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ORIGINAL ARTICLE

Comparative Study on The Effects of Oxygenates on Biodiesel From Fresh and Used Cooking Oil

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ABSTRACT
There are limitations to the use of biodiesel as a renewable fuel that need improvement. This paper focuses on comparing the fuel qualities such as the density, specific gravity, heat content, flash point, and kinematic viscosity of oxygenate-biodiesel blends. The biodiesel was produced from fresh and waste cooking oil and they were characterized and compared to ASTM standards. The oxygenated additives (ethanol, methanol and diethyl ether) were blended in the percentages 10, 20, 30 and 40% with biodiesel from fresh and waste oil. The physicochemical properties: heat content, density, specific gravity, flash point as well as kinematic viscosity were analyzed for the blends. The oxygenate addition improved the density, specific gravity, and kinematic viscosity. Oxygenate addition may be a good way of improving the properties of biodiesel.
Keywords: *Oxygenates, Biodiesel, cooking oil, physicochemical, additives.*

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INTRODUCTION

The recognition of global warming and depletion of fossil fuels has led to the search for other energy options which are environmental friendly and sustainable. Emission of greenhouse gases from fossil fuels has led scientists to turn to biofuels as an alternative source. Biofuels are fuels made from different types of biomass such as cellulose, algal oil, corn, soy, sugar cane, jatropha, camelina, rapseed, animal fat, methane, paper waste and the likes. These sources create different fuels such as bio-alcohols, plant based biodiesel and kerosene, biogas, solid biofuels and the likes [1].

Synthesis of biodiesel produces either bioethanol or biodiesel as alternatives to gasoline and petro-diesel respectively [2]. Biodiesel is synthesized from animal or vegetable fat via trans-esterification. During the trans-esterification process, triglyceride is converted to methyl or ethyl esters with the aid of an alcohol usually methanol and a base catalyst, potassium hydroxide which is more efficient than sodium hydroxide. An excess of alcohol drives the reaction towards the production of methyl or ethyl esters. The equation below shows the mechanism of conversion involved in the production of biodiesel [3]

The use of biodiesel comes with lower health problems which is possible since it has a reduced emission of carcinogenic substances. The environment is safer even with biofuel spill due to its high degradability and low toxicity [4]. The feed stock for biodiesel production is a controversial topic due to the fact that it takes up food meant to be eaten like using soy, palm kernel, castor oil and the likes. This causes a debate on which is important, food or fuel? The use of waste vegetable oil, jatropha and other nonedible oil, producing plants for the production of biodiesel is a very popular topic most especially waste cooking oil which has virtually no cost in securing it as a feed stock. 70-95% of the cost of producing biodiesel comes from the feedstock and using waste oil takes care of that cost [5]. The use of waste cooking oil in the production of biodiesel allows for its recycle seeing as its disposal holds serious damages in public sewers, waste water and even streams of flowing water [6].

Though biodiesel has promising prospects, in order to be fully accepted as an alternative to fossil fuel, its properties need to be improved upon such as the cetane number, energy density, viscosity, flash point and the likes. Modifications of the fuel properties can enable it to be well matched to that of conventional diesel. The aim of this study is to investigate the properties of biodiesel produced from fresh cooking and waste cooking oil blended with oxygenates such as ethanol, methanol and diethyl ether.

MATERIALS AND METHODS

The materials used for this research include the following: Weighing balance (ADAM AE438515 (UOM 1)), beaker, measuring cylinder, hot plate, stirring rod, oven (MODEL MINO/100/SS/F/DIG/DGW/99T, SERIAL No: Y6C038), stop watch, thermometer, desiccator, bomb calorimeter, Rheotek TCB-7 Viscometer Bath, glass capillary viscometer, crucibles, furnace (CARBOLITE, SERIAN No: 20-503174), test tubes, ice baths, round bottom flask, condenser, round bottom flask with 2 sided arm, separating funnel, flash point analyzer, GC-MS (Agilent-7890A) and IR Spectroscopy (Nicolet IR-100 FT).

Fresh cooking oil was bought from a local store with the brand name being power oil and the waste cooking oil was obtained from the American University of Nigeria's cafeteria. The oils were stored at room temperature for further use.

Biodiesel production

The oils were trans-esterified but the waste cooking oil was first esterified to reduce the high acid value.

Esterification

The round bottom flask was connected to a condenser which was attached to a ring stand. 200ml of waste cooking oil was measured and poured in a round bottom flask with 2 sided arm and heated to 50^{o}C. 0.2g of sulfuric acid was added to 60ml of ethanol and added to the oil. The oil was left to heat to 70^{o}C for one hour under constant stirring. After one hour, the mixture was cooled a bit and poured into a separating funnel and left for an hour to separate. The bottom layer was collected to be trans-esterified.

Transesterification

The product from esterification was poured into the round bottom flask set up and heated under constant stirring. A mixture of 3.418g of potassium hydroxide and 60 ml of ethanol was slowly poured into the round bottom flask and then allowed to heat to 70^{o}C for one hour. After one hour, the mixture was poured into a separating funnel and allowed to stand for 24 hours. The top layer was then collected and washed with hot water repeatedly to remove the base. The product was then heated to remove moisture from the washing. The % yield was determined by using the equation below. This process was applied to the fresh cooking oil.

$$\%Yield = \frac{\text{Volume of product}}{\text{Volume of oil used}} X\ 100$$

Characterization of the biodiesel from fresh and waste cooking oil

The biodiesel produced from the fresh and waste cooking oil were characterized using the following parameters; viscosity, density, specific gravity, ash content, heat content, pour point, cloud point and flash point.

The same methods used in the characterization of the oil samples were applied to the biodiesels

RESULT AND DISCUSSIONS

The percentage yield was calculated on a v/v percent. In the experiment, a reaction time of 60 minutes and 2% catalyst was used; the fresh and waste cooking oil yielded 61.5% and 73.5% respectively.

Confirmation of biodiesel produced using GC-MS and IR

The GC-MS for the Biodiesel from fresh oil show the presence of methyl and ethyl esters which are standard constituents of biodiesel and the same goes for that of biodiesel from waste oil.

Table 1: GC-MS of biodiesel from fresh cooking oil

Compounds	% Quality
13-octadecenioc acid, methyl ester	99%
8-octadecenoic acid, methyl ester	99%
Dodecanoic acid, ethyl ester	99%
Tetradecanoic acid, ethyl ester	99%
Tetradecanoic acid, ethyl ester	98%
Hexadecanoic acid, methyl ester	98%

Table 2: GC-MS of biodiesel from waste cooking oil

Compounds	% Quality
Methyl palmitate	99%
9-octadecanoic acid, methyl ester	99%
6-octadecanoic acid, methyl ester	98%
14-octadecanoic acid, methyl ester	98%
16-octadecanoic acid, methyl ester	98%

The GC-MS for the Biodiesel from fresh oil show the presence of methyl and ethyl esters which are standard constituents of biodiesel and the same goes for that of biodiesel from waste oil.

Table 3: Infrared spectra of biodiesel from fresh oil

Sample	Peaks	Bonds	Functional group
Biodiesel from fresh cooking oil	3100-3000	=C-H stretch	Alkenes
	1460.64	C-H bend	Alkanes
	1369.91	N-O	Nitro compounds
	1367.05-1116.69	C-O stretch	Alcohols, carboxylic acids, esters, ethers
	1750-1735	C=O stretch	Esters, saturated aliphatic
fresh Cooking oil	3006.25	=C-H stretch	Alkenes
	1367.05-1172.17	C-O stretch	Alcohols, carboxylic acids, esters, ethers
	1750-1735	C=O stretch	Esters, saturated aliphatic

Table 4: Infrared spectra of biodiesel from waste cooking oil

Sample	**Peaks**	**Bonds**	**Functional group**
Biodiesel from waste cooking oil	3005.55	=C-H stretch	Alkenes
	1458.77	C-H bend	Alkanes
	1367.05	N-O	Nitro compounds
	1367.05-1172.17	C-O stretch	Alcohols, carboxylic acids, esters, ethers
	1750-1735	C=O stretch	Esters, saturated aliphatic
Waste Cooking oil	3666.67	O-H stretch	Alcohols
	2907.50	C-H stretch	Alkanes
	1653.30	-C=C-	Alkenes

The IR chart show the functional groups alkanes, carbonyls such as esters, nitro compounds, and alkanes for both biodiesel from fresh and waste oil.

Table 5: Comparison between the produced biodiesel and ASTM standards

Property	Fresh oil	BDFO	Waste oil	BDWO	ASTM standards
Density (g/ml)	0.91	0.869	0.878	0.861	0.86-0.9
Specific gravity	0.932	0.890	0.899	0.882	0.88
Kinematic viscosity at 40^0C (mm^2s^{-1})	40.2	5.3	36.92	5.3	1.9 – 6.0
Cloud point (^{0}C)	14	13	6	13	-3 to 12
Pour point (^{0}C)	7	9	-	7	-15 to 10
Ash content wt%	<0.0000	<0.0000	<0.0000	<0.0000	<0.020
Flash point (^{0}C)	-	166.5	-	148	130 – 170
Heat content MJ/L	40.52	38.01	39.92	40.31	37
Moisture content wt%	0.055	-	0.12	-	
Acid value	0.587	-	2.24	-	< 0.5

From table 5, we observe that the properties of the biodiesel produced from the fresh and waste oil are similar to each other and also to the ASTM standard for biodiesel.

Density

From Figures 1 and 2, it can be noticed that the densities of the biodiesel reduced significantly when the oxygenates were added in various proportions. The densities of the blends do not follow a particular pattern as the percentage of oxygenates increases. In figures 3 and 4, the same can be observed in the case of the specific gravity of the blends since it is related to density. BDFO80ME20, BDWO90E10, BDWO80E20, BDWO70E30, BDWO90ME10, BDWO70E30 and BDWO60ME40 have densities similar to that of diesel fuel which is between 0.82 and 0.86 g/ml according to ASTM standards [7]. High incomplete combustion of fuels is due to the higher densities of fuels, from the results, the densities were significantly decreased and so there is high probability that complete combustion will occur adding to the increase in oxygen content [8]. The increase in Ethanol, methanol and diethyl ether reduces the densities and specific gravity significantly as compared to the B100 and is beneficial to the fuel quality as it supports complete combustion.

Figure 1: Effect of oxygenate addition on the density BDFO

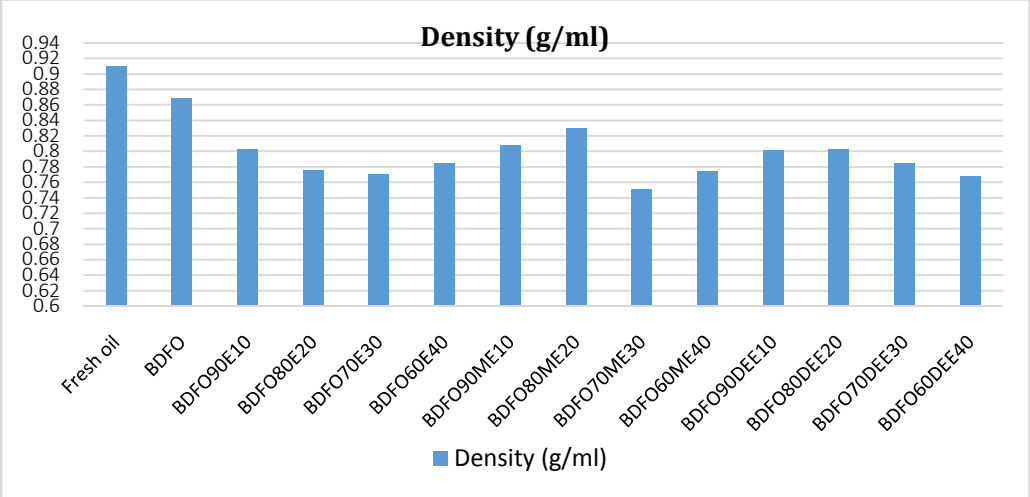


Figure 2: Effect of Oxygenate addition on the density of BDWO

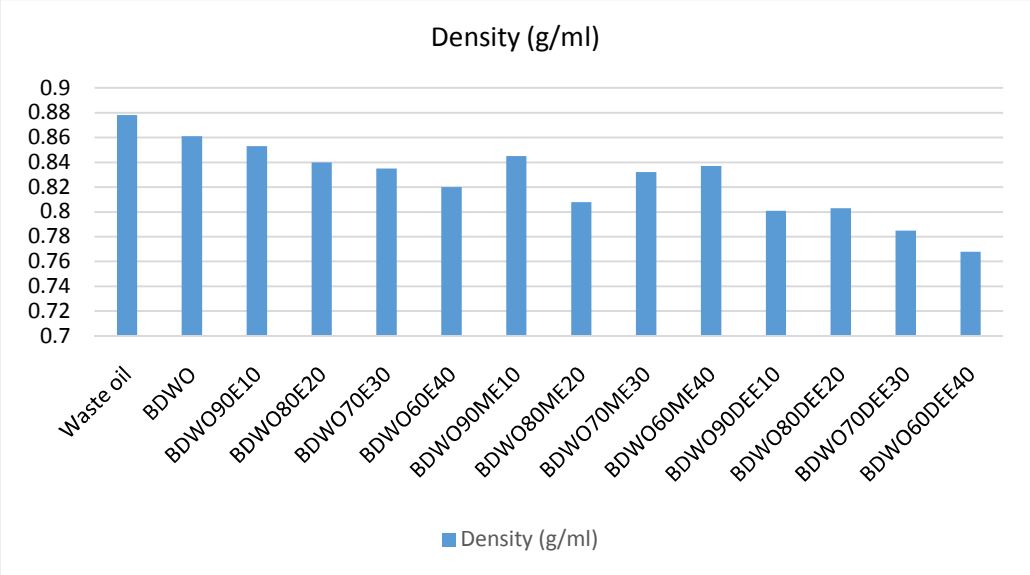


Figure 3: Effect of oxygenate addition on the specific gravity of BDFO

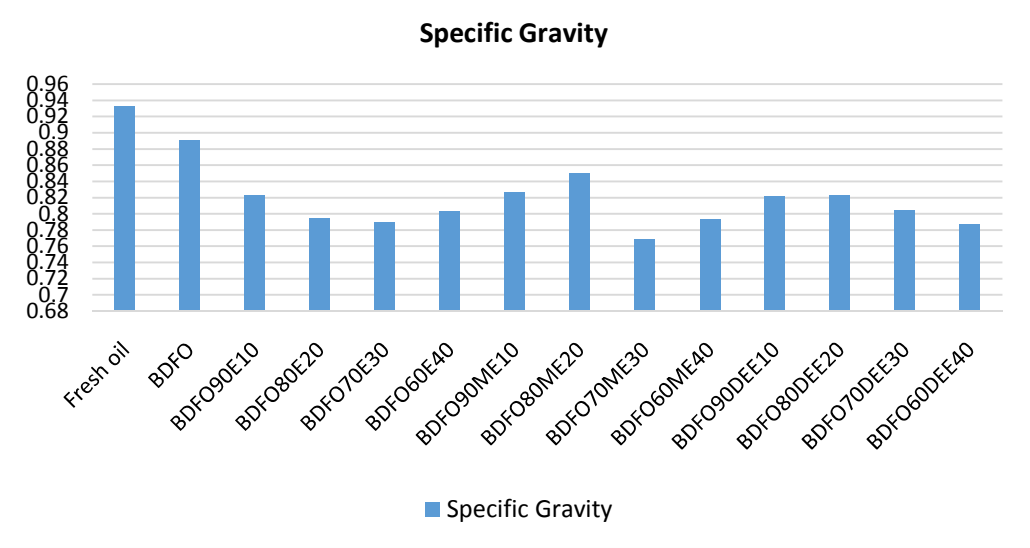
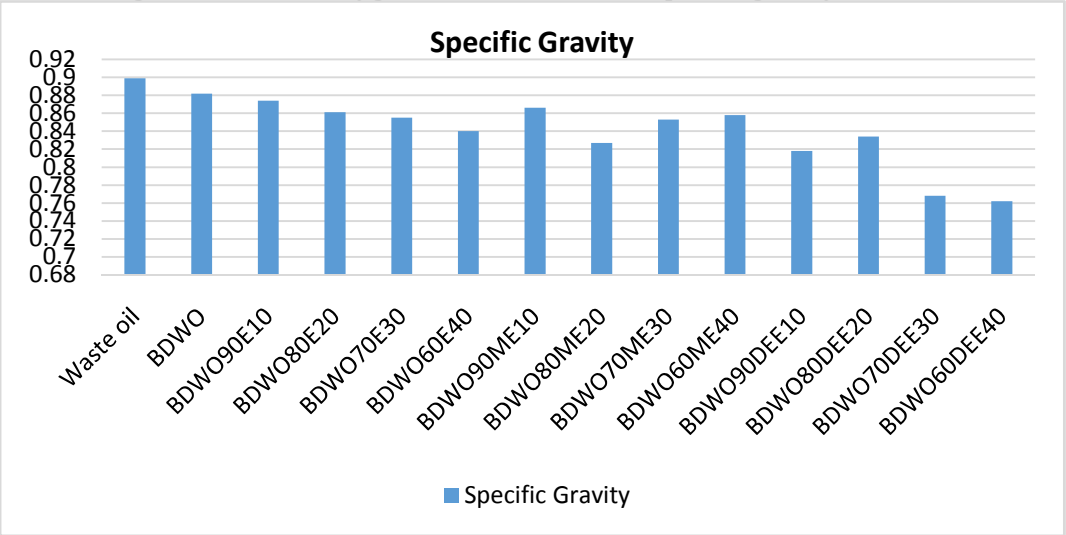


Figure 4: Effect of oxygenate addition on the specific gravity of BDWO



Kinematic viscosity

The viscosities of the blends decreased significantly as compared to the 100% biodiesel. The viscosity of each oxygenate blend was lower with increase in oxygenate percentage. BDFO90E10 had viscosity values that were closer to the BDFO followed by BDFO90ME10 and then BDFO90DEE10. The same was the case for BDWO and the oxygenate blends. We observe that diethyl ether enhances the viscosity of biodiesel more than ethanol and methanol. This can be explained by the low viscosity of diethyl ether which is 0.223 mm^2s^{-1} while that of ethanol and methanol are 0.795 mm^2s^{-1} and 0.59 mm^2s^{-1} respectively [9] [10]. From this we can deduce a trend between the viscosities of oxygenates and the effects they have on biodiesel. The lower the viscosity of oxygenate, the lower the viscosity of biodiesel-oxygenate blend. The viscosities of the blends are similar to that of diesel which is between 1.3 to 4.1mm^2s^{-1} and this suggests the use of the blends in diesel fuel engines [11]. The kinematic viscosity of the oxygenate blends are relatively low which is an advantage. Diethyl ether is more efficient at reducing the kinematic viscosity to match that of diesel.

Figure 5: Effect of oxygenate addition on the kinematic viscosity of BDFO

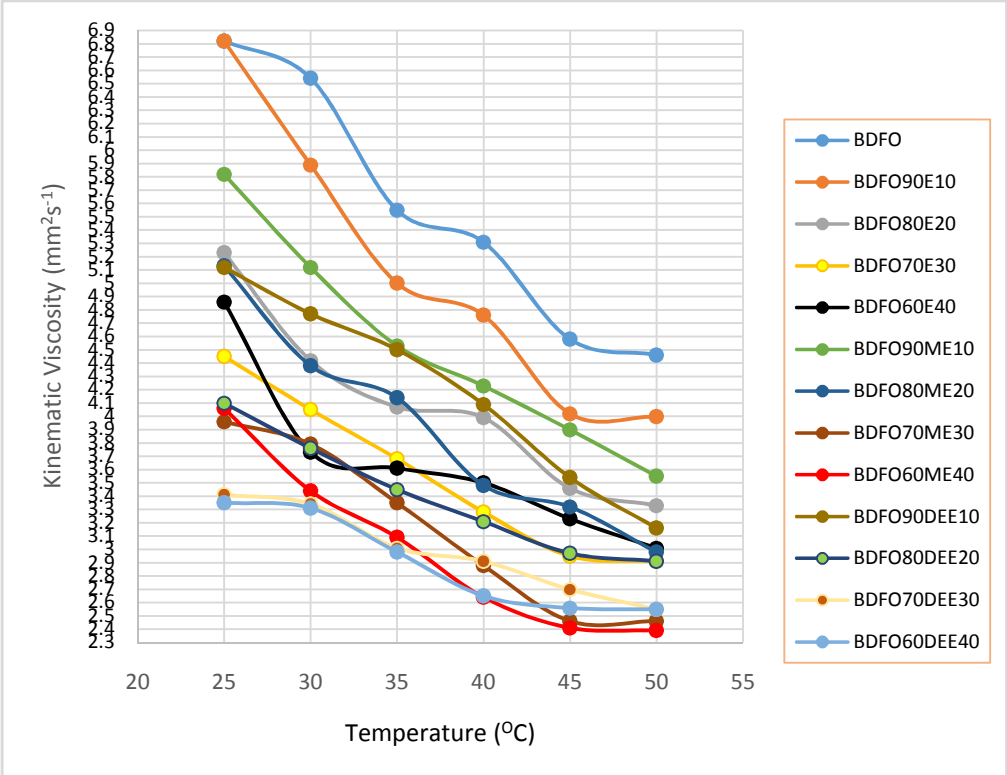


Figure 6: Effect of oxygenate addition on the kinematic viscosity of BDWO

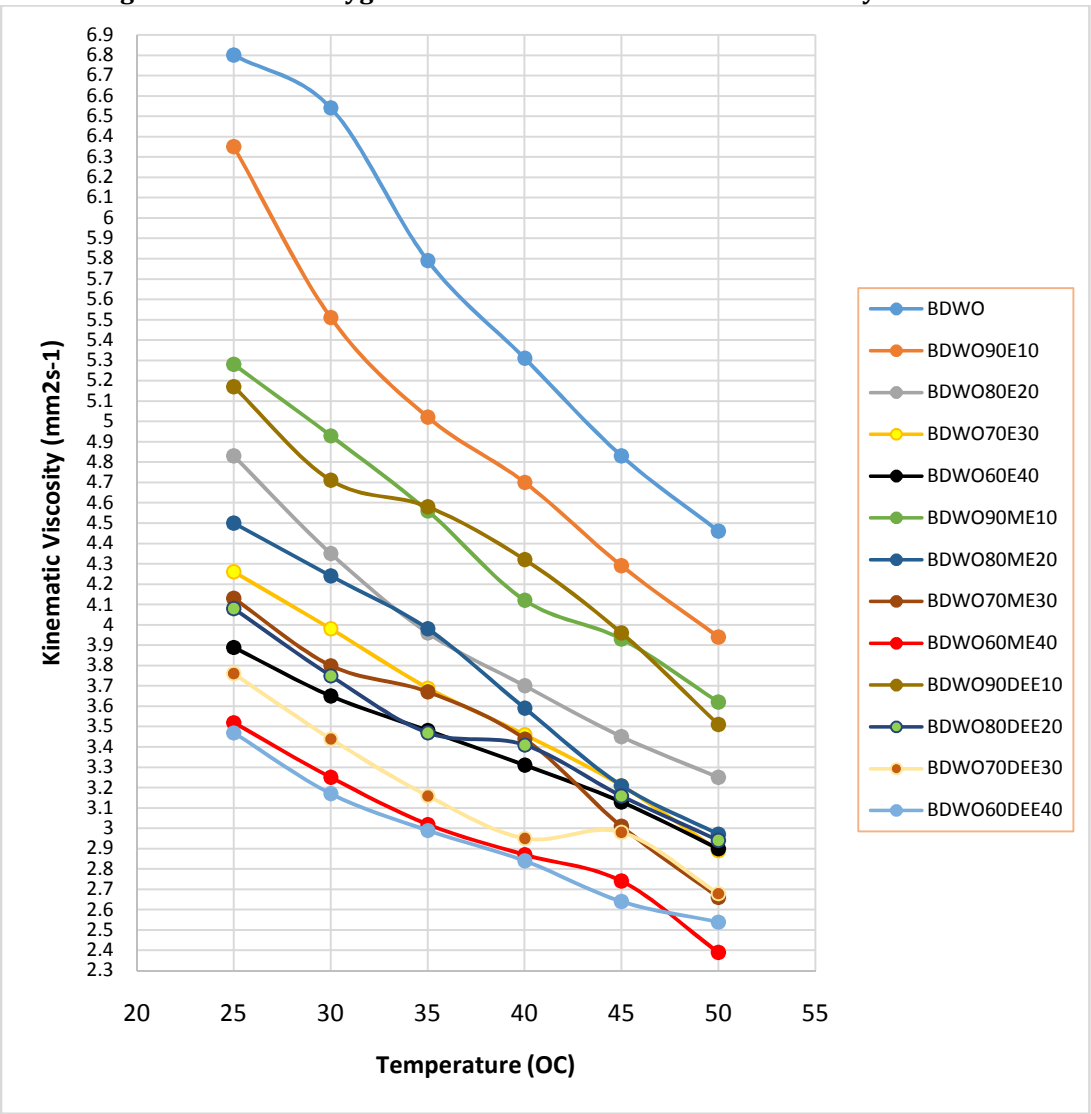


Fig. 5 and 6 compares the kinematic viscosities of biodiesel from fresh and waste oil with their various oxygenate blends.

Flash point

The biodiesel-oxygenate blends started flashing at about 16^{o}C and lower. This effect could be explained since the fuel is a mixture and the component with the lower flash point will flash first. The flash point values were within 14- to 50.9^{o}C. The flash point reduces below 16^{o}C which is a disadvantage when it comes to shipping, handling and storage but it has no effect on the performance of an engine.

Heat content

The low heat content of the oxygenated additives also explain the decrease in heat content of the biodiesel. The heat contents of ethanol, methanol and diethyl ether are 22.884, 29.847 and 33.892 respectively, all which are lower than the ASTM standard for biodiesel [9]. The length of carbon chain also determines the heat content of the fuel, the biodiesel from waste oil has longer carbon chains than that from fresh oil as suggested by the GC-MS. The heat content of the biodiesel from fresh oil showed promising values from fresh oil but that of the used oil was lower than the B100 which poses a disadvantage to the energy out of the fuel.

Figure 7: Effect of oxygenate addition on the heat content of BDFO

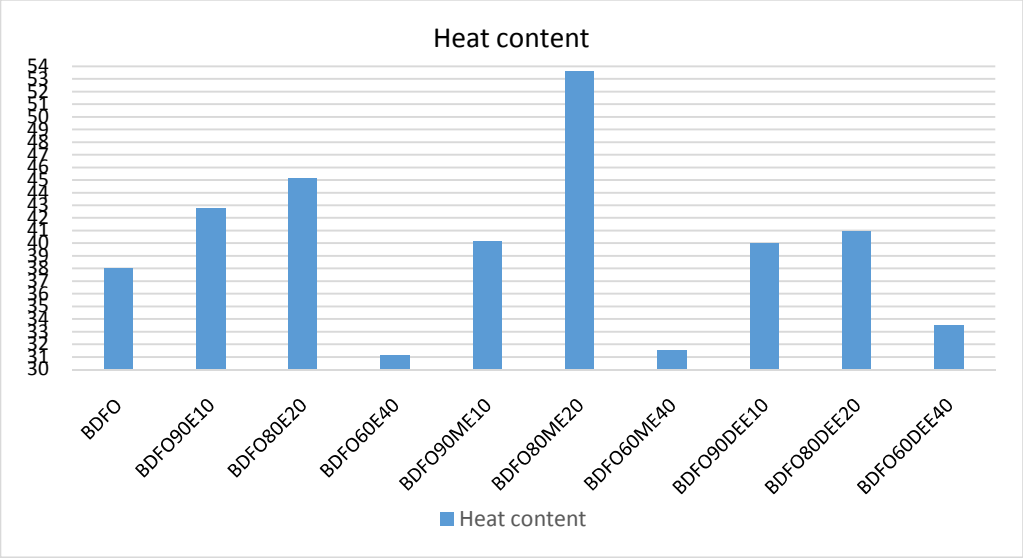
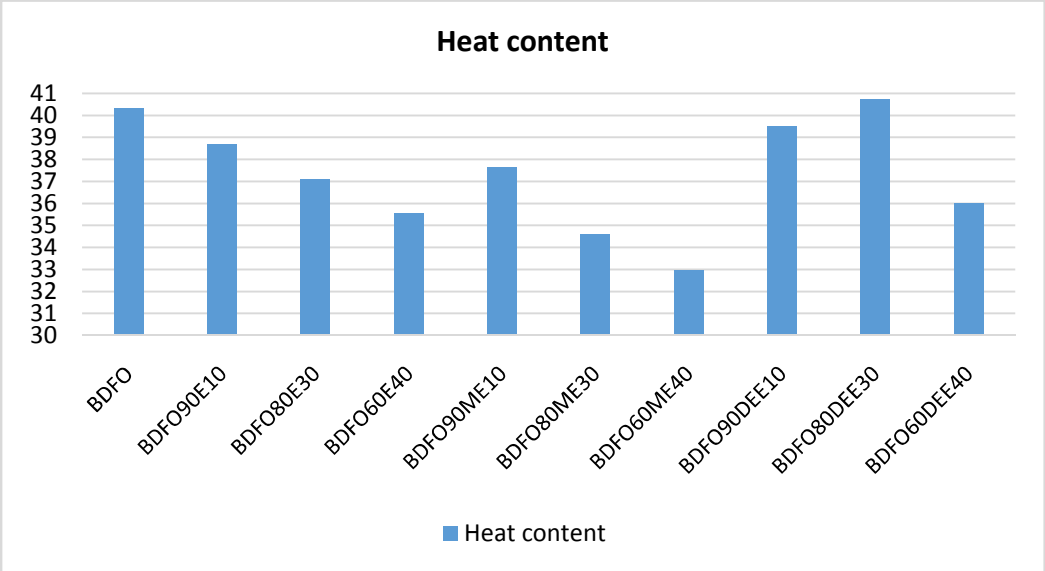


Figure 8: Effect of Oxygenates on the heat content of BDWO



In conclusion, the addition of Oxygenates- ethanol, methanol and diethyl ether exert some effect on the heat content, density, specific gravity, flash point as well as on the kinematic viscosity. Oxygenate addition have both advantages and disadvantages when it comes to the characteristics or properties of biodiesel. From this investigation, the addition of 10% oxygenate is adequate to meet commercial standards and still have environmental benefits.

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REFERENCES

1. Webb, A., & Coates, D. (2012). Biofuels and Biodiversity (Vol. Technical Series No. 65). Montreal: Secretariat of the Convention on Biological Diversity. https://www.cbd.int/doc/publications/cbd-ts-65-en.pdf
2. Okoro, L. N., Belaboh, S. V., Edoye, N. R. and Makama, B. Y. (2011). Synthesis, Calorimetric, Viscometric Study of Groundnut oil Biodiesel and Blends. Research Journal of Chemical Sciences, 1 (3) 49-52. http://www.aelsindia.com/dec_2016/6.pdf
3. Encinar J. M., Gonzalez J. F., Martinez G., & Pardal A. (2010). Transesterification of vegetable oil in subcritical methanol conditions. 18th European Biomass Conference and Exhibition, Lyon. pp. 1779-1784.
4. Romano , S. D., & Sorichetti, P. A. (2011). Dielectric spectroscopy in Biodiesel production and characterization. Green Energy and Technology , 103. ISBN 978-1-4471-5872-1

5. Arjun, C. B., Chris, W. K., & Rafiqul, I. M. (2008). Waste cooking oil as an alternate feedstock for biodiesel production. Energies 2008, 1, 3-18. http://citeseerx.ist.psu.edu/ viewdoc/ download? doi=10.1.1.360.7605 & rep=rep1&type=pdf
6. Nor, A. H., Sulaiman, H. H., & Nurrul, Y. R. (2013). Biodiesel production based on waste cooking oil. Internantional Journal of Materials Science and Engineering , Vol. 1, No. 2 December 2013. http://www.ijmse.net /uploadfile/2014/ 0519/20140519020644848.pdf
7. Aworanti, O. A., Agarry, S. E., & Ajani, A. O. (2012). A laboratory study of the effect of temperature on the densities and viscosities of binary and ternary blends of soyabean oil, soy biodiesel and petroleum diesel oil. Advances in Chemical Engineering and Science , 444-452. https://file.scirp.org/ pdf/ ACES20120400012_ 52344496.pdf
8. Obodeh, O., & Akhere, N. C. (2010). Experimental study on the effects of kerosene-doped gasoline on gasoline-powered engine performance characteristics. Journal of Petroleum and Gas Engineering, Vol. 1(2), pp. 37-40, http://www.academicjournals.org/article/article1379513294_Obodeh%20and%20Akhere.pdf
9. Nagdeote, D. D., & Deshmukh, M. M. (2012). Experimental study of diethyl ether and ethanol additives with bodiesel-diesel blended fuel engine. International Journal of Emerging technology and Advanced Engineering , , Volume 2, Issue 3, pg 195-199. http://citeseerx.ist.psu.edu/viewdoc /download? doi=10.1.1.449. 2314&rep=rep1&type=pdf
10. Brent , B., Eberhardt, J., Goguen, S., & Jimell, E. (1997, October 13). Diethyl ether as a renewable diesel fuel. Retrieved from Alternative Fuels Data Center: https://doi.org/10.4271/972978
11. Tyson, K. S., & McCormick, R. L. (2006, March). Biodiesel Handling and Use Guidelines. Colorado: U.S. Department of Energy. Retrieved from Crimson Renewable Engery: http://www.crimsonrenewable.com /biodiesel- specifications.pdf

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