Production, Characterization and Evaluation of Castor oil Biodiesel as Alternative Fuel for Diesel Engines

Bello E. I and Makanju A

Department of Mechanical Engineering
The Federal University of Technology, Akure, Nigeria

Corresponding Author: Bello E.I

Abstract
In this study, the use of castor oil methyl ester as possible alternative fuel for diesel engines was investigated. The oil was extracted in a soxhlet extractor using normal hexane as solvent. To overcome the high kinematic viscosity of the neat oil, a high molar ratio of 6 : 1 was used to produce the methyl ester. The viscosity of the ester was high and further reduced by blending with diesel fuel to reduce it to within the American Society for Testing and Materials (ASTM) D6751-02 limits for biodiesel. The biodiesel was characterized and tested in a single cylinder diesel engine. The results obtained gave properties, torque outputs and specific fuel consumption that are close to those of diesel fuel thus confirming that it can be used as alternative fuel for diesel engines. Chromatography analysis of the methyl ester shows that it contains 90% ricinoleic acid which is a monounsaturated, 18-carbon fatty acid with a high polarity hydroxyl functional group at C12 and ester linkages that makes the fuel unsaturated and with a wide range of industrial applications.

Keywords: castor oil, biodiesel, transesterification, blend, ricinoleic acid

INTRODUCTION
Biodiesel has been defined as a mono-alkyl ester of vegetable oils or animal fats (Knothe et al., 2005) and (Mittelbach and Remschmidt, 2004). It has very similar physical properties to diesel fuel and even higher cetane number which allows it to be used directly as substitute fuel for diesel engines without any modifications or as a blending agent for diesel fuel. Since it is produced from renewable and domestically grown feed-stocks, it can reduce the demand for petroleum based fuels and possibly lower the overall cost of diesel fuel. Biodiesel due to its agricultural source essentially contains no or very little sulfur and thus offers promise to reduce particulate and toxic emissions, which is one of the primary objections to diesel engines. One of such oils is castor seed oil that is obtained from castor plant Ricinus Communis which belongs to the family of euphorbiaceae. The beans contains toxin that makes the oil and cake inedible. It was chosen for the study because it widely available, has no other commercial uses and unlike vegetable oils such as soya beans, would not compete for other uses such as consumption. It grows very well on marginal land, is draught and pest resistant and has a yield of about 1413 litre per hectare when cultivated. The beans contain 35 – 55 % oil by weight for high yield breed type, has one of the highest viscosities among vegetable oils and a molecular weight of 298 (Kulkarni and Sawant, 2003)

It is a hard non-drying oil that neither become stiff with cold nor unduly thin with heat hence is used as a lubricant for jet and racing cars engines (Brown et al., 2001). It is the only source of an 18-carbon hydroxylated fatty acid with one double bond in each of the fatty acid chain and ricinoleic acid make up about 89% of the fatty acid composition (Conceicao et al., 2005 and Conceicao et al., 2007). The presence of a hydroxyl group at C12 of the ricinoleic acid, the ester linkages, double bonds and hydroxyl groups provide reaction sites that makes it unusually polar which provides sites for the production of a wide range of natural and synthetic resins, waxes, polymers and elastomers. It also has excellent emollient and lubricating properties, a marked ability to wet and disperse dyes, pigments and fillers (Azumbuja and Dias, 2006) and Ogunniyi, 2006) as well as several medicinal values (Brown, 1995). Castor oil has excellent solubility in methanol and hence theoretically an ideal oil for transesterification to biodiesel, requiring a minimum amount of catalyst and heating which can reduce costs of production.

MATERIALS AND METHODS
Oil Extraction
Castor seeds were harvested from the wild, dried, crushed and separated into seeds and shells. The seeds were packed into the extraction chamber and normal hexane poured into the round bottom flask of a soxhlet extractor. The mantle heater was set at 60°C and the oil in the seeds was leached for 8 hours after which the methanol was distilled from the castor
oils. The eight of the oil produced and the residue were measured.

MATERIALS

Anhydrous Methanol of 99.95% purity, sodium hydroxide and other chemicals were of analytical reagent grade and were obtained from Finlab Nig. Ltd. Measurement of properties were carried out in chemistry and fuel laboratories of the university while the engine tests were conducted in Agricultural Engineering internal combustion engine laboratory of the university.

ESTERIFICATION PROCESS

Determination of Optimum Conditions for Transesterification

The optimal condition for the transesterification of castor oil of Nigeria specy in terms of molar ratio, amount of catalyst required were determined by an iterative experimental design as follows:

- The mass of sodium hydroxide granulated was varied from 2.5 to 5 g in a step of 0.5 g.
- Each mass was added to 1 litre of methanol to form sodium methoxide.
- Each mass of the methoxide was mixed with the castor oil in the molar ratios of 1:1, 4:1 and 6:1 thus giving 18 samples, which were transesterified. The amount of methyl ester and glycerol produced were separated and measured for each sample. The result obtained is shown in Fig.1.

Transesterification Process

3 g/litre of sodium hydroxide was added to methanol in a mixer and stirred at 350 rpm until it is completely dissolved. It was then mixed with the castor oil in a 250 mL reactor equipped with a heater/magnetic stirred at a relatively high molar ratio of 6 to 1 to bias the reaction toward higher yield and because of the very high viscosity of the oil. It was next stirred at 1000 rpm for 3 hours at 60°C for the reaction to take place. The mixture was allowed to settle for 8 hours to drive the reaction to completion and for the mixture to separate into two layers of biodiesel and glycerol, which is denser at the bottom. The mixture was separated using a separating funnel. Tannic acid was added to the biodiesel to neutralize any remaining base catalyst and washed with distilled water to remove impurities such as diglycerine and monoglycerine, catalyst, soap and excess methanol which can affect combustion and exhaust emission. The washing was done by mixing with 20 vol.% distilled water and stirred gently for ten minutes. It was allowed to settle and it separated into two layers of pure biodiesel and hydrated methanol with the lighter biodiesel at the top, which was separated using a separatory funnel. The procedure was repeated three times (Dorado, et al., 2002) before being heated to 120°C to remove any water vapour still present.

Characterization

The main properties of the castor oil, its biodiesel and blends with diesel fuel were measured using mainly the American Society for Testing and Materials (ASTM, 1980) protocols for biodiesel fuels that are listed in Table 1. The density was measured using hydrometer to IP-160/ASTM D-1298. The specific gravity determined by using a hydrometer. In measuring the Pour point, A 45mL sample initially at 45°C is cooled at specified rate and examined at interval of 3°C to check if the sample is still flowing. The test device was Herzog CPP 97-2.

The cloud point was determined by a cloud point meter which comprises of a waveguide sensor of a total-reflection type, the wave guide sensor including a wave guide having an incidence channel, an emergency channel and a detection surface all formed on a substrate, the incidence and emergency channels intersecting along the detection surface, an incidence optical fiber connected to the entrance of the incidence channel, and an emergency optical fiber connected to the exit of the emergence channel; and a cooling/heating means in contact with the waveguide sensor for cooling/heating the waveguide sensor within a desired temperature range.

Flash point measurements were done according to method ASTM D 6751 using Kehler Model K-16270 (Pensky-Martens Closed Flash Tester). The iodine value and peroxide value 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 value and peroxide value were then calculated by the following formulae:

\[
\text{Iodine value} = \frac{B - T}{C} \times 0.001259/9, \quad (2.1)
\]

\[
\text{Peroxide value} = \frac{(T-B)}{C} \times 1000/9, \quad (2.2)
\]

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

The Heating value was determined using the oxygen bomb calorimeter

The cetane number of the biodiesel was calculated by the following formula (Willard, 2000)

\[
C_l = -420.34 + 0.166T^2 + 0.1926\log T_{150} + 6.501\log T_{50} - 0.001897T_{150}^2
\]

Where G is the API (American Petroleum Institute) specific gravity and T50 is the distillation temperature as 50 vol.% fuel sample distilled and
condensed in a unit of °F. Sulfated Ash was measured by accurately weighing 1 g of the substance into a platinum suitable dish and moisten with sulfuric acid. It was heated gently to remove the excess of acid and ignited at about 800°C until all the black particles have disappeared. It was again moisten with sulfuric acid and re-ignite. Finally a small amount of ammonium carbonate was added and ignited to constant weight.

**Carbon Residue.** This is the amount of carbon residue left at the end of the fuel combustion process and is a measure of the extent of the complete combustion of the fuel. The carbon residue (wt.%) of the biodiesel was measured by a Conradson carbon residue analyzer and calculated using the relationship:

\[
\text{Carbon residue (wt.%) = \frac{\text{weight of the total carbon residue collected after burning/ the initial weight of the liquid fuel before combustion}}{1} \times 100}
\]

Phosphorous was determined by weighing 25 mg of the sample into the schonigler flask and burnt in excess of oxygen. The product was digested with nitric acid. The content was boiled for one minute to ensure complete conversion of phosphorous pentoxide to orthophosphate. The solution was passed through a 10 cm long resin column, and the filtrate was collected in a 10 ml pyrex test tube. 2 mL of the colour development reagent was added for the absorbance reading at 650 nm for both the standards and the sample filtrate.

**Fatty Acid Profile**

The weight proportions of the composition of the saturated and unsaturated fatty acids of the oil were analyzed by a gas chromatography (GC) analyzer (GC-14A model by Shimadzu inc., Japan) with the data management system software. The size of the capillary column in the GC analyser was 30 m long and 0.25 mm in diameter. The injector was maintained at 230°C and the detector temperature was 240°C. Nitrogen was the carrier gas at a flow rate of 45.0 mL/min and pressure of 2 psi. The oven temperature was set at 40 °C, held for 1 minute, programmed to 120°C at 20°C/min and then 230°C for 35 °C/minutes. The total run time was 68.14 minutes. The knowledge of fatty acid profile is important because the dependence of biodiesel properties on the structure of fatty acid alkyl esters (Knothe,2005).

**Engine Testing**

The test engine is a Lister 8/1 VA low speed single cylinder diesel engine that is connected to an electrical dynamometer.

The specification of the engine is:
- Nominal power output: 6 kW @ 850 rev/min
- 4.5 kW @ 650 rev/min
- Bore: 114.3 mm
- Stroke: 139.7 mm
- Swept volume: 1.433 litres

The field is excited separately by current from the mains and adjusted by a rheostat. The engine is loaded by switching in the 8 electrical elements that are capable of absorbing the full output of the dynamometer and are selected by means of a selector switch. The generated current is fed to the load resistance in the generator circuit. The engine was operated at full throttle opening and the load increased gradually by switching on the load elements one at a time until the speed reduces to the minimum value at which the engine will just run smoothly. The plint fuel guage used to measure fuel consumption consists of a glass tube containing four knife-edged spacers, which are positioned to accurately calibrate the volume of fuel between them. The spring balance reading, the engine speed, revolution counter, quantity of fuel consumed and time were all recorded during each test run and used to determine the engine performance parameters. The test was done for B100 and diesel fuel.

**RESULTS AND DISCUSSION**

The seed yielded 56% oil content and the oil was like a gel, very viscosity. Fig.1 shows the biodiesel yield obtained for various combinations of catalyst amount and molar ratios. The result shows that for a catalyst amount of 3 g/litre there is not much difference between the yield for molar ratio of 4:1 and 6:1. As the molar ratio increases the yield drops slightly, but because excessive amount of methanol usually act as catalyst for other feed stocks, the most likely explanation is the high polarity of the fuel which reduces as the molar ratio is increased.

In view of the high viscosity of the oil, a high excess molar ratio of 6 to 1 was used and it gave a biodiesel yield of 92% after 3 hours of stirring. The properties of the castor oil, biodiesel, B10, B20 and diesel fuel were measured. Blending has been done because it has been reported that there is a linear increase in fuel properties value when blending and the increase up to 20% biodiesel is not significant (Ertan and Canakci, 2009). The methods and the results obtained are shown in Table 1.

The crude castor oil has a density of 0.96 kg/m³ that reduced to 0.89 kg/m³ after esterification and which is still higher than 0.85 kg/m³ for diesel fuel but can be further reduced by blending with diesel fuel. Density is important in determining the mass of fuel flowing into the engine. The specific gravity is also lower for the biodiesel. The cloud point is the temperature at which wax first become visible as the temperature is lowered. These properties can affect fuel flow and the performance of fuel pump and injector. When compared to diesel fuel, the pour point of -32 °C of B100 makes it a suitable fuel for
cold temperature and high altitude aviation applications. B20 shows good low temperature flow properties hence castor oil biodiesel can be used as petroleum diesel additive for improving cold flow properties.

Flash point which is the temperature at which the fuel can ignite when exposed to a heat source is important from the point of view of safe handling, storage and transportation. With flash points of 190 °C, 89 °C and 85 °C for B100, B20 and B10 respectively compared to 50 °C for diesel fuel, the flash point tends to increase with the amount of biodiesel present hence can be used as a flash point enhancing additive. Castor oil biodiesel can be classified as a non hazardous fuel because of its high flash point.

The iodine value of 80 will allow it to be used as alternative fuel for diesel engine that leaves very small carbon deposits on the injector and in combustion chamber thus improving life of components and increasing inter service period. The relatively very high kinematic viscosity of neat castor oil of 200 mm²/s at ambient temperature of 30 °C reduced to 15 mm²/s for the B100, 4.97 mm²/s for B20 and 4.45 mm²/s for B10 after transesterification and blending which are within the ASTM limits of (1.99 - 6 mm²/s) for biodiesel.

The heating value in the amount of energy produced when one kg of the fuel is burnt. Using a bomb calorimeter, the heating value obtained for B100 was 35 MJ/kg and is lower than the 48 MJ/kg for diesel fuel. The carbon residue and sulfated ash tests gave results that are also within the limits for biodiesel. The phosphorus increased in the methyl ester but was within the limits for biodiesel.

It can be seen from the chemical composition of castor oil shown in Table 2 that in contrast to most others vegetable oils it is a monoacid oil whose properties are dictated by the major constituent, which is ricinoleic acid and makes up 89% of the fatty acid content. The oil has a total saturation and unsaturation of 2.30% and 97.7% respectively. Fig.2 shows the variation of torque with engine speed. It has flat top like for diesel fuel and slightly lower than that of diesel fuel. The specific fuel consumption is shown in Fig.3 and has a minimum value at 1200 rpm, which is also 10% less than that for diesel fuel and consistent with the difference in heating values of the fuels.

CONCLUSION
The following conclusions can be reached from the study;

- Castor oil had very high kinematic viscosity which was reduced by using high molar ratio during transesterification but still needed to be blended with diesel fuel to bring it to the limits for biodiesel.
- The high solubility of castor oil in methanol gave very high biodiesel yield even without heating and minimum use of catalyst which, under industrial condition can lead to reduced cost of production
- The torque and power output characteristics are about 10% less than that for diesel fuel but the load carrying capacity is about 20% higher as a result of its oxygen content which allowed for more complete combustion and operate to a lower speed.
- The specific fuel consumption is 10% less than that for diesel fuel and is consistent with the difference in heating values of the fuels. The minimum specific fuel consumption occurred at 1950 rpm.

REFERENCES

AOCS American Oil Chemist Society, Official Method- Peroxide value, cd8, 1980

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


APPENDIX

Table 1. Properties of Castor oil Biodiesel, its blends and diesel fuel

<table>
<thead>
<tr>
<th>Property</th>
<th>ASTM Protocol</th>
<th>Castor oil</th>
<th>B100</th>
<th>B20</th>
<th>B10</th>
<th>Diesel</th>
</tr>
</thead>
<tbody>
<tr>
<td>Relative Density (at 35°C)</td>
<td>D1298</td>
<td>0.956</td>
<td>0.886</td>
<td>0.870</td>
<td>0.864</td>
<td>0.85</td>
</tr>
<tr>
<td>Cloud Point (°C)</td>
<td>D2500</td>
<td>4</td>
<td>7</td>
<td>-5</td>
<td>-7</td>
<td>-12</td>
</tr>
<tr>
<td>Pour Point (°C)</td>
<td>D2500</td>
<td>-15</td>
<td>-26</td>
<td>-30</td>
<td>-26</td>
<td>-20</td>
</tr>
<tr>
<td>Flash Point (°C)</td>
<td>D93</td>
<td>447</td>
<td>160</td>
<td>88</td>
<td>85</td>
<td>55</td>
</tr>
<tr>
<td>Iodine Number (mg iodine/100g)</td>
<td>-</td>
<td>159</td>
<td>80</td>
<td>80</td>
<td>806</td>
<td>-</td>
</tr>
<tr>
<td>Peroxide value</td>
<td>-</td>
<td>17</td>
<td>49.8</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Heating Value (MJ/kg.k)</td>
<td>D240</td>
<td>32</td>
<td>38</td>
<td>44.8</td>
<td>44.5</td>
<td>45</td>
</tr>
<tr>
<td>Kinematic Viscosity (mm²/s)</td>
<td>D445</td>
<td>1120.37</td>
<td>10.43</td>
<td>4.9</td>
<td>4.54</td>
<td>2.8</td>
</tr>
<tr>
<td>Cetane Number</td>
<td></td>
<td>36</td>
<td>53</td>
<td>51.6</td>
<td>51.3</td>
<td>51</td>
</tr>
<tr>
<td>Acid value (mg KOH/g)</td>
<td>-</td>
<td>0.15</td>
<td>0.01</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Free fatty acid (%)</td>
<td>-</td>
<td>0.13</td>
<td>0.26</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Sulfated Ash (%)</td>
<td>-</td>
<td>0.02</td>
<td>0.006</td>
<td>0.02</td>
<td>0.02</td>
<td>0.02</td>
</tr>
<tr>
<td>Carbon Residue (%)</td>
<td>D4530</td>
<td>0.10</td>
<td>0.037</td>
<td>.007</td>
<td>.009</td>
<td>0.05</td>
</tr>
<tr>
<td>Phosphorus mg/kg</td>
<td></td>
<td>1.85</td>
<td>3.02</td>
<td>3.08</td>
<td>3.14</td>
<td>-</td>
</tr>
</tbody>
</table>
Table 2. Fatty Acid Composition of Castor oil and other vegetable oils

<table>
<thead>
<tr>
<th>Fatty Acid</th>
<th>Class</th>
<th>Jatropha</th>
<th>Soya bean</th>
<th>Safflower</th>
<th>Castor oil</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dihydroxystearic Acid</td>
<td>C18:3</td>
<td>-</td>
<td>8.3</td>
<td>0.1</td>
<td>0.3</td>
</tr>
<tr>
<td>Eicosanoic Acid</td>
<td>C20:0</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.3</td>
</tr>
<tr>
<td>Linoleic Acid</td>
<td>C18:2</td>
<td>48.8</td>
<td>54.1</td>
<td>75.5</td>
<td>4.2</td>
</tr>
<tr>
<td>Myristic</td>
<td>C14:0</td>
<td>-</td>
<td>0.1</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Oleic Acid</td>
<td>C18:1</td>
<td>28.46</td>
<td>22.5</td>
<td>14.4</td>
<td>3.0</td>
</tr>
<tr>
<td>Palmitic Acid</td>
<td>C16:0</td>
<td>18.22</td>
<td>10.3</td>
<td>-</td>
<td>1.0</td>
</tr>
<tr>
<td>Stearic Acid</td>
<td>C18:0</td>
<td>5.14</td>
<td>4.7</td>
<td>3.3</td>
<td>1.0</td>
</tr>
<tr>
<td>Ricinoleic Acid</td>
<td>C18:1</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>89.5</td>
</tr>
<tr>
<td>Total saturated</td>
<td>-</td>
<td>23.36</td>
<td>15.10</td>
<td>3.30</td>
<td>2.30</td>
</tr>
<tr>
<td>Total unsaturated</td>
<td>-</td>
<td>76.64</td>
<td>84.90</td>
<td>96.70</td>
<td>97.70</td>
</tr>
</tbody>
</table>

\( ^a \) (El-Diwani et al., 2009); \( ^b \) (Allen et al., 1999)

Fig. 1. Variation of castor oil biodiesel yield with molar ratio and catalyst weight

Fig. 2. Variation of Torque with Engine Speed for Biodiesel and diesel

Fig. 3. Variation of Specific fuel consumption with speed for B100 and diesel