slowed down after 500°C with a weight remaining of 66 wt% at 600°C which again was similar to the sum of the ash and fixed carbon from proximate analysis in Table 1. Figure 3 also shows the weight loss for the co-pyrolysis of PS with 10 wt% BM (PSBM10 actual). The initial weight loss started after 200°C similar to that of PS on its own. However, there was a significant increase in the char yield for the PSBM10 in the temperature range 200°C to 400°C when compare with the PS on its own. At 350°C , the char formed was 53.3wt% for PSBM10 (actual) compared to only 30.9wt% for the PS. After 400°C the char formed for the PSBM10 (actual) stabilized at 23 wt% again similar to what to expect from proximate analysis. Figure 3 also shows the calculated char yield from PSBM10 (PSBM calculated), which is the calculated sum of the char remaining from the 10wt% of bone and 90wt% of PS in PSBM10. This was compared with the solid char remaining from PS only and PSBM (actual) at all the temperatures and it was discovered that the char yield was higher than that obtained from PS only and lower than that from PSBM10 actual). This indicates that there is significant interaction between the biomass and the bone during the co-pyrolysis. This might be due to the high mineral content of the bone as shown in Table 1, mainly carbonates of Ca, Na, and K, which can promote char formation [34,35]. Also, the increase in char formation occurs at the same time as the bone experience weight loss and there might be secondary reactions between the bone volatiles and the biomass that promotes char formation as shown in Figure 5.

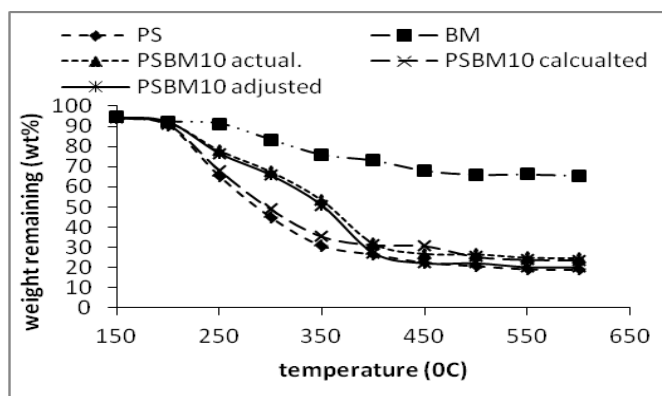


Figure 3. Comparison of remaining weight from BM, PS and PSBM10 (actual, calculated and adjusted) during fixed bed pyrolysis

Figure 4 shows the difference in char yield between the calculated and actual PSBM10 derived from the weights obtained in Figure 3. A synergetic effect was observed at 200°C increasing to a 19 wt% difference at 300 and 350°C. This difference disappear for the PSBM10 sample heated to 400°C and any difference thereafter was related to increased ash from the bone meal addition. The increase in char formation during this temperature range might be due to dehydration favored by the presence of CaO from the BM which further increases the char yield at low temperature [16], where dehydration might prevent volatiles from being released at lower temperatures due to densification of the biomass. At higher temperatures these condensed species are then released which may be responsible for the negative difference observed at 450°C. This should markedly change the composition of liquids released at higher temperatures for the PSBM10 co-pyrolysed sample.

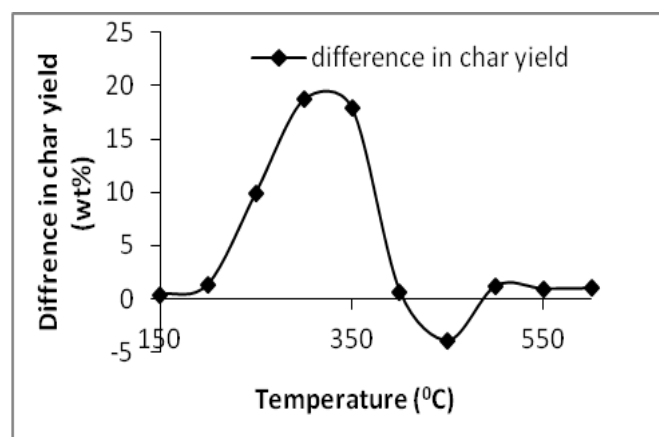


Figure 4. Difference in char yield between the actual and calculated char yield from PSBM10.

C. Bio-oil generation and characterization

Figure 5 compares the condensable liquid yield from PSBM10 with that of PS only when heated at 47°C/min to reach the desired temperature between 150°C-600°C. For the

PS only, the condensable liquids start coming off at 300°C with a yield of about 14 wt%. This yield increased to about 19 wt% for the sample heated to 550°C, showing that PS only has a limited potential to produced bio-oil [12]. The condensable liquid yield for the co-pyrolysis of PS with 10 wt% BM (PSBM10) showed a very different behavior compared to PS only. Firstly, the onset of condensable liquids was delayed from 300°C for PS to 350°C for the PSBM10, indicating that the changes in char yield observed in Figures 3 and 4 at this temperature might be related with the change in the volatilization profile. The formation of condensable liquids increased with temperature up to 550°C reaching 48 wt% at this holding temperature. For the sample heated directly to 600°C the liquid yield decreased significantly, indicating gasification reactions taking place at this temperature. The calculated oil yield was less than the actual oil recovered, but higher than that from PS only at all the temperatures which indicate a significant interaction between BM and the PS in promoting oil formation. The results indicate that co-pyrolysis of BM with PS has a significant capacity to increased the bio-oil yield by altering the release pattern on the volatile compounds.

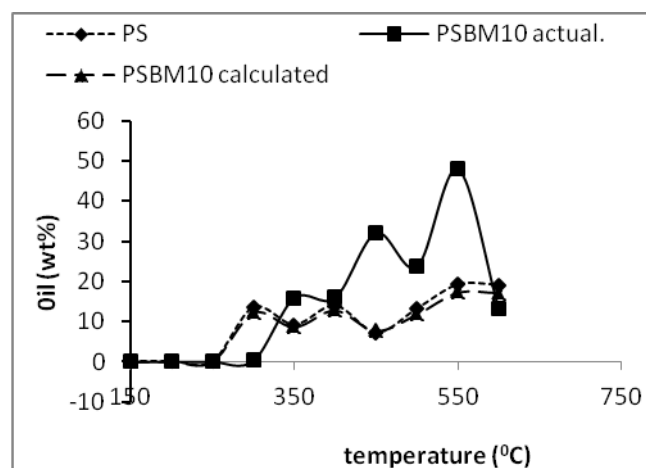


Figure 5. Comparison of the condensable liquid yield obtained from PS only and PSBM (actual and calculated).

Figure 6 compares the chromatographs of the oil produced from PS and PSBM at 550°C and heating rate of 47°C/min. More than 300 compounds were detected where the 30 most abundant were identified and quantified in Table 3. The chemical compounds identified from the bio-oils were classified into 6 groups namely: (1) Aliphatic compounds with oxygen-containing functional groups, (2) Aliphatic compounds with Nitrogen-containing functional groups, (3) Aromatic compounds with oxygen-containing functional groups and (4) Aromatic compounds with nitrogen-containing functional groups, as presented in Table 4. Table 4 shows that the most abundant chemical components of the bio-oil samples are aromatic compounds with oxygen-containing functional groups, mostly phenols and its derivatives. These were 71.1% for the PS and 74.9% for the PSBM oil. Increased

amount of phenol, 2, 6-dimethoxy was observed for the PSBM10 oil samples which were linked to the inhibition of decomposition of methoxy groups in the sample by Ca ions and increased dehydration and demethoxylation by the presence of Na ions from the bone. The next abundant group of chemical compounds in the bio-oil was aliphatic compounds with oxygen containing functional groups. They constitute about 24.1% of the PS and 20.3% of the PSBM oil. Aliphatic compounds with Nitrogen-containing functional groups were between 3-4% and this could render the application of the oil as fuel difficult [36]. The variation seen in these functional groups across the two bio-oil sample could be attributed to high ash content BM added to the PS as shown in Table 1. The higher the ash content of the biomass the more it lower the presence of the aromatic compounds containing oxygen in the resulting oil [37, 38]. Comparison between the oil from PS samples and the samples amended with bone shows that addition of bone to pistachio nut shell increase the aromatic hydrocarbon content of the resulting oil from PSBM10 by 5%, while at the same time decreasing the aromatic compounds with nitrogen containing functional group by 8%. This reduction may be due to inhibition in the decomposition of glucose units from the cellulose content of the original biomass [39] by the Ca from the bone. In a similar way, the aliphatic compounds with oxygen containing functional groups were decreased by 16% while the aliphatic compounds with nitrogen-containing functional groups were increased by 6%. This signified that bone can be used to improve the fuel quality of oil obtained from biomass through pyrolysis. This result suggested that it is possible to increase the yield of desirable chemical compounds of pyrolysis oil by amending the biomass with bone for fuel and pharmaceutical use.

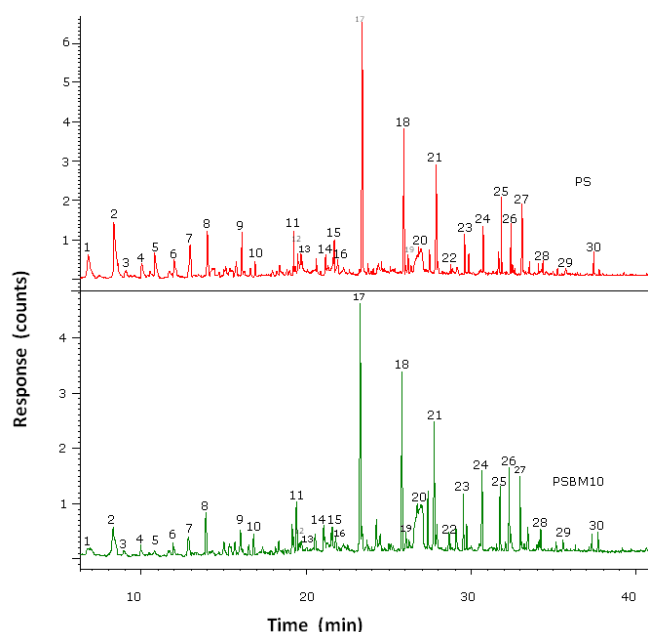


Figure 6. GC-MS analysis of bio-oil produced from PS and PSBM.

TABLE III. TENTATIVE COMPOUNDS IDENTIFIED FROM OIL PRODUCED FROM THE BIOMASS.

Retention time (min)	Name of compounds identified	Class	Formula	%area PS	%area PSBM10
6.8	Acetone	1	C ₃ H ₆ O	4.3	3.0
8.3	3-Furaldehyde	1	C ₅ H ₄ O ₂	9.4	7.6
9.0	1,1-Dimethyl propyl methyl ether	1	C ₆ H ₁₀ O	1.1	0.9
10.0	1H-Imidazole4,5-dihydro-2-methyl-	4	C ₄ H ₈ N ₂	2.0	1.6
10.8	1,2-Cyclopent-anedione	1	C ₅ H ₆ O ₂	2.0	1.7
12.0	2-furancarbox- aldehyde,5-methyl	3	C ₆ H ₆ O ₂	3.8	2.7
12.9	Oxazolindine,2,2-diethyl-3-methyl	2	C ₈ H ₁₇ NO	3.7	3.9
14.0	2-Cyclopentene-1-one,2-hydroxy-3-methyl	1	C ₆ H ₈ O ₂	0.1	0.4
16.1	Phenol,2- ethoxy	3	C ₇ H ₈ O ₂	3.2	2.0
16.9	2-cyclopentaone, 3-methyl	1	C ₇ H ₁₀ O ₂	1.0	1.7
19.2	Phenol,2-methoxy-4-methyl	3	C ₈ H ₁₀ O ₂	2.3	1.4
19.5	1,2-benzene diol	3	C ₆ H ₆ O ₂	0.9	3.2
19.7	2-furancarbox- aldehyde	3	C ₆ H ₆ O ₃	0.8	0.6
21.2	1,2,Benzodiol, 3- methoxy	3	C ₇ H ₈ O ₂	1.1	1.4
21.7	Phenol,4-ethyl-2-methoxy-	3	C ₉ H ₁₂ O ₂	1.2	1.4
21.9	2methoxy-4vinylphenol	3	C ₉ H ₁₀ O ₂	1.4	1.1
23.4	Phenol, 2, 6 dimethoxy	3	C ₈ H ₁₀ O ₃	13.6	16.2
25.9	1,2,4-Trimethoxy benzene	3	C ₉ H ₁₂ O ₃	7.2	11.2
26.2	Phenol,2-methoxy -4-(1-propenyl)-	3	C ₁₀ H ₁₂ O ₂	6.9	0.9
27.0	1,6-Anhydro-beta-D- glucopyronose	1	C ₆ H ₁₀ O ₅	1.3	3.9
27.9	Ethanone,1-(2,6-dihydroxy-4-methoxyphenyl)	3	C ₉ H ₁₀ O ₄	5.8	7.8
28.9	Ethanone,1-(3,4-dimethoxyphenyl)	3	C ₁₀ H ₁₂ O ₃	5.2	1.4
29.6	Phenol,2 6-dimethoxy-4-(2-propenyl)-	3	C ₁₁ H ₁₄ O ₃	1.8	3.2
30.7	Benzaldehyde,4-hydroxy-3,5-dimethoxy	3	C ₉ H ₁₀ O ₄	2.8	4.8
31.8	Phenol,2 6, methyl -4-(2propenyl)	3	C ₁₁ H ₁₄ O ₃	3.7	3.8
32.4	Ethanone,1-(4-hydroxy-3-5 dimethoxyphenyl)	3	C ₁₀ H ₁₂ O ₄	2.7	4.7
33.1	1-Butanone, 1-(2,4,6-trihydroxyl-3-methylphenyl)	3	C ₁₁ H ₁₄ O ₄	3.5	4.1
34.3	4-Phenyl propiophenone	3	C ₁₅ H ₁₄ O	0.7	1.1
35.7	1,7,7-Trimethyl bicyclo(2,2,1) heptan-2-one	1	C ₁₀ H ₁₆ O	4.9	1.1
37.4	3,5-Dimethoxy-4-hydroxy-cinnamaldehyde	3	C ₁₁ H ₁₂ O ₄	1.4	1.1

TABLE IV. CLASSIFICATION AND QUANTIFICATION OF CHEMICAL COMPOUNDS IDENTIFIED FROM DIFFERENT BIO-OIL.

Class	PS	PSBM10
1-Aliphatic compounds with oxygen-containing functional groups	24.1	20.3
2- Aliphatic compounds with Nitrogen-containing functional groups	3.7	3.9
3- Aromatic compounds with oxygen-containing functional groups	71.1	74.9
4-Aromatic compounds with nitrogen-containing functional groups	1.1	0.9

D. Gas generation and characterization

Figure 7 compares the non-condensable gas yield for the PS with that of the PSBM10 when heated at 47^oC/min to reach the desired temperature between 150^oC-600^oC. The PS only showed a rapid increase in the non-condensable gas yield from 34.4 wt% at 250^oC to a peak of 70 wt% at 450^oC. The yield of non-condensable gas product at virtually all temperatures from PSBM10 was suppressed compared with PS only. At 250^oC it was only 22 wt% peaking at 400^oC with only 51.9 wt% and decreasing towards 550^oC. However, for the sample heated straight to 600^oC the main product was non-condensable gases suggesting that the minerals from the BM, mainly calcium are promoting catalytic cracking of tars at this temperature. Calcium and magnesium minerals have been found to have catalytic effect on cracking tars and condensable volatiles into non-condensable gases at fixed bed and fluidized bed operating conditions, at 600-900 ^oC [40,41]. The low gas yield obtain below 600^oC from the co-pyrolysis of pistachio nut shell (PS) with 10wt% bone meal (BM) suggest a synergism between the bone matter and the pistachio nut shell, where the high nitrogen content of the BM might play a significant role. This is evident in the increased aliphatic compounds with nitrogen containing functional groups in Table 3 and a corresponding increase in nitrogen content of the char produced from PSBM10 in Figure 11.

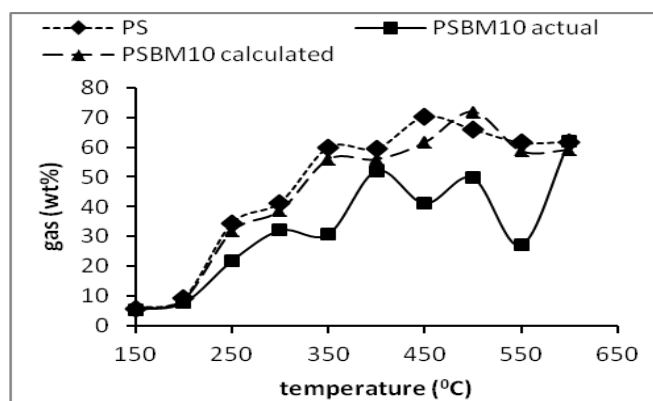


Figure 7. Comparison of non-condensable gas yield against temperature for PS and PSBM10.

Figure 8 compares light hydrocarbons from C₁ to C₄ for the gas from PS and PSBM10. Although several peaks can be observed from the GC traces of the samples, only those representing C₁ to C₄ hydrocarbons were identified and quantified. The C₂ to C₄ hydrocarbons increase with bone matter addition to PS. This was linked with a decreased in aliphatic hydrocarbons with oxygen containing functional groups as shown in Table 5. The enhanced release of H₂ and C₂ to C₄ hydrocarbons may be promoted by CaO from additions of bone matter to the pistachio which is in line with findings of Nicholas et al [42], who observed an increase in Hydrogen production when biomass was loaded with CaO at a ratio of Ca:C of 1 and 0.5. Hanaoka et al [43], also reported similar observation when Ca(OH)₂ was combined with biomass and CaO was used as bed material [44].

Table 5 shows the composition of hydrocarbons in terms of their integrated area distribution in the gas produced from pistachio nut shell and Pistachio shell mixed with bone matter. It shows a decrease in the concentration of methane and ethane from gas resulting from PSBM. The C₂-C₄ hydrocarbons shows high increase of more than 78% on the average, while the methane and ethane shows a decrease of almost 66% and 29%, respectively. This can be attributed to action of Ca⁺ in the bone matter added, which inhibit the cracking of the intermediate product. A similar observation was reported on the effect of potassium on the yield of CH₄ during pyrolysis of pine wood by Wang et al [45].

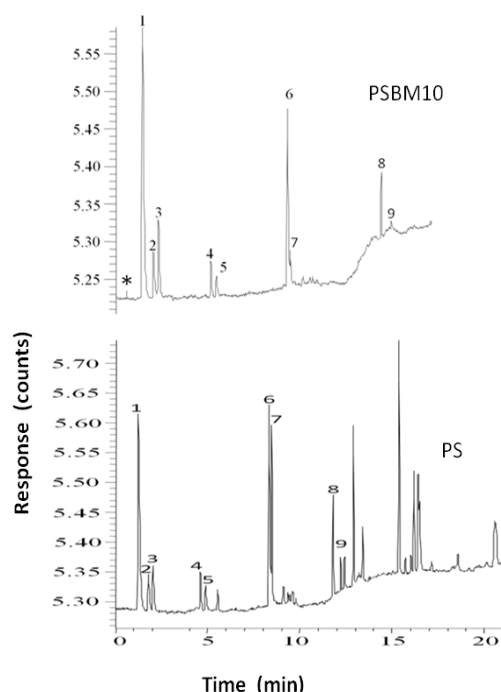


Figure 8. GC Analysis of gas from pistachio nut shell and pistachio nut shell mixed with 10wt% bone matter.

Peaks identified: (1) Methane, (2) Ethene, (3) Ethane, (4) Propene, (6) Propane, (7) Butene, and *: Hydrogen

TABLE V. COMPOSITION OF HYDROCARBON COMPOUNDS IN THE GAS FROM PISTACHIO SHELL.

	Compounds	% area (%)	
		PS	PSBM10
1	Methane	62.4	21.2
2	Ethene	8.8	6.2
3	Ethane	14.4	25.6
4	Propene	5.8	10.0
5	Propane	4.1	21.5
6	Butene	4.4	15.4
*	Hydrogen	-	<1

E. Characterization of bio-char

This section presents the result of the characterisation of biochar (actual solid remaining from PS and PSBM10).

Figure 9 compares the carbon content of the chars produced from PS with that of the PSBM10 and the yield varies with temperature. The carbon content for the PS chars increased slowly from 51 wt% at 150°C to 66 wt% at 350°C and then rapidly to 93.1wt% at 600°C which is similar to other studies [46-49]. The carbon content for the PSBM10 differed significantly. It increased rapidly from 47 wt% at 150°C to 86 wt% at 400°C. The lower value of 47wt% compared to 51wt% for the PS at this temperature was due to the addition of 10wt% BM which increased the mineral content. The rapid increase in the carbon content for the PSBM10 compared to PS is probably due to the retention of char at this temperature as shown Figure 3 and 4. Between 400°C and 600°C the carbon content slowly increases and stabilizes at 94 wt%. This could suggest stable char formation from PSBM10 at temperatures above 400°C.

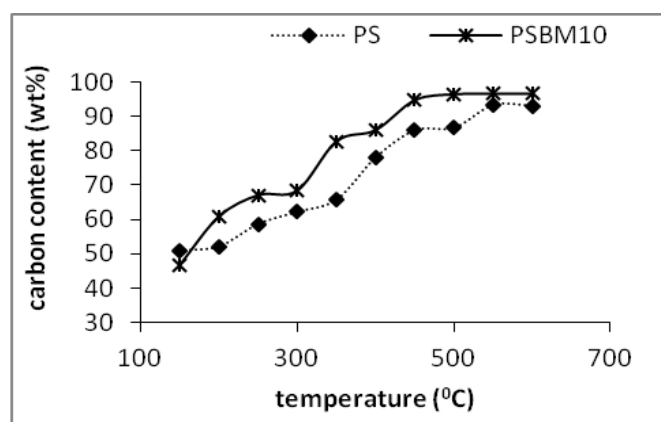


Figure 9. Comparison of carbon content against temperature for chars produced from PS and PSBM10.

Figure 10 compares the nitrogen content of the chars produced from PS with that of the PSBM10. The nitrogen

content for the chars from PS only slowly increased from 0.10 wt% at 250°C to 0.15 wt% at 600°C. This was expected since the nitrogen content of the raw PS was only 0.10 wt%. The addition of 10 wt% BM for the PSBM10 did not increase significantly the initial nitrogen content for the char at 250°C from the PSBM10. This was surprising since the overall theoretical (calculated) nitrogen content of the PSBM10 mixture should be 0.5 wt%, which may indicate that a significant proportion of the nitrogen from the BM is transferred into the gas phase at low temperatures below 300°C. However, Figure 10 shows that at 300°C the nitrogen content of the PSBM10 char was 0.22 wt% indicating that for the co-pyrolysis at 300°C the nitrogen is becoming more integrated into the char structure. As the co-pyrolysis temperature was raised the resultant chars increase rapidly in their nitrogen content reaching 0.45 wt% at 550°C. This indicates that at higher temperatures the nitrogen from the bone become fixated within the char structure. The result indicated that chars produced from co-pyrolysing biomass with bone, especially above 400°C, can trap a significant amount of the nitrogen originally contained in the feed and might be used for soil amendment purposes.

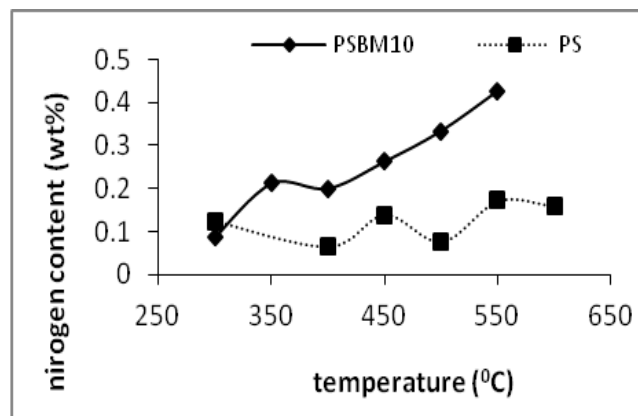


Figure 10. Comparison of nitrogen content against temperature for chars produced from PS and PSBM10.

Figure 11 compares the oxygen content of the chars produced from PSBM10 and PS. For the PS only the oxygen content decreases slowly from 43 wt% at 150°C to 29 wt% at 350°C after which there is a rapid decrease to 5.1wt% at 600°C. In contrast, the oxygen content for the chars produced from the PSBM10 decreases rapidly from 43.6 wt% at 150°C to 9 wt% at 400°C and oxygen appears to be virtually eliminated at 500°C. This supports the observation from Figure 9 where the PSBM10 chars above 400°C have the carbon content characteristics of very stable chars. Since bio-chars with high oxygen content are liable to degrade with time [3], the data suggests that char from PSBM10 can be suitable for carbon sequestration because of its low oxygen content.

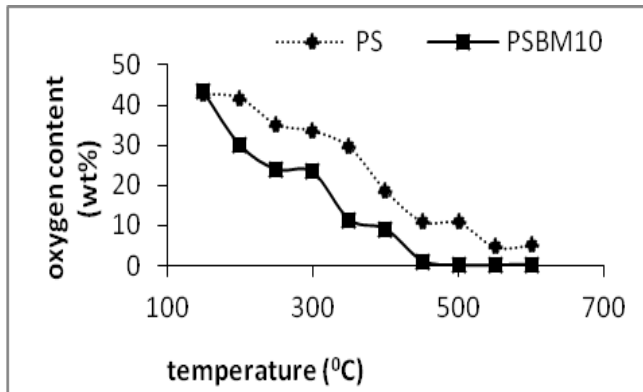


Figure 11. Comparison of oxygen content for chars produced from PS and PSBM10.

Figure 12 compares the gross calorific value (GCV) for the chars produced from PS and PSBM10 against temperature on a dry ash free basis. The calorific value for the chars from PS only increased slowly from 18 MJ/kg at 150°C to 23 MJ/kg at 350°C and then rapidly to 33.5 MJ/kg at 600°C. The PSBM10 chars behaved very different where a significant jump in the calorific value from 16 MJ/kg at 150°C to 34 MJ/kg at 400°C was observed and then stabilising at 34 MJ/kg up to 600°C. The rapid increase in calorific value for the PSBM10 compared with the PS only chars can be related to the rapid decrease in oxygen content (Figure 11) combined with the rapid increase in carbon content (Figure 9) for the PSBM10. Again the data indicate that the PSBM10 chars produced above 400°C are likely to be more stable compared with those from PS.

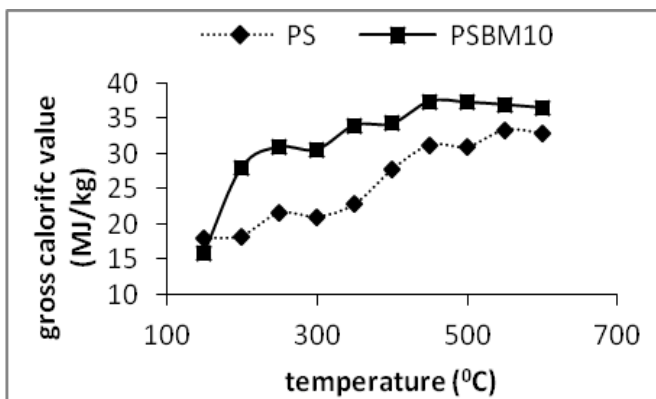


Figure 12. Comparison of gross calorific values (GCV) for the chars from PS and PSBM10 against temperature on a dry ash free basis.

F. Assessing stability by VM/FC ratio

Figure 13 compares the bio-char stability in terms of the ratio of volatile matter (VM) to that of fixed carbon (FC) content for the chars produced from PS and PSBM10 against temperature. The VM/FC ratio for the chars from PS only was about 3.50 at 200°C and decreased rapidly down to 0.30 at 350°C and decrease very slowly to 0.10 at 600°C. For the

PSBM10 chars the VM/FC ratio was about 3.20 at 200°C and started to decrease similar to the PS only chars. However, at 300°C the VM/FC ratio for the PSBM10 char was 1.60 compared to 1.10 for the PS only reflecting the retention of condensable compounds in the char at that temperature. After this, the VM/FC ratio decreased rapidly down to 0.15 at 400°C and decreased slowly after that to 0.02 at 600°C. The VM/FC ratio has been shown to correlate fairly well with the long term stability of biochar for soil amendment and carbon sequestration [50]. For a char to be stable, the VM/FC ratio must be less than one and as this ratio approaches zero the better the stability. This suggests that the chars produced from PS and PSBM10 between the temperature range of 350°C-600°C can be suitable for carbon sequestration. Above 400°C the chars from PSBM10 were likely to be more stable than that from the PS only.

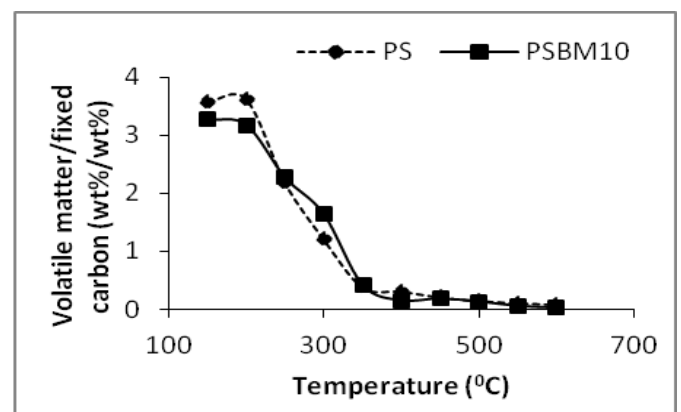


Figure 13. Comparison of the volatile matters to fixed carbon ratio against temperature for PS and PSBM10 chars.

G. Proximate and elemental analysis of bio-oil produced

Figure 13 compares the bio-char

Table 6 shows the proximate and ultimate analysis of the condensable liquids (bio-oil) obtained when heating the PS only, BM only and PSBM10 to 550°C at 47°C/min. It also compares the bio-oil yield with that from other studies. The oil yield of about 20wt% was obtained from pyrolysis of PS only in this study against 25wt% reported by Putun *et al.*, [12], which increased to 48.0wt% for PSBM10. The moisture content of the bio-oil from PS, BM and PSBM10 was 38.1wt%, 4.0wt% and 24.7 wt%, respectively, which correlates well with previous studies [16]. However, the bio-oil yield for the PS was only 20 wt% compared with 48 wt% for the PSBM10 indicating a very strong effect of the bone meal on the release of condensable organics from the pistachios. The H/C ratio for the PS bio-oil was 1.01 which increased to 1.11 for the PSBM10 bio-oil. The O/C ratio for the PS bio-oil was 0.53 which decreased to 0.50 for the PSBM10 bio-oil. The increase in the H/C and decrease in the O/C indicates an improvement in the bio-oil quality for the co-

pyrolysis with bone, where the calorific value increased from 18.5 MJ/kg for the PS bio-oil to 19.9 for the PSBM10 oil. One concern is the increase in the nitrogen content of the bio-oil to 1.2wt% for the PSBM10 bio-oil compared to only 0.2wt% for the PS.

TABLE VI. PROXIMATE AND ULTIMATE ANALYSIS OF CONDENSABLE LIQUIDS PRODUCED FROM PS, BM AND PSBM10 AT 550°C WITH A HEATING RATE OF 47°C/MIN

Properties	PS	BM	PSBM-10
Bio-oil (actual) ^a , wt%	20	13.2	48
Ash, wt%	<0.1	0.1	<0.1
Moisture, wt%	38.1	4.0	24.7
Volatile matter, wt%	48.8	90.3	52.9
Fixed carbon, wt%	13.1	5.6	22.4
N, wt% ^b	0.2	9.0	1.2
C, wt% ^b	55.6	68	56.4
H, wt% ^b	4.7	8.5	5.2
O, wt% ^b	39.6	14.4	37.3
S, wt% ^b	<0.1	<0.1	<0.1
GCV (MJ/kg) ^b	18.5	33	19.9
NCV (MJ/kg) ^b	17.5	30.5	18.8
H/C atomic ratio	1.01	1.5	1.1
O/C atomic ratio	0.53	0.16	0.50

a. as determined; b. dry and ash free

H. Proposed mechanism of interaction between PS and BM

Figure 14 shows the proposed reaction mechanisms for the interaction of bone matter with biomass during co-pyrolysis. It shows that when biomass undergoes pyrolysis it is first transform into reactive components as proposed by Broido-Shafizadeh [51] where the C-H bonds are broken with the formation of -COOH and OH groups which then combine to form H₂O and CO₂. The moisture content obtained in proximate analysis of the product (Tables 1 and 6) confirm the formation of this water since virgin biomass was dried before pyrolysis. Scanning electron microscopy combined with electron diffraction spectroscopy (SEM-EDS) analysis of the ash showed the presence of about 19 wt% of Calcium in the BM ash and only 0.4 wt% in the Pistachio shell ash. The CaO from the bone matter probably reacted with the water formed, due to high affinity of water to form Ca(OH)₂, which again react with the CO₂ formed to form CaCO₃. X-ray diffraction (XRD) analysis confirms the formation of CaCO₃ by detecting the presence of about 18 % in peak area of CaCO₃ in the PSBM10 (Figure 2 and Table 2). With the confirmation from SEM-EDS and XRD, it is highly probably that dehydration and decarboxylation is promoted by CaO from the bone matter which leads to high char yield observed in Figures 3 and 4. The consumption of water formed by CaO during the formation of Ca(OH)₂ correlate with the reduction in water content of the oil produced from PSBM10 as shown in Table

6. The increase in char yield at the expense of volatile released as shown in Figures 3, 5 and 7 could be attributed to the inhibition of the depolymerisation stage of pyrolysis by Ca⁺ from bone matter. GC-MS results from Table 4 shows reduction in aliphatic and aromatic compounds with oxygen containing functional groups. The scheme also proposes the formation of condensed char which trap nitrogen and CaCO₃. The evidence for this is shown in Figure 10 where the nitrogen content of the char formed from PSBM10 is seen to be increasing with increasing temperature of pyrolysis and in Figure 2 where the CaCO₃ content of PSBM10 is seen to be higher than that from PS alone. The high nitrogen content observed from Figure 10 and low volatile matters from Figure 13 is an indication that the char can be suitable for soil amendment while the retained carbon in the char can be suitable for carbon sequestration.

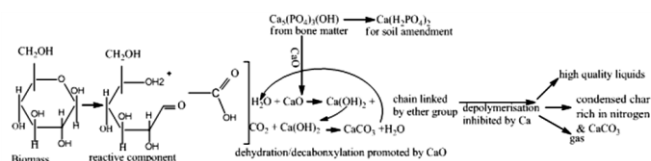


Figure 14. Proposed mechanism for the interaction of minerals from bone matter with biomass during pyrolysis.

IV. CONCLUSIONS

The addition of 10 wt% bone meal (BM) to pistachio nut shell (PS) to produced bio-chars and bio-oils up to 600°C in a fixed bed pyrolysis reactor showed that at 350°C, the char yield was 53.3wt% for the pistachio nut shell with 10 wt% bone meal (PSBM10) compared to only 30.9 wt% for the PS alone. This indicated that the PSBM10 retained condensable compounds which were released at a later temperature, where at 550°C the PSBM10 (actual) yielded 48 wt% of oil compared to only 20 wt% for the PS alone. The calorific value of the bio-oils increased from 18.5 MJ/kg for the PS bio-oil to 19.9 for the PSBM10 bio-oil which was also reflected in the increase in the H/C ratio from 1.01 for the PS bio-oil to 1.11 for the PSBM10 bio-oil indicating an improvement in the bio-oil quality for the co-pyrolysis with bone. The consumption of water formed by CaO (from bone matter) during the formation of Ca(OH)₂ suggest that bone matter addition reduces the water content of the oil produced from PSBM10. The volatile matter to fixed carbon VM/FC ratio at 300°C for the PSBM10 char was 1.60 compared to 1.10 for the PS char confirming that the bone matter addition retained more condensable compounds within the chars below 400°C. At 400°C the VM/FC ratio decreased rapidly down to 0.15 for the PSBM10 compared with 0.25 for the PS alone reflecting the release of condensable liquids from the PSBM10. The PSBM10 bio-char at 550°C contained 0.45 wt% nitrogen compared with 0.18 wt% for the PS char which suggest increased nitrogen availability in the char from co-pyrolysis with bone at this temperature. With confirmation from EA,

SEM-EDS and XRD on the reaction mechanisms between bone mater and PS, it is highly probably that dehydration and decarboxylation is promoted by CaO (from bone) which lead to high char yield. Also, increased char yield at the expense of volatile released could be attributed to the inhibition of depolymerisation stage of pyrolysis of biomass by Ca²⁺. These results indicate that a combination of bone and biomass could yield bio-chars suitable for soil amendment and possibly carbon sequestration while improve the production of bio-liquids for renewable energy.

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