Evaluation of Coconut Oil Biodiesel Fuels as Sustainable Alternatives to Petro-Diesel in Nigeria

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ABSTRACT : This work considers a viable alternative to the unsustainable dependence of Nigeria on petroleum. Coconut oil, its methyl and ethyl esters as well as blends were evaluated for both regulated and unregulated biodiesel properties. Transesterification process catalysed by sodium methoxide was used in preparing the esters. The esters, obtained in high yield and the pure oil were evaluated for biodiesel properties such as fatty acids profile, higher heating value, viscosity, density, flash point, cetane number, sulphur content, ash content, moisture and acid value. Gas chromatography was used for fatty acids profile while the American Society for Testing and Materials standards methods for biodiesel were used in evaluating each of the parameters. The values obtained were compared with international standards, particularly the India Biodiesel Standards (IBS). Also evaluated for biodiesel properties were 1:1:1 w/w blend of coconut oil, methyl ester and ethyl ester. A blend of equal weight of the ethyl ester and petro-diesel was also prepared and its properties evaluated. The qualities of the fuels were discussed with respect to applicability in compression ignition engines and environmental benignity. Coconut oil and all the fuels prepared from it were found to possess valuable biodiesel properties. The high regression between density and viscosity (0.98), flash point and density (0.94), and flash point and viscosity (0.98) of the coconut biodiesel fuels were attributed to the influence of an unregulated property - fatty acids profile of the oil. It was concluded that manufacturing of biodiesel from coconut oil is a sustainable project that can create job and wealth in Nigeria and other countries in the West Africa sub-region.

Index Terms: Biodiesel, Coconut oil, Fuel, Nigeria, Sustainable Development Agenda, Transesterification

1. INTRODUCTION

Sustainability, the contemporary agenda for the development of our world [1] should be regarded as a lifeline particularly by nations where poverty, environmental degradation and consequent disruption of peace are the order. Typical of these nations is Nigeria, a petroleum producer and exporter where the most recent available World Bank data showed that 76.46% of the population falls within the poverty headcount ratio at $3.10 a day using 2011 purchasing power parity (2011 PPP). The same source revealed that in 2010, 26% of the population lived below the national poverty line [2]. For such nations, livelihood through dependence on renewable resources is obviously a viable proposition.

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Petroleum economy is not sustainable. It is marked by supply shortage, environmental degradation and social unrest. These had driven several nations to explore alternative renewable sources of energy such as solar, wind, geothermal and plant products.

Compared to petroleum, plant products are cheaper renewable sources of energy and materials. Therefore, plant products should be considered for wealth creation in nations that have enough vacant land for agriculture. Among plant products, vegetable oils from seeds and nuts have been found to be valuable renewable sources of fuel [3].

Abbreviations IBS: Indian Biodiesel Standard. CCO: Coconut oil. ME: Methyl ester of coconut oil. EE: Ethyl ester of coconut. CME: A blend of equal weight of CCO, ME and EE. EEB50: A blend of equal weight of EE and No-2D petro-diesel. FAME: Fatty acids methyl ester.

Fuels have been prepared in good yields from oils of crops such as palm [4],groundnut [5], coconut [6], rapeseed [7], soybean [8] and jatropha [9]. The required processing methods are simple and sustainable. A few of the oils for example, groundnut oil, have been used either neat or blended to power diesel engines [10]. The alkyl esters, particularly methyl and ethyl esters of the oils have been found to have better fuel properties than the pure oil [11]. The alkyl esters, also called biodiesel, are obtained by several methods. The most effective of the methods is transesterification [12] – a process involving the heating of the oil with the appropriate alcohol in the presence of a base or acid catalyst.

Naturally, vegetable oil used in producing biodiesel in a particulars area is the oil obtained from native crops. Oil from rapeseed and sunflower is used in Europe. The most common feed oils in Asia are coconut oil, jatropha oil and palm oil. Soybean oil and waste oil are the common feedstock in Canada and the USA. Animal fat and waste vegetable oil are used in New Zealand while palm oil and soybean oil are used in Australia. Palm and coconut trees are cultivated in small, medium and large scale in Nigeria. Jatropha is grown mainly to demarcate plots of land. In Nigeria, palm oil is used mainly for nutrition and soap making. Jatropha oil has not been exploited while coconut oil is used mainly for cosmetics purposes.

Coconut, a native of the tropics which also thrives in temperate climate is one of the highest oil yielding plants. The oil content of the nut is 60 – 65%. 2,260kg or 2,689 litres of oil can be obtained from a hectare [13]. An underutilized crop with such a high content of oil is a viable solution to poverty in a monoculture economy in need of diversification such as the Nigerian economy.

Being an agricultural product, coconut oil is a renewable product and its exploitation is sustainable. However, information is essential in assessing the industrial potential of a material. There are few reports mainly from Asia (though many of them are not published in journals) about some of the biodiesel potentials of coconut and its esters. Consideration of coconut oil for biodiesel manufacturing in Nigeria and countries in the West African sub-region requires more locally generated data for the following reasons.

First, the quality of agricultural products from the same plant species varies with seasons, climates and growing conditions [14], [15], [16]. Since the physicochemical properties of biodiesel are sensitive to the quality and composition of the feedstock, data on biodiesel properties are usually generated on regional basis. Secondly, reports on technical data that can assist Nigeria in reaching informed decisions on industrial exploitation of locally produced coconut oil for biodiesel production are very scanty. Uwubanmwen et al., [17] published a review on the potentials of coconut palm in Nigeria. The potentials highlighted were application in nutrition, medicine, cosmetics, soaps and fibrous materials. The review did not mention the biodiesel potential of the oil. Alamu et al., [18] reported low yield of biodiesel from coconut oil. In the same work, findings on the viscosity and specific gravity of the coconut oil and B10 blend of the ethyl ester and petro-diesel were reported. More comprehensive data is needed.

This study was embarked upon to determine the fuel properties of coconut oil sourced locally in Nigeria, to prepare its methyl and ethyl esters and to determine the fuel properties of the esters and blends. The work reports a high yielding synthesis of methyl and ethyl esters of coconut oil.

It investigates the regulated properties – cetane number, density, viscosity, flash point, ash content, sulphur content and water content of the oil and its esters. The unregulated properties - heating values and the fatty acids profile are also reported.

2. MATERIALS AND METHODS

The oil used was a blend of coconut oil obtained from extractors in Ado Ekiti, Ibadan, and Lagos, all in south-west Nigeria. n-Hexane, absolute methanol, absolute ethanol, sodium sulphate and sodium metal

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were high grade reagents obtained from reputable dealers.

Methods for fuel properties analysis were based on the procedures of American Society for Testing and Materials (ASTM) for biodiesel. The methods are for cetane number (CN): D613; flash point (FP): D93; density: D1298; viscosity: D445; acid value (AV): D974; ash: D874; sulphur: D7039; water content: D1796; and higher heating value (HHV): D240.

3. EXPERIMENTAL

Methanol and ethanol were dried over anhydrous sodium sulphate prior to use.

3.1. Synthesis of sodium methoxide.

2.3g of freshly cut sodium metal was added in bits to 5g of dry methanol in a $250cm^3$ beaker. The vigorous reaction which was conducted in a hood at room temperature subsided and cooled to a white mass. The mass was recrystallized in methanol. Sodium methoxide, obtained as white crystals was vacuum-dried and stored in a desiccator. Melting point: 127^0C. Yield: 4.5g (83%).

3.2. Synthesis of methyl/ethyl esters of coconut oil.

A solution of 0.5g sodium methoxide in 25g methanol was added to 200g coconut oil in 1litre round bottom flask. The mixture was stirred and refluxed at 60^0C for 30minutes, poured into a separating funnel and allowed to separate into two layers. The upper layer was run into the round bottom flask and refluxed again at 60^0C for 30minutes with another 0.5g/25g sodium methoxide/methanol solution. The mixture was allowed to separate in a funnel. The lower layer was run off while the upper layer was washed thrice with distilled water. The methyl ester was dried over sodium sulphate. An identical procedure was used for the ethyl ester by simply replacing methanol with ethanol. The yields of the methyl and ethyl esters were respectively 93% and 86%.

4. RESULTS AND DISCUSSION

TABLE 1

3.3. Chromatographic analysis.

The fatty acids were determined as methyl esters. The methyl esters were prepared following a standard procedure for preparing fatty acid methyl esters (FAME) for GC analysis. 20mg of the oil was mixed with $2cm^3$ of toluene. $2cm^3$, 1.5% sulphuric acid in dry methanol was added. The mixture was stirred and incubated at 55^0C overnight. $4cm^3$ saturated solution of sodium chloride was added and vortexed. $2cm^3$ HPLC grade hexane was added followed by addition of $3cm^3$, 2% $NaHCO_3$. The mixture was also vortexed. 180µl of the upper phase was taken for GC analysis.
Gas chromatogram HP6890 powered with HP ChemStation Rev. A 09.01 [1206] software was used for the analysis with the following conditions: split injection; split ratio: 20:1; carrier gas: nitrogen; inlet temperature: 250^0C; column type: HP INNOWAX; column dimensions: 30m x 0.25mm x 0.25µm; oven program: initial temperature at 60^0C, first ramping at 12^0C/min for 20min maintained for 2min, second ramping at 15^0C/min for 3min maintained for 8min; detector: FID; detector temperature: 320^0C; hydrogen pressure: 22psi; compressed air: 35psi. The reliability of the data generated was high with the correlation curves of the various FAME standards having correlation coefficients r = 0.99964 – 0.99927.

Gas Chromatographic Result of Fatty Acid Composition (as Methyl Esters) of Coconut Oil.

Fatty acid	Concentration (%)	Carbon chain: Saturation
Caprylic acid	5.48	C8:0
Capric acid	6.44	C10:0
Lauric acid	49.60	C12:0
Myristic acid	17.15	C14:0
Palmitic acid	9.61	C16:0
Stearic acid	2.33	C18:0
Oleic acid	7.16	C18:1
Linoleic acid	2.17	C18:2

Total saturated fatty acids (%): 90.61

Total unsaturated fatty acids (%): 9.33

TABLE 2

Comparison of Biodiesel Properties of Coconut Oil (CCO), Coconut Oil Methyl Ester (ME), Coconut Oil Ethyl Ester (EE) and Blends with Indian Biodiesels Standard (IBS).

Parameter	CCO	ME	EE	CME	EEB50	IBS
Flash point (K)	535	395	415	457	403	120 (min)
Density (Kg/m^3 @ 298K)	919	869	870	874	867	860 – 900
Kinematic viscosity (mm^2/s @ 313K)	27.2	3.2	3.7	9.7	2.7	2.5 – 6.0
Cetane number	61	46	49	53	43	51 (min)
Ash (%)	0.01	0.01	0.01	0.01	0.01	0.02 (max)
Sulphur (%)	0.001	0.001	0.001	0.001	0.002	0.005 (max)
Water content (%)	0.04	0.03	0.03	0.02	0.01	0.05 (max)
Acid value (mg KOH/g)	0.43	0.16	0.19	0.23	0.07	0.50 (max)
Higher heating value (MJ/Kg)	37	42	41	40	45	-

4.1. The Fatty Acids Profile.
Due to wide variation in the fatty acid composition of vegetable oils, the fatty acid profile is not a regulated biodiesel property. However, it has been observed that this property influenced many regulated properties [19]. Hence, the effect of fatty acid profile of vegetable oils on their application as biodiesel is vital. Table 1 shows the fatty acid methyl esters (FAMEs) gas chromatographic profile of the coconut oil blend used in this work. The cities from which the coconut oil samples used to prepare the blend were obtained are well spread out in the region. Therefore the composition and properties of the oil used can be regarded as the average for coconut oil available in the region. The linearity of the calibration curves of the FAMEs has high significant ($P < 0.001$) coefficient of determination ($r^2 = 0.99$). Therefore, the data in Table 1 reflects precisely the concentrations of the various fatty acids in the oil. Unlike other vegetable oils which are made up mainly of fatty acids containing 16 or more carbon atoms, CCO is made up of 78.67% fatty acids containing less than 16 carbon atoms. These are caprylic, capric, lauric and myristic acids. The high content of medium chain fatty acids makes CCO more volatile than other vegetable oils. The fatty acids profile that confers high volatility on coconut oil also influences the viscosities, densities and flash points of the alkyl esters prepared as discussed in the next three sections.

4.2.Viscosity.
Viscosity is an internal property of a fluid which indicates resistance to relative flow of composing layers due to intermolecular attractive forces. It determines a fuel's ignition delay time, spray quality, fuel-air combustion ratio and penetration of the jet [21]. Biodiesels are generally more viscous than petro-diesel. For this reason, biodiesels lubricates engine parts such as pumps and injectors better than petro-diesel. The viscosity of ME, EE and EEB50 falls within the recommended limits of Indian Biodiesel Standards (IBS). (IBS is used mainly in this discussion because of similarities in the climate and the level of development of Nigeria and India). The specific application of these samples can be predicated on the recommendation of ASTM D975-97 Standard for the use of grade No2-D petro-diesel whose range of recommended viscosities covers the values for ME, EE and EEB50. These fuels can be used to power high-speed engines that operate for sustained periods at high load. The high viscosity of coconut oil does not prevent its use in powering engines. The viscosities of pure coconut oil at 48.9^0C and 110^0C are respectively 19.8 and $4.36mm^2/s$ [20]. These values fall within the ASTM D975-97 recommended limits of 5.5 to $24mm^2/s$ for No4-D petro-diesel - a heavy distillate fuel used in fuelling low and medium speed engines. The technical modification required for the use of CCO in such engines is the preheating of the oil to temperatures above 50^0C before injection into the combustion chamber. A hybrid engine that will start up on petro-diesel or any of the other biodiesel from CCO can be designed such that the initial heat generated can be used to heat up a CCO tank to the required temperature. Then, the engine can automatically draw CCO when the appropriate viscosity is reached.

4.3.Density.
Density is mass of a unit volume of a fluid in vacuum. Viscosity relates positively to density. Stokes equation was established on this positive relation. It has also been observed that there is high correlation between the density and viscosity values of vegetable oil methyl esters [12]. The density and viscosity of the various biodiesel fuels (excluding the blend with petro-diesel) prepared in this work correlate highly with a coefficient of 0.98. What this means is that the engine operations influenced by viscosity will similarly be influenced by density. Density of a fuel is taken into consideration when designing the processes of manufacturing, storage, transportation and distribution of fuels. Density also has direct effect on engine power. Engine power depends on the mass of fuel that reaches the combustion chamber. The mass of fuel that reaches the chamber depends on density. Pumps and injectors dose fuels by volume. Since density relates directly to mass, the higher the density of a fuel, the higher the mass of fuel burnt subject to a limit where the density may be too high for adequate metering of the fuel. With the exception of the pure

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coconut oil, the densities of other fuels prepared in this work conform to IBS.

4.4.Flash Point

Fuels are combustible materials requiring careful handling during transportation, storage and use. The parameter used to assess the combustion hazard involved in these processes is the flash point - the minimum temperature at one atmosphere at which a fuel will start burning if ignited. It is used to classify fuels according to hazard levels for transportation safety. Coconut oil and all the fuels prepared from it in this study are very safe. Their flash points are above the recommended minimum with the methyl ester being the lowest. The flash point also reflects the purity of the fuel. The presence of 0.5% methanol had been claimed to reduce biodiesel flash point 170^0C to 50^0C [22]. The values obtained in this work show that the fuels are free of methanol. In this study, flash point of the fuels studied (excluding the EEB50 blend) correlates well with density and viscosity with values of 0.94 and 0.98 respectively.

4.5.Cetane Number

Cetane number (CN) is a dimensionless primary indicator of the ease of self-ignition of a fuel in a compression ignition engine (CIE). The CN scale runs from 15 to 100. A CN of 100 was assigned to n-cetane (hexadecane, $C_{16}H_{34}$), a linear chain hydrocarbon which is highly ignitable. Its highly branched isomer, 2,2,4,4,6,8,8-heptamethylnonane is highly resistant to ignition with a CN of 15. The proportion by volume of n-cetane in a mixture of the two isomers which has the ignition characteristic as the fuel being tested is the CN of the fuel. CN is a measure of ignition delay - the time taken for a fuel-air mixture to ignite after the injection of the fuel. Fuel with too low CN will undergo incomplete combustion, produce low engine power and emit more hydrocarbon pollutants while fuel with too high CN will ignite before mixing properly with air. The combustion will be partial, heavy smoke will be produced, injector will be overheated since the fuel will ignite close to the injector, and injector nozzles will be clogged by unburned particles. The CN of CCO and CME conform to recommended standard while the CN of ME and EE are below specification for biodiesels. However, the values for all the fuels are higher than the minimum standard for petro-diesel. Therefore, actual test in engines may be necessary to assess the ignition characteristics of the esters.

4.6.Ash

In a combustion engine, ash is the residue of unburned hydrocarbon and inorganic impurities. Ash may cause wear and tear of metallic components of engines by both physical and chemical processes. It is abrasive and may cause excessive wear of the cylinder, the cylinder walls and the piston. As engine cools down, moisture may condense on ash to form solution of electrolytes which may trigger electrochemical reactions that will initiate corrosion. The ash content of all the fuels prepared in this work conforms to standard.

4.7.Sulphur.

One of the major reasons for developing alternatives to petroleum products is the need to reduce harmful emissions. Oxides of sulphur are among the noxious gases emitted from the combustion of petroleum products. Biodiesels are noted to be eco-friendly through very low emission of oxides of sulphur. The sulphur content of all the biodiesels produced from CCO is very low compared with the recommendation of IBS. They will not increase the level of oxides of sulphur in the atmosphere. To this extent, they are eco-friendly.

4.8.Moisture.

Moisture in biodiesel can come from two sources: absorption of moisture from the environment due to its hygroscopic nature and residual moisture due to improper drying during preparation. High moisture in biodiesel can increase microbial growth, free fatty acid and sediments. The increase in microbial growth can lead to clogging of fuel lines. As earlier noted, moisture can lead to wear and tear of engine parts by promoting corrosion. The moisture content of the fuels produced in this work is very low in comparison with the IBS recommendation. Low moisture content can be maintained during storage and use if the storage tank is air-tight and if filters containing drying agents are fixed in the fuel system.

4.9.Acid Value (AV). Residual mineral acid from the production process can be found in biodiesel prepared with acid catalysts. Hydrolysis of oil during storage and of the biodiesel after manufacture can also produce free fatty acids. The total acid, determined as the mass of KOH in mg required to neutralize the acidic constituents in one gram of a sample is the acid value (AV) of the sample. High AV in fuels indicates poor storage conditions, the corrosiveness of the fuel, high microbial activity and the potential of the fuel to clog fuel system. The fuels produced in this work are of very low AV. Alkaline catalyst was used thereby eliminating contamination with mineral acid. The coconut oil was used soon after extraction and the fuels were analysed soon after preparation. Throughout the experiment, moisture was kept as low as possible thus minimizing the conditions that favour hydrolysis.

4.10.Biodiesel blends. There are some properties of the CCO, ME and EE fuels which are slightly out of the IBS range. For example, the density of CCO is high while the HHV is low. Its cetane number is better than those of its esters. A blend made up of equal weights of the three fuels was prepared and its properties were studied. The density and CN of the blend conform to specification. The viscosity falls within the range for No4-D diesel which can be used to power low and medium speed engines. A blend of equal weight of the ethyl ester and petro-diesel was also prepared and studied for the following reasons. While methyl esters of oils have favourable biodiesel properties, the fact that methanol used for preparing them is obtained from petroleum reflects negatively on its greenness. Ethyl esters are considered greener because ethanol used for its preparation can be obtained from carbohydrates which are renewable agricultural products. Biodiesel is still more expensive than petro diesel. A balance between sustainability and affordability calls for compromise. This is achieved by blending biodiesel and petro-diesel. Using popular convention, B50 was prepared in this work. (B refers to the word 'blend' and '50' is the percentage of biodiesel in the blend). However, to show that it was the ethyl ester which was blended with petro-diesel, the blend was coded EEB50. Compared with IBS, all the parameters but CN were optimized in EEB50. However, the CN conforms to ASTM D975 - the American standard for petro-diesel.

5.CONCLUSION AND RECOMMENDATION

It has been shown through the results obtained in this work that the use of coconut oil for biodiesel production is sustainable. This generation will meet its needs without compromising the ability of future generations to meet their needs. Coconut oil is a product obtained from agriculture, a green process with job and wealth creating potential. The fuel manufacturing process is simple and involved the use of non-toxic chemicals. Glycerine, the by-product is highly valuable. Biodiesel is a carbon neutral, eco-friendly product. Carbon dioxide released during combustion is consumed in the photosynthetic process, making the net emission of carbon dioxide zero. Contribution to oxides of sulphur in the environment is insignificant. All the above benefits conform to the expected outcomes of the United Nations' Sustainable Development Agenda. Therefore, if Nigeria and other countries in the West Africa sub-region implement the recommendations in the next paragraph, significant assistance may be obtained from the developed nations.

Nigeria has 910,770 sq.km land area. Agricultural land, arable land, permanent cropland and forest area as percentage of land mass are respectively 78.9, 32.9, 2.9 and 14.4 [23]. Obviously, there are large swaths of land in Nigeria which can be used for large scale cultivation of coconut trees to produce enough oil for all purposes - nutritional, industrial and commercial. Biodiesel plants should be established to process the coconut oil into fuel and other valuable products. Science, technology, engineering and administration must be dynamic enough to respond to the characteristic internal and external perturbations and turbulences in the world's energy economy. Such a dynamic response can only come from adequate funding of basic and applied research, and very sound educational system whose curricular are frequently reviewed in response to challenges.

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