DEVELOPMENT OF BIO-CHAR USING NON-DIRECT FIRING SYSTEM FROM OIL PALM FROND AND ITS CHEMICAL PROPERTIES

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Abstract— **One of the vital research in this area is to locate another biomass feedstock for bio-char production since an investigation on this issue is basic in light of the fact that each country has different biomass that can used an alternative energy. There is copious measure of wastes generated from the oil palm plantation like oil palm frond (OPF) in Malaysia which greatly increased over the years are mostly left on the fields. This waste particularly can be utilizing as the feedstock in the context of the bio-char via non direct firing system. The aim of this research is to analyze the characteristics OPF as a feedstock for slow pyrolysis for production of bio-char via non-direct firing system under various temperature 400, 500 and 600^{o}C and also to analyze the chemical properties of OPF bio-char based on thermo-gravimetric analysis (TGA) for proximate analysis, CHNS/O analyzer for ultimate analysis and functional group using Fourier-Transform Infrared Spectroscopy (FTIR). The proximate analysis of raw material oil palm frond (OPF) have more volatile matter (VM) but less ash content (AC) and moisture content (MC) compared with bio-char produced at different temperature. The data of fixed carbon (FC) for OPF was lower than bio-char at 400^{o}C but higher compared to bio-char at 500 and 600^{o}C. the carbon content in OPF was less than the carbon content in bio-char produce at all three different temperatures. Meanwhile, the hydrogen, nitrogen, sulphur were high in OPF but less in bio-char produced. Furthermore, the oxygen content in OPF was less than bio-char produced at 500^{o}C but the oxygen content in OPF was high than the bio-char produced at 400 and 600^{o}C. For FTIR analysis, the spectra began to disappear with the increasing pyrolysis temperature. This result was due to functional group have rupture and progressive carbonization. It can be concluded that bio-char that were produced from OPF feedstock have different trend of chemical properties depending on the temperature.**

Keywords— **Bio-char, oil palm frond (OPF), slow pyrolysis chemical properties.**

I. Introduction

One of the center parts in human day by day life is vitality or energy. Nature manageability, financial improvement and human progress identified with this energy. The nature of energy is needed in order to fulfil the essential needs, for example, nourishment, farming and cultivating, instruction wellbeing data and other establishment organizations.

There are two types of resources that can produce the energy which are renewable and non-renewable resources. Today, non-renewable resources are commonly used by the human as the main energy resources such as fossil fuels. Fossil fuels are predicted be phased out after a year 2042, while the coal available up until 2112. [1] While the energy demand is expanding at an exponential rate influence from the exponential development of total population, the fossil fuel cannot satisfy the interest. [2].

In general, sustainable energy is the energy produced from characteristics that are consistently recharged such as biomass that would gradually help in sustainability in the world's future by making a number of discharges pollutants become close to zero which are mainly air and greenhouse gases when it meets domestic energy prerequisites. [3].

Generally, the term biomass alludes to renewable organic matter that generated by plants from daylight by means of photosynthesis process. [4]. Biomass in term of Greek, bio meaning life + maza meaning mass, in a simple words, it is a non-fossilized and biodegradable organic material that coming from plants, animals and microorganisms and also municipal solid waste [5].

The conversion of biomass into product for the uses in bioenergy relies upon the cutting edge of the technologies that are safe and cheap to change the products into value added products. One of promising ways is pyrolysis process involving the conversion of biomass into a number of energy with no oxygen with various feedstock that undergo chemical reactions. [6]; [7] [8]. Under medium temperature (~600^{o}C) in either at inert atmosphere or vacuum pressure, the conversion of biomass produces multiple fuel products such as carbonaceous char (bio-char), bio-oil and combustible gases (syngas) fractions which these product yield can be maximize by adjusting the operation condition (temperature, holding time and heating rate). [9].

The most widely preferable approach to create bio-char is the slow pyrolysis process where it involves heating process of biomass in an almost or totally free oxygen present to 300-700^{o}C [10], because it improve the measure of C that is retained and gives time for bio-char formation to occur. [11]. With non-direct firing system, the reactor is heated from the outside and strictly no oxygen from the inside. The heat being transmit through the reactor walls.

The different of bio-char from other charcoal that it has criteria that is fine-grained, highly porous charcoal material that are suitable in application of soil amendment. The commercial production of bio-char requires raw materials with high carbon content such as wood, lignite, or low-cost and available at a large quantity from agricultural waste. [5].

The upstream and downstream industry of palm oil business in Malaysia especially in terms of production and technology in the global markets is at successful rate. Oil palm plantation helps Malaysia by giving lots of benefit but also significantly contributes to environmental degradation. One of the challenges that are affect from rapid growth in the oil palm ranch is a lot quantity of biomass generated. A scenario of underutilization of the significant of hemicellulose feedstock when most of the biomass are mulch at the plantations. [12]. Oil palm frond (OPF) is reported the highest quantity of biomass from oil palm. Currently, a few quantities of OPF being used for composting while the others are dispose by direct decaying and burning on the plantation site.

The main scope of this research covers the study of OPF and OPF bio-char characterization under different temperature that undergo slow pyrolysis process.

II. METHODOLOGY

A. Oil palm frond

In this study, the oil palm frond, namely *Elaeis Guineens* were obtained from Ladang Kelapa Sawit at Kampung Seri Tiram, Kuala Selangor, Selangor Darul Ehsan, Malaysia.

B. Preparation of Milled Frond

Preparation of milled frond was started by removing the leaves attached to frond and the leather of oil palm. The frond was cut into a small size, dried in an oven that being set to 70°C for 24 hours and the required moisture content of the frond must below than 5% for preservation purpose. As the moisture content of the frond still more than 5 %, the frond was dried for another session. The dried fronds were milled by using a cutting mill with a 1mm size of molecular sieves. The milled fronds were stored in an airtight plastic bag together with silica gel at room temperature to avoid any transfer of moisture from the atmosphere.

C. Experimental Setup

A reactor, double jacket pyrolyzer (Figure 1 & Figure 2) with a dimension 118 cm in length, 14 cm in internal diameter and 24 cm in external diameter was used for non-direct firing system. The firing system from LPG gas was externally heated at the bottom of reactor. Since the firing system need to be in blue color, the air compressor was used to enhance LPG gas formation. With the attachment of N_2 gas hose at the reactor, by allowing the N_2 gas to flow through the reactor as a function to remove the oxygen and any volatiles from the reaction zone.

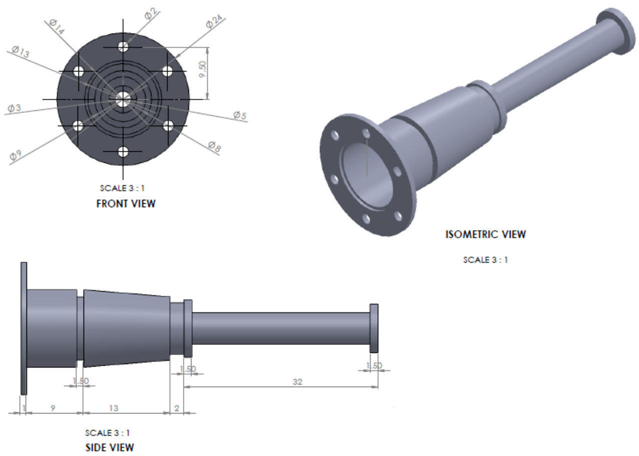

Fig. 1: The cap of double jacket pyrolyzer

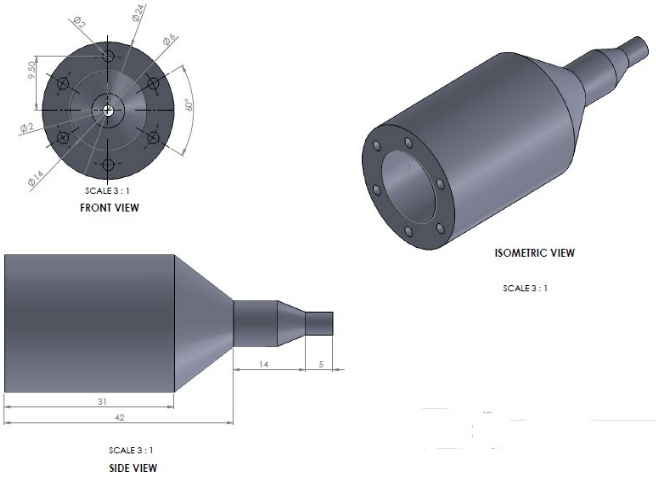

Fig. 2: Double jacket pyrolyzer

D. Preparation of Bio-char

500g of milled frond was fed into double jacket pyrolyzer reactor. The reactor was heated indirectly at constant heating rate of 20°C/min for three different temperatures: 400, 500 and 600°C and maintained to 1 hour for each temperature. N_2 gas was inserted once the target temperature had been reached. The bio-char was left inside the reactor about 24 hours for it to cool before it can be collected for further analysis.

E. Chemical Analysis

The OPF (raw material) and bio-char produced at different temperatures were further analysis for characterization based on chemical properties. Both raw material and product were characterized by using the Thermo-gravimetric analysis (TGA) for proximate analysis, and CHNS/O Analyzer for ultimate analysis and Fourier Transform Infrared Spectroscopy (FTIR) for functional group.

F. Thermo-Gravimetric Analysis (TGA)

Proximate analysis was performed on OPF and bio-char using Thermo-Gravimetric Analysis (TGA). The proximate analysis data were collected from the PerkinElmer STA6000 thermo-gravimetric analyzer by examine the weight change of material as a function of temperatures change ranging from 24.24°C to 1093.96°C with a constant heating rate of 10°C/min under a N_2 condition at a standard flow rate.

G. CHNS/O Analyzer

Ultimate analysis of Carbon (C), Hydrogen (H), Nitrogen (N), Sulphur (S) and Oxygen (O) content in the OPF and bio-char was carried by using the PerkinElmer 2400 Series II CHNS/O analyser that has a furnace capable of raising the temperature up to 1050°C. A very fine particle of oil palm frond and bio-char approximately 15-18mg was placed in the sample holder (tin capsule) and crimped before turning the instrument ON. The oxygen content was calculated by obtaining the difference.

H. Fourier Transform Infrared Spectroscopy (FTIR)

The Perkin Elmer Spectrum One FTIR Spectrometer was used to investigate and determine the presence of various functional group present in the OPF and bio-char. The sample was finely ground before pressing it into a sample holder. FTIR spectrum of sample was recorded between wave number of 515 and 4000/cm. The functional chemical groups in OPF and bio-char were identified by their FTIR absorption frequency spectra.

III. RESULTS AND DISCUSSION

A. Thermo-Gravimetric Analysis (TGA)

Table 1: Proximate Analysis of Oil Palm Frond and Bio-char produced

Proximate Analysis (%)	Oil Palm Frond	Bio-char at 400°C	Bio-char at 500°C	Bio-char at 600°C
Moisture Content	2.8097	2.8762	3.5104	6.3143
Volatile Matter	57.1088	13.946	11.9995	12.327
Ash	13.0421	31.1246	71.4471	74.7622
Fixed Carbon	27.0384	52.0532	13.043	6.5965

In general, based on Table 1, it represents the proximate analysis of raw material oil palm frond (OPF) have more volatile matter (VM) but less ash content (AC) and moisture content (MC) compared with bio-char produced at 400-600°C. The data of fixed carbon (FC) for OPF was lower than bio-char at 400°C but higher compared to bio-char at 500 and 600°C.

The moisture content (MC) for OPF from the proximate analysis was 2.8097%. In a similar work by [13], the MC of the OPF was reported to be 4%. Since the MC in OPF was low thus, it has a great prospective to be practically utilized in pyrolysis process. Therefore, there was less MC in raw materials (OPF).

The MC in bio-char increase with increasing temperature. Usually the MC of bio-char ought to be less than the OPF once exposing it to high temperature. However, with this increasing show that the bio-char might absorb some amount of moisture from the outer surroundings. The higher content of moisture content additionally was also because due to the presence of air within the reactor as the OPF did not compact very well inside the reactor.

The volatile matter (VM) for OPF from the proximate analysis was 57.1088%, Compared to study by [14] and [15] the reported percentage of VM in OPF was 76.26 % and 82.7% respectively which a bit higher than this experiment. The percentage between this data and study was slightly differ but the data in this experiment still consider high since it contains more than 50%. The VM which was high implies high reactivity and can ignite easily in thermochemical conversion such as pyrolysis for bio-char productionThe OPF with low VM content was unreactive during pyrolysis, leads to low production of bio-oils and gas. In order to produce more bio-char, higher volatility was preferable for pyrolysis process since it can be easily ignited and highly reactive in order to release more vapors emission while producing char.

As temperature increased, the VM release from bio-char shows a lower percentage with comparison to OPF. The VM in bio-char produced was less than the OPF due to low molecular volatiles have nearly vanished because of high temperature pyrolysis reaction. [17]. The dropped percentage of VM in bio-char than the OPF also because of high temperature so maximum volatiles had come out as a gaseous form containing CO_2, CO, CH_4 and H_2. [17]. The lower volatile release in bio-char is most likely due to the stronger bonding within the molecular structure of bio-char. [16]. Based on study by [18], the increasing temperature also resulted in the further crack of the volatiles fractions into low molecular weight liquids and gases instead of bio-char.

The ash content for OPF from the proximate analysis was 13.0421% which was higher than a study by [14] with 4.20%. The low ash content in OPF was preferable for thermal conversion process in order to release more vapours emission while producing char. The ash content in bio-char at 600°C was the highest with 74.7622% compared to with other bio-char at 400°C (31.1246%) and 500°C (71.4471%). This trend shows at high temperature, the elements such as carbon, nitrogen, hydrogen and nitrogen contents breaks their bonds easily compared to volatize inorganic salts, thus give higher percentage of ash. [14].

The fixed carbon (FC) was 27.0384% have been noticed in the OPF. The fixed carbon was compared with previous study by [17] reported that the amount of FC in OPF was 25.29%. This shows only a small difference.

Fixed carbon in bio-char at 400°C was 52.0532% which was high than OPF, because low temperature may condense volatile matter so the amount of solid combustible residue remains was high. The high FC indicates that the OPF will requires a long pyrolysis time to driven off the volatile matter. Moreover, the fixed carbon starts to decreased at temperature 500 to 600°C with value 13.043% to 6.5965%. It shows that the quantity of VM that contain hydrogen, oxygen, nitrogen and sulphur were driven off with the gases.

B. CHNS/O Analyzer

Table 2: Ultimate Analysis of Oil Palm Frond and Bio-char produced

Ultimate Analysis (%)	Oil Palm Frond	Bio-char at 400°C	Bio-char at 500°C	Bio-char at 600°C
Carbon	44.8775	69.1692	50.0201	72.0351
Hydrogen	8.6137	6.6265	3.6489	3.4968
Nitrogen	3.6396	2.9374	2.8760	2.5569
Sulphur	0.0024	0.0000	0.0000	0.0000
Oxygen	42.8668	21.2669	43.4549	21.9112

In general, the carbon content in OPF was less than the carbon content in bio-char produce at all three different temperatures. Meanwhile, the hydrogen, nitrogen, sulphur were high in OPF but less in bio-char produced. Furthermore, the oxygen content in OPF was less than bio-char produced at 500°C but the oxygen content in OPF was high than the bio-char produced at 400 and 600°C.

Carbon content of OPF was reasonably high (44.8775%), indicated that it has potential in producing higher purity of bio-char. Hydrogen is recorded around 8.6137% in OPF, shows that OPF can be source of energy which is environmentally friendly while having a low amount of sulphur and nitrogen (approximately 0.0024% and 3.6396%), thus can reduce negative effects on the environment. For instance, high carbon content would be desired as it was an important element in the pyrolysis process. A low content of sulphur would be desirable, as it could lower a formation of acidic compound such as acid rain when its emission react with water, oxygen. [13].

There has been a significant increase of carbon percentage in the bio-char produced, which are 69.1692%, 50.0201% and 72.0351% at 400°C, 500°C and 600°C respectively after pyrolysis. Carbon accumulates mainly due to a reduction in the levels of hydrogen and oxygen in the bio-char. High carbon content of the bio-char were linked to the high degree of aromaticity during the pyrolysis of the OPF, which produced the highly carbonized char. [19] The high carbon content was beneficial for energy source or soil adsorption of pollutants. [20]. For hydrogen, sulphur and nitrogen in bio-char produced for each temperature show a less amount than the OPF.

As the temperature increased from 400°C to 600°C, the hydrogen content decreased, from 6.6265% to 3.4968%. The decreasing in hydrogen content at higher temperature was notices due to the releasing of low molecular weight by-product containing hydroqgen.

The nitrogen content in bio-char shows a decreasing as the temperature increase to 600°C, which at 400°C (2.9374%), 500°C (2.8760%) and 600°C (2.5569%), which these values were lower than OPF. Decreasing of nitrogen percentage in bio-char with increasing pyrolysis temperature due to nitrogen complex structure did not resistant to high temperature and easily volatilized. [18]. The high temperature had causes the nitrile-N and heterocyclic-N compounds to cracked when undergo dehydrogenation.

The oxygen content remarkably increases from 21.2669% to 43.4549% with an increase in the pyrolysis temperature from 400 to 500°C. When pyrolysis temperature increased from 500 to 600°C, the decomposition of oxygenated bonds might occur, thus the content of oxygen decreased at high temperature which is 21.9112% at 600°C.

Since the OPF has high carbon content, low sulphur and nitrogen, therefore OPF was suitable as a feedstock for thermochemical conversion process. From this analysis, it shows that at temperature 600ºC was the best temperature to produce bio-char with high carbon and low oxygen content, followed by temperature 400ºC and 500ºC.

C. Fourier Transform Infrared Spectroscopy (FTIR)

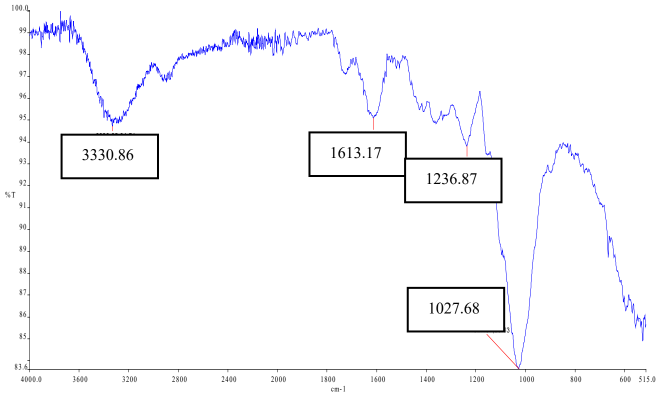

Fig. 3: FTIR Spectra of Raw Material Oil Palm Frond

The FTIR spectra of both biomass feedstock and biochars obtained at different pyrolysis peak temperatures are used to analyse the gradual loss of lignocellulosic functional groups [21] (change in the O−H stretch peak around 3330.86/cm, which dominates the feedstock's spectrum). The OPF spectra in Figure 3 showed an absorption peak at 3330.86/cm. This peak was assigned to the group of O-H stretch that specifies the bonded hydroxide in the OPF samples and also conduct the asymmetric and symmetric stretching of N-H bond. The moisture present in the OPF shows in the form of O-H group in the peak. The presence of phenolics alcohols associated with lignin of the OPF structural unit and amines from the protein content in the OPF was established by the O-H and N-H stretching. One other medium peak has been observed at 1613.17/cm which refers the C=C stretch (conjugated alkene, alkene, cyclic alkene) present in the OPF. A two strong absorption peak is also seen in 1236.87/cm which refers to the C-O stretching (alkyl aryl ether) and 1027.68/cm which implies the presence of functional group C-N stretching (amine) in the OPF. [18]

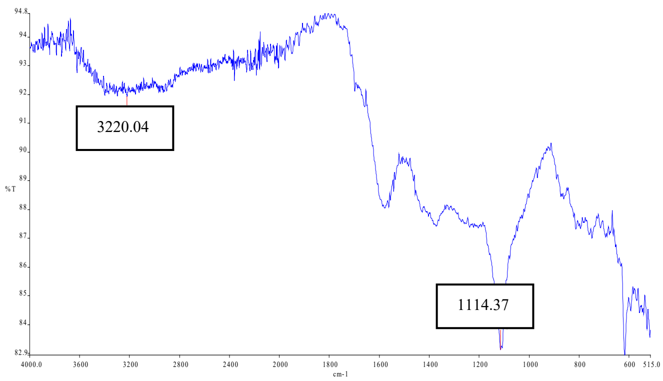

Fig. 4: FTIR Spectra of Bio-char at 400ºC

Figure 4 showed the FTIR spectra of bio-char at temperature 400ºC. There are two peaks formed which are 3220.04/cm that refers to N-H stretches since it was medium in intensity but broader in appearance. Nitrogen gas as a carrier gas during pyrolysis has created a new bond with the released H_2 from OPF. The strong absorption peak at 1114.37/cm refers to C-O stretching (aliphatic ether, secondary alcohol). As the pyrolysis occur at 400ºC, peaks O-H stretch, C=C stretch and C-N stretch disappear due to the acceleration of dehydration reaction and the cracking of volatiles matters during the pyrolysis.

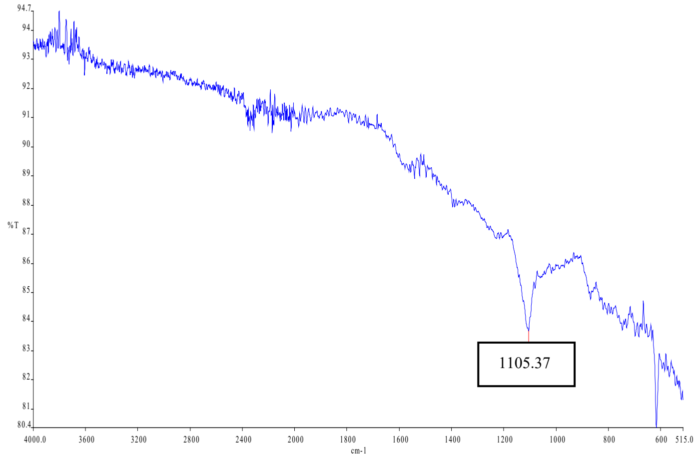

Fig. 5: FTIR Spectra of Bio-char at 500ºC

Figure 5 showed the bio-char at temperature 500ºC have a strong absorption peak at 1105.37/cm which represents the C-O stretching of (aliphatic ether, secondary alcohol). As the temperature increased to 500ºC, the functional group of N-H stretch being eliminated.

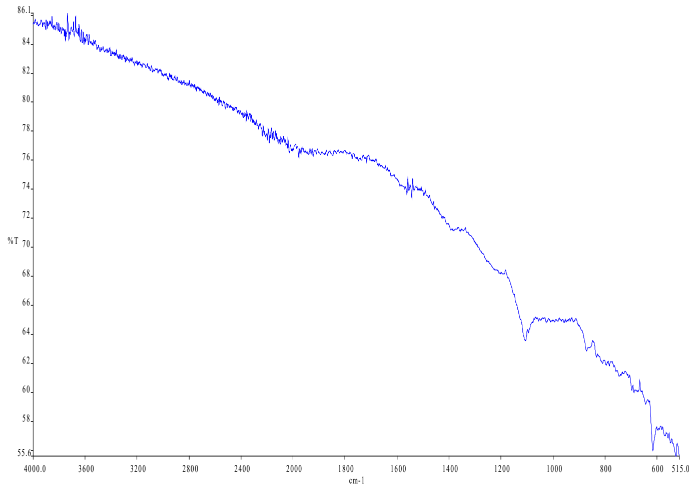

Fig. 6: FTIR Spectra of Bio-char at 600ºC

At the temperature of 600ºC, the spectra revealed the continuous loss of all functional group, which no occurrence of the bands in the 515 – 4000/cm. The symmetric C-O stretching for the OPF began to disappear with the increasing pyrolysis temperature. This result was due to functional group have rupture and progressive carbonization.

IV. Conclusion

Bio-char that were produced from OPF feedstock have different trend of chemical properties depending on the temperature. From this research project, it found that bio-char produced from OPF have a great potential in terms of improving soils and effectiveness in various application. Future research will be coordinate toward connecting bio-char properties from this finding to be use as an energy resource or for soil adsorption of pollutants.

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