Global Journal of Science Frontier Research: E
Interdiciplinary
Volume 15 Issue 4 Version 1.0 Year 2015
Type : Double Blind Peer Reviewed International Research Journal
Publisher: Global Journals Inc. (USA)
Online ISSN: 2249-4626 & Print ISSN: 0975-5896

Glycerine Analysis of Beniseed *(Sesanum Indicum)* Oil, Biodiesel and Blends

By E.I. Bello & A. Mammon
The Federal University of Technology, Nigeria

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GJSFR-E Classification : *FOR Code : 309999*

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Strictly as per the compliance and regulations of :

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Keywords: beniseed oil, biodiesel, characterization, mineral contents, fatty acid profile.

I. Introduction

Beniseed (Sesamum Indicum) belongs to the family of Pedaliaceae. It is widely grown in the North Central States of Nigeria and it is the 6th largest producer and the 5th largest exporter in the world (FAO, 1992). It has different varieties, the notable ones being white, yellow and black. The seeds are spherical, 2.5 - 3 mm diameter depending on the variety and has an oil yield of 42- 54% and protein 22 % (Hui, 1996; Bedigian, et al., 1985). It can be consumed fresh, dried or fried after dehulling. It can also be blended with sugar and usually have a milky flavor. It is also used as a paste in some local soups (Fariku et al., 2007). The oil is one of the most sought after because it contains unsaturated fatty acids and the colour vary from crystal clear to yellowish brown depending on the variety. It has excellent taste, very stability due to the presence of antioxidants such as sesamolin, Sesamine, and sesamol. It is odourless after refining and the characteristics are similar to olive oil (Weiss, 2000). It has several industrial applications that includes for the production of margarine, confections, canned sardine, corned beef, soap making and ink. (Sangha et.al, 2004, Sudhir et al., 1996; Betiku et al., 2012; Mohammed and Hamza, 2008; Njoku et al., 2009).

The oil is essentially a triglyceride and therefore, a possible feedstock for biodiesel production. Biodiesel is a form of mono alky ester of oil obtained from vegetable oil or animal fats (Knothe, 2005; Mittelbach et al., 2004; Srivastava, 2000). It is chemically simple, consisting of between six and nine fatty acid esters in the mixture. It is highly biodegradable, has agricultural source and renewable. It has inherent lubricating properties and wets the surface. The flash point is much higher than that of diesel and produces less harmful exhaust emissions. It is produced by the method of transesterification, which is the process of converting vegetable oil to esters using alcohol in the presence of a catalyst to chemically breakdown the molecules of the vegetable oil, remove glycerol from the triglycerides and replace them with radicals from the alcohol used. The reaction transforms the branched molecular structure of vegetable oil into a straight chain but smaller molecular structure, which is identical to but much longer than that of diesel fuel (Meher et al., 2006) and result in the formation of mono alkyl esters (Knothe, 2005; Mittelbach et al., 1985; Srivastava and Prasad, 2000).

Vegetable oils and animal fats are triglycerides made by living plants from fatty acids and glycerol. A triglyceride is a mixture of different glyceride esters of fatty acids in which each glycerol molecules has attached to it three molecules of long chain monocarboxyl (free fatty) acids as shown in Fig.1. Fatty acids consists of a long chain of carbon atoms with a carboxylic acid group at one end and are essential for energy storage in lipids while glycerol is a trihydric alcohol (containing three-OH hydroxyl group) that can combine with 1, 2 or 3 fatty acids to form monoglyceride, diglyceride and triglyceride respectively.

Author α: Department of Mechanical Engineering, The Federal University of Technology, Akure. Nigeria.
Author σ: Nigeria National Petroleum Company, Lagos. Nigeria.
e-mail: emmanuelbello111@yahoo.co.uk

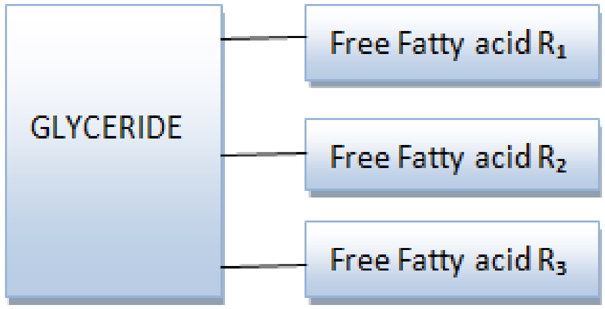

Fig.1 : Triglyceride Schematic

Transesterification is not a straight forward reaction as it occurs in a series of three reversible steps during, in which the triglyceride that consists of three fatty acid molecules attached to a glycerol backbone is first converted to diglyceride that contains two fatty acids and then to monoglyceride which contains only one molecule of fatty acid methyl ester (FAME). During the process, the reactions may not be complete and the triglycerides in the oil may still contain 3, 2 or 1 glycerol molecule(s) that have not been released. Such glyceride are said to be bounded glycerol. The sequence of deglyceriding is shown in Equations 1-3. (Schwab et al., 1997; Freedman et al., 1986; Ferella et al., 2009; Schuchardt et al., 1998).

$$\text{Triglyceride} + CH_3OH \leftrightarrow \text{Diglyceride} + \text{FAME} \quad (1)$$

$$\text{Diglyceride} + CH_3OH \leftrightarrow \text{Monoglyceride} + \text{FAME} \quad (2)$$

$$\text{Monoglyceride} + CH_3OH \leftrightarrow \text{Glycerol} + \text{FAME} \quad (3)$$

MGE is the most stable intermediate compound (Ma and Hanna, 1999) and the most important determinant of the completeness of the reaction.

The glycerol is bounded if it has not been freed from the fatty acids.

$$\text{Total glycerol} = \text{bounded glycerol} + \text{free glycerol} \quad (4)$$

As a result of incomplete reactions, small amounts of monoglyceride, diglyceride and triglyceride will remain in the biodiesel even after washing along with other impurities. They can affect the properties of the biodiesel if not limited.

For example, fatty acids are very volatile while the glycerol they are attached to has high boiling point and is more viscous. This suppresses the volatility of triglycerides, which increases the viscosity of plant oils to within the range 45 - 32 mm^2/s.

If the glycerol level in a fuel is high, because of it high viscosity, some of its contents will settle out in the fuel tank to form very viscous mixture, which can attract solid particles, increase the viscosity of the fuel and may cause blockage of filter and consequently restrict fuel flow. Such fuels are prone to coking and may thus cause the formation of deposits on injector nozzle, piston and valves that can affect fuel economy.

The concentration of each compound depends on the completion of the transesterification process. Total glycerol affects storage stability which is a measure of how well the quality of the fuel will be maintained in storage when in contact with air or water.

II. Materials and Methods

a) Oil extraction

The oil was extracted in a soxhlet extractor using n-hexane as solvent. It gave an oil yield of 48 %. This method is superior to the traditional method of oil extraction that involves grinding to flour and treating with hot water to cream out the oil. This method is slow, the yield is low and the oil produced has unpleasant odour and bitter taste (NCIR, 2002; UNIFEM, 1987; Igbo et al., 2005).

b) Fatty Acid Profile

The fatty acid profile and glyceride contents of the samples were determined using the HP 6890 Gas Chromatography analyzer equipped with a Flame Ionization Detector (FID) and HP INNOwax column (30 m x 0.25 cm x 0.20 μm film thicknesses). The carrier gas was nitrogen and the initial temperature of the oven was set at 60° C. The procedure was as reported by Bello and Otu (2012) in which the first ramping was at 10° C/m for 20 minutes and maintained for 4 minutes. The second ramping was at 15° C/min for 4 minutes and maintained for 10 minutes. The detector temperature was 320°C while hydrogen and compressed air pressures were 22 and 35 psi respectively.

c) Characterization

The oil. B100, B20 and B10 were characterized according to ASTM protocols for biodiesel.

III. Results and Discussion

The experiment was designed to monitor the concentrations of TGE, DGE and MGE in the oil, and B100 when the fatty acid profiles are being determined.

a) Concentration of TGE, DGE and MGE oil

The variation of TGE, DGE and MGE in the oil is shown in Fig.1. The oil as expected has a large concentration of TGE. DGE and MGE are intermediate compounds and are in very low concentration because no transesterification reaction that would have produced them had taken place. The highest concentration of TGE monitored was 20 000 x 10-3 mg/100g. The oil is fairly stable and contains 0.513% free glycerin.

b) Concentration of TGE, DGE and MGE in B100

Concentration of TGE, DGE and MGE in B100 is shown in Figure 2. It contains very low concentration of DGE and TGE that remained after the transesterification process. The low concentration of these compounds attests to the completeness of the transesterification reaction. The highest concentration was 0.012 mg/100g.

c) Concentration of TGE, DGE and MGE in B20

B20 contains TGE, DGE and MGE. The dorminat ones are DGE and TGE. The highest concentration is 0.007 mg/100g of DGE. As shown in Figure 3.

d) Concentration of TGE, DGE and MGE in B10

As can be seen in figure 4,TGE, DGE and MGE are present in the fuel but DGE has the highest concentration of 0.005 mg/100g. The composition of B10 and B20 are not very different.

e) Variation of TGE concentration

The variation of TGE in the 4 samples is shown in Fig. 5. The concentration is highest in the oil and only very little concentration in the other samples. The highest concentration in the oil is 20 000 x 10-3 mg/100g. The concentration decreased with time because it is an intermediate compound and peaked after 18 minutes.

f) Concentration of MGE

MGE concentration varies as shown in figure 6. It has the highest concentration in the oil of 70 x 10-3 mg/100g. The concentration of other samples is very low.

In general, triglyceride is dominant in the oil and reduced after transesterification due to removal of the fatty acids for conversion to biodiesel. Diglyceride and monoglyceride which are intermediate compounds are only present in the oil in significant amount. They are unstable compounds and easily react with air to form solid compounds in the form of sediments and gum, which can disrupt the effectiveness of fuel filters, fuel pump and injection systems. It can also cause abrasive substances to be embedded in them that can increase engine wear.

g) Physico-chemical properties of Oil and B100

The result of the characterization is shown in table 2.

Table 2 : Properties of Beniseed Oil and B100

Property	Oil	B100
Flash point (ºC)	218	165
Kinematic Viscosity (mm^2/s at 40ºC)	32.00	4.02
Lower heating value (MJ/kg)	38.20	39.90
Cetane number	50.88	58.80
Iodine value (g/100g)	108	88.20
Peroxide value (meq/kg)	0.49	0.54
Oxidation index (hrs)	18	12
Free fatty acid (%)	0.75	0.12
Acid value (mgKOH/g)	0.50	0.27
Saponification value (mgKOH/g)	190	135.6
Free Glyceride (%)	0.513	0.038

Flash points are higher than the 55oC of diesel and the oil has a flash point of 218oC which is primarily TGE.

The oil, because it is a TGE has a kinematic viscosity of 32 mm2/s and reduced to within the limits for biodiesel after transesterification and blending.

The heating values for the oil are within the range for common vegetable oils of 38 - 42 MJ/kg.

The cetane number of 50.88 for the oil is above that of diesel fuel making it a suitable fuel for diesel engine even without transesterification.

The iodine value of the oil of 108.00 makes it a semi – drying oil suitable for the production of surface coatings, decorative paints, varnishes, printing inks etc. The value for the biodiesel of 80 will not allow for high formation of carbon deposits in the engine.

Peroxide value measures the content of hydroperoxides in the oil and its low value indicates high resistance to oxidation. The value of 0.49 for the oil is low as should lead to long shelf life for the oil.

The oil is the most stable because of the TGE content and has an oxidation index of 18 hours while the B100 has a lower value of 12 hours. (Arisoy, 2008)

The low acid value (0.5 mg KOH/g oil) of the seed oil showed that it is not only edible but could also have a long shelf life. It can also be converted to biodiesel directly without pretreatment.

The high saponification value of 190.00 mg of KOH/g for the oil confirms it suitability as feedstock for the manufacture of soap and detergents.

The free glycerol contents of the oil and B100 are 0.513, 0.038% respectively. The free glycerol decreased after transesterification. The total glycerol after transesterification is below the ASTM D 6751 and EN 14214 maximum limits. Total glycerol affects storage stability which is a measure of how well the quality of the fuel will be maintained in storage when in contact with air or water.

h) Fatty Acid Profile

The fatty acid profile of Beniseed oil and B100 is shown in table 3.

Table 3 : Fatty Acid Profile of Beniseed oil and B100 (% wt)

Fatty Acid	Form	Oil	B100	Change(%)
Palmitic	C16:0	8.83	8.690	1.5
Palmitoleic	C16:1	0.056	0.0319	43.2
Stearic	C18.0	6.236	6.418	6.4
Oleic	C18:1	38.07	37.770	-0.79
Linoleic	C18:2	45.76	46.526	1.6
Linolenic	C18:3	0.062	0.0335	-45
Arachidic	C20:0	0.067	0.0360	-46.2
Behenic	C22:0	0.911	0.495	-45.7
Saturation	-	16.043	15.639	-2.5
Unsaturation	-	83.948	84.461	- 0.06

The oil is 83.948% unsaturated and does not contain any triple bond, which is responsible for the excellent shelf life. It contains mostly the oleic series of fatty acids of which oleic acid constitutes 38.07%. For industrial scale production, it will be necessary to pretreat the oil to convert some of the fatty acids to esters so that it will not inhibit biodiesel yield during transesterification.

IV. Conclusions

The banished oil and biodiesel have good fuel properties and can be blended with diesel fuel in any proportion. It has a cetane index of 57 which is one of the highest for vegetable oils. The oil is 83% saturated and has an iodine value of 108. From the results obtained, it can be used as alternative fuel for diesel engines. The complexness of the transesterification was confirmed by the low concentration of DGE and TGE.

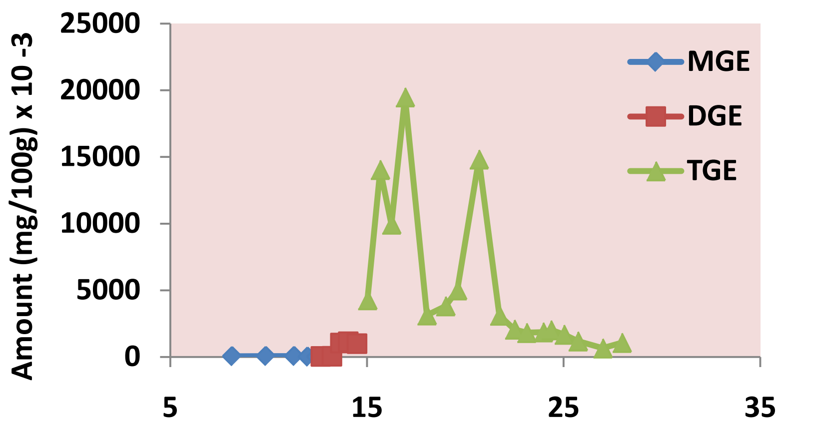

Fig. 1 : Glycerine analysis of Beniseed oil

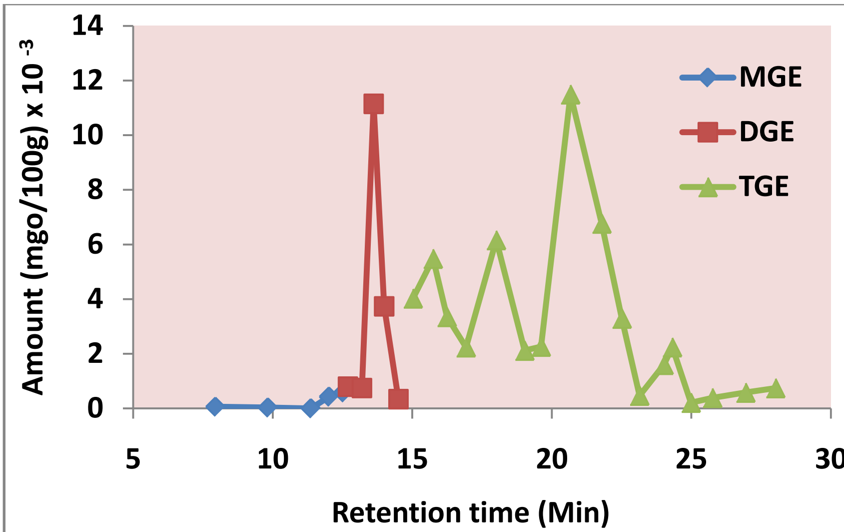

Fig. 2 : Glycerine analysis of Beniseed B100.

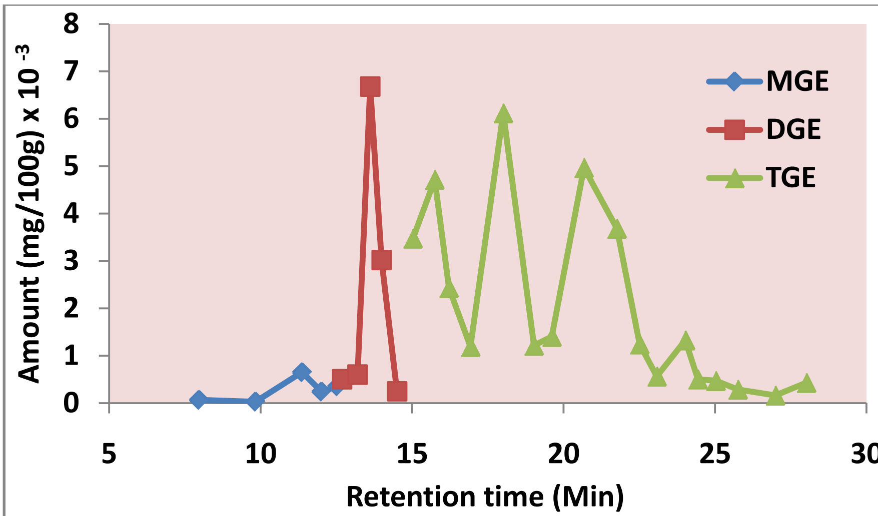

Fig.3 : Glycerine analysis for Beniseed B20

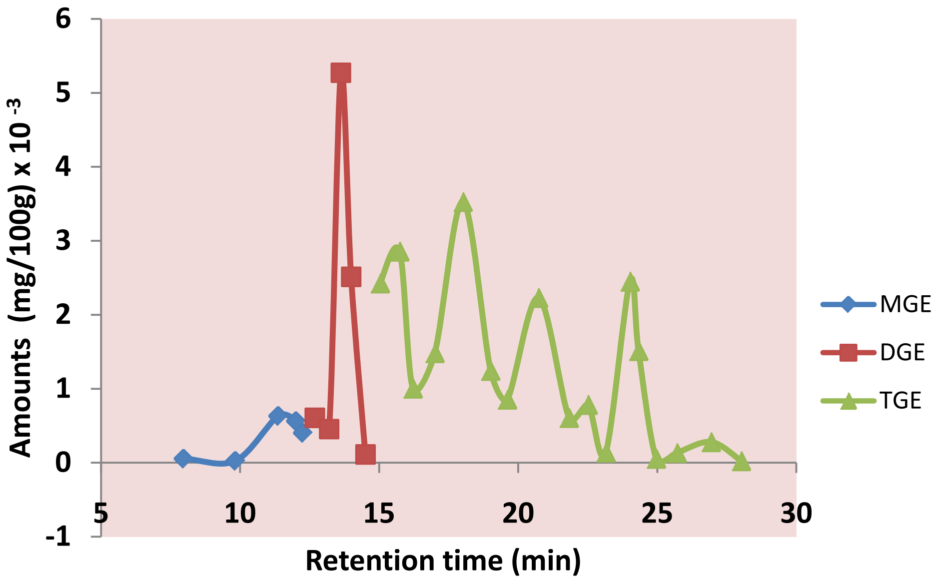

Fig. 4 : Glycerine Analysis of Beniseed oil B10

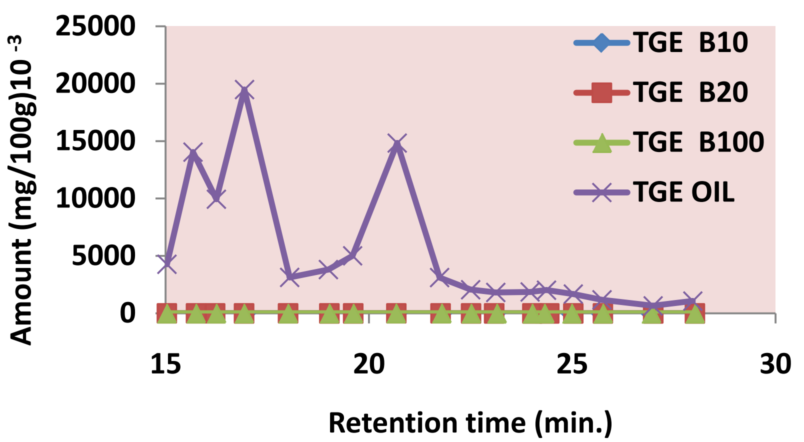

Fig. 5 : Variation of TGE in the samples

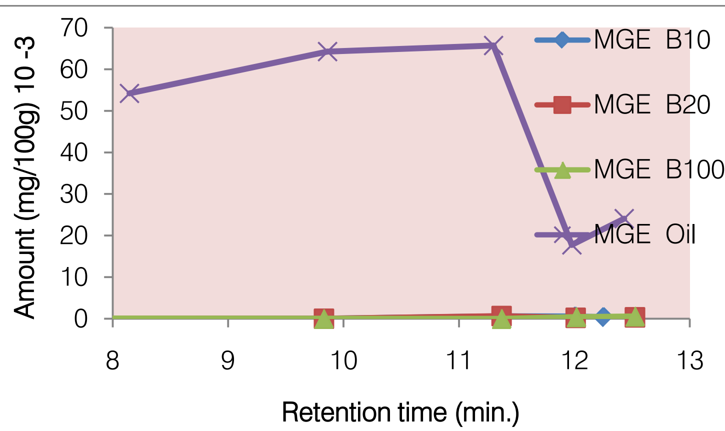

Fig. 6 : Variation of MGE in the samples

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