Biodiesel Quality and Characteristics of Transesterified *Mangifera indica* Kernel Oil

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Abstract: **The oil of common mango kernel preset with 1% w/v sodium hydroxide was used in an H_2SO_4 catalyzed reaction with methanol to produce *Mangifera indica* biodiesel having specific gravity, pour point, cloud point, flash point, calorific value and biodegradability of 0.86, 9 ^{o}C, 12 ^{o}C, 149 ^{o}C, 32.4 MJ/mol and 82.8%. The results were compared with fuel properties of the control, diesel D_2. Infrared spectral data confirmed the presence of diesel fuel functional $C=O_{stretch}$ (1734 cm^{-1}) and $C–H_{stretch}$ (2928 cm^{-1}) for esters while gas chromatographic (GC) and Mass spectral (MS) data identified ethyl stearate and ethyl (E)-9-octadecenoate as the closely most abundant esters in the biodiesel. Based on the yields and fuel properties, *Mangifera indica* biodiesel is a readily biodegradable fuel and can adequately support petro-diesel blending applications.**

Key words: Mangifera indica, **biodiesel, fuel quality, biodegradability, GC-MS**

I. INTRODUCTION

The pathway to a sustainable energy future is through the continuous development of alternative materials from available resources and biomass to add to the current stock. An important consideration is on cleaner burning fuels which are better for optimum engine performance, greater lubrication and that leave fewer particulate deposits behind, reducing emissions associated with the life cycle of combustion fuels, environmental pollution and the greenhouse gas, CO_2, responsible for global warming. Countries that have to import oil and other petroleum products and are heavily dependent on other nations for their energy needs can become self dependent through domestic production of clean fuels, such as biodiesel, bioethanol and biogas from waste agricultural products [1].

Biodiesel is a renewable and volatile fuel made up of mono-alkyl esters of fatty acids with long chain lengths derived from vegetable oils (or animal fats) and show similar physicochemical properties as petroleum-based diesel [2]. The vegetable oils are trans-esterified with lower molecular weight alcohols, for example, methyl, ethyl, propyl or butyl alcohol, in the presence of a catalyst, to generate linear esters and the byproduct glycerol. The reaction is reportedly affected by the type of feedstock, alcohol, molar ratio of triglycerides to alcohol, type and amount of catalyst, reaction temperature, reaction time and free fatty acid and water content of the vegetable or animal feedsock [3]. Feedstocks with high free fatty acid content (>2%) such as those previously reported for *Mangifera indica* species require a combined two-stage process – pretreatment by a base (e.g. NaOH) and transesterification (by either a strong acid, base or solid nano-materials) – to minimize soap production and maximize the amount of biodiesel produced as well as to eliminate engine corrosion problems [4, 5]. Several methods for carrying out transesterification reactions for biodiesel production have been reported including the common batch process, supercritical processes, ultrasonic and even microwave methods [6, 7].

$$Oil + alcohol \xrightarrow{catalyst} Biodiesel + glycerin$$
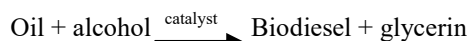
As is the case with petroleum fuels, commercial-grade biofuels are required to also conform to international standards such as American Society of Testing Materials (ASTM D6751), European Number (EN 14125) etc, to be suitable for use in diesel engines. A good biodiesel is also expected to be readily biodegradable in case of spillage. Currently, much stricter definitions in the form of quality standards have been established to gain wider acceptance from engine manufacturers, distributors, retailers and end users, in order to ensure trouble free operation in diesel engines. Achieving this requires the most important aspects of biodiesel production to be taken care of: complete reaction, absence of free fatty acids and removal of glycerin, catalyst, alcohol and odours [8, 9].

Mangifera indica (Common mango) plant is found as a large evergreen tree with dense foliage and drought tolerant, being able to withstand seasonal dry periods for up to 8 months. There is an abundant supply of mango seeds in Nigeria especially from fruit processing industries and the seeds are generally cheaper since they are considered product waste. The seed kernel is solitary, oblong, encased in a hard, compressed fibrous endocarp and the oil is solid at room temperature. The usefulness of the whole mango kernel, the defatted kernel flour and the oil is yet to gain industrial attraction in African countries [10]. In this work, the quality and composition of Mango kernel biodiesel was evaluated and compared with conventional diesel fuel.

II. MATERIALS AND METHOD

Sample Preparation

Mangifera indica (common mango) were collected from peeled industrial waste fruits, dried for 3 weeks and decorticated with the aid of a knife to obtain the seed kernel.

The kernels were crushed and sieved to obtain fine powder and the moisture content was determined after oven-drying 3 g of the powder to constant weight. 300 g of the sample was soxhlet extracted with petroleum ether at 60 ^oC to obtain *Mangifera indica* kernel oil (MIKO). All reagents used for the experiments were analytical grade quality. The oil was recovered by evaporating off the solvent using a rotary evaporator and then drying in an oven at 105 ^oC at 1 hour intervals until all traces of solvent still present had gone off. Oil quality parameters of the extract such as Iodine value, Peroxide value, Saponification value, and Acid value were determined based on the AOAC methods for food analysis adopted by Oshieke and Jauro, 2012 [11].

Biodiesel Production

The oil of *Mangifera indica* kernel was mixed with 1 mL 1% NaOH with stirring for 15 minutes at 45 ^oC. The slightly soapy mixture was washed with water and oven dried at 100 ^oC overnight. Methanol (10 mL) was added to 1 mL dry sulphuric acid in a 250 ml conical flask and stirred for 15 minutes. The mixture was transferred to 45 ml of the pretreated *Mangifera indica* kernel oil (at 60 ^oC) in another flask with continuous stirring for 3 hours. The resulting mixture was poured into a separating funnel and left overnight. The lower layer was drained off leaving the upper layer (biodiesel). The biodiesel was washed with water several times until a clear product was obtained. The clear biodiesel was then filtered through a cotton wool sprayed with anhydrous Magnesium sulphate in order to absorb any trace of water present. The biodiesel yield was calculated as the percentage of the volume ratio of biodiesel produced to oil used.

Biodiesel yield = $\frac{\text{Volume of biodiesel collected}}{\text{Volume of sample oil used}}$ x 100

Fuel Properties

A Density bottle was used to determine the specific gravity and the kinematic viscosity was determined using a viscometer.

Flash Point, Pour Point and Cloud Point

The flash point, cloud, pour point, calorific value were determined and compared with petro-diesel D_2 according to the method described by Jauro and Adams (2011) [12]. 10 mL of the biodiesel was slowly heated at constant rate and the temperature at which a test flame caused the vapour above test flask to make a pop sound as if to ignite was recorded as the flash point. The Cloud Point was noted as the temperature at which a distant cloudiness appeared in the fuel (10 mL) placed in an ice bath, and the Pour Point was recorded at the temperature which the freezed fuel started to flow. The same procedures were repeated using the D_2 diesel.

Flames Test and Calorific Value

A wick was dipped into the test tube containing a small quantity of biodiesel and placed on a watch glass. The wick was then lit and allowed to burn. The rate of burning, the colour of the flame and the amount of smoke given out were observed. The same procedure was repeated using diesel D_2. Thereafter, 100g of the water was put into a copper vessel and heated for 10 minutes, with the biodiesel as the burning fuel. The temperature of the water before and after heating for 10 minutes was recorded. The procedure was repeated with the same amount of diesel D_2 using different wicks of the same height as the one for biodiesel. The calorific value was then calculated as follows:

$$\text{Calorific value} = mc\Delta\Theta$$

Where; *m* = *mass of water*

c = *specific heat capacity of copper*

$\Delta\Theta$ = *temperature rise of water after 10 minutes*

Biodegradability test

The CO_2 evolution method for determining biodegradability of chemical substances was employed (EPA, 560/6-82-003) [12]. A 500ml Erlenmeyer flask containing 100ml of inoculums (prepared from contaminated soil and raw domestic sewage water 14 days before the experiment), 150ml of deionized water, about 5ml of the biodiesel, and reservoir holding 10ml of Calcium hydroxide, $Ca(OH)_2$, solution suspended in the flask to trap CO_2 that evolved from the media. The test flasks were sealed and kept in a dark cupboard for 28 days. The 10ml of $Ca(OH)_2$ was removed after 7 days, 10 ml of distilled water was added and titrated with 0.1N HCl to the phenolphthalein endpoint to determine the CO_2 evolved. Each time, the reservoir was refilled with fresh 10ml $Ca(OH)_2$. The sample was analyzed at time zero and weekly during the 28-day period. The same procedure was carried out for the diesel D_2 and for the control. The percentage CO_2 evolution was calculated as follows:

% CO_2 evolution = $\frac{TF - CF}{C}$ x 100

Where,

TF = ml of 0.1 N HCl required to titrate $Ca(OH)_2$ samples from the test flask;

CF = ml of 0.1 N HCl required to titrate $Ca(OH)_2$ samples from the control flask;

C = A constant (equal to 16.67 ml of carbon substance)

Infrared Analysis

The infrared information for analysis of bond types and possible functional groups present in the biodiesel was obtained using the Shimadzu FITR-8400S Fourier Transform Infrared (FTIR) Spectrophotometer.

Gas Chromatographic/Mass Spectrometry (GC/MS)

By combining the above two techniques-qualitative and quantitative, the number of chemicals present in the biodiesel

was determined. This analysis was done on the SHIMADZU GCMS-QP2010 Spectrophotometer. The temperature programme used was 70 ^{o}C for 5 minutes then ramped up at 5 ^{o}C/minute up to 250 ^{o}C and then rose to 300 ^{o}C at 20 ^{o}C/minute. The injection port was held at 280 ^{o}C and 1 ml of the sample was injected.

III. RESULTS AND DISCUSSION

Yields

The physical and chemical properties of *Mangifera indica* Kernel oil used to produce *Mangifera indica* methyl esters are presented in Table 1. The oil yield was 12% at sample moisture content of 4.33%. This is lower than the 30% benchmark rating for fuel based oil seeds. However, on the sustainability front, material, energy and environment rule (MEE 1% rule), the 12% oil yield is suitable enough to be included in a unit industrial process and the oil can better serve as a substitute for commercial biodiesel production that uses mechanical pressing method for the oil extraction.

Table 1 Properties of *Mangifera indica* kernel oil (MIKO)

Parameters	MIKO
Moisture content (%)	4.33
Oil yield (%)	12
Specific gravity	0.8608
Colour	Pale yellow
Smell	Pleasant
Free fatty acid value (%)	3.43
Acid value (%)	6.83
Saponification value (meq/kg)	204.8
Peroxide value (meq/kg)	8.4
Iodine value (g/100g)	17.8

Biodiesel Yield

The fuel yield relative to the initial amount of *Mangifera indica* kernel oil utilized for the process was 66.7 %. By calculation, 1 ton of waste mango seeds would be expected to generate 80 litres of MIKO biodiesel from 120 litres of the extracted oil using solvent extraction method. This figure is good but higher yields of 90 – 100 % are more economically acceptable. One case for accepting the biodiesel yield is that by neutralizing free fatty acids in the oil sample with NaOH, the fuel quality of the biodiesel has been greatly improved. 25.5ml of glycerol was also obtained from an initial oil stock (of 45ml) used for biodiesel production. The amount is quite high since the amounts of by-products for any chemical reaction should be significantly lower than that the required product (30ml).

Fuel Quality

The biodiesel burns slowly with a smoky flame while diesel, D_2 burns more vigorously with thick sooty flame. The energy available from the fuel (32.4 MJ/mol) is lower than that of

Diesel D_2 (43.4 MJ/mol). This can be interpreted as the fact that diesel D_2 is more volatile than *Mangifera indica* methyl esters leading to higher heating value.

The flash point for the biodiesel is 149 ^{o}C and diesel D_2 is 80 ^{o}C. The higher flash point of the biodiesel translates to level of safety in combustible transport and storage. Increasing the proportion of biodiesel in blending cases with diesel D_2, elevates the flash and ignition temperatures making the blended fuel safer for use. The lowest temperature for the oil flow, the pour point, 9 ^{o}C was much higher than for diesel D_2 (–10 ^{o}C). The fuel will be most useful in tropical regions, in colder regions of the world; heating mechanisms will be needed to keep the fuel warm and flowing during use or at rest. A better performance in temperate countries can be expected from the fuel when blended with diesel D_2. The minimum temperature at which wax-like crystals appeared in the fuel, cloud point, when cooled (12 ^{o}C) is very high compared to –5 ^{o}C for diesel D_2. The crystallike-like materials may not cause lubrication problems, but the remaining unwax-like areas of the liquid fuel may have lower properties relative to the fully mixed fuel. Flow-improvement additives can modify these values and create an optimum fuel for diesel engines [13].

The kinematic viscosity of the *Mangifera indica* biodiesel, 3.94 mm^2/s at 60 ^{o}C is slightly higher than diesel, D_2 (3 mm^2/s). This difference is needed to improve the properties of the fuel when blending with diesel D_2.

Table 2 Comparison of fuel properties of MIKO, MIME and Diesel D_2

| Property	MIKO Biodiesel	Diesel D_2	ASTM standard
Specific gravity	0.86	0.87	0.82 *min.*
Pour point (^{o}C)	9	-10	*NA*
Cloud point (^{o}C)	12	-5	*NA*
Flash point(^{o}C)	149	80	100 *min.*
Kin. viscosity (mm^2/s at 60°C)	3.94	3.0	1.9-6.0
Calorific value (MJ/mol)	32.4	43.4	*NA*

NA – not available, min. – minimum

Biodegradability

The percentage consumption rate of the biodiesel is shown in Table 3. By employing the biodegradative potentials of organisms in a relatively simple setup, the extent of detoxification and volume reduction of the biofuel in oil spill situations was evaluated. The synthesized biodiesel was 54% biodegraded on the seventh day compared to 13.8% for diesel D_2. After 28 days, MIKO biodiesel was 82.78% mineralized while only 28.19% of diesel D_2 was consumed. Microbial consumption >80% in 28 days shows that the biodiesel is readily biodegradable and not persistent in the environment in case of clean up after spillage.

Table 1 Carbon dioxide (CO_2) evolution from biodiesel and diesel D_2 from inoculum

Day	Inoculums	
	Mangifera indica Biodiesel (%)	Diesel D_2 (%)
0	0.00	0.00
7	53.99	13.80
14	62.99	19.80
21	76.19	24.60
28	82.78	28.19

The microbial consumption trajectory for the both diesel D_2 and MIKO biodiesel in Figure 1 is almost similar for the duration of the biodegradation test, with regression values of 0.9875 and 0.9855, respectively. The microbes degraded the test samples at relatively the same linear progression on the area of contact available for consumption with the biodiesel providing more surface area at 9.957 compared to 4.797 for diesel D_2.
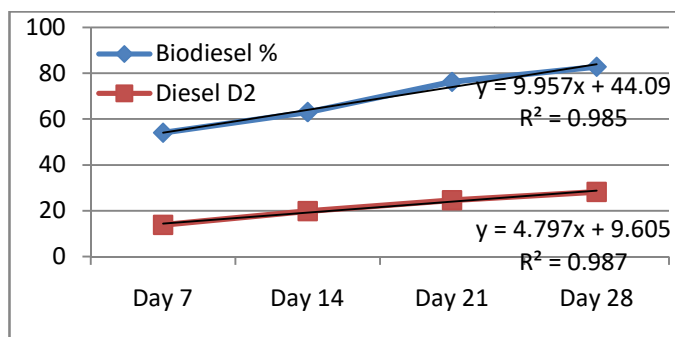

Figure 1 Enzyme activity for CO_2 evolution

Functional Groups

Infrared spectra (figure 2) show 10 peaks with five of them above the fingerprint region. There is the carbonyl $C=O_{stretch}$ (1734 cm^{-1}), strong acyl $C–O_{stretch}$ at 1177 cm^{-1} and $C–H_{stretch}$ sp^3 at 2928 cm^{-1} and $C–H_{bend}$ sp^3 at 1356 cm^{-1} for saturated esters. Also, a weak absorption band at 3471 cm^{-1} represents $N–H_{stretch}$ (for amines) and another weak $C–H_{bend}$ sp^2 at 720 cm^{-1} (for cis-disubstuted alkenes) showed that the biodiesel contains some amounts of nitrogen and unsaturated alkenes.
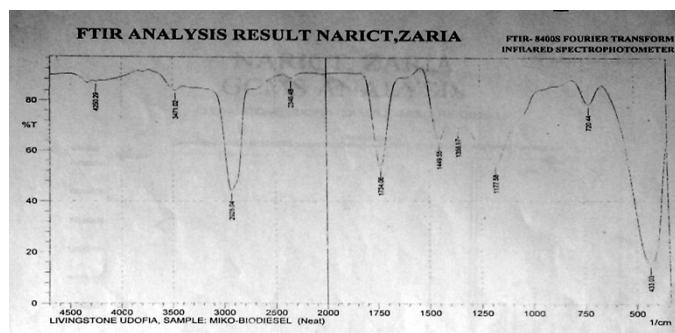
Figure 2 Infrared spectrum of *Mangifera indica* biodiesel

GC-MS analysis of Mangifera indica Biodiesel

Gas chromatography (GC) separates the components of a mixture and mass spectroscopy (MS) characterizes each of the components individually. The Gas chromatogram (Figure 3) of the biodiesel showed 18 peaks of which 8 are prominent. The MS fragmentation pattern is consistent with 10 of the identified components including ethyl laurate (C12:0), ethyl myristate (C14:0), ethyl palmitate (C16:0), ethyl oleate (ethyl (E)-9-octadecenoate C18:1), ethyl stearate (C18:0), propyl stearate (C18:0), isobutyl stearate (C18:0), ethyl nonadecanoate (C20:0, arachidic acid ethyl ester), glyceryl-1,3-distearate and 2-hydroxy-2-methyl hexanone. The remaining eight peaks alternate between C16 and C24 saturated and unsaturated esters. The fifth peak identified as ethyl palmitate, the ethyl oleate (peak 6) and the ethyl stearate (peak 7) collectively make up 76.51% and 68.15% of the peak areas and heights, respectively. From the data, the biodiesel contains approximately 52% saturated entities and 48% unsaturated esters. Ethyl oleate is the most abundant ester, 34.48%, while ethyl stearate and ethyl palmitate follow closely with 31.26% and 10.77% contents. The results show that the fatty acid profile is reduced for the biodiesel compared to those reported for *Mangifera indica* oil but with a lofty ester saturation level that slightly affects its cold flow properties [14].
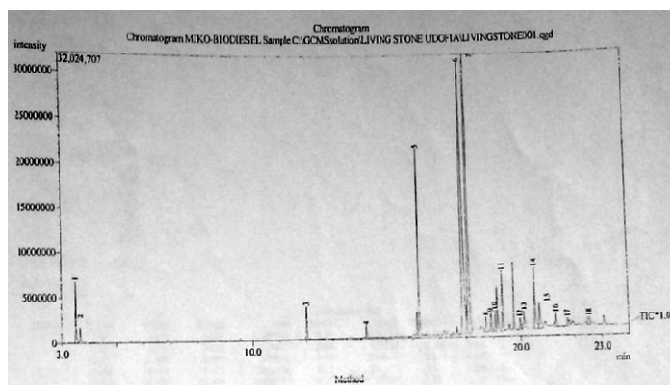
Figure 3 Gas chromatogram of *Mangifera indica* biodiesel

IV. CONCLUSIONS

Biodiesel is a clean, non-toxic, biodegradable, efficient and sustainable energy alternative to the non-renewable petroleum-based fuels. *Mangifera indica* biodiesel has a promising potential to contribute its 12% oil content to the global biofuel market. Increasing the quantity of NaOH used to catapult the process is not cost effective but can effectively reduce the saturation level of the fuel for temperate applications. The consumption of the biodiesel shows a readily biodegradable fuel, one less environmental concern as it relates to effects of industrial activities. The by-product glycerin has varied applications, water and alcohol can be removed to produce 80-88% pure glycerin. Currently, glycerin has been used in the production of lactic acid which if used or sold, in combination with other products can also affect the final cost per liter of the resulting biodiesel.

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