International Journal of Innovation and Applied Studies
ISSN 2028-9324 Vol. 22 No. 1 Dec. 2017, pp. 44-53
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http://www.ijias.issr-journals.org/

Transesterification of Waste Cooking Oil with Methanol and Characterization of the Fuel Properties of the Resulting Methyl Ester and its Blends

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ABSTRACT: Rapid exhaustion of fossil fuels and the increase in environmental concerns have promoted recent attention towards converting various oils into fuels (biofuels) as alternatives to petroleum diesel. Methanol was used to trans esterify waste cooking oil using the molar ratios of 1:3, 1:6, 1:9 and 1:12 (oil to methanol) in the presence of potassium hydroxide (KOH) as catalyst and 65^0C activation temperature. The physicochemical properties of the resulting methyl ester of standard molar ratio (1:6) and its blends were investigated and the resulting properties were compared with that of fossil fuel. These properties were also compared with standard values of biodiesel using European Standard (EN 14214), United States Standard (ASTM D6751) and South African Standard (SANS 1935). Results from the variation of the molar ratio of oil to methanol i.e. 1:3, 1:6, 1:9 and 1:12 showed that the percentage yield of methyl ester increased as the molar ratio increased until at 1:9 where the percentage yield of methyl ester started to decline which might be as a result of excess methanol present in the reaction. The value of each of the physicochemical properties for biodiesel (B100) was close to that of petroleum diesel (B0) and almost the same as European Standard (EN 14214), United States Standard (ASTM D6751) and South African Standard (SANS 1935) when compared. The study concludes that waste cooking oil methyl ester and its blends compare favorably with fossil diesel in terms of physicochemical properties and the values are within the acceptable standards.

KEYWORDS: Biodiesel Blends, Glycerol, Methyl Ester, Physicochemical Properties, Transesterification.

1 INTRODUCTION

Rapid exhaustion of fossil fuels and the increase in environmental concerns have stimulated recent attention towards alternatives for petroleum based fuels. Methyl ester has created vast awareness in different countries all over the world because of its renewability, improved gas emissions, better combustion characteristics and its biodegradability. Attention has always been focused on the ever threatening problem of the country such as; Continuous depletion of oil and other fossil fuels, Dependence on the import of sources of energy and Increase in the price of conventional fuels such as diesel and petrol. The fuel modification is mainly aimed at reducing the viscosity to get rid of flow and combustion-related problem. For these modifications in fuel characteristics, there are mainly four processes named as dilution or blending, micro-emulsification, transesterification and pyrolysis.

Among all these techniques, the transesterification seems to be the best choice, as the physical characteristics of fatty esters are very close to those of diesel fuel and the process is relatively simple. The commercial method used for the biodiesel production is the transesterification also known as alcoholysis [1]. Transesterification is the process of using an alcohol of low molecular weight (e.g. methanol, ethanol, butanol), in the presence of a catalyst such as sodium hydroxide or potassium hydroxide, to break the molecule of the raw renewable oil chemically into methyl or ethyl esters of the renewable oil with glycerol as a byproduct. Methyl ester refers to a vegetable oil-or-fat based diesel fuel consisting of long chain alkyl esters. It is an attractive alternative to fossil fuels; it is biodegradable, non-toxic and has low combustion and emission profiles as compared to petroleum fuels. Biodiesel can be produced from vegetable oils, animal fats or waste cooking oils by transesterification with an alcohol in order to substitute fossil fuels [2], [3], [4]. Many works have used methanol [5], [6], [7], [8] as alcohol reactant which is mainly produced by oxidation processes of methane, a natural gas component, hence, a non-renewable energy. Methanol is preferable to ethanol because it is very cheap and due to its dissolving power for vegetable oils, it has low toxicity and renewable origin. Various factors such as Free Fatty Acid (FFA) content, water content, amount/type of catalyst, vegetable oil to alcohol molar ratio or temperature can affect the process [9], [10], [11]. Methyl ester can be blended with petroleum diesel. In the case of mixtures, the respective proportion of methyl ester in petrol diesel should be indicated. E.g. B20 means a mixture of 20% methyl ester and 80% petroleum diesel; B75 means a mixture of 75% methyl ester and 25% petroleum diesel while B50 means 50% methyl ester and 50% petroleum diesel. B100 means pure methyl ester and B0 means pure petroleum diesel. In this study, the physicochemical properties of the waste cooking oil methyl ester (WCOME) and its blends with petroleum diesel in the ratios of 25% (B25), 50% (B50), 75% (B75) together with pure petroleum diesel 0% (B0) were investigated and percentage yield of methyl ester for each molar ratio of oil to methanol of 1:3, 1:6, 1:9 and 1:12 was also investigated as well.

2 METHODOLOGY

2.1 BIODIESEL PRODUCTION

The process employed was transesterifcation because it was a simple and fastest way of producing biodiesel as recommended by Van Gerpen [12] and almost all the literature consulted supported the use of the method in producing biodiesel. Transesterifcation of oil was carried out with methanol at a molar ratio of 1 to 6 (1:6) in the presence of potassium hydroxide (KOH) as a catalyst and 65^0c reaction temperature. One hundred gram (100g) of oil was weighed into 250 mL flat bottom flask fitted with a condenser. The oil was preheated for about thirty (30) minutes to increase the reaction of the oil with methanol. 1% KOH (by weight of oil) was dissolved in 21.7g of methanol (equivalent to 1:6 of oil to methanol) in a separate beaker to give potassium methoxide. This solution was added to the preheated oil and stirred for two hours on a magnetic stirrer. The condenser was placed on top of the mixture setup to condense any vaporized liquid (such as methanol) back to liquid which consequently returned into the mixture as liquid methanol. After two hours, the entire mixture was poured into a separating beaker and left for twelve hours to separate into two phases, where the glycerol settled at the bottom of the separating funnel and the methyl ester at the top of the funnel [12]. This is possible because the two liquids have different densities. The tap at the base of the separating funnel was opened to allow the run of glycerol into one container while the biodiesel followed after the flow of glycerol has ended as shown in figure 1

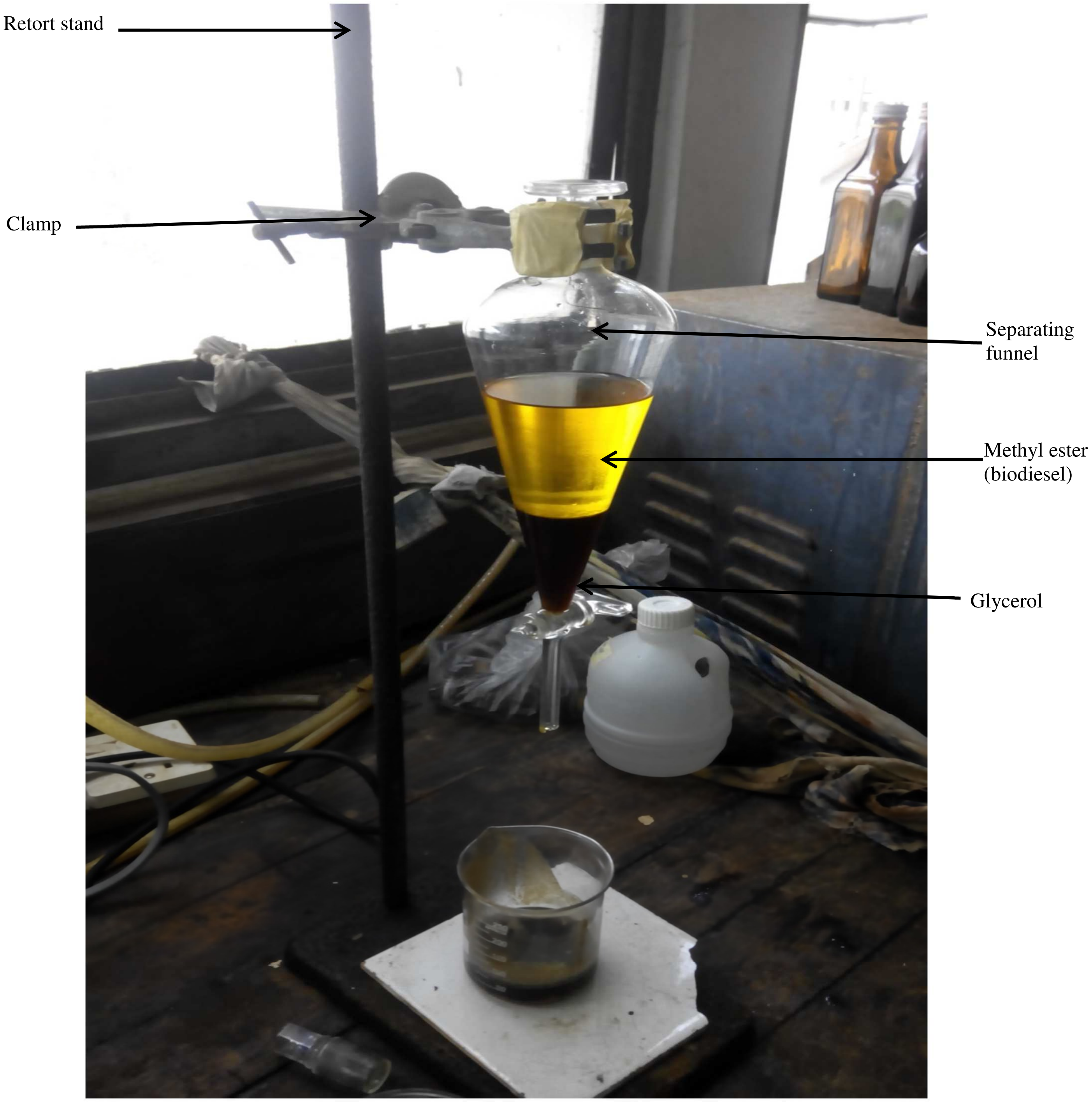

Figure 1. Methyl Ester Separation Using Separating Funnel during Experiment

2.2 PERCENTAGE YIELD OF METHYL ESTER ON MOLAR RATIO VARIATION

Four different molar ratios of oil to methanol were investigated (1:3, 1:6, 1:9, 1:12) and the percentage yield of biodiesel for each ratio was calculated accordingly. While the mass (100g) of oil was kept constant to maintain its ratio of ONE (1) and the amount of potassium hydroxide as a catalyst (1g or 1% KOH) was also kept constant together with other reaction conditions. But mass of methanol varied depending on each ratio. While 10.85g of methanol was used for 1:3, 21.7g was used for 1:6, 32.55g of the same methanol was used for 1:9 and 43.4g was used for 1:12. The percentage yield of biodiesel for each ratio was calculated using:

$$\text{Percentage Yield} = \frac{\text{Mass of methyl ester produced}}{\text{Mass of oil used}} \times 100$$

2.3 CHARACTERISATION OF METHYL ESTER AND ITS BLENDS (PHYSICOCHEMICAL PROPERTIES)

2.3.1 DETERMINATION OF DENSITY (RELATIVE DENSITY)

The density of oil was measured using density bottle. A clean and dry density bottle of 25mL capacity was weighed with the stopper on it (W_0). It was then filled with the oil, stopper inserted and immersed in a thermostated water bath at 40^0c until it equilibrates with the temperature. The water that oozed out from the stopper was wiped dry and weighed to give (W_1). The oil was substituted for water after washing and drying the bottle and reweighed to give (W_2).

$$\text{Relative Density} = \frac{\text{Mass of oil } (W_1 - W_0)}{\text{Mass of equal volume of water } (W_2 - W_0)}$$

2.3.2 DETERMINATION OF KINEMATIC VISCOSITY

Viscosity measurement was performed using kinematic viscometer. The viscometer was first calibrated using glycerol and viscometer constant Ka was obtained. The viscosity of oil was determined at 40^0c so as to be able to compare with the standard values. The time of flow of each oil sample under gravity through the capillary of the viscometer was measured at known temperature. Then viscosity was calculated using:

Viscosity = Calibration Constant × Mean Time of Flow of Oil.

Calibration constant used was 0.09827

2.3.3 DETERMINATION OF FLASH POINT AND SMOKE POINT

A clean and dry crucible filled with 20mL of biodiesel was placed on a regulated heating mantle; a thermometer was clamped to touch the biodiesel but not touching the bottom of the crucible. The biodiesel was stirred and a flame was passed over the surface of the biodiesel at 30^0c interval. The temperature at which the smoke started coming out from the biodiesel is the ***smoke point*** while the temperature at which the smoke ignites is the ***flash point***. (ASTM D-93)

2.3.4 DETERMINATION OF CETANE NUMBER (CN)

Cetane number of biodiesel was calculated according to the expression given below [13]:

$$CN = 46.3 + (5458/SV) - (0.225 \times IV)$$

Where SV = Saponification Value; IV = Iodine Value

2.3.5 DETERMINATION OF IODINE VALUE (IV)

Accurately weighed 0.25 g oil sample was put into a conical flask and dissolved with 10 mL chloroform ($CHCl_3$) and 25 mL Hanus reagent was added. The flask was placed in the dark for about 30 minutes with occasional shaking. 10 mL KI solution was added with thorough shaking. Traces of iodine on stopper were washed down with 100 mL of distilled water and 25 mL of the solution obtained was titrated with standard 0.1 M sodium thiosulphate solution with constant shaking until the yellow solution turned almost colourless. Two drops of freshly prepared starch indicator were added and the titration continued until the blue-black colour disappears. Blank determination was also performed. The iodine value (IV) was calculated using the expression below (EN 14214):

$$IV = \frac{(B-S) \times 126.9}{\text{Weight of oil (g)}}$$

Where B = Blank titre value; S = Sample titre value; 126.9 = Atomic mass of Iodine

2.3.6 DETERMINATION OF ACID VALUE (AV) AND PERCENTAGE FREE FATTY ACID (FFA)

Accurately weighed 5.0 g of each oil sample was weighed into a conical flask. 50 mL of methanol was neutralized by adding 2 or 3 drops of phenolphthalein indicator and few drops of 0.1 M KOH to produce a faint pink colour. The mixture was added to the oil and was boiled on water bath for few minutes until the oil globulised. The mixture was titrated with 0.25 M KOH solution until a pink colour persists for about one minute was obtained. The percentage free fatty acids and the acid value were calculated from the expression below [14]:

$$\text{Acid value} = \frac{\text{Titre Value} \times M \times 56.1}{\text{Weight of oil (g)}}$$

Percentage FFA = Acid value / 1.99

Where M = molarity of KOH,

56.1 = molar mass of KOH

2.3.7 DETERMINATION OF SAPONIFICATION VALUE (SV)

An alcoholic KOH solution was prepared by crushing 40 g KOH and 45 g CaO. The mixture was well ground and dissolved with a little portion of methanol. The content was transferred to a two litres volumetric flask and made up to two litres with methanol. The flask was shaken vigorously for a few minutes and left overnight. The resulting content of the flask was filtered into a clean volumetric flask [14]. Two grams of each sample was weighed into a 250 mL quick-fit flask, 25 mL of alcoholic KOH was added and the content was refluxed for one hour on the magnetic stirrer. After refluxing, the flask was allowed to cool and the condenser was washed with little distilled water. The excess unreacted KOH was titrated with 0.5 M HCL using phenolphthalein indicator. The same procedure was carried out for a blank determination [14]. The Saponification value (SV) was calculated from the expression below:

$$SV = \frac{(B - S) \times 56}{\text{Weight of Sample (g)}}$$

Where B = titre value of Blank; S = titre value of the Sample; 56.10 = molar mass of KOH.

3 RESULTS AND DISCUSSION

3.1 PERCENTAGE YIELD OF METHYL ESTER ON MOLAR RATIO VARIATION

The variation of the molar ratio of methanol to oil showed that the percentage yield of biodiesel increased as the ratio increased except at 1:9 where the percentage yield of biodiesel started to decline as shown in figure 2. This might be as a result of excess methanol present in the mixture, because, excess methanol hinders the formation of biodiesel [15].

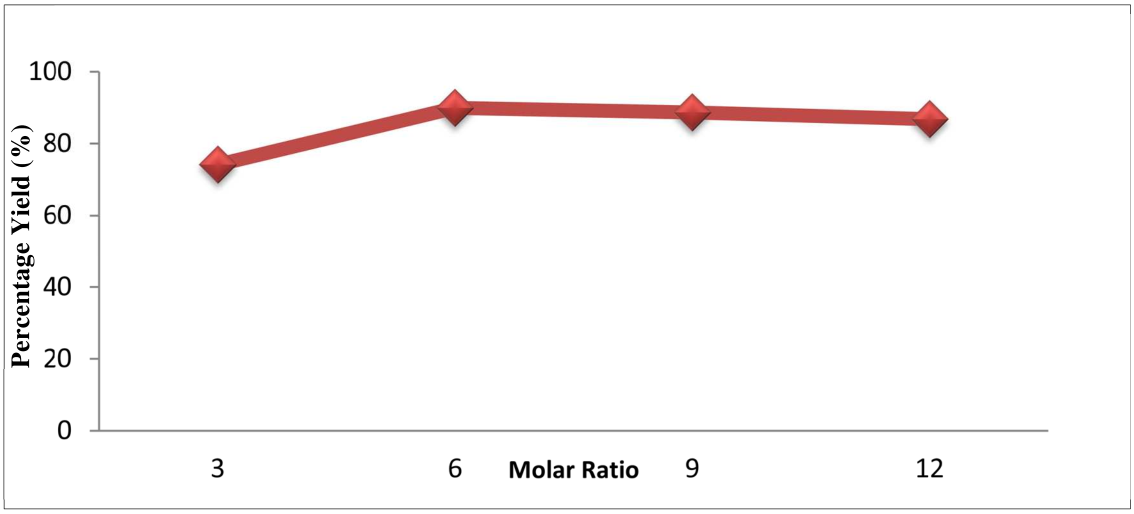

Figure 2. Percentage Yield of Methyl Ester on Molar Ratio Variation

3.2 PHYSICOCHEMICAL PROPERTIES OF PRODUCED METHYL ESTER AND ITS BLENDS

The results from the investigations of physicochemical properties of the produced methyl ester and its blends showed that for almost all the physical properties, such as Density, Viscosity, Flash Point (FP), Cetane Number (CN) and Smoke Point (SP), the magnitude of each property increased as the percentage of the biodiesel blend increased except for some chemical properties such as Iodine Value (IV), Saponification Value (SV) and Peroxide Value (PV). But generally, the value of each of these properties for biodiesel (B100) was almost the same as European Standard (EN 14214), United States Standard (ASTM D6751) and South African Standard (SANS 1935) as shown in table 1 and figures 3 to 7.

Table 1 Physicochemical Properties of produced Methyl Ester and its Blends and Comparison with Standard Values.

FUEL PROPERTY	UNIT	Bo	B25	B50	B75	B100	European Biodiesel Standard (EN 14214)		United States Biodiesel Standard (ASTM D6751)		South African Biodiesel Standard (SANS 1935)	
							LIMITS		LIMITS		LIMITS	
							MIN.	MAX	MIN.	MAX	MIN.	MAX
Ester Content	% (m/m)	-	-	-	-	89.93	96.5	-	-	-	96.5	-
Density at 40^0C	Kg/m^3	830	844	849	859	860	860	900	-	-	860	900
Viscosity at 40^0C	mm^2/s	3.91	4.00	4.80	5.50	6.00	3.5	5.0	1.9	6.0	3.5	5.0
Flash Point	^0C	65	95	110	130	178	120	-	93	-	120	-
Cetane Number	-	65.80	66.72	67.09	67.40	68.63	51	-	47	-	51	-
Acid Value	mgKOH/g	0.70	1.12	1.12	1.25	1.40	-	0.50	-	0.50	-	0.50
Iodine Value	I/100g	115.75	114.49	113.33	112.67	111.67	-	120	-	-	-	140
Smoke Point	^0C	45	50	70	80	95	-	-	-	-	-	-
Saponification Value	mgKOH/g	119.85	118.20	117.90	117.50	115.01	-	-	-	-	-	-
Peroxide Value	mgKOH/g	9.00	7.00	4.00	2.00	1.50	-	-	-	-	-	-

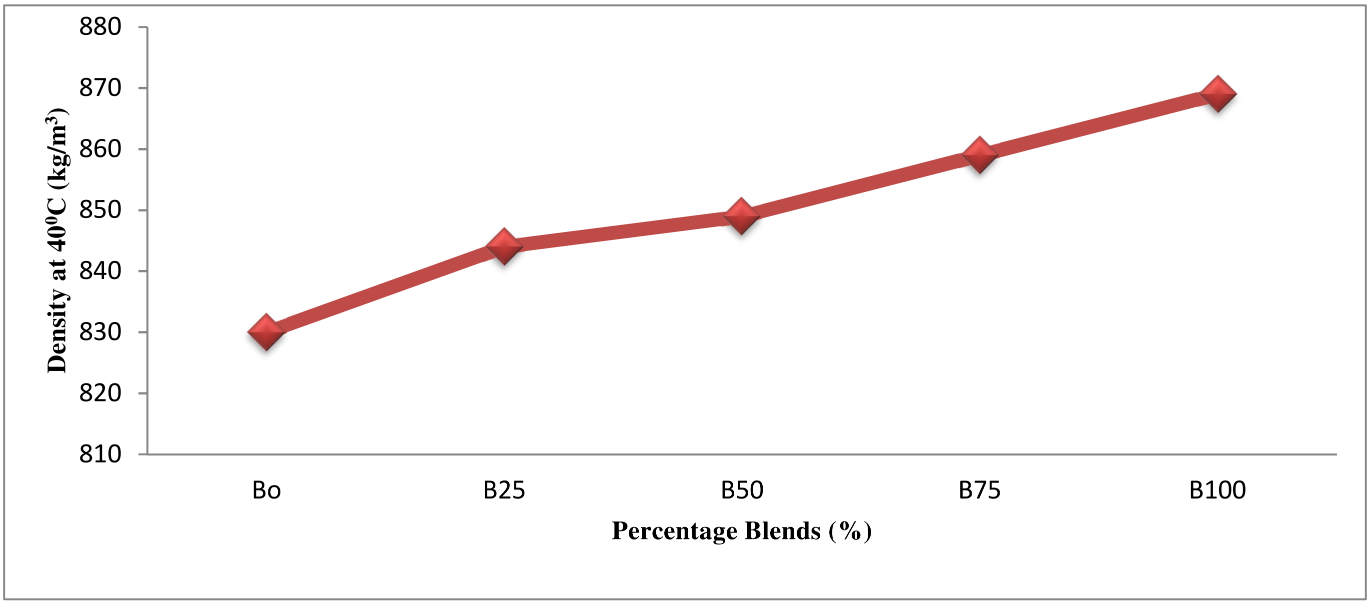

Figure 3. Effects of Methyl Ester Blends on Density

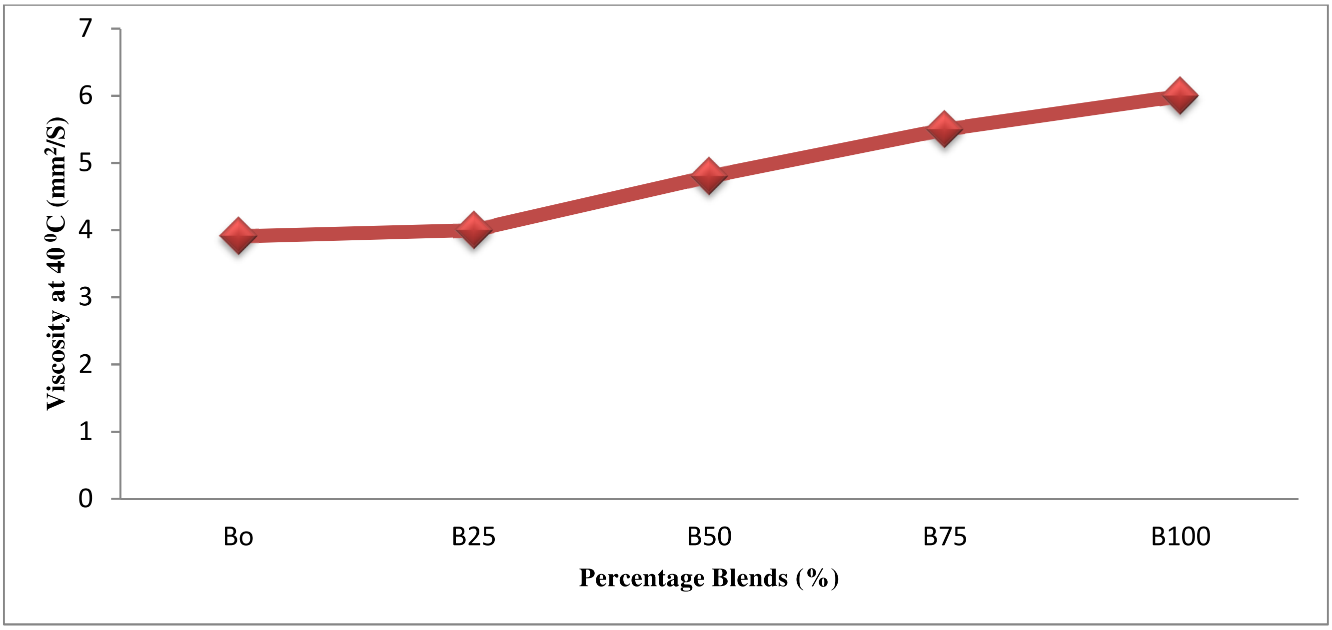

Figure 4. Effects of Methyl Ester Blends on Viscosity

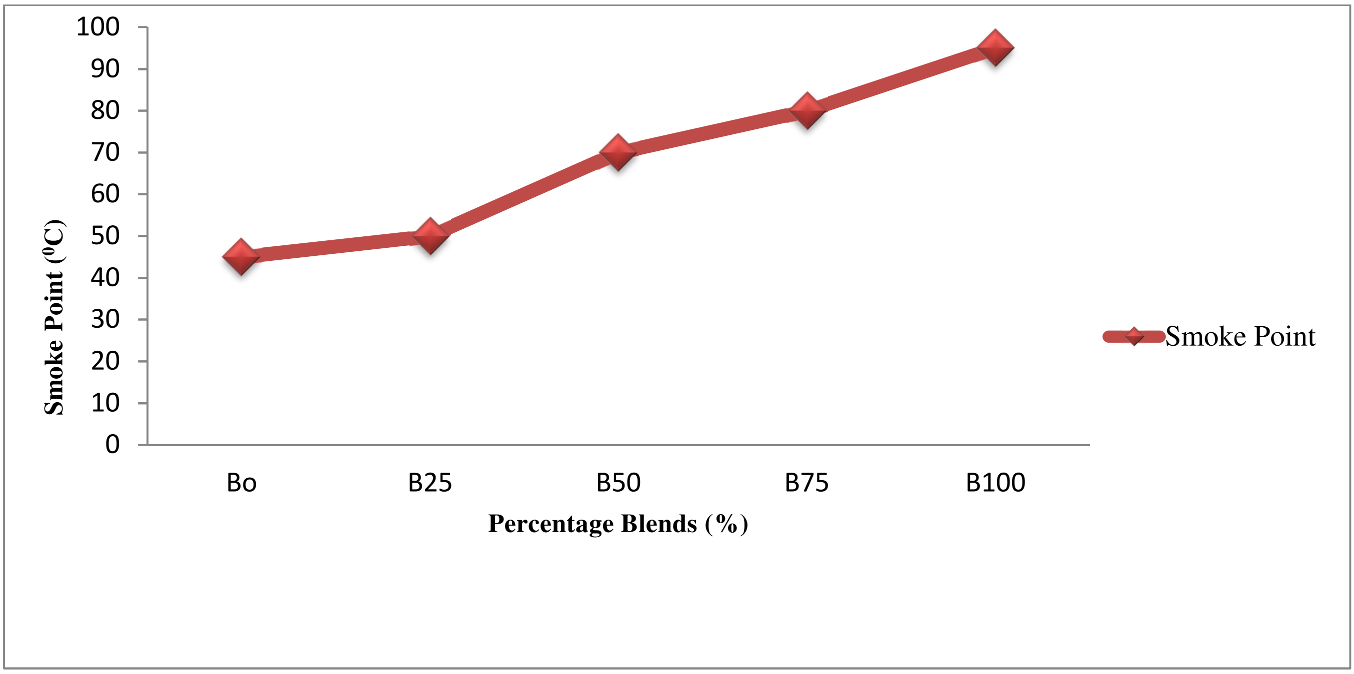

Figure 5. Effects of Methyl Ester Blends on Smoke Point

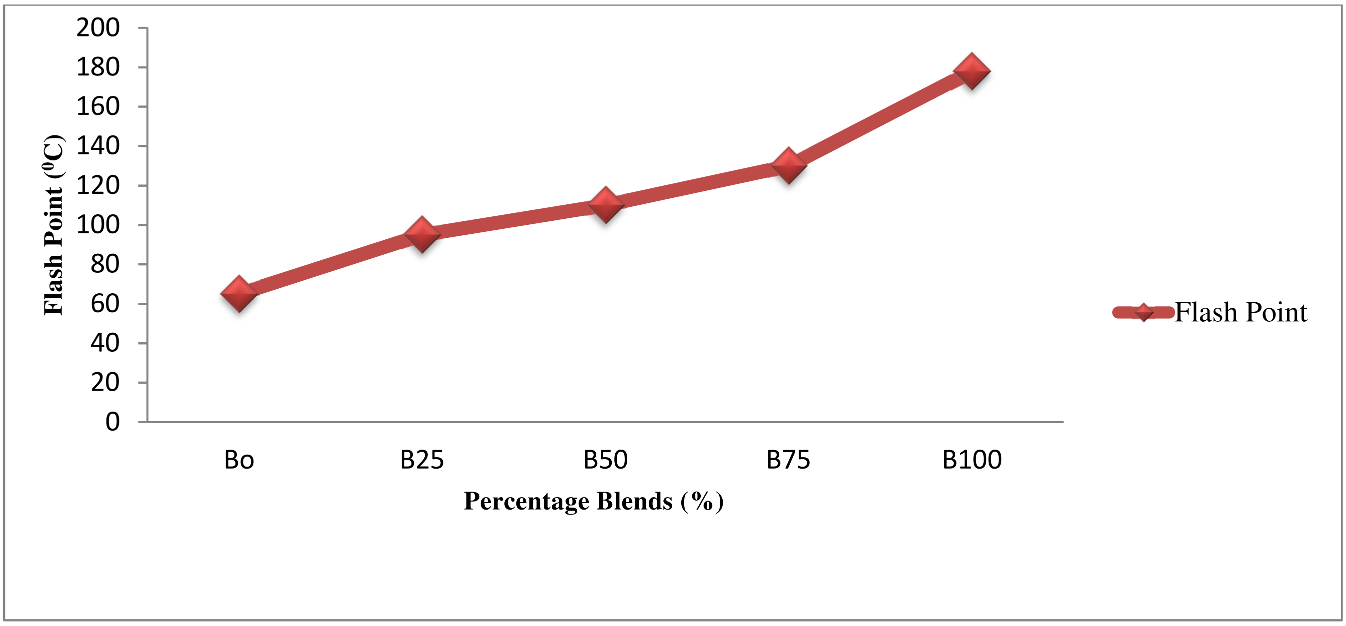

Figure 6. Effects of Methyl Ester Blends on Flash Point

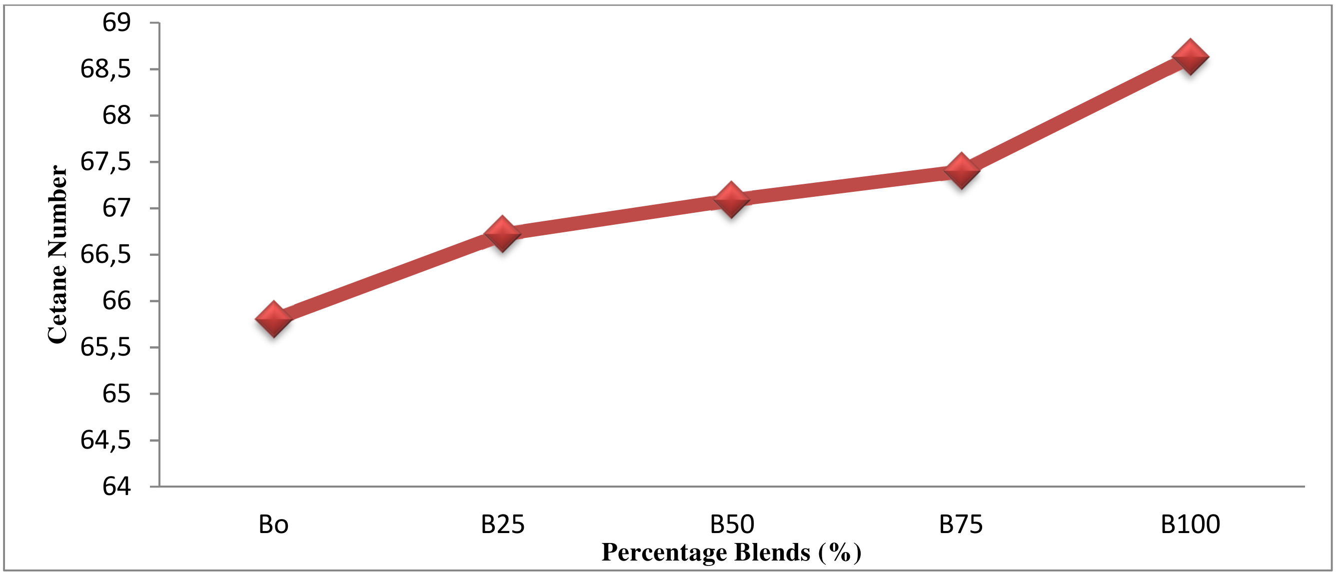

Figure 7. Effects of Methyl Ester Blends on Cetane Number

4 CONCLUSION

The production of methyl ester (biodiesel) was possible using transesterification of waste cooking oil with methanol in the presence of potassium hydroxide (KOH) as a catalyst at 65^0c. The separation of biodiesel from glycerol was done using separating funnel with the biodiesel at the top because of its lower density compared to the denser glycerol which settled at the base of the funnel. Also, the variation of the molar ratio of methanol to oil showed that the percentage yield of biodiesel increased as the ratio increased except at 1:9 where the percentage yield of biodiesel started to decline which might be as a result of excess methanol present in the mixture. Because for higher molar ratios, the separation of the glycerol was difficult, as the methanol excess hinders the decantation by gravity [15] so that the apparent yield of esters decreases since part of the glycerol remains in the biodiesel phase. Moreover, results from the investigations of physicochemical properties of the produced biodiesel and its blends showed that for almost all the physical properties, such as density, viscosity, flash point, cetane number and the smoke point, the magnitude of each property increased as the percentage of the biodiesel blend increased. But generally, the value of each of these properties for biodiesel (B100) was almost the same as European Standard (EN 14214), United States Standard (ASTM D6751) and South African Standard (SANS 1935). Also, the values were observed very close to those obtained for ordinary normal diesel (Bo). The study concludes that waste cooking oil methyl ester compares favorably with fossil diesel in terms of physicochemical properties and its values are within the acceptable standards.

REFERENCES

[1] Eman, N., Ali, C.I.T. Characteristics of Biodiesel produced from Palm Oil via Base Catalyzed Trans esterification, (2013). Vol. 53, pg. 7-12.
[2] Demirbas, A., and Karsliogu, S. Biodiesel production facilities from vegetable oils and animal fats, (2007). Energy Sources Part A 29, 133–141.
[3] Encinar, J.M., Gonzalez, J.F., and Rodrıguez-Reinares, A. Ethanolysis of used frying oil. Biodiesel preparation and characterization, (2007). Fuel Process Technol. 88, 513–522.
[4] Kouzu, M., and Hidaka, J.S. Transesterification of vegetable oil into biodiesel catalyzed by CaO: (2012) a review. Fuel 93, 1–12.
[5] Darnoko, D., and Cheryan, M. Kinetics of palm oil transesterification in a batch reactor. J. Am. Oil Chem. Soc. (2000) 77, 1263–1267.
[6] Fukuda, H., Kondo, A., Noda, H. Biodiesel fuel production by transesterification of oils. J. Biosci. Bioeng, (2001) 92, 405–416.
[7] Sharma, Y.C., and Singh, B. Development of biodiesel from karanja, a tree found in rural India, (2008). Fuel 87, 1740–1742.
[8] Srivastava, P.K., and Verma, M. Methyl ester of karanja oil as an alternative renewable source energy, (2008). Fuel 87, 1673–1677.

[9] Freedman, B., Pryde, E.H., and Mounts, T.L. Variables affecting the yields of fatty esters from trans esterified vegetable-oils, (1984). J. Am. Oil Chem. Soc. 61, 1638–1643.

[10] Meher, L.C., VidyaSagar, D., and Naik, S.N. (2006). Technical aspects of biodiesel production by Trans esterification — a review. Renewable Sustainable Energy Rev., (2006). 10, 248–268.

[11] Sharma, Y.C., Singh, B., and Upadhyay, S.N. Advancements in development and characterization of biodiesel: (2008) a review. Fuel 87, 2355–2373.

[12] Gerpen, J.V. Biodiesel Processing and Production. Fuel Processing Technology, (2005).Volume 86(10) on pages 1097-1107.

[13] Mohibbe, A., Amtul, W., and Nahar, N.M. Prospect and Potential of Fatty Acid Methyl Esters of Some Non – traditional Seeds Oils for use as Biodiesel in India, (2005). Biomass Bioner. 29: 293 -302.

[14] AOAC, Official methods of analysis of the association of official analytical chemists, (1991). Analytica Chimica Acta, Volume 242 on page 302.

[15] Feuge, R.O., Gros, A.T. Modification of vegetable oils. VII. Alkali catalyzed interesterification of peanut oil with ethanol, (1949). *J. Am. Oil Chem. Soc.* **26:** 97-102.