Effects of a Combustion Enhancer Fuel Additive on Diesel and Biodiesel Standards

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Abstract - Fossil fuel is a limited resource and thus there is need for developments in the field of nanofluid technology for a more environmental friendly and energy-efficient alternative fuels. This issue will be addressed with a combustion enhancer fuel additive for improved fuel consumption and significantly reduce the greenhouse gas emissions. The fuel additive atomizes the fuel on injection which remarkably reduce the unburned fuel fragments in the combustion stage, and this improves the combustion process, but its impact on fuel quality needs to be determined. The aim is to determine the effect of different fuel additive dosages (2, 3 and 4 ml/l) on all diesel fuel properties. Three types of diesels was identified namely SASOL 10ppm, SASOL 50ppm and Shell 50ppm these diesels was analyzed to determine a baseline for all fuel properties to comply to the technical performance of the SANS, EN and ASTM diesel standards. All the analysis is repeated on the same diesel types blended with 5%wt. biodiesel. The small dosages of additive proved minor decreasing effects on properties like viscosity, cetane number, 90% distillation temperature and lubricity. Whereas major effects was observed in the flash point where the dosage of 0-4 ml/l fuel additive decreased the flash point from 69°C – 37°C. The optimum dosage was determined to be 2.3ml/l in diesel and 3.4ml/l when the diesel is blended with 5 %wt. biodiesel to remain within specification of the diesel fuel standards.

Index Terms--Additive, Alternative fuels, Biodiesel, Combustion enhancer, Diesel

I. Introduction

Energy is globally recognized as one of the most important factors that affect human development and economic growth. Petrochemical fuel is the largest worldwide source of energy compared to coal, nuclear, natural gas and renewable energy [1]. A high population growth rate has led to an increase in motorization and industrialization which led to a rise in the demand for fossil fuels. Increased use of fossil fuels has increased global warming through an increase in carbon dioxide in the atmosphere [2]. Fossil fuel is a limited resource and thus there is need for developments in the field of nanofluid technology for a more environmental friendly and energy-efficient alternative fuels [3]. There are two ways to address this problem, firstly with an alternative fuel like biodiesel to replace fossil fuels. This solution was determined to be a non-feasible solution and some modifications to the engine may be required. Biodiesel in South Africa is made from different types of recycled vegetable oil and are very prone to oxidation [4]. Thus biodiesel is not an advantage to this problem. However there is an alternative for an increase in compression injection engine performance by using additives that require no modification to the engine [5]. Thus this issue will be addressed with a combustion enhancer additive for improved fuel consumption and significantly reduce the greenhouse gas emissions. All the diesel standards allow additives to improve performance quality they also recommend the use of additives as long as they are used in an appropriate amount without any known harmful side effects [6],[7],[8]. The additive is dosed in very small portions 2-5mL/L. Various tests and experiments was performed with the same product and is sufficiently discussed and documented and an 8-15% fuel saving was achieved [9]. Different fuel properties would be considered for this research by focusing on optimizing the atomization which improve the combustion process for an improved engine performance by using diesel, biodiesel and fuel additives. Atomization is achieved when bulk liquids breakup in small droplets in an atomizer or injector.[10] There are some main parameters that plays a role on fuel atomization at the injection phase and the droplet burning in the combustion chamber. These properties have the largest impact on atomization namely: Density, viscosity, surface tension, latent heat of vaporization, specific heat capacity, thermal conductivity, heat of combustion and boiling point [1]. An increasing fuel viscosity cause an instable spray at the fuel breakup in the fuel jet that delay atomization. Fuel with higher surface tension resist the formation of small fuel droplets in the atomization process [11]. The additive is used to compromise for these parameters for better spray patterns in the combustion chamber that contribute to better engine performance. The key aspect of this study is to investigate diesel engines and observe the best alternatives to delay fossil fuel depletion. The characteristics of different diesel fuels combined with biodiesel and additives would be researched for a solution to fossil fuel depletion and environmental protection. All the diesel properties is considered to determine the fuel combustion. Sulfur content is a good indication of the cleanliness or quality of diesel. Sulfur cause traces of wearing and corrosion that lead to a significant effect on engine life. Copper strip corrosion test is to measure the possibility of corrosion in the engine fuel system for components as brass, bronze or copper. Crude oil contains traces of sulfur compounds that lead to corrosion effects [12]. A compression ignition engine fuel like diesel can measure the combustion or ignition quality with a parameter called cetane number. Where using fuel with a higher cetane number value the compression ignition engine would reduce exhaust smoke, increase power output and reduce combustion noise [13]. Liquid density also known as specific gravity of fuels plays an important role in spray characteristics, injection pressure and droplet breakup

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this influence the emissions and the combustion. The flash point temperature fuel property is mainly for storage purposes. Hence flammable vapors would form if fuels are spilled above their flash point that are likely to explode if ignited [14]. Viscosity is the measurement of a liquid's resistance to flow. Liquids flow less readily when the viscosity is greater. Kinematic viscosity have an influence on the spray and atomization characteristics in the combustion chamber [15]. Lubricity is the ability of diesel fuel to lubricate the fuel system to protect relative fuel supply equipment and pumps from wear when contacting with metal surfaces. Oxidation stability indicates the store stability of diesel in the presence of water and air diesel fuel oxidize.

II. Experimental

A. Methodology

Three diesel types namely SASOL 10ppm and SASOL 50ppm that was obtained from the Sasol gas station nearest to the refinery (-26.817494, 27.830306) and Shell 50ppm (-26.700032, 27.094052) was labelled, prepared and analyzed to determine a baseline. Repeated samples of the different diesel types was prepared by different dosages of 2, 3 and 4mL/L fuel additive the additive was obtained from Raventech CC. All the dosage was carefully measured with MBI smart pipette for the most accurate dosages. Three types of biodiesel from different suppliers namely NWU Potchefstroom, J-Bay biofuels and KMS biofuels across South Africa was analyzed and the biodiesel with the highest quality was chosen for further research where all the diesel samples mentioned above was prepared and blended with 5 wt.% biodiesel.

B. Diesel Standards

Fuel standards are used to regulate fuel quality for the industry. The specifications of the SANS 342 (South Africa), EN 590 (Europe) and ASTM D975 (USA) standards are compared in Table 1. There are some similarities and small variations.

TABLE I
COMPARISON OF THE SOUTH AFRICAN, EUROPEAN AND AMERICAN

Property	Units	SANS 342	EN 590	ASTM D975	Test method
Sulfur content, max[a]	mg/kg	50	50	50	D5453
Biodiesel content (FAME), max	%vol	5	7	5	EN 14078
Cetane number, min[a]		45	51	40	D613
Density ,20°C	kg/m³	800 min	820 to 845	820 to 845	D4052
Distillation temperature(90%, vol recovery), max	°C	362	360	360	D86
Flash point, min	°C	55	55	52	D93
Copper strip corrosion rating, max	Rating	Class 1	Class 1	No. 3A	D130
Cold filter plugging point	°C	-4 to 3	-5 to 5		D6371
Water content, max	%vol	0,035	0,02	0,05	D4377
Total contamination, max	mg/kg	24	24		EN 12662
Carbon residue, max	%mass	0.3	0.3	0.35	D4530
Viscosity at 40 °C	mm²/s	2.2 to 5.3	2 to 4,5	1,9 to 4,1	D445
Oxidation stability, min	hours	20	20	20	EN 15751
Ash content, max	%mass	0,01	0,01	0,01	D482
Lubricity, max	µm	460	460	520	D6079

[a] min refers to minimum and max to maximum

C. Analysis of diesel properties

1) Density and Cetane Number by FTIR

The ERASPEC FTIR with diesel fuel module was used to measure the density and cetane number using Fourier transform infrared (FT-IR) that use an interferometer was to send a unique type of infrared frequencies simultaneously to a beam splitter then through the sample. The special inferno gram signal spectrum detected and processed to obtain the data. Thus, the use of the interferometer results was extremely fast measurements. The standard test method for density using ASTM D7777 and a correlation to cetane number using the ASTM D613.

2) Flash point by Pensky-Martens

The flash point was measured with the ERAFLASH with diesel module that use a technique called Pensky-Martins automated closed-cup apparatus. A small sample was placed in a closed temperature controlled cup with an electric spark mechanism above the sample to ignite the flammable vapors that form as the sample was heated. This is a standard test method that comply with ASTM D93.

3) Viscosity by Ostwald's viscometer

The Ostwald viscometer consist of two storage bulbs which is separated by a capillary. According to the ASTM D445 the temperature of the liquid must be kept constant at 40°C as viscosity is a function of temperature, therefore a warm bath was used. The liquid was pulled up to the upper storage bulb by suction. The time was measured that the liquid take to drain by gravity between two markers. The equipment was calibrated distilled water as reference with known density and viscosity. Next the viscosity of the diesel is determined by using (1):

$$\eta_1 = \frac{\eta_0 \times \rho_1 t_1}{\rho_0 \times t_0} \quad (1)$$

Where t is the time the liquid drain through the capillary, ρ is the density and η is the viscosity.

4) Copper strip corrosion

The copper strip corrosion test is rated according to the ISO 2160 standard. The samples was heated to 100°C and a copper strip inserted in the sample for 3 hours where after it was compared and rated according to the ASTM D130 table.

5) Distillation Curves with GC-MS

The diesel samples was analyzed using the GC-MS: Agilent 7890A GC with 5975C MSD with a 1µl injection and a split inlet at 250°C and 29.352 kPa. The Vf-5ht Ultimetal column is 50m long, 0.25mm in diameter and a film thickness of 0.1 µm. This was to characterize all the alkanes in the diesel. From these results one can draw a simulated distillation curve to determine the 90% distillation temperature as required in the diesel standards. The distillation curve is an indication of the amount that would boil off at a specific temperature in diesel fuel.

6) Water content

The water content in diesel was measured by Karl Fischer auto titration method that uses coulometric titration to detect small amounts of water in a diesel sample.

7) Lubricity

The lubricity was measured using a high frequency reciprocating rig. These analysis was outsourced to the Chemical engineering department at the University of Pretoria.

8) ICP

The inductively coupled plasma mass spectrometry equipment have the ability to detect metal concentrations in a substance. This technique was used to determine the sulfur content in diesel and the sulfur, phosphorus, Sodium, Magnesium, Potassium and calcium content in the biodiesel. These analysis was outsourced to Wearcheck.

D. Biodiesel standards

There are a number of fuel property standards that are essential to diesel engines and proper operation. The South African and USA diesel standards allow a maximum of 5% biodiesel blend where the European diesel standards allow a maximum of 7% biodiesel blend. In Table II the properties of the SANS 1935 is listed to compare to the analysis.

TABLE II
REQUIREMENT FROM THE SANS 1935 BIODIESEL STANDARDS

Property	**Units**	**SANS 1985**	**Test method**
Ester content	%mass	96,5 min	SANS 54103
Density at 15°C	kg/m³	860-900	ISO 3675
Kinematic viscosity at 40°C	mm2/s	3,5-5	ISO 3104
Flash point	°C	101 min	ISO 2719
Sulfur content	mg/kg	10 max	ISO 20846
Carbon residue	%mass	0.3 max	ISO 10370
Cetane number		51 min	ISO 5165
Sulphated ash content	%mass	0,02 max	ISO 3987
Water content	mg/kg	500 max	ISO 12937
Total contamination	mg/kg	24 max	SANS 52662
Copper strip corrosion	rating	Class 1	ISO 2160
Oxidation stability	h	6 min	SANS 54112
Acid value	mg KOH/g	0,5 max	SANS 54104
Iodine value	g /100g of FAME	140 max	SANS 54111
Linolenic acid methyl ester	%mass	12 max	SANS 54103
Methanol content	%mass	0,2 max	SANS 54110
Monoglyceride content	%mass	0,8 max	SANS 54105
Diglyceride content	%mass	0,2 max	SANS 54105
Triglyceride content	%mass	0,2 max	SANS 54105
Free glycerol	%mass	0,02 max	SANS 54105
Total glycerol	%mass	0,25 max	SANS 54105
Group I metals(total Na ,K)	mg/kg	5 max	EN 14538
Group II metals(total **Ca** ,Mg)	mg/kg	5 max	EN 14538
Phosphorus content	mg/kg	4 max	SANS 54107

E. Analysis of biodiesel properties

All the analysis that was performed on the diesel was repeated on the biodiesel with addition of the following analysis.

1) Linolenic acid methyl ester with GC-FAME

The FAME GC: Agilent 7820A GC with a 1µl injection and a split inlet at 250°C and 400.78 kPa. The HP-88 column is 100m long, 0.25mm in diameter and a film thickness of 0.2 µm. This is to characterize a wide range of fatty acid methyl ester in the biodiesel from C6:0 to C18:3.The FID detector is calibrated at 350°C with 40mL/min H_2 flow,450mL/min Air flow and 1mL/min He(make up) flow. By the use of calibration curves the linolenic acid methyl ester content can be determined.

2) Free and total glycerol titrations

The free glycerol is all the unbounded glycerol in the substance where the total glycerol consist of the free and bound glycerol from uncovered triglycerides. To prepare a sample for total glycerol one need to boil the biodiesel and condense for a period of time to separate the bound glycerol from the triglycerides. The same titration methods was performed on free and total glycerol content in each sample.

III. RESULTS AND DISCUSSION

A. The effect of adding the combustion enhancer on Diesel standards

Most of the parameters of the diesel was analyzed and are presented. First each diesel type was analyzed to determine a baseline. When comparing Sasol 50ppm and Sasol 10ppm, two diesels that are manufactured at the same refinery. In table IV the Sasol 10ppm's sulfur content was not below 10 ppm and thus it does not comply with the standards. In table III the baseline diesel and the diesel with 2 ml/L additive comply to the SANS 342 and EN 590 where the diesel with 3ml/L comply with the ASTM D975 standard and all the diesels with 4ml/L additive was below all standards.

TABLE III
SASOL 50PPM FUEL PROPERTIES

	Units	SASOL 50ppm baseline	SASOL 50ppm + 2ml/L Additive	SASOL 50ppm + 3ml/L Additive	SASOL 50ppm + 4ml/L Additive
Sulphur content	mg/kg	20	18	19	21
Cetane Number		56.5	53.5	55.2	53.1
Density @ 20°C	kg/m^3	0.829	0.829	0.829	0.829
90% Recovery temperature	°C	350.1	343.9	347.7	340
Flashpoint	°C	65	57	**52**	**46**
Copper strip corrosion	Rating	Class 1	Class 1	Class 1	Class 1
Carbon residue	%mass	1.9	1.9	1.9	1.9
Water content	%mass	0.003	0.003	0.005	0.004
Total Contamination	mg/kg	2	1.6	4	1.6
Lubricity	um				
Viscosity@40°C	mm^2/s	2.35	2.31	2.3	2.26

TABLE IV
SASOL 10PPM FUEL PROPERTIES

	Units	**SASOL 10ppm baseline**	**SASOL 10ppm + 2ml/L Additive**	**SASOL 10ppm + 3ml/L Additive**	**SASOL 10ppm + 4ml/L Additive**
Sulphur content	mg/kg	**18**	**17**	**17**	**16**
Cetane Number		59.1	56.7	57.2	57.4
Density @ 20°C	kg/m^3	0.818	0.819	0.818	0.819
90% Recovery temperature	°C	346	346	346	346
Flashpoint	°C	69	57	**52**	**53**
Copper strip corrosion	Rating	Class 1	Class 1	Class 1	Class 1
Carbon residue	%mass	1.9	1.9	1.9	1.9
Water content	%mass	0.003	0.003	0.003	0.002
Total Contamination	mg/kg	2.9	2.8	4	3.2
Lubricity	um				
Viscosity@40°C	mm^2/s	2.24	2.27	2.27	2.24

TABLE V
SHELL 50PPM FUEL PROPERTIES

	Units	Shell 50ppm baseline	Shell 50ppm + 2ml/L Additive	Shell 50ppm + 3ml/L Additive	Shell 50ppm + 4ml/L Additive
Sulphur content	mg/kg	25	20	23	22
Cetane Number		67.9	65.7	68.9	66.2
Density @ 20°C	kg/m^3	0.821	0.82	0.82	0.82
90% Recovery temperature	°C	345.6	342.3	346.8	344.3
Flashpoint	°C	70	58	**51**	**49**
Copper strip corrosion	Rating	Class 1	Class 1	Class 1	Class 1
Carbon residue	%mass	1.7	1.7	1.7	1.7
Water content	%mass	0.005	0.003	0.002	0.006
Total Contamination	mg/kg	3.7	4.5	2.9	4
Lubricity	um				
Viscosity@40°C	mm^2/s	2.95	2.89	3	3

Due to the fact that small portions of combustion enhancer is added to the diesel ≤ 4 ml/L for optimum combustion performance stated by [8] had minimal to no effect on all the diesel parameters except flash point. Some small decreasing effects was picked up in density, viscosity, cetane number, 90% distillation temperature and lubricity.

B. Effect of the combustion enhancer on flash point

When adding the combustion enhancer it significantly reduce the flash point linear. In order to comply to the SANS and EN diesel standards the optimum dosage of the additive is 2.2 – 2.3 ml/L and 2.7 – 3ml/L for the ASTM diesel standard shown in figure 1. Lines was added between the dots for a guide to the eye. The flash point is a property implemented in the standards for handling or proper safety storage of diesel fuels. This means that if diesel have a flash point below standard the diesel would have no negative impact on the engine or engine performance. Even all filling stations are equipped with tanks that can store petrol on their premises and the flash point of petrol is below -35°C.

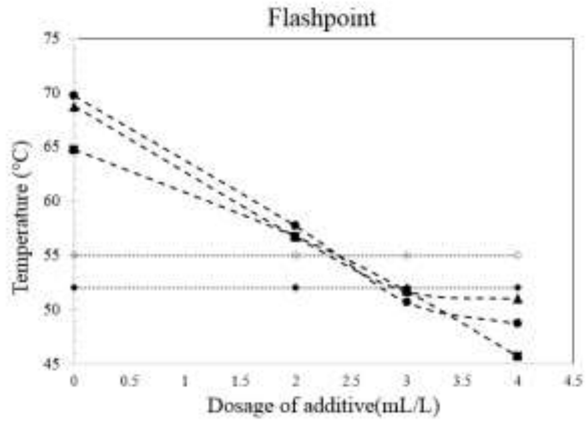

Fig. 1 Effect of the additive on Flashpoint where (▲) SASOL 10ppm, (■) SASOL 50ppm and (●) Shell 50ppm

All the same analysis was done on the same diesel samples with a 5%wt. biodiesel blend. Which increased the flash point making the optimum dosage of additive 3 – 4 ml/L depending on the type of diesel shown in figure 2. Lines was added between the dots for a guide to the eye.

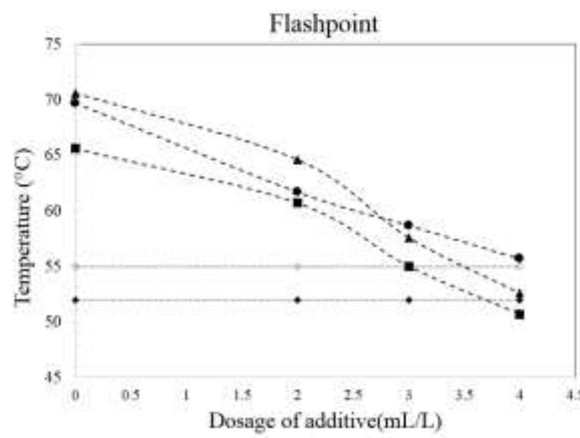

Fig. 2 Effect of additive with 5%wt. biodiesel blend on flashpoint where (▲) SASOL 10ppm, (■) SASOL 50ppm and (●) Shell 50ppm

C. Minor decreasing effects on the following diesel properties

In figure 3a) a baseline of Shell 50ppm gave a wear scar of 454µm and 3b) Shell 50ppm+ 4mL/L additive gave a wear scar of 442µm. This means that the additive gives the diesel fuel a better lubrication ability that is an advantage for engine life over the long run.

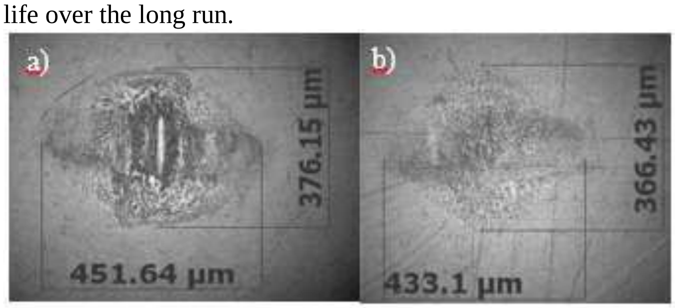

Fig. 3 Effect of additive on lubricity, a): Shell 50ppm baseline b): Shell 50ppm + 4ml/L additive

In figure 4 it is noted that the additive cause a small decrease in the viscosity with all the samples. A lower viscosity cause a better spary pattern of the fuel when injected in the combustion chamber that leads to a more complete combustion and better engine performance. When the diesel samples was blended with a 5%wt. Biodiesel the viscosity rised by a factor.

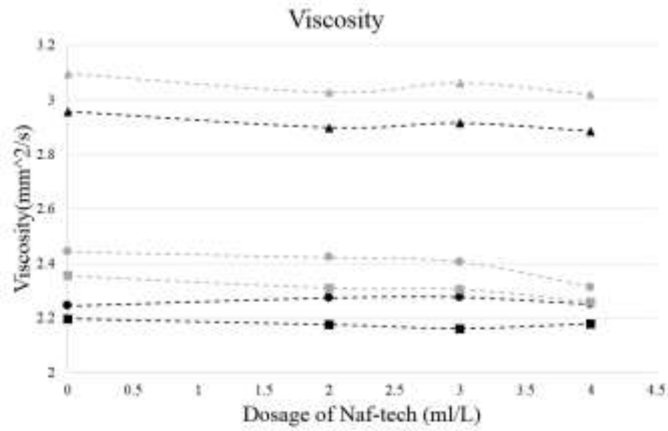

Fig. 4 Effect of additive on viscosity where (●) SASOL 10ppm, (■) SASOL 50ppm and (▲) Shell 50ppm and (●) SASOL 10ppm+5%wt. biodiesel, (■) SASOL 50ppm+5%wt. biodiesel and (▲) Shell 50ppm+5%wt. biodiesel

D. Biodiesel analysis

Three biodiesel types was analyzed and the biodiesel of the highest standard was determined to be J-Bay Biofuels complying with all the standards except the oxidation stability was below standard. The biodiesel was blended with an antioxidant additive which raised the oxidation stability from 1.25 to 11.5 hours as shown in figure 5 to obtain a biodiesel that comply to the technical performance of the SANS 1935 standard. This biodiesel was blended 5%wt. in all the diesel samples to determine the effect.

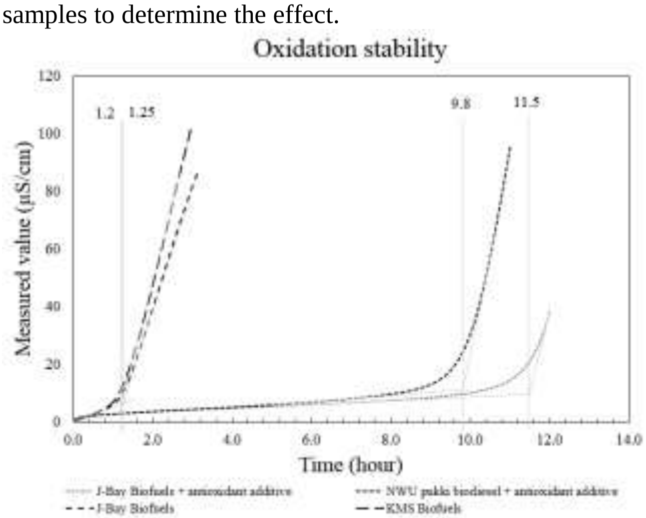

Fig. 5 Impact of antioxidant additive on Oxidation stability

In Table VI is the results from the different biodiesel suppliers. The biodiesel from J-Bay biofuels was determined to be the best and was used in this research. The NWU Pukki biodiesel had a high acid value. Where the KMS Biofuel have a very low flashpoint and may contain other additives.

TABLE VI
BIODIESEL RESULTS

	NWU Pukki Biodiesel	J-Bay Biofuels	KMS Biofuels
Sulphur content	109	113	176
Cetane number	53.4	58.2	56.4
Density	0.8335	0.8335	0.8335
Flash point	170.5	170.5	**67.6**
Copper strip corrosion	Class 1	Class 1	Class 1
Water content	0.012	0.02	0.016
Viscosity	4.45	4.57	4.6
Ester content	89	91	84
Phosphorus content	4	5	14
Acid value		6.5	7
Free glyerol	0.016	0.018	0.02
Total Glycerol	0.1	0.18	0.05
Oxidation stability	9.8	11.5	1.2
Linolenic Acid methyl ester	0	0	0
Group I metals(Na and K)	10	11	1
Group II metals(Ca and Mg)	6	4	6

IV. CONCLUSION

This article concludes that the combustion enhanced diesel is a promising alternative solution to diesel fuel and the additive had little to no effect on all the properties due to the fact that small amounts is dosed for better performance the flash point however reduced significantly. As little as 2.5ml/l would reduce the flash point below the SANS 342 and EN590 standard. Further studies should be done for a controlled fuel additive applicator equipment to ensure compliance to diesel standards.

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