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Effect of diesel-biodiesel and diesel-biodiesel-ethanol blends on physical and chemical properties of *Karaya* biodiesel

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Abstract
In this study Karaya crude oil was converted to Biodiesel using two step transesterification reaction to reduce the free fatty acid and kinematic viscosity of crude oil. The produced biodiesel was identified using GC-MS techniques, the results shows that 96.83% of triglycerides were converted to biodiesel. Physical and chemical properties of Karaya biodiesel met the requirements of ASTM D 6751. B20 blend of biodiesel with Diesel met the requirements of ASTM D 7467. Biodiesel-Diesel-Ethanol blends were investigated and compared also with standard method ASTM D 7467 and had met all standard requirements except for Flash point. The flash point of pure biodiesel was 158ºC, reduced to 70 ºC in the B20 blend and reduced to 14 ºC, 16 ºC and 18 ºC in D60 B20 E20, D80 B10 E10 and D80 B15 E5 respectively.

Keywords: biodiesel, transesterification, blend, ethanol, flash point

1. Introduction
The rise in global temperature resulting from energy generation and Consumption has become a very worrisome phenomenon to many stakeholders in different progressive sectors. Rise in environmental temperature and changes in related processes are directly connected to increasing anthropogenic Greenhouse gas (GHG) emissions such as nitrogen oxides, methane and carbon dioxide in the atmosphere [3].

Renewable energy is energy supplies by natural processes. All renewable energy comes ultimately from the sun as in solar heating systems or indirectly as in hydroelectric power, wind power, and power from biomass fuels. Since 20th century, the number of developing countries having a renewable energy has increased [4]. Biofuels one of the most renewable energy sources was used to reduce dependence on fossil fuels and to conserve the environment by reducing toxic gas emissions.

Biodiesel is defined as a fuel comprised of mono-alkyl esters of long chain fatty acids derived from vegetable oils or animal fats [5]. It has similar physico-chemical properties of conventional fossil fuel and can consequently, entirely or partially substitute fossil diesel fuel in compression ignition engines [6].

Karaya (*Fam*. *Sterculia setigera*) is a multi-purpose savanna tree which spreads naturally in Southern Sudan. The species is the main source of the internationally accepted gum karaya. It grows up to 15m high, the seeds have greenish yellow color. *Karaya* seeds contain 25.65% fiber, 3.45% ash, 11.12% carbohydrates, 24.10% protein and 25.25% crude oil [7].

2. Materials and Methods
2.1 Materials
Crude *Karaya* oil was previously extracted in. Other chemicals were supplied from Pan Reac AppliChem, SDFCL and SIGMA ALDRICH.

2.2 Methods
2.2.1 Biodiesel production
The *Karaya* crude oil was acid treated to reduce high fatty acid composition using 2% Sulfuric acid in 0.60 w/w methanol, the mixture was added to the heated oil at (60 °C), and kept on steering at 2500 rpm for 2 hours, then the content was kept in separation funnel for 24 hours. The upper layer of treated oil with low fatty acid was transferred to 500 ml beaker and heated up to 60°C at a steering speed of 2500 rpm, methanolic NaOH was added in a ratio of 6:1 methanol to oil, and the mixture was left steering for 2 hours. The mixture was removed from the hot plate and transferred to a separation funnel [8, 9].

2.2.2 Identification of *Karaya* Biodiesel and Ester content using Gas Chromatography - mass spectrometry (GC-MS)
Shimadzu GC-MS model (QP2010- Ultra) equipped with capillary column (Rtx-5ms- 30m×0.25 mm×0.25µm) was used to verify the conversion of the lipids to methyl ester qualitatively and quantitatively. The Sample was injected by using split mode, helium was used as carrier gas with flow rate 1.61 ml/min, the temperature program was started from 60°C with rate 10°C/min to 300°C. The sample was analyzed using the scan mode in the range of m/z 40-550, the total run

time was 24 minutes [10, 11]. Sample components were identified by comparing their retention times and mass fragments with those available in the National Institute of Standards and Technology (NIST) library.

2.2.3 Biodiesel blending

2.2.3.1 Diesel-Biodiesel blend: Biodiesel and fossil diesel were kept at same temperature of 25 °C to assure the homogeneity of the blends and the temperature of biodiesel while blending should be above its cloud point by minimum 25-30 °F. The biodiesel should be also free from water and sediments before starting the blending [12].

B20 blend which contains 20% biodiesel and 80% fossil diesel was prepared volumetrically in 500 mL batches using graduated cylinders of 250 ml and 50 ml, and stirred with speed of 2500 rpm for 30 min. to homogenize the blends.

2.2.3.2 Diesel-Biodiesel-Ethanol blends: Diesel-Biodiesel-Ethanol blends were prepared by the same procedure of biodiesel-diesel blend. Three blends with different ratios were prepared, Table 1 and kept in tightly closed bottles to minimize ethanol evaporation.

Table 1: Diesel-Biodiesel-Ethanol blends ratio

Blend	Biodiesel	Diesel	Ethanol
D60 B20 E20	60%	20%	20%
D80 B10 E10	80%	10%	10%
D80 B15 E5	80%	15%	5%

2.2.4 Physical and chemical properties of *Karaya* Biodiesel and its blends

Physical and chemical properties of Fossil diesel and B 100 (Pure Biodiesel) were determined according to ASTM D 6751. B20 and Diesel-Biodiesel-Ethanol blends were characterized according to ASTM D7467 "Standard Specification for Diesel Fuel Oil, Biodiesel Blend (B6 to B20)" following additional tests were carried out also for the set of the samples; water content, density at 15 ºC, Color, pour point (PP) and cold filter plugging point (CFPP). Table 2 shows the methods and instruments used for physical and chemical properties.

Table 2: Methods and Instruments used for physical and chemical properties

Tests	Method	Instrument	Imstrument Model
CFPP, °C	Astm d 6371	Normalab analis	Cloud and Pour test cabinet
Total Acid Number, mgKOH/g	Astm d 974	Si analytic	TitroLine 7000
Calorific Value, MJ/Kg		Parr	6400 Isoperibol Calorimeter
Flash Point, °C	Astm d93	Stanhope-seta	1366-3 P
Copper Strip Corrosion (3 Hours @ 100ºC), Rating	Astm d130	Stanhope-seta	15157-0 T
Phosphorus content, mg/kg	Astm d4951	Agilent icp	5110 ICP-OES
Sulfur Content, mg/kg	Astm d 4294	Oxford	TWIN-X

3. Results and discussion

3.1 Identification of *Karaya* Biodiesel and Ester content using Gas Chromatography - mass spectrometry (GC-MS)

The ester composition in biodiesel is important factor as it is affecting many properties of biodiesel such as; Cetane number, cold properties and stability [13]. Table 3 shows the fatty acid methyl esters which were found in the *Karaya* biodiesel and their yield. The total ester content in the biodiesel was 96.83% of the total components of produced *Karaya* biodiesel which indicate successful biodiesel production and prove that the triglycerides were converted to methyl ester. The methyl esters with higher percentage were in the order Palmitic Acid methyl ester, Oleic Acid methyl ester and Linoleic Acid methyl ester with percentage of 19.66 %, 18.97% and 17.58% respectively. Saturated FAME was found with less percentage of 27.84% and the great majority of FAME was found for unsaturated fatty acid methyl ester which is good indicator for the biodiesel feed stock as the saturated FAME affecting the engine due to formation of gum [14]. The great majority of FAME was found for unsaturated fatty acid methyl ester with percentage of 48 %.

Table 3: Ester content of *Karaya* Biodiesel

No.	Fame	GC % Yield	Common Name	Formula
1	C16:0	19.66	Palmitic Acid ME	$C_{17}H_{34}O_2$
2	C16:1	2.37	Palmitoleatic Acid ME	$C_{17}H_{32}O_2$
3	C17:1	2.03	10-heptadecanoic Acid ME	$C_{18}H_{34}O_2$
4	C18:0	8.18	Stearic Acid ME	$C_{19}H_{38}O_2$
5	C18:1	7.10	Methyl2-OCTYLcyclopropene-1-heptanoate	$C_{19}H_{34}O_2$
6	C18:2	17.58	Linoleic Acid ME	$C_{19}H_{34}O_2$
7	C18:1	18.97	Oleic Acid ME	$C_{19}H_{36}O_2$
8		20.94	OTHER ESTERS	
Total		96.83		

3.2 Physical and chemical properties of biodiesel blends

Table 4 shows the physical and chemical properties of *Karaya* Methyl ester and Fossil diesel in comparison with the limits of standard method ASTM D 6751. The results show that *Karaya* methyl ester had met the requirements of the standard method limits. The fossil diesel also met with all parameters of ASTM D 6751 except the flash point as the minimum limit of fossil diesel as per ASTM D 975 is 38°C, the flash point of fossil diesel was found 63.0 °C.

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

TESTS	ASTM D 6751	*Karaya* Methyl Ester	Fossil Diesel
Kinematic Viscosity @ 40ºC, cSt	1.9 - 6.0	5.272	2.483
Cloud Point, °C	REPORT	6	-4
Pour point, °C	-	6	-15
CFPP, °C	-	3	-9
Color, ASTM	-	L 3.0	L2.0
Density @15ºC, g/ml	-	0.8873	0.8300
Free Fatty Acids (as Oleic acid), %FFA	-	0.14	0.069
Total Acid Number, mgKOH/g	Max. 0.50	0.31	0.12
Flash Point, °C	Min. 93	158.0	63.0
Water Content, wt%	-	0.1	<0.05
Copper Strip Corrosion (3 Hours @ 100ºC), Rating	Max. 3	1B	1A
Sulfated Ash, Wt%	Max. 0.02	0.007	-
Sulfur Content, % mass	Max. 0.05	0.012	0.010
Phosphorus content, mg/kg	Max. 10	1	-

Table 5 shows the physical and chemical properties of Biodiesel blends in comparison with ASTM D 7467. B20 blend had successfully met all the requirements of ASTM D 7467. However, cold properties have no specification limits in the standard method as they depend on the equipment design, operating conditions and weather situation in the country which uses the fuel and mostly additives will be used to maintain the limits required [15]. Color is important feature since the color is easily noted by the user of the product and mainly used for the purpose of manufacturing quality [16].

Table 5 shows the Ethanol blends met the standard requirements in Kinematic Viscosity, total acid number, copper corrosion and sulfur content. Flash point and water content of ethanol blends had not met the standard requirements. The flash point which is less than the room temperature due to the volatility of ethanol will assist the combustion of the blend in the CI engine but it will be dangerous for storing and transporting.

Table 5: Physical and Chemical properties of *Karaya* Biodiesel Blends

TESTS	ASTM D 7467	B 20	D60B20E20	D80B10E10	D80B15E5
Kinematic Viscosity @ 40ºC, cSt	1.9 – 4.1	2.908	2.660	2.924	3.175
Cloud Point, °C	-	-3	+5	+3	+4
Pour point, °C	-	-6	+3	0	+3
CFPP, °C	-	-12	-2	0	-1
Color, ASTM	-	L 2.5 (2.3)	L 2.0 (1.6)	L 1.5 (1.4)	L 2.0 (1.7)
Density @15ºC, g/ml	-	0.8416	0.8352	0.8347	0.8392
Total Acid Number, mgKOH/g	Max. 0.3	0.19	0.17	0.20	0.20
Flash Point, °C	Min. 52	70.0	14.0	*16.0*	18.0
Water Content, wt%	0.05	<0.05	0.259	0.056	0.049
Copper Strip Corrosion (3 Hours @ 100ºC), Rating	No. 3	1A	1A	1A	1A
Distillation Temperature, 90% vol recovered	Max. 343	343	-	-	-
Sulfur Content, % mass	Max. 0.05	0.009	0.0046	0.0059	0.0062

4. Conclusion

The following conclusions can be drawn from this study.

1. *Karaya* oil has a high free fatty acid and high viscosity; both were successfully reduced by acid esterification.
2. *Karaya* biodiesel was produced through two step tranestrification with Biodiesel yield of 96.83%.
3. 27.84% of Ester content of *Karaya* Biodiesel was saturated FAME.
4. Produced *Karaya* Biodiesel had met the requirements of ASTM D6751.
5. B 20% blend of Biodiesel-Diesel had met the requirements of ASTM D 7467.
6. Biodiesel-Diesel-Ethanol blends had met requirements of ASTM D 7467 for S500 grade except flash point and water content.

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