The future of fossil fuels of energy has necessitated the need to search for renewable alternatives. Thus, *Carica papaya* seed oil (CPSO) was employed as feedstock for the production of biodiesel by methanolysis. The seed was obtained locally, dried, and extracted with n-hexane. The CPSO was analyzed for specific gravity, viscosity, iodine value, and saponification value, among others using standard methods. The oil was transesterified by two-stage catalysis with oil to methanol mole ratio of 1:9. The biodiesel produced was subjected to standard fuel tests. The seed has an oil yield of 31.2% which is commercially viable. The kinematic viscosity of the oil at 313 K was 27.4 mm$^2$s$^{-1}$ while that of *Carica papaya* oil methylester (CPOME) was reduced to 3.57 mm$^2$s$^{-1}$ and the specific gravity was 0.84 comparable with other seed-oil biodiesels and number 2 diesel. Other oil properties were compared favourably with seed oils already documented for biodiesel synthesis. CPOME's cloud and pour points were 275 K and 274 K, respectively, and relatively higher than other biodiesels and number 2 diesel. CPOME exhibits moderate corrosion of copper strip. The methanolysis improved the fuel properties of the CPOME similar to other biodiesels. CPSO therefore exhibits a potential for biodiesel production.

1. Introduction

The major parts of all energy consumed worldwide come from fossil sources (petroleum, coal, and natural gas). However, these sources are limited and nonrenewable and will be exhausted in the future. The price volatility of fossil-based fuels, monopoly in the crude-oil market, energy crisis associated with technological advances are some of the justifications for continuous quest and renewed drive for alternative, cheaper, and renewable energy sources [1, 2]. There is a global clamour for sustainable development and environmental conservation. This has also increased the tempo of researches on the application of biotechnology for other sources of fuel [3]. Thus, there is global interest in sourcing for eco-friendly, clean-burning, and renewable alternative sources of energy such as energy from biomass, wind, solar, hydroelectricity, geothermal, and hydrogen, among others. Alternative and renewable fuels have the potential of solving many of the current social problems and concerns, from air pollution and global warming to other environmental improvements and sustainability issues [4].

Furthermore, over dependency on petroleum reserves for energy supply and the increasing demand for energy are indicators that supply will not meet demand with time. There is therefore need for research efforts in developing vegetable oils and its derivatives as alternate fuels for engines. Biodiesel, one of such alternative fuels, is produced from renewable biological sources such as vegetable oils and animal fats. Biodiesel is a clean burning ester-based, oxygenated fuel synthesized from natural, renewable sources such as virgin or used vegetable oils and animal fats [5, 6]. The act of producing this fuel, biodiesel, is commonly referred to as transesterification or alcoholysis. The process involves reacting seed oils from some plants, vegetable oils, or animal fats with a short-chain aliphatic alcohol (typically methanol or ethanol) [7, 8]. The best way to use vegetable oil as fuel is to convert it into biodiesel by alcoholysis which is aimed at increasing the volatility and reducing the viscosity thereby
improving the fuel properties. The alcoholysis generally may be methanolysis or ethanolysis based on the alcohol used and the production process may be by catalytic or by non-catalytic supercritical processes. Biodiesel fuel production has been attempted through noncatalytic supercritical fluids (methanol and ethanol) method [9]. Some seed oils have been investigated for biodiesel production but competitive applications has limited their commercial exploration [8, 10]. Some of the seed oils are applied in food and other industrial applications. Thus, the application of some other seed oils that has been classified as underutilized for biodiesel production needs to be further researched into. Therefore, this study is focused on investigating an underutilized seed oil from Carica papaya for production of biodiesel. The annual global production of Carica papaya is placed at over 10 million tons, which places papaya as one of the extremely important fruit crop [11, 12]. The fruit pulp is used as food for human and the foliage is used in fishery livestock feeding [13], but there is no well-documented use for the seed or the seed oil. The aim of this study is therefore to produce biodiesel fuel by methanolysis of Carica papaya seed oils using a two-stage catalytic method and to characterize the fuel relative to other biodiesel and standard diesel fuels.

2. Materials and Methods

2.1. Materials. Carica papaya seed used for this study is majorly produced in Mexico, Florida, Hawaii, Nigeria, South Africa, Sri-Lanka, India, Canary Islands, Malaysia, and Australia with Nigeria being the leading producer (748,000 Mt per annum). It has a typical/average percentage weight composition in the region, seed (8.5%), skin (12%), and pulp (79.5%) [13]. The seed used for this study was obtained in local Nigerian markets, dried, and graded; n-hexane solvent was used for oil extraction; potassium hydroxide which was dissolved in glycerol and sulphuric acid was the catalyst used for the two-stage methanolysis reaction with methanol as the transesterifying agent. The first stage catalytic process is to avoid the problem of soap formation with sulphuric acid before the methanolysis with KOH. All reagents used for the methanolysis and the characterization were of analytical grade.

2.2. Extraction and Characterization of the Seed Oil. The dried, graded seed was extracted with n-hexane using the Soxhlet extractor until the seed in the Soxhlet has been defatted with resulting cleared coloured n-hexane. The mixture of the seed oils and hexane was separated using a rotary evaporator to guide against denaturing the oil with high heat. The content of the oil in the seed was calculated to evaluate the percentage oil content of the seed. The extracted oil was kept in a refrigerator to guide against peroxidation of the oil until analysis and biodiesel synthesis were completed.

The following characterized steps were undertaken on the seed oil: specific gravity, refractive index using the methods reported by [14-16] while saponification value, iodine value, viscosity, and unsaponifiable matter were determined by the methods described by the Association of Official Analytical Chemist [17]. The specific gravity was determined with specific gravity bottle and the refractive index was measured with the aid of Abbe refractometer (Optic Ivymen System) at 313 K. Viscosity of the oil was measured using Rotational Viscosimeter (P-Selectra Typ ST-2001L) at 313 K. The saponification value was obtained by adding alcoholic KOH solution to the sample and heated on a boiling water bath. The excess KOH was titrated with 0.5 M HCl using phenolphthalein as indicator to assess the quantity of KOH used up in saponification [17]. Iodine value was evaluated by weighing about 0.3 g of the oil accurately and dissolving it in 20 mL of Wij’s solution. The flask was closed, shaken, and kept in the dark for 60 min at room temperature. Then 20 mL of potassium iodide solution was added and followed by the addition of 100 mL of distilled water. The liberated iodine was slowly titrated with 0.1 N sodium thiosulphate solution until the yellow colour just disappeared and starch solution was added. The resulting blue colour was discharged by further titration with thiosulphate. A blank analysis was carried out alongside. Furthermore, the measuring of the unsaponifiable matter was carried out by taking a known weight (2 g) of oil, saponifying it with 20 mL of 0.1 N ethanolic KOH under refluxing, and extracted with diethyl ether. The ether was distilled to almost dryness and a few millilitres of acetone were added and evaporated off. The flask is dried at 80°C till no further loss occurs and weighed to calculate the unsaponifiable matter.

2.3. Methanolysis Process. The transesterification of the Carica papaya seed oil (CPSO) with methanol was carried out using a two-stage method. Sulphuric acid (2%) was added to CPSO with continuous stirring with magnetic stirrer for an hour. This first stage acid hydrolysis was followed by the addition of 0.4 g KOH catalyst prepared in 0.4 g glycerol and addition of methanol in oil to methanol mole ratio of 1:9 [18]. The mixture was stirred for 2 hrs at 373 K and at ambient pressure for the conversion of CPSO to the Carica papaya oil methyl esters (CPOME). After the methanolysis of the oil, the glycerol recovery was achieved by the separation of the biodiesel from the glycerol phase in a separating funnel for 4 hrs. After the withdrawal of the glycerol, the CPOME was washed with water to remove traces of glycerol. The total ester yield of the biodiesel was calculated using stoichiometric mole ratio of the experimental yield relative to theoretical yield of the CPOME taking the mean molecular weight of the fatty acid in CPSO as 282 g/mol. The equation of reaction of the methanolysis is presented in Figure I.

2.4. Fuel Properties. The produced biodiesel was characterized by the determination of specific gravity, viscosity, flash point, pour point, cloud point, copper strip corrosion test, and sulphated ash content [19, 20]. The viscosity and specific gravity were determined using the same procedure earlier reported above for CPSEO.

The cloud point was measured by placing the oil in a thermostated vessel set at 263 K and the temperature of the oil drops at an interval of 1°C from ambient temperature. The temperature at which the oil settles and form cloud
was observed as the cloud point. The pour point was also determined on the oil by conditioning the oil in a thermostated vessel at 263 K and measuring the temperature at which the oil did not flow when tilted. At an interval of 1-2°C temperature drop the sample was tilted to observe movement within 5 sec. The temperature at which no movement was observed was recorded for the pour point. Flash point was determined in accordance with the modified method for closed cup flash point determination of AOCS [21].

Furthermore, determination of copper corrosion test was carried out using the method of the American Society for Testing and Material (ASTM) [22]. The methyl esters were placed into a chemically clean and dry 25 mm by 150 mm test tube; the copper strip was slide into the test tube after being polished. A vented cork was placed at the top of the tube before placing it in a bath maintained at 50 ± 1°C. The content of the tube was shielded from strong light during the test. After 3 h ± 5 min in the bath, the copper strip was examined and compared with standard. The copper strip corrosion test is to assess the corrosion tendency of the fuel on metals and engines.

The sulphated ash was determined to assess inorganic content and gross emission properties of the fuel. This was determined by weighing a known small amount of the sample in a previously weighed crucible. The crucible and sample were heated carefully till the content ignites with flame. The temperature was maintained for uniform burning until no fume or smoke was evolved. The crucible was allowed to cool to room temperature, 2-3 mL of sulphuric acid (H$_2$SO$_4$) was added, it was heated further until no fume was observed and transferred into muffle furnace and heat at 500°C for 1 hour. The temperature of the furnace is allowed to cool and the crucible transferred into desiccators after which it was weighed. The sulphate ash was determined with the expression

$$\text{%ash} = \frac{\text{weight of ash}}{\text{weight of oil}} \times 100.$$  \hspace{1cm} (1)

The cetane number of the methyl esters was calculated using the equation reported by Krisnangkura [23],

$$\text{CN} = 46.3 + \frac{5458}{\text{SV}} - (0.225 \times \text{IV}),$$  \hspace{1cm} (2)

Table 1: Results of characterization of *C. papaya* seed oil.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>CPSO</th>
<th>LSO$^{ab}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific gravity</td>
<td>0.926</td>
<td>0.924</td>
</tr>
<tr>
<td>Kinematic viscosity (m$^2$/s$^{-1}$ at 313 K)</td>
<td>27.4</td>
<td>27.2</td>
</tr>
<tr>
<td>Refractive index</td>
<td>1.4501</td>
<td>nd</td>
</tr>
<tr>
<td>Saponification value (mg KOH/100 g oil)</td>
<td>107.99</td>
<td>187.7</td>
</tr>
<tr>
<td>Iodine value (g-I/100 g oil)</td>
<td>86.7</td>
<td>156.7</td>
</tr>
<tr>
<td>Unsaponifiable matter (%)</td>
<td>1.1</td>
<td>nd</td>
</tr>
</tbody>
</table>

CPSO: *Carica papaya* seed oil; LSO: linseed oil; nd: not determined; $^{ab}$Demirbas 2005 [18]; Demirbas 2009 [1].

where CN = cetane number, SV = saponification value, and IV = iodine value.

All analyses were carried out in three replicates to assess reproducibility of method and precision of results.

3. Results and Discussion

3.1. Oil Yield and Characterization. The yield of the oil from *C. papaya* seed was determined as earlier stated. The mean percentage oil yield was 31.18 ± 0.1%. The result of the oil content of the *C. papaya* indicates that the seed has relatively high oil content and is considerable for commercial or industrial applications. The oil yield of the seed therefore makes it suitable for consideration in the biodiesel production. Badami and Daulatabad [24] reported the fatty acid composition of *Carica papaya* seed oil to be lauric acid (0.4%); myristic acid (0.4%); palmitic acid (16.2%); stearic acid (5.0%); arachidic acid (0.9%), behenic acid (1.6%); hexadecenoic acid (0.8%); oleic acid (74.3%); linoleic acid (0.4%). This implies that the unsaturated fatty acid of the seed oil is more than the saturated one. The implication of this is that the oil will not solidify easily when applied in engines but will flow as oil and not fat. Likewise, palmitic and oleic acids amounting to 90% of the fatty acid will most likely give good fuel properties. The characterizations carried out on the seed oil were specific gravity, viscosity, refractive index analysis, saponification value, iodine value, and unsaponifiable matter. The results of these characterizations are presented in Table 1.
Specific gravity and viscosity of oil are important properties that are always considered in oil which will serve as feedstock for biodiesel. The specific gravity of the C. papaya seed oil (CPSO) is comparable with specific gravity reported for linseed oil and other seed oils that have been documented as good feedstock for biodiesel [1, 18, 25]. This makes it suitable oil for biodiesel synthesis trial. Further, the viscosity which measures the flow property of a fluid and determines ease of flow of vegetable oil in engine, if used directly, was assessed in the oil. The observed kinematic viscosity of the oil at 313K was 27.4 mm$^2$s$^{-1}$ which was comparable with the viscosity also reported for linseed oil and with many other seed oils that have been applied for biodiesel production [18]. The viscosity of CPSEO is high for its direct application in engines when compared with 2.60 mm$^2$s$^{-1}$ that has been documented as suitable for petrol diesel [2] or against 4.40 mm$^2$s$^{-1}$ recommended for number 2 diesel fuel by ASTM 975 and documented in literature [8, 18]. Thus, the reduction of the viscosity of the oil by transesterification is essential to its potential application as biodiesel.

Other parameters studied in the oil which are of interest to biodiesel production were the saponification value and iodine value. The iodine value measures the degree of unsaturation in total fatty acids of the oil. The percentage of unsaturation in it is predominantly oleic acid which amounts to 74.3% of the total fatty acids of the oil. The percentage of unsaturation in CPSEO is lower than linseed oil which has C18:1 (18.9%), C18:2 (18.1%), and C18:3 (55.1%) [1, 18]. It therefore implies that CPSEO may be more stable to deterioration than the linseed oil. The unsaponifiable matter in CPSEO is another important property that may contribute to the fuel properties of its biodiesel product because some of the unsaponifiable matters are waxes which may affect the cloud and pour points of the product. The unsaponifiable matter amounts to 1.1% which is moderately high.

### 3.2. Characterization of Biodiesel from C. papaya Seed Oil

After the transesterification of CPSEO, the two phases generated were the C. papaya oil methylester (CPOME) and glycerol. The CPOME was separated and characterized based on the following parameters: viscosity, specific gravity, flash point, cloud point, pour point, cetane number, and copper strip corrosion, among others. The values were compared with other biodiesel produced from other feed stocks and with petroleum diesel. The results of the characterization carried out are presented in Table 2 and are discussed in this section.

Specific gravity of biodiesel fuels reported in literature is between the ranges 0.87 and 0.89 [18, 27]. The higher the value of specific gravity of the fuel is, the more dense the fuel will be. This will affect a number of the fuel's properties, particularly the flow and the volatility. The specific gravity observed for CPOME was 0.840 which is comparable with petroleum diesel and other biodiesels (Table 2). Generally, the specific gravities of other biodiesels cited were slightly higher than those of petroleum diesel which is 0.840 but that of CPOME is the same as petroleum diesel.

The viscosity is another fuel property which will measure the ease of fuel in engines. A less viscous fuel will flow easily in the engine. Thus, a drop in the viscosity is desirable and improves on the fuel for application in engines. The kinematic viscosity of the biodiesel was significantly reduced from 27.4 mm$^2$s$^{-1}$ for the oil to 3.57 mm$^2$s$^{-1}$ for the biodiesel. This is because of the transesterification that has converted the triglyceride to methyl esters of the fatty acids which have shorter chains than the triglyceride. The viscosity obtained for the CPOME was slightly higher than the standard for petroleum diesel. It was, however, comparable with some seed oils that have been reported for biodiesel production (Table 2).

Moreover, the pour point which is the lowest temperature at which a fuel is observed to flow under the conditions of the test was evaluated in CPOME. A slightly higher pour point was observed for the CPOME (274 K) than other biodiesels and petroleum diesel which indicates a relatively high amount of wax in fuel form on the unsaponifiable matter in the oil. Generally, pour point data indicates the amount of long-chain

### Table 2: Fuel properties of biodiesel from C. papaya seed oil compared with others.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>CPOME$^a$</th>
<th>BOME$^b$</th>
<th>LSOME$^c$</th>
<th>Diesel$^{bd}$</th>
<th>ASTM B100$^e$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific gravity</td>
<td>0.840</td>
<td>0.860</td>
<td>ND</td>
<td>0.840</td>
<td>0.86–0.90</td>
</tr>
<tr>
<td>Kinematic viscosity 313 K (mm$^2$s$^{-1}$)</td>
<td>3.57</td>
<td>3.98</td>
<td>3.36</td>
<td>2.60</td>
<td>1.9–6.0</td>
</tr>
<tr>
<td>Copper strip corrosion</td>
<td>No. 3</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>No. 3</td>
</tr>
<tr>
<td>Flash Point (K)</td>
<td>389</td>
<td>348</td>
<td>449</td>
<td>325</td>
<td>403</td>
</tr>
<tr>
<td>Pour point (K)</td>
<td>274</td>
<td>270.5</td>
<td>ND</td>
<td>231</td>
<td>278</td>
</tr>
<tr>
<td>Cloud point (K)</td>
<td>275</td>
<td>ND</td>
<td>ND</td>
<td>247</td>
<td>278</td>
</tr>
<tr>
<td>Sulphated ash content (%)</td>
<td>0.02</td>
<td>0.017</td>
<td>0.01</td>
<td>0.01</td>
<td>0.02</td>
</tr>
<tr>
<td>Cetane number</td>
<td>77.3</td>
<td></td>
<td></td>
<td>47</td>
<td></td>
</tr>
</tbody>
</table>

$^a$This study. $^b$Mean value of triplicate analysis. $^c$Deshmukh and Bhuyar (2009) [2]. $^d$Demirbas (2009) [1]. $^e$ASTM 975, ASTM 6751-03a.
paraffins found in a fuel. Handling and transporting fuels is difficult at temperatures below their pour points. It therefore implies that biodiesel made from CPSO will be difficult to handle and transport especially in temperate region. Often, chemical additives known as pour point depressants are used to improve the flow properties of such fuel as CPOME. Thus, the use of chemical additive to improve the flow properties of the fuel is recommended for this fuel.

The cloud point of CPOME was also determined. Cloud point of a fluid is the temperature at which dissolved solids are no longer completely soluble, precipitating as a second phase giving the fluid a cloudy appearance. It is the temperature below which wax in diesel or biowax in biodiesels forms a cloudy appearance. The cloud point of CPOME was also higher than other biodiesels and petroleum diesel (Table 2). High cloud point is not also desirable in fuel because the presence of solidified waxes thickens the oil and clogs fuel filters and injectors in engines [27]. The wax also accumulates on cold surfaces (e.g., pipeline or heat exchanger fouling) and forms an emulsion with water. Therefore, cloud point indicates the tendency of the oil to plug filters or small orifices at cold operating temperatures. It may therefore be necessary that the CPOME be applied as blend with petroleum diesel for effective application especially in cold regions of the world.

Another fuel property determined was the cetane number. Cetane number is the ability of fuel to ignite quickly after injection into engines. Higher cetane number ensures better ignition of the fuel in the engine. This is therefore one of the important parameters which are considered during the choice of suitable oil for transesterification for use as biodiesel. Generally, fatty acid methyl esters with higher cetane number are favored for use as biodiesel. However, this increase of cetane number implies decrease in iodine value which means there will be increase in saturated fatty acid composition. This situation will lead to the solidification of fatty acid methyl esters at low temperature typical of temperate region of the world. Therefore, an upper limit of cetane number (65) has been specified in US biodiesel standard [28]. The cetane number obtained for CPOME (77.3) was above the ceiling standard recommended for biodiesel. This result corroborate the results obtained for the pour and cloud point. It may therefore imply that CPSO contains some waxes that are responsible for the obtained results.

The corrosive tendency of the CPOME on engine when applied was assessed by carrying out a copper strip corrosion test. From the method of determination the copper is allowed to stay in the fuel for 4 hours at 313 K which simulates conditions in which fuel may be applied. The corrosion test shows that the biodiesel moderately corroded the copper strip and may have corrosion tendencies on engines. This may be confirmed further with corrosion studies of the fuel on different alloys and metal materials. Also, the ash test which indicates the amount of metallic constituents in the fuel and the emission or pollution tendency was assessed. The ash left after completely burning the fuel usually consists of stable metallic salts, metal oxides, and silicon oxide. The ash could be further analyzed for individual elements. The sulphated ash obtained for CPOME was comparable with other biodiesels and petroleum diesel (Table 2) which implies that it has acceptable inorganic content. It can also be inferred that the emission properties of the fuel will be moderate.

4. Conclusions

The study has attempted to synthesize biodiesel from Carica papaya seed oil and has found that the oil exhibits a potential for biodiesel production. The seed has sufficient oil content and the oil has suitable properties which are comparable with other oils that have been applied for biodiesel production. The transesterification process improved the fuel properties of the CPOME. The CPOME has comparable properties with other biodiesels that have been reported in the literature and with petroleum diesel. High pour point and cloud point was, however, observed for CPOME but can be addressed by using CPOME as blend with petroleum diesel or with addition of pour point depressants.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

References


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