International Journal of Multidisciplinary Research and Development
Online ISSN: 2349-4182, Print ISSN: 2349-5979
Impact Factor: RJIF 5.72
www.allsubjectjournal.com
Volume 4; Issue 11; November 2017; Page No. 24-27

Synthesis and characterization of the oil and biodesil from *Sterculia setigera* Del (Karaya) Seeds

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Abstract
This study aims to identify a sustainable source of energy from natural and environmentally friendly resources. The oil from *Karaya* seeds was extracted using three techniques; chemical soxhelet extraction, cold chemical extraction and mechanical pressing. Percentage yields were 32.4%, 26.0 % and 18.2% respectively. Fatty Acids profile shows that the oil contained, approximately, 97% saturated fatty acids Palmitic, Myristic and Heptadecanoic, and 3% unsaturated fatty acids Palmitoleic and Linolenic. Acid catalyzed esterification reduced fatty acids content from 15.88% to 1.56%. Treated oil was Transesterified. The results indicate that the physicochemical properties of *Karaya* methyl esters are within standard limits of.

Keywords: biodiesel, extraction, karaya, transesterification, fatty acids

1. Introduction
Energy demands are, rapidly, increasing due to fast industrialization and the increased number of vehicles on the road [4]. Fossil fuels are the main sources of energy all over the world. [5]. The reserves of fossil fuels are diminishing with their, daily, increasing demand due to their non-renewable nature [6]. Nowadays, researchers are looking for alternative, renewable, economically viable and environmentally friendly sources of energy [7]. One of the most important, sustainable, energy sources is Biodiesel which is suggested as being an alternative fuel for diesel.
Biodiesel is a liquid fuel, technically known as a mono alkyl ester, made from fats or oils and alcohols. Biodiesel one of the sources of the renewable energies which can be produced in different conditions and considered as one of the best alternative energy sources made from renewable biological sources such as vegetable oils and animal fats [8]. Biodiesel is yield of transestrification reaction of vegetable extracted oil and alcohol [9]. This product can be used pure or blended with fossil diesel. There are many advantages of using biodiesel such as it is biodegradability, low emission profile, non-toxicity [10] and higher flash point [11].
Transesterification reaction can be performed using acid or alkali but the alkali such as NaOCH3, KOH and NaOH are preferred due to their non-corrosive nature and reactivity [12].
Sterculia Setigera Del belongs to *Sterculiaceae* family; it is commonly known as Karaya and locally as Tartar tree. It is widespread in tropical savanna forest and it grows in Sudan in southern Kordufan and Blue Nile states. The tree is medium sized with horizontally spreading branches, grows to a maximum height of 15 m. The bark is smooth, fibrous and thick, grey-purple. The seeds are purplish- black with yellow-brown puffy aril in the top and it is surrounded by a shell and a thin 2-3 mm layer of pulp, covered by sharp brown bristles. It contains 10–15 seeds in each shell. The shell is grey-green and sometimes brown [13]. One of the products of the Karaya tree is the Karaya gum and it is widely used in pharmaceutical industry, food industry as a thickener and emulsifier and also used in textile industry [14].

2. Materials and Methods
2.1Materials
Dried *karaya* seeds were collected from Al Azaza Forest east of Al Rusaires city in the Blue Nile State of Sudan. Chemicals used for extraction, oil treatment and biodiesel production were from SIGMA ALDRICH and SDFCL.

2.2 Methods
2.2.1 Oil Extraction
Karaya seeds were oven dried for 12 hours. Then the oil was extracted by two chemical extraction and mechanical pressing methods. Chemical extraction methods were cold Solvent extraction and Soxhlet, system, Solvent extraction. N-Hexane was used as a solvent in both methods.
Cold extraction was carried using 250 g of seeds. Seeds were placed in 1 liter beaker and 500 ml of N-Hexane were added, and then kept for 36 hours at room temperature under steering at 1000rpm. The solvent was evaporated [15].
In the Soxhlet method; 1000 g of the seeds were added to 2000 ml of n-Hexane in the Soxhlet round bottom flask, heated to 60 °C for 8 hours. The extracted oil and solvent were transferred to a rotatory evaporator to remove the n-Hexane [16].
In the mechanical pressing method, Chinese automatic presser model ZX 10 of 3ton capacity was used. 5 kg of seeds were pressed and the oil was filtered.
Eq. 1 was used to calculate the oil yield from all oil extraction methods.

$$oil\ yield = \frac{weight\ of\ oil}{weight\ of\ seeds}\ X\ 100 \qquad (1)$$

2.2.2 Fatty Acid Profile of *Karaya* crude oil
0.3g of crude oil sample were weighted into a 250 ml round

bottom flask, 6 ml of 0.5 M methanolic NaOH were add to the sample and boiled for 2.5 min. 1% Sulfuric acid, in methanol, was added to the mixture, shaken, and kept overnight at 50°C. 2 ml of hexane were added and well steered. Enough saturated NaCl was added for lowering. 1 ml of the upper Hexane layer was transferred to a glass stoppered tube; anhydrous Na_2SO_4 was added to Hexane layer and kept in vial. The dried sample was subjected to GC analysis.

2.2.3 Free Fatty Acid Treatment

2% concentrated Sulphuric acid, in 100 ml of methanol were added to 500 ml of hot crude Karaya oil. The mixture was kept at 55 °C for two hours with continuous stirring at 3000 rpm (STUART SB 162). The mixture was transferred to a separating funnel and allowed to settle for 24 hours. The lower layer of glycerol, sulfuric acid and unreacted methanol was separated from the upper layer of treated oil. The oil was washed three times with warm distilled water at 40 °C to remove impurities and soap. [17]

2.2.4 Transesterification Reaction

500 ml of acid treated oil were placed into a 1 L beaker and heated up to 60 °C, 100 ml of fresh methanolic Sodium Hydroxide were added under stirring at 3000 rpm for two hours. The mixture was transferred to a separating funnel and kept for 24 hours. Then the lower, glycerol layer was drained and the upper biodiesel layer was washed, three times, with warm distilled water to remove soap, methanol and remaining glycerol [18].

2.2.5 Identification of *Karaya* methyl ester

The conversion of *Karaya* oils to biodiesel was investigated using Fourier transform infrared spectroscopy (FTIR).Thermo Nicolet iS5 FT-IR spectrophotometer (Germany), equipped with a ZnSe crystal attenuated total reflectance (ATR) cell was used to obtain the IR spectrum [19]

2.2.6 Physicochemical properties of Karaya Crude oil and Biodiesel

Free fatty acid was determined according to AOCS method Ca-5a-40 and calculated as oleic acid. Total acid number was carried out according to ASTM method D 974. Saponification number was determined according to ASTM method D 94. Iodine number was determined according to ASTM method D5554. Density @ 15°C and Kinematic Viscosity was carried out according to ASTM method D 4052 and D 445 respectively. Calorific value was carried out according to ASTM method D2015. Water content of Crude oil was determined by Coulometric Karl Fischer Titration according to AOCS method Ca 2e-84.

Flash point, Copper strip corrosion, Kinematic viscosity, Sulphated ash, Acid Number, density, cloud point (CP), pour point (PP), cold filter plugging point (CFPP), Water content, Color, and Sulphur Content were carried out according to ASTM method D 6751.

3. Results and Discussions

3.1 Oil Extraction and Fatty acid profile

Table 1 shows percentages oil yields. Soxhlet system showed the highest efficiency of oil extraction in comparison to cold solvent and mechanical extraction.

Table 1: Oil yield from Karaya seeds using different extraction Methods.

No.	Extraction method	Oil yield, wt%
1	Soxhlet solvent Extraction	32.4
2	Cold Solvent Extraction	26.0
3	Mechanical Pressing	18.2

Table 2 shows fatty acid composition of Karaya oil with 96% saturated fatty acids concentration and 3% of unsaturated acid. The fatty acid profile of Karaya oil consist, mainly, of Palmitic, Myristic and Heptadecanoic acid and for the acids are Palmitoleic Acid, Linolenic unsaturated acids. These acids are commonly available in vegetable oils.

Table 2: Fatty Acids composition of *Karaya* crude oil.

Fatty acid	Formula	Structure	Area %
Palmitic Acid	$C_{16}H_{32}O_2$	C16:0	56.4
Myristic Acid	$C_{14}H_{28}O_2$	C14:0	32.8
Heptadecanoic acid	$C_{17}H_{34}O_2$	C17:0	6.45
Palmitoleic Acid	$C_{16}H_{30}O_2$	C16:1	1.64
Linolenic Acid	$C_{18}H_{30}O_2$	C18:3	1.25
Stearic Acid	$C_{18}H_{36}O_2$	C18:0	1.06
Tri decanoic acid	$C_{13}H_{26}O_2$	C13:0	0.21
Cis-11-Eicosenoic acid	$C_{20}H_{38}O_2$	C20:1	0.13
Undecanoic Acid	$C_{11}H_{22}O_2$	C11:0	0.075

3.2 High Free Fatty Acid Treatment and Transestrification Reaction

The presence of high free fatty acid in fuel may cause corrosion of internal engines parts and thus it will affect the engine performance [20]. Also high free fatty acids in raw materials of biodiesel can cause soap formation and low yield of biodiesel and the separation of the methyl ester from glycerin will be difficult. The maximum limit of free fatty acid in crude oil should be less than 2% [8], The maximum limit of total acid number in biodiesel is 0.5 mg KOH/g as per ASTM D6751 standard specifications of Biofuel. The free fatty acid content as oleic acid in Karaya crude oil was reduced from 15.88 % to 1.56 % and total acid number was reduced from 37.4 mg KOH/g to 3.54 mg KOH/g.

Fig..1 and Fig..2 shows the FTIR spectrum of Karaya oil and Karaya methyl ester respectively the spectra show similar absorbance peaks at 2922, 2853 due to C-H stretching, and absorbance around 1741 and 1743 which represent of C=O Carbonyl group. New peak appeared at 1436 cm-1which represent of methoxy group (O-CH3) which indicates the conversion of oil to methyl ester [21] Another new peak appeared at 1195.67 cm-1 which represent C-O.

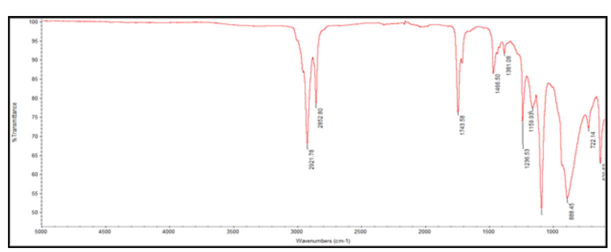

Fig 1: FTIR spectrum of crude *Karaya* oil

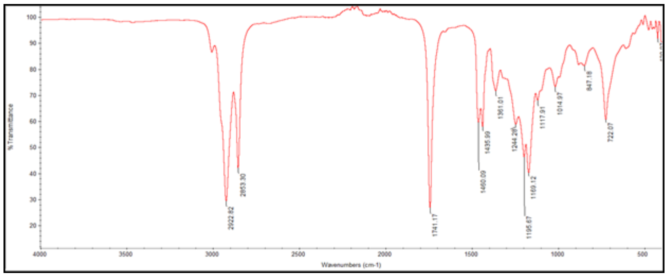

Fig 2: FTIR spectrum of *Karaya* methyl ester

3.3 Physicochemical characteristics of *Karaya* Crude oil and *Karaya* Biodiesel

Karaya oil and Karaya Biodiesel properties were determined according to ASTM and AOCS standard methods. Karaya crude oil was compared with *Chicha* oil and *Egusi melon* oil; however the results suggest that most parameters are in the same range with other oils except the Free Fatty acid and total acid number which is very high for Karaya oil (15.88 % FFA and 37.4 mg KOH/g respectively). The ratio of free fatty acids is the main factor determining the method of production of biodiesel, in either one or two step production.

Biodiesel properties were compared with ASTM D 6751 and EN 14214 standards specifications. Table 4.3 shows that all physical and chemical properties of *Karaya* biodiesel meet ASTM D6751 standards and most of EN 14214 standard parameters except for Kinematic viscosity and Sulfur content.

Table 3: Physical and Chemical properties of *Karaya* crude oil comparison with *Chicha* oil and *Egusi melon* Oil.

TESTS	METHOD	*Karaya* Oil	*Chicha* Oil [a]	*Egusi melon* Oil[b]
Kinematic Viscosity @ 40ºC, cSt	ASTM D445	37.43	51.95	31.52
Cloud Point, °C	ASTM D2500	19	-	-
Pour point, °C	ASTM D97	15	-	-
Color, ASTM	ASTM D1500	(2.8) L3.0	-	-
Density @15ºC, g/ml	ASTM D4052	0.9157	0.8600	0.9053
Free Fatty Acids (as Oleic acid), %FFA	AOCS Ca-5a-40	15.88	-	0.49
Total Acid Number, mgKOH/g	ASTM D 974	37.4	8.05	0.98
Iodine Value, g/ml	ASTM D 5554	50.91	-	-
Saponification Value, mg KOH/g	ASTM D94	180.35	-	204.44
Calorific Value, MJ/Kg	ASTM D 2015	45.97	32.8	39.37
Water Content, wt%	AOCS Ca 2e-84	3.7	-	-
Phosphorus content, mg/kg	ASTM D4951	0.031	-	-

a [22], b [23]

Table 4: Physical and Chemical properties of *Karaya* Biodiesel.

TESTS	METHOD	ASTM D 6751	EN 14214	Karaya Methyl Ester
Kinematic Viscosity @ 40ºC, cSt	ASTM D445	1.9 - 6.0	3.5-5.0	5.272
Cloud Point, °C	ASTM D2500	REPORT	-	6
Pour point, °C	ASTM D97	-	-	6
CFPP, °C	ASTM D 6371	-	-	3
Color, ASTM	ASTM D1500	-	-	L 3.0
Density @15ºC, g/ml	ASTM D4052	-	0.860-0.900	0.8873
Total Acid Number, mgKOH/g	ASTM D 974	Max. 0.50	Max. 0.50	0.31
Calorific Value, MJ/Kg	ASTM D2015	-	-	38.84
Flash Point, °C	ASTM D93	Min. 93	Min. 101	157.0
Copper Strip Corrosion (3 Hours @ 100ºC), Rating	ASTM D130	Max. 3	Max. 1	1B
Sulfated Ash, Wt%	ASTM D874	Max. 0.02	Max. 0.02	0.007
Phosphorus content, mg/kg	ASTM D4951	Max. 10	-	1
Sulfur Content, mg/kg	ASTM D 4294	Max. 500	Max. 10	120

4. Conclusions

The following conclusions can be drawn from this study.

- Highest yield of oil was gained from Chemical extraction using soxhlet and it was more serviceable than the cold extraction and mechanical pressing.
- Karaya oil content 97% of saturated fatty acids and 3% of unsaturated fatty acid.
- Acid esterification process was reduced 90% of FFA content in the oil.
- *Karaya* bio diesel was, successfully, synthesized using Alkali transestrification and proven using FTIR.
- The Physical and Chemical properties of *Karaya* biodiesel met the requirements of both ASTM D6751 and EN14214 standards.

Acknowledgement

The authors would like to acknowledge the technical support of Africa Technology Park.

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