Base Catalysed Transesterification of Horned Melon (*Cucumismetuliferus*) Seed Oil to Biodiesel

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Abstract: **- Base catalyzed transesterification was carried out on horned melon seed oil as potential feed stock for biodiesel production. The oil was extracted by soxhlet extraction method and transesterified to methyl ester at methanol to oil ratio of 5:1, 60^{o}C reaction temperature, 2hours reaction time using sodium hydroxide as catalyst (0.5%wt/wt, 0.75%wt/wt, 15wt/wt and 1.25% wt/wt) to obtain optimum yield. The horned melon seed oil, methyl ester were characterized using ASTM protocols and results shows; specific gravity (0.95 ± 0.006, 0.8695 ± 0.0019), refractive index (25^{o}C)(1.4612± 0.0001, 1.4411 ± 0.0002), kinematic viscosity (mm^{2}/s) (5.16 ± 0.013, 3.36 ± 0.011), flash point (^{o}C) (239 ± 1.63, 165 ± 1.47), acid value (mgKOH/g) (0.6883 ± 0.018, 0.436 ± 0.016), free fatty acid value (mg/g) (0.3379 ± 0.0017), Saponification value (mgKOH/g) (163 ± 0.95), carbon residue (553^{o}C) (0.021 ± 0.0045). All the properties measured are within SON/NIST standards for edible oil and ASTM 651 limits for biodiesel.**

Keywords: **renewable energy, biodiesel, horned melon, SON/NIST, transesterification, ASTM**

I. INTRODUCTION

The major part of all the energy consumed worldwide comes from fossil sources such as coal, petroleum and natural gas. However, these non-renewable sources will be exhausted in the near future (Aguilera and Sorreli, 2009). Thus the search for alternative sources of renewable and sustainable energy sources such as hydro, biomass, wind, solar, geothermal, hydrogen and nuclear is of vital importance. Alternative new and renewable fuels have the potential to solve many of the current social problems such as dwindling price of petroleum crude and environmental concerns like air, water pollution and global warming caused by fossil fuels (Demirbas, 2005).

Biofuels as an alternative fuel for engines is becoming increasingly important due to diminishing petroleum reserves and environmental consequences of exhaust gases from petroleum fueled engines (Demirbas, 2009). The term biofuel or renewable energy is referred as a solid, liquid or gaseous fuel that are predominantly produced from biomass, biofuels are non-polluting, locally available, accessible, sustainable and reliable fuel obtained from renewable sources (faith et al., 2011). Among other reasons biofuels are considered as relevant technologies by both developing and industrialized countries; energy security, environmental concerns, foreign exchange saving and socio-economic issues related to the rural sector of all countries in the world (Demirbas and Dincer, 2005).

Biodiesel is defined as alkyl ester of vegetable oil and animal fat (Knothe,2005). They are renewable and environmentally friendly energy sources that can be produced from plant oil and animal fat. Several techniques are available for biodiesel production but most commonly used is transesterification; in which triglycerides are reacted with alcohol usually methanol in the presence of an alkaline catalyst to provide mono alkyl esters (biodiesel). Many factors affect the biodiesel yield and economics, the most important factors are alcohol type, alcohol/oil molar ratio, reaction temperature, contact time, catalyst type and moisture content of the reactants (Moher *et al*., 2006).

Transesterification is the process of exchanging the organic group R^{II} of an ester with the R^{I} group of an alcohol. This reaction is often catalyzed by addition of an acid or a base catalyst. The reaction can also accomplish with help of enzymes (biocatalyst) particularly lipases.

African horned melon (*Cucumismetuliferus*) is an annual vine in the cucumber and melon family, *Cucurbitaceae*. It fruits has horn-like spines hence the name "Horned melon". The ripe fruit is orange in color with its seeds engrossed in gelatin like substances. Over 350 plus oil-bearing crops have been tested that belong to *cucurbitaceae* plant family made up of 750 genera and 750 species (Giwa*et al*., 2010). The seed oil can serve as potential feed stockfor biodiesel production because of its high oil content.

II. MATERIALS AND METHODS

Sample Collection and Preparation

The Horned melon fruits were collected from FederalGovernment College and also purchased from building material market, Jos Plateau State. The fruits were cut into two and seeds incrusted in the pulp were removed, rinsed with distilled water andsun dried on the straw mattresses for five day. The seeds werecrushed using a mortar and pestle and sieved through a 125 mesh screen.The moisture content was determined by drying in a drying oven (Memmerl mark) while the ash was obtained after mineralization by drying the grinded sample previously dried (AOAC method 1984).

Oil Extraction

15g of the grinded seed was transferred into the thimble of the soxhlet extractor that incorporates a condensation system. The mantle heater was set at 60^{o}C close to the evaporation temperature of hexane (64^{o}C). The oil was leached for 8 hours and the hexzane in the oil was recovered in a vacuum rotary extractor operated at 75^{o}C. The oil obtained was weighed and the percentage oil yield was calculated.

Characterization of the Oil

The properties of the oil were first measured to determine if pretreatment was necessary or not before alkaline transesterification. It was found that the free fatty acid value (FFA) of the oil was 0.03379 ± 0.077 mg KOH/gm (oleics) which is within limits for direct alkaline transesterification without acid pretreatment (Ramadhas, 2009).

Tranesterification Procedure

Transesterification was carried out using a laboratory scale reflux condenser in the laboratory of the department of chemistry, University of Jos, Nigeria. The Methanol and sodium hydroxide used were of analytical grade. Methanol was used as the reagent because it is a low cost and short-chain alcohol that reacts fast. Transesterification was carried out by varying the concentration of the catalyst from 0.5% w/w, 0.75%w/w, 1.00%w/w and 1.25%w/wof the oil while oil to methanol ratio was constant at of 5:1, temperature of 60 ^{o}C for 2 hours, after which the mixture was poured into a seperatory funnel and allowed to settle for 3 hours so that the reaction can be driven to completion and for the mixture to separate into methyl ester and for the glycerol at the bottom to be drained off by gravity. The excess methanol in the ester was removed in a flash evaporator. To remove any impurity, the methyl ester was washed in distilled water of volume ratio 3 to 1 three times. Finally, the washed methyl ester was dried by passing it through anhydrous sodium sulphate (Na_2SO_4)(Shinas *etal*.,2009).

Determination of Fuel and Physiochemical Properties

The fuel and physiochemical properties of the horned melon seed oil and its fatty acid methyl ester (FAME) were determined following American Society for Test and Materials (ASTM) and American oil Chemist Society (AOCS) methods and undertaken in NASCO laboratory, Jos, Nigeria and Chemistry laboratory of the l University of Jos, Nigeria. Fuel and physiochemical properties examined include flash point, kinematic viscosity, specific gravity, carbon residue, refractive index, acid value, free fatty acid value and saponification value.

III. RESULTS AND DISCUSSION

Table 1:Properties of Horned melon seed oil

Parameters	Horned Melon Oil	SON/ NIST
Moisture content%wt/wt	3.290 ± 0.0352	NM
Ash content%wt/wt	4.150 ± 0.040	NM
Acid value mgKOH/g	0.6883 ± 0.018	7.0 max
Free fatty acid value mg/g	0.3379 ± 0.017	3.5 max
Sap value mgKOH/g	163 ± 0.95	195 – 205
Specific gravity	0.95 ± 0.006	0.891 – 0.926
Refractive index (25^{o}C)	1.4612 ± 0.0001	1.4612– 1.4707
Flash point (oC)	239 ± 1.63	NM
Kinematic viscosity (mm2/s @ 40^{o}C)	5.16 ± 0.013	NM

NM-Not Mentioned

SON- Standard Organisation of Nigeria

NIST-

Table 2: Fuel properties of Horned melon seed oil methyl ester

Parameters	Horned melon seed biodiesel	USA ASTM D6751
Specific gravity	0.8695 ± 0.0091	0.86 -0.90
Refractive Index	1.4411 ± 0.0002	1.33 -1.66
Flash point (^{o}C)	165 ± 1.47	130 min
Kinematic viscosity	3.36 ± 0.011	1.9 – 6.0
Acid Value	0.436 ± 0.016	0.05 max
Carbon residue 553^{o}C	0.021 ± 0.0045	0.05max

NM- Not Mentioned

USA - United States of America. ASTM- American Standard of Testing and Materials

The oil content of horned melon seed was found to be 14.62% which is lower than 24.62 % reported by Hassimi*et al*., 2007. It can be noted from Fig 1 that methyl ester yield increased with increase in catalyst concentration. The yield (79.4%) was highest at 1.25% wt/wt catalyst concentration at 60^{o}C reaction temperature, 5:1 methanol to oil ratio and 2hours reaction time.

The moisture content (3.290 ± 0.0352) and ash content (4.150 ± 0.040) of the horned melon seed as shown in Table 1 compared favorably with Hassimi *et al*., 2007.The result presented on Table 1 was all within Standard Organisation of Nigeria (SON) and NIST for edible oil.

Specific gravity: This refers to the ratio of the density of a substance to the density of a reference substance, this affect the weight of the diesel fuel with regard to transportation of the fuel. The specific gravity of the raw oil and methyl ester are 0.95 ± 0.006 and 0.8695 ± 0.0019 respectively. The result for the raw oil was higher than SON/NIST standard for edible oil while the result for the methyl ester is within ASTM specification for biodiesel.

Refractive index: The refractive index was 1.468 and reduced to 1.366 after transesterification. Refractive index is a measure of purity of the fuel.

Kinematic viscosity: The kinematic viscosity of the horned melon seed oil and methyl ester are 244.52 and 6.6 mm^2/s respectively. Viscosity is an important property of biodiesel since it affects the operation of fuel injection equipment, particularly at low temperatures when the increase in viscosity affects the fluidity of the fuel or leakage at high temperature when too thin.

Flash Point: Flash point measurements were done according to method ASTM D6751 using Kehler Model K-16270 (Pensky-Martens Closed Flash Tester). It is a measure of flammability of fuels and thus an important safety criterion in transport and storage. Horned melon seed oil has a flash point of 239^{o}C and the value for methyl ester is 165^{o}C which although are below the minimum for biodiesel, are higher than that for diesel fuel.

Acid number and Free Fatty Acid value: This is the quantity of base required to titrate a sample to a specified end point. It is a measure of free fatty acid in biodiesel. Excessive free fatty acid in the fuel can be corrosive and may be a symptom of water in the fuel or poor production or subjected to oxidative degradation. The acid values of the oil and methyl ester are 0.6883 mg KOH/gm and 0.436 mg KOH/gm respectively.

Carbon residue: The carbon residue of a fuel is the tendency of carbon deposit to form under high temperature condition in an inert atmosphere; the carbon residue when the methyl ester was combusted is 0.021 ± 0.0045 wt/wt which is within the ASTM D651limits (0.5max). Carbon residue is affected by impurities and the presence of additives in the fuel. The methyl ester gave lower carbon residue and this may be attributed to the highlevel of oxygen content in the fuel which results into more complete combustion and hence reduced carbon residue Lin *et al*., (2009).

IV. CONCLUSION

Horned melon seed oil can be converted to methyl esters and the properties are within the limits for biodiesel. Flash point which is the temperature at which the fuel can ignite when exposed to a heat source is important from the point of view of safe handling, storage and transportation. The raw oil has a flash point of 239^{o}C which reduces to 165 ^{o}C after transesterification and makes horned melon methyl ester much safer than diesel fuel.It can hence be used as alternative fuel or blended with diesel for engines**.**

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