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Methanol and glyceride contents of Egunsi melon oil, its biodiesel and blends with diesel fuel

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Biodiesel is gradually being accepted worldwide as suitable alternative fuel for diesel engine. Rigorous purification is however required to meet the American Society for Testing and Materials (ASTM) and European Union (EU) standards for biodiesel because of unfavorable properties and the multitude of feed stocks with different properties that can be used. Two of such impurities that must be kept within limits are methanol and glyceride. Egunsi melon oil selected for the study was transesterified using sodium hydroxide as catalyst and methanol as reagent and then washed with distilled water. The fatty acid profile, the amount of methanol and glyceride in the oil, (B100) 100% biodiesel and, B10 (10% biodiesel blend with 90% diesel) and B20 (20% biodiesel blend with 80% diesel) were measured by Gas chromatography equipped with flame ionization detector. They were also characterized to determine their suitability for use in diesel engine. The triglycerides, free and total glyceride content of the oil are all outside the limits, while those of B100, B10, and B20 are within the limits. The measured fuel properties are also within the limits, hence egunsi melon oil biodiesel and blends can be used as alternative fuel for diesel engines without major modifications.

Key words: Egunsi melon oil, biodiesel, blends, methanol, glyceride.

INTRODUCTION

Diesel fuel is extensively used to power diesel engines on trucks, marine vessels, electrical power generating sets and earth moving equipments. The source of the crude oil is fast depleting and it has adverse effects on the environment because of harmful exhaust emissions, noise pollution and environmental degradation. The search for alternative fuels has been focused on vegetable oils but the use is handicapped by the high viscosity and poor cold flow characteristics. To overcome these problems, the viscosity is normally reduced by blending (Bello and Makanju, 2011) or transesterification (Doranto et al., 2009, Canakci and Van Gerpen, 1999). The more common method is by transesterification to biodiesel which also improve properties such as cetane number, viscosity, and oxidative stability (Bello and Makanju, 2011) to the limit required for a standard diesel engine operation. Biodiesel has been described as the mono alkyl ester of vegetable oil or animal fats (Knothe, 2005; NBB, 1997).

Biodiesel is chemically simple, consisting of six to nine fatty acid esters and has similar physical properties to diesel fuel. It also has higher cetane number than diesel fuel which allows it to be used as substitute fuel in diesel engines without major modifications. Biodiesel is carbon neutral, as oil yielding plant absorbs more carbon dioxide than that added to the atmosphere when used as fuel

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(Antolin et al., 2002; Hoekman et al., 2012; Lang et al., 2001; lin et al., 2009; Vincente et al., 2004). It is also highly biodegradable, environment friendly and non toxic (Makareviciene and Janulis, 2003; Focke et al., 2012; Pinto et al., 2005).

Transesterification 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. It has also been defined as the displacement of ester by another ester (Otera, 1993). 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).

Transesterification is not a straight forward reaction as it occurs in a series of three reversible steps during, 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 bound glycerol. The sequence of deglyceriding is shown in Equations 1-3. (Schwab et al., 1997; Freedman et al., 1986; Ferella et al., 2009).

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

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

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

Triglyceride or triacylglycerol (TAG) has three fatty acid molecules attached to the glycerol backbone and it is fairly stable. Diglyceride or diacylglycerol (DAG) , has two fatty acids radicals and exists in the 1,2 form and the 1,3 form depending on how the fatty acids are attached to the glycerol molecule and monoglyceride or monoacylglycerol (MAG), has only one fatty acid radical per molecule of glycerol (Schuchardt et al., 1998). It is the most stable intermediate compound (Ma and Hanna, 1999) and the most important determinant of the rate of reaction.

The glycerol is bonded if it has not been freed from the fatty acids. Glycerol is a trihydric alcohol (containing three-OH hydroxyl group) that can combine with up to three fatty acids to form monoglyceride, diglyceride and triglyceride depending on the number of fatty acids combined.

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

Due to incomplete reactions, small amounts of monoglyceride, diglyceride and triglyceride will remain in the biodiesel during the settling process along with other impurities. They can affect the properties of the biodiesel if not removed. For example, fatty acids are as volatile as diesel while the glyceride they are attached to have high boiling point and suppresses the volatility which make plant oils viscous.

Egunsi melon oil selected for this study belongs to the cucurbitaceous plant family made up of over 750 genre and 750 species (Giwa et al., 2010). It is a crawling crop that is widely grown in tropical Africa for its seeds which is processed by deshelling, drying and grinding into a paste that is added to vegetable soup to confer aroma, improve taste and to thickening. It has an oil content of about 50% and protein of 30% (Achu et al., 2005). It is usually intercropped with standing crops like maize and corn to suppress weeds. The oil content is the main attraction for possible use as source of oil but it is also self sustaining as it is widely grown in several West African countries (Bello and Makanju, 2011).

MATERIALS AND METHODS

The methanol, sodium dioxide, sodium sulphate and distilled water used for the experiments were of analytical grade and purchased from Finlab Laboratory, in Akure, Nigeria. The equipment used are soxhlet extractor, Gas chromatography equipped with Flame Infrared Detector, biodiesel reactor, separating funnel, blending cylinder with heater and magnetic stirrer. The fuel properties and standards used for the characterization are listed in Table 1.

Oil extraction

For the purpose of this study, Egunsi melon seeds were planted in a garden and harvested 4 months later. No fertilizer was used and it was not irrigated either. The fleshy gourds were harvested and soaked in water for two weeks to allow loosening of the fleshy contents, such that the seeds will fall off and be easily collected. The seeds were dried in the sun at an average measured ambient temperature of 35°C for 5 days and then deshelled in a machine built for this purpose. The deshelled seeds were dried further in the sun to reduce the moisture content to 8%. The oil was extracted by soxhlet extractor using n-hexane as solvent and operated at 60°C. The oil was leached for 8 h while the mantle heater was set at 60°C. The residual n-hexane in the oil was removed using a vacuum rotary evaporator operated at 75°C.

The Free Fatty Acids (% oleic acid) content of the oil was first measured to determine if pretreatment was necessary before alkaline transesterification, as it has been reported that too high acid content during alkaline transesterification can react with the catalyst to form soap which can inhibit biodiesel yield (Ramadhas et al., 2009). This was found to be 0.12%, which was lower than the 3 % baseline often reported (Ramadhas et al., 2009; Sahoo et al., 2007; Ghadge and Raheman, 2006), hence no pretreatment was necessary.

Transesterification and blending procedures

Transesterification was carried out using a laboratory scale biodiesel reactor in the Chemistry Laboratory of the Federal University of Technology, Akure. The anhydrous methanol was

Table 1. Biodiesel properties and test methods.

Property	Unit	Protocol	ASTM Limits D6751	EN Limits 14214
Density at 15°C	kg/m^2	ASTM D1298	860-900	860-900
Pour point	°C	ASTM 2500	-	-
Cloud point	°C	ASTM2500	-	-
Flash point	°C	ASTM D93	130 min	120 min
Kinematic viscosity	mm^2/s at 40°C	ASTM D445	1.9-6.0	3.5-5.0
Lower heating value	kJ/kg	ASTM D240	-	-
Cetane index	-	ASTM D613	47 min	-
Iodine value	g/100 g	EN14111	120	-
Peroxide value	meq/kg	EN14111	-	-
Oxidation index	Hours	ASTM D2709	3 min	6 min
Saponification value	mg KOH/g of oil	EN14111	-	120 max

mixed with 0.9 % w/w of sodium hydroxide as catalyst and the mixture mixed with the oil at an excess molar ratio of 6:1 instead of the stoichiometric ratio of 3:1, to shift the reversible reaction to the product side to increase the yield and allow its phase separation from the glycerol to be formed (Keera et al., 2010). The reactor was stirred at 600 rpm and at a constant temperature of 60° C for 60 m after which the mixture was poured into a decanter and allowed to settle for 3 h so that the reaction can be driven to completion and for the mixture to separate into biodiesel and denser glycerol at the bottom to be drained off by gravity.

The excess methanol in the ester was removed in a flash evaporator. The biodiesel was then washed by mixing with distilled water at a volume ratio of 3:1 and stirred gently. This was done three times until it became clear (Dorado et al., 2002) thus indicating that most of the unreacted oil components (monoglyceride, diglyceride and triglyceride), sulfur, trace metals, catalyst, salts and pigmentation in the biodiesel had been removed. The mixture was allowed to settle for 30 m for the pure biodiesel and the impurities at the top to be separated. Finally, the biodiesel was heated to 110° C for any water in it to evaporate and then dried by passing over anhydrous Na_2SO_4 to remove any water still present. Blending was done at a temperature of 25° C well above the cloud points of both contents and in a stainless steel vessel to prevent degenerating reactions associated with the use of vessels made from brass, bronze, copper, lead, tin and zinc.

Characterization

The main properties of the oil, its biodiesel and blends were measured using mainly the American Society for Testing and Materials and European Union EN protocols for biodiesel fuels as shown in Table 1. The flash point was determined in a Pensky-Marten closed flash tester (Kehler-model K-16270), cloud point was determined using a high precision cloud point meter while the kinematic viscosity was by glass capillary viscometer. For the heating value, the microprocessor controlled Isoperil oxygen bomb calorimeter model 6200 was used.

The vacuum distillation temperature was determined according to the ASTM D1160 Method using the reduced pressure advanced distillation curve apparatus, which consists of a distillation unit and a vacuum pump. The distillation pressure was set between 1 kN/m^2 and 83 kN/m^2 and the uncertainty for each measurement was less than 1° C. The distillation temperatures were set to correspond to 50 % of the biodiesel distilled and condensed. The cetane index of the biodiesel was calculated by the following formula (Willard, 1997):

$$CI = -420.34 + 0.016G^2 + 0.192G(logT_{50}) + 65.01(logT_{50})^2 - 0.0001809T_{50}^2$$

Where G is the API (American Petroleum Institute) specific gravity and T_{50} is the distillation temperature at 50 % volume fuel sample distilled and condensed in a unit of °F. Other properties are as shown in Table 1.

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 Agge (2011).

RESULTS AND DISCUSSION

Table 2 shows the fatty acid profiles of the oil, B100 and B20. The oil contained mainly 62.35% linoleic, 13.23% oleic, 12.88% palmitic acids and was 78.90% unsaturated. The profile for B100 and B20 followed the same trend and the results obtained are similar to those obtained by Giwa et al. (2010) that are superimposed on Table 3.

The fatty acid profile of biodiesel has strong influence on properties such as cetane number and cloud point (Knothe, 2005; Ramadhas et al., 2009; Freedman and Bagby, 1987). Since linoleic is the dominant acid, the property of the biodiesel is dictated by it. Blending has very little effect on the proportion of the fatty acids presents. The methanol and glycerides contents are shown in Table 3. The methanol content in Egunsi melon seed oil is 0.02% and below the maximum allowed by EN 14214. It however, increased to 0.104% after transesterification due to residual methanol that escaped the settling and washing processes but decreased with blending. The amount of methanol in B100 depends on the molar ratio and the effectiveness of the washing process. Specification of methanol value can lower flash

Table 2. Fatty acid profile of Egunsi melon seed oil, B100 and B20.

Fatty acid	Form	Egunsi melon seed oil	Egunsi melon seed oil B100	B20	*Egunsi melon seed oil B100
Lauric	C12:0	-	0.79	0.78	-
Myristic	C14:0	-	0.88	0.87	-
Palmitic	C16:0	12.88	10.27	10.23	11.49
Palmioleic	C16:1	0.74	0.96	0.95	0.06
Stearic	C18:0	6.70	10.36	10.32	9.72
Oleic	C18:1	13.23	12.84	13.67	17.95
Linoleic	C18:2	62.35	62.46	62.22	61.41
Linolenic	C18:3	2.42	1.44	0.94	0.23
Total Unsaturation		78.90	77.90	77.78	79.65

*Giwa et al. (2010).

Table 3. Methanol and glyceride contents of Egunsi melon oil.

Property (% mol/mol)	Egunsi melon seed oil	Egunsi melon seed oil			Limits	
		B100	B10	B20	ASTM D6751	EN 14214
Methanol content	0.002	0.104	0.023	0.01	0.03	0.020
Triglyceride	98.837	0.004	0.006	0.004		0.20
Monoglyceride	0.001	0.168	0.038	0.019		0.08
Diglyceride	0.001	0.009	0.003	0.002		0.20
Free glycerol	0.982	0.013	0.004	0.003	0.020 max	0.020
Bound glycerol	98.839	0.181	0.047	0.025		
Total glycerol	99.821	0.194	0.051	0.028	0.240	0.25

point and result in excessive evaporation, high vapour pressure in the fuel system and anhydration.

The triglyceride in the oil reduced after transesterification due to conversion of the fatty acids to biodiesel while the monoglyceride and diglyceride increased because they are intermediate compounds. High levels of diglyceride and monoglyceride, which are unstable when exposed to the air can lead to the formation of gums and sediments, which can cause filter plugging, increase combustion chamber deposits, and gumming of the injection systems components, as well as increased engine wear.

The bound and free glycerol decreased after transesterification and decreased further with blending. If the glycerol level in a fuel is high, some of its contents will settle out in the storage tank to form very viscous mixture, which can affect fuel flow 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 total glycerol after transesterification and blending is below the ASTM D 6751 and EN 14214 maximum limits. The concentration of each form depends on the completion of the transesterification process. Total glycerol affects storage stability which is a measure by how well the quality of the fuel will be maintained in storage when in contact with air or water.

Table 4 shows the characterization results. The pour points are at sub-zero degrees while the cloud points are just above zero which are lower than those of diesel and hence limits their use in cold regions. Flash point reduced after transesterification but decreases with increasing amount of diesel in the blend due to the diluting effects of diesel that has lower flash point (Ertan and Canakci, 2001). The kinematic viscosity of the oil was 37.05 mm^2/s and reduced to within the limits for biodiesel after transesterification and blending. Viscosity affects fuel atomization, spread and penetration of injected fuel, and fuel burning efficiency. Hoekman et al. 2012 reported that the higher viscosity of biodiesel can lead to inferior atomization and spray, resulting in a larger mean liquid droplet diameter and a longer ignition delay. The heating value did not change much after transesterification but increased with blending due to the higher heating value of diesel.

Biodiesels usually have heating value of 10% lower than that of diesel because of the oxygen content which

Table 4. Properties of EMS Oil, its biodiesel and blends with diesel Fuel.

Property	Egunsi melon seed oil	Egunsi melon seed oil B100	B20	B10
Density (kg/m$^{2)}$	912	885	859	856
Pour point (°C)	15	-4	-1	0
Cloud point (°C)	23	1	3	2
Flash point (°C)	172	144	93	84
Kinematic viscosity (mm^2/s at 40 °C)	32.31	3.85	2.88	2.77
Lower heating value (kJ/kg)	37.05	37.10	42.10	42,75
Cetane index	47.65	55.20	46.89	45.85
Iodine value (gI_2/100g)	115.23	103.55	27.41	18.27
Peroxide value (meq/kg)	18	19.70	16	15.30
Oxidation index (Hrs)	15	7	14	25
Saponification value (mg KOH/g of oil)	203.36	210.38	169.70	165.70
Distillation temperature T_{50} °C	337	335	275	270

has low heating value and occupies about 10% of the total volume. The cetane index increased as usual after transesterification but reduces with increasing amount of diesel in the blend because of the lower cetane number of diesel. Iodine value of the oil was 115.23 gI_2/100g of which triglyceride was the major component and the value decreased after transesterification and with increasing proportion of diesel. Peroxide value increased after transesterification and decreased with increasing amount of diesel in the blending.

The oxidation index of the oil was 15 h which can be attributed to triglyceride which is naturally occurring. The oxidation index for B100 was 7 h and increased with the amount of diesel in the blend. The saponification value increased from 203.36 mgKOH/g to 210.38 mg KOH/g after transesterification because of the effect of alkaline catalyst used, but reduced with blending as diesel does not contain saponifying catalyst.

The distillation temperature T_{50} of the oil and B100 differs by 2°C but reduced to 275 °C and 270 °C for the B20 and B10 respectively, because diesel contains much heavier components.

Conclusion

Egunsi melon oil has 78.90% saturation and the major constituent is 62.35 % linoloic acid. After transesterification, the triglyceride of the oil reduced from 98.83 % to 0.004 % for B100. The free, bound and total glycerol values are within the ASTM limits.

The physico-chemical properties of the fuel are similar to those of diesel fuel thus confirming that it can be used in diesel engine with little modification. The properties of blendings tend toward those of diesel as the proportion of diesel increases.

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