Biodiesel Fuel from Differently Sourced Local Seed Oils: Characterization, Effects of Catalysts, Total Glycerol Content and Flow Rates

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Abstract — The recently observed depletion in the petroleum resources, which also mainly constituted carbon dioxide emission and global warming problems call for renewable and sustainable alternative fuels. Oils were extracted from various seeds: Jatropha curcas (Botuje), Pentaclethra macrophylla (Apara) and soybean, using petroleum ether (40-60°C). Alkali catalyzed transesterification of the oils (biodiesel production) in the presence of different kinds of alcohol (methanol, ethanol and propanol) were carried out using sodium hydroxide as catalyst. In the case of Jatropha oil, potassium hydroxide served as catalyst. Effect of catalysts to obtain optimum biofuel was established. In the case of soybean oil, fatty acid methyl ester, FAME, (96%), fatty acid ethyl ester, FAEE, (84%) and fatty acid propyl ester, FAPE, (37.50%) were produced. In waste palm kernel oil, methyl ester (72.92%) and ethyl ester (46.25%) were obtained. In refined palm kernel oil, methyl ester (70.83%), ethyl ester (66.67%) and (14.17%) propyl ester were produced. However, only methyl ester conversion (20.83%) was possible in Pentaclethra macrophylla oil. In Jatropha curcas using KOH catalyst, only methyl ester (80%) formation was possible. Moreover, yields were affected as the alcohol alkyl became bulkier giving relatively lower value of biodiesel. Sulphur content (0.01) obtained for each of the biofuel was satisfactory when compared with ASTM standard (0.05 maximum). The cetane value of soybean oil (45.5), refined palm kernel oil (46) and used oil (44.6) were quite reasonable compared with the special standard (47). The combustion energy of the fuels from refined palm kernel oil, waste palm kernel oil and soybean are 39, 36 and 45.5 respectively. The total glycerol content (Gc) of the methyl and ethyl esters emanated from soybean are quite reasonable and fell within standard.

Keywords: biodiesel, flow rates, local seed oils, total glycerol content, transesterification

1 INTRODUCTION

Among liquid biofuels, biodiesel is gaining acceptance and market share as diesel fuel in Europe and the United states. Biodiesel has become more attractive recently because of its environmental benefits and the fact that is made from renewable resources [1]. Moreover, they have practically no sulfur content, offer no storage difficulty, and they have good lubrication properties.

The substitutions of petrodiesel oil by renewable fuels produced within some countries generate high foreign exchange savings, even for the major oil exporting countries. Consequently, project or research in this direction potentially would serve to solve economical problems and improve economy of developing countries.

Considerable research has been done on vegetable oils as diesel fuel. Feedstock commonly used includes: palm oil, sunflower oil, coconut oil, rapeseed oil and tung oil. Animal fats, although mentioned frequently, have not been studied to the same extent as vegetable oils. Some methods applicable to vegetable oils are not applicable to animal fats because of natural property differences. Oils from algae, bacteria and fungi also have been investigated [2]. Microalgae have been examined as a source of methyl ester diesel fuel [3]. Terpenes and latexes also were studied as diesel fuels [4].

Some natural glycerides contain higher levels of unsaturated fatty acids. Their direct uses as biodiesel fuel are precluded by high viscosities. Fats, however, contain more saturated fatty acids. They cannot be used as fuel in a diesel engine in their original form. Because of the problems, such as carbon deposits in the engine, engine durability and lubricating oil contamination, associated with the use of oils and fats as diesel fuels, they must be derivatized to be compatible with existing engines. Therefore, the work reported herein describe the formation of biodiesel in its various derivatives (methyl-, ethyl- and propyl-) from local seed oils while studying the effects of catalysts and glycerol as it affect flow rates on conversion.

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2 MATERIALS AND METHODS

2.1 Seeds collection, extraction and analysis

Seeds were collected from different locations. Pentaclethra microcarpa (Apara) seeds were collected from Ijebu Ode and Lafenwa market in Abeokuta, Ogun state. Refined palm kernel oil (PKO) was bought from Adatan market, Abeokuta. Soybean was obtained from Kuto market in Abeokuta, Ogun state. Waste/used cooking oils were obtained from different beans cake sellers from Sabo and Carwash; Abeokuta, in Ogun state. Jatropha curcas was collected from University of Agriculture Abeokuta and Asero, Abeokuta in Ogun state. These places are located in the Western part of Nigeria.

The seed shells were cracked to remove the seeds, sun dried and later oven dried to constant weight. Oil from the seeds was obtained by the method of soxhlet extraction using petroleum ether (40-60°C).

Physical analyses of vegetable oils were conducted according to the AOCS standard test methods. The following parameters: iodine value, acid value, peroxide value, saponification value, refractive index and free fatty acid were determined on each sample of the extracted oil as well as used/waste cooking oil. These routine analyses on different seed oils were carried out using AOCS (1978) and Cordex Alimentarious (CAC/RM 9/14-1969).

2.2 Alkali-catalyzed transesterification process

2.2.1 Preparation of Alkoxide

The solvents (methanol, ethanol and propanol) were distilled before use to ascertain purity. Sodium methoxide, ethoxide and propoxide (Na+CH3O-) were prepared by dissolving 0.20g NaOH (catalyst) in 20ml methanol, 20ml ethanol or 20ml propanol respectively. The solutions were thoroughly mixed until the whole alkali dissolved in each solvent. The procedure was repeated using 0.35g, 0.50g, 0.75g and 1.0g NaOH.

Also, potassium methoxide, ethoxide and propoxide (K+CH3O-) were created by mixing 0.20g KOH (catalyst) in 20ml methanol, 0.20g KOH in ethanol and 0.2g KOH in 20ml propanol respectively. The procedure was repeated by dissolving 0.35g, 0.50g, 0.75g and 1.0g KOH in methanol, ethanol or propanol.

2.3 Fuel Characterization

The fatty acid alkyl esters were characterized for their physiochemical and fuel properties. The parameters includes: total acid value, cetane number (CN), iodine number and saponification value. Chemical analyses of vegetable oils were conducted according to the standard test methods: Bomb calorimeter was used to determine HHV in KJ/g, ASTM D613 for CN and ASTM D5453 for sulphur content, while AOCS (1978) and Cordex Alimentarious (CAC/RM 9/14-1969) was used for IV, saponification value (SV), acid value and free fatty acid. Instrumental analyses of the biodiesel fuel were carried out by Nigeria liquefied Natural Gas company (NLNG), Bonny Island at International Energy Services Limited. Port Harcourt, in Nigeria.

Total glycerol content Gs (wt% on mass of biodiesel fuel) was determined using the formula:

\[ G_s = 0.1044W_{TG} + 0.1488W_{DG} + 0.2591W_{MG} + W_G \]

where WTG, WDG, WMG and W_G are amounts of triglycerides, diglycerides, monoglycerides and free glycerol respectively.

3 RESULTS AND DISCUSSION

Biodiesel has become more attractive recently because of its environmental benefits and the fact that it is made from renewable resources [1].

In this study, potential of locally sourced seed oils and waste/used cooking oils were established for the development of biodiesel using alkali-catalysed transesterification. The transesterification experiments using methanol, ethanol and propanol (solvents) were carried out on oils from; Jatropha curcas (Botuje), Pentaclethra macrophylla (Apara) and soybean. Refined palm kernel oil and used palm kernel oil were used as well. Sodium hydroxide (NaOH) was used as catalyst in all the oils for transesterification processes with the exception Jatropha oil where potassium hydroxide (KOH) was used instead. The two catalysts were used effectively with the hope to optimizing biodiesel conversion condition. The catalysts exhibited a pronounced effect on methyl ester, ethyl ester and propyl ester formation with evidence of good conversion. However, in the transesterification process, addition of excess amount of catalyst gave rise to the formation of emulsion, which increased the flow rate and led to the formation of gels. Ramadhas, et al., reported [5] failure in transesterification process and the phenomenon was attributed to insufficient amount of catalyst added.

Alkali-catalysed transesterification of soybean oil was studied. Successful transesterification reaction produced two liquid phases: ester and glycerine. Phase separation was observed within 5 minutes. Complete separation took about 20 hours as expected in the alkali-catalyzed transesterification process.

3.1 Effect of catalyst (NaOH) on Ester Formation Using soybean oil

The transesterification of soybean oil with methanol, ethanol and butanol, using 1% concentrated sulfuric acid, was unsatisfactory when the molar ratios were 6:1 and 20:1 [6]. A 30:1 ratio resulted in a high conversion to methyl ester. In this study, alkaline transesterification of soybean oil using NaOH in methanol, ethanol and propanol was considered to produce sodium alkoxide (Na+CH3O-).
Fig. 1: Effect of NaOH (catalyst) on biodiesel conversion from soybean oil in different solvent media.

Result in figure 1 indicates highest conversion (96%) in the case of methyl ester derivative of the oil at catalyst concentration of 6.25 x 10⁻¹M. Lower conversions were also obtained at catalyst concentrations of 4.38 x 10⁻¹M and 0.25 x 10⁻¹M giving 72% and 84% for the seed shells were cracked to remove the seeds, sun dried and later oven dried to constant weight. Oil from the seeds was obtained by the method of soxhlet extraction using petroleum ether (40-60°C).

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**4.2 Effect of catalyst (NaOH) on transesterification of used/waste palm kernel oil (PKO)**

Figure 2 reveals the significant effect of catalyst on biodiesel formation from used or waste PKO. The alcoholysis of used/waste cooking oil was successful in methyl ester and ethyl ester formation but failed in propanol as solvent. At NaOH concentration of 0.25 x 10\(^1\)M, methyl ester produced was insignificant, and this shows that the catalyst concentration was not enough to break the fatty acid in the triglyceride of waste oil [5].

However, at increased concentrations of 4.38 x 10\(^{-1}\)M, 6.25 x 10\(^{-1}\)M, 9.38 x 10\(^{-1}\)M and 12.5 x 10\(^{-1}\)M, conversions of 72.92%, 60.40%, 59.25% and 41.67% respectively were obtained. Optimal condition for methyl ester production in waste oil was evident at 4.38 x 10\(^{-1}\)M NaOH (catalyst) concentration, with 72.92% conversion. Ethyl ester formation in waste oil was highest at a very low catalyst concentration of 0.25 x 10\(^{-1}\)M with 46.25% yield. However, propyl ester formation was not successful. Thus, only methyl ester and ethyl esters were obtained from used cooking oil using alkali-catalyzed transesterification method.

**4.3 Effect of catalyst on biodiesel formation in refined palm kernel oil using NaOH (catalyst) in alcohol**

Figure 3 is the graph showing optimal condition for methyl ester, ethyl ester and propyl ester conversion as a function of catalyst in refined palm kernel oil. The amount of catalyst used in transesterification process affects the efficiency of the process as reported by Ramadhas, et. al., [5].
Fig. 3: Effect of NaOH (catalyst) on biodiesel conversion from refined palm kernel oil in different solvent media.

Methyl ester was produced at NaOH concentrations of 0.25 x 10^{-1}M, 4.38 x 10^{-1}M, 6.25 x 10^{-1}M, 9.38 x 10^{-1}M and 12.5 x 10^{-1}M, with biodiesel conversions of 25%, 41.67%, 70.83%, 64% and 60.42% respectively.

Moreover, ethyl esters were obtained at two NaOH (catalyst) concentrations; 4.38 x 10^{-1}M and 6.25 x 10^{-1}M, with conversions of 66.67% and 40% respectively.

Propyl ester was obtained at 0.25 x 10^{-1}M and 4.38 x 10^{-1}M catalyst concentrations. The percentage conversions at these concentrations were 10% and 14.17% respectively. However, these conversions were very low relatively.

Thus, optimal biodiesel conversion was evident at NaOH concentration of 6.25 x 10^{-1}M (70.83%) in CH₃OH, 4.38 x 10^{-1}M (66.67%) in C₂H₅OH and 4.38 x 10^{-1}M (14.17%) in C₃H₇OH.

4.4 Effect of catalyst on biodiesel formation in Pentaclethra macrophylla (Apara)

Pentaclethra macrophylla (Apara); locally sourced seed oil was investigated as an alternative feedstock for fatty acid alkyl ester production. The oil content of 45% proves the oil to be promising as one of the feedstock considered for biofuel. This is because seeds with high oil content are considered for biodiesel as reported by Karaosmanoglu [7].

Biodiesel production using Pentaclethra macrophylla was not satisfactory. Only methyl ester conversion was possible at 0.25 x 10^{-1}M NaOH concentration with 20.83% conversion. At other catalyst concentrations, in different solvent media; ethanol and propanol, there was no evident of biodiesel conversion.

4.5 Biodiesel fuel properties

Table 1: Characteristics of biodiesel fuel from differently sourced feedstock.

<table>
<thead>
<tr>
<th>Test Method</th>
<th>Specification</th>
<th>PKO biodiesel</th>
<th>PKO oil biodiesel</th>
</tr>
</thead>
<tbody>
<tr>
<td>ASTM D6751 – 07B</td>
<td>Sulphur</td>
<td>0.05 max</td>
<td>0.01</td>
</tr>
<tr>
<td>ASTM 613</td>
<td>Cetane number</td>
<td>47</td>
<td>46</td>
</tr>
<tr>
<td>ASTM</td>
<td>Combustion energy</td>
<td>Bomb calorimeter</td>
<td>39</td>
</tr>
</tbody>
</table>

ND: Not determined

The results of the analyses shown in table 1 reveals sulphur content of 0.01 for all the biodiesel emanated from soybean oil, Pentaclethra oil, Jatropha oil, used palm kernel oil and refined palm kernel oil. The maximum sulphur content according to USA ASTM D-6751 is 0.05. Judging from this view, the fuels are satisfactory due to low sulphur in them. This means that they are not prone to knocking in combustion ignition engine [8].

Cetane number is a measure of the ignition performance of a diesel fuel obtained by comparing it to reference fuels in standardized engine test. The higher the cetane number, the better the ignition ability of the fuel. Cetane number scale of diesel fuel covers the range from 0-100. However, typical testing is in the range of 30-65 cetane number. (Destination: D 613-05). The cetane number of biodiesel varies, usually in the range of 48-67 depending on the feedstock [9].

The cetane number of biodiesel fuel from soybean oil, waste/used cooking oil and palm kernel oil were found to be 45.5, 44.6 and 46 respectively. Therefore, the cetane value of soybean oil and that of palm kernel oil are quite reasonable compared with the special standard (47). Niehaus et. al. [10] and Schwab et. al., [11] reported the cetane number of biodiesel from soybean oil that was thermally decomposed and distilled in air and nitrogen sparged with a standard ASTM distillation apparatus to be 43.3. Fangrui et. al. reported [12] that the cetane number of transesterification reaction is still better and higher than those of thermally cracked oil. This...
is demonstrated in this study where the value of cetane number of soybean oil is 45.5, higher than biodiesel obtained by thermal decomposition.

However, from table 1, the combustion energy (high heating energy) of the fuels from refined palm kernel oil, waste palm kernel oil and soybean are; 39, 36 and 45.5 respectively. Biodiesel obtained from soybean oil has high combustion power of 45.5.

4.6 Biodiesel flow rates

The essence of transesterification process is to lower the viscosity of oil. Table 2 shows the flow rates of feedstock with their corresponding biodiesel at their optimal conditions. Flow rate is dependent on viscosity. It is evident that there is reduction in the viscosity of biodiesel compared with their corresponding feedstock, due to the increase in the flow rate of biodiesel compared with their corresponding feedstock. These results further indicate a complete transesterification and derivatization.

<table>
<thead>
<tr>
<th>Feedstock</th>
<th>Flow rate (cm³/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Jatropha curcas</td>
<td>2.00 3.67 - -</td>
</tr>
<tr>
<td>Pentaclethra macrophylla</td>
<td>1.60 2.50 - -</td>
</tr>
<tr>
<td>Waste palm kernel oil</td>
<td>2.40 4.00 2.00 1.00</td>
</tr>
<tr>
<td>palm kernel oil</td>
<td>2.33 2.33 2.00 1.00</td>
</tr>
<tr>
<td>Soybean oil</td>
<td>2.30 3.63 2.50 0.50</td>
</tr>
</tbody>
</table>

Result obtained (table 2), to a large extent shows significant increase in the flow rate of the biodiesel as the oil was transformed. The result in the case of methyl ester from Jatropha (3.67), methyl ester from used oil (4.00), ester from refined palm kernel oil (3.33), ester from soybean oil (3.63) and ester from Pentaclethra oil (2.50), clearly indicates transesterified oil in its various derivatives. In all cases, FAME exhibited a general increase in flow rate over other derivatives (FAEE, FAPE) and this phenomenon accounts for reduction in oil viscosity. The increase in the flow of ester compared with their corresponding feedstock is encouraging and may not constitute blockage in diesel engine.

4.7 Total Glycerol content (Gc) of soybean biodiesel

Among the specification standards of biodiesel fuel, total glycerol content(Gc) is one of the most important characters, since glycerides significantly affect other fuel properties such as viscosity, pour point, amount of carbon residue etc. causing problems on filterability and deposition on the injection and combustion chamber.

4 CONCLUSIONS

Of the several methods available for producing biodiesel, transesterification of natural oils and fats is currently the method of choice. The purpose of the process is to lower the viscosity of the oil or fat. Although blending of oils and other solvents lowers the viscosity, engine performance problems, such as carbon deposit and lubricating oil contamination, still exist. In this present study, a high efficient transesterification has been described; optimal condition for alkyl conversion in each sample oil has been determined. Therefore, catalysts concentration significantly affects overall conversion of biodiesel. It has been evaluated in this work also the influence of various fatty acid derivatives (methyl-, ethyl- and propyl esters) on biodiesel flow rate. Methyl esters of most of the oils increases oil flow rates significantly when compared to other. The results on the total glycerin content of the biodiesel emanated from soybean are quite impressive and conform favourably to standard. This phenomenon hopefully is another factor that would justify preclusion of unwanted combustion chamber deposition and filterability problems.

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