Torrefaction of Mangrove Wood by Introducing Superheated Steam for Biochar Production

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Abstract. Torrefaction by superheated steam was carried out over mangrove wood in a rotary kiln carbonizer. The mangrove wood was obtained from Kuala Sepetang, Malaysia. The current biochar production process still applies the traditional carbonization method, which requires 30 days in hot air. The torrefaction process using superheated steam was performed by manipulating the operating time at 30, 60, 90, and 120 min operating at 300°C. The high heating value (HHV) for raw mangrove wood to solid char product raised from 16.7 MJ/kg up to about 30 MJ/kg. The HHV was 29.7 MJ/kg after 60 min torrefaction. The carbon percent increases from 47.4% to above 70%. For bio-oil products, the superheated steam torrefaction produces various acids, alcohols, ketones, and aldehydes range from 249 ml to 335 ml. In contrast, torrefaction products via hot air carried-out in Kuala Sepetang have a liquid that contains acetic acid, butanoic acid, and phenol. Torrefaction of mangrove wood by superheated steam significantly reduced the biochar production period from 30 days to one-hour operation.

1. Introduction

Fossil fuel such as petroleum, coal, and natural gas is one of the most abundant materials used as fuel globally, and Malaysia is one of the countries that used fossil fuel. However, this kind of energy is non-renewable and cannot be replenished once used. When fossil fuel is used as burning material to generate power, it leads to an increase in greenhouse gas emissions, a global energy crisis, and, most importantly, fossil fuel reserves will decline as the world's population keeps increasing. For keeping the world below an average temperature increase, which has a catastrophic consequence, 80% of all fossil fuels in the ground need to be left [1]. Therefore, renewable energy resources can be used as an alternative fuel to replace the existing fossil fuel to generate energy. Renewable energy can be divided into a few types, such as solar energy, wind energy, hydropower, geothermal energy, and biomass energy. According to Kabberger [2], renewable electricity is cheaper per unit of energy than oil, where the price is about the same price as fossil methane but still higher than coal. This kind of energy is, however, not fully explored and exploited. Among these renewable examples, biomass is promising alternative energy. Five significant sectors contribute to Malaysia's biomass energy, such as forestry (wood product), rubber cultivation, cocoa cultivation, sugar cane cultivation, and oil palm cultivation [3]. Biomass contributed about 14% of the approximately 340 million barrels of oil equivalent of energy used every year.

Biomass is organic material produced by the growth of microorganisms, plants, and animals. It is a renewable and sustainable energy source that can generate electricity and other forms of energy. By
burning biomass, which comes from plants, carbon dioxide is released. However, through the European Union and United Nations frameworks, carbon dioxide has been classified as a renewable energy source. The photosynthesis process will use carbon dioxide back into new plants.

Mangrove wood charcoal production at Kuala Sepetang, Taiping, Perak, is one of the world's highest quality charcoal and requested a lot from Japan, Arab, and Korea. Although the request for mangrove wood charcoal is high, charcoal production is being monitored by the Department of Forestry Perak due to the limitation of mangroves' logging. The traditional method's charcoal production requires 60 to 90 days using hot air between 100˚C to 200˚C in a traditional igloo reactor (conventional slow pyrolysis kiln). Due to the lengthy time taken, this study has considered the use of superheated steam as a new alternative.

Torrefaction is the thermal pretreatment of biomass in an inert atmosphere between 200˚C to 300˚C in order to upgrade solid biomass fuel. Nitrogen is the standard carrier gas used to provide a non-oxidizing atmosphere. Through the torrefaction process on biomass several benefits can be achieved, such as higher energy density, lower atomic O/C and H/C ratios, lower moisture content, higher water-resistivity, improved grindability, and more uniform properties. Using superheated steam as a pretreatment process will open up the fibers and makes the biomass polymer more accessible for subsequent operation such as fermentation, hydrolysis, or densification. Therefore, superheated steam is a valuable and essential technology to improve the recovery of sugars and other useful biomass compounds. Materials with favorable properties such as high heating value (HHV), low moisture absorption, and excellent pelletizing properties.

Upon subjected to superheated steam, volatile matter removed from the solid biomass will be carried by the carrier gas that enters the reactor chamber. In the condenser system, the volatile matter will condense and produce a thick liquid. According to Mamvura and Danha [4], hydrogen gas and oxygen gas's reaction during torrefaction is freely bound moisture. The liquid product produces through the torrefaction process includes sugars, alcohols, polysugars, aldehydes, furans, and ketones. Lipids are present inside the liquid product, such as benzene, phenol, fatty acids, terpenes, tannins, and waxes.

2. Methodology

2.1. Rotary kiln and apparatus setup

Figure 1 shows the flow diagram of a rotary kiln carbonizer (Tanaka Tech, Japan) to perform the torrefaction process by superheated steam. The carbonization furnace was connected with an evaporator, where the evaporator will vaporize distilled water into superheated steam (300˚C) at a constant flow rate of 1.0 mL/min by a pump. The superheated steam flowed into the right furnace then into the rotary kiln furnace. Samples were torrefied in the rotary kiln where volatile matter, tar, and gas are released. All the components removed from the rotary kiln flowed into the left furnace and quenched to cool the volatile matter and tar extracted from solid samples. The internal temperatures of the rotary kiln were measured with a thermocouple. The water-soluble organic and tar condensed in the round bottom flask were measured. The non-condensable gas was not measured due to the small amount of gas obtained.

2.2. Raw material preparation

For this research project, the raw material was obtained from the charcoal factory at Kuala Sepetang, Perak. The raw materials were easy to prepare because it does not need any chemicals. However, the mangrove wood was cut into nearly identical sizes, roughly a diameter of 9.5 cm and 8.7 cm in length. The mangrove woods will be oven-dried for 24 h in an oven at 80˚C to avoid damage, fungal growth, and remove surface moisture. After 24 h of drying, the wood was cut again into four sections from end to end to increase the reaction's surface area. The samples were stored in zipping load plastic bags 0.45kg each. The samples were labeled as Tor30min, Tor60min, Tor90min, and Tor120min, denoting the torrefaction time of 30, 60, 90, and 120 min, respectively.
2.3. Torrefaction process of mangrove wood
The mangrove woods were torrefied with superheated steam using a rotary kiln carbonizer. The lid of the furnace was opened, and the sample was put inside. After the kiln was tightly closed, the rotary kiln was inserted into the rotary kiln furnace, and the furnace lid was tightly closed. The torrefaction temperature 300°C for all samples, while the residence time for each process was varied at 30, 60, 90, and 120 minutes.

The instruments that are attached were the ribbon heater and cooler. The ribbon heater heated the connector pipeline, connecting the cooling system and the right furnace at 200°C to avoid the tar from solidified. The cooler was turned on together with the water pump, and the temperature was set at 20°C. The right furnace was set at 250°C, the left furnace was set at 200°C, and the evaporator temperature was set at 300°C. The body furnace was 50°C for 1 min and step up to 300°C for 20 min, and the temperature was fixed at 300°C for 5 h. The body furnace's initial temperature heated the kiln at the rate of 13.5°C/min until it reached 320°C. Lastly, the body furnace temperature was fixed for 300 min at 320°C to allow the kiln furnace to reach 300°C to promote the torrefaction process to occur. 300 ml distilled water inside the conical flask was used to produce superheated steam, where the pump rate was 1 ml/min.

2.4. Solid Characterization

2.4.1. Determination of Mass Yield Percent. The mass yield was defined as the percentage of solid fuel retained after torrefaction. The mass yield was calculated using the mass of mangrove wood used and the mass after the mangrove wood torrefied. The formula can be referred to as follows:
\[ y_M = \frac{\text{The mass of solid after torrefaction}}{\text{Mass of mangrove wood used}} \times 100\% \]

where \( y_M \) is mass yield (%).

2.4.2. **Ultimate Analysis.** Carbon (C), hydrogen (H), nitrogen (N), sulfur (S), and oxygen (O) content were measured using a CHNS analyzer (CHNS LECO, CHN628 & 628S). Álvarez-Álvarez et al. [5] claim that chemical analysis is crucial for calculating the HHV of biomass and material balance. For wood fuel, standard ASTM E870-082 (2013) is used to determine the ultimate analysis. %O was calculated using the formula below:

\[ \%O = 100\% - (\%C + \%H + \%N + \%S) \]

2.4.3. **Higher Heating Value.** The heating value is a unit fuel quantity at 1 atm and 25˚C, where it is burned with sufficient dry air. The heat obtained is called the heating value when the combustion gas is cooled to 25˚C. For this experiment, the heating values were on the HHV basis and calculated using data obtained from elemental composition. According to Demirbas (2016)[, the formula to calculate HHV in unit MJ/kg using elemental composition was as follows:

\[ \text{HHV (MJ/kg)} = (33.5\%C + 142.3\%H - 14.5\%N - 15.4H\%\) \]

2.5. **Liquid Characterization**

2.5.1. **Gas Chromatography-Mass Spectrometry (GCMS).** The condensed bio-oil from the condensing system will be analyzed using GCMS to check the liquid's product and compare the juice obtained from the library data with the literature obtained. Table 1 shows the GCMS setting for component identification.

| Column                    | Zebron ZB-5 (30m x 25mm LD x 0.25um) |
|---------------------------|-------------------------------------|
| Injection Volume          | 1.0 μL                              |
| Injection Temp.           | 200˚C                               |
| Column Flow               | 1.76 ml/min                         |
| Carrier Gas               | Helium                              |
| Split Ratio               | 1/100                               |
| Oven Temperature Program  | Rate (˚C/min) Temperature (˚C) Hold time (min) |
|                           | 120.0. 250.0. 36.0                  |
|                           | 33.0 250.0 0.0                      |
| MS Temperature            | 250˚C                               |
3. Results and Discussion

3.1. Temperature Profile on Carbonizer

Figure 2 shows the temperature ramping profile of Torr30min, where the furnace step-up temperature (blue), kiln temperature (orange), and the kiln temperature (green). All other samples also showed the same phenomena, therefore only Torr30min is shown. The external furnace temperature (T3) was increased to 325°C with heating rate 13.5°C/min. The kiln internal temperature (T5) did not increase as rapid as the furnace due to the electric current, which was limited to 30A to avoid electric failure. Temperature between 200°C until 300°C is an ideal temperature for hemicellulose to decompose, which causes rapid temperature increase, as shown by the 'green' line as proven by Chen et al. [6]. This temperature rise is controllable. Removing the condensable product is vital to reduce the temperature overshoot and avoid condensed tar on biomass char that can interfere with self-ignition [7]. After some time, the temperature on the 'green' line shows a decrease in temperature. This drop indicated that the cellulose decomposed more than hemicellulose decomposed [7]. For temperatures between 275°C to 300°C, cellulose has severely deteriorated, and they are an endothermic process. For them to decompose, they required heat, and as a result, the temperature inside the kiln decreased slowly. Through experience with several trials and errors, the temperature's overshoot can be severe if the treatment time increases. In this research, the torrefaction time varied at 30, 60, 90, and 120 min. The furnace temperature was adjusted during the experiment to maintain the temperature at 300°C.

3.2. Torrefaction product

Steam was used as a gas carrier to carry volatile matter produced inside the kiln chamber. Therefore, the inlet of steam should be included in the chemical equation to ensure the reaction's material balance is balanced. The chemical equation for this system is equation (5).

\[
\text{Biomass}_{(s)} + \text{Steam}_{(g)} \rightarrow \text{Biochar}_{(s)} + \text{Bio} - \text{oil}_{l} + \text{Pyrolysis gas}_{(g)}
\]

\[
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\]
According to Chen et al., [6] biomass components consist of cellulose, hemicellulose, lignin, inorganic minerals, and organic extractives. They also claim that the first three components, cellulose, hemicellulose, and lignin, are the main components in biomass, and each biomass species has its weight percent. Mangrove wood can be considered a hardwood, consisting of 45% cellulose, 30% hemicellulose, 20% lignin, and 5% organic extractive. Table 2 below summarizes the properties of cellulose, hemicellulose, and lignin in biomass.

Table 2. Properties of cellulose, hemicellulose, and lignin, as reported by Chen et al. [6].

| Structure             | Cellulose | Hemicellulose | Lignin          |
|-----------------------|-----------|---------------|-----------------|
| Formula               | \((C_6H_{10}O_5)_m\) | \((C_5H_8O_4)_m\) | \([C_9H_{10}O_3.(OCH_3)_{0.9-1.7}]_m\) |
| Atomic O/C            | 0.83      | 0.80          | 0.47-0.36       |
| Atomic H/C            | 1.67      | 1.60          | 1.19-1.53       |
| Thermal decomposition | 315-400   | 220-315       | 160-900         |
| temperature (°C)      |           |               |                 |
| Component             | Glucose   | Xylose, glucose, mannose, galactose, arabinose, and glucuronic acid | Phenyl propane |
| Thermal behavior      | Endothermic | Exothermic   | Exothermic      |

Table 3 shows the mass after the torrefaction, the inlet of superheated steam, condensed liquid, and volatile matter obtained. Pyrolysis gas was not measured because almost no gas was produced.

Table 3. Mass after torrefaction, superheated steam inlet, condensed liquid, and volatile matter.

| Samples | Mass after torrefaction (kg) | Superheated Steam Inlet (mL) | Condensed liquid (mL) | Volatile Matter (mL) |
|---------|------------------------------|------------------------------|-----------------------|----------------------|
| Tor30min | 0.160                      | 166                          | 249                   | 83                   |
| Tor60min | 0.151                      | 185                          | 272                   | 87                   |
| Tor90min | 0.155                      | 215                          | 270                   | 55                   |
| Tor120min | 0.164                     | 249                          | 335                   | 86                   |

Figure 3 shows a summary of the torrefaction product for biochar (solid) and condensed volatile matter. Theoretically, the mass of the biochar will decrease while the volume of volatile matter increases as the treatment time increased. The dashed blue and red line indicates the final theoretical mass (kg) of solid and theoretical condensed volatile matter (mL) without water included. This theory was supported by the evidence provided by Mamvura and Danha [4], where longer operating time will cause more hemicellulose, cellulose, and lignin decomposed overtime. However, the increase in operation time will result in temperature overshoot due to the decomposition of hemicellulose was an exothermic reaction. For product Tor90min and Tor120min, the temperature overshoot causes less deterioration of volatile matter, which affects the final mass of both products.
3.3. Biochar characterization

3.3.1. Mass yield. Figure 4 represents the effect of operating time on the mass yield of torrefied mangrove wood. The mass yield based on Eq. 1 for Tor30min to Tor60min decreased from 35.71% to 33.71% with increasing time. However, the mass yield increased from Tor60min (33.71%) to Tor120min (36.77%). The mass yield was expected to decrease as operating time increases. However, due to the temperature overshoot, the mass yield for 90 min and 120 min have slightly different from the theoretical mass yield. A decrease in mass yield is due to cellulose and hemicellulose decomposition, as supported by Mamvura and Danha [4].

3.3.2. Ultimate analysis. Figure 5 shows the elemental analysis of natural mangrove wood (MW), torrefied products, and coal from Kuala Sepetang. The carbon content increased from 47.43% to 79.10% for Tor30min. As the operating time increases, the amount of carbon content for Tor60min, Tor90min, and Tor120min decrease to 75.7%, 75.8%, and 71.6%. This drop is due to many hemicelluloses and celluloses decomposed during the torrefaction process with time. In comparison, Kuala Sepetang Coal has lower carbon content, which is 64.83%. For the content of sulfur, the natural mangrove wood has 0.095% sulfur content. As torrefaction process conducted at 30min, 60min, 90min and 120min, the sulphur content reduced to 0.081%, 0.041%, 0.071% and 0.074% respectively. However, for the igloo
reactor (slow pyrolysis kiln) at Kuala Sepetang, the sulfur content was 0.021%. For the removal of sulfur inside biomass, the igloo reactor performed better than the torrefaction process because the igloo reactor (slow pyrolysis kiln) has a longer operation time that allows sulfur to be removed slowly.

![Elemental analysis of raw mangrove wood (MW), torrefied products, and coal from Kuala Sepetang.](image)

**Figure 5.** Elemental analysis of raw mangrove wood (MW), torrefied products, and coal from Kuala Sepetang.

3.3.3. Calorific value (HHV). Figure 6 shows the theoretical and experimental HHV of raw and torrefied mangrove wood. The observed HHV was obtained from Bomb Calorimeter analysis, while the theoretical HHV was calculated using elemental data proposed by Demirbas [8]. The HHV for the Tor30min increased to 28.8 MJ/kg from 16.7 MJ/kg by observing the experimental HHV. As the torrefaction time increased, the HHV slightly increased for Tor60min (29.7 MJ/kg) and Tor90min (29.6 MJ/kg). However, for Tor120min, the HHV drops to 27.3 MJ/kg. Drop-in HHV for Tor90min and Tor120min was due to temperature overshoot, where the longer the treatment time, the harder the temperature to be controlled.

Furthermore, endothermic reaction to decompose cellulose also contributed to the decline of HHV due to temperature drop. According to Chen and Kuo [9], for torrefaction duration less than 1 h, thermal degradation of biomass is rapid and becomes sluggish after 1 h. Figure 6 shows the HHVs for torrefaction treatment for 60 min, 90 min, and 120 min were almost identical. Therefore, the 60 min torrefaction is the optimum time to produce high HHV biochar and reduce the energy required to heat the kiln. The theoretical HHV was calculated by using the method by Demirbas [8]. Compared to the experimental HHV, the value calculated by elemental data is almost analogous to the experimental data. This similarity proves that the Demirbas [8] elemental data can be used for other mangrove wood torrefied treatment to get a rough estimation of HHV. Compared to coal produced from Kuala Sepetang, the biochar produced by the torrefaction using superheated steam delivered a higher HHV useful for solid fuel. The higher HHV is due to more oxygen being removed from the biomass, which fulfills the torrefaction process’s initial intention in removing oxygen content inside biomass.
### 3.3.4. Van Krevelen diagram.

The O/C ratio against the H/C ratio plot or van Krevelen diagram was plotted to compare the torrefied mangrove wood with coal, as shown in Figure 7. It is desirable to have a higher ratio for the H/C but lower for the O/C. The natural mangrove has a larger proportion of O/C and H/C as compared to torrefied samples. As the natural mangrove being torrefied, the O/C is significantly reduced as oxygen is being removed during the torrefaction process. However, the H/C ratio needs to be maintained as high as possible because a lower H/C value indicates that only ash is present and is not suitable for solid fuel properties. The coal from Kuala Sepetang has a higher O/C ratio, while the torrefied sample has a lower O/C ratio. It is proven that the torrefaction by injecting superheated steam is better than the igloo reactor (slow pyrolysis kiln) injected by hot air to reduce the oxygen content inside biomass. However, the igloo reactor (slow pyrolysis kiln) is better in minimizing the drop in the H/C ratio. For different torrefaction times, the sample torrefied sample at 60 min and 90 min is the optimum time to increase oxygen content reduction while minimizing the H/C ratio reduction. Figure 5 shows that the carbon content decreased as the operating time increased due to thermal degradation of hemicellulose and cellulose. Therefore, to reduce carbon content removal, the optimized torrefaction time should be taken into account.
3.4. **Bio-oil characterization**

Bio-oil product was analyzed using GCMS to characterize the liquid's organic content. Figure 8 and Figure 9 show the GCMS of liquid from Kuala Sepetang and liquid from Tor30min. The Tor30min product has products containing oxygen atoms consisting of ketones, alcohols, and aldehydes from the data library. Tor30min has 16.8% oxygen atom, while Kuala Sepetang Coal has 30.3% oxygen based on Figure 5. Therefore, the torrefaction process by injecting superheated steam is proven to reduce the biomass's oxygen content rather than the igloo reactor (slow pyrolysis kiln) injected with hot air used at Kuala Sepetang. The use of superheated steam has a high potential to recover by-products, such as acetic acid and formic acid, from the torrefaction process rather than using nitrogen gas where it is removed in the form of flue gas into the atmosphere [10]. Water has a higher condensation point than inert gas, making it easier to recover torrefaction by-products. Compared to the by-products from Kuala Sepetang, more by-products were observed when torrefaction was performed by superheated steam. Stelt [11] stated that the main condensable torrefaction volatiles is acetic acid and water. The reaction for acetic acid is made up of carbon solid, hydrogen gas, and oxygen gas. Acetic acid is worth mentioning because it was present in both Kuala Sepetang and torrefied products. The acetic acid formation is caused by the thermolysis of acetyl radicals linked to the xylose units of hemicellulose that decomposed during the torrefaction process [11].

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**Figure 7.** Raw mangrove wood, torrefied sample, and coal from Kuala Sepetang under van Krevelen diagram.
4. Conclusion

In this study, mangrove wood was torrefied at 300°C by superheated steam. The effect of operating time on the HHV and carbon content analyzed by the CHNS analyzer was investigated. The HHV of torrefied mangrove wood rapidly increased for torrefaction below 60 min, but a small increment if more than 60 min. The highest HHV obtained was 29.7 MJ/kg, where the operating time was 60 min. The increasing and decreasing trend of HHV can be related to carbon content inside the bio-char. As the treatment time increased, the biomass's carbon content decreased due to hemicellulose's thermal degradation and cellulose.

In comparison, Kuala Sepetang coal has lower carbon content (64.8%), proving the torrefaction process is better than the igloo reactor (slow pyrolysis kiln) practiced in Kuala Sepetang. Not only that, the duration to make biochar reduced from almost one-month to one day. The operating time also influences the sulfur content inside the biomass. The longer the operating time, the more sulfur was removed from the solid biomass. The torrefaction relation of the H/C and O/C ratio was correlated using the van Krevelen diagram. When operating time was reduced, the ratios became closer to the coal, which means that torrefied mangrove wood has great potential to be an excellent solid fuel due to lower H/C and O/C ratios, especially for operating time 30 minutes and temperature 300°C. The mass yield percent
decreased as the operating duration increase due to thermal degradation of hemicellulose and cellulose. Considering for HHV with the H/C and O/C ratios, the optimum torrefaction process time for mangrove wood is 60 min.

The content of the liquid product was analyzed by using GCMS. The liquid obtained from the torrefaction process by injecting superheated steam will produce a liquid that contains acetic acid, ketones, aldehydes, acids, and alcohols. Therefore, by injecting superheated steam, the oxygen content was reduced inside the biomass. This liquid product is sold as mangrove vinegar in Kuala Sepetang to prevent pesticides. In the igloo reactor (slow pyrolysis kiln) method by hot air, the liquid product is obtained after a lengthy one-month duration. However, through the torrefaction by injecting superheated steam, this process to obtain the liquid is shortened to an hour.

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