Characterizations of Bio-char from Fast Pyrolysis of Meranti Wood Sawdust

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Abstract. In this research, Meranti wood sawdust (MWS) was pyrolyzed in a fixed bed drop-type pyrolyzer under an inert condition. The first part of the study is to determine the influence of pyrolysis temperature (450, 500 and 550 °C) on the yield of pyrolysis products. Pyrolysis of the waste MWS material generated the highest amount of bio-char with approximately 38 wt.% at pyrolysis temperature of 450 °C. Next, the char product (from pyrolysis at 450 °C) was analyzed to compare its characteristics with the raw MWS feedstock. The major component of the char is carbon element, significantly contributed to its high calorific value. TGA profile shows the MWS char could withstand high temperature of up to 400 °C. Under extensive heating, particle size of the bio-char from SEM images decreased due to breakage and shrinkage processes.

1. Introduction
Depleting fossil fuel resources calls for alternative energy assets. Economic and environmental concerns are the main driving forces for exploiting new sustainable sources of fuel. Biomass is one of the key potential energy resources in Malaysia to overcome increasing energy needs while being environmentally friendly. Malaysia produces many agricultural, plantation, and forestry residues which could be converted into valuable fuels and chemical products. These waste materials have no or little economic values and often present as a disposal problem. In 2010, Malaysia’s annual log production was approximately 24 million m³ [1]. Multiplying by the ratio of wood waste of 0.78, about 18 million m³/year of wood waste was generated [2]. Among hardwood waste, Meranti wood sawdust (MWS) is a significant residue from logging and deforestation in Malaysia [3]. Meranti is a local and common name or otherwise scientifically known as Shorea sp. [3].

Thus, there is a need to convert these by-products into useful and profitable bioenergy and biomaterials products. One of the promising techniques to accomplish that is through a fast pyrolysis process. Fast pyrolysis is the heating of an organic material, for instance wood, at a high temperature (450 to 550 °C) and short retention time (a few seconds of vapor product), in the absence of oxygen or air. So, the material does not combust as no oxygen is present. However, the three main biomass pseudo-components of cellulose, hemi-cellulose, and lignin that form the material are thermo-chemically decomposed into charcoal and volatiles. Some of these volatiles could be condensed into liquid, called bio-oil. All that is left is the carbon latticework of the charred material, called bio-char [4,5]. So, pyrolysis of lignocellulosic biomass yields three products: one liquid, bio-oil; one solid, bio-
char, and one gaseous, non-condensable gas. Therefore, pyrolysis of waste materials into pyrolysis products could add a substantial economic value and promote a greener environment [5,6].

Pyrolysis of different biomasses produces different yields and characteristics of products. Meranti wood has been chosen for this study because for the meantime, pyrolysis of Meranti wood research has not been reported in any literature. The aims of this study are to determine the effect of pyrolysis temperature on the products yield and to analyze the MWS feedstock and its bio-char product.

2. Materials and methods

2.1. Preparation of raw materials
Meranti wood sawdust was collected from sawmills in Perak, Malaysia. The biomass was dried in a drying oven (Memmert, 100-800 model) for 24 hours at 105 °C to minimize the free moisture that could affect the performance of pyrolysis reaction [4]. Then, the biomass was sieved to the size range of 0.15-0.5 mm. By referring on the author’s previous research review, smaller particle size favours higher rate of fast pyrolysis reaction [6]. However, very small particles are difficult to handle. The raw feedstock is stored in an air-tight container.

2.2. Experimental setup
Figure 1 shows the schematic diagram of a fixed bed drop-type pyrolyzer used to carry out fast pyrolysis of the feedstock for the present study. The experimental setup was connected to vacuum and nitrogen gas lines used to create an inert condition. A biomass holder zone was created by closing two ball valves. The design would allow the biomass to drop inside the heated zone only after the desired temperature reached up. The pyrolyzer consisted of a cylindrical reactor made of stainless steel with 53 mm internal diameter and 155 mm height. The reactor was installed inside an electrical heater and was insulated to minimize heat loss. A thermocouple was inserted inside the reactor to record the pyrolysis temperature. The reactor was connected to two condensers to improve the condensation efficiency and immersed in a cooled ethylene glycol bath to condense the pyrolysis vapors into bio-oil at below -10 °C. The outlet of the vapor-trap was connected with a gas sampling bag to collect the non-condensable gases (NCG). The bio-char was accumulated in the reactor.

Figure 1. Schematic diagram of the fixed bed drop-type pyrolyzer [7]
2.3. Pyrolysis procedure
In all experiments, 10 g of feedstock was put into the reactor. The first part of the study is to determine the impact of pyrolysis temperature on the distribution of pyrolysis products. The biomass was dropped to the fast pyrolysis zone under several temperatures (450, 500 and 550 °C). Duration of the experiment was held at the selected temperature for 10 minutes. The pyrolysis reaction produced bio-char, bio-oil, and non-condensable gases. The char and bio-oil yields were determined based on the weight changes of the reactor and condensers, respectively, before and after the experiment. The mass of the char and bio-oil are given within the experimental error of < ±3 wt.%, as shown in Figure 2. The yield of non-condensable gases was calculated using a mass balance equation [7]:

\[
\text{Bio-char (wt.\%)} + \text{bio-oil (wt.\%)} + \text{NCG (wt.\%)} = 100 \text{ (wt.\%)} \quad (1)
\]

2.4. Analysis of feedstock and pyrolysis product
The second part involves the analyses of raw MWS and MWS char product from the pyrolysis reaction at 450 °C. The proximate analysis of moisture, ash, and volatile contents was performed according to ASTM E871-82, D1102-84, and E872-82 standards, respectively [8,9,10]. Fixed carbon content was determined by the difference of the three analyses. The elemental analysis was carried out using a Perkin Elmer 2400 CHN Analyzer. The O content was determined by the difference of the C, H, and N. The calorific value was measured by an IKA-WERKE C2000 bomb calorimeter. All the aforementioned analyses were repeated at least twice to verify the reproducibility and then averaged. Thermogravimetric analysis (TGA) was performed using a TA Instruments model QA50 with 60 mL/min of N\textsubscript{2} flow rate at a heating rate of 10 °C/min. Morphology analysis was done via a TM3030 Scanning Electron Microscopy (SEM).

3. Results and discussion
3.1. Impact of pyrolysis temperature on products yield
After each pyrolysis experiment, the products namely bio-char, bio-oil, and non-condensable gases were obtained. Calculation of pyrolysis products yield was based on mass percentage. It is well known that the key parameter among operational factors of pyrolysis reaction is the pyrolysis temperature [4,5,11]. For the present study, pyrolysis experiments of MWS were performed at various temperatures (450, 500 and 550 °C). The effect of pyrolysis temperature on products yield is illustrated in Figure 2. Pyrolysis of MWS generated the highest amount of bio-char with 38.7 wt.% at pyrolysis temperature of 450 °C. As pyrolysis temperature increased from 450 to 550 °C, the bio-oil and non-condensable gases yields increased. As contrast, the yield of char decreased because of the continuous volatilization reaction became more preferred. Similar pattern of pyrolysis products distributions were observed by other researchers [11,12,13].

![Figure 2. Pyrolysis of MWS](image)
The experimental setup of this study is a complete closed system. It is possible, therefore, that a high percentage of product recovery is anticipated. Based on the carbon balance calculation between input (feedstock) and output (pyrolysis products), the recoveries for the pyrolysis of MWS in this research was 98.6\%, by using the equation \[12\]:

\[
\text{Product recovery} = \frac{m_{\text{char}} + m_{\text{oil}} + m_{\text{gas}}}{m_{\text{feedstock}}}
\]  

(2)

3.2. Characterization of raw MWS and MWS bio-char

The main characteristics of the feedstock and char product samples are summarized in Table 1. As expected from the proximate analysis, moisture content of the bio-char has decreased when compared to the initial feedstock due to a dehydration reaction from the heating process. In addition, the moisture content for the raw MWS feedstock is low when comparing to other lignocellulosic biomass from colder countries, mostly contributed by the hot climate in Malaysia [11,13,14]. For ash content, it is easy to assume that the ash content is higher after the pyrolysis process. However, this data must be interpreted with caution because after multiplying the percentage of ash in char with the yield of char, the calculated ash content of the char remained constant. During pyrolysis process, some of volatile matter decomposed into vapors, hence showing a reduced amount of volatile matter in the char. In term of fixed carbon, more than half of the MWS char contained fixed carbon substance. This finding, while preliminary, suggests that the MWS char could withstand higher temperature.

| Properties                | Raw MWS          | MWS char         |
|---------------------------|------------------|------------------|
| Proximate analysis (wt.\%)|                  |                  |
| moisture                  | 6.2 ± 0.3       | 2.9 ± 0.2       |
| ash                       | 1.2 ± 0.1       | 3.0 ± 0.2       |
| volatile matter           | 69.9 ± 1.7      | 42.5 ± 1.0      |
| fixed carbon              | 22.7            | 51.6            |
| Elemental analysis (wt.\%)|                  |                  |
| C                         | 41.7 ± 0.1      | 84.9 ± 0.3      |
| H                         | 5.7 ± 0.1       | 2.3 ± 0.1       |
| N                         | 0.1 ± 0.1       | 0.4 ± 0.1       |
| O                         | 52.6            | 12.4            |
| Calorific value (kJ/g)    | 19.6 ± 0.8      | 28.5 ± 1.2      |

The major component of the char was carbon element, which had a composition of approximately double than the original feedstock. The calorific value of the char was significantly higher than the feedstock. These results might explain a good correlation between the carbon content and calorific value. There are, however, other possible factors such as the structural or chemical bond of the char that could affect the calorific value [4,11,13]. Some of the suggested applications for bio-char are as carbon sequestration agents, soil improvers, activated carbons or catalysts [13,14,15]. On the other hands, it is apparent that the calorific value of bio-char is very high, indicating a potential usage as a solid fuel. The calculated energy consumption of the experiment was approximately 7200 J.

Figures 3 and 4 display the thermogravimetric, TG (in wt.\%) and differential thermogravimetric, DTG (in wt.\%/°C) curves for the raw MWS and MWS bio-char. High rate of decomposition for raw MWS started approximately at 250 °C whereas for MWS char took place after 400 °C. The highest rate of decomposition for MWS char happened at approximately 650 °C. These findings further corroborate the previous statement that the MWS char could withstand to a higher temperature. It has been established that pyrolysis of lignocellulosic biomass could be divided into four stages which are dehydration (removed at temperature above 105 °C), followed by decomposition of hemicellulose which mainly occurs between 210 to 310 °C. It decomposes easier than cellulose or lignin as it comprises of amorphous structure and rich in branches. Next, cellulose is broken down at around 300 to 400 °C. Thermal stability of cellulose is higher than hemicellulose as it is made up of a long
polymer of glucose without branches. The activities of chemical bonds in lignin cover a widespread range which leads to the decomposition of lignin occurring in a broader range of temperature between 150 and 900 °C [4,16,17]. Based on the guidelines and TGA data, the lignocellulosic compound of a biomass could be estimated. Hence, Figure 3 shows the estimated lignocellulosic composition of the raw MWS.

**Figure 3.** TGA and DTG of raw MWS

**Figure 4.** TGA and DTG of MWS char
Figure 5 and 6 exhibit the morphology of the raw MWS and MWS bio-char. In this analysis, five measurements from five particle samples were performed. Focusing closely through the SEM instrument at 180x magnification, the particle size of the char decreased when compared to the raw feedstock, as shown in Figure 5. Further magnifying to microporous level, as shown in Figure 6, the structures of the feedstock undergo breaking and shrinking mechanisms from extensive heating, to form charred materials. The average vessel sizes decreased from 0.018-0.027 mm (MWS raw feedstock) to 0.010-0.013 mm (MWS char). These observations were consistent with the report by Alvarez et al. [14]. It is projected that the degree of structure breakage will increase with the higher pyrolysis temperature.

**Figure 5.** Comparison of raw MWS with MWS char (magnification: 180X)

**Figure 6.** Comparison of raw MWS with MWS char (magnification: 500X)

4. Conclusions
The effect of pyrolysis temperature on the products yield and the characterization of the bio-char were discussed. Pyrolysis of MWS generated the highest amount of bio-char with 38.7 wt.% at 450 °C. Major component of the MWS char is carbon element, with 84.9 wt.% and its calorific value is high,
which is 28.5 kJ/g. The particle size of the char decreased, due to the breakage of the structure from high heating of pyrolysis reaction. High decomposition rate for MWS char started approximately at 400 °C, indicating the char could withstand to a high temperature. A further study, which takes more varieties of wood feedstock into account, needs to be undertaken before the association between pyrolysis of different woody types and its pyrolysis products yield and characterizations are more clearly understood.

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