Characterization of *Terminalia Catappa Linn* Oil, *Linn* Oil-based Methyl Ester and its Blends

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Abstract

Compression ignition (C.I.) engine related problems are often caused by non-compatibilities in terms of physico-chemical properties of the fuels used. Hence the importance of using fuels with appropriate physico-chemical properties in C.I. engines. This need for using fuels with appropriate physico-chemical properties, the reason for other researchers to effectively tap in to potential use of Terminalia Catappa Linn oil and the great awareness worldwide to the need to replace fossil fuels with renewable fuels calls for investigation of local sources of such renewable fuels. To this end, this work is on renewable fuel oil extracted from the seed of *Terminalia Catappa Linn* (TCL), a very common plant found in most tropical southern Nigeria. After extracting the seed oil of TC, it was trans-esterified and the methyl ester produced was blended with fossil diesel and characterized to determine their suitability for use as a diesel or C.I. engine fuel. Potassium hydroxide was used to reduce the activation energy for quick production of oil methyl esters (major product) and glycerol (by-product) after which some important physico-chemical properties of the T.C.L oil, methyl ester fuel and their blends were examined. For the 100% methyl ester composition, the Kinematic viscosity showed a remarkable reduction of about 71.5% from untrans-esterified oil to trans-esterified fuel. Specific gravity also showed a significant reduction from 0.926 to 0.888 which is very close to that of automotive gas oil (AGO, 0.83). The flash point (145.3 ^{O} C) and the pour point (-2.7 ^{O} C) are very good results for storage logistics and cold starting of the compression ignition (CI) engine respectively. Although the acid value of TC methyl ester of 2.36

(mg KOH/g) as against 0.06 (mg KOH/g) for diesel fossil fuel oil signifies low quality of TC methyl ester as compared to diesel fuel, yet its iodine value of 83.2 as against 11 for diesel fossil fuel denotes that the T.C. methyl ester has potential for a high degree of stability against oxidation. Thus, with reference to ASTM standards, this study concludes that the physico-chemical properties of the methyl ester of *Terminalia Catappa Linn* (TCL) and its blends are within the acceptable range for use in C.I. engines.

Keywords: Characterization, *Terminalia Catappa Linn* (TCL), Trans-esterification, diesel fuel, AGO, methyl ester, physico-chemical properties

Introduction

Perhaps the most crucial issue facing human civilization today is its over dependency on the energy stored within the carbon-carbon bonds of the fossil fuels such as coal, crude oil and natural gas (Samukawa, 2000). Fossil fuels require long formation times in the earth's crust (up to millennia in some cases) while their current rate of utilization in the world is much faster than their formation rate. This disequilibrium of current use rate and formation rate in the earth's crust had led to limited reserve of fossil fuel. In view of this problem of limited reserve, and associated problems of rapidly increasing prices of petroleum products, the depleting nature, the environmental issue and the greenhouse gases effect (GHGs), have stimulated more and more interest in the investigation of vegetable oils as substitutes to fossil fuel (Dmytryshyn, 2004, Wang et al., 2006, Nanthagopal, 2012; Shahabuddin et al., 2013 and Özener et al., 2014). Batidzirai et al., 2006 corroborated by Gupta et al., 2007; Alamu et al., 2007b; Alamu et al., 2008; Wang et al., 2013; Kumar et al., 2013; Ramjee et al., 2013 and Özener et al., 2014 reported that modern biofuels have a promising long term renewable energy source. The authors also agree that the biofuels had potential to address both environmental impacts and security concerns posed by current dependence on fossil fuels. *Terminalia Catappa Linn* is a large, spreading tree now distributed throughout the tropics in coastal environments. The tree is tolerant of strong winds, salt spray, and moderately high salinity in the root zone. It grows principally in freely drained, well aerated, sandy soils. The species has traditionally been very important for coastal communities, providing a wide range of non-wood products and services. It has a spreading, fibrous root system and plays a vital role in coastline stabilization. It is widely planted throughout the tropics, especially along sandy seashores, for shade, ornamental purposes, and edible nuts. Information abounds on the extraction, trans-esterification and characterization of the methyl ester produced from the seed of groundnut, cashew nut and walnut. However, there is limited information on the extraction, trans-esterification and characterization of the methyl ester produced from the nut/seed of *Terminalia Catappa Linn*. In order to gain a better understanding in to the suitability of *Terminalia Catappa Linn* based-methyl ester in internal combustion engines and to overcome dearth of information on the extraction, trans-esterification and characterization of the oil *Terminalia Catappa Linn* seed and methyl ester produced from the oil of the nut/seed, this work extracted, trans-esterified and characterized in particular the oil and methyl ester produced from the oil of the seed.

Methodology

Materials preparation

Some seeds of *Terminalia Catappa* Linn were collected under the trees of *Terminalia Catappa Linn* at Jaja Clinic at the University of Ibadan. Foreign materials and dirt which were found in the seed were separated from the oilseeds by winnowing. The cleaned oilseeds were then broken up using the traditional method of stone cracking from which 210 grams of nuts were obtained from the seeds. The nuts obtained were dried at 105 ^{O}C for 24 hours and subsequently ground in a mill at the Department of Food Technology of the Faculty of Technology of the University. The grounded/powdered sample was stored in a polythene bag and kept in a refrigerator at 4 ^{O}C until when needed for further processing

Oil extraction and biodiesel synthesis

Oil extraction process

Oil was extracted in five-successions from 200 g of the milled sample using 500 ml-Soxhlet-apparatus and n-hexane as solvent. The Soxhlets apparatus was charged with 40 g of the milled/powdered sample of *Terminalia Catappa* Linn through muslin cloth placed in a thimble of the apparatus. A round bottomed flask containing 150 ml of n-hexane was fixed to the end of the apparatus and a condenser was tightly fixed at the bottom end of the extractor. The whole set up was heated up in a heating mantle at a temperature of about 70 ^{O}C. The excess solvent in the oil was recycled by heating in a heating mantle at temperature of 70 ^{O}C after the extraction. Quantity of oil extracted was determined gravimetrically. The oil yield was evaluated as the ratio of the weight of the extracted oil to the weight of the *Terminalia Catappa* Linn sample as defined in equation 1

$$Percentage\ oil\ yield = \frac{weight\ in\ grams\ of\ extractedoil}{weight\ in\ grams\ of\ powdered\ sample} x100 \qquad (1)$$

Methyl ester production process

Trans-esterification reactions were performed in a 50 ml-batch reactor. The batch reactor comprises 50 ml capacity Pyrex flask placed on a hot plate with magnetic stirrer. The flask was charged with a known weight of the oil and preheated to 50 ^{O}C. Following preheating; a known weight of potassium hydroxide pellet was dissolved in a known volume of anhydrous methanol and was quickly transferred into the pre heated oil. The reaction mixture containing methanol, TC oil and the catalyst (KOH), with a molar ratio of alcohol (6): oil (1): catalyst (0.2) was further heated on the hot plate under continuous steering. At the boiling temperature of the alcohol (78 ^{O}C), the mixture was allowed to reflux for 1, 2, 3 and 4hrs. Two layers of liquid were noticed. The flask was covered by a stopper to prevent methanol escaping as the reaction proceeded. In order to separate the two layers of liquid, separation by gravity was used. This was achieved by transferring the resulting mixture into a separating funnel and allowing it to settle for 24 hours. Two phases separated out clearly, the glycerol being the heavier fluid was then tapped off the bottom of the separating funnel leaving behind methyl ester in the separating funnel. The methyl ester left in the funnel was then washed with warm distilled water to remove residual catalyst, glycerol, methanol and soap. The washed methyl ester left in the separating funnel was then tapped off into a Pyrex flask where it was further dried over $MgSO_4$. The final product was the methyl ester of *Terminalia Catappa* Linn known as biodiesel and the yield was calculated in terms of % (w/w) as described in Equation 2 below.

$$\%\ experimental\ yield\ of\ methyl\ ester = \frac{weight\ of oil - weight\ of\ glycerol}{weight\ of\ reaction\ mixture} x100 \qquad (2)$$

Determination of the physico-chemical properties of Terminalia Catappa Linn oil and Linn oil based methyl ester

Physico-chemical properties such as kinematic viscosity, specific gravity, flash point, calorific value, pour point, acid value and iodine value were determined for both the biodiesel and diesel-fuels using ASTM standards.

Determination of specific gravity and density

Room temperature was measured and recorded. The dry pycnometer was then weighed when empty, when filled with distilled water and when filled with oil or methyl ester and their respective weights were recorded. From the values, the specific gravity was estimated using equation 3 and density calculated using equation 4.

$$Specificgravity = \frac{mass\ of\ oil/methyl\ ester}{mass\ of\ equal\ volume\ of\ water} \tag{3}$$

$$Density = \frac{mass\ of\ oil/methyl\ ester}{volume\ of\ oil/methyl\ ester} \tag{4}$$

Determination of kinematic viscosity

The viscometer was filled with the oil/methyl ester and placed in the water bath that has been preheated to a steady state temperature of 40 ^{O}C for 30 mins to attain uniform temperature with the water. The sample was sucked up the capillary tube and the time taken (in seconds) for the oil/methyl ester to flow from upper mark of the capillary arm to the lower mark was taken. This time was multiplied with the constant (C = 0.03318) of the viscometer to obtain the viscosity at 40 ^{O}C

Determination of flash point

Pensky Martens closed cup tester was used for the determination of the flash point of the oil and biodiesel. The cup was filled to the mark and then placed inside the apparatus. The apparatus was switched on after which stirring began. When the sample temperature was approximately 30 ^{O}C which was below the anticipated flash point, the test fame was lowered onto the oil/methyl ester with the aid of the lever handle at every 4-5 ^{O}C rise in temperature. The flash point was read at the instant when the oil/methyl ester caught fire and the fire was not sustained.

Measurement of pour point

Oil/Methyl ester sample was heated in a test tube above 100 ^{O}C; the oil/methyl ester was then allowed to cool to room temperature. This sample was thereafter introduced into the pour point cabinet pot. The temperature at which the entire oil/methyl ester in the test tube ceased to flow was read and taken as the pour point.

Determination of net calorific value

An Oxygen Bomb Calorimeter was used to perform this test. A sample of test oil/fuel and pure oxygen was charged in to bomb calorimeter, and the initial weight of the sample and ambient temperature were recorded. The sample was ignited; the final temperature and weight of the sample were recorded again after ignition, and the heat of combustion was calculated (At ambient temperature of 25°C).

Determination of acid value

Acid value is a measure of the free fatty acids in oil. Normally, fatty acids are found in the triglyceride form, however, during processing the fatty acids may get hydrolyzed into free fatty acid. The higher the acid value found, the higher the level of free fatty acids which implies decreased oil/fuel quality. Acceptable levels for all oil/fuel samples should be below 0.6 mg KOH/g (measured in potassium hydroxide per gram) (AOCS Official Method Cd 8-53, 2003). Each oil/fuel sample (1.0 g) was weighed and dissolved with 50 ml of ethanol in a conical flask. Two drops of phenolphthalein indicator were added and titrated to pink end point with 0.1 N potassium hydroxide solutions (KOH). (This persisted for 15 minutes). Acid value was calculated using equation 5 below.

$$\text{Acid value} = \frac{56.1\, V\, C}{m} \tag{5}$$

Where 56.1 is equivalent weight of KOH, V is the volume in ml of standard volumetric KOH solution used, C is the exact concentration in KOH solution used (0.1 N); m is the mass in grams of the test portion (1 g).

Determination of iodine value

0.4 g of the sample was weighed into a conical flask and 20 cm^3 of carbon tetrachloride was added to dissolve the oil/fuel. Thereafter, 25 cm^3 of Dam's reagent was added to the flask using a safety pipette in a fume chamber. A stopper was then inserted and the content of the flask was vigorously swirled. The flask was then placed in the dark for 2 hours 30 minutes. At the end of this period, 20 cm^3 of 10 % aqueous potassium iodide and 125 cm^3 of water were added using a measuring cylinder. The content was titrated with 0.1 M sodium thiosulphate solutions until the yellow colour almost disappeared. Few drops of 1 % starch indicator were added and the titration continued by adding thiosulphate drop-wise until the blue coloration disappeared after vigorous shaking. The same procedure was used for blank test and other samples. The iodine value (I.V) was calculated using equation 6

$$I.V = \frac{12.69\, C\, (V_1 - V_2)}{M} \qquad (6)$$

Results and Discussion

Physico-chemical properties of the oil extracted and methyl ester synthesized

Figure 1 shows plot of specific gravity and kinematic viscosity against percentage biodiesel concentration in the blend of TCL Methyl ester and fossil diesel. It was observed that as the percentage biodiesel concentration increases in the blend, both the specific gravity and kinematic viscosity increase.

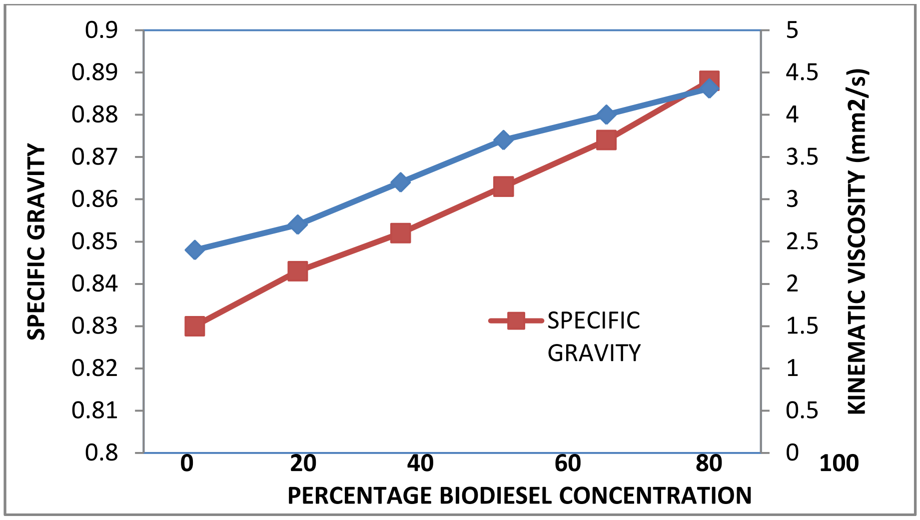

Figure 1: Plot of specific gravity and Kinematic viscosity against percentage biodiesel concentration

This observation is in order, as the specific gravity (0.888) and kinematic viscosity (4.31 mm^2/s) of the TCL oil methyl ester (biodiesel) are higher than that of fossil diesel which are 0.83 and 2.4 mm^2/s respectively as shown in Table 1, thus blending diesel with more TCL biodiesel should actually raise the mixture specific gravity and kinematic viscosity as does. However, as it can be observed in the same Table 1, the kinematic viscosity and the specific gravity of the parent TCL seed oil have been reduced from 15.11 mm^2/s, 0.926 to 4.31 mm^2/s, and 0.888 respectively by trans-esterification. There was a significant reduction of about 71.5 % in the viscosity of the oil after trans-methylation process. Viscosity of TCL oil seed at 15.11 mm^2/s if not significantly reduced, may cause severe problem in the fuel filter and the engine.

Table 1: Properties of various blends of biodiesel and fossil diesel, oil of *Terminalia Catappa Linn* and singular fossil diesel (B0)

Property	Petrol diesel (B0)	B20	B40	B60	B80	B100	Oil of *Terminalia Catappa L.*
Kinematic viscosity @ 40⁰c (mm²/s)	2.4	2.7	3.2	3.7	4.0	4.31	15.11
Specific gravity	0.83	0.843	0.852	0.863	0.874	0.888	0.926
Flash point (⁰C)	49	65	77	89	108	145.3	263.7
Calorific Value (MJ/Kg)	41.86	39.26	38.54	38.12	37.41	36.97	_
Density at 20⁰C (Kg/m³)	820	_	_	_	_	873	910
Pour point (⁰C)	-15	-12.2	-10.3	-7.2	-4.5	-2.7	13.9
Oleic acid (%)	_	_	_	_	_	0.16	0.5
Acid value Mg KOH/g	0.06					2.36	7.59
Iodine value	11	-	-	-	-	83.2	83.92

The plot of calorific value and flash point against percentage biodiesel concentration in the blend of TCL biodiesel and fossil diesel is as shown in figure 2; it was observed that as the percentage biodiesel concentration increases in the blend, the calorific value decreases while the flash point increases. This is in order because, the calorific value and the flash point of the TCL oil methyl ester (biodiesel) are lower and higher than that of fossil diesel respectively as shown in Table 1, thus increasing the TCL biodiesel in the blend should reduce the calorific value and increase the flash point of the mixture. The lower figure of calorific value of TCL oil methyl ester is a testimony to the higher energy content of fossil diesel (41.86 MJ/kg) to methyl ester of TCL oil (36.97 MJ/kg), however, as the difference is not much, this is not a major setback. The higher flash point in the TCL oil methyl ester will be helpful in the handling and storage processes.

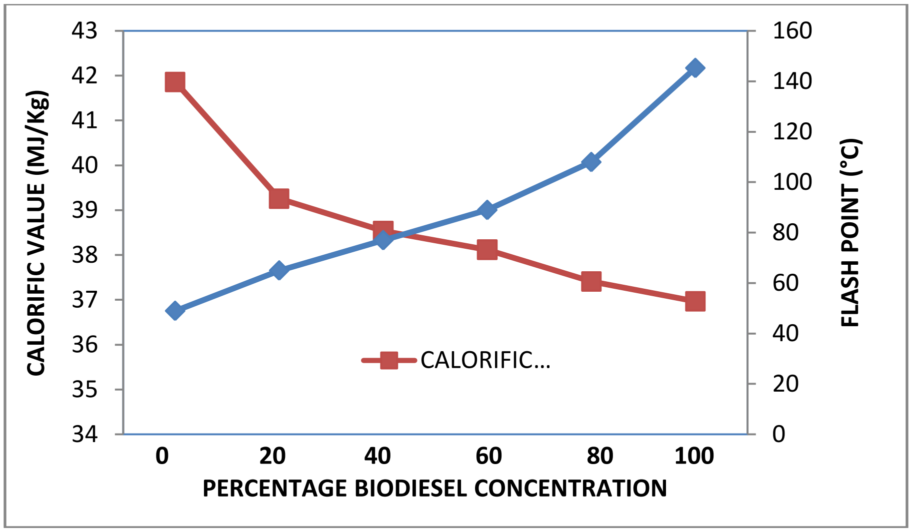

Figure 2: Plot of calorific value and flash point against percentage biodiesel concentration

Figure 3 shows the plot of pour point against percentage centration of biodiesel, as noticed, as percentage biodiesel concentration increases in the blend, the value of pour point increases. The observation is consistent as the pour point (-2.7 ^{O}C) of the TCL oil methyl ester (biodiesel) is higher than that of fossil diesel which is -15 ^{O}C as shown in Table 1, thus blending diesel with more TCL biodiesel should actually raise the mixture pour point as does. This higher pour point noticed for TCL biodiesel is particularly important as problem of cold starting in diesel engine will be easily handled and overcome. Table 1 gives the acid value of TCL biodiesel as 2.36 (mg KOH/g) and that of fossil diesel as 0.06 (mg KOH/g) respectively. Thus TCL biodiesel is inferior to fossil diesel in this respect as the higher the acid value found, the higher the level of free fatty acids which translates into decreased oil quality. Acceptable levels for all oil samples should be below 0.6 mg KOH/g (measured in potassium hydroxide per gram) (AOCS Official Method Cd 8-53, 1998). This high acid value of TCL oil methyl ester however makes the TCL oil a suitable ingredient for soap manufacture. Still in Table 1, the iodine value for TCL biodiesel is 83.2 as against 11 for fossil biodiesel, this high iodine value for TCL biodiesel denotes high degree of unsaturation of the oil caused by the extent of oxidation and degree of heat treatment during oil processing. The implication is that the biodiesel can exist as liquid in room temperature very importantly; the result points out that such a biofuel can present a suitable degree of stability against oxidation. There is no sign of water content in the biodiesel. Therefore, long time storage will be enhanced and hydrolytic degradation will be hampered. Combustion will also take place efficiently. The comparison between the TCL oil based methyl ester and fossil diesel (AGO) as shown in Table 2 were close most especially in the area of specific gravity and that of the kinematic viscosity and met acceptable ranges, according to EN 14214 and ASTM D6751 specifications. This will particularly afford blending the biodiesel with AGO in any ratio.

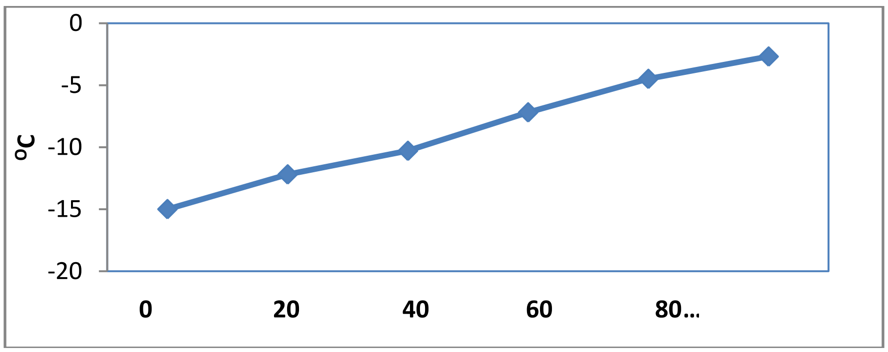

Figure 3: Plot of pour point against percentage centration of biodiesel

Besides, the properties of *Terminalia Catappa Linn* oil based methyl ester and that of the methyl ester from other oil sources as shown in table 2 gave good agreement.

Table 2: Some fuel properties of methyl ester from *Terminalia Catappa* Linn oil and specifications from ASTM D 6751 and EN 14214

Property biodiesel from	*Terminalia catappa* oil[a]	Soybean oil	Palm oil	EN 14214	ASTM D6751
Iodine value	83.2	136.4[b]	54.5[a]	120 max	_[f]
Density at 20⁰C (kg/m³)	873	885[e]	880[e]	860-900[e]	_[f]
Kinematic viscosity at 40⁰C (mm²/s)	4.3	4.5[c,d]	5.7[c,d]	3.5-5.0	1.9-6.0
Calorific value	36.97	33.50[c]	33.50[c]	_[f]	_[f]

a Experimental results
b Ferrari et al.(2005)
c Prasad and Srivastana, (2000)
d Determined at 37.8^{0}C
e Determined at 15^{0}C
f No specified limit

Conclusion

Terminalia Catappa Linn oil, *Linn* oil-based methyl ester and its blends had been characterized. The values obtained show that the kinematic viscosity of the trans esterified oil (methyl ester) has been greatly reduced when compared with un trans-esterified oil. The values obtained for each blend were unique on its own case and are characterized by the percentages of methyl ester in the blend. In the case of 100% methyl ester, the values obtained were very close to that of conventional diesel and are within the acceptable ones by the ASTM standards for biodiesel. Thus making it suitable as a fuel in internal combustion engines

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