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Properties of Biodiesel from *Calophyllum inophyllum* L. (Calophyllaceae) Oil Referring to another Oleaginous Plants of Madagascar

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Abstract Foraha, scientifically known as *Calophyllum inophyllum* L. from Calophyllaceae family was studied for biodiesel production. This study analyzed the physical and chemical properties of the fatty acid methylic esters from Foraha oil in comparison with biodiesel from different oil sources and gasoil diesel. Oil from Foraha is dark green with relatively high density (0.9431 ±0.00161 at 20°C) caused by undesirable components in the oil. Its acid number is high (44.9873±0.41167mg of KOH). Hydrolysis and oxidation of triglyceride are favored by chlorophyll. Oleic acid (37.83%) and the linoleic acid (38.87%) are the main components of oil. The transesterification of triglyceride was done using methanol [1: 6] with NaOH (1% w/w) as the basic catalyst. The reaction was carried out at 65°C, during 90mn. The efficiency of conversion achieved 80.83%. There was an increase in the density (0.8958±0.0099) and viscosity (at 20°C is 34.3253 ±0.1765 cSt) of biodiesel. There was an increase in the acid value (30.9360 ±0.5500mg of KOH/g) when stored for 4 months. Ash content did not exceed 500ppm. During combustion, the calorific value was slightly lower than gasoil. However, there was an increase in the number of methylic esters having a linear unsaturated chain. Thus, production of chlorophyll by Foraha should be limited to increase production of methylic esters.

Keywords *Calophyllum inophyllum,* Chlorophyll, Unsaturation, transesterification, biodiesel

Introduction

The research of an alternative to gasoil becomes more and more attractive for the increasing demand in energy and the dependence to the fossil products. The green fuel stands like an energizing renewable and non-toxic resources [1]; it contributes to the management of the fossil resources and forecasts of its weariness.

The biodiesel is a green fuel exploiting the oleaginous plant, it appears under three forms: pure vegetable oil, fatty acid of methylic ester and hydrogenated vegetable oil [2]. The biodiesels are categorized in three generations according to the raw materials used for its manufacture. The first generation of the biodiesel remains the most producible on an industrial scale; it is gotten from the different plant oils or waste oils [3,4]. Multiple are the reasons that justify the choice of the oleaginous plants cultivated for energizing ends: valorization of non-edibles oils [5-7], energizing output [8], and valorization of the waste oils [9-11].

This present survey uses the physical and the chemical properties of the made biodiesel to choose the parents oils. Some properties of fuel are determinative for its combustion in the engine. The similarity to the properties of petroleum diesel is crucial for the physicals properties; the density and the viscosity assure the adaptability without modification in the engine [12]. The power value and flammability of fuel assure its better combustion and in part the power of the engine. In addition, the combustion of fuel emits greenhouse gaseous. The pollution of the atmosphere is consequently a constraint to be managed by reducing emission gaseous.

"*Calophyllum inophyllum* L." belonging to the Calophyllaceae family was investigated to produce biodiesel. Does its methylic ester is physically and chemically a good fuel?

This present work aims to conduct a comparative analysis of biodiesel properties from Foraha referring to three other different unsaturated oils: peanut, cotton, jatropha, and gas oil.

The activities carried out with the Foraha are described in this article: its extraction, its characterization, its transesterification and the determination of its properties. The results obtained with the three other vegetable oils are analyzed in the analytical and comparative analysis.

Materials and Methods

Foraha plant is a tree of 10 to 15 m tall, and its robust trunk is sometimes crevassed. Its leaves are oblong, broad, large, and have many veins visible on the underside; its flowers are very fragrant, each of which forms 4 whites petals half notes and many stamens [13]. Its fruit is globular, formed by two well-sown oleaginous seeds between them [14]. The tree is native to East Africa and it thrives on the cost of the Indian Ocean. It is adapted to areas with warm and rainy climate. These factors make its cultivation simply, without the requirement of pesticides and irrigation. Therefore, it is indeed ecological and economical production of seed oil. In facts, cultivation of Foraha for energy production would lead to the reforestation of the littorals. The plant has high values of several byproducts: first, its precious dense and hard red wood is perfect raw material for sculpture, or manufacture of furniture. Moreover, the bark and leaves are used in traditional medicine. The oil also has cosmetic values. Its healing values assure dermal restructuring [15; 16].

Seventy kilograms of fruit samples were collected in February 2017 in Mananjary which is located in the south-east of Madagascar (S27° 13'; E48° 20', 0-10m above sea level). Fruits were dried and husked, producing 21.2 kg of seeds. Oil from seeds was extracted by mechanical pressure and by extraction using solvent (hexane) of the fatty oilcake according to the method described by Soxhlet.

The density was determined by the method of weighed report to the mass of distilled water in the unchanged condition, following the process of ASTM D1217 - 15. The acid was determined by following the procedures described in the standard normalized ASTM D664, quantifying the present free fatty acids in a known quantity of oil with a solution of KOH. The iodine value was determined by following the method described in ASTM D5768-02 through addition of unsaturated halogens then quantified the halogens not fixed by thiosulfate of sodium. The saponification of oil follows the ASTM D5558 – 95process in which with a quantity known of KOH and the dosage of the remaining KOH with the HCl determined the indication of saponification.

Where IE is esterification number, IS denotes saponification, and IA is the acidic number. This data was used to determine the amount of NaOH required for its transesterification.

The profile of fatty acid oils was identified by chromatograph in gaseous phase following the method ASTM D1945 – 14 exploiting the equilibrium in concentration of the present compounds between two phases on contact that settles to every instant. The separation takes place by the differential affinity of the constituent. The position of the peak identified the compound and the area calculated its amount. The equipment is based on a capillary column and a furnace set adjusted initially to 190°C, the temperature of the injection is 240°C and the temperature in the Flam Ionization Detector is 260°C. Nitrogen was used as a carrier gas.

This process replaced the alkyl radical of the glycerol with methyl. The reagents used were: oil and methanol with a ratio of 1:3 molars of methanol reacting with 1 molar of triglyceride. An excess of methanol improved reaction efficiency. The latter is catalyzed by a strong bases (NaOH) with a quantity 1% w/w to the triglyceride. The operation is carried out at 60°C with a heating system and a reflux fitting. The magnetic stirrer facilitates the initiation of the reaction by promoting phase contact. The reaction lasted 90mn and a foam appears to the surface and reversal color of the phases takes place (dark green to clear solution). Washing with water follows the operation to eliminate glycerol, soap, and other impurities. The washings are dried by the silicate gel for 2 to 3 days (until the solution becomes clear).

The process was the same in determining the density of the plant oil. Thus, the results were used to compare with the plant oil (ASTM D1217 - 15). The method normalized ASTMD 445 d determined the viscosity kinematics which measured the length of liquid out-flow between the two features of the viscometer, using the law of Poiseuille and supposing that the liquid is Newtonian (viscosity constant to constant temperature). The measure of the power calorific is driven according to the norm ASTMD 240; it was done by burning the sample in the calorimetric case then increased the temperature of distilled water. The ash content of the ester was measured by the mass of the sample charred reported in its initial mass. This determination uses the method by calcination (ASTMD 482).

An analysis of variance (ANOVA) proceeded by a test of homoscedasticity was used to test variations of the oil characteristics and the ester properties. The analyses were made using XLStat-pro 2010 software.

Results and Discussion

The extracted oil was dark green, 5.34 liters were obtained from the seed pressing and 0.93 liters were extracted from oilcake using a solvent (Fig. 1). Dark green color of the oil signifies the presence of chlorophyll (pigment responsible of this tint) in high quantity. The oils constituted of triglyceride and other minor components [17]. Triglyceride is composed of three fatty acids that can be saturated or not. The proportion of the various fatty acids in the oil confers different intrinsic and physicochemical properties. Although some of these components have valued interests in therapeutic and cosmetic usage, they are considered impurities in the manufacturing of biodiesel.

Figure 1: Seeds, oil, and biodiesel

The main results are presented in the table 1. The means identified with the same letter are the column representing statistically homogeneous groups at a 5% probability level according to the Newman-Keuls test.

Table 1: Properties of oils

Oil type	Density	Acid number Mg of KOH/g	Iodine value Dg of Iodine/g	Saponification number mg of KOH/g
Foraha	0.9431 ±0.0016	44.9873 ±0.4116	115.82 ±2.17	176.78 ±13.60
Peanut	0.9170 ±0.0001	1.0379 ±0.0637	103.88 ±2.50	178.69 ±3.86
Jatropha	0.9213 ±0.0006	15.0363 ±0.8091	96.71 ±1.92	183.23 ±6.23
Cotton seed	0.9199 ±0.0005	1.3050 ±0.0791	95.53 ±0.73	203.68 ±7.10

Foraha oil has relatively a high density ($F= 888.00$; $p< 0.0001$). Oil is generally heavier than gasoil especially when oil is rich in impurities. The acid number value of the Foraha oil is higher than other unsaturated oil. Its iodine value (95.6424 ± 11234) classified it as a semi-siccative oil. Conferring to this data, the fatty acids include some unsaturation. These are easy oxidize and polymerize which turn the oil to be more acidic. The profile of fatty acid confirmed that oil contains more unsaturated fatty acid (Fig. 2). The palmitic acid (14.14%), oleic acid (37.83%) and linoleic acid (38.87%) were the main components of oil (Table 2).

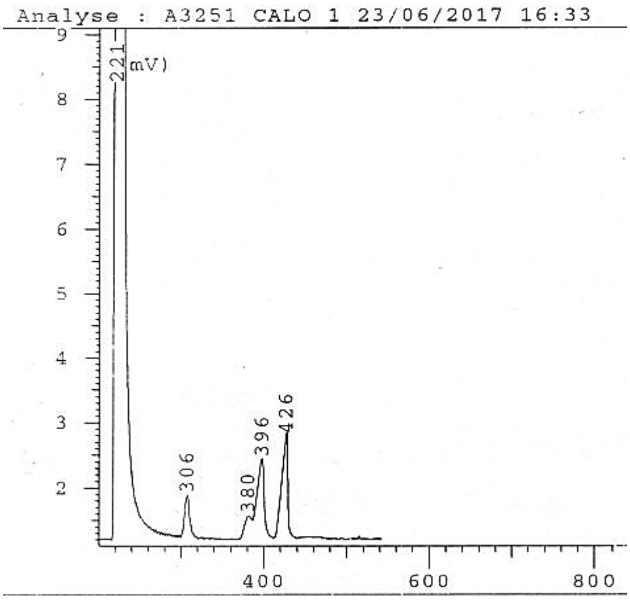

Figure 2: Composition of oil

Table 2: Profile of fatty acid of the oil of Foraha

Symbols	None	Founded value
C 16:0	Acid palmitic	14.17 %
C 18:0	Acid stearic	9.12 %
C 18 :1w9	Acid oleic	37.83 %
C 18 :2w6	Acid linoleic	38.87 %

Given by chromatographic areas of made biodiesel, efficiency of conversion achieved 80.83%. The neutralization of oil is an essential process have a better output.

The density of Foraha biodiesel is relatively lower than oil; while the diesel is between 0.845 and 0.860. The methylic form of fatty acid is less viscous than the pure vegetable oil but relatively high compared to conventional diesel. The Foraha viscosity at 20°C is 34.3253 ±0.1765centiStokes while diesel oil has a maximum viscosity of 7Cst at this temperature. Freshly made biodiesels does not present any risk to be acidic. Even to 4 months of storage, acid of the ester from Foraha is still 30.9360±0,5500mg of KOH / g.

The calorific value of the Foraha biodiesel is relatively lower than other calorific value of the biodiesel rich in unsaturated fatty acid and value of diesel gasoil. Refining oil, especially the elimination of the chlorophyll was proven to be necessary. This refining can improve the density, viscosity and it reduce the ash content of the ester. The energizing output of the biodiesel is comparable to diesel oil in relation to its lower calorific power per unit of volume. The difference was caused by the presence of the carboxyl group previously mentioned; the carbon and hydrogen are oxidized and reduced the energy. The oxygen on the other hand, oxides them. Ash content which was relatively higher than that of diesel oil came from non-burnt impurities. These results are shown on table 3.

Table 3: Biodiesel properties

	Density (at 20°C)	**Viscosity (centiStokes at 20°C)**	**Acid number (mg de KOH/g)**	**Calorific value (KJ/l)**	**Ash content %**
Foraha	0.8958± 0.0099bc	34.3253± 0.1765	30.9360± 0.5500	29813.01± 1.2247	5.2065± 0.0115
Peanuts	0.8891± 0.0015	86.5719± 0.5055	2.0971± 0.0970	34045.84± 0.8367	1.0352± 0.0080
Jatropha	0.9341± 0.0056	10.3732± 0.1278	4.9323± 0.1291	37982.56± 1.4832	0,9624± 0.0085
Cotton seed	0.9108± 0.0020	44.6971± 0.8320	1.6707± 0.0478	35403.03± 1.4832	1.0789± 0.0046
Gas oil	0.83 to 0.85	3 to 7	0.50	36855	3.50
Biodiesel ASTMD6751-12	0.86 to 0.9	1.9 to 6	0.50	38400	2.00

Conclusion

Four physical and chemical properties, and the fatty acid profile of Foraha oils were examined. Seven properties of the methylic ester manufactured with this oil were investigated and compared to three other biodiesel and to diesel gasoil. The Foraha ester is rich in chlorophyll and in unsaturated fatty acid. Its density and viscosity is higher than diesel gasoil. Ash (5.2065%/3.50%) content isn't comparable to diesel gasoil. Its acid number (30.9360± 0.5500 mg of KOH/g/0.5mg of KOH / g) and calorific value (29813.01±1.2247KJ/l /36855 KJ/l) can be improved by bleaching the oil. During transesterification, it was found out that chlorophyll has affinity to the methanol thus methanol can be used to clarify oil. The decolorized Foraha oil is recommended for biodiesel production. The diversification of the exploited plants is encouraged to ecological findings. Cultivation of this plant contributes in reforestation of east island littoral. Minor components of oil have high value and it can be recovered by refining the oil.

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