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Fatty Acid Methyl Esters of Melon Seed Oil: Characterisation for Potential Diesel Fuel Application

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Abstract

Fatty acid methyl esters (FAME), biodiesel, are alternative diesel fuels usually obtained from renewable sources, mainly, vegetable and animal oils through transesterification among other processes. Melon seed oil was extracted from melon seeds bought from a local market, degummed and alkali refined using standard methods. FAME of the oil was produced using methanol in the molar ration of 1:6, 1% sodium hydroxide catalyst at the reaction temperature of 60°C for the duration of 1h. Results obtained showed that the fatty acid methyl esters had a specific gravity of 0.8786, viscosity of 6.24 centistokes, pH of 7.23, heating value of 36.34 J/g and flash point of 148°C. The FAME yield was 87.35% under the reaction conditions that applied. The infrared spectra of both the refined oil and the methyl esters from it, showed peaks at 1721.3cm^{-1} and 1167.8cm^{-1} (C=O and C-O stretches large and medium absorbance's) for oils and methyl esters. Generally, the fuel properties of the FAME compared with values obtained under the same conditions for conventional petroleum diesel that was sourced from a retail outlet;

suggesting that biodiesel from MSO could be used alone or in blends with petrodiesel to power compression ignition (diesel) engines.

Keywords

Fatty acid methyl esters; Biodiesel; Melon seed oil; Transesterification; Flash point.

Introduction

The ever-increasing population of both the developing and developed nations of the world and the consequent increase in their diesel consumption and the non-renewability of diesel source (petroleum), as well as the adverse environmental effects of diesel burning are some of the factors that has made alternatives to petroleum diesel very attractive [1-3]. The air pollution occasioned by diesel use has been identified to be one of the reasons for climatic changes that result in frequent heavy rains, hurricanes and floods that threaten lives and properties [4]. Biodiesel life cycle analysis showed 78% reduction in CO_2 (greenhouse gas) emissions relative to petrodiesel [5]. The unpredictable price fluctuations of crude oil in the international market have also been a major source of concern in total dependence on diesel fuel. Report by Rudolf Diesel in 1900 showed that vegetable oils could be used as diesel fuel [6]. The very low cost of petroleum at the time of this proposal by Rudolf did not help the development of triglycerides as diesel substitute. The direct use of vegetable and animal oils and/or oil blends was found to be unsatisfactory and impractical for both direct-injection and indirect type diesel engines. This is as a result of the high viscosity (10 times greater than diesel), acid composition, and free fatty acid content of such oils, as well as gum formation due to oxidation and polymerization during storage and combustion, carbon deposits, lubricating oil thickening and poor cold engine start-up fuel atomization [3, 7-10]. A number of measures have been adopted to solve the above problems of straight-run vegetable oil in its use as diesel fuel. These are dilution of diesel fuel with vegetable oil [11-13] and pyrolysis of vegetable oil in the presence of air or nitrogen to yield hydrocarbons suitable as diesel [13,14]. Also, microemulsification to give isotropic, clear or translucent thermodynamically stable dispersions of oil, water, a surfactant/cosurfactant microemulsion [10, 15,16] and transesterification involving the displacement of an alcohol (glycerol) by another alcohol in a process similar to hydrolysis with water [7] are some other methods.

Jatropha [1], palm kernel and coconut [3], Cynara cardunculus L [8], soap nut and jatropha [17], palm, palm kernel and ground palm oils [18], soybean [19], and waste vegetable oils [20], have been transesterified and characterized for biodiesel use. Various esters ranging from methyl, ethyl, propyl to butyl esters have been produced from the oils using different reaction conditions. Efforts are still on in various laboratories to identify more vegetable oils that could be used as sources of biodiesel in many countries.

Transesterification process is a set of three consecutive chemical reactions between esters generally and mainly triglycerides and simple alcohols. The reaction is usually very slow to be of any industrial value and as such catalysts, which can be acidic, basic, organic or enzymatic, are usually used to achieve reasonable conversion at short time. Also, since the reaction is reversible as 1 mole of the triglyceride reacts with 3 moles of the alcohol, as shown in Figure 1, removal of one of the products or an increase in the mole ratio of one of the reactants can be used to drive the reaction to the right (alkyl ester formation).

Usually, the methanol to oil/triglyceride mole ratio is made greater than 3:1; 6:1 and above for most oils [2, 8, 21].

$$\begin{array}{lllll} CH_2COOR_1 & & & CH_3COOR_1 & CH_2{-}OH \\ | & & & & | \\ CHCOOR_2 & + 3CH_3OH & \xrightarrow[\Delta]{NaOH} & CH_3COOR_2 & + CH{-}OH \\ | & & & & | \\ CH_2COOR_3 & & & CH_3COOR_3 & CH_2{-}OH \end{array}$$

Figure 1. *Typical Transesterification Reaction Equation*

In this paper, we report a work carried out with melon seed oil which has been identified elsewhere [22] as possible industrial oil and proposals made as to how it could be produced to meet both the domestic and industrial needs like the case of soybean oil. Fuel properties of the fatty acid methyl esters obtained from the oil were determined and compared with that of conventional petroleum derived diesel fuel.

Materials and Methods

Melon seeds were bought from Ogige market in Nsukka-Nigeria, ground and extracted with 60-80°C boiling range petroleum ether and the solvent recovered using a rotary evaporator. The oil was degummed to remove phosphatides, alkali-refined to get rid of the free fatty acids, and heated to, and held at 105°C for 30 min. to expel moisture. The acid, saponification and iodine values of the freshly extracted oil were determined using ASTM methods. Methanol was a product of Merk, Darmstadt, Germany and is of 99.7% purity, while the sodium hydroxide was a product of Loba Chemie GmbH Switzerland. All other regents were of analytical grade unless otherwise stated.

Preparation of Sodium Methoxide

0.35g of NaOH was added with care into a beaker containing 40cm^3 of methanol, and stirred vigorously until the NaOH dissolved completely to form sodium methoxide. The solution was heated to 60°C and held at that temperature.

Production and Purification of Biodiesel

The transesterification reaction was carried out in a three-necked 500ml round bottom flask equipped with a thermometer, condenser and stirrer. 100ml of melon seed oil was put in the flask and heated to 60°C. The catalyst solution also at 60°C was gradually introduced into the flask containing the oil. The temperature of the system was maintained at 65±2°C for 1h with the stirrer operating at 150rpm [8].

At the end of 1h the reaction was assumed to have reached completion [8] and immersing the flask in a cold water bath was applied to quench the reaction. The method of Ikwuagwu et al [23] was used to separate the biodiesel (upper layer) from the glycerol (lower layer) using a separating funnel. The biodiesel was washed with about 15% by weight of warm distilled water and about 5% $NaHCO_3$ three times to a neutral pH to remove the catalyst, glycerol and other impurities. Rotary evaporator was used to recover completely the excess methanol in the biodiesel at the boiling temperature (67°C) of methanol. The moisture remaining in the product was removed with anhydrous Na_2SO_4 which was subsequently filtered off and the product dried at 105°C for 10 min, cooled and weighed. The glycerol was also purified according to the methods of De Filippis et al [24]. The above experiments were performed in duplicate and the average values obtained.

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Characterization of the Biodiesel Produced

The biodiesel produced was characterized for its absolute viscosity using Ferranti portable viscometer model VL, refractive index using Abbe refractometer, specific gravity using specific gravity bottle, flash point using a cup adapted to serve as the Pensky-Martens flash point cup, pH using a consort pH meter model P 107 and the heat of combustion using Hewlett Adiabatic Bomb Calorimeter model 1242. The colour of the product was determined by virtual means and the density by using density bottle. Fourier Transform Infrared (FTIR) spectra of the refined oil as well as the biodiesel produced were run to confirm the methyl esters in the products. The physicochemical properties determined for the raw, refined and FAME of the MSO was determined, also in duplicates, for conventional petroleum diesel obtained from a commercial depot at Nsukka.

Results and Discussion

The FTIR spectra of the refined oil and biodiesel both showed peaks at 1721.3cm^{-1} and 1167.8cm-1 similar to that reported in the literature [25], indicating that the carbonyl (C=O) and C-O in the oil is retained in the methyl esters. These mid-infrared region peaks were absent in petrodiesel and their presence have been used [26] to confirm cases of adulteration in petrodiesel.

The properties of the raw and refined oils are shown in Table 1. From the table, the viscosities of the raw and refined oils are 33.29 and 31.02 mms^{-1}, respectively. These viscosity values are lower than the 49.9 and 37.06 mm^{2}s^{-1} reported for soybean oil [19] and by far larger than the 1-6 mm^{2}s^{-1} recommended for biodiesel by ASTM, and 3.5 –5.0 mm^{2}s^{-1} recommended by BIS standard [27].

Table 1. Some physicochemical properties of raw and refined MSO

Properties	**Raw Oil**	**Refined Oil**
Colour	Golden yellow	Golden yellow
Specific Gravity	0.9138	0.9013
Viscosity (mm^{2}s^{-1})	33.29	31.02
Iodine value (mgI/g sample)	121.8	119.29
Acid value (mgKOH/g)	2.08	0.93
Saponification value	192.5	191.6
Flash Point (°C)	186	181
Heat of Combustion (kJ/g)	38.74	38.43

The high viscosity of the triglycerides is a major contributing factor to the onset and severity of durability problems when using vegetable oils directly in diesel engines [28].

The acid value was significantly reduced in the refined oil to 0.93. The viscosity of the biodiesel produced at 27°C, as shown in Table 2, was 6.24mm^{2}s^{-1} while that of petrodiesel was 4.43mm^{2}s^{-1}. The 6.24mm^{2}s^{-1} reported in this work for biodiesel is within the limit recommended at 40°C for biodiesel and the 4.43 mm^{2}s^{-1} for the commercial petrodiesel similar to 1.3 to 2.1mm^{2}s^{-1} (at 40°C) that of low sulphur grade petrodiesel reported by Peterson et al [29] for eight biodiesel fuels from vegetable oils. Values as high as 6.8 and 6.7mm^{2}s^{-1} have been reported for cotton seed and rapeseed methyl esters at 21 and 40°C respectively [28]. The value also is a remarkable reduction to that of the refined oil and will give good atomization in diesel engines.

The heat of combustion of 38.34 reported for MSO biodiesel is not significantly lower than that of the refined MSO, though it is lower than 42.89 obtained for the control, petrodiesel. It is also lower than 39.8 kJ/kg reported for sunflower and soybean [28].

Table 2. Fuel properties of the MSO-Biodiesel and commercial petrodiesel

Properties	**MSO-Biodiesel**	**Petrodiesel**	**ASTM Values**
Colour	Clear yellow liquid	Clear liquid	-
Sp. Gravity	0.8786	0.8347	0.8347
Viscosity (Cst)	6.24	4.43	1.9-6.0
pH	7.23	7.76	-
Iodine Value	115.5	76.2	-
Heat of Combustion	36.34	42.89	-
Flash Point	148	79	≥ 100.00

Biodiesels have been reported to have slightly lower energy content per unit volume which tends to cause a corresponding reduction in maximum power, maximum toque, and fuel economy [30].

Specific gravity has been described as one of the most basic and most important properties of fuels [31] because of its correlation with cetane number, heating values and fuel storage and transportation [32-33]. The specific gravity obtained for the MSO biodiesel lies within the standard range of 0.87-0.90 [31] and slightly higher than the petrodiesel standard range of 0.81-0.86, as seen in Table 2. The petrodiesel used in this study gave specific gravity of 0.8347 that is 0.95003 times that of the MSO biodiesel. Similar trends had been reported by other workers [29, 31,32].

The near-neutral pH of the biodiesel produced is a welcome development to circumvent the corrosion problems associated with extremes of pH in the metallic components of engines. Also, the flash point of 148°C obtained in the MSO biodiesel is within the ASTM standard, as seen in Table 2, and will not predispose the product to fire outbreak in case of accidents during haulage of the material as opposed to the petrodiesel flash point of 79. Vehicles used in transportation of petrodiesel usually catch fire when involved in accidents because of the low flash point of petrodiesel.

Conclusions

Melon seed oil has been used to produce methyl ester (biodiesel) and the characteristics of the product indicates that it is potential fatty oil for biodiesel production.

There is now a growing list of various industrial applications of melon seed oil aside of its domestic use as a soup thickener in Nigeria and some other West African countries.

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