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Comparative Investigation of Prosopis Africana Seed Oil as a Biodiesel and Edible Oil

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ABSTRACT

The global and urgent need for alternative and renewable energies to fossil fuels has necessitated this study. The use of African Mesquite (*Prosopis Africana*) seed oil as biodiesel and edible oil was investigated. The seed was subjected to soxhlet extraction using petroleum ether (60 – 80^{o}C) as a solvent and mechanical expression to extract its oil. The oil yields of 18% and 23.6% were obtained respectively from the two processes. The clear, golden-yellow and transparent liquid (oil extract) was subjected to chemo-physical and thermal analysis to ascertain its composition in the raw state. A stimulated distillation using a GC-MS analyzer gave a 95% stable yield of diesel at the temperature range of 325 – 330^{o}C. The products were made up of alkanes, alkenes, aromatics and carboxylic acids members ranging from 10 to 20. The distillation curve displays the trend of yields with temperature. The fatty acid profile from the GC-MS analyzer showed that the oil has 63% linolenic acid with 0.08% free fatty acids. From the results, the oil favourably compares with NAFDAC's specifications for edible oils and also presents great potentials for biodiesel when transesterified or thermally cracked. Based on the oil composition and prospects for biodiesel, an ASTM distillation apparatus was used to thermally pyrolyze it to produce biodiesel.

Keywords: biodiesel, prosopisafricana, comparative investigation, chemo-physical properties, analysis, edible oil.

1.0 INTRODUCTION

There is currently an increased global demand for alternatives to fossil fuels and hence researchers have seen the dire need and the urgency to plunge into action. This is as a result of the incessant increase in the prices of fossil fuels; petrol diesel and other fractions. They are no doubt non-renewable; the sources of fossil fuels are diminishing and the surging demand for energy has been on the increase since the nineteenth century. The supply however depends on the availability and the acceptability of fuels and how easily they can be delivered. Equally, the exhaust gases (flue) or products of combustion from diesel combustion engines continually pollute the environment, its environmental impacts on lives of communities, vegetation and aquatic lives also contribute in misbalancing the ecosystem.

Biodiesel as a renewable source of energy is non-toxic, biodegradable and available to be implemented immediately and currently the best substitute for diesel today. Biodiesel is a name used to describe a clean burning alternative fuel, produced from domestic, renewable resources [1].

Based on these facts, African Mesquite (Prosopisafricana) oil, its biodiesel and blends were produced and comparatively analyzed for their physio-chemical properties viz a viz; acid value, relative density, carbon residue content, water content (crackle test), kinematic viscousity, flash point, cloud point, ash content, pour point, cetane number, calorific value, engine performance test, combustibility test and so on.

Prosopis oil seeds are in abundance in the savannah and sub-savannah regions of the world and in Nigeria, have not been effectively utilized except as food condiment or seasoning around the Benue, Kogi, South-eastern areas, outside which, they are left out unutilized. Mindful of other production processes, the biodiesel was produced thermally at appropriate temperature(s) and will be used to substitute the transesterified biodiesel and petroleum diesel as alternative energy resource after comparison with the standard Automotive Grade Oil (AGO).

Also, the bond structure/stability of the samples in relation to diesel was monitored using a Fourier Transform Infrared (FTIR) Spectrophotometer.

The results obtained were compared with the standard fossil fuel diesel – Automotive Grade Oil (AGO) using ASTM, IP, AOAC and NAFDAC standards. The suitability of the oil, its biodiesel, the blends and the new method of production will be brought to limelight. Based on the findings of this research work, due recommendations will be proffered on the possibility of enlisting prosopis seed oil as a potential biodiesel in the biodiesel diary after those of jatropha, canola, soybeans and so on; its blends at different ratios with petrol-diesel for use in diesel engines, and establishing another method for producing biodiesel viz a viz, thermal conversion or pyrolysis also called depolymerization method at different temperatures. Ideally, biodiesel could be produced solely from vegetable oils that provide all the needed constituents. This will make the biodiesel industry completely independent from fossil-based resources and the biodiesel will be truly a bio-based product, which in turn will further increase the energy security of our country and enhance the environmental benefits of biodiesel and prepare ground for the emergence of bio-refinery in Nigeria.

When the diesel engine was invented, vegetable oils were used as the first liquid fuel after coal dust. (www.biodiesel.org). However, their use was abandoned when comparatively inexpensive petroleum-based fuels became available.

The petroleum-based fuels, besides offering an economic advantage were free from so many of the problems which have been with the use of vegetable oils as fuels. The problems associated with the use of vegetable oils are injector fouling; ring sticking and varnish build up on the cylinder walls. These problems could be attributed to the high viscousity of vegetable oils and to the reactivity of the polyunsaturated fatty acids components of the triglycerides. Researches have shown that viscousity and other attendant problems can be overcome by different reactions to form biodiesel. These include: transesterification process, thermal cracking/pyrolysis, micro emulsification, and algae production to form fuels which are called biodiesel.

Although biodiesel may seem like a recent innovation, it was first used over a century ago. (Fangruiand Milford, 1999).Dr. Rudolf Diesel, the inventor of diesel engine, designed it to run on coal dust suspended in water, heavy mineral oil, and vegetable oils. When Dr. Diesel demonstrated his engine at the World Exhibition in Paris in 1900, it was running on 100% peanut oil [2].

Through its economic interest, there is no doubt that fossil fuels play a vital role in the generation of energy to drive automobiles and mechanics but recent informed survey has indicated that at the present rate of energy consumption, since the fossil oil is the major source of energy, there is continued decline in the quantity of crude petroleum which serves as a source for diesel oil production. Moreover, the rate of replacement is not commensurate to the rate of consumption. For instance, at the end of 1986, there was sufficient oil remaining to last 34 years, natural gas for some 58 years, and coal, 219 years in Nigeria [3].

Nigeria's contribution to biodiesel production has just begun with researches at top gear towards its eventual kick-off. At present, the emphasis is on Biofuel/bioethanol production with the federal government's establishment of its plants and ethanol crop plantations across the country. This research work is one of such.

2.0 MATERIALS AND METHODS

50kg of African mesquite seeds and 5 litres of automotive grade oil (AGO) used as standard and for blends were purchased from Modern Market in Makurdi, Benue State and Conoil Filling Station in Effurun, Delta State respectively.

ASTM standard methods for distillation of petroleum products D86-82 was used to thermally decompose the vegetable oil. ASTM standard distillation equipment AE 133-78 was used with minor modifications. A sample of AGO was obtained from Conoil Filling Station, Effurun, DeltaState. The prosopis seeds were sent for bulk soxhlet extractor using petroleum ether (60-80^{o}C) as solvent to the Biochemistry department of the University of Nigeria, Nsukka, Nigeria. For mechanical extraction, it was carried out at a local oil mill in Makurdi. In addition to chromatographic and mass spectrometric analysis of the distillates and blends, samples of oil were comparatively and chemo-physically analyzed at the petroleum/chemical laboratory of Light-House Petroleum Engineering Services Company, a leading analytical laboratory in Nigeria and Petroleum Training Institute (PTI), both in Effurun, Delta State of Nigeria. Engine performance test using diesel test engine was conducted at the Mechanical Engineering department workshop of Federal University of Agriculture (UNIAGRIC), Makurdi, Nigeria.

The prosopis seeds having hard cotyledonious shell were crushed (dehuled and dehuled), milled and ground to coarse powder. They were sieved to remove shells and inner transparent membranes and dried for two to three days before being ready for extraction. For the mechanical press, after crushing and ground, they were toasted and poured into the oil expeller for extraction.

American Oil Analytical Chemists (AOAC) official methods 981:11 for oils and fats for preparation of samples were employed (Firestone and Yurawecz, 2006). This was done by using clear sediment free-liquid sample of oil after extraction, direct and inverting the container several times.

Three samples of the seeds were prepared for the percentage oil yield determination:

(1) Pre-treated samples (P1): Heated/boiled for about five hours, manually dehuled dried and ground to powder.

(2) Untreated samples (P2): crushed, sieved and ground to powder.

(3) Fermented samples (*gbaye*) (P3): Heated/boiled for five hours, dehuled and fermented and ground to powder: the sample is odourous.

Weight of initial mass of sample (10g) was determined before solvent extraction using hexane and petroleum ether. Weight of oil after concentration and drying was determined and the percentage calculation with respect to the initial weight of 10g was determined to give the percentage oil yields of each sample.

2.5 litres x 5 bottles of petroleum ether (60 – 80^{o}C) were used to extract oils from the 50kg of prosopis seeds using bulk soxhlet extractor, 2 - 4 litres by volume. The following methods were used for the chemo-physical analysis: Flash point, (ASTM D 92/93 Method); Moisture content/volatile matter, (ASTM 4377 Method); pour point,

$$\% \, H_2O \text{ content} = \frac{w_1 - w_2}{w_1} \times 100\% \quad (1)$$

(ASTM D 97 Method); Cloud point, Carbon residue, (ASTM D 189 Method);

$$\% \text{ Carbon content} = \frac{w_2}{w_2 - w_1} \times 100\% \quad (2)$$

w_2 = weight of crucible + oil,

w_1 = weight of crucible + residue.

Kinematic viscousity, (ASTM D 445); density/specific gravity, (ASTM D 4052/ISO-AOAC Methods);

Kinematic viscousity, V = C x t (3)

C = Tube calibration constant

T = Average flow time.

$$D_T \text{ (g/mL)} = \frac{w - w_1}{v_T} \quad (4)$$

Where w and w_1 = weight (g) of Pycnometer empty and filled with test sample; v_T = volume of Pycnometer (mL) at temperature, T (20^{o}C)

To calculate specific gravity 20^{o}C of sample at temperature,

$$\text{Specific gravity @ } 20^{o}\text{C} = \frac{D_{20}}{d_{H_2OT}} \quad (5)$$

Index of refraction, (AOAC Official Method 921.08);

$$R = R^1 + K\,(T^1 - T) \quad (6)$$

[4], JAOAC, 1986). Melting and boiling point, (AOAC Official Method 920.157) (Lewkowitsch, 1921, JAOAC, 1986). Iodine value, (IUPAC-AOCS-AOAC Method); Fatty acid profile (FFA),

$$\text{Acid value} = \frac{titre(ml)x(5.01)}{weight \triangleright of \triangleright sample} \quad (7)$$

The FFA figure is usually calculated as oleic acid (1ml of 0.1M NaOH 0.0282g oleic acid) in which case, the acid value = 2 x FFA. For most oils, acidity begins to be noticeable to the palate when the FFA calculated as oleic acid is about 0.5 -1.5% [5]. Calorific value, (bomb calorimetry); Saponification value,

$$\text{Saponification value} = \frac{(b - a)x(28.05)}{wt(g) \text{ of sample}}$$

(8)

Peroxide value/stability, multiply the values obtained by 2 = mEq/kg of peroxide oxygen of sample (ml M per kg) (Onwuka, 2005). Trace metals, (AAS/ Spectroil Method) [6]. Stimulated distillation, (ASTM 86); and FTIR, and ASTM standard methods for Cetane number index, (ASTM D613); distillation (ASTM D86); viscosity, (ASTM D445); density, (ASTM D4052); chromatography of fatty acid and sulphur content, (ASTM D4294) of petroleum fuels. Pyrolysis experiments were carried out at temperatures ranging from 350–400^{o}C using the ASTM bench home-made 5 L stainless still batch distillation unit. The vegetable oil (500ml) was introduced into the pyrolysis reactor and then heated by an external electric resistance. Using an in-tank method of petroleum blending, the biodiesel (pyrolyzate) obtained after chemo-physical screening were blended with AGO earlier obtained from Conoil Filling Station at different proportions. They include, B10, B20, B30, B40, B50, B60, B70, B80 and B90. B100 represents 100% pyrolyzate (biodiesel). The blends were centrifuged for homogeneity before proceeding with fuel analysis using ASTM standards.

Engine performance test was carried out by testing the biodiesel in a four-cylinder, 30 hp Kubota engine (V1305) on a dynamometer. The speed was varied by ramping up and then back down again to eliminate hysteresis in the measurements. Torque, power, and airflow were recorded for each speed increment.
The consumption tests were done by filling the fuel tank with the test fuel then weighing it with a digital scale accurate to 1 gram.

3.0 RESULTS AND DISCUSSION

The percentage oil yield of Prosopisafricana seed is in the range of 18 to 24%, with the treated seeds presenting the highest yield. The yield from the fermented seeds which is used as food condiment was quite low but promissory. The yields from using petroleum ether were higher than the yields from hexane. See Tables 1 and 2.

Table 1: Percentage Oil yield using Petroleum Ether as a solvent

Sample	Initial weight of sample (g)	Weight of flask (g)	Weight flask + oil (g)	% Oil Content
P1	10	95.91	98.27	23.6
P2	10	95.91	98.03	21.2
P3	10	95.91	97.71	18

P1 - Pre-treated Prosopis seeds sample, P2 - Untreated Prosopis seeds sample, P3 - Fermented Prosopis (*gbaye*) sample.

Table 2: Percentage Oil yield using Hexane as a solvent

Sample	Initial weight of sample (g)	Weight of flask (g)	Weight of flask + oil (g)	% Oil Content
P1	10	95.91	98.11	22.0
P2	10	95.91	97.99	20.8
P3	10	95.91	97.55	16.4

In describing the chemo-physical properties of *prosopisafricana*, Table 3 gives a clear picture. Density, which with some conversions gives the specific gravity falls within the permissible limit of the ASTM, ISO and API specification which ranges from 0.875 to 0.95 kg/m^3 (Kinast, 2003, Knothe*et al*, 2006). The flash and pour points of 113^{o}C and -13 respectively as obtainable with other vegetable oils are above the minimum recommendation of ASTM which is 100^{o}C making the oil and its biodiesel flammably safe for handling and haulage. The kinematic viscousity is expected high (12.16 cSt) quite above specification for biodiesel (1.9 – 6.5 cSt). The viscousity of vegetable oils is usually high and that is the major challenge for biodiesel production. But it is expected that when converted to biodiesel, the specification would have been met and indeed Table 6 justifies this claim. The biodiesel and their blends fell comfortably within specification. That is the breakthrough! Other parameters in Table 1 present prosopis oil as a potential biodiesel material and edible oil within ASTM and NAFDAC's specifications. The free fatty acid content is quite minimal and overall, there is no significant toxic trace element(s) contained in the oil. The heating value is quite promissory with low moisture content.

Table 4 is the fatty acid profile of the oil; percentage saturated which is predominantly linolenic and oleic acids are high enough for biodiesel for high cetane numbers whether estimated or calculated. The unsaturated free fatty acid is very low and commendable (Kinast, 2003).

Table 3: Physico-chemical properties of prosopis oil

S/N	Test	Unit	Result
1	Density @ 20°C	Kg/m^3	0.925
2.	Refractive Index 40°C	N/A	1.447
3.	Saponification Valu	mg KOH/g	190
4.	Iodine value (wijis)	g/100g	11
5.	Peroxide Value	Meq/kg	6
6.	Free Fatty Acid	%	0.08
7.	Kinematic Viscous @ 40°C	cSt	12.16
8.	Iron Content	mg/kg	1.37
9.	Copper Content	mg/kg	0.03
10.	Sulphur Content	mg/kg	< 0.05
11.	Flash Point	°C	113
12.	Pour Point	°C	-13
13.	Cloud Point	°C	
14.	Moisture Content	Mass %	0.04
15.	Carbon Residue	Mass %	0.13
16.	Melting Point	°C	18
17.	Heating Value	kJ/kg	43,729
18.	Total Acid	mg/kg	7.14
19.	Ash Content	%	0.008

Table 4: Fatty Acid profile

Fatty Acid	**Saturated (%)**	**Unsaturated (%)**
Lauric (C-12)	0.5	-
Palmitic (C-16)	4.5	-
Oleic (C18)	29	0.08
Linoleic (C 18: 2)	63	-
Total	**98**	**0.08**

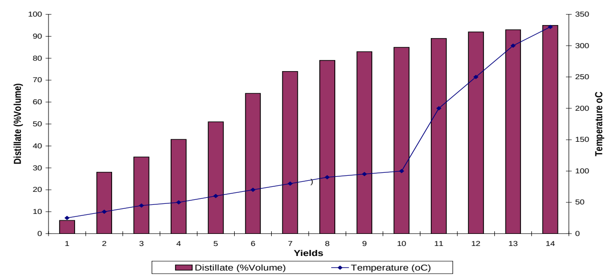

Fig. 1: Distillation Curve of Prosopis Oil

Fig. 1 presents the stimulated distillation curve of prosopis oil with temperature using GC analyzer. The curve lines position the highest yield in volume of diesel thermally produced when prosopis was pyrolyzed. At temperature of 325 – 400°C, the distillates were obtained with the action of sodium hydroxide as a catalyst to yield the polar and non polar components. The non-polar component which is our biodiesel contains alkanes, alkenes, aromatics and carboxylic acids members ranging from 10 to 20.

Table 6 is the comparative analysis of prosopis biodiesel, AGO and AGO blends of prosopis. The table speaks for itself. Prosopis biodiesel favourably compares with AGO if not better. Biodiesels have low acid contents, sulphur content, carbon residue/ash content, somewhat higher heating values, less prone to the formation of polyaromatichydrocarbons (PAHs) and pollutants [7]. These are clearly shown in the Table 6.

4.0 CONCLUSION

The comparative investigation of African Mesquite (*Prosopis Africana*) seed oil presents the facts that the savannah and sub savannah perennial tree plant presents great potential for edible oil and biodiesel. Although the nutrient value was not ascertained as it bothers beyond the scope of this work, the chemo-physical properties clearly highlights its edibility according to NAFDAC.s specification for edible oils and can well be enlisted as one of such. The Biodiesel potential which is the main thrust of this paper cannot be underestimated as this work x-rays. Also the possibility of thermal conversion process/pyrolysis also called depolymerisation as a biodiesel production option is however brought to limelight. Several of such works highlighting thermal conversion process have been noted (Dunn, 1999; Schwab *et al*, 1988). The products were made up of alkanes, alkenes, aromatics and carboxylic acids members ranging from 10 to 20 at the temperature range of 300 - 400^{o}C. The distillation curve displays the trend of yields with temperature. Overall, the oil favourably compares with NAFDAC's specifications for edible oils and also presents great potentials for biodiesel when transesterified or thermally cracked.

Table 6: Comparative Analysis of *Prosopis Africana* Oil, its biodiesel, biodiesel-AGO blends and Diesel (AGO)

Sample	Density @ 20°C	Calorific value (kj/kg)	Total Acid (mg/g)	Carbon Residue % Wt	H_2O Content % Wt	Flash Point °C	Viscousity @ 40°C cSt	Ash Content %	Pour Point °C
Diesel (AGO)	0.8701	44,938	0.23	0.17	0.03	120	2.00	0.006	
PO	0.925	43,729	7.14	0.13	0.04	113	12.16	0.008	-13
B100	0.9104	44,147	4.25	0.12	0.03	94	2.65	0.005	-15
B90	0.9064	44,357	6.30	0.28	0.025	97	2.69	0.005	-14
B80	0.9023	44357	6.13	0.25	0.035	99	2.52	0.005	-13
B70	0.8983	44,543	5.25	0.25	0.03	102	2.46	0.005	-13
B60	0.8943	44,543	4.55	0.23	0.03	104	2.39	0.0045	-13
B50	0.8903	44,543	3.36	0.19	0.03	107	2.33	0.004	-13
B40	0.8862	44,543	5.22	0.18	0.03	109	2.26	0.005	-13
B30	0.8822	44,752	6.02	0.094	0.03	112	2.20	0.005	-12.5
B20	0.8782	44,752	5.40	0.08	0.03	115	2.13	0.005	-12
B10	0.8741	44,938	5.60	0.078	0.03	117	2.07	0.006	-12

PO-Prosopis Oil, B100-100% prosopis biodiesel (pyrolyzate), B90-90%prosopis, biodiesel + 10% AGO, B80-80% prosopis biodiesel + 20% AGO, B70-70% prosopis biodiesel + 30% AGO, B60-60% prosopis biodiesel + 40% AGO, B50-50% prosopis biodiesel + 50% AGO, B40-40% prosopis biodiesel + 60 % AGO, B30-30% prosopis biodiesel + 70 % AGO, B20-20% prosopis biodiesel + 80 % AGO,
B10- 10% prosopis biodiesel + 90 % AGO

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