A Study of Biodiesel (Ethyl Ester) Production from Grease/Oil Rich Sludge through Acid-Catalytic Ethanol Transesterification and It’s Fuel Specifications

Kappaput Thong-Innatra, Gritsanaruk Theeraraj, Chumporn Yuwaree, Kitikorn Charmondusit and Rungrat Hutacharoen*
Faculty of Environment and Resource Studies, Mahidol University, Nakhon Pathom 73170, Thailand

Abstract

The objective of this study is to produce biodiesel from grease/oil rich sludge which was trapped from the canteen of Mahidol University’s Salaya campus. The biodiesel was produced through the process of transesterification reaction in the presence of an acidic catalyst of concentrated sulfuric acid. 100% excess ethanol was used to accomplish the reaction at the molecular ratio of 30:1 (ethanol to grease) at 90°C for 90 minutes. The finished product contained 95.17% biodiesel by volume with an API gravity value of 0.90 g/cm³ at 15°C, a viscosity value of 8.69 mm²/s at 40°C, a flash point value of 184°C, and a heat value of 9,685.35 cal/g. The blending with petroleum based diesel or baseline diesel (commercial diesel) at the proportions of 5, 10, 15, and 20 percent showed no statistical significant difference at the 0.05 level. In addition, the engine performance of the blends had slightly higher engine torque and engine power than baseline diesel. In conclusion, this study found that the conversion of the canteen’s trap grease into ethyl ester had the potential to be a diesel substitute, particularly at the blending ration of 15%.

Key Words: trapped grease / biodiesel / transesterification

1. Introduction

Due to the world’s increasing demand for non-renewable petroleum and the never-ending rise in petroleum prices in the oil market, and Thailand, as an agricultural oil importing country using petroleum for agriculture, transportation, electricity generation, industry, and commercial sectors, multiple options for seeking substitutable alternative energy sources, such as bio energy, solar energy, and wind energy, as well as biodiesel (ester from of grease conversion), have been introduced. Donkathin (2000) noted that the grease/oil traps at food services such as restaurants, canteens, and cafes with floor surface sizes of less than 100, 100-200, and more than 200 square meters, had a grease and oil content as high as 129.49, 57.61, and 86.53 milligrams per liter respectively. Such grease/oil rich sludge produced from food services in Bangkok inevitably sinks into the water system, which accumulates over time and contaminates the water supply. Therefore, the extraction of these grease and oil pollutants (grease/oil rich sludge) and subsequent conversion into valuable compounds such as esters or biodiesel¹ through transesterification

¹ According to Directive 2003/30 EC of the European Parliament, the term biodiesel is any methyl ester produced from vegetable or animal oil of diesel quality. ASTM defines biodiesel fuel as monoalkyl esters of long fatty acids derived from a renewable lipid feedstock such as vegetable oil or animal fat (Demirbas, 2009).
reaction to substitute some portion of diesel in machine combustion is certainly one beneficial option. It will not only provide a less expensive form of biodiesel fuel and lessen the water pollution problem, but will also provide an alternative approach to solving the problems of climate change and ecosystem destruction.

It is well known that a variety of biogrease/oil matter can be used to produce biodiesel, such as vegetable oils, waste vegetable oil, and animal fat including tallow, lard, and non-edible oils (Demirbas, 2009 and Demirbas, 2008). The most common way to produce biodiesel is through transesterification reaction, a chemical catalyzed reaction involving grease/oil and alcohol to yield fatty acid alkyl esters. Transesterification reaction using alkaline catalysts, as well as acidic catalysts, have received the greatest attention and are the highlight of this study. As all such waste materials can be used for the production of biodiesel (Bhatti, 2008), it is very feasible that waste grease/oil rich sludge from canteens and restaurants display the same characteristics and can be used as a raw material for biodiesel production. Moreover, in the chemical catalyzed reaction by excess alcohol, the study preferred and intended ethanol alcohol, in stead of methanol. Which is feasible at the local consumer level, particularly in view of self sustainability and the capability of communities to derive their own fuel from agricultural products. And in view of global climate change, biodiesel produced this way is a biologically renewable resource.

2. Materials and Methods

2.1 Conceptual Framework

Raw biodiesel in this study came from the grease and oil traps of the central canteen of Mahidol University’s Salaya campus. Synthetic transesterification reaction occurred in the presence of an acidic catalyst. The blended fuels were studied at biodiesel to petroleum diesel ratios of 5%, 10%, 15%, and 20% (B5, B10, B15, and B20 respectively). The stages of approach are outlined in Figure 1.

2.2 Biodiesel production

2.2.1 Selected procedure for grease conversion

Demirbas (2002) reviewed the production process of biodiesel from vegetable oil using catalytic and non-catalytic alcohol in transesterification reaction and other methods. Their study identified the influencing factors on transesterification reaction to be molar ratio of glycerides to alcohol, catalysts, reaction temperature, reaction time, and content of free fatty acids and water in grease/oil matter. Zhang (2003) reported that biodiesel production under alkaline catalytic reaction with purified vegetable oil used fewer instruments and fewer raw materials than biodiesel production under acidic catalytic reaction but at a higher cost; while acidic catalytic reaction conditions were technically more feasible.

---

2 Transesterification (alcoholysis) is the chemical reaction between triglycerides and alcohol in the presence of a catalyst to produce mono-esters. Stoichiometrically, three moles of alcohol are required for each mole of triglyceride but in practice, a higher molar ratio is employed in order to displace equilibrium for greater ester production.
Moreover, the study mentioned that biodiesel quantity tended to increase as the proportion of grease/oil matter and alcohol, temperature, and reaction time were extended. Furthermore, Mohamad Al-widyan and Al-Shyoukh (2002) studied the utilization of ethyl esters from vegetable oil waste as biodiesel for diesel engines. Their study concluded that the best conditions for transesterification reaction were with 2.25 M H₂SO₄ and 100% excess ethanol resulting in a specific gravity of 0.8737 from an initial value of 0.916 in three hours of reaction time, and that the biodiesel had the behaviour of a Newtonian fluid. Moreover, Loisamutr (1999), experimented with biodiesel from used vegetable oil in transesterification reaction with a sulfuric catalyst at 90°C for one hour, and showed the specific fuel consumption of a one piston, 11 Hp diesel engine using baseline diesel to be higher than the studied biodiesel. In research by Klongdech (2000), biodiesel from the used oil of McDonald’s restaurants blended with baseline diesel at 20%, 30%, 40%, and 50% was tested with a one piston 7.5 Hp diesel engine.

The study found that emissions of carbon monoxide, nitrogen oxide, and black smoke tended to decline when the percentage of biodiesel in the blends increased. Therefore, grease/oil rich sludge as the raw material of biodiesel production through acidic-catalyzed transesterification reaction, for which literatures had been studied, was considered to be the production procedure of this study. As well as, in the presence of catalyzing with excess ethanol alcohol, which literatures did not present any difference from methanol.

### 2.2.2 Production procedure

The grease/oil rich sludge³ was collected from the grease and oil traps of the central canteen, Mahidol University, Salaya. Production procedures of Demirbas (2002), Zhang (2003), and Mohamad Al-widyan and Al-Shyoukh (2002) were applied. Firstly, 1 ml of HCl (conc.) was added to every 80 g sample of grease/oil rich sludge to retain the grease structure. The waste amount was then separated and the pH reduced to 2 (each

---

³ The entire grease/oil rich sludge sample in this study was collected one time
A 20 g sample of waste used 0.3 ml of concentrated HCl. The acidic sample was heated for four hours at 103°C for water dehydration in an oven. The dried samples were then ground to a fine mixture as possible. Separated 100 g samples of ground matter were then added to 200 ml of hexane solvent in a reflux extraction set and heated at 90°C for four hours. The solvent solution was then evaporated in an evaporator at 85°C for 15 minutes. Secondly, for transesterification reaction, the extracted grease was heated to 80°C in a flask mixed with an amount of ethanol (only half of the calculated volume was used, see Table 3 and the remark for calculation), optimized to pH 3 by H₂SO₄ (conc.), stirred for one hour, and then left to cool. The mixture was then washed with deionized water, and separated to remove impurities. The clean product was then transferred to another flask (a round bottomed flask) to which the remaining ethanol (calculated volume) was added having had its pH adjusted to 3 again using H₂SO₄ (conc.). The flask was then combined with the reflux and heated at 90°C for 90 minutes. After that, the solution was poured into a separatory funnel and left to separate into two layers: the ethyl ester in the upper layer and the unwanted solution in the lower layer. Finally, the ethyl ester (biodiesel) was separated and cleaned by shaking with deionized water, and poured through sodium sulfite for water elimination.

2.3 Quantity and quality determination

The quantity and quality of biodiesel production was determined by volume measurement, fuel property tests, and engine performance tests as follows:

2.3.1 Fuel property

Fuel property testing was conducted using the following processes:
1) Kinematics viscosity, at 40°C: ASTM D-2270-93
2) API gravity, at 15°C: ASTM D-1298-99
3) Flash point: ASTM D-93-99a
4) Heat value by bomb calorimeter: ASTM C56

2.3.2 Engine performance

Testing was conducted by measuring the performance value of engine torque and engine power using petroleum diesel (baseline diesel) blended with biodiesel at the volume ratio basis of 100:0 (baseline diesel), 95:5 (B5), 90:10 (B10), 85:15 (B15), 80:20 (B20), and 0:100 (B100).

3. Result and Discussion

3.1 Quantity of the extracted grease

The variables affecting ester formation (Demirbas, 2009) were reaction temperature, pressure, molar ratio, water content, and free fatty acid content. The most important variables affecting ester yield during transesterification reaction were molar ratio of alcohol to grease and reaction temperature. Meher (Demirbas, 2009 and Meher et al., 2006) used a 6:1 molar ratio during acid esterification and a 12:1 molar ratio during alkaline esterification. However, due to the typical characteristics of the grease/oil rich sludge in this study, the most accurate molar ratio was 4:1. Meanwhile, in consideration of the effect of reaction temperature, Demirbas (2009) showed that a temperature higher than 323 K had a negative impact on the production yield of neat oil, but had a positive effect on the production yield of waste oil with higher viscosities. Furthermore, the presence of water and free fatty acids (FFA) in the
raw material during transesterification reaction caused soap formation, decreased the yield of alkyl esters, reduced the effectiveness of the catalyst, and induced an increase in viscosity (Demirbas, 2009 and Demirbas, 2006). Canakci and Gerpan (1999) insisted that even a small amount of water (0.1%) during transesterification reaction will decrease ester conversion from vegetable oil. Moreover, Canakci and Gerpan (1999) found that the alkaline catalyzed transesterification process was not suitable for the production of esters from unrefined oils and the high saturated fatty acid sample, and that acid esterification was typically recommended for producing biodiesel from high FFA oils. The quantity of extracted grease is shown in Table 1, where 600 g of grease/oil rich sludge could provide, on average, 325.27 g of grease or 54.20 % of dry waste. Which the aforementioned transesterification product (see 2.2.2) performed the dark red in color and emitted a bad smell with various pH and components as shown in Tables 2 and 3. As well, it can be concluded that with this procedure 600 ml of grease/oil rich sludge can be converted into 571 ml of ethyl ester (biodiesel), giving a conversion efficiency of 95.17%. The pH of the product was 1.3 and 6.3 on average after washing several times (at least 3 times).

In addition, the proportion of alcohol and grease (computed from gas chromatography) revealed that grease had a total saturated fatty acid content of 90.03% and a total unsaturated fatty acid content of 9.97% (see Table 3). The proportion of ethanol and grease could be calculated5 and set to an ethanol to grease ratio of 4:1.

3.2 Fuel specific test

The ASTM D 6751 standard identifies that certain parameters for pure biodiesel (B100) must be met before being used as a pure fuel or before being blended with a petroleum based diesel fuel. Biodiesel specifications (Demirbas, 2009 and ASTM D6751-02: requirements) remark kinematic viscosity at 40°C to be 1.9-6.2 mm²/s (ASTM D445), flash point to be 130°C (ASTM D 93), and API gravity to be 0.86-0.90 g/cm³ (ASTM D1298). Additionally, another international standard describing the minimum requirements for biodiesel produced from rapeseed fuel stock (EN 14214: requirements for biodiesel) remark density at 15°C to be 860-900 kg/m³ (methods EN ISO 3675 and EN ISO 12185) and flash point to be over 101°C (Demirbas, 2009 and method ISO CD 3679e). This study therefore employed a fuel specific test to determine the quality of the converted grease/oil rich sludge (biodiesel) as a diesel substitute by measuring kinematics viscosity, API gravity, flash point, and heat value, as shown in Table 4.

triglyceride, the MW of the grease is 289.94*3, which is equal to 869.82. The alcohol used in the reaction was 30:1 by mole with the grease. The volume of alcohol could be determined by formula where the volume (ml) equalled the molecular mass divided by the density (g/ml). Therefore, when the molecular weight of the ethyl alcohol was 46.07 and the density was 0.719 g/cm³, 30*46.07 = 1382.1 of alcohol was used. So, the final volume used was 1382.1/0.719 or 1922.25 ml. For 95% alcohol solution, the volume of the ethyl alcohol must be 1922.25*100/95 = 2023.42 ml. Similarly, as the molecular weight of the grease was 869.83 and the density was 0.904 g/ml, the volume of the grease used in this study was 962.20 ml, using the same equation. Consequently, the proportion, theoretically, of ethanol and grease by volume in the reaction was 3.2 Fuel specific test

The ASTM D 6751 standard identifies that certain parameters for pure biodiesel (B100) must be met before being used as a pure fuel or before being blended with a petroleum based diesel fuel. Biodiesel specifications (Demirbas, 2009 and ASTM D6751-02: requirements) remark kinematic viscosity at 40°C to be 1.9-6.2 mm²/s (ASTM D445), flash point to be 130°C (ASTM D 93), and API gravity to be 0.86-0.90 g/cm³ (ASTM D1298). Additionally, another international standard describing the minimum requirements for biodiesel produced from rapeseed fuel stock (EN 14214: requirements for biodiesel) remark density at 15°C to be 860-900 kg/m³ (methods EN ISO 3675 and EN ISO 12185) and flash point to be over 101°C (Demirbas, 2009 and method ISO CD 3679e). This study therefore employed a fuel specific test to determine the quality of the converted grease/oil rich sludge (biodiesel) as a diesel substitute by measuring kinematics viscosity, API gravity, flash point, and heat value, as shown in Table 4.

In addition, the proportion of alcohol and grease (computed from gas chromatography) revealed that grease had a total saturated fatty acid content of 90.03% and a total unsaturated fatty acid content of 9.97% (see Table 3). The proportion of ethanol and grease could be calculated5 and set to an ethanol to grease ratio of 4:1.

5 When SN is the saponification value of the fatty acid, SNₙ is the saponification value of ethyl ester of each fatty acid from SNₙ*X. The ethyl ester molecular weight was calculated and equal to 56*1,000/ΣSNₙ, since SNₙ was 193.14, the ethyl ester MW was 289.94. As transesterification reaction can provide three molecules of ethyl ester from one molecule of greased, the MW of the grease is 289.94*3, which is equal to 869.82. The alcohol used in the reaction was 30:1 by mole with the grease. The volume of alcohol could be determined by formula where the volume (ml) equalled the molecular mass divided by the density (g/ml). Therefore, when the molecular weight of the ethyl alcohol was 46.07 and the density was 0.719 g/cm³, 30*46.07 = 1382.1 of alcohol was used. So, the final volume used was 1382.1/0.719 or 1922.25 ml. For 95% alcohol solution, the volume of the ethyl alcohol must be 1922.25*100/95 = 2023.42 ml. Similarly, as the molecular weight of the grease was 869.83 and the density was 0.904 g/ml, the volume of the grease used in this study was 962.20 ml, using the same equation. Consequently, the proportion, theoretically, of ethanol and grease by volume in the reaction was 2023.42:962.20 or approximately 2.1:1. With 100% excess ethanol, the real proportion used was therefore 4046.84:962.20 or approximately 4:1.
Table 1: The quantity of grease extracted from canteen grease/oil sludge (weight in gram)

<table>
<thead>
<tr>
<th>Samples</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sludge</td>
<td>600</td>
<td>600</td>
<td>600</td>
<td>600</td>
<td>600</td>
<td>600</td>
<td>600</td>
<td>600</td>
</tr>
<tr>
<td>Grease</td>
<td>325.25</td>
<td>325.22</td>
<td>326.25</td>
<td>325.23</td>
<td>325.45</td>
<td>324.02</td>
<td>325.16</td>
<td>325.18</td>
</tr>
</tbody>
</table>

(Con’t table)

<table>
<thead>
<tr>
<th>Samples</th>
<th>9</th>
<th>10</th>
<th>11</th>
<th>12</th>
<th>13</th>
<th>14</th>
<th>15</th>
<th>AVG.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sludge</td>
<td>600</td>
<td>600</td>
<td>600</td>
<td>600</td>
<td>600</td>
<td>600</td>
<td>600</td>
<td>600</td>
</tr>
<tr>
<td>Grease</td>
<td>325.40</td>
<td>324.25</td>
<td>324.64</td>
<td>325.05</td>
<td>325.33</td>
<td>325.34</td>
<td>326.23</td>
<td>325.27</td>
</tr>
</tbody>
</table>

Table 2: The volumes and pH values of the bio-diesel synthesis

<table>
<thead>
<tr>
<th>Time</th>
<th>Volume of grease (ml)</th>
<th>Volume of ester (ml)</th>
<th>pH Unwashed</th>
<th>pH Washed</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>600</td>
<td>576</td>
<td>1.0</td>
<td>5.7</td>
</tr>
<tr>
<td>2</td>
<td>600</td>
<td>572</td>
<td>1.3</td>
<td>6.3</td>
</tr>
<tr>
<td>3</td>
<td>600</td>
<td>567</td>
<td>1.3</td>
<td>6.2</td>
</tr>
<tr>
<td>4</td>
<td>600</td>
<td>569</td>
<td>1.5</td>
<td>6.9</td>
</tr>
<tr>
<td>Total</td>
<td>2400</td>
<td>2284</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Average</td>
<td>600</td>
<td>571</td>
<td>1.3</td>
<td>6.3</td>
</tr>
</tbody>
</table>

Table 3: The Quantity of Fatty Acid Composition and C-10 Saponification value of the ethyl ester

<table>
<thead>
<tr>
<th>Fatty Acid Composition</th>
<th>% Quantity</th>
<th>SN</th>
<th>%X</th>
<th>SNx</th>
</tr>
</thead>
<tbody>
<tr>
<td>Myristic acid</td>
<td>2.00</td>
<td>218.80</td>
<td>2.00</td>
<td>4.38</td>
</tr>
<tr>
<td>Palmitic acid</td>
<td>71.87</td>
<td>197.22</td>
<td>71.87</td>
<td>141.74</td>
</tr>
<tr>
<td>Stearic acid</td>
<td>16.16</td>
<td>179.52</td>
<td>16.16</td>
<td>29.01</td>
</tr>
<tr>
<td>Total Saturated fatty acid</td>
<td>90.03</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Oleic acid</td>
<td>9.97</td>
<td>180.68</td>
<td>9.97</td>
<td>18.014</td>
</tr>
<tr>
<td>Total Unsaturated fatty acid</td>
<td>9.97</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total fatty acid</td>
<td>100.00</td>
<td>100.00</td>
<td>100.00</td>
<td>193.14</td>
</tr>
</tbody>
</table>

Source: Department of Agriculture, The Ministry of Agriculture. Analysis through requested of C.P No.3203/48 and calculation by the study (as mentioned).
Kinetic viscosity: ASTM D445-88

It is recognized that high viscosity induces poor atomization of the fuel spray. Furthermore, the average viscosity of biodiesel and biodiesel blends increases rapidly as the temperature decreases, and at normal conditions, the viscosity of biodiesel is slightly greater than that of petro-diesel. However, transesterifying oil, grease, and fat into acid/alkyl esters actually reduces viscosity. In addition, the kinematic viscosity of fuel at 40°C (the acceptable temperature for kinematic viscosity calculation specified in biodiesel standards) is 1.9-6.2 mm²/sec for ASTM D6751 and 3.5-5.0 mm²/sec for EN 14214 (Demirbas, 2009, ASTM D6751-02 requirements, and references herein). This report and references herein further specified the effects of molecular structure on kinematic viscosity, particularly a reduction in viscosity from a shorter chain length by the introduction of cis-double bonds; while trans-double bonds had a less significant effect on viscosity. And branched esters had viscosity values similar to that of their straight chain counterparts.

Table 4: The fuel specific test

<table>
<thead>
<tr>
<th>Samples Parameter</th>
<th>Pure petroleum-based diesel</th>
<th>B5</th>
<th>B10</th>
<th>B15</th>
<th>B20</th>
<th>B100 (Pure synthesis biodiesel)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Viscosity (mm²/sec)</td>
<td>3.54</td>
<td>3.69</td>
<td>3.70</td>
<td>3.90</td>
<td>4.15</td>
<td>8.69</td>
</tr>
<tr>
<td>API Gravity (g/cm³)</td>
<td>0.83</td>
<td>0.84</td>
<td>0.84</td>
<td>0.84</td>
<td>0.85</td>
<td>0.9</td>
</tr>
<tr>
<td>Flash Point (°C)</td>
<td>68.5±1.5</td>
<td>74</td>
<td>76±2</td>
<td>71</td>
<td>76</td>
<td>181±1</td>
</tr>
<tr>
<td>Heat Value (Cal/g)</td>
<td>10,389.11</td>
<td>10,505.36</td>
<td>11,803.64</td>
<td>12,669.16</td>
<td>11,587.26</td>
<td>9,685.35</td>
</tr>
<tr>
<td>Smoke feature</td>
<td>Dark black</td>
<td>Black</td>
<td>Black</td>
<td>Black</td>
<td>Black</td>
<td>Pale black</td>
</tr>
</tbody>
</table>

With an OH group in the chain, such as that found in methyl ricinoleate, aliphatic hydrocarbons allowed for a slight increase in viscosity. The study also found that the viscosity increase for hydrocarbons was smaller than that for fatty acid/alkyl esters when the chain length increased. In this study, as the content of biodiesel in blends B5, B10, B15, and B20 increased, the viscosity also increased. Viscosity values for all blends were in the acceptable range under ASTM and EN regulations at 1.9-6.2 and 3.5-5.0 mm²/sec respectively, as shown in Figure 2. There was no statistical significant difference in viscosity values among the blends at the 0.05 level.

Figure 2: The viscosity test
However, if the study considered the relation between biodiesel content and viscosity, the viscosity value was above that for petro-diesel (baseline diesel in this study) by 0.15 mm$^2$/s for B5 and 0.16 mm$^2$/s for B10, and increased linearly to 0.36 mm$^2$/s and 0.61 mm$^2$/s for B15 and B20. Whether or not the blending equation or empirical correlations can be adopted to determine kinematic viscosity for various biodiesel fractions awaits further study.

### 3.2.2 API gravity: ASTM D1298

API (American Petroleum Institute) gravity is a measure of the relative density of liquid petroleum and the density of water or the specific gravity of fuel. A low value of specific gravity of a fuel or biodiesel is an indication of a complete reaction and the removal of unwanted compounds such as glycerine. The influence of molar ratio, temperature, and catalyst quantity on the specific gravity of biodiesel was studied by Miao and Wu (2006). This study mentioned that the specific gravity of the biodiesel product decreased sharply with a reaction time of up to two hours using a molar ratio of 30:1 and up to four hours using molar ratios of 45:1 and 56:1, after which the specific gravity was almost constant. Moreover, Benjumea et al. (2008 and references herein) indicated a linear specific gravity-temperature relationship for soybean oil biodiesel and diesel blends. In this study, the lowest API gravity value was detected in the petroleum based diesel at 0.83 g/cm$^3$; while all blends gave higher values as their biodiesel content increased. For the most part, the API gravity of the blends was out of the acceptable range of ASTM regulations (0.86-0.90 g/cm$^3$, ASTM, 1994a), as shown in Figure 3. There was no statistical significant difference in API gravity values among the blends at the 0.05 level.

![Figure 3: API Gravity test](image)

### 3.2.3 Flash point: ASTM D93 and ASTM D92

The flash point is a measure of the temperature at which a fuel becomes a mixture that can ignite when exposed to a spark or flame; a higher flash point, for instance, is a safety feature for the handling, transportation, and storage of a fuel. Generally, the flash point of neat biodiesel is typically greater than 90°C; lower flash points measured in some studies might have been caused by residual alcohol forming during biodiesel production (Engine Manufacturers Association, 1995). This could possibly also be the cause of the large range of flash points for experimental biodiesel making it difficult to compare flash points of biodiesel with various raw material sources (Michael, 1998), in particular from during the different extraction and synthesis procedures. In this study, the highest flash point was with B100 (pure biodiesel) at 184°C and the lowest flash point was with baseline diesel at 68.5°C. Most of the blends had a slightly higher
flash point than baseline diesel but this increase was not directly proportional to the increase in percentage of biodiesel in the blends. The closest flash point to baseline diesel was with B15 at 71°C. All blends performed in the acceptable ranges specified by ASTM D93 at 130°C (D93) and EN 14214 at 101°C (ISO CD 3679e), see Figure 4. For flash point values, there was no statistical significant difference between the blends and the petroleum based diesel at the 0.05 level.

3.2.4 Heat value: ASTMD2015

The heat value (sometimes called calorific value or heat of combustion) is an important property in defining the energy content and efficiency of a biodiesel. The heat value is obtained by the complete combustion of a unit quantity of sample fuel (including biodiesel products and blends) in an oxygen-bomb colorimeter. A high heat value indicates the most ideal properties of a fuel. In general, the heat value of a fuel increases with an increasing number of fuel molecules (carbon number), and also increases as the ratio of carbon and hydrogen to oxygen and nitrogen increases (Demirbas, 2009). In this study, there was no statistical significant difference among the blends and the baseline diesel at the 0.05 level. B15, with the highest heat value of 12,669.16 cal/g, was higher than the baseline diesel by 17.99%, see Figure 5; while the pure biodiesel (B100), with the lowest heat value of 9,685.35 cal/g, was lower than the baseline diesel by 6.7%, and lower still than the findings by Ramadhas (2005) in a high FFA rubber seed oil study, which showed that the heat value was lower than the baseline diesel by 4%. This was not in agreement with Benjumea (2008) in the study of palm oil biodiesel-diesel blends who found that the heat value of blends decreased in direct proportion to the biodiesel content.

Moreover, as seen in Table 4 and Figure 5, the heat values of the blends increased with biodiesel content until 15%, after which the heat value dropped to be as low as pure biodiesel (B100). These values showed no statistical significant difference but the process mechanisms are recommended for further study. In this study, it was assumed that the grease/oil rich sludge sample collected from the canteen was the end result of a cooking process with numerous additives. Moreover, the conversion reaction into ethyl ester was achieved through violent reactions at intense temperatures and in acidic conditions. These violent reactions were assumed to destroy the molecular bonds of the compounds in the grease/oil rich sludge, such as fatty acids, triglycerides, and fatty esters, since the energy content in pure biodiesel, which is partly based on bond energy being released, caused the energy content or heat value to be low. In addition, the heat value of the blends increased when the content of biodiesel increased up until B15 at which point the heat value decreased to that of pure biodiesel. This might be due to the effects of viscosity as mentioned in 3.2.1 and engine power as mentioned in 3.3.2. The authors recommend that further study of these effects be undertaken.
3.3 Engine Performance

Petroleum based diesel and all blends were tested for their engine performance using a high-speed diesel engine of the Nissan type: TDG21-C43524, 2,494 cc, 4 cylinders, 90 Hp. Details are as follows:

3.3.1 Engine Torque Performance

Engine torque is the ability of an engine to produce force from the axis of rotation to the point of application. Radu et al. (2009 and references herein) evaluated the performance of a direct injection diesel engine fuelled by 50% biodiesel (obtained by transesterification reaction of used vegetable oil) and 50% petro-diesel. The study found that the most significant characteristics affecting the combustion of the biodiesel blends were with fuel delivery such as injection duration, pressure wave propagation time, and average injection rate. The study noted that a lower pressure wave propagation time and auto ignition delay of the biodiesel blends caused combustion with a lower heat release rate, which led to a decrease in engine power and torque; while the higher oxygen content, cetane number, and shorter auto ignition delay led to a higher thermal efficiency. Throughout experimentation in this study, the engine’s parameters were controlled into a fixed mode, in particular injection duration, pressure wave propagation time, and average injection rate. The highest engine torque was in the range 149.57-152.60 Nm, and the lowest engine torque was in the range 120.70-122.79 Nm at various engine speeds as shown in Table 5.

Table5: Engine Torque Performance.

<table>
<thead>
<tr>
<th>Blended Fuel (Diesel : Bio-diesel)</th>
<th>Highest Engine Torque</th>
<th>Lowest Engine Torque</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Torque(Nm) Speed (rpm)</td>
<td>Torque(Nm) Speed (rpm)</td>
</tr>
<tr>
<td>Diesel</td>
<td>150.12 1812</td>
<td>122.56 4191</td>
</tr>
<tr>
<td>B5</td>
<td>149.57 2142</td>
<td>122.79 4187</td>
</tr>
<tr>
<td>B10</td>
<td>152.60 1993</td>
<td>122.67 4193</td>
</tr>
<tr>
<td>B15</td>
<td>151.88 2178</td>
<td>120.70 4190</td>
</tr>
<tr>
<td>B20</td>
<td>151.80 1922</td>
<td>121.87 4197</td>
</tr>
</tbody>
</table>

The torque values of all blends were nearly equal to that of diesel fuel at all speeds. However, the blends seemed to produce slightly higher torque values than baseline diesel at speeds of 1,500-3,000 rpm. After that, performance dropped slightly at 3,100-3,900 rpm, and then increased again at the baseline value of 4,000 rpm. However, when all measurements underwent statistical analysis for correlation R values, the values were in the range 0.97-0.99. The study can conclude that all blends could be a suitable replacement for petroleum based diesel in terms of engine torque performance.

3.3.2 Engine Power

Engine power describes the motive power to a system. Usta et al. (2005, and references herein) defined that the addition of biodiesel to a petroleum based diesel fuel had an effect on its heat value and engine power. In experiments, Usta give two reasons for this change in engine power performance as a result of the
addition of biodiesel. Firstly, all biodiesel contained approximately 10% oxygen (by weight) that can be used in combustion. This was the probable reason for a more complete combustion thereby increasing the torque and power at the starting stage of combustion. Secondly, the biodiesel fuel was pumped into the diesel engine cylinder on a volumetric basis and the density of the biodiesel blend was higher than that of the petroleum based diesel. Therefore, a larger mass flow rate for the same fuel volume was pumped into the engine resulting in an increase in torque and power. Meanwhile, the more viscous blend meant less internal leakage in the fuel pump. And furthermore, when the biodiesel content continued to increase in the blend, the power decreased to be below that of the diesel fuel due to a lower heat value and a higher viscosity resulting in slightly poorer atomisation and combustion. This study also concluded a similar trend in the thermal efficiency of engines.

The reasons given by Usta were compatible with this study as power performance varied from 73.51 to 74.47 Hp and the engine speed varied from 3932 to 3982 rpm. All blends and the baseline diesel had the same correlation by R value between engine speed and power at the value of 0.99 (see Table 6 and Figure 7). The engine power increased as the biodiesel content in the blends increased from B5 to B10 with engine performance at 73.76 Hp and 74.47 Hp respectively. After that, engine power gradually decreased as the biodiesel content in the blends increased (B15 and B20), as shown in Table 6 and Figure 7. From this, it can be seen that the content of biodiesel blends B10, B15, and B20 were in the acceptable range for petroleum substitution, which was harmonized by Usta et al. (2005) using a mathematical equation to determine that maximum power can be obtained by adding approximately 17.5% biodiesel or B17.5 in this study.

Table 6: Engine Power Performance

<table>
<thead>
<tr>
<th>Blended Fuel</th>
<th>Highest Engine Power</th>
<th>Lowest Engine Power</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Diesel:Bio-diesel)</td>
<td>Power(Hp)</td>
<td>Speed (rpm)</td>
</tr>
<tr>
<td>Diesel</td>
<td>73.83</td>
<td>3979</td>
</tr>
<tr>
<td>B5</td>
<td>73.76</td>
<td>3970</td>
</tr>
<tr>
<td>B10</td>
<td>74.47</td>
<td>3982</td>
</tr>
<tr>
<td>B15</td>
<td>73.51</td>
<td>3893</td>
</tr>
<tr>
<td>B20</td>
<td>73.66</td>
<td>3932</td>
</tr>
</tbody>
</table>
Figure 6: Engine torque performance in correlation with baseline diesel.
Petroleum based-diesel B5 (5% of biodiesel) and Petroleum based-diesel

Petroleum based-diesel B10 and Petroleum based-diesel

Petroleum based-diesel B15 and Petroleum based-diesel

Petroleum based-diesel B20 and Petroleum based-diesel

Figure 7: Engine power correlation in correlation with baseline diesel
4. Discussion

In comparison, the study of Donkathin (2000) reported that waste grease when mixed with sawdust had a heat value in the range 6,117-7,065 cal/g. So, the conversion of trapped grease into biodiesel in this study could raise the fuel heat value more than a mixture of waste grease and sawdust. Moreover, Demirbas (2002) showed a similar potential for methyl esters and the ethyl esters; while Mohamad Al-widyan and Al-Shyoukh (2002 and references herein) noted that ethyl ester produced from used vegetable oil yielded better engine performance than baseline diesel. In addition, Krongdech (2000) reported that methyl ester of used oil had less potential in comparison to diesel. In this study, the fuel blends with ethyl ester by the aforementioned procedure performed slightly better than baseline diesel. The mono-alkyl esters of grease/oil rich sludge through acid-catalyst ethanol transesterification reaction tended to be more suitable for petroleum diesel substitution. In other words, the canteen’s trap grease had potential to be transformed into ethyl ester or biodiesel by the study procedure. Those blends with biodiesel content below 20% had the potential to be a substitute for petroleum based diesel. For the blends B5, B10, B15, and B20, B15 displayed the best performance in comparison to baseline diesel. But conversion details such as unit cost, environmental impact, and more such indicators have to be further investigated. It has to be noted also that in this study engine performance using all blends was fairly smooth with no visible abnormal vibrations or any other problems. Furthermore, all blends, including 100% ethyl ester (B100), performed at acceptable values for all essential engine performance parameters. Even though the baseline diesel fuel used in this study was a domestic diesel fuel, in which some specifications were different from the No. 2 diesel fuel used in most other relevant studies, the study presented a real situation for a biodiesel substitution for regular fuel.

At last, the authors agree with Gerpen (2005) who stated that there were at least five reasons that justify the extension of biodiesel development in the future: i) it provides a market for excess production of vegetable oils, animal fats, grease/oil rich sludge, ii) it will decrease, although will not eliminate, the country’s dependence on imported petroleum, iii) it is renewable and does not contribute to global warming due to its closed carbon cycle. A life cycle analysis of biodiesel showed that overall CO$_2$ emissions were reduced by 78% compared to petroleum based diesel fuel, iv) the exhaust emissions of carbon monoxide, unburned hydrocarbons, and particulates from biodiesel were lower than with regular diesel fuel, except for oxides of nitrogen (NOx), which this study recommends further justification, v) when biodiesel is added to petroleum diesel fuel at 1-2%, it can convert fuel with poor lubricating properties, such as modern ultra-low-sulfur diesel, into an acceptable fuel.

5. Conclusion

In conclusion, this study found that the transesterification of grease/oil rich sludge from the University’s canteen was quite feasible in terms of production. For the diesel-biodiesel blends at 5, 10, 15, and 20 percent, engine performance was quite high compared with regular diesel. This was not in agreement with the study of Zhang et al. (2003) on acidic-catalyzed reactions of used oil materials in which it was noted that there was a worsening trend of engine performance as the biodiesel ratio increased. This study however showed that the threshold performance of biodiesel content was approximately 20% (B20), after which
engine performance worsened. Furthermore, the authors would like to emphasize that in this study there was no statistical difference between the four blends (B5, B10, B15, and B20) and the baseline diesel (B0) at the 0.05 significance level.

6. Reference


ASTM standard D6751. Standard specification for bio-diesel fuel (B100) blend stock for distillate fuels. ASTM. West Conshohocken, PA.


Donkathin, N. 2000. Introduce the mixture of grease oil rich sludge from restaurants with saw dust to be as the fuel. Master Degree of Environmental Technology Management, Graduate school, Mahidol University.


Klongdech, S. 2000. The development of used vegetable oil quality to substitute diesel fuel. Master Degree of Environmental Technology, King Mongkut's University of Technology Thonburi.


