The Study of Crude Palm Oil

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Abstract

The study of Crude Palm Oil (CPO) was conducted to utilize liquid waste as bioenergy in the form of biodiesel. The Industrial Liquid waste of CPO processing was used and found methyl ester in biodiesel. The process had mainly two reactions namely esterification and transesterification. The analysis showed that liquid waste had methyl esters as hexadecanoate, octadecanoate and 8,11-octadecadienoate.

Keywords – CPO, Bioenergy, Esterification, Transesterification, Methyl esters.

1. Introduction

Biodiesel is produced from different triglyceride sources, which is an alternative fuel to petro-diesel. The biodiesel is mono-alkyl esters produced from various lipid feedstocks including vegetable oils, animal fats, etc. Furthermore, it has been accepted as a fuel and fuel additive worldwide. There were so many varieties of oil examined as biodiesel, for instance, vegetable oil, animal fat, algae oil, and vegetable oil waste [1]. One of potential renewable raw materials to produce biodiesel is crude palm oil (CPO) [2]. This is the need of fuel for the development of industry and and country as population increases. The greatest fuel consumption is identified in the sector of industry and transportation and causes fuel insufficiency [3]. The production of unrefined oil reached 18 million barrels per day in some areas and it decreases to 700,000 barrels per day at present [4]. So the limited investment in new oil resource exploration and increased domestic fuel consumption turned a country to be oil importer [5]. Furthermore, the use of fossil-based fuel is not considered environmentally friendly because it boosts the concentration of carbon dioxide (CO₂). This gas enhances greenhouse effect that contributes to the event of global warming [6], [7]. The development of alternative energy resources, therefore, should be carried out to substitute diesel-based fuel. One alternative energy resource which is widely developed is biodiesel [8]. Biodiesel (methyl-ester) is proposed to substitute fuel-based fuel due to
vegetable oil-based fuel which is renewable and environmentally friendly [9]. CPO processing biodiesel is biodegradable and non-toxic; it also has low CO$_2$ emission and sulfuric gas content [10]. The utilization of CPO of agricultural and victuals needs as the raw material of biodiesel is categorized as the first generation of biodiesel [11]. Liquid waste of palm oil is one of the renewable raw materials of biodiesel. Liquid waste of palm oil has 0.5–1% of oil content which can be processed as biodiesel [12]. The great amount of palm oil liquid waste within palm oil processing is considered as environmental pollution; in spite of that fact, it is a quite potential raw material to be processed as vegetable-based fuel which is economical in price and sumptuous in supply. Direct use of vegetable oil as the fuel of diesel still exhibits a weakness in term of its higher viscosity than diesel petroleum. This high viscosity of vegetable oil disturbs the process of injection and atomization of fuel [13]. To overcome these problems, the process of converting vegetable oil into methyl-ester through the transesterification process with catalyst should be carried out [14] for biodiesel [15].

2. Experimental

2.1. Degumming process

The fixed amount of 150 mL of CPO industrial liquid waste was heated at the temperature of 104 °C for an hour and distilled. To the he obtained liquid, 6 mL of H$_3$PO$_4$ 85% is added up and distilled for 30 min. The sample is centrifuged for 3 min by the speed of 600 rpm and separated gum from the oil.

2.2. Esterification process

The above obtained degummed liquid (85.10 g) is added with 63.36 g of methanol and 2 mL of H$_2$SO$_4$ 98%. This mixture is heated for 3 h within the temperature of 55 to 60 °C and stirred by magnetic stirrer. Oil and methyl-ester are separated from glycerol and water as by-products of esterification process by using centrifuge.

2.3. Transesterification process

The liquid of esterification process [16] is weighed (69.00 g) and CaO catalyst is added up with the variations of catalyst content of 1, 2, 3, and 5%; each of them is dissolved in 52.00 g of methanol and heated within the temperature 55 to 60 °C for 3 h. Methyl-ester [17],[18], formed is separated from glycerol and residual catalyst by using centrifuge.
2.4. Characterization

The produced biodiesel was characterized by Gas Chromatography-Mass Spectroscopy (GC-MS).

3. Results and discussion

The CPO biodiesel is a form of long chain fatty acid ester and has 14 to 22 the number of carbon atom lying in the long chain \([19], [20], [21], [22]\). The building blocks o are methyl ester and were analysed using GC-MS. The results were exhibited in Fig. 1 and Table 1 given below.

![Figure 1](image)

Fig. 1. GC-MS Chromatogram of biodiesel samples.

<table>
<thead>
<tr>
<th>Retention time, Rt (minutes)</th>
<th>Compounds identified</th>
<th>Molecular formula</th>
<th>Composition (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>19.70</td>
<td>Methyl hexadecanoate</td>
<td>C(<em>{17})H(</em>{34})O(_2)</td>
<td>12.80</td>
</tr>
<tr>
<td>20.00; 24.80</td>
<td>Hexadecanoic acid</td>
<td>C(<em>{16})H(</em>{32})O(_2)</td>
<td>3.20</td>
</tr>
<tr>
<td>21.30</td>
<td>Methyl 8,11-octadecadienoate</td>
<td>C(<em>{19})H(</em>{34})O(_2)</td>
<td>10.20</td>
</tr>
<tr>
<td>21.40</td>
<td>Methyl 9-octadecenoate</td>
<td>C(<em>{19})H(</em>{36})O(_2)</td>
<td>19.90</td>
</tr>
<tr>
<td>21.60</td>
<td>Methyl octadecanoate</td>
<td>C(<em>{19})H(</em>{38})O(_2)</td>
<td>5.70</td>
</tr>
<tr>
<td>21.60</td>
<td>9,12-octadecadienoate acid</td>
<td>C(<em>{18})H(</em>{32})O(_2)</td>
<td>0.52</td>
</tr>
</tbody>
</table>

Table 1. Methyl ester of biodiesel according to the results of GC-MS analysis.
<table>
<thead>
<tr>
<th>Retention time, Rt (minutes)</th>
<th>Compounds identified</th>
<th>Molecular formula</th>
<th>Composition (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>21.70; 26.24</td>
<td>9-octadecenoate acid</td>
<td>C_{18}H_{34}O_{2}</td>
<td>3.30</td>
</tr>
<tr>
<td>24.20</td>
<td>cyclohexane</td>
<td>C_{6}H_{12}</td>
<td>1.30</td>
</tr>
<tr>
<td>24.30</td>
<td>Propanenitrile</td>
<td>C_{3}H_{5}N</td>
<td>4.30</td>
</tr>
<tr>
<td>24.36</td>
<td>3-butyl phenol</td>
<td>C_{10}H_{14}O</td>
<td>6.30</td>
</tr>
<tr>
<td>24.38</td>
<td>Phenol</td>
<td>C_{6}H_{6}</td>
<td>0.940</td>
</tr>
</tbody>
</table>

The results show that there was a substance of methyl hexadecanoate in methyl ester with the retention time of 19.70 and the composition of 12.80%. Molecular ion of C_{17}H_{34}O_{2}^{+} presented fragmentation by releasing C_{3}H_{7} radical and produced fragments by m/z 227 originating from C_{14}H_{27}O_{2}^{+}, while the bottom peak lies in m/z 74 originating from C_{3}H_{5}O_{2}^{+}. The mass spectrum of methyl hexadecanoate given below in Fig. 2.

![Mass spectrum of methyl hexadecanoate.](image)

Fig. 2. Mass spectrum of methyl hexadecanoate.

The results of GC-MS analysis indicate that there was a substance of methyl octadecanoate with the retention time of 21.60 and the composition of 5.70%. The mass spectrum of methyl octadecanoate was written by m/z 298 originating from the molecular ion of C_{19}H_{38}O_{2}^{+} resulted from methyl octadecanoate. Molecular ion of C_{19}H_{38}O_{2}^{+} experiences radical fragmentation by releasing C_{3}H_{7} radical and produces fragments by m/z 225 originating from C_{16}H_{31}O_{2}^{+}. The peak of m/z 129 originating from C_{7}H_{13}O_{2}^{+} resulted from C_{16}H_{31}O_{2}^{+} which releases C_{5}H_{10}. Molecular ion of C_{7}H_{13}O_{2}^{+} experiences McLafferty reorganization by releasing C_{3}H_{5}O_{2} and it produced the peak within m/z 55 originating from C_{4}H_{7}, while the peak of m/z 87 comes from C_{4}H_{7}O_{2}^{+} originating from the fragment of C_{19}H_{38}O_{2}^{+} releasing C_{15}H_{31} radical. The bottom
peak lies in m/z 74 originating from $\text{C}_3\text{H}_6\text{O}_2^+$. The pattern of mass fragmentation of methyl octadecanoate is given in Fig. 3.

![Mass spectrum of methyl octadecanoate.](image)

**Fig. 3.** Mass spectrum of methyl octadecanoate.

The results of GC-MS analysis of methyl 8, 11-octadecadenoate with the retention time of 21.30 and the composition of 10.20% is an isomer compound of methyl linoleate which has the same molecular formula that is $\text{C}_{19}\text{H}_{34}\text{O}_2$. The mass spectrum of methyl 8, 11-octadecadenoate was written by m/z 294 originating from the molecular ion of $\text{C}_{19}\text{H}_{34}\text{O}_2^+$ which is formed when it is exposed by 70 eV of electron. Molecular ion of $\text{C}_{19}\text{H}_{34}\text{O}_2^+$ undergoes fragmentation by releasing $\text{CH}_3\text{O}$ radical and it produces the peak by m/z 263.

![Mass spectrum of methyl 8, 11-octadecanoate.](image)

**Fig. 4.** Mass spectrum of methyl 8, 11-octadecanoate.
originating from \( \text{C}_{18}\text{H}_{31}\text{O}^+ \). The peak lies in m/z 220 originating from \( \text{C}_{16}\text{H}_{28}^+ \) formed by McLefferty reorganization of \( \text{C}_{18}\text{H}_{31}\text{O}^+ \) releasing \( \text{C}_2\text{H}_3\text{O} \). The peak lying in m/z 95 originates from \( \text{C}_7\text{H}_{11}^+ \) coming from \( \text{C}_{18}\text{H}_{31}\text{O}^+ \) releasing \( \text{C}_9\text{H}_{19} \) radical. The mass spectrum of methyl 8,11-octadecanoate contains bottom peak by m/z 67 originating from \( \text{C}_4\text{H}_7 \). The pattern of fragmentation of 8,11-octadecanoate can be seen in Fig 5.

Fig. 5. Mass spectrum of methyl 9-octadecanoate.

The results of GC-MS analysis of methyl 9-octadecadinoate indicate that the retention time required was 21.42 with the composition of 19.90%. The mass spectrum of methyl 9-octadecanoate was written by m/z 296 originating from the molecular ion of \( \text{C}_{19}\text{H}_{36}\text{O}_2^+ \) which is formed when exposed by 70 eV of energy. Molecular ion of \( \text{C}_{19}\text{H}_{36}\text{O}_2^+ \) releases \( \text{C}_3\text{H}_6\text{O}_2 \) radical and produces fragments by m/z 222 originating from \( \text{C}_{16}\text{H}_{30} \) which then releases \( \text{CH}_3 \) radical which forms the peak of m/z 207 originating from \( \text{C}_{15}\text{H}_{27}^+ \). The peak of m/z 180 originating from \( \text{C}_{13}\text{H}_{24} \) which undergoes fragmentation by releasing \( \text{CH}_2 \) radical produces peak by m/z 166. Molecular ion of \( \text{C}_{19}\text{H}_{36}\text{O}_2^+ \) can also experience fragmentation by releasing \( \text{CH}_3\text{OH} \) and it produces the peak within m/z 264 originating from \( \text{C}_{18}\text{H}_{32}\text{O}^+ \). The peak with m/z 111 originating from \( \text{C}_7\text{H}_{11}\text{O}^+ \) releases \( \text{CH}_2 \) radical and produces m/z 97 originating from \( \text{C}_6\text{H}_5\text{O}^+ \); while the bottom peak originates from \( \text{C}_4\text{H}_7^+ \) with m/z 55.

4. Conclusion
Palm-biodiesel existed as an efficient energy source, the reduction of environmental impact, an increment of job opportunities, enhancement of energy security, and waste utilisation. Besides, palm-biodiesel had been noted as a viable and practical alternative or additive to petro-diesel through its excellent characteristics such as clean-burning, nontoxicity, renewability, sustainability, and acceptability. On top of that, it also has benefits including its cheaper cost and more positive carbon benefits than other major biodiesel sources [24]. The present study shows that there were several methyl esters like methyl hexadecanoate, methyl 9-octadecanoate, methyl octadecanoate and methyl 8,11-octadecadienoate with different percentage.

References


[23] Biodiesel Production from Palm Oil, Its By-Products, and Mill Effluent: *energies* Review, Aug, 2018