Effects of Blending on the Properties of Biodiesel Fuels

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Abstract
Most vegetable oils are too viscous for direct use as diesel engine fuel hence they are transesterified to biodiesel to modify their properties. Transesterification involves transformation of the molecular structure hence change in the properties. The objective of this paper is to quantify the changes in selected properties after transesterification and blending with diesel fuel using cashew, rubber and egunsi seed oils as case studies. The oils were transesterified and the properties measured following the ASTM protocols. The results obtained show that properties such as flash points, acid and iodine values reduced while others like cetane number increased with blending. Blending can hence be used to modify the properties of biodiesels.

Keywords: biodiesel, diesel, transesterification, blending, fatty acid profile, properties.

INTRODUCTION
Vegetable oil is a mixture of different glycerides of fatty acids called triglyceride, which is a chemical compound that is structurally one molecule of glycerol esterified to three molecules of long chain monocarboxylic (fatty) acids and this is responsible for the very high viscosity and poor cold flow properties of vegetable oils. The relatively high viscosity of vegetable oils and the consequential poor fuel atomization characteristic, fuel injector blockage and cold starting problems, makes them unsuitable for use in neat form as diesel engine fuel making it necessary to convert vegetable oil to esters by the method of transesterification to produce biodiesel (Canakci and Van Gerpen, 1999; Scholl and Sorensen, 1993; Wagner and Peterson, 1982; Bagby and Freedman, 1987; Bagby and Freedman, 1989; Barsic and Humke, 1981; Bartholomew, 1981; Blumberg et al., 1982). Transesterification is the process of converting vegetable oil to esters and uses alcohol in the presence of a catalyst to chemically break down the molecules of the vegetable oil during which the glycerol from the triglycerides are removed and replaced with radicals from the alcohol used. It has also been defined as the displacement of ester by another ester (Otera, 1993). The reaction transforms the complex branched molecular structure of vegetable oil into a smaller straight chain molecular structure, identical to but much longer than that of diesel fuel (Meher et al., 2006) and results into the formation of mono-alkyl esters (biodiesel) of the vegetable and glycerol as shown in Fig.1. (Knothe et al., 2005; Mittelbach et al., 1985; Srivastava and Prasad, 2000). The glyceride backbone is turned to glycerol as a byproduct. This structural rearrangement affects the properties of the resulting biodiesel and the changes depend mainly on the properties of the attached fatty acids (Freedman et al., 1986; Ma and Hanna, 2005; Van Gerpen, 2005).

\[\text{Triglyceride} + \text{Methanol} \rightarrow \text{Biodiesel} \text{ and Glycerol}\]

Fig.1. Transesterification Process

Biodiesel has been defined as a mono-alkyl ester of vegetable oils or animal fats (Knothe et al., 2005; Lois, 2007; NBB, 1997; Mittelbach and Remschmidt, 2004). Biodiesel is chemically simple, consisting of between six and nine fatty acid esters in the mixture and has very similar physical properties to diesel fuel. It has a higher cetane number than diesel fuel which allows it to be used as substitute or blending fuel in diesel engines without any modifications. Glycerol on the other hand is a trihydric alcohol (containing
three -OH hydroxy groups) that can combine with up to three fatty acids to form monoglycerides, diglycerides, and triglycerides, depending on the number of fatty acids combined (Schudartt et al., 1998). Biodiesel is similar to diesel fuel except that it contains oxygen in addition to the carbon and hydrogen molecules and can hence be used as direct substitute or blending fuel in diesel engines in accordance with the dreams of Rudolf Diesel (1858-1913), who was quoted to have remarked that "The use of vegetable oils for engine fuels may seem insignificant today. But such oils may become in the course of time as important as the petroleum and coal tar products of the present time". The objective of this study is to investigate the effects of blending on selected properties of biodiesel using cashew seed, rubber seed, and egunsi seed oils as case studies.

MATERIALS AND METHODS

Materials
Cashew (Anarcardium Occidentale), Rubber (Hevea Brasiliensis) and Egunsi (citrullus colocynthis) seeds were procured from a local dealer and the oils were extracted by solhlet extractor.

Characterization of the Oil
The properties of the oils were first measured to determine if pretreatment was necessary or not before alkaline transesterification. It was found that the free fatty acid value (FFA) of rubber seed oil was 23.68 mg KOH/g (oleic) which is too high for alkaline transesterification as it can react with the catalyst to form soap which can inhibit methyl ester yield (Ramadhas et al., 2009). The others have free fatty acids below 2% and hence did not require pretreatment.

Transesterification Procedure
Transesterification was carried out using a laboratory scale biodiesel processor in chemistry laboratory of the Federal University of Technology, Akure. Rubber seed oil was first esterified with anhydrous methanol at a molar ratio of 9:1 using 1%(v/v) sulfuric acid (H$_2$SO$_4$) as catalyst to transform the free fatty acid into ester thereby reducing the FFA value of the oil to less than 2% (Ramadhas et al., 2009; Sahoo et al., 2007; Ghadge and Raheman, 2006). The alkaline transesterification was also done using anhydrous methanol at a molar ratio of 6 to 1 and 3g/litre of sodium hydroxide as catalyst. The processor was stirred at 1000 rpm (Dorado et al., 2002) and at a temp of 60 °C for 2 hours, after which the mixture was poured into a decanter and allowed to settle for 3 hours so that the reaction can be driven to completion and for the mixture to separate into methyl ester and for the glycerol at the bottom to be drained off by gravity. The excess methanol in the ester was removed in a flash evaporator. To remove any impurity, the methyl ester was washed in distilled water of volume ratio 3 to 1 three times. Finally, the washed methyl ester was dried by passing it through anhydrous sodium sulphate (Na$_2$SO$_4$) (Schinas et al., 2009). The procedure was repeated for cashew and egunsi seed oils Blending was done by stirring gently and limited to 10% (B10) and 20% (B20) biodiesel in diesel fuel because B20 is the most economical ratio and has been used widely.

Fatty Acid Profile
The fatty acid composition of the oils, their methyl esters and blends with diesel (B10 and B20) and the standard sample of free fatty acid were determined by chromatography analyzer following the modified AOAC 965.49 and AOAC 996.06 official methods. The fatty acid methyl esters were separated using HP 6890 Gas Chromatography analyzer powered by HP ChemStation Rev A 09.11 [1206] software and equipped with a flame Ionization Detector (FID) and HP INNOWax column (30 m x 0.25 cm x 0.20 μm film thickness) The carrier gas was nitrogen and the oven initial temperature was at 60 °C. The first ramping was at 10 °C/min for 20 min and maintained for 4 minutes. The second ramping was at 15 °C/min for 4 minutes and maintained for 10 minutes. The detector temperature was 320 °C while hydrogen and compressed air pressures were 22 and 35 psi respectively Bello et al.,2011. The proportion of the various fatty acids for cashew, rubber and egunsi seeds oils are shown in Table 1.

Determination of Fuel and Physiochemical Properties
The fuel and physiochemical properties of the oils, their methyl esters and blends were determined following ASTM, AOCS methods and undertaken in McDonald laboratory in Warri, Delta state of Nigeria and fuel laboratory of the Federal University of Technology, Akure. Kinematic viscosities: The kinematic viscosity was determined with a Herzog GmbH MP-480 that involves measuring the time for a fixed volume of the fuel to flow under gravity through a capillary at a known and closed temperature. Kinematic viscosity = Calibration constant (mm$^2$/s) x mean time of flow (s). Flash Point: The flash points measurements were done according to method ASTM D6751 using Kehler Model K-16270 (Pensky-Martens Closed Flash Tester). Heating Values: The lower heating values were obtained using the oxygen bomb calorimeter (Parr Instrument company, US.) following the ASTM D240 method. The lower heating value of vegetable oils depends on the composition of the fatty acids, where grown and its vintage among other factors. Cetane Number: The cetane number of the biodiesel was calculated using equation 1. (Willard, 1996).
Cetane (CN) = -420.94 + 51.66T + 0.1926$\log(T_{50})$ + 65.01$\log(T_{50})^2$ + 0.0001089$T_{50}^4$

where $G$ is the API (American Petroleum Institute) specific gravity and $T_{50}$ is the distillation temperature as 50 vol. % fuel sample distilled and condensed in a unit of °F.

Iodine Values: The iodine values were analyzed, based on the methods of the American Oil Chemists' Society (AOCS cd8, 1980) by titration with 0.01 N sodium thiosulfate for the mixture of tested fuel and chemical reagents until they were light blue and light yellow, respectively.

The iodine values were then calculated as shown.

Iodine Value = \((B - T) \times C \times 0.001269 / Y\).

where $B$ and $T$ are denoted as the amounts (in mL) of sodium thiosulfate titrated for the blank sample and tested sample, respectively; $C$ is the molar concentration (in mol/L) of sodium thiosulfate; and $Y$ is the weight (in g) of the tested sample.

Acidic Number: The acid number, which is expressed as mg KOH/g, was determined by titrating with 0.01 N potassium hydroxide for the mixture of tested fuel and chemical reagents until the appearance of the color pink.

Oxidative Stability: A glass ware apparatus for ASTM D 2274 was used for the oxidation stability test. The fuel was made to degrade by heating and oxygenating the sample in a shorter period of induction time. Oxygen was bubbled for 16 hours while the fuel was held at 95 °C. Thereafter, the fuel sample was filtered to measure the amount of any insoluble that was formed. Finally, the amount of time that the fuel could be stored before deterioration by forming acids was then estimated.

Carbon Residue: Carbon residue for each sample was determined by heating a sample to 500 °C in nitrogen filled chamber at controlled rate to ensure that the sample cokes and does not combust. The formed volatile compounds were flushed from the chamber by nitrogen, and the mass of the remaining coke determined. The test is designed to simulate the formation of carbon deposits in the engine by the fuel.

Sulfated Ash: Isotemp muffle furnace was used for ash analysis. Each residue was allowed to cool down and thereafter treated with sulfuric acid and heated to 750 °C until oxidation of carbon was complete. The ash was then cooled, retreated with sulfuric acid and heated to 750 °C to constant weight. To obtain the sulfated ash content of the samples, the final weight was divided by the initial weight and then multiplied by 100 to express as percentage.

RESULTS AND DISCUSSION

Blending the biodiesels with diesel fuel resulted into a mixture with fuel and physiochemical properties that are superior in many respects to those of diesel. The two fuels blended very well with diesel fuel without segregation or adverse chemical reactions in the three cases.

Flash Point

The oils and their B100s have higher flash points than the ASTM limits for biodiesel as shown in Fig.2. The Flash point reduced for B10 and then increased again for B20 suggesting that as the proportion of biodiesel increases the flash point also increases. Blending with diesel reduces flash point up to B10 and thereafter increases again. For ratios lower than B10, the mixture has flash point that approaches that of diesel and above B20 approaches the properties of B100. The flash points of all the unblended biodiesels are above 120 °C which make them safe fuels from the point of views of storage and transportation.

Kinematic Velocity

Transesterification reduces the kinematic velocity of cashew rubber and egunsi oils of 54.92, 74.31 and 32.31 mm²/s respectively to within the 1.6-6 mm²/s limits of biodiesel. Since diesel has lower kinematic velocity than B100, blending will therefore tend to reduce the value for the mixture at low ratio and the converse. Of the three vegetable oils tested, rubber seed oil has the highest kinematic velocity followed by cashew and egunsi oils in this order. The result is shown in Fig.3. Kinematic viscosity affects fuel flow and atomization of fuel when injected.

Heating Value

No significant change in heating values were observed after transesterification of the three vegetable oils and confirms the report of Lague et al. (1987) that heating value is not affected by transesterification. However, upon blending to B10 the value increased by an average of 15% because diesel has higher heating value than biodiesels. The higher the amount of biodiesel in the mixture, the lower the heating value. The trend is shown in Fig.4. Heating value is a measure of the heat energy in the fuel and the higher value the more the energy released after combustion.

Cetane Value

Cetane value (CN) is a measure of the ignition quality of diesel fuels and one of the prime indicators of the quality of diesel fuel. It relates to the ignition delay time of a fuel upon injection into the combustion chamber, it influences ease of starting, duration of white smoke after start up, drivability before warm up and intensity of diesel knock at idle. Biodiesel has a higher cetane number than diesel fuel because of its oxygen content and also because the fatty acids present in the fuel have very high octane number. It increased after transesterification with cashew nut oil having the highest cetane number of 63.83, followed by egunsi seed of 52.56 and rubber seed oil of 55.20 as shown in Fig.5. Cetane number decreases with blending but increases again as from B20. The decrease is due to the high percentage of diesel which has a cetane number of 44.46.
Acid Value
The acid value of rubber seed oil is the highest at 47.13 mgKOH/g followed by cashew at 4.56 and egunsi at 1.05 as can be seen in Fig.6. Rubber seed oil was transesterified by first converting the free fatty acids to ester before transterification with methanol and this reduced the acid value to 0.45. The values for B10 are lower than B100 but as from B10 are lower than B100 but as from B20 it starts to increase. The values for B100, B10, B20 are within the ASTM limits for biodiesel of 0.80.

Iodine Number
Iodine number is a measure of the total unsaturation within a mixture of fatty acids, and is expressed in grams of iodine which react with 100 grams of biodiesel. Unsaturation can lead to deposit formation and storage stability problems with biodiesel. Fuels with higher iodine number tend to polymerize and form deposits on injector nozzles and piston when heated. Iodine value is an indication of the drying quality of the oil. The iodine value decreased between 5-12% after transesterification as shown in Fig.7, and decreased further with blending because of the diluting effect of the diesel.

Oxidation Stability
Biodiesel ages because of their nature origin and aging properties vary with method of production, feedstock, exposure to sunlight, heat and atmospheric oxygen. They can cause the fuel to form insoluble sediments and gums, which are associated with fuel filter plugging and deposits within the injection system and the combustion chamber. It leads to increased viscosity, corrosion and acid value. The oils are less stable after transesterification except egunsi oil which has the highest oleic acid value, but they all increased at B10 before decreasing at B20 because of the increasing ratio of diesel fuel used for blending as shown in Fig.8. For maximum oxidative stability, blending should be limited to 10% B10.

Sulphated Ash
This is the alkaline catalyst residue remaining after a fuel sample has been carbonized, and the residue subsequently treated with sulfuric acid and heated to a constant weight. It is a measure of the mineral ash residue when a fuel is burned. It is an important test for biodiesel because it is an indicator of the quantity of residue metals in the fuel that came from the catalyst used in the transesterification process. The raw oils have relatively high sulphated ash values compared to 0.02 maximum recommended by ASTM. B100 has a value of 0.03, 0.03 and 0.02 for cashew nut rubber and egunsi seed oils respectively as shown in Fig.9. No differences were observed between the values for B10 and B20.

Carbon Residue
The carbon residue test gives the remaining part when a sample of biodiesel has been subjected to thermal decomposition and hence a measure of the coking tendency of the fuel. It involves heating the fuel to a high temperature in the absence of oxygen to simulate very simplified burning conditions in an engine. Most of the volatile part of the fuel will vaporize and be driven off but a portion may decompose and pyrolyze to hard carbonaceous deposits. This is particularly important in diesel engine because of the possibility of carbon residue clogging the fuel injectors. After transesterification the carbon residue decreased. All the B10s reduced to 0.03 but at B20, cashew nut oil methyl ester decreased to 0.02 while rubber seed and egunsi melon increased to 0.04 and 0.05 respectively. All values after transesterification and blending are below the ASTM maximum for biodiesel as can be seen in Fig.10.

CONCLUSIONS
Blending biodiesel with diesel can be employed to increase heating value and oxidation stability. However, since diesel has flash point and cetane number less than B100, their values would be reduced by blending. Kinematic viscosity, Acid value, sulphated ash, carbon residue and corrosion are reduced by blending. B20 is the best blend as far as engine performance parameters such as heating value and cetane number are concerned. The properties of blends can be predicted for higher blend proportions by extrapolation of the properties trend between B10 and B20 (Aiptekin and canakci, 2009).

REFERENCES

ASTM. American Society of Testing and Materials. ASTM D6751-02 Requirements for Biodiesel ASTM, Easton, Maryland, USA.


APPENDIX

Table 1. Fatty Acid Profile of cashew seed oil and its methyl Ester.

<table>
<thead>
<tr>
<th>Acid</th>
<th>Form</th>
<th>Oil</th>
<th>B100</th>
</tr>
</thead>
<tbody>
<tr>
<td>Capric</td>
<td>C10:0</td>
<td>1.367</td>
<td>2.225</td>
</tr>
<tr>
<td>Lauric</td>
<td>C12:0</td>
<td>1.832</td>
<td>2.984</td>
</tr>
<tr>
<td>Myristic</td>
<td>C14:0</td>
<td>0.587</td>
<td>0.957</td>
</tr>
<tr>
<td>Palmitic</td>
<td>C16:0</td>
<td>28.867</td>
<td>23.134</td>
</tr>
<tr>
<td>Palmitoleic</td>
<td>C16:1</td>
<td>3.162</td>
<td>5.155</td>
</tr>
<tr>
<td>Stearic</td>
<td>C18:0</td>
<td>4.061</td>
<td>5.573</td>
</tr>
<tr>
<td>Oleic</td>
<td>C18:1</td>
<td>34.479</td>
<td>31.648</td>
</tr>
<tr>
<td>Linoleic</td>
<td>C18:2</td>
<td>5.673</td>
<td>7.616</td>
</tr>
<tr>
<td>Linolenic</td>
<td>C18:3</td>
<td>20.971</td>
<td>20.709</td>
</tr>
</tbody>
</table>

Total Saturation: 36.715 34.871
Total unsaturation: 63.285 65.128

Table 2. Fatty Acid Profile of rubber seed oil and its methyl Ester

<table>
<thead>
<tr>
<th>Acid</th>
<th>Form</th>
<th>Rubber seed Oil</th>
<th>B100</th>
</tr>
</thead>
<tbody>
<tr>
<td>Palmitic</td>
<td>C16:0</td>
<td>19.32</td>
<td>19.65</td>
</tr>
<tr>
<td>Stearic</td>
<td>C18:0</td>
<td>3.87</td>
<td>5.48</td>
</tr>
<tr>
<td>Oleic</td>
<td>C18:1</td>
<td>23.74</td>
<td>27.82</td>
</tr>
<tr>
<td>Linoleic</td>
<td>C18:2</td>
<td>37.90</td>
<td>35.17</td>
</tr>
<tr>
<td>Linolenic</td>
<td>C18:3</td>
<td>15.16</td>
<td>11.90</td>
</tr>
</tbody>
</table>

Total Saturation: 23.19 25.13
Total unsaturation: 76.81 74.87

Table 3. Fatty Acid Composition of Egusi oil and its Methyl Ester

<table>
<thead>
<tr>
<th>Fatty Acid</th>
<th>Form</th>
<th>Egusi Oil</th>
<th>EMOME</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lauric</td>
<td>C12:0</td>
<td>-</td>
<td>0.79</td>
</tr>
<tr>
<td>Myristic</td>
<td>C14:0</td>
<td>-</td>
<td>0.88</td>
</tr>
<tr>
<td>Palmitic</td>
<td>C16:0</td>
<td>12.88</td>
<td>10.27</td>
</tr>
<tr>
<td>Palmitoleic</td>
<td>C16:1</td>
<td>0.74</td>
<td>0.96</td>
</tr>
<tr>
<td>Stearic</td>
<td>C18:0</td>
<td>6.70</td>
<td>10.36</td>
</tr>
<tr>
<td>Oleic</td>
<td>C18:1</td>
<td>13.23</td>
<td>12.84</td>
</tr>
<tr>
<td>Linoleic</td>
<td>C18:2</td>
<td>62.35</td>
<td>62.46</td>
</tr>
<tr>
<td>Linolenic</td>
<td>C18:3</td>
<td>2.42</td>
<td>1.44</td>
</tr>
</tbody>
</table>

Total saturation = 19.52 22.30
Total unsaturation = 80.48 77.70