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Characterization of Fuel Properties for the Biodiesel-Petro-Diesel Blends Dosed with the FPC

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I. Introduction

Due to the fluctuating cost of common petroleum products (petro-diesels) and the need to reduce fuel consumption worldwide, there has been a renewed investment in the development of the alternative energy sector in South Africa (White Paper, 2006). According to Pradhan and Mbohwa (2014), South Africa is the largest energy consumer amongst the African countries as it contributes to about 31% of Africa's primary energy consumption. The highest energy demands have been predominantly attributed to the transport sector. In light of this, the Department of Minerals and Energy (DME) initiated the development of a Bio-fuels Industrial Strategy in the year of 2005, to systematically quench these growing energy demands (White Paper, 2006). Later, the Position Paper was published in terms of National Energy Act 34 of 2008. However, challenges such as biodiversity, impacts on food security, lack of understanding of the new technology and slow agricultural development due to land use changes have stalled the targeted biofuel commercialization potential over the years (Avinash A. et al, 2014; Mobida E. et al, 2014).

Nevertheless, studies have been conducted in recent years to investigate the economic viability of biodiesels derived from vegetable or animal fats as well as synthetic diesels from biomass, biogas, natural gas, and coal (Avinash A. et al, 2014; Mobida E. et al, 2014). A detailed account on the production of biodiesel can be found elsewhere (Mittelbach M. and Gangl S., 2001; Kivevele T. and Huan. Z.,2015).The effects of different formulations of biodiesel and petro-diesel blends on fuel flow properties such as density and viscosity have been investigated by numerous scholars (Mittelbach M. and Gangl S. 2001; Kivevele T. and Huan. Z., 2015, Enmeremadu C.C., 2011). All these studies aided in developing a knowledge base on the potential alternative fuel sources and the effects of blending different fuels in order to create a better fuel economy.

In addition, successful reports on studies aiming on the reduction of fuel consumption in South African UD60 diesel trucks using a homogenous catalyst called the Fuel Performance Catalyst (FPC) have been reported by Mosesane et al (2015). Elsewhere, scholars such as Zhang (2009) also reported positive results on the performance of this catalyst. The FPC is a homogenous diesel additive made from ferrous picrate with a complex concoction of short-chain alkyl benzenes (±87%), n-butanol (±12%), dioctyladipate (±1%) and a common plasticizer (Zhang, 2009). Although the fuel consumption studies have been documented, there is still a knowledge gap on the effects of the FPC on the stability of the density and viscosity of pure petro-diesels, biodiesels and their blends. Characterization of these properties is crucial as they determine the ease of flow and atomization in diesel engines (Schwab A.W. et al., 1987).

Numerous researchers have investigated different biodiesel-petro-diesel blends on various diesel engines to examine fuel performance characteristics such as exhaust emission parameters (Durbin, T. D. et al, 1999), energy output, thermal efficiency and other fuel performance associated properties (Nwafor, O.M.I. and Rice, G., 1996; Misra, R.D. and Murthy, M.S., 2011). Their formulations showed comparable performance in relation to the pure diesel. Their results also showed a reduction in harmful exhaust gas emissions by the biodiesel-petro-diesel blends as compared to the pure diesel feeds. Common blends may range from a ratio(s) of 2:98% (B2) up to 100% (B100) by volume. Although biodiesels are miscible with petro-diesel in a variety of proportions, not all formulations may be used in diesel engines as an increase in biodiesel concentration

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increases both fuel density and viscosity (Enmeremadu C.C., 2011). According to the Engine Manufacturers Association (EMA), blends of up to 20% biodiesel and 80% petro-diesel (B20) can be used in nearly all diesel equipment and are compatible with most storage and distribution equipment. Blending ratios higher than B20 may clog up the engine piping systems and also necessitate engine modifications (Schwab A.W. et al., 1987). Hence, the warranty on most new engines only allows a maximum of B 20 to be used as reported by Enmeremadu (2011). Biodiesel blends of up to 20% have been reported to reduce emissions of hydrocarbon (HC), carbon monoxide (CO), sulphur dioxide (SO_2), and particulates as well improve the engine performance (Balat and Balat, 2008; Zhang et al, 2003).

In this regard, this work aims at studying the effect of the FPC on the flow properties namely; density and viscosity of biodiesel-petro-diesel mixtures of different ratios. Flash point tests have also been incorporated to the test matrix to account for the minimum temperature at which the fuel burns when subjected to an external heat source. This work forms part of the biodiesel-petro-diesel blending investigations in terms of Act 120 of 1997 in line with the position taken by the South African petroleum regulators (White paper, 2006 and Green Cape, 2013).

II. Materials and Methods

The biodiesel used was produced by Matayo Bio-fuels Pty Ltd, South Africa using the Fuel Meister 2 which requires vegetable oil with about 0% to 10% Free Fatty Acid (FFA) content. Samples of biodiesel and petro-diesel (50ppm Sulphur) were collected from the Matayo storage tank and the local Garankuwa filling station respectively. The experiments were carried out in two stages namely: (i) FPC and Biodiesel-Petro-diesel blending and (ii) Fuel blend property characterization involving density, viscosity and flash point investigations. All measurements were carried out in at least three repetitions. For each set of conditions, the mean was used for analysis.

a) Fuel blending

The fuel blends formulated in this work are made up of a volume by volume (Vol %) mixture of biodiesel and petro-diesel at ratios of 10:90, 20:80 and 30:70 to expand the test range. These were given acronyms of B10, B20 and B30 respectively. The FPC dosed batch of the B10, B20 and B30 blends was added to the experiment matrix at an FPC: Biodiesel-petro-diesel ratio of 1:10 000 by volume. FPC dosages were made using a Gilson micropipette. All blending was performed at room temperature. All doses of biodiesel or FPC were added to the petro-diesel under continuous mixing by a magnetic stirrer in a 500mL beaker.

b) Fuel density and viscosity determination

The fuel density was analyzed as a function of temperature using a Rudolph Research Analyzer - Automatic Density Meter in accordance with ASTM D1250 standard. Viscosity was measured using a Brookfield DV II + Pro Viscometer as per ASTM D7467-13 standard. All samples were subjected to a temperature range of 20-80˚C with 5˚C increments.

c) Fuel flashpoint determination

The fuel flashpoint investigations were conducted using a Normalab Flashpoint Tester which was set at 60˚C as per NFEN 22719 standards. Samples of 75mL were poured into a flash point cup which was connected to the regulator bath to steadily increase the sample temperature from 20˚C to a maximum of 80˚C.

III. Results and Discussion

a) Fuel blending

In the Fig. 1 are shown the density data obtained for the pure biodiesel (B100), petro-diesel (B0) and the fuel blends (B10-30) studied as a function of temperature. The Fig. 1a represents the study where the FPC was not added to the fuel while the FPC dosed fuel tests at a 1: 10 000 FPC to Fuel ratio are depicted on Fig.1b. The collected data shows are linear decline in fuel density as the temperature increases irrespective of its blend formulation and catalyst dosage.

A fuel concentration packing order can be observed on both density plots where for blended fuel the reduction in biodiesel content translates results of reduced density. For instance, when referring to Fig. 1a, the density curve packing order is a follows: B100>>B30>B20>B10>B0. Referring to Fig.1a, the pure petro-diesel appeared to have lower density in comparison the pure biodiesel by 6.08% when taking the mean of the resulting density range. Blending proved to generate a median density with respect to both biodiesel (B100) and petro-diesel (B0) pure fuels as depicted on Fig 1 irrespective of the FPC dose investigated. To establish the line of fit, the fuel blend results were observed to be congruent with the work of Enweremadu et al (2011), whereby blend formulations data set followed the equation (1) that follows:

$$\rho = AT + B \tag{1}$$

Where ρ represents the density of the blend (g/cm³), A and B denote the fitting curve coefficients for the temperature range, T (˚C) investigated. Taking a blend with common concentration of FPC undosed biodiesel blend of B20 in this study and the data was best modelled by equation (2) that follows:

$$\rho = -0.0007T + 0.8696 \tag{2}$$

When equation (2) is used, the fitting curves produced a regression coefficient of R^2=0.9999. For the

FPC dosed fuel, the data set followed the equation (3) that follows:

$$\rho = -0.0007T + 0.8704 \qquad (3)$$

The regression coefficient obtained from the line of fit was $R^2=0.9999$. It can be observed that the fuels showed equivalent values of "A" and minor deviation in "B" which was translated to a standard deviation of 0.0005657. The summary of the fitting curve coefficients and R2 values are represented on Table 1. When comparing the complete data set of the FPC dosed and undosed fuel, a maximum standard deviation of 2.7305×10^{-4} was obtained as shown on Table 2. With regards to the values of the mean density for the FPC dosed fuel, one may deduce that the influence of the FPC on fuel density was insignificant for the studied samples as evidenced by the low standard deviation values.

b) Effect of FPC on fuel viscosity

Biofuel has been reported by numerous scholars to exhibit high viscosity as compared to petro-diesel (Franco Z. and Nguyen Q.D., 2011; Misra R.D. and Murthy M.S., 2011; Geacai S. et al, 2015). This often causes poor fuel atomization crucial for combustion in combustion chambers leading to injector chocking and the accumulation of carbon in the engines (Schwab A.W. et al., 1987). One solution often proposed is the efficient biodiesel-petro-diesel blend formulation which then leads to the attainment of acceptable flow properties as conducted in this work. On the Fig.2, the viscosity data for the blend formulations presented in the previous section is depicted. It can be observed that fuel viscosity decreases with an increase in operating temperature for the both FPC dosed and undosed fuel. The relationship between viscosity and temperature for the data collected was discovered to follow a power fitting curve as in equation (3) that follows:

$$\nu = cT^d \qquad (4)$$

Where ν is the fuel viscosity (cP), c and d are the fitting curve coefficients. The summary of the fitting coefficients for the investigated fuels is displayed on Table 3. From the regression coefficient values (R^2), it can be deduced that the fitting curve represented by equation (3) can be used to predict the fuel viscosity as a function of temperature since $R^2>0.96$ for the majority of the blends. The expected packing order exhibited on the density curves in previous section where the highest values were obtained at high biodiesel concentration was also realized on the viscosity curves as seen on Fig. 2.

The FPC dosed fuel blends followed a similar trend, with the curves approaching a similar value of 95.8 cP at 80 ˚C. Having B30 approaching B20, more statistical analysis was needed to validate the presence of variance in the mean data sets of the FPC dosed and undosed fuels. A comparative study of the FPC dosed and undosed fuels depicted on Table 4 shows that there is variance in the means of viscosity since ANOVA(n=13, P=0.05) F test value of 494.140 is greater than F_{crit} of 2.604, requiring further t-Test analysis assuming unequal variance between the two data sets of n=13 each. From the Table 4, the difference between the B30 sample means of 134.6297 and 132.759 cP for the FPC undosed and dosed fuels respectively can be observed. The significance of the standard deviation (Std. Dev) of 1.3228 was investigated using the t-Test. The statistical analysis showed a t_{stat} value of 0.1466 which is greater than the $t_{critical}$ value of 2.064 and this justify that there was no need to reject the null hypothesis as the observed difference between the mentioned sample means is not convincing enough to conclude that the average viscosity values differ significantly. The comparative study on Table 4 still shows insignificant variance between FPC dosed and FPC undosed blends as the t_{stat} values are lesser than those of the $t_{critical}$ values.

c) Effect of FPC on fuel flash point

The flash point temperature of biodiesel is the minimum temperature at which the fuel will ignite (flash) in the presence of an ignition source. Flash point varies inversely with the fuel's volatility (Sivaramakrishnan and Ravukumar, 2012). Biodiesels have been reported to have higher flash and fire points than the petro-diesel by Odeigah Edith et al (2012). From the Table 5, it can be observed the flash point values generally increase with an increase in biodiesel concentration. When comparing the FPC undosed and dosed blends, the results showed a slight increase in flash point of B10 samples while at higher blend concentrations, the FPC dosage marginally lowered the flash point of all investigated blends. Nevertheless, the observed increase in flash point as blend concentration increases may be considered as good results with respect to safety and fuel handling requirements. At the same time having FPC lower the flash point marginally can be good for ignition of fuel in combustion ignition engines. This can be attributed to the observed reduction in fuel viscosity and density as discussed in the previous section, although the deviation is insignificant.

IV. Conclusion

The results have revealed that at an FPC: Diesel fuel dosage ratio of 1: 10 000, the FPC did not have significant effects on both density and viscosity of the fuel when temperature was steadily increased from 20°C to 80°C. An increase in blend concentration resulted to an increase in flash point. This was considered as good safety feature for fuel handling purposes.

Finally, the results presented in this paper should not be presumed to be the final answer to properties studied in this work on the specific biodiesel-petro diesel blends used but rather be used as an aid in the dosing, testing and blending of other biodiesel blends from other sources.

V. Abbreviations

FPC – Fuel Performance Catalyst

DME – Department of Minerals and Energy

EMA – Engine Manufactures Association

HC – Hydrocarbon

CO – Carbon monoxides

SO_2 – Sulphur dioxide

NFEN – French regulations and standards

FFA – Free Fatty Acids

Vol % – Volume by volume percentage

ASTM – American Society for Testing and Materials

ANOVA – Analysis of Variance

Std. Dev – Standard deviation

R^2 – Regression coefficient or Correlation factor

F_{crit} – F-test critical value

t_{crit} – t-test critical value

t_{stat} – t-test statistical analysis value

B0, B10, B20, B30, B100 – Biodiesel 0% (Pure diesel), Biodiesel 10%, Biodiesel 20%, Biodiesel 30%, Biodiesel 100% (Pure biodiesel).

VI. Acknowledgements

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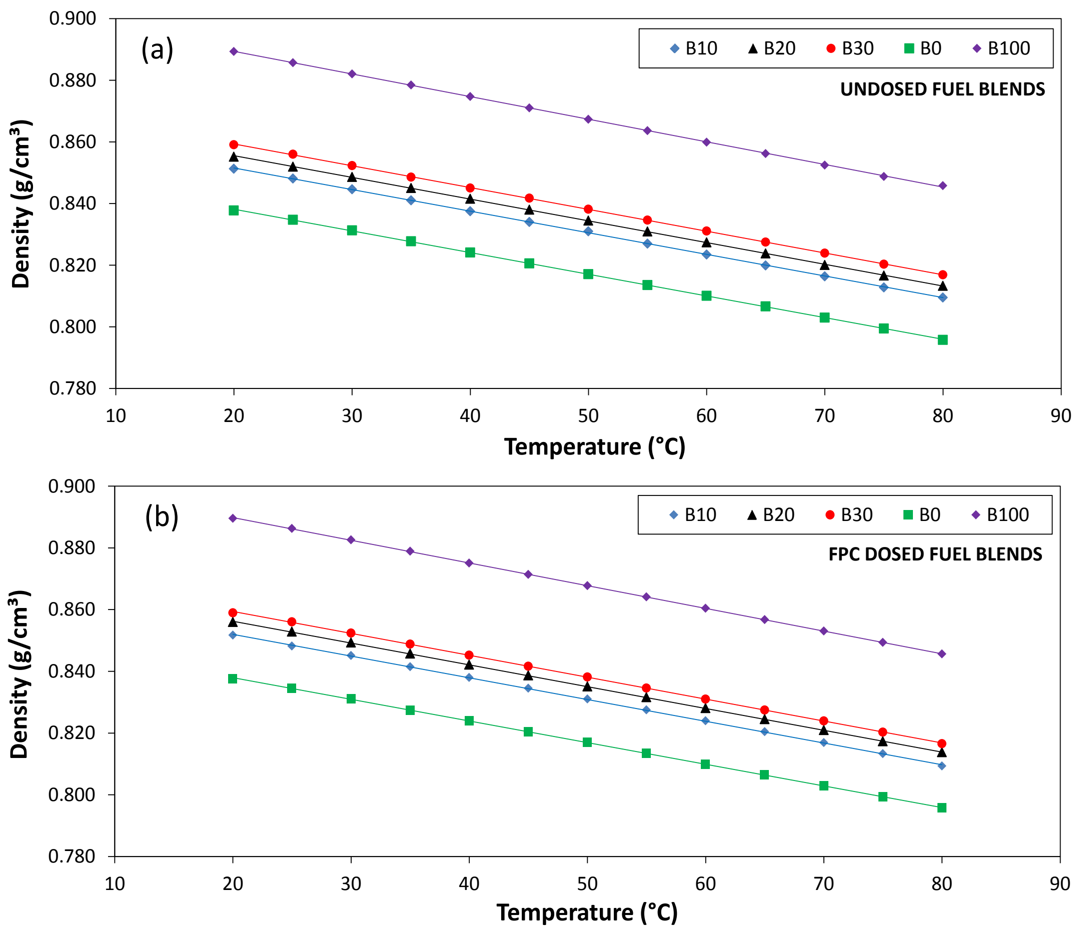

Fig. 1 : Fuel density as a function of temperature for the: (a) FPC undosed and (b) dosed Biodiesel-petro-diesel blends (B10-B30%, Vol %)

Table 1 : Density fitting curve coefficients for the FPC undosed and dosed Biodiesel-petro-diesel blends

FUEL BLEND	UNDOSED FUEL			FPC DOSED FUEL		
	Coefficients		Regression	Coefficients		Regression
	A	B	R^2	A	B	R^2
B100	-0.0007	0.9040	0.9999	-0.0007	0.9045	0.9999
B30	-0.0007	0.8735	0.9999	-0.0007	0.8736	0.9999
B20	-0.0007	0.8696	0.9999	-0.0007	0.8704	0.9999
B10	-0.0007	0.8656	0.9998	-0.0007	0.8660	0.9998
B0	-0.0007	0.8522	0.9999	-0.0007	0.8520	0.9999

Table 2 : Mean density comparative study for the FPC undosed and dosed Biodiesel-petro-diesel blends

FUEL BLEND	UNDOSED FUEL	FPC DOSED FUEL	COMPARATIVE STUDY
	Density (g/cm³)	*Density (g/cm³)*	*Std. Dev.*
B100	0.8674	0.8677	2.7305×10^{-4}
B30	0.8381	0.8381	3.6262×10^{-6}
B20	0.8353	0.8350	1.9001×10^{-4}
B10	0.8305	0.8309	2.4549×10^{-4}
B0	0.8171	0.8169	$1.2293 \times 10\text{-}^{4}$

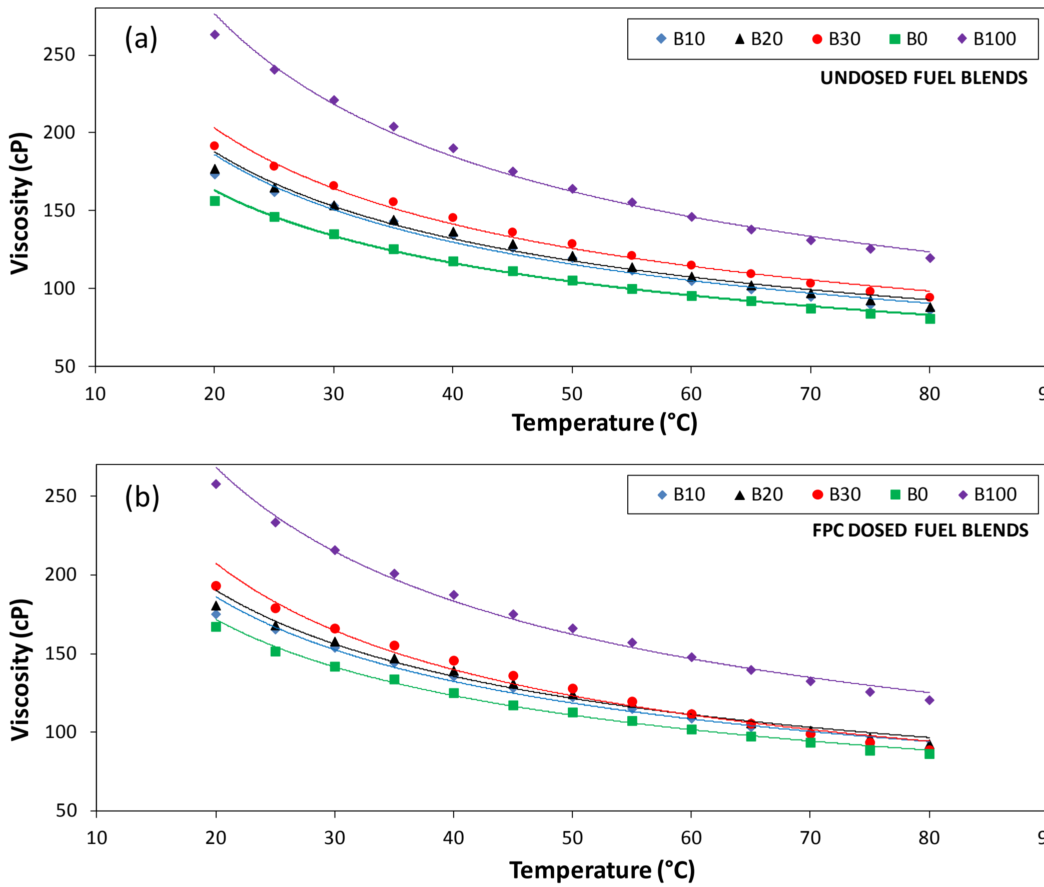

Fig. 2 : Viscosity data plotted as a function of temperature for the FPC dosed and undosed petro-diesel, diesel and relevant blends (B10-B30%, Vol %)

Table 3 : Viscosity model coefficients for the FPC undosed and dosed biodiesel-petro-diesel blends

FUEL BLEND	UNDOSED FUEL			FPC DOSED		
	Coefficients		*Regression*	*Coefficients*		*Regression*
	C	*d*	*R^2*	*c*	*D*	*R^2*
B100	1573.10	-0.580	0.9922	1397.10	-0.551	0.9903
B30	971.12	-0.522	0.9846	1140.90	-0.569	0.9767
B20	860.73	-0.508	0.9811	823.53	-0.489	0.9844
B10	879.95	-0.519	0.9766	812.27	-0.492	0.9821
B0	697.41	-0.485	0.9936	718.68	-0.478	0.9930

Table 4 : Summary of experimental data for flash tests of biodiesel-diesel blends

PROPERTY	BLEND CONDITION	FUEL BLEND				
		B0	B10	B20	B30	B100
Flash point (°C)	*Undosed fuel*	70	71	78.5	78.5	137
	FPC dosed fuel	69	74.5	76.5	78.5	124.5

Table 5 : Mean density comparative study for the FPC undosed and dosed Biodiesel-petro-diesel blends

	UNDOSED FUEL	FPC DOSED FUEL		ANOVA		t-Test	
BLEND	*Viscosity (cP)*	*Viscosity (cP)*	*Std. Dev.*	*F*	*F-critical*	*t-stat*	*t-critical*
B100	175.5077	174.2308	0.9029	722.55	2.604	-0.073	2.064
B30	134.6297	132.759	1.3228	494.14	2.604	0.146	2.064
B20	125.8077	129.2052	2.4024	266.422	2.604	-0.305	2.064
B10	123.6205	126.0923	1.7478	417.775	2.604	-0.073	2.064
B0	111.0923	118.1615	4.9987	54.7	2.604	-0.667	2.064

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