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DETERMINATION OF BIO-ENERGY POTENTIAL OF PALM KERNEL SHELL BY PHYSICOCHEMICAL CHARACTERIZATION

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Abstract

Palm Kernel Shell (PKS) is an economically and environmentally sustainable raw material for renewable energy industry. To this vane its physicochemical properties were determined for its most viable application in Renewable Energy options such as bioenergy and biomass utilization. Its higher heating values determined by bomb calorimetric method are 22.94 and 25.27MJ/kg on dry and dry ash free bases respectively while its thermo-gravimetric behavior shows that it can completely decompose between 400℃ and 500℃. Its compositional analysis by 72% sulphuric acid hydrolysis and High Pressure Liquid Chromatography (HPLC) analysis of structural carbohydrates show that its lignin, cellulose and hemicellulose compositions are respectively 50%, 7% and 26%. Under high resolution scan electron microscope, (SEM), PKS contains natural micro pores that enable it release volatile matter necessary for bio-energy production. The results of the ultimate analysis show that the raw material contains high carbon and moderate hydrogen content. These are responsible for the large value of its higher heating value. These results show that PKS possess valuable potential to supplement the energy supply of developing countries through sustainable renewable energy technologies.

Keywords: palm kernel shell, bioenergy, thermogravimetric analysis, pyrolysis, gasification

1. Introduction

Oil Palm nativity had been associated with the tropical rainforest of West Africa but has spread to most of the equatorial tropics of South-East Asia and America[1,2]. It forms part of foreign income earner for most of Asian countries such as Malaysia, Indonesia and Thailand. In oil palm processing for palm oil and palm kernel oil production, palm oil fibre, effluent, kernel shell and empty fruit bunch are regarded as wastes. According to Luangkiattikhun et al., [2] and Pansamut et al., [3] about 0.07 tons of palm shell, 0.103 tons of palm fibre and 0.012 tons of kernel are produced as the solid wastes for every ton of oil-palm fruit bunch being fed into the palm-oil processing plant. The amount of each component waste generated from palm oil (PO) and Palm Kernel Oil (PKO) processing may be attributed to the type of oil palm species dominant in the quantity being processed.

Dura and Pisifera are the two major species of oil palm being cultivated. Whereas the Dura is thick shelled with thin mesocarp, the Pisifera species is thin shelled with thicker mesocarp. This invariably contributes to the amount of palm oil, palm kernel oil and palm kernel shell that can be obtained from the species. However, improved varieties of the former are being cultivated with the assistance of advances in plant genetic technology.

According to, FAO [4], over 20 tonnes of bunches/ha/yr can be produced with improved varieties. For instance, Palm Plantations of Australia have developed a species of Dura that can yield up to 35.65 tons ha-1 by the 6th year [5]. A typical fresh palm fruit bunch can produce about 5–7% PKS per bunch [4]. This invariably suggests the relative abundance of PKS per oil palm harvest.

The major consideration and utilization of PKS has been energy production through direct combustion processes. However, it has been proposed for use as concrete reinforcement in construction indus-

try [6-8], production of palm kernel shell concrete [9, 10], production of admixture with Portland cement to form concrete [11], production of activated carbon for industrial use [12] while, for minor considerations, Ibhadode and Dagwa [13] have considered it as substitute in manufacture of auto lining. These have not attained high social acceptance due to the limitations of the PKS quality in meeting technical standards required in these industries.

Palm Kernel Shell as one of the 'wastes' accruing from oil palm processing, can be suitably converted to renewable energy by applying suitable thermochemical process. Gasification, torrefaction and fast pyrolysis are the three common thermochemical processes recently applied to biomass conversion to obtain higher energy density fuels. Fast Pyrolysis is the thermal decomposition of biomass for bio-char, bio-oil and combustible gas production in the absence of oxygen while gasification is thermal decomposition of biomass in the presence of oxidative substance – usually controlled air. Reduced feedstock transportation from point of production to consumption destination is the merit that fast pyrolysis holds over gasification while its ability to harness other bio-energy components such as liquid and gaseous fuels gives it preference to torrefaction.

However, the present thermochemical processes are preferred to the traditional combustion of PKS because of their environmental friendly output. In order to adopt this or any other biomass sample for any of the thermochemical processes, their physical and chemical properties need to be determined with a view to adopting their most valuable conversion method. For instance, Miskam et al [14] characterized saw dust from local furniture manufacturers in Malaysia in order to determine its potential as feedstock for cyclone gasifier. They found that ground saw dust is a better option than large size particles for the gasifier. In the same vein, Sharifah and Suzana [15] introduced aggregated matrix method as alternative and quick method for characterizing biomass for thermochemical process.

The physicochemical properties of interest determined in our study include the moisture and ash content, the heating values, the compositional analysis as well as the ultimate analysis. The thermogravimetric analysis (TGA) and the morphology of the sample pore structure were also determined. The moisture content affects the energy value of any fuel hence, the importance of determining the moisture content. Heating values are important parameters for measuring the energy content of biomass samples. It is vital to study the thermal behavior of PKS to understand its behavior at high temperature applications as well as to know the right temperature for a particular application.

PKS is a typical plant material; hence the compositional analysis for the determination of its structural carbohydrates and lignin composition is vital. The composition helps in understanding its thermal behavior since the cellulose and hemicelluloses decompose at much lower temperature than the lignin [16]. The major objective of the paper is to determine the properties of PKS that can justify its use in bioenergy production.

It is therefore the aim of this paper to fully characterize the sample to determine the aforementioned properties that will inform the end users for its application in bioenergy production as a means of maximizing the potential of the residue in oil palm processing.

2. Materials and Methods

The palm kernel shells used were obtained from local palm oil processors in Nsukka Local council of Enugu State Nigeria which was a mixture of shell from different species of oil palm viz: Dura and Pisifera. This is because it is unusual to sort the species during palm oil processing. In commercial oil production, both species are usually cultivated. The climatic conditions of Nsukka and most of the South Eastern Nigeria, such as mean annual rainfall of 1,981mm [17], make it possible for commercial production of oil palm in the area. The samples were air dried and milled through a mesh 40 (425μm) screen. The properties determined include moisture content, heating values, percentage ash, structural carbohydrates and lignin. The morphology and thermal behavior of the samples were determined through scan electron microscopy and thermogravimetric analyses respectively.

The moisture content of the sample was determined according to the methods specified in ASTM D4442-92 (2003) (Standard Test Methods for Direct Moisture Content Measurement of Wood and Wood-Base Materials) and NREL/TP510-42621 (Determination of total solid and total dissolved solids in biomass), at a temperature of 105℃ for 24 hours. It involves the continual weighing and reheating every 1hr until a constant weight was observed to $\pm$0.02g of the previous weight. In all mass (weight) measurements, a Citizens analytical balance (CX265) was used while the Fischer Scientific Isotemp oven was used in the moisture analysis tests. Aluminum pans were used after preheating in the oven for 4 hours. Two replicate samples were used and the average taken as representative moisture content of the samples.

ASTM D5865 (Standard Test Method for Gross Calorific Value of Coal and Coke) was used for the heating value determination on dry basis using the oven dried samples. The PAAR 1341 oxygen bomb calorimeter, standardized using benzoic acid pellets was used to determine the gross caloric value (HHV) while the net calorific value (LHV) was calculated using wt% of hydrogen resulting from elemental analysis

of the sample. The samples were pelletized using the PAAR pellet press 2811. Combustion was in excess of oxygen at a pressure of 30atm using 45C10 fuse wire while the temperature of 2kg of water surrounding the bomb was measured using a mercury thermometer. The ash content was determined on both wet (as received) and dry basis according to ASTM D3174-04 (Standard Test Method for Ash in the Analysis Sample of Coal and Coke from Coal) at 950℃. Porcelain crucibles containing PKS were placed in a Fischer Scientific Isotemp Model 58 electric muffle furnace for combustion. The ash content, defined as the residue remaining after igniting the sample at 950℃ for 4 hours was calculated as percentage of the original quantity of the sample PKS.

Thermogravimetric Analysis for the determination of the thermal behavior of the sample was carried out using the TGA Q500 V20.10 Build 36 machine while being steadily heated in the presence of nitrogen gas flow at 40 ml/min. Approximately 18.5 milligrams of sample was heated from room temperature to 600℃ at a heating rate of 25℃/min.

For the determination of the lignin and structural carbohydrate content of the sample PKS, two-step acid hydrolysis method as provided by NREL/MRI laboratory analytical procedure – TP-510-42618 (Determination of Structural Carbohydrates and Lignin in Biomass), was used. The sample was analyzed as received using 72% sulfuric acid to decompose all structural carbohydrates. The insoluble lignin was filtered using filtration crucibles and later ashed at 575℃Ṫhe acid soluble lignin was determined using a Shimadzu UV spectrophotometer 1800 at wavelength of 320nm. The structural carbohydrates were analyzed by high performance liquid chromatography with detection by refractive index using D-cellobiose, D(+)glucose, D(+)xylose, as calibration standards for determination of cellulose and hemicellulose components of the sample.

The anatomical structure of the sample was observed using a JEOL JSM-6400V (lanthanum hexaboride electron emitter) scanning electron microscope (JEOL Ltd., Tokyo, Japan) after coating it with osmium (∼10 nm thickness) in an NEOC-AT osmium coater. The digital images were acquired using Analysis Pro software version 3.2 (Olympus Soft Imaging Solution Corp., Munster, Germany).

3. Results and Discussion

3.1. Physical and chemical properties

The table 1 shows the result of the physicochemical parameters experimentally determined. It reveals that the sample has high calorific values conforming to its high carbon and hydrogen content as well as low moisture content. The higher heating values are 21.5, 22.9 and 25.3MJ/kg on as received, dry and dry and ash free bases respectively. The available energy from the biomass is reported as the lower heating value when the energy required to evaporate water of reaction in the calorimeter experiment is removed from HHV. Thus the values for LHV are smaller as reported in table 1. When placed side by side with other biomass materials of wood origin such as Pine, Aspens, Birch and Oak woods [18] the LHV for PKS indicate that larger energy values can be obtained from PKS, even though it has higher ash content of 8.7% and 9.2% on as received and dry bases respectively, than the samples mentioned above. The heating value compares very well with 25.46MJ/kg, on dry basis, obtained by Olufayo [19] for palm kernel shell and higher than 17.66MJ/kg for coconut shell [16]. The values obtained in this work is higher than 19.64MJ/kg obtained by Ezeike [20]. This could be because of higher moisture content of Ezeike's sample than used in this work. It was also shown by Ezeike that heating value has an inverse relationship with moisture content.

Table 1: Physical and chemical properties of the PKS sample.

		Value		
	Property	Ar	db	daf
Physical	Moisture content (%)	6.11	-	-
	HHV (MJ/kg)	21.5	22.9	25.3
	LHV (MJ/kg)	20.2	21.7	23.9
	Ash (%)	8.7	9.2	-
Ultimate analysis	C (%)	47.0	50.0	
	H (%)	6.0	5.6	
	N (%)	0.7	0.72	
	Cl (ppm)	84	89	
	O (%) (by difference)	38.0	35.0	
	S (%)	<0.08	<0.08	

Ar (as received), db (dry basis), daf (dry and ash free)

The reason for high values of the energy density of the PKS may be associated to the high carbon and hydrogen contents as revealed by the ultimate analysis result (table 1).

The ash value is less than that for rice straw used by Tsai et al [21] and higher than values for sugarcane baggasse and coconut shell. Even though the ash value reported is also higher for most woody biomass, the sample can still be considered a useful feedstock for bio-oil production. In bio-oil production through fast pyrolysis technique, high ash content tend to reduce the amount of liquid products from the biomass material. This is because ash tends to catalytically crack the liquid into non-condensable gases. It tends to also reduce the yield of bio-char that is a requirement for water treatment agent in form of Activated Carbon.

The values of the ultimate analysis (table 1) compare well with the values reported for rice straw, sugarcane baggasse and coconut shell, by Tsai et al [21]; for Pine, Aspens, birch and Oak woods by Shen et al

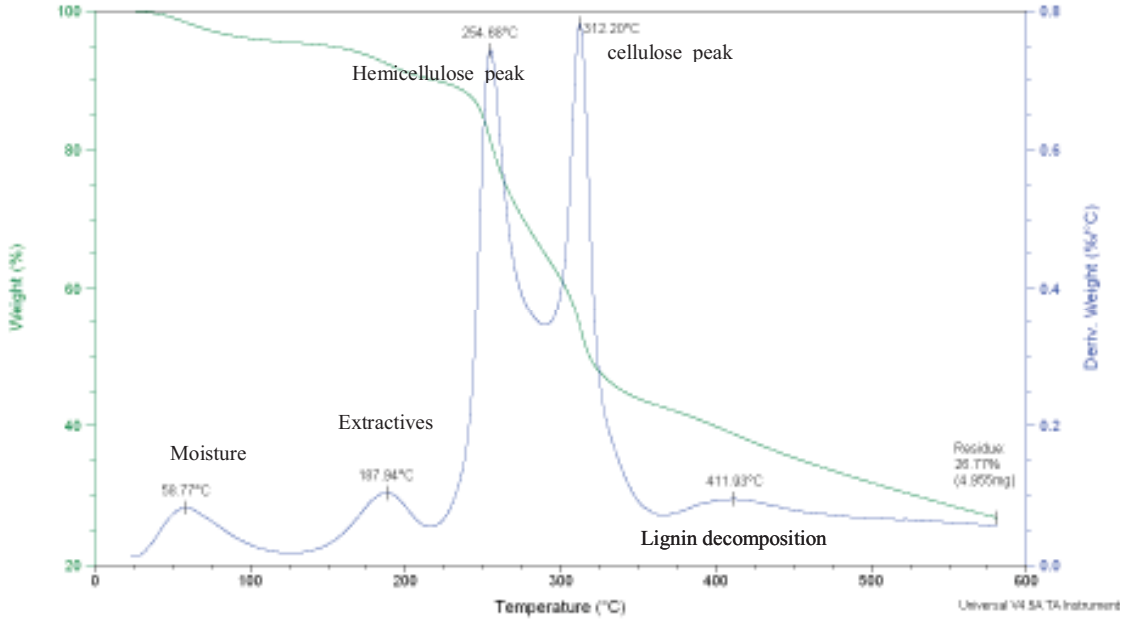


Figure 1: TGA and DTGA of PKS.

[18], for cassava rhizome and cassava stalk by Pattiya et al [22] and for saw dust by Qiang et al [23]. There is a narrow range for the values of carbon and hydrogen for all the materials while the oxygen content of PKS is less than those of the others. This implies that better bio-oil quality with less oxygen content may be obtained through the pyrolysis of PKS than from these feedstock. Oxygen content of bio-oil or biomass sample tends to lower the heating values of the fuels as well as cause instability in the products of pyrolysis or gasification.

Similarly, it can be affirmed that since these biomass materials have been successfully converted to bio-energy through laboratory analytical methods [22,23] and by bench scale method [18,21], it follows that PKS is a potential feedstock for bioenergy production. The fuel derived from it can be environmentally friendly since it possesses less sulphur and nitrogen.

3.2. Thermogravimetric analysis (TGA)

Thermogravimetry plot (figure1) shows the thermal behavior of the sample which is important parameter in the design of reactors for the pyrolysis of the sample. TGA of the PKS shows derivative weight loss/℃ with remarkable mass loss at 58.77℃ corresponding to about 6%. This is probably moisture which confirms that the sample contains about 6.11% moisture (Table 1). According to Chen and Kuo [16], thermal decomposition of hemicellulose occurs at temperatures ranging from 150 to 350℃. Similarly, cellulose decomposes at temperatures in the range of 275 to 350℃, while lignin gradually decomposes at temperatures between 250 and 500℃ [24, 25]. In the light of this, the three peaks around 187.94, 254.68 and 312.20℃ on the figure 1 may be volatiles resulting from the decomposition of inorganic materials, hemicellulose and cellulose respectively. This also agrees with the suggestion by [26] that cellulose and hemicelluloses decomposition take place around 300℃.

Similarly, the peak around 411.93℃ may be volatiles that result from lignin which decomposes at much higher temperature than the others. This conforms to suggestions by [2] for palm shell and fibre decomposition. The five peaks obtained in this work show the reaction schemes during the pyrolysis of the sample. The difference in the number of peaks obtained by [2] and that of this work may be explained due to the difference in the pretreatment given to the samples. Whereas the sample used by [2] was washed and dried at 110℃ which might have taken care of moisture and some volatiles, the sample used in our analysis was air dried at ambient temperature not exceeding 35℃Ḟrom the above, the peak representing the volatiles from inorganic material represent about 6% of the total mass of the sample while Hemicellulose is estimated at about 26% which conforms to the result of structural carbohydrate determination reported in Figure 2. Cellulose and lignin are major components of a typical plant material and are usually decomposed at much higher temperature than the extractives and water. This shows mass losses at 312.20℃ and 411.93℃ with estimated values of 6% and 48% respectively which confirms the compositional analysis result in Figure 2. There is a mass residue of 26.77% at temperature close to upper tem-

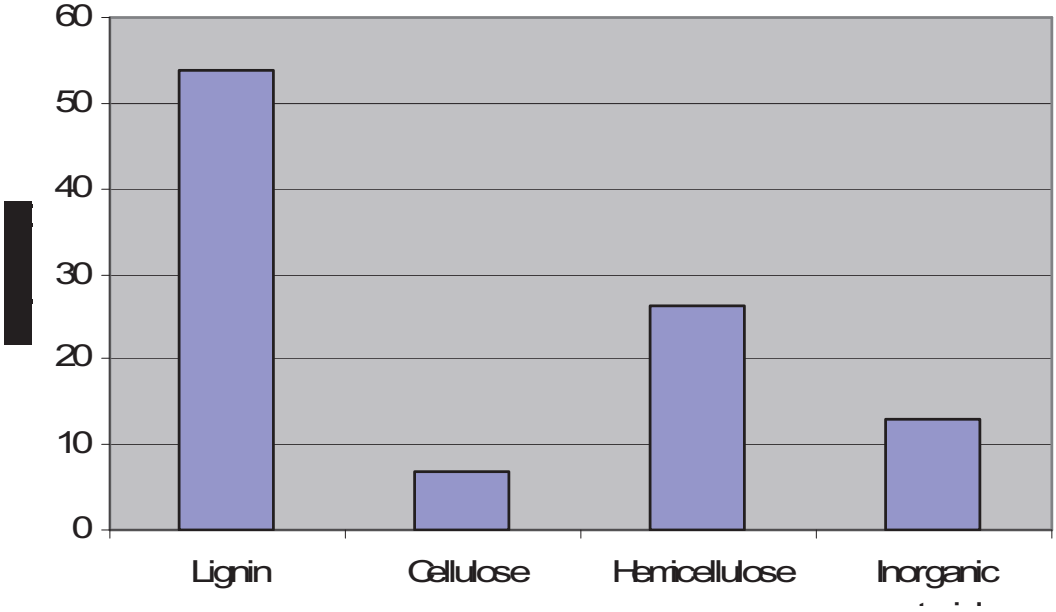


Figure 2: The % structural composition of the PKS sample.

perature limit of the reaction. This corresponds to some lignin that would decompose at much higher temperatures above gasification temperature of 600℃. This implies that gasification at 600℃ and above will completely decompose the feedstock for energy production. Hence, the TGA can be used to estimate the chemical composition of the sample as well as its thermal behavior. The PKS has thermal behavior similar to those of wood samples used for bio-energy production.

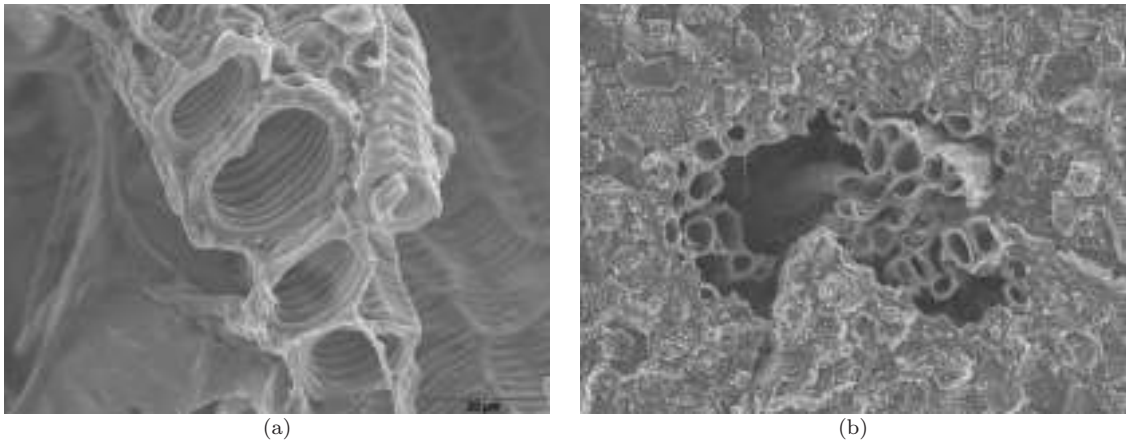
3.3. Chemical composition

The chemical composition of biomass samples especially wood is quite different from those of fossil fuels such as coal, oil shale, petroleum crude etc. The major chemical constituents of wood biomass are cellulose, hemicellulose, lignin and extractives. Cellulose fibers are responsible for the strength of the wood. Different wood samples have different constituents of the compounds. Figure 2 presents the percentage (%) chemical composition of the sample showing the presence of large concentration of lignin and very little cellulose. These values are different for most woody samples as proposed by [27]. This may suggest that PKS even though a plant material may have slight different plant composition from those of wood. The large percentage of these carbohydrates and lignin in the sample suggests that the feedstock could be a good material for fast pyrolysis work. This is confirmed by the TGA result showing a total decomposition of the sample within a small temperature range of 200 – 600℃This also agrees with predictions of thermal decomposition of biomass samples as suggested by [2, 16, 25, 28]. It also implies that maximum fast pyrolysis yield of PKS could be obtained at temperature close to and below 500℃ as suggested by Bridgwater [29] for biomass materials while at temperature above 600℃ gasification technology can be used to convert PKS to gaseous fuel.

3.4. Scan electron microscopy

The SEM images shown in figures 3(a) and (b) are the morphology revealing the heterogeneous structure of the palm kernel shell in its natural form. They show that the sample is made up of micro-pores through which the kernel probably exchanged air and liquids with the outer layers in order to sustain its life. The shape of biomass materials are important property in the design and function of thermochemical reactors. The shape affects the fluidization behavior and feeding system performance during thermochemical processing of biomass materials [30]. The images reveal that PKS is not homogenous and contains the pores through which volatiles are released during thermochemical processes. This implies that the PKS has the potential to expel volatiles when subjected to thermal processes for bio-oil and synthesis gas production.

When compared with the SEM of other biomass materials treated with heat, such as tea waste by Uzun et al., [31] it shows that there is likelihood for more pore opening and increase in pore size when volatiles are expelled under heat treatment. This is confirmed by the SEM of the resulting bio-char of the PKS as shown in figure 4. The images acquired both for the PKS sample and its Bio-char scan reveal that the pores are naturally present and can be formed due to volatilization during char production. The results have much



(a) (b)

Figure 3: Scan electron microscope images of fresh PKS.

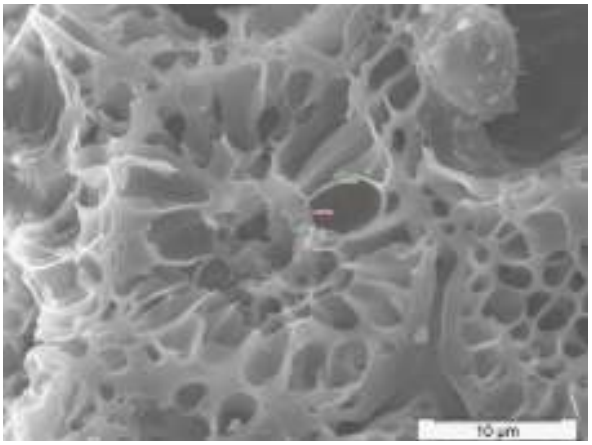


Figure 4: Scan electron microscopic image of the PKS biochar.

to say concerning its suitability for water treatment and energy production.

This implies that under pyrolytic process, pore sizes and macroporosity increased as proposed by Guerrero et al [32] and Apaydin-Varol et al., [33]. The presence of natural pores were responsible for the rapid mass loss (devolatilization) at temperature 225℃ and 400℃ as shown in the TGA result in figure1. This shows that the sample can be easily converted to liquid and gaseous fuels by thermochemical processes. Most biomass materials used for bio-oil production are thermally degraded between 450℃ and 600℃ [30, 34]. Thus fast pyrolysis can be favored.

4. Conclusion

Palm Kernel Shell is characterized for its useful application in bio-energy production. These results will enable oil palm producers to realize the value to which PKS should be placed during palm oil processing. PKS is a potential feedstock for bio-oil, bio-char and biogas production through fast pyrolysis and/or gasification process. It can be affirmed that since the biomass materials outlined above have been successfully converted to bio-energy through laboratory analytical methods and by bench scale pilot plants, it follows that PKS with similar or better qualities from this characterization analyses, is a potential feedstock for bioenergy production. The fuel derived from it can be environmentally friendly since it possesses less sulphur and nitrogen. It is a source of green energy when used as feedstock for thermochemical conversion other than for direct combustion. The combustion of the sample should be compared vis-á-vis bio-oil/ syngas production for cleaner energy and higher thermal capacity of the products. The environmental effect of direct combustion of PKS is the basis for adopting thermochemical conversion as better option. In addition to the above, biochar production or torrefied PKS can be another advantage over combustion or use of PKS in other mechanical applications.

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