Fuel Characteristics of Biodiesel Produced from a High-Acid Oil from Soybean Soapstock by Supercritical-Methanol Transesterification

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Abstract: A supercritical methanol transesterification method was applied to produce biodiesel from the high-acid oil of soybean soapstock. The fuel properties of biodiesel produced with various molar ratios of methanol to raw oil were analyzed and compared in this experimental study. Oleic acid (C18:1), linoleic acid (C18:2), and palmitic acid (C16:0) were the three main compounds in the high-acid oil-biodiesel. The saturated fatty acid content of the high-acid oil increased significantly due to the supercritical-methanol transesterification reaction. The fuel characteristics of the resulting high-acid oil, including the specific gravity and kinematic viscosity, were also greatly improved. The saturated fatty acid content of the biodiesel produced from the high-acid oil was higher than that of biodiesel from waste cooking oil produced by the subcritical transesterification using a strongly alkaline catalyst. The high-acid oil-biodiesel that was produced with a molar ratio of methanol to raw oil of 42 had the best fuel properties, including a higher distillation temperature and cetane index and a lower kinematic viscosity and water content, among the biodiesels with different molar ratios.

Keywords: biodiesel; high-acid oil; saturated fatty acids; supercritical-methanol transesterification
1. Introduction

Biodiesel is a renewable fuel that has superior biodegradability, better lubricity, and is better for the environment than petroleum fuel. The use of biodiesel as an alternative fuel for diesel vehicles, coastal ships, and merchant vessels also results in fewer poisonous emissions into the atmosphere [1]. Moreover, biodiesel that leaks or is discharged from marine vessels into the ocean generally decomposes into less harmful components and causes much less pollution to the ocean environment [2].

The higher cost of biodiesel is currently the main obstacle to its widespread use as an alternative to petroleum-derived fuel, particularly in application in marine vessels. Biodiesel is produced from vegetable oils, animal fats, or algae, generally through a transesterification reaction. The price of the feedstock typically accounts for 75% of the cost of manufacturing biodiesel. Lower-cost feedstocks such as used cooking oil or rubber oil are thus preferable to reduce the cost of production. However, those feedstocks generally have a high moisture content and free fatty acid content, which may cause saponification, leading to a lower conversion rate and poorer fuel quality. It has been suggested that such feedstocks should be pretreated to achieve a moisture level of less than 0.06 wt % and a free fatty acid content of less than 0.5 wt % [3].

A supercritical fluid is a fluid that is under a temperature and pressure that is higher than its corresponding critical temperature and pressure. The diffusion coefficient of a supercritical fluid is greater than in its liquid phase, and it thus has more intense contact with other reactants to boost the reaction rate. The viscosity of a supercritical fluid is lower than in its liquid phase, giving it greater fluidity [4]. Soybean soapstock is a lipid-rich by-product of the refinement of soybean cooking oil [5]. So-called high-acid oil is produced from the acidification reaction of soybean soapstock with sulfuric acid and water steam. High-acid oil derived from soybean soapstock generally contains as much as 59.3 wt % free fatty acids, and thus cannot be directly transesterified using a strong alkaline catalyst [6].

With supercritical-fluid transesterification, the moisture and free fatty acids in the feedstock do not hinder the production of biodiesel. On the contrary, their presence may even enhance the conversion of the feedstock to fatty acids methyl esters [7]. No catalyst is required and fewer post-treatment processes are needed in supercritical-fluid transesterification, which reduces the manufacturing cost. Soapstock, which is generally composed of 50 wt % water, alkaline lipids, and triacylglycerols and a high level of free fatty acids and other nonpolar components, is a by-product of the refining of vegetable oils such as soybean oil. The production rate of soapstock is about 6 vol % of the refined oil [8]. High-acid oil is produced from the reaction of soybean soapstock with sulfuric acid and water steam at about 110 °C. Soybean soapstock and high-acid oil are mostly used as raw feedstocks for fatty acid and soap production, and in animal feeds. The use of high-acid oil from soybean soapstock as the raw material for biodiesel production is currently limited, primarily due to its high water and free fatty acid contents, which make it unsuitable for alkaline-catalyst transesterification [9]. No investigations of the fuel properties of biodiesel produced with high-acid oil from soybean soapstock through supercritical-methanol transesterification have been published. This study thus used the high-acid oil from soybean soapstock as the feedstock for biodiesel production using supercritical-methanol transesterification, and analyzed and compared the fuel properties of biodiesel produced with various
molar ratios of methanol to high-acid oil to evaluate its potential as an alternative fuel for land vehicles and marine vessels.

2. Experimental Details

The high-acid oil from soybean soapstock was provided by the Central Union Oil Corp. of Taiwan. The high-acid oil was transesterified with supercritical-methanol to produce high-acid oil-biodiesel under various molar ratios of methanol to high-acid oil (referred to as the M/H molar ratio). Higher methanol/oil molar ratio than 12 is suggested for commercial supercritical-methanol transesterification systems for biodiesel production [10]. Lower M/H molar ratios have been found to cause lower fatty acid methyl esters (FAME) conversion and require higher critical temperature and longer transesterification time [11]. Hence, the M/H molar ratio was set between 12 and 50 in this study. The fuel properties of the biodiesel were analyzed, including the heating value, flash point, cetane index, and kinematic viscosity. The experimental details are described in the following sections.

2.1. Preparation of the Biodiesel

The supercritical-methanol reacting system was manufactured by the Jeouu Rong Industrial Corp. in Taiwan. The system was composed of a reacting tank, feeding pump, temperature-control unit, cooling vessel, and anti-explosion stainless tank. The maximum tolerable pressure and temperature of the reacting system was 27.6 MPa and 450 °C, respectively [12]. The volume of the reacting tank was 5000 cm³. The experimental setup of the supercritical-methanol reacting system is illustrated in Figure 1.

**Figure 1.** Experimental setup of the supercritical methanol transesterification system for the production of biodiesel from high-acid oil.
Activated acidic clay was used to absorb the impurities and decolorize the crude high-acid oil produced from the acidification of the soybean soapstock. After the pretreatment process, the high-acid oil was poured into the reacting tank and mixed with methanol to form various molar ratios of methanol to high-acid oil (M/H molar ratio) ranging between 12 and 50. The reacting mixture was then heated to a temperature of 350 °C in the reacting tank, which far exceeded the corresponding critical temperature (239 °C) of methanol. The supercritical-methanol transesterification reaction proceeded under the same reactant temperature for 30 min. The product was then either kept motionless or centrifuged to separate the crude biodiesel in the upper layer from the glycerin in the bottom by the difference in gravity between the two compounds. The crude biodiesel was then heated to 110 °C for 10 min to remove any unreacted compounds, water, methanol, or other volatile impurities. The fuel properties of the biodiesel product were then analyzed.

2.2. Analysis of the Fuel Properties of the Biodiesel

A gas chromatography (GC) analyzer (GC-14A model by Shimadzu Inc., Kyoto, Japan) with the Chromatography Data Management system (Advantech Inc., Taipei, Taiwan) was used to analyze the weight proportions of the fatty acids in the high-acid oil-biodiesel produced by the supercritical-methanol transesterification system. The capillary column in the GC analyzer was 0.25 mm in diameter and 30 m long.

The heating value of the biodiesel was analyzed with an oxygen bomb calorimeter (1261 automatically adiabatic model, Parr Instrument Co., Moline, IL, USA) [13]. A capillary viscometer (501 23/Iic, Schott Gerate Inc., Mainz, Germany) at a constant temperature of 4 °C inside a water tube was used to measure the kinematic viscosity of the fuel. The water content in the biodiesel was analyzed by a volumetric Karl Fischer Titration unit (DL31 model, Mettler Toledo Ltd., Zurich, Switzerland). A Conradson carbon residue analyzer was used to measure the carbon residue in units of wt %.

The distillation temperatures of the biodiesel samples T10, T20, T50, and T90, which stand for distillation temperatures corresponding to 10, 20, 50, and 90 vol % of the distilled and condensed liquid fuel, respectively, were measured by a distillation temperature analyzer (HAD-620 model, Petroleum Analyzer Inc., Pasadena, TX, USA). The cetane index (CI) of the biodiesel samples was calculated from the specific gravity (SG) and distillation temperature T50 using the following formula [14]:

\[
CI = -420.34 + 0.016 G^2 + 0.192 G (\log_{10} T_{50}) + 65.01 (\log_{10} T_{50})^2 - 0.0001809 T_{50}^2
\]

where \( G = 141.5/SG - 131.5 \).

3. Results and Discussion

3.1. Fuel Characteristics of the High-acid Oil and Its Biodiesel Product

The fuel characteristics of the raw high-acid oil from the feedstock and its biodiesel product transesterified in the supercritical-methanol reacting system under a molar ratio of methanol to high-acid oil of 42 are compared in Table 1. The heating value of the high-acid oil-biodiesel was slightly greater after the transesterification process. Moreover, the water content and kinematic
viscosity of the raw high-acid oil were significantly higher than those of the high-acid oil-biodiesel. The carbon residue, acid value, and specific gravity of the raw high-acid oil were reduced after the transesterification reaction. This implies that the fuel properties of the high-acid oil-biodiesel were significantly improved and superior to those of the raw high-acid oil following supercritical-methanol transesterification.

Table 1. Fuel properties of the high-acid oil and its biodiesel product with a molar ratio of methanol to high-acid oil of 42.

<table>
<thead>
<tr>
<th>Fuel property</th>
<th>Fuel type</th>
<th>High-acid oil</th>
<th>Biodiesel product</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heating value (MJ/kg)</td>
<td></td>
<td>39.03</td>
<td>39.55</td>
</tr>
<tr>
<td>Carbon residue (wt %)</td>
<td></td>
<td>0.28</td>
<td>0.25</td>
</tr>
<tr>
<td>Specific gravity</td>
<td></td>
<td>0.912</td>
<td>0.884</td>
</tr>
<tr>
<td>Water content (wt %)</td>
<td></td>
<td>0.787</td>
<td>0.154</td>
</tr>
<tr>
<td>Kinematic viscosity (mm² s)</td>
<td></td>
<td>35</td>
<td>5.2</td>
</tr>
<tr>
<td>Flash point (°C)</td>
<td></td>
<td>-*</td>
<td>118</td>
</tr>
<tr>
<td>Acid value (mg KOH/g)</td>
<td></td>
<td>-*</td>
<td>0.8</td>
</tr>
<tr>
<td>Cetane index</td>
<td></td>
<td>-*</td>
<td>45.49</td>
</tr>
<tr>
<td>Iodine value (g I/100g oil)</td>
<td></td>
<td>-*</td>
<td>62.6</td>
</tr>
</tbody>
</table>

*: Not available.

3.2. Fatty Acid Composition

The relative weight compositions of the biodiesel produced from the high-acid oil in the supercritical-methanol transesterification reacting system at molar ratios of methanol to raw high-acid oil of 24 and 42, commercial biodiesel from waste cooking oil produced by subcritical transesterification with a strong alkaline catalyst, and the raw high-acid oil used for the biodiesel production were analyzed and compared with a gas chromatography analyzer. The fatty acids in the high-acid oil-biodiesel primarily comprised 38.91 wt % oleic acid (C18:1), 25.38 wt % linoleic acid (C18:2), and 22.31 wt % palmitic acid (C16:0), as shown in Table 2. These three fatty acid compounds accounted for 86.5 wt % of the total fatty acid content. By comparison, the fatty acids in the raw high-acid oil were mainly unsaturated fatty acids, including 50.01 wt % linoleic acid (C18:2) and 24.77 wt % oleic acid (C18:1). The unsaturated fatty acid content in the raw high-acid oil was as high as 82.02 wt %. The saturated fatty acid content significantly increased by about 82% in the supercritical-methanol transesterification reaction, which was from 17.98 wt % in the raw high-acid oil to 32.88 wt % in the high-acid oil-biodiesel product. The higher saturated fatty acid content would cause higher oxidative and thermal stability, leading to a slower deterioration rate of the lipid characteristics [15]. The saturated fatty acid content of the high-acid oil-biodiesel produced by supercritical-methanol transesterification was also significantly higher than that of a biodiesel produced from soybean soapstock by subcritical strong alkaline transesterification in a previous study, which was 21.20 wt % [5].

The saturated fatty acid composition of the waste cooking oil biodiesel (29.71 wt %) produced by subcritical methanol transesterification appeared to be lower than that of the high-acid oil-biodiesel, as
shown in Table 2. Oleic acid (C18:1), linoleic acid (C18:2), and palmitic acid (C16:0) were the three main fatty acids in the waste cooking oil-biodiesel. The high-acid oil-biodiesel also had the highest saturated fatty acid among the three products, and thus the greatest thermal and oxidative stability, which would retard its fuel deterioration in high-temperature environments or long-term storage.

3.3. Kinematic Viscosity

Viscosity is directly related to the atomization, lubricity, impinging distance, and burning efficiency of a liquid fuel. Biodiesel generally has a higher viscosity than petro-diesel, and thus has inferior atomization and spray, resulting in a larger mean liquid droplet diameter and a longer ignition delay [16]. Figure 2 shows that the kinematic viscosity of the biodiesel samples decreased as the M/H molar ratio increased.

**Figure 2.** Kinematic viscosity of the biodiesel produced with various molar ratios of methanol to high-acid oil by supercritical-methanol transesterification.

![Kinematic viscosity graph](image)

The kinematic viscosity of the biodiesel with an M/H molar ratio of 42 was the lowest, at 5.2 mm$^2$/s, as shown in Figure 2. The kinematic viscosity of methanol (0.7 mm$^2$/s) is considerably lower than that of the high-acid oil, which was 35 mm$^2$/s at 20 °C. Hence, an increase in the M/H molar ratio reduced the kinematic viscosity of the reactant mixture of the high-acid oil and methanol, and in turns that of the biodiesel product. The high-acid oil was primarily composed of triglycerides with longer carbon chains and a greater molecular weight. A higher M/H molar ratio of the reactant mixture thus caused the formation of more unsaturated fatty acids [17]. Hence, the biodiesel produced from high acid oil with molar ratio of methanol to oil of 42 was found to have significantly lower kinematic viscosity than that of the biodiesel with molar ratio of methanol to oil of 24 in Figure 2. The supercritical-methanol transesterification reaction produced fatty acid methyl esters from the high-acid oil with significantly shorter carbon chains, leading to the much lower kinematic viscosity shown in Table 2 and Figure 2.
Table 2. Comparison of the fatty acid composition (wt %) of the high acid-oil biodiesel produced with molar ratios of methanol/raw oil of 24 and 42 with that of waste cooking oil biodiesel and the raw high-acid oil.

<table>
<thead>
<tr>
<th>Type of fatty Acids</th>
<th>Biodiesel from high-acid oil with M/H = 24</th>
<th>Biodiesel from high-acid oil with M/H = 42</th>
<th>Biodiesel from waste cooking oil</th>
<th>High-acid oil</th>
</tr>
</thead>
<tbody>
<tr>
<td>Palmitic acid (C16:0)</td>
<td>23.45</td>
<td>22.21</td>
<td>22.99</td>
<td>12.79</td>
</tr>
<tr>
<td>Palmitoleic acid (C16:1)</td>
<td>0</td>
<td>0</td>
<td>1.316</td>
<td>0</td>
</tr>
<tr>
<td>Stearic acid (C18:0)</td>
<td>10.17</td>
<td>9.91</td>
<td>5.32</td>
<td>4.69</td>
</tr>
<tr>
<td>Oleic acid (C18:1)</td>
<td>36.75</td>
<td>38.91</td>
<td>36.64</td>
<td>24.77</td>
</tr>
<tr>
<td>Linoleic acid (C18:2)</td>
<td>26.49</td>
<td>25.38</td>
<td>29.24</td>
<td>50.01</td>
</tr>
<tr>
<td>Linolenic acid (C18:3)</td>
<td>1.94</td>
<td>2.82</td>
<td>3.11</td>
<td>7.23</td>
</tr>
<tr>
<td>Behenic acid (C22:0)</td>
<td>1.20</td>
<td>0.76</td>
<td>1.4</td>
<td>0.50</td>
</tr>
<tr>
<td>Saturated fatty acids</td>
<td>34.82</td>
<td>32.88</td>
<td>29.71</td>
<td>17.98</td>
</tr>
</tbody>
</table>

3.4. Water Content

The existence of water in liquid fuel enhances its hydrolysis, resulting in the deterioration of the fuel characteristics, particularly for biodiesel. The water content of a fuel generally increases with storage time once oxidative instability is initiated, which is governed by the peroxidation chain mechanism [18]. The more extensive formation of primary oxidation products such as hydroperoxides and conjugated dienes then continuously occurs from the decomposition of unsaturated fatty acids [19], leading to the rapid degeneration of fuel properties such as the flash point, cetane index, and heating value. The presence of water in liquid fuel may also induce the formation of microorganisms and speed up the corrosion of metallic engine parts [20]. Hence, reducing the water content in liquid fuel to as low a level as possible is preferable to retain stable and superior fuel characteristics.

An increase in the M/H molar ratio appeared to reduce the water content in the biodiesel produced in this study, as shown in Figure 3.

Figure 3. Water content of the biodiesel produced with various molar ratios of methanol to high-acid oil by supercritical-methanol transesterification.
This is probably because water was more likely to be deposited in the raw high-acid oil than in the neat methanol. Water that had bonded with viscous glycerin in the oil phase was also less likely to be distilled away during the post-treatment of the biodiesel product. It follows that the biodiesel samples produced with a lower M/H molar ratio had higher water content.

### 3.5. Distillation Temperature

The distillation temperature is one of the main indicators of the volatility and distribution of light to heavy chemical compounds in a liquid fuel. A lower distillation temperature of \( T_{50} \) generally implies a lower content of heavier compounds in a liquid fuel, which causes a longer ignition delay and a greater degree of knocking. In contrast, a higher distillation temperature of \( T_{90} \) indicates a higher content of heavier compounds, which may cause a slower vaporization rate and inferior atomization of liquid fuel.

The biodiesel products of the high-acid oil had higher distillation temperature values but a narrower temperature range than premium diesel, as shown in Figure 4. The trends in the curves in Figure 4 are similar to those of the biodiesels made from waste parts of marine fish oil and animal fats [21,22].

**Figure 4.** Comparison of the distillation temperatures of the biodiesel produced with various molar ratios of methanol to high-acid oil by supercritical-methanol transesterification.

Knothe [23] found that biodiesel containing a higher content of mono-unsaturated fatty acids such as oleic acid (C18:1) generally has a higher distillation temperature. The biodiesel sample produced with an M/H molar ratio of 42 appeared to have a higher distillation temperature than that produced with an M/H molar ratio of 24 due to the higher mono-unsaturated fatty acid content of the former of 38.91 wt % compared with that of the latter of 36.75 wt %, as shown in Table 2. A lower volatile compound content also causes an increase in the distillation temperature of liquid fuel. The supercritical-methanol transesterification process used in this study was carried out under a significantly higher temperature.
than the traditional subcritical transesterification reaction. Hence, the biodiesel products of the former process had higher distillation temperatures than the products of the latter process because they had fewer volatile compounds.

### 3.6. Cetane Index

The cetane index of a liquid fuel represents its compression ignition quality for diesel engines. A higher cetane index translates into a shorter ignition delay, a faster engine cold-start, a smoother combustion process, and a higher burning efficiency. The cetane index is frequently influenced by the structure of fatty acids, the saturated fatty acid content, and the length of the carbon chains in a fuel. Longer carbon chains associated with a higher saturated fatty acid content result in a higher cetane index [24].

The cetane indices of the biodiesel products increased as the M/H molar ratio increased, as illustrated in Figure 5. This is because a higher M/H molar ratio resulted in a higher $T_{50}$ distillation temperature, as shown in Figure 4. The specific gravity of the biodiesel product was found to decrease with the increase of the M/H molar ratio in this study. Therefore, lower specific gravity of the biodiesel produced with a higher M/H molar ratio is also responsible for the higher cetane index according to the formula of cetane index. In addition, the higher saturated fatty acid content of the biodiesel samples produced with a higher M/H molar ratio also explains their higher cetane index.

**Figure 5.** Cetane index of the biodiesel produced with various molar ratios of methanol to high-acid oil through supercritical-methanol transesterification.

### 4. Conclusions

The experimental results demonstrate the potential of using such biodiesel products as an alternative fuel for land vehicles and marine vessels. The main conclusions of this study are summarized as follows.
(1) Oleic acid (C18:1), linoleic acid (C18:2), and palmitic acid (C16:0) were the three main compounds found in the high-acid oil-biodiesel, whereas the raw high-acid oil was primarily composed of unsaturated fatty acids. The saturated fatty acid content of the high-acid oil-biodiesel was significantly increased.

(2) The level of saturated fatty acids in the biodiesel produced from the high-acid oil by supercritical-methanol transesterification was higher than in the waste cooking oil-biodiesel produced by subcritical transesterification of a strong alkaline catalyst.

(3) The fuel properties of the biodiesel produced by the supercritical-methanol transesterification system were much better than those of the raw high-acid oil, particularly the specific gravity, water content and kinematic viscosity.

(4) An increase in the molar ratio of methanol to high-acid oil resulted in an increase in the kinematic viscosity, distillation temperature, and cetane index and a decrease in the specific gravity, kinematic viscosity, and water content of the high-acid oil-biodiesel.

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References


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