Synthesis of Biodiesel From Avocado Seed Waste Through Esterification And Transesterification Processes

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ARTICLE INFORMATION

Received 09 August 2023
Accepted 15 September 2023
doi.org/10.35313/fluida.v16i.sp1.5342

ABSTRACT

The avocado seed is a food waste that contains vegetable oil. The amount of avocado seed waste is very abundant, but there is no optimal processing or utilization. Fossil fuels as an energy source can experience scarcity because these energy sources are non-renewable. This research has important implications in waste management and development of renewable energy sources. One type of renewable energy is biodiesel. Biodiesel is an environmentally friendly alternative fuel made from vegetable oil. The use of biodiesel as an alternative fuel has advantages including being easier to decompose in nature and reducing emissions when compared to diesel oil. One type of plant that can be used as raw material for making biodiesel is avocado. This study aims to utilize avocado seed waste as a raw material for biodiesel synthesis and to test its characteristics that have not been found in previous studies in the form of analysis of acid value, density, and oxidation stability. The method used in the synthesis of biodiesel was esterification and transesterification reactions using methanol solvent with a mole ratio of avocado seeds to methanol of 1:6 and the addition of H₂SO₄ catalyst as much as 0.5% of the weight of oil for the esterification process and the addition of NaOH catalyst as much as 1% of the weight of oil for the transesterification process. This study complements previous research on biodiesel from avocado seeds and compares the obtained biodiesel characteristics to the Indonesian National Standard (SNI) 04-7182:2015. The final results of this study were 34.61%, 0.98 mg-KOH/g, 977 kg/m³, and 318 minutes for biodiesel yield, acid value, density, and oxidation stability, respectively.

Keywords:
Avocado seeds
Biodiesel
Characteristics
Esterification
Transesterification

INTRODUCTION

The demand for fuel increases with the development and use of transportation. So far, the use of transportation has depended on the existence of fossil fuels as the main energy source which can experience scarcity because fossil energy sources cannot be renewed. This is supported by the statement of the Minister of Energy and Mineral Resources (ESDM), Arifin Tasrif that Indonesia’s oil reserves will only be available for the next 9.5 years [1]. Therefore, innovation is needed from environmentally friendly fuels so that they can be used as alternative energy from renewable materials.

Biodiesel is an environmentally friendly alternative fuel made from vegetable oil. In Indonesia, the government launched the B30 program, namely blending 30% biodiesel with 70% diesel fuel, which was implemented on 1 January 2020 [2]. From this program, the development of biodiesel has a great opportunity to be implemented in Indonesia. The national standard that must be met for the biodiesel used is the Indonesian National Standard (SNI) 04-7182:2015. The 2015 SNI revised SNI 04-7182-2006 and SNI 7182:2012 [3].

To produce biodiesel according to SNI, one type of plant that can be used as raw material for making biodiesel is avocado. Avocado production in Indonesia (Figure 1) has increased every year and recorded for 2022, the total production is 865,780 tonnes/year [4]. According to several
studies, avocado seed waste contains oil of 3-30% (w/w) depending on the ecological and racial characteristics of the plant [5].

The yield of biodiesel produced is also another aim to be obtained in this research. The optimum operating conditions used refer to studies that have been carried out by several previous researchers [6].

METHODS
This research was conducted at the Process Unit Laboratory, Department of Chemical Engineering, Politeknik Negeri Bandung. The stages of the process in details are described as follows.

Tools, equipment, and materials
The tools and equipment used in this study were oven, soxhlet extractor, grinder, two-neck flask, thermometer, condenser, measuring cup, separating funnel, Erlenmeyer, burette, stative, clamps, beaker, pycnometer, analytical balance, measuring pipette, paper pH, hot plates, centrifuges, centrifuge tubes, distillation equipment, test tubes and compressors.

The materials used were 15 kg of avocado seeds from a juice seller around the Cigugur Tengah Cimahi City, NaOH p.a, KOH p.a, methanol 96% p.a, H₂SO₄ 97% p.a, n-hexane, distilled water, 96% ethanol, phenolphthalein indicator.

Process Stages
In this research, several working procedures were carried out including the avocado seed pre-treatment, extraction, esterification, transesterification, and analysis.

Pre-treatment of Avocado Seeds
Pre-treatment of avocado seeds was the initial treatment by cleaning them from dirt, drying them in the sun for 2-3 days and continued by drying them in an oven at 110°C until a constant weight was obtained. The next step was reducing the size of avocado seeds using a grinder and sieving avocado seeds until a size of 120 mesh was obtained.

Avocado Seed Oil Extraction
The 120 mesh avocado seeds were extracted using the soxhletation method with a reaction time of 2 hours, a temperature of 65°C, and n-hexane solvent. The extracted solution was then separated from avocado seed oil and n-hexane using a distillation apparatus. After obtaining pure
avocado seed oil, free fatty acid analysis was carried out.

**Esterification**

The esterification process was done with a mole ratio of avocado seed oil to methanol of 1:6 and an acid catalyst (H₂SO₄ solution) of 0.5% (w/w). The esterification process with stirring was kept at 60°C and the reaction time was 2 hours. A separation process was carried out using a centrifuge at 3000 rpm for 30 minutes to remove residue from the esterification process. After that, washing with distilled water was carried out until the pH of the product became neutral. After that, analysis of free fatty acids was carried out.

**Transesterification**

The transesterification process was carried out with a mole ratio of avocado seed oil to methanol of 1:6 and 1% (w/w) of alkaline catalyst (NaOH). The transesterification process with stirring was kept at 65°C and the reaction time was 2 hours. Furthermore, the separation process was carried out using a centrifuge to form 2 phases: the top layer (methyl ester) and the bottom layer (glycerol).

**Analysis of Avocado Seed Oil Biodiesel**

Determination of the acid value of biodiesel was carried out by titration using 0.1 N KOH. The titration was carried out twice and the acid value was calculated using the following formula:

\[ \text{Acid Value} = \frac{V_{KOH} \times N_{KOH} \times 56.11}{\text{grams of sample}} \]  

Determination of the density of biodiesel was carried out using a pycnometer. Oxidation stability was measured from the Induction Period value obtained by the Rancimat method [10]. The sample required for the Rancimat method of oxidation stability analysis was 6 grams with the boiling temperature maintained at 110 °C. For 30 minutes, conductivity measurements were carried out until a spike in conductivity occur and the measurement was then stopped.

**RESULT AND DISCUSSION**

**Pre-treatment of Avocado Seeds**

The drying process was stopped when the weight of the dried avocado seeds had a relatively constant value (±5%). In this case, it was considered that the water content contained in the avocado seeds had completely evaporated.

From 15 kg of wet avocado seeds, the dry sample weight produced after drying was 4.1 kg or 27.33% (w/w) of the avocado seed sample before drying. The water content in avocado seeds is 73.66% [11]. The percentage of evaporated water content from the results of this study is almost the same value as their research, which is 72.2%, this shows that the water content in avocado seeds evaporates completely. Data on the drying of avocado seeds can be seen in Table 1.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Wet Sample Weight (kg)</th>
<th>Dry Sample Weight (kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Avocado Seeds</td>
<td>15</td>
<td>4.1</td>
</tr>
</tbody>
</table>

From the 4.1 kg dry sample weight, then a size reduction and sieving process were carried out to obtain a size of 120 mesh. This size is to obtain the condition that the smaller the particle size of the avocado seed, the wider the contact area between the material and the solvent. This also affects the length of extraction time. The wider the contact area between the material and the solvent, the faster the extraction process.

**Avocado Seed Oil Extraction**

The extraction process takes 2-3 hours depending on the weight of samples put in the filter paper. For a 250 mL soxhlet, generally the sample weight placed is around 30-40 grams.

From 4.1 kg of dried avocado seed samples, 310 grams of oil was produced with a volume of 325.39 mL or 7.56% (w/w) of the dried avocado seed sample. Avocado seeds contain 3-30% (w/w) of oil depending on the ecological and racial characteristics of the plant [5]. The level of maturity also affects the oil content because ripe fruit has a low water content and a high oil content [12]. Data from the extraction of avocado seed oil can be seen in Table 2.
Table 2. Results of Extraction of Avocado Seed Oil

<table>
<thead>
<tr>
<th>Dry Avocado Seed Weight (kg)</th>
<th>Mass of Avocado Seed Oil (grams)</th>
<th>Avocado Seed Oil Volume (mL)</th>
<th>Avocado Seed Oil Oil Content (%w/w)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.1</td>
<td>310</td>
<td>325.39</td>
<td>7.56</td>
</tr>
</tbody>
</table>

Esterification of Avocado Seed Oil

The esterification process is a conversion step from free fatty acids to esters with the help of an acid catalyst. Esterification must be done to reduce the free fatty acids in the extracted avocado seed oil. From the calculation, it was obtained free fatty acids (FFA) of 14.4%. Because the FFA obtained is >2%, the transesterification process cannot be carried out directly. Avocado seed oil with a high free fatty acid content will cause a saponification reaction because the FFA reacts with an alkaline catalyst if the transesterification process is carried out. Therefore, it is necessary to carry out the esterification process which aims to reduce the %FFA value. The following data from the esterification process can be seen in Table 3.

Table 3. Data from the Esterification Process

<table>
<thead>
<tr>
<th>FFA Before Esterification</th>
<th>FFA After Esterification</th>
</tr>
</thead>
<tbody>
<tr>
<td>14.4%</td>
<td>0.72%</td>
</tr>
</tbody>
</table>

The decreased %FFA value (Table 3) indicates that the esterification process has successfully converted free fatty acids into methyl esters and water as a by-product. Because the esterification process is carried out using an acid catalyst, it is necessary to wash it so that the acid catalyst does not react with the base catalyst during the transesterification process which can cause a decrease in the yield of biodiesel produced. In this study, the washing process was carried out seven times using distilled water until the pH was the same as the pH of the distilled water to ensure that no residual acid catalyst (H₂SO₄) was left in the esterification results [10]. After the washing process, three layers are formed, namely the upper layer is methyl ester, the middle layer is a mixture of methyl ester and distilled water, and the bottom layer is water. The washing process in this study used a centrifuge with a rotational speed of 3000 rpm for 1 hour and produced 24.75 grams of methyl ester.

Transesterification of Avocado Seed Oil

The transesterification process of avocado seed oil produced a by-product in the form of glycerol. The Glycerol by-product is shown in Figure 2.

Figure 2. Separation Results After the Transesterification Process

Figure 2 shows that the results of the separation formed 2 layers: the top layer is methyl ester and the bottom layer is glycerol. The yield obtained was 34.61%. This low yield can be caused by several factors, including the presence of wasted products during the washing process due to the separation process carried out using a centrifuge which results in not all of the methyl ester being carried away but also wasted along with the washing water in the centrifuge tube. Another reason is that the acid catalyst during the esterification process was not completely wasted. The excess acid (excess H₂SO₄) was predicted to be carried to the top layer and then reacted with the alkaline catalyst (NaOH) in the transesterification stage. Another possibility is a saponification reaction between all unconverted free fatty acids into methyl esters which react with an alkaline catalyst (NaOH) to produce products in the form of soap and glycerol [13].

Analysis of Avocado Seed Oil Biodiesel

Crucial parameters analyzed include acid value, density, and oxidation stability. The test results are compared with SNI 7182: 2015 as shown in Table 4.
Table 4. Results of Parameter Analysis of Avocado Seed Oil Biodiesel

<table>
<thead>
<tr>
<th>No</th>
<th>Parameter</th>
<th>Test Result</th>
<th>SNI Standard</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Acid Value</td>
<td>0.98 mg-KOH/g</td>
<td>0.5 mg-KOH/g, max</td>
</tr>
<tr>
<td>2</td>
<td>Density</td>
<td>977 kg/m³</td>
<td>850-890 kg/m³</td>
</tr>
<tr>
<td>3</td>
<td>Oxidation Stability</td>
<td>318 minutes</td>
<td>480 minutes</td>
</tr>
</tbody>
</table>

The acid value test carried out in duplo resulted in a value of 0.98 mg-KOH/g. The acid value of the biodiesel produced is greater than the acid value required by SNI 7182:2015. The acid value resulting from this study is close to the results of the Hiwot study which obtained an acid value of 0.89 mg-KOH/g [14]. The high result of the acid value from this study indicates that there are still free fatty acids contained in biodiesel. The higher the acid value, the higher the ability of biodiesel to corrode the engine [15].

The density parameter obtained is 977 kg/m³, which does not meet SNI-7182:2015. This high-density value indicates the presence of glycerol, fatty acids that are not converted to biodiesel, and residual methanol contained in the biodiesel. The high-density value is caused by the incomplete separation between biodiesel and glycerol [16].

The value of oxidation stability is obtained through the Rancimat method, a test carried out by injecting a certain amount of heat and oxygen. The oxidation reaction of biodiesel forms peroxides and other products from the degradation of fatty acids. The compound formed is flowed through the air into a beaker containing distilled water, and then changes in conductivity are measured continuously every 30 minutes. The content of organic acids is detected through the increase in conductivity. The oxidation stability testing equipment is assembled as shown in Figure 3.

The Induction Period (IP) is the time measured from the start of heating to a spike in oxidative activity occurs. This IP value indicates the stability of oxidation in oil or grease or the resistance of biodiesel not to experience degradation due to oxidation by oxygen and heat within a certain period of time.

The value of oxidation stability is inversely proportional to the acid value [17]. The lower the oxidation stability, the higher the acid value is obtained.

The results of this study are in accordance with the theory. The acid value obtained was 0.98 mg-KOH/g possibly
because avocado seeds contain unsaturated fatty acids such as linoleic acid and oleic acid which cause the oil to oxidize easily. To obtain biodiesel from avocado seed oil so that it can be stored for a long time, it is necessary to add antioxidants.

Several researchers added antioxidants to obtain IP above 480 minutes [18, 19]. The synthetic antioxidants most often used in biodiesel include propyl gallate (PG), pyrogallol (PY), butylated hydroxyanisole (BHA), and tetra-butyl hydroquinone (TBHQ) [18]. Antioxidant TBHQ showed the best oxidative stability in used cooking oil biodiesel, followed by PY, PG, BHA, and BHT. Oxidation stability increased from 3.01 hours to 22.3 hours after TBHQ antioxidant addition, 20.07 hours after PY antioxidant addition, 15.10 hours after PG antioxidant addition, to 7.24 hours after BHA antioxidant addition, and 6.27 hours after BHT antioxidant addition [20].

CONCLUSION

The synthesis process of avocado seed biodiesel was carried out through 2 processes, i.e. esterification and transesterification with a biodiesel yield of 34.61%. The characteristics of biodiesel from avocado seeds had an acid value of 0.98 mg-KOH/g, a density of 977 kg/m³, and an oxidation stability of 318 minutes or 5.3 hours. These three parameters do not meet the requirements of SNI 7182:2015.

ACKNOWLEDGEMENT

We would like to express our special thanks to Politeknik Negeri Bandung for providing funding assistance and research equipment.

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