Insight into Possibility of Producing Biokerosene From Jatropha Curcas Plant in Nigeria

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Abstract: In this research project, a non-edible vegetable oil was produced from jatropha curcas seed through chemical extraction method using the soxlet apparatus as a substitute fuel for kerosene lamps and its usability was investigated as pure oil and as a blend with ethanol. Biodiesel produced from jatropha oil was analyzed, from the analysis, properties such as free fatty acid content, acid value, pour point, viscosity @ 400C, density, specific gravity etc. where determined. The oil had 14% free fatty acid content, density of 920.43, specific gravity of 0.92.

Bio-kerosene production in this project attempted two methods which are; distillation of the biodiesel and blending of the biodiesel with ethanol to raise the cetane number to that close to the cetane number of fossil kerosene. Distillation of the biodiesel using the distillation apparatus to remove the light end of the biodiesel to produce a lighter liquid with low flash and boiling point compare to the biodiesel. The distillation temperature used was about 1750C-3250C, this is the boiling temperature range for fossil kerosene.

The second approach focused on blending biodiesel with ethanol, with aim to improve the cetane number. Ethanol was blended with biodiesel at different percentage; E5B95 (5% ethanol, 95% biodiesel), E20B80 (20% methanol, 80% biodiesel), E50B50 (50% methanol,50% biodiesel), E70B30(70% methanol, 30% biodiesel). Each sample was analyzed for its physicochemical properties and compared with that of fossil kerosene.

Introduction
Biodiesel is defined by ASTM International as a fuel composed of mono-alkyl esters of long-chain fatty acids derived from renewable vegetable oils or animal fats meeting...
the requirements of ASTM D6751. Biodiesel is receiving increased attention as substitute, non-toxic, biodegradable, and renewable diesel fuel. Its properties vary depending on the oil feedstock and alcohol used but it can always be used as a direct substitute for diesel fuel (Fernando, 2004). A sustainable bio-fuel has two favorable properties which are its availability from renewable raw material and its less negative environmental impact than that of fossil fuels. Various vegetable oil extraction and trans-esterification technologies are currently used in the production of biodiesel fuel. As an alternative fuel, vegetable oil is one of the renewable fuels (Fernando, 2004; Bryan, 2009). Vegetable oil is a potentially inexhaustible source of energy with an energetic content close to that of Diesel fuel. The vegetable oil fuels have not been acceptable because they were more expensive than petroleum fuels. The major problem associated with the use of pure vegetable oils as fuels, for diesel engines, is caused by the high fuel viscosity in compression ignition, practically the high viscosity of vegetable oils ranges from (30-200 Centistokes) as compared to that to diesel (5.8-6.4 Centistokes) (Chakraborty and Sarkar, 2008). There are more than 350 oil bearing crops identified, among which only sunflower, safflower, soybean, jatropha curcas, cotton-seed, rape-seed and peanut oils are considered as potential alternative fuels for diesel engines. There are different ways the viscosity can be reduced; Trans esterification seems to be the best choice, as the physical characteristics of fatty acid esters (biodiesels) are very close to those of Diesel fuel and the process is relatively simple (Fernando, 2004; Chakraborty and Sarkar, 2008; Falasca, Ulberich and weldman, 2006; Aldo, Okullo, Temn, Ogwok, and Ntalikwe, 2011).

**Energy Content of Biofuels**

1. The energy content of biodiesel is about 90% that of petroleum diesel.
2. The energy content of ethanol is about 50% that of gasoline.
3. The energy content of butanol is about 80% that of gasoline.
4. Most biofuels are at least as energy dense as coal, but produce less carbon dioxide when burned.
5. The lower energy content of biofuels means vehicles travel shorter distances on the same amount of fuel. This has to be taken into account when considering emissions.

Every single part of the plant can be useful for human consumption directly or indirectly. Below are some of its uses (Chakraborty and Sarkar, 2008):

1. The Jatropha oil has its characteristic which is similar to diesel, a distillate from crude oil. So cars can use this oil with little change in their design.
2. It is used as a domestic livestock for skin diseases, sore and rheumatism.
3. The roots are believed to serve as an antidote for snake bites.
4. A dark blue die is extracted from the bark which serves as a coloring matter for clothes, fishing nets and lines.

**Materials**

The materials and reagents used in carrying out the research are as follows: Jatropha oil, Potassium
hydroxide (KOH), Sodium hydroxide (NaOH), Hydrochloric acid (HCl), Sulphuric acid, Isopropyl alcohol, Sodium methoxide, Phenolphthalein Additives. The instruments and equipment used in carrying out this study are: Soxhlets apparatus, Heating mantle/hot plate, Brookfield viscometer, Refrigerator, Conical flasks, weighing balance, Measuring cylinders, Beakers, Magnetic stirrer, Liebig condensers, Thermometer (capable of measuring both negative and positive temperatures), Pipettes and burette, Distillation apparatus, methanol (99% purity)

Methodology

A. Oil Extraction
1. A standard weight of Jatropha seed is crushed and placed in a three necked flask of reasonable capacity to accommodate the material.
2. Hexane was used as a solvent for the extraction of the oil. The volume of hexane needed was determined by the ratio of 6:1.
3. A reflux condenser was connected to the flask and placed in a heating mantle with a set temperature of 55oC - 60oC
4. The mixture was allowed to stir for about 8 hours. The solvent mixture and resulting oil were filtered to remove suspend solids.
5. The mixture was placed in a rotary evaporator to evaporate the solvent and thus, Jatropha oil was obtained.

B. Free Fatty Acid Test
The acid value is defined as the number of milligrams of potassium hydroxide required to neutralize the free fatty acids present in one gram of fat. It is a relative measure of rancidity as free fatty acids are normally formed during decomposition of oil glycerides. The value is also expressed as percentage of free fatty acid calculated as oleic acid.

i. Principle
The acid value is determined by titrating directly the oil/fat in an alcohol medium against standard KOH or NaOH solution.

ii. Analytical importance
The value is a measure of the amount of fatty acid which has been liberated by hydrolysis from the glycerides due to the action of moisture, temperature and or lipolytic enzyme lipase.

iii. Procedure
• Prepare a known base solution (weigh one gram of KOH and dissolve in in one liter of distilled water.)
• Take 10ml of isopropyl alcohol using syringe and put into a small beaker.
• Measure out 1ml of sample oil using syringe, pour into the small beaker containing the 10ml isopropyl alcohol, the mix (titration solution)
• Add few drops of phenolphthalein into the titration solution
• Using syringe, take 20ml to 50ml of your know base solution
• Titrating the (oil, propyl alcohol and phenolphthalein) against the base solution by adding drops of the base solution using the syringe into the titration solution until it turns pink.
• Titration value is recorded.

C. Acid Value Determination
Two grams of sample was dissolved in 50 cm3 of mixed neutral solvent (25 cm3 diethyl ether with 25 cm3 ethanol carefully neutralized with
0.1 M NaOH using 1 % phenolphthalein solution, the mixture was titrated with 0.1 M NaOH aqueous solution with constant shaken to faint pink color.

**i. Calculation**

\[
\text{Acid Value} = \frac{\text{Titre Value} \times 5 \times 61 \times 0.0026}{\text{Weight of Sample (g)}} = \left(\frac{\text{mg KOH}}{g}\right)
\]

\[
\text{FFA} = \frac{\text{Acid Value}}{2} = \left(\frac{\text{mg KOH}}{g}\right)
\]

**D. Determination of Saponification Value**

The saponification value is the number of mg of potassium hydroxide required to saponify 1 gram of oil/fat.

**i. Principle**

The oil sample is saponified by refluxing with a known excess of alcoholic potassium hydroxide solution. The alkali required for saponification is determined by titration of the excess potassium hydroxide with standard hydrochloric acid.

**ii. Analytical importance**

The saponification value is an index of mean molecular weight of the fatty acids of glycerides comprising a fat. Lower the saponification value, larger the molecular weight of fatty acids in the glycerides and vice-versa.

**iii. Procedure**

0.5 M KOH was prepared in 95 % ethanol, 2g of oil sample was weighed and 25 cm of the KOH was added, 25 cm3 of the blank solution was also measured into a conical flask, the two sample were then connected to a reflux apparatus and allowed to boil for an hour until the reflux is completed, 1 cm3 of phenolphthalein was added to the mixture and the resulting mixture was titrated while hot against 0.5 M HCl acid solution, the volume of the acid used to attained the end point was recorded, the blank determination was carried out using the same procedure described above until the color changes from blue to transparent white, then the volume of acid used was noted.

**iv. Calculation**

\[
\text{Saponification value} = \frac{56.1 \times T \times (V_2 - V_1)}{M}
\]

Here, \(T\) = molarity of the standard KOH solution used, \(V_0\) = volume of acid used for the first titration with oil sample, \(V_1\) = volume of acid used for the second titration of the blank solution, \(M\) = mass of the oil sample used.

**E. Viscosity Determination**

Viscosity is the measure of material resistance to flow, higher viscosity materials flows with great difficulty and a material with less viscosity flow more easily. Viscosity is important to diesels and biodiesels because it has impacts on the operation of some engine components such as the fuel pump. The viscosity of a fluid is a measure of its resistance to gradual deformation by shear stress or tensile stress. For liquids, it corresponds to the informal notion of "thickness".

**i. Procedure**

400 cm3 of oil sample was poured into the cup of “Clandom Viscometer, Model VT – 03 Viscometer”, the lowest number spindle was selected and screwed into the underside of the viscometer, the cup containing sample was carefully locked into position so that the spindle cone would be completely immersed in the sample, the machine was switched on and pointed deflection on the machine
scale was observed for about ten seconds and allowed to stabilize, after which the position of the pointer on the scale was read off, this gives the value of viscosity of the oil sample in centipoises.

F. Density Determination

I. Definition
Density is an important physical property of a material or any matter, as each compound and element has a specific density associated with it. Density defined in a qualitative manner as the measure of the relative "heaviness" of objects with a constant volume.

II. Procedure
• The mud balance was cleaned properly to avoid any contamination of the oil sample.
• Fill the already cleaned and dried cup to the top with the oil sample.
• Place the lid on the cup and set it with a gentle rotational motion. Be sure that some oil is expelled through the hole in the cup as this will ensure the cup is full and also will free any trapped air or gas.
• Cover the hole in the lid with a finger and clean all oil from the outside of the cup and arm. Then thoroughly dry the entire balance.
• Place the balance on the knife edge and move the rider along the outside of the arm until the cup and arm are balanced as indicated by the bubble.
• Read the mud weight and specific gravity at the edge of the rider towards the cup.

G. Production of Biodiesel
The process of producing Bio Diesel can be as simple or as tasking as you want it to be, though the more effort you go through, the more percentage of oil you will be able to convert to biodiesel, and the better quality biodiesel you will have as a result. The first step of the process is to reduce FFA content in vegetable oil by esterification with methanol and acid catalyst. The second step is transesterification process, in which triglyceride portion of the oil reacts with methanol and base catalyst to form ester and glycerol. The acid catalyst is generally sulfuric acid while the base catalyst is usually sodium or potassium hydroxide. Product from the reactions is separated into two phases by gravity. The upper portion is then purified by water washing process to meet the biodiesel fuel standards.

i. Esterification
Esterification is mainly the reaction between alcohols and carboxylic acids to make esters. It also looks briefly at making esters from the reactions between acyl chlorides (acid chlorides) and alcohols, and between acid anhydrides and alcohols.

The esterification reaction is both slow and reversible. The equation for the reaction between an acid RCOOH and an alcohol ROH (where R and R' can be the same or different) is:

\[
R-COOH + ROH \rightleftharpoons RCOOR + H_2O
\]

ii. Trans-esterification (alcoholysis)
Trans-esterification of oils (vegetable, used cooking oil) is the most well-known method of producing biodiesel. Trans-esterification, also known as alcoholysis is the reaction of a fat or oil (triglyceride) with an alcohol to form fatty acid alkyl esters, methyl and ethyl esters (which are excellent
substitutes for biodiesel) and glycerol as shown in the reaction below;
CH2-OOC-R1 R1-COO-R’ CH2-OH
CH-OOC-R2 + 3R’OH R2-COO-R’+ CH-OH CH2-OOC-R3 53
COO-R’ CH2-OH

Triglyceride Alcohol Esters Glycerol (Vegetable oil) trans esterification as an industrial process is usually carried out by heating an excess of the alcohol with vegetable oils under different reaction conditions in the presence of an inorganic catalyst. The reaction is reversible and therefore, excess alcohol is used to shift the equilivium to the products side. The alcohols that can be used in the trans-esterification process are methanol, ethanol, propanol, butanol and amyl alcohol, with methanol and alcohol being frequently used. The reactions are often catalyzed by an acid, a base or enzyme to improve the reaction rate and yield. Alkali-catalyzed trans-esterification is much faster than acid-catalyzed trans-esterification and is most often used commercially (Ma, & Hanna, 1999; Ramachandran, Suganya, Gandhi, & Renganathan, 2013; Agrawal, 2007). The alkalis which are used include sodium hydroxide, potassium hydroxide, and carbonates. Sulphuric acid, sulfonic acids, and hydrochloric acids are the usual acid catalysts. After trans-esterification of triglycerides, the products are a mixture of esters, glycerol, alcohol, catalyst and tri-, di- and monoglycerides which are then separated in the downstream (Ma & Hanna, 1999; Freedman, Butterfield, & Pryde, 1986; Demirbas, A, 2005). The process of trans-esterification brings about drastic change in viscosity of the vegetable oil. The high viscosity component, glycerol, is removed and hence the product has low viscosity like the fossil fuels. The biodiesel produced is totally miscible with mineral diesel in any proportion. Flash point of the biodiesel is lowered after trans-esterification and the cetane number is improved. The yield of biodiesel in the process of trans esterification is affected by several process parameters which include; presence of moisture and free fatty acids (FFA), reaction time, reaction temperature, catalyst and molar ratio of alcohol and oil.

iii. The effect of reaction time
The reaction time in the esterification and trans-esterification process because both processes experience an increase in conversion rate which increases the yield.

iv. The effect of reaction temperature
For both processes, the reaction temperature was close to the boiling point of methanol (550C - 600C). The top of the heating vessel should be covered to avoid evaporation of methanol during the esterification and trans-esterification process.

H. Biodiesel Production Process in Laboratory Environment
For this process, 250ml of jatropha oil will be used
• Filter oil remove particles or solid suspension.
• Heat oil to about 80oC - 100 oC to remove moisture: this is very important.
• Allow oil to cool to about 55oC
• Measure out methanol equal to 17% of the volume of oil used. For 250ml oil, 43ml of methanol is used.
• Measure out sulphuric acid: 1 liter of oil to 1.5 ml of sulphuric acid. For 250 ml oil, 0.4 ml is used.
• Mix methanol, sulphuric acid and oil for 2 hours @ 55 - 60°C.
• The mixture is left for 12 hours.
• Prepare methoxide: 3% methanol by volume of the 250 ml oil is measured: 2.5 g of KOH is dissolved in the methanol.
• Add methoxide to oil and mix for 1 hour.
• Pour the mixture into a separating funnel (two phase separation appears), allow glycerol to settle then drain off.
• Water wash the biodiesel with warm water and dry
• Determine the physical and chemical properties of the biodiesel.
• Carryout 3-27 test on biodiesel.

I. Production of Bio-Kerosene
Two methods were used in a quest to achieve this:

(i) Distillation of biodiesel
(ii) Blending of biodiesel with ethanol.

i. Distillation of biodiesel
In an aim to produce bio-kerosene, I distilled the produce biodiesel at a temperature range of (175°C - 3250°C). This temperature range was used because it’s the boiling point of fossil kerosene.

ii. Blending of biodiesel with ethanol
Blending of biodiesel with ethanol at different percentage; E5B95 (5% ethanol, 95% biodiesel), E20B80 (20% methanol, 80% biodiesel), E50B50 (50% methanol, 50% biodiesel), E70B30 (70% methanol, 30% biodiesel).

iii. Flash point determination
The flash points of the blends are determined through the use of an Automatic flash point tester closed cup.

Results and Discussion

Table 1: Results of the Analysis of Chemical and Physical Properties of Jatropha Oil

<table>
<thead>
<tr>
<th>PROPERTIES OF JATROPHA OIL</th>
<th>Frequency</th>
</tr>
</thead>
<tbody>
<tr>
<td>Free Fatty acid (FFA %)</td>
<td>14%</td>
</tr>
<tr>
<td>Acid value (mgKOH/g)</td>
<td>28</td>
</tr>
<tr>
<td>Pour point (°C)</td>
<td>5.0</td>
</tr>
<tr>
<td>Viscosity @ 40 °C (cst)</td>
<td>36</td>
</tr>
<tr>
<td>Viscosity @100°C (cst)</td>
<td>14.4</td>
</tr>
<tr>
<td>Density (kg/m³)</td>
<td>920.4</td>
</tr>
<tr>
<td>Specific gravity (mgKOH/g)</td>
<td>0.92</td>
</tr>
<tr>
<td>Saponification value (mgKOH/g)</td>
<td>187</td>
</tr>
</tbody>
</table>
Table 2: Physiochemical Analysis of the Jatropha Oil Biodiesel

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pour point (°C)</td>
<td>2</td>
</tr>
<tr>
<td>Viscosity (cst)</td>
<td>4.8</td>
</tr>
<tr>
<td>PH value</td>
<td>8</td>
</tr>
<tr>
<td>Density (kg/m^3)</td>
<td>874.73</td>
</tr>
<tr>
<td>Specific gravity</td>
<td>0.875</td>
</tr>
</tbody>
</table>

Table 3: Flash Point Analysis of the Various Biodiesel Ethanol Blends.

<table>
<thead>
<tr>
<th>BLENDS</th>
<th>B100</th>
<th>B95E5</th>
<th>B80E20</th>
<th>B50E50</th>
<th>B30E70</th>
<th>B100</th>
</tr>
</thead>
<tbody>
<tr>
<td>FLASH POINT (°C)</td>
<td>175</td>
<td>125</td>
<td>98</td>
<td>52</td>
<td>25</td>
<td>13</td>
</tr>
</tbody>
</table>

Figure 1: Chart showing Percentage by volume of Biodiesel to Ethanol

1.5 Discussion
The aim of this paper is to produce bio-kerosene from jatropha oil. The physical and chemical properties of jatropha oil and jatropha biodiesel are showcase in table 1 and 2 respectively. Initial method to produce bio-kerosene was to distill
bio-diesel at the boiling point of fossil kerosene, but this method was not a success.

The second method was to blend bio-diesel with a solvent that will raise the cetane number of the bio-diesel to that close to kerosene, solvent such as acetone peroxide, alkyl nitrate 56 ethanol. Ethanol was chosen because of its availability compared to others. Acetone peroxide wasn’t used because it’s an unstable solvent.

Blending of ethanol with bio-diesel was a successful one as shown in figure 1, but solubility of the mixture is a problem. Ethanol solubility in bio-diesel reduces with increase in ethanol percentage. From table 3, the flash point of the blends reduces as the percentage by volume of ethanol increases. This shows that ethanol has a great effect on the flash point.

1.6 Conclusion

Pure bio-kerosene production might not have been a success, but with further analysis better solvent (non-fossil) could blended with bio-diesel to improve the cetane number, such that the flash point of the blend would very close to that of fossil kerosene. Bio-fuels has shown to have advantages over fossil fuels because of low greenhouse gases emission when its being combusted. Blending of bio-diesel with fossil diesel reduces carbon emission.

Large scale bio-diesel Production Company would provide jobs and other source of fuels to reduce dependency on fossil fuel.

References


American Oil Chemists' Society, 63(10), 1375 - 1380.
