Physico-Chemical Properties of Bio-diesel from Wild Grape Seeds Oil and Petro-Diesel Blends

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Abstract: - The swiftly depleting conventional fossil fuel resources and increasing environmental distress has considerably popped up research curiosity in renewable energy fuel for internal combustion engines. Accordingly, in this research work, biodiesel from wild grape seed (Lannea Microcarpa) was blended with petro-diesel in a ratio of 5:95, 10:90, 15:85 and 20:80 and pure fossil diesel designated B5, B10, B15, B20 and B0 respectively. The physico chemical properties of the biodiesel/petro diesel blends were determined. The properties are specific gravity, viscosity, flash point, calorific value, sulphur content, copper strip corrosion, colour, diesel index, cetane number, and cloud point. It was observed that, 9 out of the 10 properties determined conform to ASTM standards except for the colour which was dark brown for the oil and biodiesel, and brown for the automotive gasoline oil. The specific gravity and viscosity increase with percentage increase of biodiesel in the blends. The sulphur content, calorific values, cetane number and diesel index decrease with increase in the percentage biodiesel from the blends. The colour of the samples does not conform to the ASTM standards. All the samples have the best ASTM value for copper strip corrosion and as such, they could be run in any diesel engine without any fear of corrosion tendencies. Whence, Wild Grape seed biodiesel is physically okay, chemically stable, environmentally friendly and economically viable for use in compression ignition engine as a blend to partly replace the automotive gasoline oil.

Keywords: – Biodiesel, Blend, Physico-Chemical Properties, Wild Grape Seeds

I. INTRODUCTION

Biodiesel means fatty acid methyl ester or mono-alkyl esters derived from vegetable oil or animal fats for use in diesel engines (Nigerian Bio-Fuel Policy and Incentives, 2011). Biodiesel is an alternative for or an additive to diesel fuel, that is derived from the oils and fats of plants, like sunflower, canola, Jatropha, neem seed oil (Ambuman and Sing, 2010). With fuel prices increasing and growing environmental awareness, the need to consider alternative energy and fuel sources are becoming a necessity. One alternative is the use of biodiesel fuel which is becoming more and more popular today (Haresh, 2008).

The physico-chemical properties of fuel are the fuel specifications that define and set the quality standards. For biodiesel, physico-chemical properties are a set of property specifications measured by specific American Society for Testing and Material (ASTM) test methods such as ASTM 6751 – 02 (Gerpen et al., 2004). This specification must be met for a fatty acid ester product to carry the designation “biodiesel fuel” or “B100” or for use in blends with any petroleum-derived diesel fuel (Gerpen et al., 2004). These properties are termed physico-chemical properties which include but not limited to: specific gravity, viscosity, flash point, calorific value, cetane number, acid value, volatility, and saponification value.

There exist in Nigeria, a set of problems due to exploration, refining, transportation and final combustion of the petroleum products in which diesel fuel is not an exception. There are environmental catastrophes like oil spills, acid rains and depletion of the ozone layer. Recently, the Federal Government of Nigeria has removed its subsidy on petroleum products which lead to rise in prices of the products. Therefore, there is need to surmount these challenges and as such, we have to search for alternatives and or additives that will wholly or partially replace the expensive petroleum products. There alternatives are supposed to be locally abundant, environmentally friendly and economically viable. In the light of the above, this work therefore seeks
to evaluate the physical and chemical properties of transesterified wild grapes seeds oil/petro-diesel blends. Result of this study is expected to contribute to the existing database of locally available alternative energy resources with the objective of reforming the global energy and environmental predicaments.

II. MATERIALS AND METHODS

2.1 Materials

2.1.1 Sample Collection

The seeds to be used in this work is botanically called *lannea microcarpa*; it is also referred to as wild grapes in English and "Faru" in Hausa, the main language in Northern Nigeria. The sample was obtained from Kankia local government, Katsina State of North Western Nigeria.

2.1.2 Extraction Procedure and Biodiesel Production

Seed sample was washed and dried. The oil was extracted from the sample using the mechanical press engine driven expeller. The oil yield from the sample was initially 12.5% with very high free fatty acid (FFA), and then later increased to 37.5% after the free fatty acid was reduced using acid esterification reactions on the sample. The free fatty acid was 42% but reduced to 2.52 after a repeated esterification reaction. Alkali esterification reaction was carried out on the sample and bio-diesel was produced. The biodiesel was blended with fossil diesel in a ratio of 5:95, 10:90, 15:85 and 20:80 and a pure petro-diesel sample kept for control purpose as B5, B10, B15, B20 and B0 respectively.

2.2 Determination of Physico-Chemical Properties

The physico chemical properties of the biodiesel produced were determined as follows:

2.2.1 Measurement of the specific gravity:

The specific gravity of the samples was measured at room temperature of 27 °C using a Fisher brand hydrometer (size 0.795-0.910, accuracy 0.001). The measurement was performed according to the method adopted by Coronado et al. (2009). The hydrometer is a graduated glass tube filled with air and fitted with a weight.

- To measure specific gravity, a hydrometer and a large graduated cylinder were obtained
- The graduated cylinder was filled with the sample and the hydrometer was then dropped into the blend.
- The point at which the hydrometer floats gives the measurement of the specific gravity.
- Hydrometer readings were taken at temperatures between 16 °C to 30 °C.

2.2.2 Measurement of viscosity:

The viscosities of the samples were measured with a viscometer at 40 °C (Sivaramakrishnan et al., 2011). According to Adebayo et al. (2011) the viscosity at 40 °C (313k) is measured following the ASTM D445 method using a calibrated viscometer with a calibration constant of 0.1057. In this research, the determination of viscosity was done following the Institute of Petroleum (IP) method by Milner and Whiteside, (1986). This involves measuring the time of flow of the sample between two marked points on the Ostwald viscometer (Nafi’u et al., 2012).

2.2.3 Flash point

The flash point of the biodiesel/diesel blends was determined by the method of ASTM D93, using the Pensky-Martens closed cup tester. The determination of the flash point of biodiesel was done in the temperature range of 60 °C to 190 °C by an automated Pensky-Martens closed cup apparatus according to the standard method of testing flash point. The flash point determination was carried out by heating a sample of the fuel in a stirred container and passing a flame over the surface of the liquid. If the temperature was at or above the flash point, the vapour was ignited and an easily detectable flash would be observed. The fire point has produced sufficient vapour to maintain a continuous flame (Babgy et al., 1987).

2.2.4 Cetane number:

The cetane number was determined using a portable cetane/octane metre. The cetane index of the biodiesel-diesel blends was determined by the ASTM D.976 method (Kywe and Oo, 2009).

2.2.5 Cloud point:

The cloud point was determined by visually inspecting for a haze to become visible as the fuel is cooled in a refrigerator.

2.2.6. Calorific value

The calorific values of the biodiesel/diesel blends were measured using a bomb calorimeter. A known amount of fuel was placed in a crucible. The crucible was then placed over a ring and a fine magnesium wire touching the fuel sample is stretched across the electrodes. The lid was tightly screwed and the bomb was filled with oxygen up to 25 atmosphere pressure. The initial temperature was recorded.

The electrodes were then connected to a 6 V battery and the circuit was completed. As soon as the circuit was completed and the current was switched on, the fuel in the crucible burnt with the evolution of heat.
Heat liberated by burning of the fuel increases the temperature of water and the maximum temperature attained was recorded.

2.2.7 Pour point:
The pour point was determined by the ASTM D.97 method (Kywe and Oo, 2009). 3.0 g of the blend was placed into a test tube in which a thermometer was inserted through a cork which was used to cover the mouth of the test tube. The test tube was placed in a refrigerator and observed at 10 minute intervals for a period of two hours. The test tube was removed and tilted to ascertain if the oil flowed or moved, until it showed no movement when the test tube was held horizontally for seconds; it was said to be solidified. The pour point was then taken at the temperature of 5 °C above the solid point.

2.2.8 Total sulphur Content:
The total sulphur content was determined using X-ray analyses of the fuel samples. This test method covers the determination of total sulphur by monochromatic, wavelength-dispersive X-ray fluorescence (MWDXRF) spectrometry in single-phase biodiesel, diesel fuels, and refinery process streams used to blend bio-diesel and petro-diesel. The precision of this test method was determined by an inter laboratory study using representative samples of the fuels.

2.2.9 Copper strip corrosion
A three inch copper strip was prepared by cleaning and polishing all sides so that no discoloration or blemishes were visible. The strip was then placed in the test samples and held for 3 hours at 100 °C as the typical starting point. At the end of the exposure period, the strip was removed, wiped cleaned and matched with coloured reproduction strips characteristic of the descriptions.

2.2.10 Diesel Index
The diesel index was calculated using the following equation:

\[
\text{Diesel Index} = \frac{\text{aniline point}(\circ F) \times \text{degrees API}(60\circ F)}{100}
\]

III. RESULTS
The physico chemical properties of the various biodiesel blends with pure diesel are presented in table 1 and illustrated in figures 1 to 7.

Table 1: Physico Chemical Properties of Biodiesel from Wild Grape Seeds/Diesel Blends

<table>
<thead>
<tr>
<th>Sample</th>
<th>Specific Gravity</th>
<th>Sulphur % (wt)</th>
<th>Calorific Value</th>
<th>Flash Point (°C)</th>
<th>Viscosity @ 40°C (mm²/s)</th>
<th>Cetane Number</th>
<th>Cloud Point (°C)</th>
<th>Colour (ASTM)</th>
<th>Diesel Index</th>
<th>Copper Strip Corrosion</th>
</tr>
</thead>
<tbody>
<tr>
<td>B0</td>
<td>0.8645</td>
<td>0.202</td>
<td>10,831</td>
<td>75</td>
<td>3.93</td>
<td>44</td>
<td>-5</td>
<td>&lt;3.5</td>
<td>47</td>
<td>1a</td>
</tr>
<tr>
<td>B5</td>
<td>0.8645</td>
<td>0.191</td>
<td>10,831</td>
<td>60</td>
<td>4.19</td>
<td>44</td>
<td>-13</td>
<td>6.5</td>
<td>47</td>
<td>1a</td>
</tr>
<tr>
<td>B10</td>
<td>0.8655</td>
<td>0.181</td>
<td>10,827</td>
<td>45</td>
<td>4.21</td>
<td>41</td>
<td>-12</td>
<td>&lt;8</td>
<td>44</td>
<td>1a</td>
</tr>
<tr>
<td>B15</td>
<td>0.8665</td>
<td>0.171</td>
<td>10,823</td>
<td>40</td>
<td>4.28</td>
<td>39</td>
<td>-15</td>
<td>&lt;8</td>
<td>40</td>
<td>1a</td>
</tr>
<tr>
<td>B20</td>
<td>0.8673</td>
<td>0.155</td>
<td>10,820</td>
<td>40</td>
<td>4.42</td>
<td>36</td>
<td>-18</td>
<td>&gt;8</td>
<td>37</td>
<td>1a</td>
</tr>
</tbody>
</table>
Figure 1: Specific Gravity of Biodiesel Blends

Specific Gravity of Biodiesel Blends

Figure 2: Total Sulphur of Biodiesel Blends

Sulphur Content of Different Blends

Figure 3: Calorific Values of the Blends

Calorific Values of the Blends
Figure 4: Flash Points of Biodiesel Blends

Figure 5: Viscosities of Biodiesel Blends

Figure 6: Cetane Values of Biodiesel Blends
IV. DISCUSSIONS

The graph of specific gravity against blends is presented in figure 1. From the graph, pure diesel (B0) and 5% biodiesel blend (B5) have the lowest specific gravity of 0.8645 each, B10 has 0.8655 with B15 and B20 having 0.8665 and 0.8675 respectively. The ASTM standard for specific gravity for diesel fuels and biodiesels is from 0.8000 to 0.9000, and all the blends fall within this range and hence, conform to the required standard for specific gravity. Therefore, the specific gravities of all the samples B0, B5, B10, B15 and B20 of wild grape seeds biodiesel/diesel blends are within the acceptable limit.

The sulphur content of the biodiesel blends are shown in figure 2. It is seen that, sulphur content decreases with increase in the percentage biodiesel from the blends. The sulphur content of the petro diesel is 0.202 by weight from test. It reduced to 0.191, 0.181, 0.171 and 0.155 with increase in biodiesel content from 5% through 10% and 15% up to 20% respectively. This shows that the wild grape seed biodiesel is capable of reducing the emission of sulphur dioxide into the atmosphere. The sulphur content of the pure biodiesel which was not captured on the table is 0.04 wt %. This is within the standard range of ASTM D5453 which allows a maximum of 0.05 wt % for total sulphur content in a given biodiesel.

The calorific values of the pure diesel as well as the different blends are presented in figure 3. B0 and B5 blends have the same calorific values, while there was decrease in the values with increase percentage of biodiesel in the blends. The calorific value of B20 was the lowest and that of the B0 was the highest. The calorific values are decreasing with percentage increase of biodiesel in the blends. The calorific value of B0 and B5 are the same; this is because, with 5 % of biodiesel in the blend, the quantity of biodiesel in the blend is not enough to alter the calorific value of the blend.

Figure 4 shows the respective flash points of the pure diesel and the biodiesel blends B0, B5, B10, B15 and B20. The minimum flash point for biodiesels according to ASTM 6751-02 D93 test method is 100 °C and the maximum is 170 °C. The flash point range for pure diesel is 60 °C to 80 °C. While the ones obtained in this test have the highest flash point as 75 °C of the petro diesel which is within the standard. The lowest was 40 °C for B15 and B20. From B5 to B10, there was a slight decrease in flash point and further decrease was also observed between B10 and B15.

Figure 5 presents the graphical variation in viscosity of the biodiesel blends. The viscosity of the pure diesel was 3.93 mm²/s at 40 °C. There was increase in viscosity with corresponding increase in biodiesel percentage in the blends. B5 has a viscosity of 4.19mm²/s and B20 has 4.42 mm²/s. The ASTM range for viscosity is between 1.9mm²/s and 6.0mm²/s. The standard for diesel fuel is 1.3mm²/s to 4.1mm²/s. Hence, both the petro diesel and the blends have conforming viscosities.

The various cetane numbers are presented in the figure 6. The ASTM standards for cetane number of biodiesel are 48-65. It was observed that, with increase in biodiesel blends, there was a corresponding decrease in cetane number from B10 through B15 to B20.
Therefore, the knocking tendency of the engine increases with an increase in the percentage of the blend. However, at 5 % blend, there was no any change in cetane number; it was same 44 as the petro diesel cetane index, this is because, there is no any significant change with 5 % blend as compared to B0 as it was also observed with specific gravity and calorific value.

The values of the cloud point of the samples are presented in table 2. According to Gerpen et al. (2004) there is no any standard limit for cloud point. From the table 3, however, the cloud point of the samples are: -5 °C, -15 °C, -12 °C, -15 °C and -18 °C for B0, B5, B10, B15 and B20 respectively. The trend of the curve starts from its highest value for B0, then goes down to the lowest value for B20.

The petro- diesel used in this experiment has a very bad colour likewise the biodiesel produced and the blends. The colour of the biodiesel was dark brown (Coffee Colour), while that of the pure diesel used (B0) was light brown. From table 2, the values of the colours for B0 and B5 were >3.5 and 6.5 respectively, these are the minimum colour codes of the samples produced. The ASTM standards for colour codes of biodiesels is <3. Hence the colour of the samples does not conform to the ASTM standards.

From table 2, the respective values for copper strip corrosion for B0, B5, B10, B15 and B20 were presented as 1a each. This is very interesting, as it shows that all the samples have the best ASTM value for copper strip corrosion and as such, they could be run in any diesel engine without any fear of corrosion tendencies. The ASTM value for copper strip corrosion is 3max (Maximum value of 3).

The diesel indices of the pure diesel and those of the blends are presented in figure 7. The diesel indices of pure diesel and 5 % biodiesel are the same, whereas for B10, B15 and B20 it reduces with increase in the percentage of the biodiesel present in the blends.

V. CONCLUSIONS
The specific gravity and viscosity of the biodiesel blends increase with percentage increase of biodiesel in the blends. With increase in the percentage biodiesel there was corresponding decrease in sulphur content, calorific values flash point, diesel index and cetane numbers.

The pure diesel used in this experiment has a very bad colour likewise the biodiesel produced and the blends. The colour of the biodiesel was dark brown (Coffee Colour), while that of the pure diesel used (B0) was light brown.

The entire blends have the best ASTM value for copper strip corrosion and as such, could be run in any diesel engine without any fear of corrosion tendencies. Besides the colour, all the physico chemical properties of the blends conform with ASTM standards.

REFERENCES