Effect of Fatty Acid Methyl Esters on the properties of Biofuel from *Ricinus communis* (Castor) Seeds Oil

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Abstracts: **This paper studied the effect of fatty acid methyl esters on the properties of biofuel produce from the seeds oil of Ricinus communis. Oil was extracted from the seeds using soxhlet extractor with n-hexane; and then Transesterified using single alkali hydrolysis to biodiesel. The biodiesel produced was analyzed for it fatty acid profile using GM-MS and fuel properties using ASTM Methods. The result obtained show the presences of 10-undecenoic acid methyl ester as the dominant ester with the percentage of 51.19%, 9,12-Octadecadienoic methyl ester 18.85%, Octadecanoic acid methyl ester 8.27%, Hexadecanoic acid methyl ester 8.27%, 9-Hexadecenoic acid methyl ester 6.33%, and 2-Octadecenoic acid methyl ester 3.42% other fuel parameters like density, carbon residue, acid value and other fuel properties determined showed compliance with ASTM Specifications. The results infer that the oil from castor seeds possess some beneficial properties tha are suitable for biofuel production.**

Keywords: **Effect, Ricinus communis seed oil, Transesterification, fatty acid, fuel properties**

I. INTRODUCTION

Energy is very important and all aspects of human activities are hinged to it. The operations of our technological society depend upon the production and use of large amount of energy. Nations are fast developing industrially and in social status, as a result, more individuals own cars, trucks, heavy duty machines, power generating plants and other forms of mechanical devices which operate using one form of fuel or the other. There is therefore an exponential increase in the use and demand for fuel in terms of power generation, transportation and mechanized agriculture. The sources of fuel to run these engines have so far been extracted from our stock of fossil fuel such as crude oil and to a lesser extent coal and natural gas, which are finite and environmentally intolerable (OPEC, 1994).

Fast depletion of fossil fuels resulting in unpredictable increase of crude oil prices and growing worldwide concern for environmental degradation have necessitated the expeditious identification of alternative sources of energy to replace traditional fossil fuels (Gerhard, 2009). A very key feature of alternative sources of fuel energy is that they are well suited for decentralized development i.e can be domesticated to meet the needs for social and economic progress, especially in rural communities where fossil fuels may be difficult or expensive to obtain (Vicente *et al*., 2005).

The focus on the use of renewable feedstock's for supplementing and possible replacement of fossil fuels to secure future energy supplies continues to be accorded great priority. In this connection, biodiesel which mainly consist of mixture of alkyl esters remain one of the promising liquid alternative fuel to supplement the petroleum-based diesel fuel (petrodiesel). The fatty acids profile of biodiesel is an essential feature that corresponds to that of its parent oil or fat. Thus, biodiesel fuels derived from different sources can have significantly varying fatty acid profiles and properties. Various specifications that a biodiesel fuel must meet as contained in biodiesel standards, (such as American Society for Testing and Materials (ASTM) D6751 and EN 14214 in Europe) can be traced or associated to the composition and structure of the fatty esters comprising the biodiesel. Some of these specifications that are related to fuel quality include cetane number, acid value, and cold-flow properties in form of the cloud point or cold-filter plugging.

II. MATERIALS AND METHODS

The plant seeds of *Ricinus communis* (Castor) are named in Hausa as *Dan kwasare* . The sample of castor seeds were obtained from National Research Institute for Chemical Technology (NARICT) Zaria in Kaduna State**.** The seeds collected were cleaned by removing foreign materials such as ticks, stains, leaves, sand and dirt. The dried seeds were then mechanically dehulled to remove the seed coat. Removal of the seed coat was imperative because the seed coat contained little or no oil and more importantly its inclusion would make extraction less efficient. The seeds were milled into fine powder and stored in airtight polythene bag prior to the commencement of analysis.

Extraction of Oils

Oil from the crushed sample was extracted using Soxhlet method with n-hexane as extracting solvent. This process was carried out by placing powdered sample (50 g) in a thimble covered with cotton wool and inserted into a Soxhlet extraction chamber, n-hexane 200 cm^3 was poured into the receiving flask and condenser was mounted on it. The whole assembly was placed in a heating mantle and heated at 60 ^oC

for six hours. The receiving flask was cooled and the thimble removed. The set up was reassembled for solvent recovery. The extraction was repeated until appreciable amount of oil from each of the samples was obtained. The solvent was recovered and oil content determined (Swehla, 1996).

The percentage oil yield of each sample was determined using equation 1

$$\%\ \text{Oil yield} = \frac{B-A}{W} \times 100 \qquad (1)$$

Where; W is the weight of the sample in (g)

B is the weight of the empty thimble + sample before extraction

A is the weight of the thimble + sample after extraction.

Determination of Acid Value

Acid value measure the amount of free fatty acid present per gram of the sample oil, which is determined by titration with a standard solution of potassium hydroxide (Verma, 2001).

Procedure

The oil sample (2 g) was weighed into a conical flask (250 cm^3) and propan-2-ol (50 cm^3) was added to ensure complete dissolution. 3 drops of phenolphthalein indicator were added and mixed thoroughly. The mixture was titrated with KOH (0.1M) to faint pink colour end point (AOAC, 1990).

The acid value was calculated using equation 2.

$$\text{Acid value} = \frac{56.1 \times TV \times 0.1MKOH}{2g\ \text{ofthe oil}} \qquad (2)$$

Where TV = Titre value,

56.1= Molar mass of KOH

Determination of Free Fatty Acid (FFA)

The procedure employed for the determination of Acid Value applies to free fatty acids. The free fatty acid was calculated using equation 3

$$FFA = \frac{28.2 \times TV \times 0.1MKOH}{2g\ \text{sample Oil}} \qquad (3)$$

Transsterification

The transesterification is the reaction of a triglyceride with alcohol to produce esters and glycerol. The reaction is often catalyzed by an acid, base or enzymes (Demirabas, 2005). Base-catalyzed reaction is employed for vegetable oil having low free fatty acid content. The formation of methyl esters by transesterification of vegetable oils requires three moles of alcohol stoichiometrically (Sokoto et al.,2011)

The transesterification of 3:1 molar ratio of methanol to *Ricinus communis* (Castor oil) was done by dissolving 0.20 g of KOH in 7.5 cm^3 of methanol , then mixed with 20 g of the extracted *Ricinus communis* (Castor) oil in a 250 cm^3 round bottom. The content was stirred on magnetic stirrer for 5 minutes. The resulted mixture was heated on a water bath thermo set at 60 °C for one hour. The mixture obtained was transferred into separating funnel which was allowed to separate under gravity overnight, two distinct layers were observed, a thick brown layer (glycerol) at the bottom with a yellowish colour layer constituting the upper layer (biodiesel) (Demirabas, 2005).

The methyl ester obtained was purified by neutralization with dilute, phosphoric acid (pH 4.0), then washed with hot distilled water until the washed water has a pH of 7.0. The residual water was removed by drying the methyl ester over heated anhydrous sodium sulphate (Demirbas, 2008).

Analysis of the Transesterified Product using GC-MS.

The samples were subjected to GC–MS analysis using a Gas Chromatograph. The technique involves separation of alkyl esters in the mixture into their components based on boiling point and polarity, the oven temperature programmed at 120 °C and was initially held for 1min and was increased to temperature 220 °C (heId 15 min) at a rate of 4 °C/min. Helium was used as the carrier gas, the derivatized sample (1.0µl) was injected into the gas chromatograph at injector temperature (230 °C) and detected at temperature (250 °C).The injected sample in the gas chromatograph was separated on a column (30m ×0.25 mm). The detector elutes components material from the column at a certain retention time (i.e., the time after which a compound comes out from the column) and shown by a peak in the chromatogram (i.e., the record of the chromatographic analysis). The acquired chromatographs were scanned in scan mode and the components identified based on software matching with mass spectra.

Calculation of the Degree of unsaturation

Degree of unsaturation (DU) was determined based on the percentages of monounsaturated and poly unsaturated FAMEs in each of the biodiesel using equation (Ramos *et al*., 2009)

$$DU = (\text{monounsaturated Cn: 1wt\%}) + 2(\text{polyunsaturated Cn: 2,3wt\%})$$

III. RESULTS AND DISCUSSION

Table 1: Methyl Fatty acids Ester of from Castor seeds Biodiesel . The methyl ester composition in biodiesel produced from castor oil shown in Table 1, indicate the presence of 51.19% 10-undecenoic acid methyl ester, 18.85% 9,12- Octadecadienoic methyl ester, 8.27% Octadecanoic acid methyl ester, 8.64% Hexadecanoic acid methyl ester, 6.33% 9-Hexadecenoic acid methyl ester, 3.42% 2-Octadecenoic acid methyl ester and others. The fatty acid methyl ester profile of biodiesel produced from castor seed oil contains high number of double bond (unsaturation) within carbon chain. The presents of unsaturation gives an excellent lubricity property to the biodiesel, thereby increasing diesel engine performance when compared with diesel fuel (Knorthe, 2005

Table 1: Methyl fatty acids esters of castor biodiesel

Methyl esters	Approximate composition %
10-undecenoic acid methyl ester	51.I9
Hexadecanoic acid methyl ester	8.64
Octadecenoic acid methyl ester	8.27
9,12-octadecedienoic methyl ester	18.86
2-Octadecenoic acid methylester	3.42
9-Hexadecenoic acid methylester	6.33
Other non Methyl ester	3.20

Similarly the methyl ester show small amount of saturated fatty acid methyl ester which reduced the cloud point,pour point and also oxidative stability of fuel (Weiksner,2006) . The methyl ester profile is one of the factors that determine the suitability of any feedstock for use in biodiesel fuel production (Knothe, 2009). From the result in Table 1 it shows that, the most abundant ester in castor biodiesel is monounsaturated methyl 10-undecenoic acid , it is good with respect to stability of biodiesel as higher degree of unsaturation in the fatty acid methyl esters limits its suitability for use as a fuel due to high polymerization tendency as result of peroxidation (Gaby and Peter, 1997).

Specific Gravity

The density of petroleum products is usually expressed as a specific gravity and measured at a specific temperature commonly 20^0C (Dunn *et al*., 1996). It is an important property in diesel engine performance, since fuel injection operates on a volume metering system (Song, 2000). As shown in Table 2, castor diesel (0.90g/cm^3). This value is similar to those of sunflower and diesel fuel (0.86 and 0.85g/cm^3) reported by (Barnwal and Sharma, 2006).The specific gravity obtained in this study conform to ASTM standard specification for biodiesel fuel range (0.86 to 0.90g/cm^3) depending on the feedstock used. The slight difference in densities of biodiesel is attributed to fatty acid composition of ester and purity of feedstock (Enweremadu *et al*., 2011).

Carbon residue in Table 2 shows that castor biodiesel (0.02%) this value is lower than the ASTM limit (0.05%). This is an indication that the fuel burn completely with lesser or no emission of carbon monoxide which is a potential Greenhouse gas. The complete combustion of the fuel lessen carbon deposits on the nozzle of diesel engine (Zheng *et al*., 2000*)*

Acid value is a measure of the acid constituent in fuel; it is a good indicator of the quality of the fuel. The common acid constituents are free fatty acid which has high tendency for corrosion and also a symptom of water in the fuel (Gbadge and Raheman,2005). The maximum limit of acid content in biodiesel was 0.8 mgKOH/g (ASTM 1998). The results obtained in Table 2, shows that castor diesel has the value (0.16 mg/kg) . This value is within the ASTM limit, which indicates that they have less tendency of causing wear is storage tank and fuel system.

Pour point is the temperature at which the amount of wax from biodiesel is sufficient to gel the fuel, from the result in Table2, it show that castor diesel has pour point value of (50^0F). Thiis value are within the range reported for biodiesel (5 to 50^0F) as recommended by ASTM D6751 Standard (1999). The biodiesel sample could be handled and stored safely without solidifying, but when the fuel are to be used in cold area, they would have to be preheated or blended with some additives that would reduce the pour point (Hassan and Sani, 2006).

Flash point is the key property in determining the flammability of fuel (Gerpen *et al*., 2004). The flash point is the lowest fuel temperature at which application of ignition source cause the vapour of the fuel sample to ignite under the prescribe test condition. The result obtained in Table 2 castor diesel was (170^0C), this value is within the range of biodiesel fuel 100 to 170^0C (NREL, 2004). This values indicate that the biodiesel produced is essentially free from methanol as even small amount of methanol can reduce the flash point, affect fuel pump seals (Gerpen *et al*, 2004), according to Bapjai and Tyagi (2006) reported that biodiesel with flash point greater than 93^0C is classifying it as a non flammable and hazardous from the perspective of storage and fire hazard, therefore biodiesel is much safer than petro diesel.

Table 2: Fuel properties of Castor Methyl Ester.

Fuel Parameters	Values
Specific gravity(g/cm$^{3)}$	0.90
Carbon residue (%)	0.02
Acid value (mgKOHg^{-1})	0.16
Flash point (^{0}C)	170
Pour point (^{0}C)	50.00
Saturated fatty acid	17.49
Mono unsaturated	82.51
Polyunsaturated	0.00
Degree of unsaturated	82.51

The types of fatty acid methyl esters (% wt) and degree of unsaturation (DU) of the biodiesels produced from the seed oils of castor, shows the percentage saturated fatty acid (17.49 %). Monounsaturated ester (82.51 %), biodiesels with high value of monounsaturation are associated with high cetane numbers, the results in Table 2 indicate high cetane number due to high value of monounsaturation, and also polyunsaturated methyl esters in castor biodiesel was not detected. Hence, feedstock with high percentage of polyunsaturated acid is not suitable for usage as biofuel. The result in Table 2 infers that the produced biodiesel will be stable owing to the absence of polyunsaturated fatty acid.

Therefore, it could be deduce that castor biofuel has some of the viable characteristic of being a good material for biofuel production.

IV. CONCLUSION

The results from this studies reveal that the oil can be extracted from the seed of *Ricinus communis.* The physicochemical properties of oil show that they possess suitable properties for biodiesel. The samples gave high percentage oil yield when compared with the percentage yield of other related literature like those of cotton seed and jatropha seed oils. Also most of the fuel properties conform to the ASTM and EN standard. This implies that the seed oils are good raw material for biodiesel production and can be used in diesel engine.

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