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PILOT SCALE BIOCHAR PRODUCTION FROM PALM KERNEL SHELL (PKS) IN A FIXED BED ALLOTHERMAL REACTOR

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ABSTRACT

Oil palm biomass wastes such as oil palm fronds (OPF), empty fruit bunches (EFB) and palm kernel shells (PKS) are amongst the most abundantly available agricultural residues in Malaysia. Of these, an average 0.16 t PKS per tonne crude palm oil (CPO) is commonly used in palm oil mills as boiler fuel to generate steam and electricity, while the remaining unused 0.20 t PKS per tonne CPO are often sold as fuel. In order to diversify and add value to the remaining PKS, it is proposed to convert it into biochar to sequester CO_2 and improve the productivity of low-fertility soil. In this study, PKS was carbonised under allothermal conditions at various temperatures (400°C to 600°C) and residence times (30 and 60 min) using the biochar experimenters kit (BEK). Biochar yield decreased from 52.1 ± 15.5 wt% at 400°C (30 min) to 33.4 ± 1.4 wt% at 600°C (60 min), while pH, elemental and fixed carbon content increased with temperature and residence time. The VM/FC (0.25 to 0.60) and O/C (0.12 – 0.23) ratios suggest that PKS biochar is an effective carbon sink with a half-life in soil > 100 years.

Keywords: oil palm biomass, pyrolysis, fuel properties, soil application.

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INTRODUCTION

Biomass is organic matter derived from living organisms with a renewed availability including agricultural wastes, wood / forestry residues, animal manure and municipal waste. In Malaysia, oil palm biomass is one of the most abundant agricultural wastes generated (Mekhilef *et al*., 2011). The oil palm biomass is generally harnessed from: (1) upstream plantation (trunk and fronds) and (2) midstream palm oil milling (empty fruit bunches produced after fresh fruit bunches stripping, mesocarp fibre after oil screw processing and palm kernel shells - PKS - after nut cracking process) (Kong *et al*., 2014). In 2014, about 4.46 million tonnes of PKS residues were produced which increased to 4.56 million tonnes (Wafti *et al*., 2017) in 2015 and 4.72 million tonnes in 2016 (Loh, 2017). PKS has been used as a source of energy for combined heat and power generation in palm oil mills (Vijaya *et al*., 2008). However, based on a life cycle study of 12 mills by Vijaya *et al*. (2008), only approximately 45% of PKS is utilised with the remainder sold as fuel to external parties. Owing to the high lignin and fixed carbon content of original PKS (Abnisa *et al*., 2011; Choi *et al*., 2015) conversion of PKS to carbon-negative biochar appears to be a promising alternative. Many studies have found that biochar can mitigate global warming (Shepherd *et al*., 2009; Woolf *et al*., 2010), help plants to access more nutrients through physico-chemical processes that allow for the better utilisation of 'soil inherited'

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or 'fertiliser-derived' nutrients (Sohi *et al*., 2009), improve soil pH and permeability of loamy soils (Martinsen *et al*., 2014).

Over many centuries, charcoal has been made using various forms of earth kilns for metallurgical, cooking, heating and medical applications (Kortzfleisch, 2009). However, the traditional charcoal production technology releases condensable and non-condensable gases into the environment causing health concern. Modern biochar production technology must meet stringent emission criteria while producing high-quality, stable biochar at an affordable price. Several technologies have been proposed over the past decade such as top-lit updraft gasifiers (Nsamba *et al*., 2015), Kon-Tiki earth kiln (Cornelissen *et al*., 2016), improved retort kiln (Adam, 2009) and the biochar experimenter kit (BEK) (Boateng and Mullen, 2013). The BEK is a unit that can be operated in various modes enabling researchers and practitioners to produce and characterise biochar under allothermal, autothermal, batch and continuous operation conditions. Autothermal may be defined as a process in which heat is generated from reactions within the reactor to support endothermic pyrolytic processes while allothermal refers to heat that is produced outside the reactor and transferred through a wall into the interior of the reactor to drive endothermic reactions (Karellas, 2015; Nsamba, *et al*., 2015; Rauch, *et al*., 2014; Stiller and Hochrinner, 2016). The flexible platform of the BEK enables researchers to report comparable yields in contrast to highly customised reactor types currently used (*Table 1*). Apart from that, the BEK is relatively easy to operate as it can feed the original form of granular biomass such as PKS and therefore potentially save time, energy and cost. The quantity produced is also sufficient to conduct nursery and field trials compared to laboratory-scale pyrolysis reactor (*Table 1*).

Table 2 summarises the various process conditions used for the production of biochar. Generally, the generation of solid, liquid and gaseous products from biomass pyrolysis primarily depends on the feedstock used as well as operating conditions such as temperature, heating rate, residence time and oxidising agent (Shafizadeh, 1982). The biochar yield under a slow pyrolysis condition is higher than in fast pyrolysis which produces mainly bio-oil. Most studies used laboratory-scale fixed bed reactors at temperatures ranging from 400°C to 800°C with a PKS biochar yield of 23 to 39 wt%. Only one study is available in which PKS biochar was produced at pilot-scale conducted at one temperature and holding time (Kong *et al*., 2013).

This study therefore aims to investigate the effect of pyrolysis temperature and residence time on biochar and bio-oil yields at pilot-scale under fixed-bed allothermal conditions using the BEK and as-received PKS. In addition, the physico-chemical properties of biochar were determine and the potential for soil application discussed.

TABLE 1. REACTOR TYPE AND PROCESS CONDITIONS USED FOR CARBONISING PALM KERNEL SHELL (PKS)

Reactor type	Capacity	Particle size (mm)	Temperature (°C)	Residence time (min)	Biochar yield (wt%, dwb)	Bio-oil	Reference yield (wt%)
Fluidised-bed [au]	0.3-2 kg feed	1-2	479 – 555	30 – 197	21 – 23	50-53	Choi *et al*. (2015)
Fixed bed [al]	20 kg	As received	400	60	29	NR	Kong *et al*. (2013)
Fixed bed [al]	0.15 kg	1.7-2.0	400 – 800	60	24 – 35	36 - 46	Abnisa *et al*. (2011)
Fluidized-bed [au]	0.94 kg hr^{-1}	0.125-1.400	478	NR	23	52	Kim *et al*. (2014)
Fixed bed [au]	0.1-0.4	10-20	500	60	32	51	Lee *et al*. (2013)
Fixed bed [al]	0.5	As received	400 – 800	55 – 167	31 – 39	NR	Titiladunayo *et al*. (2012)

Note: au - autothermal; al - allothermal; NR - not reported; dwb - dry weight basis.

TABLE 2. BIOMASS PYROLYSIS BASED ON THREE DIFFERENT CONDITIONS

Pyrolysis mode	Temperature (°C)	Vapour residence time	Liquid yield (wt%)	Gas yield (wt%)	Char yield (wt%)
Fast	500	1-2 s	60-75	13-20	12-20
Intermediate	500	5-30 s	40-50	25	25-30
Slow	400	hr-days	25-30	25-35	30-40

Source: Kantarelis *et al*. (2013).

MATERIALS AND METHODS

Sample Preparation

PKS (*Figure 1*) was obtained from Sime Darby Palm Oil Mill in Labu, Negeri Sembilan, Malaysia. Prior to biochar production, the collected PKS was air-dried by spreading on a rain-sheltered concrete floor for a few days followed by drying in an oven at 103°C until the moisture content was <10 wt %.

Experimental Procedures

The BEK, a multi-mode manual pyrolysis machine supplied by All Power Labs (USA) was used to produce biochar from PKS with bio-oil as a side product (*Figure 2*). It consists of a cylindrical reactor and two cylindrical hoppers; one for feeding the biomass to the reactor, and the other for collecting the biochar. There are several pyrolysis modes available, *i.e.* bypass mode, retort mode and sweep gas mode. In this study, the bypass mode (*Figure 3a*) was used during start up burning propane gas to heat up the PKS (20 kg) in the reactor. Once the reactor reached 100°C, the heat was generated by burning the syngas released from pyrolysing PKS using retort mode (*Figure 3b*).

Figure 1. Raw palm kernel shell (PKS) from palm oil mill.

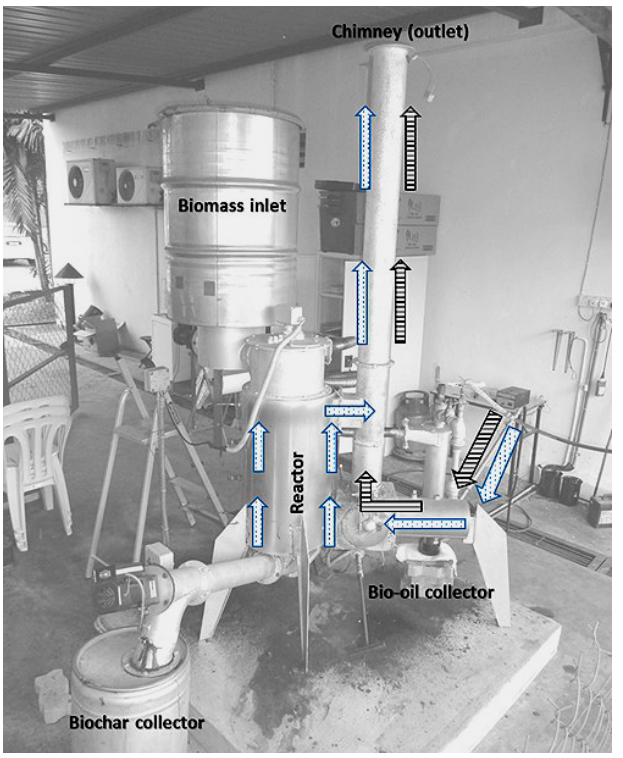

Figure 2. The biochar experimenter's kit (BEK); white arrows for bypass mode and black arrows for retort mode (outer layer of the reactor).

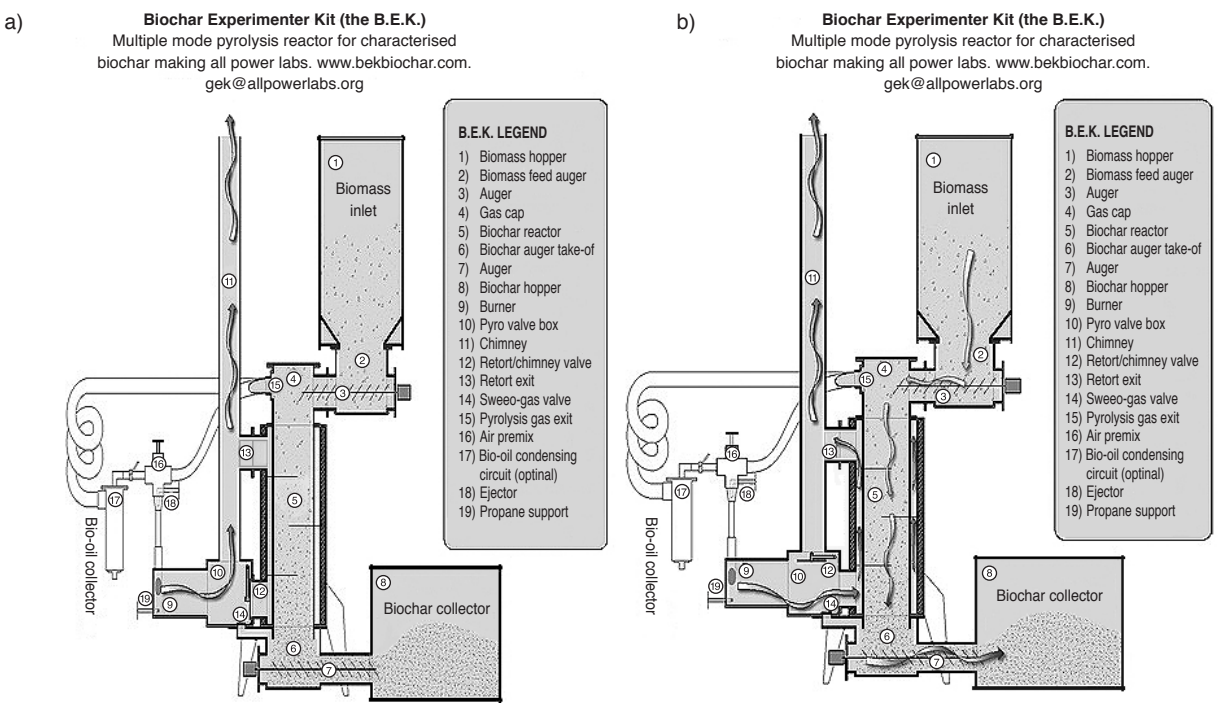

Figure 3. (a) Bypass mode layout and (b) retort mode.

Two pyrolysis parameters were monitored, *i.e.* temperature (400°C to 600°C) and residence time (30 and 60 min). All experiments were performed in triplicate in batch mode and results presented as mean values. The biochar produced was collected from the second hopper (No. 8, *Figure 3b*), then cooled overnight prior to physico-chemical analyses. Bio-oil was collected from the condenser unit at the end of the run using a pre-weight glass beaker.

The biochar yield was calculated using Equation (1):

$$\text{Biochar yield (wt\%)} = \frac{W_{bc}}{W_0} \; x \; 100 \quad \text{Equation (1)}$$

where W_0 is the dry weight of raw PKS (kg), and W_{bc} is the weight of biochar produced (kg).

The bio-oil yield was calculated using Equation (2):

$$\text{Bio-oil yield (wt\%)} = \frac{W_{bo}}{W_0} \; x \; 100 \quad \text{Equation (2)}$$

where W_0 is the dry weight of raw PKS (kg), and W_{bo} is the weight of bio-oil (kg) collected from the condenser.

Physico-chemical Characterisation of PKS and Biochar

Prior to characterisation, the biochar samples were ground using a Dickson AFY-300 grinder and used as it was for analysis. For pH determination, Enders *et al*. (2012) protocol was followed using a calibrated pH meter (BP3001 Trans Instruments). However, instead of 1 M KCl, deionised water was used. The proximate analysis was carried out by thermal gravimetric analysis (TGA) (Leco TGA 701) according to ASTM D5142. Calorific value (CV) of biochar was determined with a bomb calorimeter (Leco AC-600) according to ASTM D5865-07. Ultimate analysis was done using a CHNS analyser (Leco 628) according to ASTM D5373, and the oxygen (O) content calculated by difference (Equation 3; Titiladunayo *et al*., 2012). The raw PKS was analysed in a similar manner.

$$\text{O(wt\%)=100-C(wt\%)-H(wt\%)-N(wt\%)-S(wt\%)-Ash(wt\%)} \quad \text{Equation (3)}$$

RESULTS & DISCUSSION

Biochar and Bio-oil Yield

The PKS pyrolysis product distribution (*Figure 4*) was found to range from 33 - 52 wt% (dwb) for biochar (*Figure 5*), 1 - 5 wt% (dwb) for bio-oil and 43 - 64 wt% (dwb) for pyrogases. Results generally show a decrease in biochar yield with temperature and residence time which agrees with literature cited in *Table 2*. The relatively higher yields of biochar at lower temperature (400°C) are attributed to the thermal breakdown resistance of lignin (Ma *et al*., 2015). Comparing the PKS biochar yield with yields from other biomasses under similar process conditions it can be seen that PKS biochar yield is greater (Lee *et al*., 2013; Titiladunayo *et al*., 2012). According to Lehmann *et al*. (2006), Thomsen *et al*. (2011) and Kong *et al*. (2014), lignin is an important factor for biochar production. Several authors reported a PKS lignin content ranging from 44 wt% (Abnisa *et al*., 2013) to 50 wt% (Loh, 2017) which are

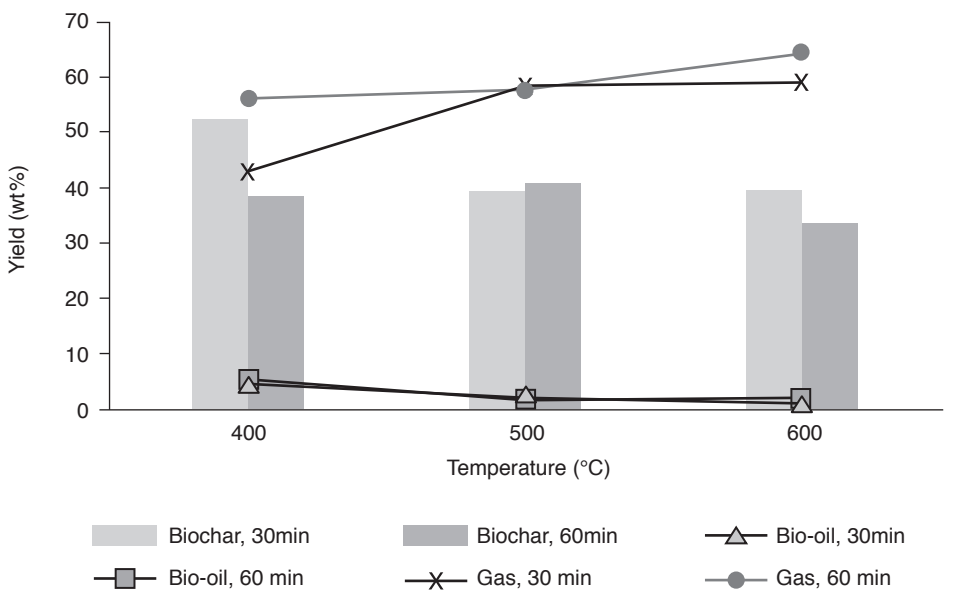

Figure 4. Palm kernel shell (PKS) pyrolysis product yield distribution at different temperature and residence times.

Figure 5. Fully carbonised palm kernel shell (PKS) biochar.

amongst the highest values found in plant biomass (Mohan *et al*., 2006). Although the crystallinity of cellulose also plays an important role, lignin possesses a more complex, aromatic structure that resists volatilisation and thus facilitates biochar formation.

The relatively low bio-oil yields (*Figure 4*) may be attributed to the condenser temperature which appears to be >100°C thus primarily collecting high molecular weight, organic condensable substances and less water. Sukiran *et al*. (2009) also reported that the amount of water in the bio-oil is a function of the gas leaving the collector as well as the extent of secondary reaction or cracking reactions in the reactor. The presence of water can affect the physical, chemical and combustion properties of the bio-oil (Ibrahim *et al*., 2012), where a high water content reduces the calorific value but improves viscosity and stability (Sukiran *et al*., 2009). In laboratory-scale studies where bio-oil was collected at temperatures close to 0°C, the oil yield was 52 wt% while the water content constituted 42 wt% of the bio-oil (Kim *et al*., 2013). According to Wang (2013), fresh bio-oil generally appears in one phase however long-term storage can cause its separation into two phases as the heavier substances segregate and deposit at the bottom. In this study, we found that the bio-oil appeared as a single phase even after long-term storage. The physical appearance of bio-oil PKS was dark-brown, viscous, yet free-flowing liquid with a pungent coal odour.

Physico-chemical Characteristics of PKS and PKS Biochar

Results from the proximate and ultimate analyses of PKS and its biochar produced at different temperatures and residence time are summarised in *Tables 3* and *4*. Proximate results for raw PKS are in agreement with Kawser and Ani (2000) and Ma *et al*. (2015) who reported very similar values. Compared to its raw form, pyrolysis enhanced fixed carbon (FC), ash content and carbon content of PKS by factors of 2.4 - 3.2, 1.7 – 4.7 and 1.2 – 1.5, respectively. The volatile matter (VM) of PKS biochar (20-39 wt%) was lower than the raw PKS (71 wt%). Increasing the pyrolysis temperature caused a significant loss of VM content in the biomass due to the decomposition of hemicellulose, cellulose and lignin components, respectively (Thangalazhy-Gopakumar *et al*., 2010; Mukherjee *et al*., 2011; Rafiq *et al*., 2016). The VM/FC ratio of raw PKS was 3.18 while for PKS-biochar the ratios decreased with increasing temperature and residence time (*Table 3*). Similar trends were reported by Lee *et al*. (2013) for raw (3.73) and pyrolysed PKS (0.15). According to Amonette *et al*. (2010) and Novak and Busscher (2013), a VM/FC ratio of < 1.0 is indicative of a good biochar stability in the soil suitable for carbon sequestration suggesting that all PKS biochars produced with the BEK meet this criterion and can therefore be considered as a suitable carbon sink.

The elemental composition of raw and PKS biochar as well as pH are provided in *Table 4*. The pH of biochar is an important parameter in biochar-soil interactions associated with nutrients mobility (Gomez-Eyles *et al*., 2013). The pH of PKS biochar ranged from pH_{H2O} 6.7 to 7.8 and increased as temperature and residence time increased. The pH in this study was similar to values reported by

TABLE 3. PROXIMATE ANALYSIS OF PALM KERNEL SHELL (PKS) AND PKS BIOCHAR

Properties	Unit	Raw PKS	PKS Biochar					
			30 min			60 min		
Temperature	°C	-	400	500	600	400	500	600
Calorific value	MJ kg^{-1}	19.5±0.6	26.7±2.8	25.1±5.1	29.9±0.6	29.0±0.3	27.9±0.21	28.3±1.2
Moisture content	wt%	4.86±1.29	2.20±0.08	3.00±0.04	4.07±0.18	2.46±0.07	3.26±0.16	3.80±0.08
Volatile matter (VM)*	wt%	70.7±2.0	38.6±1.1	34.6±1.7	22.8±2.5	31.6±0.5	25.2±0.8	20.0±5.3
Ash content*	wt%	2.17±0.59	6.07±0.88	3.73±0.34	5.12±0.63	6.23±0.62	10.3±5.2	5.28±0.29
Fixed carbon (FC)*	wt%	22.2±2.2	53.2±1.8	58.7±1.8	68.0±2.3	59.7±0.9	61.3±4.7	70.9±0.4
VM/FC	-	3.18	0.73	0.59	0.34	0.54	0.41	0.28

Note: ± SD - standard deviation; * dwb - dry weight basis.

Kong *et al*. (2013) who found that the value of PKS biochar at 400°C was pH_{H2O} 6.9, and Lee *et al*. (2013) reported a pH_{H2O} 6.99 at a temperature of 500°C. Biochars ($pH_{biochar} >> p_{soil}$) are known to increase soil pH which helps to alleviate aluminum root stress (Manickam *et al*., 2015). The PKS biochar with the highest C content (74.2 wt%) was obtained at 500°C for 30 min reaction. The H and O contents of PKS decreased during pyrolysis probably caused by dehydration and decarboxylation reactions (Li *et al*., 2007; Jindo *et al*., 2014; Yu *et al*., 2016). In addition, aromatisation and the formation of light molecular weight hydrocarbons during pyrolysis could also reduce the H content (Kim *et al*., 2010; Mantilla *et al*., 2014).

The sulphur (S) content in raw and pyrolysed PKS was below the detection limit, while nitrogen content was found to range from 0.17 wt% in raw to 0.77 wt% in pyrolysed PKS. The low concentrations of S and nitrogen (N) content in PKS is a common feature of ligno-cellulosic material due to a lack of proteins in non-reproductive plant components while animal residues have a typical S and N content of 2.3 wt% and 12 wt%, respectively (Vassilev *et al*., 2010). Sulphur content in PKS was reported in literature to vary from below detection limit (BDL) (Kawser and Farid, 2000), 0.04 wt% (Asadullah *et al*., 2013), 0.1 wt% (Ma *et al*., 2015) and 0.38 wt% (Asadieraghi and Wan Daud, 2014). Increased levels of inorganic S in plants is indicative of cultivation on acid sulphate soils, soil contamination with sulphur due to acid rain or excessive sulphur fertilisation requiring the plants in all cases to store S compounds such as SO_4 and sulphate esters in plant fluids and vacuoles (Knudsen *et al*., 2004). The N content ranged from 0.37 wt% (Kawser and Farid, 2000) to 0.76 wt% (Asadieraghi and Wan Daud, 2014) and was found to be greater in pyrolysed PKS arguably due to pre-concentration effects caused by the volatilisation of hemicellulose and cellulose while proteins either react with cellulose to form glycosylamines (Maillard reaction) or form cyclic amides such as 2,5-diketopiperazine (DKP) (Hansson *et al*. 2003; Becidan *et al*., 2007; Liu *et al*., 2017) which lock up N at temperatures below 400°C. However, as pyrolysis temperature increases, N content in pyrolysed PKS decreased (*Table 4*) probably due to the decomposition of DKP and glycosylamine resulting in the formation and release of HCN, HNCO and NH_3 (Hansson *et al*., 2003; Becidan *et al*., 2007; Liu *et al*., 2017). Although major and trace nutrients in PKS and PKS biochar were not analysed in this study, Loh (2017) showed that PKS can be potentially used as animal feed ingredient and soil amendment (Loh *et al*., 2013). It can therefore be anticipated that the derived PKS biochar will also inherit these properties.

The H/C and O/C molar ratios are important indicators of the presence of polar functional groups, hydrophilic nature of the surface (Chen *et al*., 2008; Kearns *et al*., 2014) as well as biochar's stability (Spokas, 2010). The H/C ratio of raw PKS was found to be 2.02 while ratios of 1.36 to 1.47 were reported by numerous authors (Kawser and Ani, 2000; Asadullah *et al*., 2013; Asadieraghi and Wan Daud 2014; Ma *et al*., 2015). Raw PKS had an O/C ratio of 0.61 which agrees well with literature values ranging from 0.513 to 0.818 (Kawser and Ani, 2000; Asadullah *et al*. 2013; Asadieraghi and Wan Daud 2014; Ma *et al*., 2015). The H/C molar ratio of PKS biochar ranged from 0.52 and 0.97, while the O/C ratio varied between 0.12 and 0.23 (*Table 3*). H/C and O/C ratios of < 0.7 and < 0.4 respectively indicate a good degree of carbonisation of biochar (Kuhlbusch, 1995; Zheng *et al*., 2010; Kung *et al*., 2013) and its suitability for biochar-soil interaction (Camps-Arbestain *et al*., 2015; IBI, 2015). The H/C and O/C ratios decreased as pyrolysis temperature increased (Krull *et al*., 2009; Spokas 2010; Enders *et al*., 2012). According to Spokas (2010), biochars with an O/C ratio of < 0.2 can attain half-life > 1000 years while O/C ratio > 0.6 have an estimated half-life of < 100 years. Therefore, it shows that O/C ratio of PKS biochars reported here have an expected

TABLE 4. ULTIMATE ANALYSIS OF PALM KERNEL SHELL (PKS) AND PKS-BIOCHAR

Properties	Unit	PKS	Biochar					
			30 min			60 min		
Temperature	°C	-	400	500	600	400	500	600
pH	-	6.28±0.08	6.63±0.05	6.89±0.15	7.30±0.20	6.65±0.01	7.08±0.02	7.75±0.23
C	wt%	49.2±0.2	67.4±2.4	74.2±0.3	72.8±2.8	72.5±0.5	66.3±0.6	61.0±1.2
H	wt%	8.26±0.06	4.21±0.05	4.71±0.02	3.18±0.04	3.90±0.02	4.49±0.11	4.93±0.07
N	wt%	0.17±0.03	0.64±0.01	0.72±0.01	0.77±0.02	0.73±0.01	0.43±0.01	0.37±0.02
S	wt%	BDL	BDL	BDL	BDL	BDL	BDL	BDL
O	wt%	39.7±2.3	21.8±0.7	16.6±0.2	18.1±0.04	16.7±0.3	18.6±0.2	28.5±0.1
C/N (molar)	-	332	123	120	110	117	182	195
H/C (molar)	-	2.02	0.75	0.76	0.52	0.65	0.81	0.97
O/C (molar)	-	0.61	0.23	0.15	0.17	0.16	0.15	0.12

Note: ± SD - standard deviation; BDL - below detection limit of the method used.
C - carbon. O - oxygen. S - sulphur. H - hydrogen. N - nitrogen.

half-life of at least 100 to 1000 years thus playing a potentially important role in locking up carbon while improving plant growth in low-fertility soils.

The C/N ratio of biochar indirectly relates to N mineralisation/immobilisation during biochar-soil-microorganisms interactions in decomposing organic materials (Ameloot *et al*., 2015). A C/N ratio of 20 is commonly attributed to organic substrates adequate for microbial soil function (Loh *et al*., 2013). Cayuela *et al*. (2014) stated that the C/N ratio is the main element to indicate the N_2O emission where high C/N ratio influences the reduction of soil N_2O emission (Brassard *et al*., 2016). Biochar with a C/N ratio of < 30 showed negative effects towards N_2O emissions compared to higher C/N which can reduce N_2O emission of the soil (Ameloot *et al*., 2013). The C/N ratio of PKS biochars produced here was found to be between 110 - 195 which indicates that N_2O emissions from PKS amended soil are low.

Further studies should be carried out to test the effect of biochar on plant growth in low fertility soil under various fertilisation regimes. Predicted stability in soil should be confirmed experimentally. Stack emission monitoring should be carried out to determine emission factors for regulated gases to demonstrate compliance with legislation. In addition, an energy balance and cost-benefit analysis need to be carried out to demonstrate the sustainability of this technology.

CONCLUSION

PKS biochar was successfully produced at pilot-scale under different temperatures and residence times. The PKS biochar yield ranged from 33 – 52 wt% which was amongst the highest reported in literature and found to decrease with pyrolysis temperature and residence time. All PKS derived biochars had VM/FC and O/C ratios of < 0.60 and < 0.23 respectively, and are expected to be stable in soil for > 100 years. The high C content in the biochar of up to 74 wt% combined with its stability demonstrates its potential to sequester and store carbon in soil. The pH of the PKS biochar was neutral to alkaline suggesting its ability to increase pH of highly acidic soils and alleviate aluminum root stress. The high C/N ratio of PKS biochar suggests that N2O emissions from PKS biochar amended soil will be low. Overall, this study demonstrated the suitability of PKS biochar for the amendment of and carbon sequestration in degraded soils.

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