The characteristics of palm oil plantation solid biomass wastes as raw material for bio oil

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Abstract. Indonesia is the largest palm oil plantations estate in the world. It reached 11.30 million hectares in 2015 and increased up to 11.67 million hectares in 2016. The advancement of technology recent, the solid waste of palm oil plantation can be reproduced become bio oil through pyrolysis hydrothermal process and utilized for biofuel. The purpose of this research was to analyze the characteristics of feedstock of bio oil of solid waste of palm oil plantations estate. The feedstock used was derived from solid waste of palm oil plantations in Riau Province. Characteristic analysis of waste oil included chemical compound content (cellulose, hemicellulose, lignin), ultimate analysis (C, H, N, O, S) to know height heating value (HHV). The result of analysis of chemical content showed that solid waste of palm cellulose 31.33 – 66.36 %, hemicellulose 7.54 – 17.94 %, lignin 21.43 - 43.1. The HHV of hydrothermal pyrolysis feedstock was 15.18 kJ/gram - 19.57 kJ/gram. Generally, the solid waste of palm oil plantations estate containing lignocellulose can be utilized as bio oil through hydrothermal pyrolysis. The CG-MS analysis of bio oil indicated hydrocarbon contents such as pentadecane, octadecane, hexadecane and benzene.

1. Introduction
Indonesia has the largest palm oil plantation field in the world with 11.67 million ha, that produced 33.50 million tons of Crude Palm Oil (CPO) in 2016 [1]. CPO produces biomass solid wastes not only on the plantation but also in the palm oil mill. The palm oil plantation wastes consist of trunks and fronds, while mill wastes consist of processed fresh fruit bunch that, in turn, produces empty fruit bunches (EFB), palm kernel shells (PKS) and mesocarp fibers (MF). The biomass solid wastes have already been utilized to fulfill some needs such as trunks and fronds to substitute wood, empty fruit bunches to substitute compost material, kernel shells, and mesocarp fibers as boiler fuel in the palm oil mill.

Fossil fuel used as driving force for the machine has already reported causing environmental pollution through the emission of gases. The limitation in the use of fossil fuel has been implemented by mean of utilizing renewable energy such bio oil. Bio oil can be created by taking advantage of biomass.
through a process called pyrolysis. The advantage of using bio oil as an energy source is that it reduces gas emission, decreases CO$_2$ emission level in the atmosphere that leads to a decrease in green house effects.

Biomass is considered as clean energy, because it contains negligible amount of nitrogen, sulphur and ash compared to conventional fossil fuels, which results in lower emission of SO$_2$, NO$_x$, and soot than do conventional fossil fuels [2,3]. In addition, CO$_2$ released from biomass is resolved into plants by photosynthesis.

The chemical composition of palm oil plantation biomass solid waste needs to be investigated in order to obtain characteristics that fit the need of bio oil raw materials. One of the raw material requirements in the burning process is a biomass waste that contains lignocellulose. The aim of the present study was to analyze the characteristics of bio oil raw material from palm oil plantation biomass solid waste and determine the characteristics of bio oil from selected waste materials. The results of the present study are expected to determine raw material criteria and production process of bio oil in a specific and sustained way (zero-waste concept).

2. Materials and Methods

2.1. Biomass Powder Preparation
Palm oil plantation solid waste consisting of fronds, trunks, empty fruit bunch, palm kernel shell and palm mesocarp fiber were brought from a palm oil plantation in Riau Province. Biomass was processed into powder at a size that passed through a 40-mesh size filter and restrained to a 60-mesh size filter (using a hammer mill).

2.2. The Analysis of Pyrolysis Raw Material Chemical Compounds
Prior to chemical components analysis, the generated waste powder was dried to reach a water content of 15%. Chemical components such as cellulose, hemicellulose, and lignin levels were analyzed by mean of TAPPI (Tappi 1989) [4] procedures. The ultimate analysis was using CHNO/S analyzer to determine the Carbon, Hydrogen, Nitrogen contents. The oxygen contents was determined by difference as following : $O = 100 - (C + H + N)$ [5]. The evaluation of chemical element components such as carbon, hydrogen, nitrogen, oxygen, and sulfur in palm oil biomass waste was performed in reference to ASTM D 3172 – D 3175 [6].

2.3. Pyrolysis Of Biomass Solid Waste
Biomass solid waste pyrolysis was carried out by mean of a hydrothermal reactor that can operate up to a maximal temperature of 350 °C. BSW powder was processed into a size of 40 mesh which was mixed with EFB liquid smock at a ratio of 1:1 and Hydrogen gas flowed across the reactor at a pressure of 10 bar. The reactor was turned on and left on to reach a temperature of 350 °C and a constant heat was maintained for an hour. Afterward, the mentioned reactor was switched off and left for 24 hours. Subsequently, fractionation was performed to obtain liquid smock and bio oil. During the fractionation process, the reactor was turned on to reach a maximal temperature of 400 °C (until the total absence of condensed smock). The high heating value (HHV) determination was carried out by analyzing the chemical element components of bio oil and the chemical compound content using a GC-MS device.

3. Results and Discussions

3.1 The characteristics of palm oil plantation solid biomass wastes
Palm oil plantation biomass solid wastes such as fronds, trunks, empty fruit bunch (EFB), palm kernel shell, and palm mesocarp fiber can be used as fuel energy source. Energy conversion can be carried out by direct burning, pyrolysis, gasification, and torefaktion. The characteristics of a biomass will
affect its role as fuel. Palm oil biomass waste contains lignocellulose (cellulose, hemicellulose) and lignin that play roles in energy conversion processes such as pyrolysis. Figure 1 determined the characteristics of palm oil biomass waste, from which the most suitable waste will be determined as raw material for pyrolysis that produces bio oil.

![Figure 1. The characteristics of palm oil plantation solid biomass wastes](image)

The dominant chemical compounds in palm oil biomass waste are lignocellulose (cellulose, hemicellulose) and lignin. The mentioned chemical compounds are the main materials for the pyrolysis process to produce a liquid product, charcoal, and gas. Pyrolysis is a thermal decomposition occurring in the absence of oxygen at high temperatures (300 °C – 500 °C) [7,8]. According to [9], there are fundamental differences in characters when the process of pyrolysis is carried out with cellulose, hemicellulose, and lignin, and during the process, the first to unravel is hemicellulose at 200 – 315 °C, while cellulose starts to unravel at 300 -355 °C with a thick residue. Lignin ravels at a temperature of 160 – 900 °C. Pyrolysis results using cellulose and hemicellulose produced organic compounds (C=C, C=O-C), while lignin was observed to produce more methane gas compound (CH₄) due to the fact that it perfectly unraveled at high temperature (900 °C) [10,11]. The present research was aimed at producing liquid product i.e. bio oil at a temperature of 300 – 350 °C.

The characteristics analysis results of palm oil biomass (Figure 1) through chemical component and proximate analyses revealed that lignocellulose compound was higher in trunks, fronds, and EFB, while the highest heat value was observed in Palm kernel shells and EFB. Lignin percentage was higher in palm kernel shells compared to other wastes, and when used as pyrolysis raw material, it will produce the acid compound. However, if a lignocellulose content material is used as raw material in pyrolysis, it will result in the production of flammable compounds such as phenol.

3.2 Pyrolysis of Empty Fruit Bunches (EFB)

Empty palm oil bunches used in the present study were processed into powder with a size of 40 mesh and a water content of 12 %. Pyrolysis uses hydrothermal process (slow pyrolysis) by adding liquid smock from EFB. The ratio between the liquid smock and EFB powder was 1:1, and the maximal temperature was 350 °C with a hydrogen bar of 10. The pressure during pyrolysis process ranged between 60- 85 bar. The purpose of adding Hydrogen gas to the process was to accelerate the termination of carbon chains that influenced the obtained bio fuel. The pyrolysis of EFB using
hydrothermal reactor resulted in 2 types of the liquid i.e. liquid smock and a thick black liquid called bio oil as shown in Figure 2.

Figure 2. Liquid yield from hydrothermal pyrolysis

Hydrothermal pyrolysis of the remaining lignocellulosa solids took place at higher temperature, producing intermediates that could undergo an extraordinary variety of reactions such as isomerization, dehydration, fragmentation and condensation reactions and ultimately form liquid oils, gas and char [12]. The present research focused on the bio oil and the results of the characterization analysis revealed that the liquid had a pH of 5 which was close to the normal pH (in general, bio oil pH is relatively low). In Table 1, a significant difference, in terms of water content, was observed in a research conducted by [13] that resulted in high water content. Indeed, the high the water content is, the low the burning value. Besides water, a high oxygen content is not needed in fuel burning process. Indeed, the HHV value in the present study was close to that of fossil fuel used in motorized vehicles.

| Component | Bio oil | Bio oil a | Light Fuelb | Heavy Fuelb |
|-----------|---------|-----------|-------------|-------------|
| Moisture  | %       | 15 – 30   | 65          | -           | -           |
| pH        | 5       | -         | -           | -           |
| C         | %       | 76        | 86,0        | 86,0        | 85,6        |
| O         | %       | 10,69     | 78,83       | 0           | 0,6         |
| H         | %       | 9,51      | 9,64        | 13,6        | 10,3        |
| S         | %       | 1,91      | 0,02        | < 0,18      | 2,5         |
| N         | %       | 1,90      | 0,2         | 0,2         | 0,6         |
| Higher Heating Value (HHV) | MJ/kg | 39,19 | 30,58 | - |
| Low Heating Value (LHV)    | MJ/kg  | 37,12     | 28,48       | 40,3        | 40,7        |

a [14], b [15]

From Table 1, the chemical composition of bio oil was complex mixture of degradation product of EFB constituents namely cellula, hcellululosa and lignin. The bio oil composition depends on type of raw material (biomass) and the pyrolysis condition [16]. The GC-MS analysis was carried out to observe the chemical compound content that was close to that of an environmentally friendly fuel. The presence of pioneer compounds that could be developed into fuel was the hydrocarbon group or easily flammable compound. The GC-MS analysis result is presented in Table 2 and phenol compound was observed to be the most dominant compound (56.6%), followed by hydrocarbon (19.5%) and acids (3.43%). The presence of hydrocarbon compounds that are easily flammable such as pentacene, Hexadecene, Heptadecene, Octadecene and other compounds are potential compounds to be
developed into alternative fuel with upgrading process. Side product of bio oil are charcoal and gases can use more application such as activated carbon using various activation methods and use as absorbents to eliminate pollutants in wastewater treatment [17].

Table 2. The GC-MS analysis dominant result of bio oil chemical compound

| Chemical compound           | Value (%) |
|-----------------------------|-----------|
| Phenol (3,5-Dioctoxyphenol)  | 56.6      |
| Acetic acid                 | 3.43      |
| Tetradecane                 | 2.71      |
| Pentadecane                 | 8.17      |
| Hexadecane                  | 1.57      |
| Heptadecane                 | 2.19      |
| Tridecane                   | 2.07      |
| Heptadecanone               | 1.25      |
| Cyclopentanone              | 1.01      |
| Benzene                     | 3.01      |
| Decane                      | 1.41      |

4. Conclusions
Research on bio oil raw material characteristics from palm oil plantation solid waste such as fronds, trunks, empty fruit bunch (EFB), palm kernel shell and mesocarp fibers showed that each material contained different lignocellulose and lignin levels. The results of the present study revealed that the raw material required for pyrolysis (to produce bio oil) is the one that contains high cellulose level with a high HHV value and a low lignin. Pyrolysis results of EFB in producing bio oil revealed the presence of hydrocarbon that can be developed into fuel to substitute fossil fuel.

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