# PRODUCTION AND CHARACTERIZATION OF BIO-OIL FROM PYROLYSIS OF GAHARU WASTE

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*Abstract*— **Gaharu is known as the most expensive wood in the world because it can be used in many cultures for its distinctive fragrance, and used extensively in incense and perfume. However, the gaharu residue are still not been used for any purpose and just been drawn as waste. In this research, the gaharu waste was used to produce bio oil as alternative for replaced the depending on the petroleum source. The method used for the experiment was slow pyrolysis. Firstly, the gaharu waste was collected at Bukit Larut, Kuala Lipis and then dried it at room temperature before ground and sieved it for the experiment. The reactor used in this research was fixed bed reactor with electrical furnace heat externally. The mass of the product bio oil produced was measured to analyze the percent yield of bio oil obtained. The experiments were conducted at differences range of temperature that are 400, 500 and 600 ˚C. The heating rate used was constant at rate 1000°c/min and the nitrogen supply at flow rate 0.5 liter/min. The product of bio oil then characterized using Fourier Transform Spectroscopy (FTIR),Gas Chromatography (GC-MS), Bomb calorimeter and CHNS analyzer, Thermo gravimetric Analysis (TGA). From the result obtained after pyrolysis, at the temperature 500°c was indicated as the best condition to give the highest product yield. The maximum yield of the bio oil produced from these conditions was 26.8%. Based on GCMS and FTIR analysis, it was shown that the pyrolysis oils from gaharu waste contains complex compounds mostly functional groups of phenol, alcohols, ketones, aldehydes and carboxylic acids,aromatic and also carbonyl structures. The heating value for the bio oil produced also lower than petroleum that was 23.75 MJ/kg.**

*Keywords*—**Biomass, Bio-oil, Gaharu waste, Pyrolysis, Bio-oil characterization.**

## I. INTRODUCTION

Biomass, wood, wind, sunlight are some of the renewable form of energy resources that are finite or exhaustible to obtain and has high potential to use for energy production. However, these types of renewable energy are less applied in the industries and transportation usage compare for our primary energy supply like fossil fuels, petroleum, charcoal that are exist as non -renewable energy. The excess use of non-renewable energy may cause a major pollution to the sea, land, environment, increased concentration of acid rain as well as can cause high release of greenhouse gas such as sulphur dioxide ($SO_2$), nitrogen dioxide ($NO_2$) and carbon monoxide (CO) to environment.

Biomasses process is one of the primary renewable energy in the world that are include wood waste, industrial and agriculture residue, municipal solid waste, and animal waste. According to Sukiran *et al* (2011) the biomass consumption get high attention from most developing countries due to their economy value mostly based on agriculture and forestry. The highest potential for energy from biomass is considered the renewable energy source that contributed to the energy desires of modern society for the developed and developing economies global (McKendry, 2002). The product from biomass naturally contain high percent value of hydrogen and produce a larger volatile component as well as produces a more reactive char after devolatilization or pyrolysis. Besides, the biomass feedstocks also has high content of hydrogen and carbon and it can be converted into valuable fuel and other chemical product (Phillips *et al*,.2016). The technology of the biomass become attract most of the industries to use these source as their primary source to obtain energy for industrial use other than use the fossil fuel and coal which is non-recycle resource.

Biomass is a process that can produce large energy in variety of way such as biochemical and thermochemical. The biochemical process including fermentation and anaerobic digestion, while for the thermochemical like the process combustion, gasification and pyrolysis (Salehi *et al*.,2009). However, pyrolysis is the most attractive thermochemical process because it is simplicity and higher conversion of biomass and it solid waste into liquid product. Pyrolysis process commonly used for converting biomass into three different phases there are liquid phase called bio oil or bio fuel, which is mixture of water and organic molecules, produce a solid phase that is known as bio-char which is residue product from the pyrolysis process and other phase is non-condensable gases. This is a process of thermal decomposition of organic component that can produce high quality of the yield tar like bio oil, bio fuel and bio crude without present of oxygen and the optimum temperature is about 500˚c (Islam *et al*,. 2010). In this process the feed material is put in the fixed bed pyrolysis reactor and heated at the high temperature. Furthermore, the inert gas like nitrogen gas is used for assisting the gases mixture to dispose of the reactor.

The bio oil or crude oil produce from pyrolysis process contains carboxylic acids, alcohols, aldehydes, esters, ketones, heterocyclic derivatives and phenol compound. (Demiral *et al*.,2012). These compounds very useful as a fuel for produce energy. The advantages of bio oil are easily to transport and store.

It can be transported cost effectively to centralized refineries and can be as feedstock for producing Fisher-Tropsch fuel from syngas, when the liquid use as gasifier feedstock (Mullen *et al*,.2010). Besides that, bio oil also used as feedstock in the process of refineries petroleum for produced high value of chemical product.

There are some of the plant that have potential to used for pyrolysis process in order to producce of bio oil such as corncorb, sugarcane bagasse, empty fruit bunch and gaharu. Gaharu also known as agarwood is a resin product which is produced from particular trees and get high in commercial value and it is one of the most expensive wood in the Malaysia and world. According to Santoso *et al* (2011) gaharu is the rare product of two to four classes in the family *Thymelaeaceae*, with *Aquilaria Agallocha* and *Aquilaria Malaccensis* the is indicate as best known species. Gaharu has been used since back during our ancestor time as a fragrant wood that is widely used for religious, medicinal and aromatic preparations (Zich *et al.,* 2001). Gaharu essential oil is highly demand from most of the country including Malaysia due to the special usage of this plant. They are use them for religious ceremony, in perfume and toiletry product such as soap, shampoo and use as a traditional medical preparation (Ismail *et al*.,2014). Mostly, gaharu oils are mixture of sesquiterpenes, sesquiterpene alcohols, oxygenated compounds, chromone derivatives and resin (Nik Yasmin *et al.,* 2008). The amount of chemical compound present in the gaharu can identify their quality and grade of the gaharu.

The effect of reaction condition in the study is reaction temperature in furnace on the product yield in a batch slow pyrolysis system were investigated using fixed bed reactor in order to determine the optimum pyrolysis temperature to produced maximum yield of bio oil. Moreover, the pyrolysis product such as bio oil from gaharu waste, obtained at the conditions of maximum product yields then were analyzed by using gas chromatography (GCMS), Fourier Transform Infrared(FTIR), Bomb Calorimeter, Thermogravimetric (TGA) and Elemental Analyzer CHNS to determine possibility of the bio oil to be used as one of the source of renewable fuel.

## II. METHODOLOGY

### A. Materials

The gaharu waste sample in this study has been taken from Bukit Larut, Taiping. For the experiment, the gaharu waste sample was dried in room temperature for a day, grounded in a high speed rotary grinder and then sieved it to get small size. The particle size range was between 0.40 mm < dp <0.6 mm. Then, the sample was dried overnight at 100˚c in the oven to reduce the moisture content.

### B. Fixed Bed Pyrolysis Temperature

The major components of the system of pyrolysis are fixed bed reactor, furnace heater, liquid condenser and iced cooled liquid collectors. The dimension of the reactor is 47cm in length and the diameter is 7.8cm. The volatile material produced from the reactor passed through two sequential condenser to 10˚c. Nitrogen gas was supplied to the reactor in order to maintain the inert atmosphere in the reactor and also to dispose the pyrolzed vapor products to the condenser. The pyrolyzed vapor then condense into liquid product in the condenser as bio oil and collected in bio oil collector. The bio oil product were weight using measuring balance in order to get the yields of the liquid produce

### C. Experimental Procedure

The 250g of gaharu waste sample are weight by measuring balance then put it in the fixed bed reactor which is connected to the nitrogen gas tank. In order to determine the operating condition that can give maximum product for bio-oil yield the three different types of temperature are used in this experiment there were 400°c, 500°c and 600°c. This experiment was conducted with a condensation temperature of -10˚c. The nitrogen gas are used to move the pyrolyzed vapor was at 0.5 Liter/min and the heating rate also fixed constant at rate 1000˚c/min. The apparatus was held at adjusted temperature in 60 min or until no release of gas is detected. Liquid product were condensed in ice cooled traps. The yield of the oil produced also can be calculated by using the yield formula.

$$yield\ (\%) = \frac{amount\ of\ product\ (g)}{total\ mass\ feed\ (g)}\ x\ 100$$

### D. Characterization

The sample of gaharu waste was analyzed by Elemental Analyzer CHN-OS (FlashEA) to determine the elemental content and Thermogravimetric (METLER TOLEDO) analysis also perform to determine the moisture content and fixed carbon contain in the sample. The gross calorific value in the sample also can be determined by using Bomb Calorimeter (IKA WERKE) .We also conduct these type of analysis method for the bio oil produce after the pyrolysis. Table 1 show the elemental analysis and the calorific value of biomass raw material gaharu waste before pyrolysis.

**Table 1: Main Characteristic of Gaharu waste**

| | |
|---|---|
| Elemental analysis (wt%) | |
| Carbon | 49.32 |
| Hydrogen | 5.35 |
| Nitrogen | 0.63 |
| Oxygen | 44.70 |
| Heating Value (MJ/kg) | 17.34 |

Besides, after the pyrolysis of the gaharu waste, the functional group that present in the bio oil was analysed by using Perkin-Elmar Model Fourier Transform Infrared (FTIR) spectrometer. Bio oil of gaharu contains hundreds of chemicals compound, accurate analysis result of bio oil are difficult to obtain using the existing gas chromatography equipment. Therefore, gas chromatography (CGMS) was carried out in order to indicate the chemical compound in bio oil. The GC-MS analyses was performed on Agilent technology model with Varian 450-GC system equipment with Varian 240 mass spectrometer., fitted with capillary coloum with dimension 30m x 0.25m x 0.25um. The injector and detector temperature was 180˚c with carrier gas helium was use as carrier. GC oven was heated to 60˚c for 1 minute then increased to 270˚c at the rate of 6˚c/min and the hold time for 10 minutes. Then, one microliter of bio oil from gaharu was dilute with hexane solution and take one micrometer of the solution and injected into the coloum. Moreover, to determine whether the bio oil meet regulatory requirements for industrial fuels the Bomb Calorimeter had been used in the analysis product. The value of gross caloric value obtained from the analysis then compare with the commercial calorific value such as diesel and petrol.

## III. RESULTS AND DISCUSSION

### *A. The effects of pyrolysis temperature on yield of the product*

**Figure 1:** Bio oil produce from pyrolysis of gaharu waste

Figure 1 it can be seen obviously the the yield of liquid produce at temperature 500°c is at 26.8% of yield are higher amount compared to the temperature 400°c and 600°c which are 26% and 24% of yield produce. The production of bio oil yield are low at the lower reaction temperature due to the reaction temperature was not high enough for complete fast pyrolysis (Park *et al*.,2008) and the heat was sufficient to break hemicellulose compound only and mainly produce gas carbon monoxide(CO) and carbon dioxide ($CO_2$) gases (Pulun *et al*.,2005).However, when the temperature increseased the cellulose were break down first then at the high temperature also, the lignin began to crack down to form char, water and heavy oil. The yield of bio oil produced increased vigorously at temperature 500°c. According to Salehi *et al*.,2009 the maximum liquid yield can be obtained at the reaction temperature 500°c with high heating rates and short vapour residence times .This is due to the decomposition of organic and specific product and secondary volatiles at temperature above 500°c (Salehi *et al*.,2009).Besides, when the temperature higher than 500°c the amount bio oil yield will be decreased slowly. This is because of the thermal cracking of the gaharu occur and make the oil content and moisture content in the plant decreased.On the other hand, based on the result the yield of char form were increased when the temperature of furnance low. The yield of char is getting higher at the temperature 400°c compared to the other temperature while the yield of the gas produce are higher at the temperature 600°c. The higher treatment temperature can led to bio cracking of the plant resulting higher gas yield, lower bio oil and bio char yield (Demiral *et al*.,2012).Furthermore, the increased in gas yield is due to secondary cracking of the pyrolysis vapors at higher temperatures. The secondary decomposition of the char at higher temperatures can produce non condensable gaseous products, and may cause increase of the gas yield (Laresgoiti *et al*.,2004) .Figure 2 show the graph of product of liquid, char and gases form after the pyrolysis of gaharu waste in the three different types of temperature.

**Table 2: Characteristic of Bio Oil**

| | |
|---|---|
| Elemental analysis(wt%) | |
| Carbon | 58 |
| Hydrogen | 7.38 |
| Nitrogen | 0.43 |
| Oxygen | 34 |
| Heating Value (MJ/kg) | 26.64 |

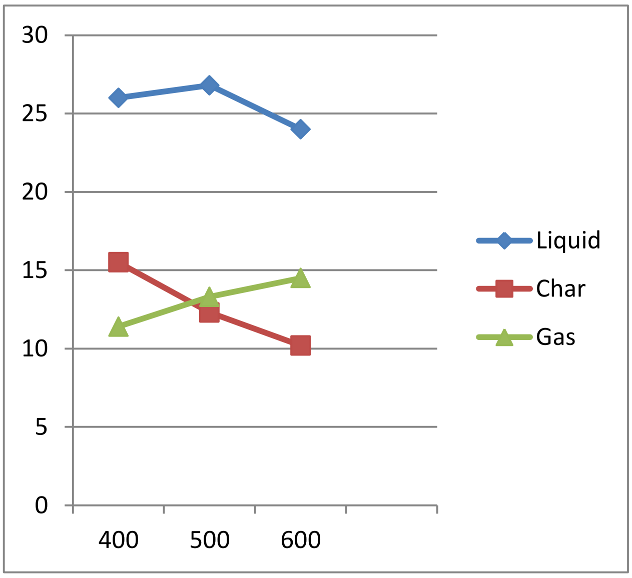


**Figure 2**: Yield of bio-oil, bio-char and gases pyrolysis form (%)

### *B. Characterization*

The elemental composition and heating value of bio oil are shown in table 2. The amount weight percent of carbon is the highest value that is 58% and the sulfur content is the very little in the bio oil of gaharu. The oil composition also contains low oxygen content than the original feedstock. According to Demiral *et al* (2009) the production of transport fuel not favorable for the oil which content high oxygen content because they are tendency to produce high amount of carbon monoxide (CO) and carbon dioxide ($CO_2$). Besides, the calorific value of the gaharu bio oil obtained after analysis is 26.64 MJ/Kg at pyrolysis temperature 600°c. This value was not as high as the calorific value of the commercial heating oil which is around 25-40 MJ/Kg (Salehi *et al*.,2009).

The Fourier Transofrm Infrared (FTIR) spectra of bio oil with different temperature are given in figure 3. The bio oil contains high amount of phenols and alcohol. At the temperature 400°c alcohol group stretch appear at the peak 3314.24cm$^{-1}$. There are also exist a peak at wavelength 1635.03cm$^{-1}$ that present for amides (C=O) and alkenes group (C=C). At this temperature also indicates the present of the ketone group at the 1279.23cm$^{-1}$.The present of carboxylic acid is indicated by the absorbance peak of O-H vibration between 3400-2400 cm$^{-1}$ when the pyrolysis temperature at 500°c. The peak carboxylic acid is started to increase at wavelength 3326.35 cm$^{-1}$. There are also increased in alcohol content group at to the peak 3326.35 cm$^{-1}$. The absorbance peak at 1635.26 cm$^{-1}$indicates the present of the alkenes, amines and aromatics group.. According to Lievens *et al*.,2011, FTIR spectra of bio-oil in the range of 1490-1850 cm$^{-1}$ could provide detailed information on various carbonyl group in bio oil. This is shown that the biomass sample contains of cellulose, hemicellulose and also lignin (Chen *et al*.,2010). The amount of carboxylic acid and alcohol are decrease at peak 3320.04 cm$^{-1}$ when they are heat at the 600°c.Two peak are start to appear at the wavelength 2923.99cm$^{-1}$and 2853.38 cm$^{-1}$. These small peak represent the functional group of aldehydes (C-H).At the peak 1634.50 cm$^{-1}$ there are indicated the present of amine and alkene groups. Alkanes group ($CH_2$) also exist at the peak 1456.88 cm$^{-1}$ and also present of the ethers and ketones group at the peaks between 1300 to 1000cm$^{-1}$. The liquid fraction in the bio oil contains numerous types of functional group such as carboxylic acid, alcohols, esters, ketones, aldehydes, heterocyclic derivatives and phenol compound (Demiral *et al*.,2012).

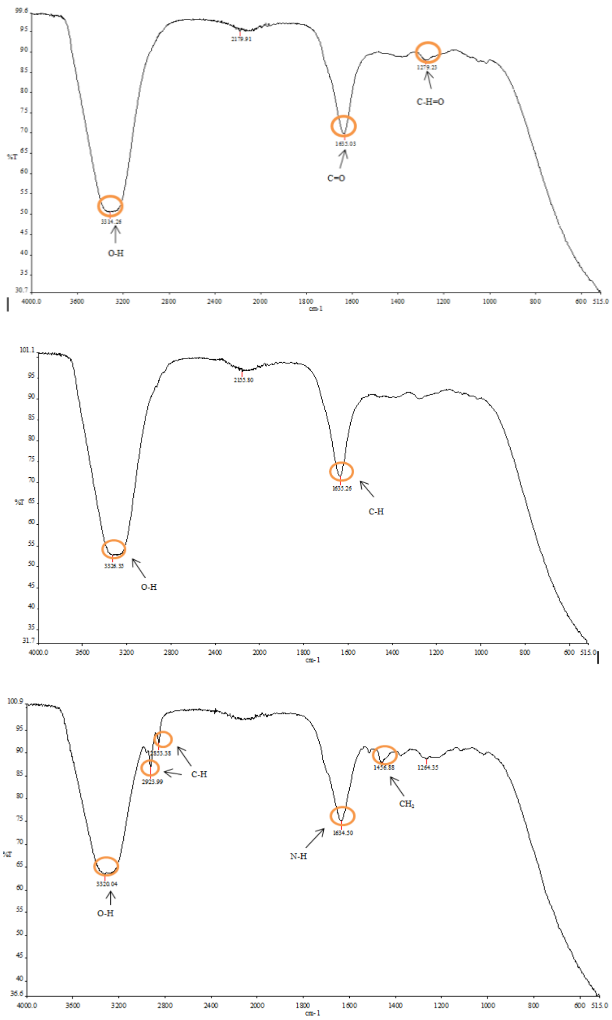

**Figure 3:** The FTIR Spectra of bio oil at the temperature a) 400°c b) 500°c and c) 600°c

GCMS is use in this study to determine the chemical compound present in the bio oil of gaharu. From the result obtained, about more than 25 compounds were determined in the bio oil of gaharu in temperature 400°c and more than 26 compound present in temperature 500°c and only about 19 compound are indicated in the pyrolysis temperature 600°c. The determined products were categorized into seven major functional groups including phenols, aldehydes, ketones, acid, benzene and alcohol and we found that phenol compound is the major component contains in the bio oil, they are including piperidin-1 methyl, phenol 4 methyl, phenol 3,4-dimethyl, phenol- 3-ethyl, 2-butonone,3 phenyl, phenol 2-metxoy-4-methyl that are present in the 400°c pyrolysis of bio oil. Where, in the pyrolysis temperature 500°c they are present of compound such as phenol 2 methyl, phenol 3,4 dimethyl, phenol 3 ethyl, phenol 2-methoxy-4-methyl, 2-butone 3-phenyl and phenol 4 methyl. Besides, at temperature 600°c the compound present are piperidine, 1 methyl, 1H-imidazole,2-propyl, phenol 2 methyl, phenol 4 methyl, citronellyi isobutyrate, phenol 3 ethyl, Phenol, 2-methoxy-4-methyl and 2-butane,3-phenyl. The common substructure in lignin is 2-methoxyphenol and this compound are present in bio oil after pyrolysis(Salehi *et al.*,2009). Lignin also can be converted to phenolic compound by the process of thermal degradation and this compound can be used as intermediates in synthesis of pharmaceuticals, synthesis of various types of polymer as well as can be used for production of adhesives (Kim *et al.*, 2015). Table 3 shows the component present in the gharu bio oil at differences temperature with their retention time, amount and purity component.

**Table 3:** Components in the Bio Oil at differences temperature.

| Temperature | Component | Retention Time(min) | Amount (%) | Purity(%) |
|---|---|---|---|---|
| 400°c | Piperidin-1 methyl | 3.958 | 0.00326 | 8.6 |
| | Phenol, 4-methyl | 5.540 | 3.05 | 91 |
| | Phenol, 3,4-methyl | 7.069 | 1.1 | 87 |
| | Phenol, 3-ethyl | 7.485 | 0.915 | 76 |
| | 2-Butanone,3-phenyl | 9.351 | 2.73 | 94 |
| | Caryophyllene | 11.038 | 0.0424 | 13 |
| 500°c | Phenol, 2-methyl | 6.349 | 2.02 | 93 |
| | Phenol-3,4-dimethyl | 9.158 | 1.21 | 86 |
| | Phenol 3, ethyl | 9.823 | 0.888 | 73 |
| | Phenol 2-methoxy-4 methyl | 10.769 | 1.14 | 78 |
| | 2-butone, 3-phenyl | 12.627 | 3.12 | 93 |
| | Phenol, 4 methyl | 13.961 | 0.0591 | 20 |
| 600°c | Piperidin-1 methyl | 4.368 | 0.00669 | 20 |
| | 1H-1 midazole, 2-propyl | 8.765 | 0.00665 | 36 |
| | Phenol, 2-methyl | 11.753 | 0.748 | 81 |
| | Phenol, 4-methyl | 12.656 | 1.18 | 82 |
| | Citronellyi | 15.892 | 0.0247 | 47 |
| | isobutyrate | 18.818 | 0.399 | 83 |
| | Phenol, 3-ethyl | 17.894 | 0.744 | 90 |
| | Phenol, 2-methoxy-4- methyl | 20.174 | 1.19 | 79 |
| | 2-Butone,3-phenyl | | | |

## IV. CONCLUSION

Biomass process is indicated as the best alternative renewable source which important to reduce depending to fossil fuel source. Biomass technology also can help to reduce the environmental impact from dirty gas emission. Pyrolysis process is the best conversion technologies among thermochemical process to liquefaction and convert biomass to different product. Gaharu waste is the best organic compound that can give high quality of bio oil from pyrolysis process.

In this study, gaharu waste sample was pyrolysed in the fixed bed reactor at different temperature. The maximum oil yield of 26.8% was produced at the pyrolysis temperature of 500°c at the constant holding time for 5 minutes and the nitrogen supply at flow rate 0.5 liter/min. The higher calorific value of bio oil is 23.75 MJ/Kg and this value is closer to the petroleum fraction which is 40 MJ/Kg. FTIR and GCMS analysis showed the bio oil composition contains complex compound mostly composed of alcohol, carboxylic acid, ketones, aldehydes, aromatic and carbonyl structure.

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