Extraction and characterization of biodiesel from cashew nuts and shells oil \textit{(Anarcadium occidentale)}

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Citation

Abstract
The extraction, production and characterization of biodiesel from cashew nut and shell were done using standard procedures. Solvent extraction method was used in the extraction with a percentage yield of 35.5% and 51.60 % for the shell and nut oil respectively, the extracted oils were characterized and subsequently used in the production of biodiesel. Upon characterization of the oil, (the nut and the shell oil), it was observed that the nut/shell oil have these values (173.91/189.34mgKOH), (23.76/36.76mgI\textsubscript{2}/g), (0.29%/4.6%), for saponification value, peroxide value, and % free fatty acid respectively. The biodiesel produced was also characterized and shown to have a viscosity of 10.75 at 40°C, acid number (3.079mgKOH), flash point (204.6°C), pour point (7.8°C) and cloud point (12°C). Some of the above properties of the biodiesel met the standard as specified by the American Standard Test Method (ASTM) for biodiesel, with few modification required where variations were observed. The required result obtained show the viability of producing biodiesel from cashew nut oil and the inability of the shell oil to yield biodiesel because it is not a triglyceride.

1. Introduction

Petroleum products are primarily used for transport and powering spark-ignition engines and compression-ignition (diesel) engines all across the world. Globally, the transport sector accounts for over 40% of fossils energy resources (Abigor et al., 2000). With the growing concerns for the environmental problems of fossil fuel exploration, rising prices of imported refined petroleum products and the constant emission of pollutant to the atmosphere, the importance of finding alternative sources of energy cannot be over emphasized. Thus, there is the need to develop cleaner fuels such as ethanol and biodiesel from renewable energy sources like cashew nut oil, sugar cane, corn, cassava, plant oils, rubber seeds, jatropha curcas, castor seed amongst others. Virgin vegetables are very viscous that they do not burn completely, forming deposits in the fuel injector of diesel engines (Murugesan et al., 2009). Their direct use in the fuel engines is problematic.

Currently, biodiesel is considered a real alternative to diesel fuel due to the following advantages: It can reduce the dependence on crude oil foreign imports and enhance...
energy security. It can reduce greenhouse emissions and lower harmful emissions. It is biodegradable, non-toxic and renewable. It can help improve rural economics since the agricultural surplus is used as raw materials (Fukuda et al., 2001).

Furthermore, Biodiesel has many advantages which include: higher cetane number, it contains no aromatics, almost no sulphur and 10-12% oxygen by weight. Biodiesel fueled engines produces less carbon monoxide; CO, hydrocarbon and particulate emissions. Biodiesel improved the lubricity which result in longer engine component life (Goodrum and Geller, 2005).

2. Experimental

2.1. Sample Collection and Preparation

The samples were collected from a compound in Ugbojiobo in Benin City, stored at room temperature for one month to reduce the moisture and subsequently de-shelled. The nut and shell were dried in the oven at a temperature of 105°C to remove the remaining moisture until a constant weight was achieved.

2.2. Extraction of Oil

The nuts were milled so that the oil could easily be extracted using solvent extraction. After extraction, analysis such as free fatty acid value, density determination, moisture content, saponification value and peroxide value were carried out.

10g of the milled sample was weighed and inserted into the extracting thimble covered with a cotton wool free from substances normally soluble in petroleum ether. The extractor was made to sit in 250ml round bottom flask containing 85ml of petroleum ether (60-80°C). The condenser was connected to reflux for 8 hours to ensure complete extraction of the oil present in the sample. After extraction, the round bottom flask was detached from the set up to recover the petroleum ether using a rotary evaporator. The flask was dried further in the oven to completely remove the solvent and the percentage yield calculated (AOAC, 1990).

Calculation

\[
\text{Oil Content (\%)} = \frac{\text{weight of oil}}{\text{weight of sample}} \times 100
\]

2.3. Characterization of the extracted oil

2.3.1. Saponification Value

2g of the oil was weighed into two clear and dry Erlenmeyer flask (250ml). 25ml of alcoholic potassium hydroxide was added. The flask was covered with a cork having long tube to act as the condenser. It was heated in the water bath for 30 minutes. The flask containing the saponification solution was removed from the heat source, shaken well and titrated against standard acid, using 2 drops of phenolphthalein as the indicator. A blank was carried out using the same quantity of alcoholic potassium hydroxide and phenolphthalein but without the oil.

2.3.2. Peroxide Value

1g of the oil was accurately weighed into a clean dried boiling tube. 1g of powdered KI and 20ml of the solvent mixture (2:1 of Glacial acetic acid and chloroform) was added. The tube was transferred to the boiling water to boil vigorously for 30 minutes. 25ml of water was added and swirled. It was titrated against 0.002N Na₂S₂O₃ solution until yellow colour almost disappeared. 0.5ml of starch solution was added, shaken vigorously and titrated carefully until the blue colour disappears. A blank was titration run afterwards.

2.4. Free Fatty Acid Determination

2.5g of the oil was weighed accurately into the conical flask. 2.5ml of neutralized alcohol was added and boiled on a water bath. It was shaken well to dissolve the fatty acid. The alcohol was added to provide a medium for dissolving the fatty acid. 1ml of phenolphthalein indicator solution was added to the solution while hot and titrated against 0.1N sodium hydroxide; NaOH. The end point was reached when the pink colour persists for 30 seconds.

2.5. Biodiesel Synthesis from Cashew Nut Oil

40g of the oil was dispensed into a 250ml round bottom flask, containing 20ml of methanol equipped with a thermometer, reflux condenser and a magnetic stirrer. The reaction flask was placed on a water bath mounted on a magnetic stirrer hot plate and then heated to 60°C. The catalyst solution also at 60°C was gradually added into the flask containing the oil. The temperature of the system was maintained at 60°C for 45 minutes. After the reaction time, the two layer mixture was extracted with n-hexane and carefully transferred to separating funnel and left overnight. The glycerol, due to difference in density was left to run off. The biodiesel was washed with warm distilled water to a neutral pH to remove the catalyst, glycerol and other impurities. A rotatory evaporator was used to recover the excess methanol and n-hexane in the biodiesel at their boiling temperatures of 64.7°C and 60°C respectively. The moisture remaining in the product was removed with anhydrous Na₂SO₄ which was subsequently filtered off and
the clear, golden yellow fatty acid methyl ester (biodiesel) was dried at 105°C for 10 minutes cooled and weighed. The biodiesel produced was then characterized to determine the kinetic viscosity, flash point, cloud point, pour point and acid value using standard analytical technique with a comparison drawn using the ASTM standard.

2.6. Biodiesel Characterisation

2.6.1. Kinematic Viscosity

The test was carried out using a capillary tube viscometer test method. The oil sample was placed into a glass capillary u-tube. The sample was drawn through the tube using suction until it reaches the start position indicated on the tube’s side. The suction was released, allowing the sample to flow back through the tube under gravity. The narrow capillary section of the tube controls the oil flow rate.

Afterwards the kinematic viscosity was determined from the time it takes to flow from the starting point to the stopping point using a calibration constant supplied for each tube.

Calculation

\[
g = \text{acceleration due to gravity} \\
D= \text{diameter of capillary} \\
L= \text{average distance between upper layer menisci} \\
V= \text{timed volume of liquid passing through the capillary} \\
\rho= \text{flow rate}
\]

\[
\text{Kinematic viscosity} = \frac{gD^2L^4}{128\pi V^2}\rho
\]

2.6.2. Flash Point

The specimen was placed in the cup of the tester with the lid closed. It was heated at a slow constant rate and ignition source (lighted a match stick) was directed into the cup at regular interval. The flash point was taken at the lowest temperature at which application of ignition source causes the specimen to ignite.

2.6.3 Cloud Point

The test sample was poured into a test jar to a level approximately half filled. A cork carrying the test thermometer was used to close the jar. The entire test subject was then placed on a constant temperature cooling bath to prevent excessive cooling. The sample was taken out every 1°C and inspected for cloud formation, (wax formation). The temperature at which the first appearance of wax crystal was detected in the sample was recorded as the cloud point.

2.6.4 Pour Point

The sample was kept in a test jar and allowed to cool in a bath to allow the formation of paraffin wax crystals. At every 3°C, the test jar was removed to check for surface movement. It was observed that when the sample was tilted it did not flow, when the jar was held horizontally to 5 second, it still did not flow, the temperature at which it flows on being tilted was immediately recoded as the pour point temperature.

3. Results and Discussion

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Units</th>
<th>Nut Oil</th>
<th>Shell Oil</th>
</tr>
</thead>
<tbody>
<tr>
<td>Saponification value</td>
<td>(mgKOH)</td>
<td>173.91</td>
<td>189.34</td>
</tr>
<tr>
<td>Peroxide value</td>
<td>(mg L/g)</td>
<td>23.76</td>
<td>36.76</td>
</tr>
<tr>
<td>%FFA</td>
<td>(%)</td>
<td>0.27</td>
<td>5.48</td>
</tr>
<tr>
<td>Moisture content</td>
<td>(%)</td>
<td>13.0</td>
<td>10.75</td>
</tr>
<tr>
<td>Relative density</td>
<td></td>
<td>0.8869</td>
<td>0.9459</td>
</tr>
</tbody>
</table>

From the results above, we can see that the saponification value, peroxide value and the free fatty acid of the shell oil is greater than those from the nut oil.

The higher saponification value of the shell oil indicates that, the shell oil can form soap easily than the nut oil when in contact with a base. As natural oils and fats are mixture of triglycerides, the saponification number will depend upon the relative sample; butter and coconut oil contain large quantities of short chain fatty acid and glycerides and have high saponification values. Therefore, the smaller the molecular weight of the fat, the greater the saponification number and vice versa. Saponification value of oil is an index of average molecular weight of the triglyceride composition of the oil. Values above 200mg/KOH indicate the presence of fatty acids of low or fairly low molecular weight, while values below 190 mg/KOH is an indication that high molecular weight fatty acids is present

Also, its higher peroxide value indicates that the shell oil contains more peroxides than the nut oil and also of higher rancidities than the nut oil. The higher value recorded is an evidence that the extracted oil has high peroxide values, which is above the allowable level for edible oils, and the implication is that the oil has undergone hydrolytic oxidation.

In other words, the nut oil is of higher quality than the shell oil because the higher the rancidity factor (value) of an oil, the more the deterioration with accompanying effect on the shelf life of the oil and viability of biodiesel production from the oil.

The FFA of the shell oil is very much greater than the nut oil, indicating the level of acidity in the oil than the nut oil. FFA determination helps in knowing whether ageing has taken place in the oil and also weather the oil has undergone hydrolytic change and the ease with which the conversion reaction will take place. Oils with very high free fatty acid values will react with alkali catalyst to produce soaps that inhibit the conversion reaction to biodiesel and make washing of the finished product more difficult. The high acidity of these oils was also reflected in the high acid value of the biodiesel obtained from the oil.

Also, it was observed that the nut oil contains more moisture than the shell oil, hence the higher percentage moisture content which invariably affects the shelf life of these oil. Higher moisture content poses higher rate of deterioration due to higher microbial activities.

The values of the density and moisture of these oils falls within the range of values obtained by Aremu and Akinwumi, (2014) as 0.91 and 8.90% respectively.

The above properties of these oils (peroxide value and
acidity) gave insight into the better quality of the nut oil for biodiesel production as seen from the results in table 2.

### Table 2. Properties of Cashew Nut Oil Biodiesel

<table>
<thead>
<tr>
<th>Classification</th>
<th>Nut Oil</th>
<th>ASTM STD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kinematic viscosity at 40°C</td>
<td>10.75mm²/s</td>
<td>1.9-6.0mm²/s</td>
</tr>
<tr>
<td>Flash point (closed cup)</td>
<td>204.6°C</td>
<td>130°C min</td>
</tr>
<tr>
<td>Pour point</td>
<td>7.8°C</td>
<td>-</td>
</tr>
<tr>
<td>Cloud point</td>
<td>12°C</td>
<td>-</td>
</tr>
<tr>
<td>Acid value</td>
<td>3.079mg/KOH/g</td>
<td>0.80max</td>
</tr>
</tbody>
</table>

From the research carried out, the kinematic viscosity was determined to be 10.75mm²/s. This was however too high because it was above the standard specified by ASTM (1.9 – 6.0 mm²/s). So there is a tendency that it can cause fuel flow problems and lead to stall out or fuel pump failure. Thus, to increase the performance there is need for it to be blended with other diesel with a view to reducing its high viscosity.

The cloud point and pour point was determined to be 12°C and 7.8°C respectively. Although no ASTM standard has been specified for these parameters, the values obtained were however within the other biodiesel previously analyzed by Audo (2012) as 12°C and 15°C for cloud and pour point respectively.

The acid value was determined to be 3.079mgKOH/g. The acid value determined from the biodiesel produced in the presence of anacardic acid a non-triglyceride. However, it should be noted that the shell oil did not produce biodiesel because it is not a triglyceride, hence cannot be converted to biodiesel. This observation was supported by Redhakrishnan et al., (2014) and Velmurugan and Loganathan (2011).

However, the shell oil contains between 71-82% anacardic acid and could be used directly in engines or blended with other diesel fuel for optimum performance according to Redhakrishnan et al., (2014).

### 4. Conclusion

This research has shown the great prospects in the utilization of cashewnut oil in the production of biodiesel and the characteristics of the diesel thus produced with an insight into the necessary modifications to be done on few properties with little variations from the stipulated ASTM standard. The results obtained also verified previous claims of the inability of the cashew shell oil to yield biodiesel because of the high presence of anacardic acid a non-triglyceride.

### References


