Improving the Quality of Fast Pyrolysis Bio-oil (Liquid Fuel) using Thermal Distillation Method

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Authors' contributions

This work was carried out in collaboration among all authors. Author MH and Author FAR designed the study, performed the experimental analysis, wrote the protocol, and wrote the first draft of the manuscript. Author KQ, and Author MD managed the analyses of the study. Author HK and Author DQ managed the literature searches. All authors read and approved the final manuscript.

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Original Research Article

ABSTRACT

Oil palm biomass generates an abundance via the oil palm industry such as Palm kernel shell (PKS), empty fruit bunch (EFB), frond, trunk.

Problem Statement: The main issue nowadays is global warming; one of the factors is the increment of CO₂ content in the atmosphere. In order to reduce the CO₂ content in the atmosphere, biomass is used, as it is a renewable, sustainable, and cost-effective alternative energy source that needs to be adopted in the energy mix. The objective of this study was to improve the quality of bio-oil.

Approach: In this research, an empty fruit bunch (EFB) was utilized in a fixed bed reactor, and pyrolysis oil was upgraded via a thermal distillation reactor. The temperature of pyrolysis was 500 °C, and the temperature of thermal distillation was 100 °C. Gas chromatography-mass spectroscopic and ultimate analysis was utilized to investigate chemical composition.

Results: The maximum distilled bio-oil yield was 60-65 % at 100 °C. The heating value of bio-oil was 21 MJ/kg, and distilled bio-oil was 30 MJ/kg. The density of bio-oil was 1035 g/mL, and distilled

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bio-oil was 980 g/mL

**Conclusion:** The results showed that the distilled bio-oil obtained from EFB bio-oil has a high heating value low oxygen content than it can use as fuel in engines.

**Keywords:** Biomass; empty fruit bunch; bio-oil; distillation; pyrolysis.

1. INTRODUCTION

Bio-oil is a liquid product of pyrolysis, with its color properties being dark brown that consists of black liquid, often being characterized by the smoky odor. This bio-oil is a complex mixture of oxygenated compounds consisting of water that comes from the moisture inside the biomass itself [1]. In addition, bio-oil has a small amount of coal particles and alkali metals that have been dissolved during the pyrolysis chemical reaction [2]. Generally, the bio-oil composition depends on the parameters and types of biomasses being used and the operating conditions applied in the process. Besides that, bio-oil can be described as an aqueous microemulsion resulting from cellulose, hemicelluloses, and lignin fragmentation [3].

The dependency on the process conditions and the initial mass feedstock significantly affects the properties of bio-oil being produced. Bio-oil comprises 20–25 % water, 25–30 % water-insoluble pyrolytic lignin, 5–12 % organic acids, 5–10 % non-polar hydrocarbons, 5–10 % hydro sugars, and 10–25 % other oxygenated compounds [4]. Therefore, the bio-oil produced from fast pyrolysis can be utilized directly without upgrading as a fuel oil for combustion in a boiler or a furnace. However, the viscosity of fast pyrolysis bio-oil increased during storage because of slow polymerization or condensation reactions [5]. Therefore, bio-oil usage as fuel requires upgrading to improve storage stability and heating value.

One of the easiest ways to utilize the bio-oil for transportation fuel is to combine the bio-oil with diesel directly. However, the bio-oil from fast pyrolysis is immiscible with hydrocarbons but can emulsify it by using surfactants by the ratios of 25, 50, and 75 %. In addition, these emulsions were major stable than the original bio-oil [3]. Fast pyrolysis bio-oil also can be upgraded by hydrotreatment using catalysts. The oxygen contents significantly decrease by using catalysts. However, this method is quite expansive, and the catalyst is easily deactivated [5].

Thermal Distillation of bio-oil from fast pyrolysis is a suitable method for upgrading bio-oil. This method improved the heating value, corrosivity, and storage stability of fast pyrolysis bio-oil (liquid fuel).

2. METHODOLOGY

2.1 Fast Pyrolysis Bio-oil Preparation

A fixed bed reactor made of stainless steel was utilized to produce bio-oil via fast pyrolysis of empty fruit bunch EFB. The reactor dimension is 50 cm in height and 10 cm in diameter. About 200 g of the biomass was placed in the reactor. This reactor is vertically positioned, and N₂ gas was introduced inside the reactor at an injection amount/speed of 200 ml/min from the bottom, passing through the top of the reactor. The nitrogen injection replaced the air from the reactor and allowed the pyrolysis reaction to occur under anaerobic conditions. The gases formed from the pyrolysis inside the reactor flowed out along with N₂ from the top of the reactor. The mixture of gas was passed through two condensers. The first condenser was cooled using dry ice. The vapor temperature was reduced to around 60 °C, and the circulation of iced water reduced the temperature of the second condenser, where it was cooled to around 5 °C. [6]. Figure 1 shows the schematic diagram of bio-oil production via fast pyrolysis.

2.2 Distillation of Bio-oil

The method used to upgrade the bio-oil is via a reactor and stirring hotplate that will assist the distillation process through some modifications made. Firstly, put the bio-oil inside the reactor and provide about 100 °C with a stirring hotplate. After that, pyrolysis bio-oil was separated into tar and 10 fractions of bio-oil. The distilled bio-oil fraction yield is 60 – 65 %. Figure 2 shows the Thermal distillation product yields from fast pyrolysis of bio-oil at temperature 100°C [7].
2.3 Analytical Analysis

2.3.1 Ultimate Analysis

This analyzer was used for the ultimate analysis, whereby in the biomass, the carbon, sulphur, hydrogen, and nitrogen percentages are obtained by calculating the oxygen's differences from the four elements. Thermo Fining Flashed, model 1112 with helium gas as the carrier, was used for the ultimate analysis, and the ASTM standards (ASTM D5373-02) was carried out following the ultimate analysis. The organic material is homogeneous, where the carbon, nitrogen, hydrogen, and sulphur are determined using CHNSO series instruments. Also, high-temperature combustion is used to remove the elements from the material. This combustion process runs on a normal 2 mg sample encapsulated tin or silver capsule. The sample is then dropped into the furnace while the oxygen is injected. The oxygen-rich environment is used to heat the sample; SOx, NOx, H2O, and CO2 are the CHNSO analysis products. These gases, which are carried through the system by helium carrier, are swept through the oxidation tube...
packed with copper sticks (which removes oxygen) to complete the conversion of SO2. The result is displayed as the weight percent of C, S, N, and H of gases that were passed through four infrareds [8].

2.3.2 GC-MS

The bio-oils chemical composition was tested using GC-MS (Auto System XL GC/Turbo Mass MS, Perkin Elmer) by a quadruple detector and a DB-1MS capillary column (30 m × 0.25 mm inner diameter × 0.25 μm thickness). Helium (UHP) was used as the carrier gas with a constant 1.2 mL/min flow. The primary temperature of oven temperature program was set at 40 °C and continued for 4 min, rising by 5 °C/min to 250 °C, which continued for another 10 min. The injector temperature was 250 °C. The volume of the injected sample (10% of bio-oil in chloroform) was 1 μL. Electron ionization (EI) was used in the MS (Auto System XL GC/Turbo Mass MS, Perkin Elmer). Standard mass spectra with 70 eV ionization energy were recorded with a scanned range from 0 to 1200 amu. The computer recording matches the mass spectra that were performed using the NIST98 and WILEY7.0 library, and the retention time of known species injected in the chromatographic column was used for the identification of the peaks [9].

3. RESULTS AND DISCUSSION

3.1 Characterization and Chemical Composition of Bio-oil and Distilled Bio-oil

The distilled bio-oil water content is 17.14 % it is much lower than the water content of fast pyrolysis bio-oil 35- 50 % it is due to raw material moisture. This finding is comparable with [10] studies. The pH of distilled bio-oil is 2.95; it is much lower than fast pyrolysis bio-oil 3.3 [11]. The low pH of bio-oil represents a high probability of corrosivity than some metals [5]. The oxygen content of distilled bio-oil is 34.7 % which is lower than pyrolysis bio-oil 40- 50 %. The decline of oxygen content in distilled bio-oil is much more important than the fast pyrolysis because the high oxygen content in fuels transportation is not good [12]. Because of low oxygen content, high carbon, and hydrogen content, distilled bio-oil has a higher calorific value 30 MJ/kg. The Density of bio-oil is 1035 g/mL, which is higher than the bio-oil fraction 980 g/mL. The calorific value of bio-oil is 21 MJ/kg, and it is closer to [13] Finding around 23.48 MJ/kg might be because of water content in the bio-oil. Table 1 shows the fast pyrolysis bio-oil and distilled bio-oil properties.

Table 1. Properties of fast pyrolysis bio-oil and distilled bio-oil

<table>
<thead>
<tr>
<th>Properties</th>
<th>Fast pyrolysis bio-oil</th>
<th>Distilled bio-oil</th>
</tr>
</thead>
<tbody>
<tr>
<td>H2O (wt. %)</td>
<td>35- 50</td>
<td>17.14</td>
</tr>
<tr>
<td>pH</td>
<td>3.3</td>
<td>2.95</td>
</tr>
<tr>
<td>Density (g/mL)</td>
<td>1035</td>
<td>980</td>
</tr>
<tr>
<td>HHV (MJ/kg)</td>
<td>21</td>
<td>30</td>
</tr>
<tr>
<td>C (wt. %)</td>
<td>45- 49</td>
<td>58.8</td>
</tr>
<tr>
<td>H (wt. %)</td>
<td>5.0- 6.0</td>
<td>6.90</td>
</tr>
<tr>
<td>O (wt. %)</td>
<td>40- 50</td>
<td>34.7</td>
</tr>
<tr>
<td>N (wt. %)</td>
<td>0.02</td>
<td>0.19</td>
</tr>
</tbody>
</table>

Table 2. some composition of fast pyrolysis bio-oil and distilled bio-oil

<table>
<thead>
<tr>
<th>Composition</th>
<th>Bio oil (%)</th>
<th>Distilled bio-oil (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene, (1,1dimethylethoxy)</td>
<td>8.03</td>
<td>1.20</td>
</tr>
<tr>
<td>Phenol, 2,6-dimethoxy</td>
<td>3.50</td>
<td>2.56</td>
</tr>
<tr>
<td>Phenol, 4-methyl</td>
<td>8.80</td>
<td>1.43</td>
</tr>
<tr>
<td>Phenol, 3-methyl</td>
<td>8.58</td>
<td>1.60</td>
</tr>
<tr>
<td>Phenol, 2,6-dimethoxy</td>
<td>3.90</td>
<td>1.50</td>
</tr>
</tbody>
</table>
GC-MS analysis was carried out with bio-oil to determine the type of possible compounds and nature in the bio-oil, and distilled bio-oil. Based on Table 2, fast pyrolysis bio-oil is a mixture of organic compounds which are including water, acids, and hydrocyclic substance. The fast pyrolysis of bio-oil contains 8.03 % Benzene, (1,1-dimethylethoxy), 8.03 % Phenol, 2,6-dimethoxy, 3.50 % Phenol, 4-methyl, 8.80 % Phenol, 3-methyl, 8.58 and phenol,2,6-dimethoxy 3.90 %.

Table 2 shows distilled bio-oil is indicated the carbocyclic acid, and heterocyclic are much lower content than pyrolysis bio-oil. Benzene, (1,1-dimethylethoxy), 1.20 wt. % Phenol, 2,6-dimethoxy, 2.56 % Phenol, 4-methyl, 1.43 wt. % Phenol, 3-methyl, 1.60 % and phenol,2,6-dimethoxy 1.50 %. The GC-MS analysis results show that the phenol derivative is the major group of compounds existed in both bio-oil, and distilled bio-oil. The highest area percentage for pyrolysis bio-oil was Phenol, 4-methyl 8.80, and for distilled bio-oil was Phenol, 2,6-dimethoxy 2.56 % [14].

4. CONCLUSION

Although the bio-oil obtained from different biomass have different compounds. These Bio oils have high oxygen content and are not stable, and their compositions quickly change during storage. Fast pyrolysis bio-oil may use as a fuel or source of chemical feedstock, but it needs some methods to improve the heating value and storage stability. Thermal distillation is one of the effective and simple methods to reduce the oxygen content of fast pyrolysis bio-oil. Distilled bio-oil is more stable compared to fast pyrolysis bio-oil. The higher heating value HHV of distilled bio-oil is 30 MJ/kg, which is much higher than fast pyrolysis bio-oil.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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