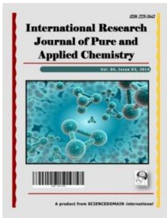

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Biodiesel Produced from *Azadirachta indica* and *Hevea brasiliensis* Seeds Oil: Effect of Additives on Cold Flow Properties

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Authors' contributions

This work was carried out in collaboration among the authors. Authors CSE, VOA and EBA designed the study and wrote the protocol. Authors OJO and CSE preformed the statistical analysis, managed the literature search and wrote the first draft of the manuscript. All the authors read and approved the final manuscript.

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ABSTRACT

This study is aimed to evaluate the effect of additives on cold flow properties of biodiesel fuel obtained from *Azadirachta indica* and *Hevea brasiliensis*, readily available seed oil in Nigeria. The seed oils were converted to biodiesels via transesterification and additives kerosene, Eva, Ethanol, Cristol and Lubrizol were added to evaluate the cold flow properties. The results showed that biodiesel produced from *Azadirachta indica* and *Hevea brasiliensis* has closed properties to diesel. Effects of ethanol, kerosene and commercial additive on cold flow behaviour of this biodiesel revealed that kerosene and EVA improve the cold flow properties when blended up to 20%. Though, lower blends (2%) with cristol and Lubrizol 7671 shows better lowering of cold flow properties of biodiesels from *Azadirachta indica* and *Hevea brasiliensis* seed oils. This will lead to development of biodiesel as an alternative source of energy to diesel.

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Keywords: Azadirachta indica; Hevea brasiliensis; biodiesel; ethanol; pour point; cloud point; commercial additives.

1. INTRODUCTION

Around the globe, there has been a considerable awareness of developing biodiesel as an alternative fuel in recent years due to its environmental benefits with similar engine performance and durability to the petroleum diesel. In most of the developed nations efforts point to the use of biodiesel blends up to 20% (B20) for both on-road and off-road applications in the near future. However, the tendency of crystallization formation at low temperature may limit its usage. Hence a significant problem of biodiesel is that its usage exhibits cold start problems due to the long chains that increase cloud point, pour point, cold-flow plugging point (CFPP) [1].

The cloud point is described as the temperature at which the smallest observable cluster of wax crystals first appears, while the pour point is the lowest temperature at which movement of biodiesel is observed, and the cold filter plugging point is an estimation of the lowest temperature at which a fuel will give trouble-free flow in certain fuel systems. There are two primary ways of increasing the cold flow properties of biodiesel blends; the addition of cold flow additives and winterization of the biodiesel component prior to blend preparation. Several investigators have studied the cold flow properties of biodiesel and biodiesel blends based on different types of vegetable oils [2-5].

The cold flow properties of biodiesel fuels are dependent on the feedstock (specific type of oil, fat or grease) from which they are made and the level of saturated fat. Since, transesterification process does not alter the fatty acid composition of vegetable oil feedstock, biodiesel made from feedstock containing higher concentrations of high melting point saturated long-chain fatty acids tends to have relatively poor cold flow properties [4].

Therefore, with the enormous advantages in properties biodiesel compared to diesel, improvements of its low temperature flow characteristics still remains one of the major challenges when using biodiesel as an alternative fuel for diesel especially in low temperature environment. Hence, the need to define different additive to improve low temperature flow characteristics of biodiesel from different feedstocks becomes imperative. This paper is aimed to evaluate the effect of additives on cold flow properties of 100% biodiesel fuel obtained from *Azadirachta indica* and *Hevea brasiliensis*.

1.1 Mechanism and Impact of Cold Flow Properties on Biodiesel

At low temperatures, high amount of saturated fatty acid in the fuel causes high melting point components which lead to nucleation and growth of solid crystals. Exposing the fuel to temperatures below cloud point for a relatively long time causes solid crystals to grow and form interlocking networks. This ceases the flow and lead to starvation of fuel in the engine and its operation in that condition [6].

2. MATERIALS AND METHODS

2.1 Sample Collections and Oil Extraction

Dried *Azadirachta indica* seeds were obtained from the National Research Institute for Chemical Technology, Zaria, Nigeria, while the dried *Hevea brasiliensis* seeds were obtained from the Rubber Research Institute Benin, Nigeria. The seeds were cleaned by removing debris using hand picking method, dried to constant mass in an oven at 50°C for 72 h, dehauled to remove the seed coat, and the seeds dried at 50°C for another 48 h. The oil was extracted by oil expeller. The seeds were fed to a series of expellers to receive a mild pressing on continuous basis, as each screw press gradually increased the pressure on the incoming material through the interior of a closed barrel [7].

The extracted oil were drained out through a small gap between positioned hardened steel bar in the barrel cage. The oils were dark colour, with neem oil being more viscose and denser. The oils were filtered using muslin cloth to remove dirt and other inert materials. The oils were heated in flasks up to near boiling point to remove water contaminant, allowed to cool to room temperature (27°C) and taken for biodiesel production [7].

2.2 Production of Biodiesel

The Free fatty acid (FFA) content of the biodiesel was determined using ASTM standard methods by initially determination of acid value by neutralization reaction using 0.1 M KOH, hence the FFA is evaluated by dividing the acid value by 2. The neem oil had 0.78% Free Fatty Acid (FFA) content and was found suitable for direct transesterification. The rubber seed oil had high FFA content of 16.58% and was refined, as the yield of esterification process decreases considerably where FFA value > 2 % [8]. The FFA of rubber seed oil was reduced below 2 % using para toluene sulphoni lic acid as catalyst prior to transesterification [7]. A round bottom flask was used as laboratory scale reactor vessel, and a hot plate with magnetic stirrer was used for the heating. After series of experiments, the optimized reaction/heating time of 60 min, agitation speed of 375 rpm, temperature of 55°C, and alcohol to oil molar ratio of 6:1 (*Azadirachta indica*) and 9:1 (*Hevea brasiliensis*) were used for production of their methyl esters (Biodiesel). The methyl esters were tested according to ASTM standards.

2.3 Refining Process

2.3.1 De-waxing

Rubber oil was subjected to de-waxing process to remove the wax; the oil was cooled to 5°C, where the wax was converted into crystal form. Then, the wax was separated and the de-waxed oil was collected.

2.3.2 Degumming

Degumming converts the phosphatides in rubber seed oil to hydrated gums which are insoluble in oil and readily separated as sludge. In this process, 1litre of oil from above de-waxing step was measured in a beaker, heated to 60°C, and then 1%v/v phosphoric acid was added and mixed thoroughly. The mixture was maintained at 60°C for 1 hr, and hot water was added, and then mixed thoroughly. The mixture separated into two layers, the heavy phase which contained phosphatides, pigments and other impurities was then separated.

2.3.3 Neutralizing

The oil from degumming process was mixed with 100 ml of 1 M NaOH, which mixed with the free fatty acids forming soap. The mixture was heated to 60°C by continuous stirring for 1 hr to remove the free fatty acid.

2.4 Fuel Properties

The physic-chemical properties of the *Azadirachta indica* and *Hevea brasiliensis* oil based biodiesel (B100) and their various blends with diesel were evaluated using the ASTM standards procedure.

2.5 Cold Flow Study

Three samples (40 ml each) were collected for each biodiesel sample to study the effect of different cold flow improver on the samples. A 40 ml mixture of biodiesel fuel and 5% and 10% each for kerosene, 1 and 2% each for Eva, Ethanol, Cristol and Lubrizol 7871 (cold flow improvers) was tested, the procedure was again repeated twice. The cold flow properties of the biodiesel with and without additives were evaluated by ASTM D6371 using cold filter plugging point (Model Linetronic Technologies Newlab 200) at Delhi University of Technology, Delhi, India. Bath temperature of the equipment was at -34°C before the sample oil was inserted into the equipment and then the equipment started. The starting temperature of the sample in the equipment is noted and the cold filter plugging point temperature (CFPP) also noted. The laboratory temperature varies from 15°C to 25°C. The power supply is 230 volts ± 10%, hot, neutral, ground, and uninterrupted, without electrical noise and perturbation equipped with ground fault intensity devices (15Ma).

3. RESULTS AND DISCUSSION

3.1 Characterization of Biodiesel from *Azadirachta indica* and *Hevea brasiliensis* Oil

The fuel properties of neem methylester (NME) and rubber methylester (RME) and their blends in comparison with that of biodiesel are shown in Tables 1 and 2. Most fuel properties of NME and RME and their blends are compared to those of diesel. The results obtained show that, the transesterification process improved the fuel properties of the oil with respect to acid number (mgKOH/gm), density (g/cm3), kinematic viscosity (40°C), cetane number, calorific value (MJ/kg), cold filter plugging point (CFPP) (°C), flash point (°C), carbon residue (%), ester content (%) and API gravity.

The comparison of these properties with diesel shows that the methyl esters of *Azadirachta indica* and *Hevea brasiliensis* oil have relatively close fuel property values to that of diesel. Hence, no hardware modifications are required for handling the biodiesel and their blends in the existing engine.

The calorific values of all the biodiesel and their blends are lower than that of diesel because of their oxygen content. The presence of oxygen in the biodiesel helps for complete combustion of fuel in the engine. Addition of small quantity of biodiesel with diesel increases the flash point of diesel. Hence, it is safer to store biodiesel-diesel blends as compared to diesel alone. As also observed from these results, there is a good correlation between the flash point and cold filter plugging point (CFPP).

3.2 Cold Flow Properties

As shown in Fig. 1, the cold filter plugging point (CFPP) of any fuel represents the cold flow properties of the fuel. These properties for various test fuels are represented in Fig. 1. The cold filter plugging point of diesel has been found to be -9°C. The cloud points of NME100 and RME100 are found to be 5°C and 3°C respectively. It is clear from figure that cold filter plugging point increased with increase in biodiesel concentration, CFPP is a criterion used for low temperature performance of the fuels and Nigeria having a tropical climate, no problem is envisaged with the cold flow characteristics of blends of different biodiesel fuels with diesel in lower concentration having CFPP marginally higher than diesel. The above results suggest that with up to 40% substitution of biodiesel in diesel, cold flow properties of biodiesel-diesel blends are as good as neat diesel.

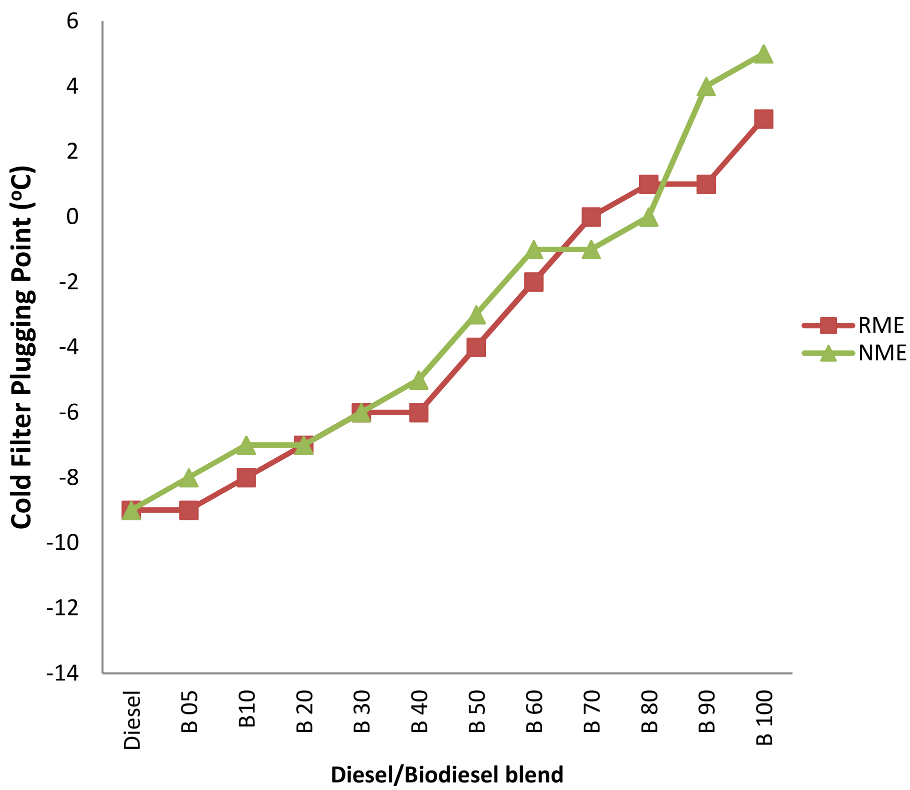

Fig. 1. Variation of cloud point of various test fuels

Table 1. Properties of biodiesel and its blends from neem seed oil

Samples	Acid number (mgKOH/gm)	Density (g/cm^3)	Kinematic viscosity (40°C)	Cetane number	Calorific value (MJ/kg)	CFPP (°C)	Flash point (°C)	Carbon residue (%)	Ester content (%)	API gravity
Diesel	0.21	0.8329	2.957	55.6	45.821	-9	65	0.05	N/A	38.39
B 05	N/A	0.8354	3.072	56.1	45.54	-8	71	0.05	N/A	37.88
B10	N/A	0.8375	3.197	56.9	45.264	-7	79	0.04	N/A	37.46
B 20	N/A	0.8429	3.432	57.9	44.731	-7	89	0.02	N/A	36.37
B 30	N/A	0.8506	3.671	58.5	44.054	-6	101	0.02	N/A	34.85
B 40	N/A	0.8547	3.882	59.6	43.514	-5	114	0.02	N/A	34.06
B 50	N/A	0.8571	4.116		42.992	-3	124	0.01	N/A	33.59
B 60	N/A	0.8627	4.415		42.461	-1	139	0.01	N/A	32.52
B 70	N/A	0.8685	4.621		41.8709	-1	151	0.01	N/A	31.42
B 80	N/A	0.8759	4.814		41.3061	0	163	0.01	N/A	30.05
B 90	N/A	0.8805	5.047		40.1273	4	171	0.01	N/A	29.20
B 100	0.16	0.8824	5.27	50.8	40.178	5	183	0.01	94.6	28.86

Table 2. Properties of biodiesel and its blends from rubber seed oil

Samples	Acid number (mgKOH/gm)	Density (g/cm3)	Kinematic viscosity (40°C)	Cetane number	Calorific value (MJ/kg)	CFPP (°C)	Flash point (°C)	Carbon residue (%)	Ester content (%)	API Gravity
Diesel	0.21	0.8329	2.957	55.6	45.821	-9	65	0.05	N/A	38.39
B 05	N/A	0.8359	3.052	56.2	45.2097	-9	79	0.05	N/A	37.78
B10	N/A	0.83842	3.104	57.5	44.612	-8	93	0.05	N/A	37.27
B 20	N/A	0.8434	3.598	58.5	43.9847	-7	107	0.05	N/A	36.27
B 30	N/A	0.8496	3.671	60.5	43.351	-6	119	0.04	N/A	35.05
B 40	N/A	0.8512	3.882	60.9	42.4609	-6	134	0.03	N/A	34.74
B 50	N/A	0.86089	4.286		42.1647	-4	148	0.02	N/A	32.86
B 60	N/A	0.86604	4.597		41.568	-2	155	0.02	N/A	31.89
B 70	N/A	0.873	4.759		41.3256	0	161	0.02	N/A	30.58
B 80	N/A	0.879	4.971		40.9214	1	175	0.01	N/A	29.48
B 90	N/A	0.88258	5.097		40.3251	1	189	0.01	N/A	28.83
B 100	0.13	0.8881	5.27	49.8	39.7	3	197	0.01	92.8	27.83

3.3 Effect of Additive on Cold Flow Properties of Biodiesel

Cold filter plugging point (CFPP) of a fuel reflects its cold weather performance. At low operating temperature fuel may thicken and might not flow properly affecting the performance of fuel lines, fuel pumps and injectors. Although most of the properties of biodiesel fuels are comparable with that of diesel fuel but the cold flow behaviour of this fuels are very poor. Figs. 2 - 6 shows the reduction in cold filter plugging point (CFPP) of RME and NME when blended with kerosene, EVA, ethanol, cristol and Lubrizol 7671. A CFPP of 5°C and 3°C was observed for B100 NME and RME, respectively. The reduction in CFPP was from 5°C to -1°C and 3°C to -5°C, when blended with 10% of kerosene and up to -2°C and -4°C when blended with 2% of EVA for NME and RME, respectively. Similarly, the reduction in CFPP from 5°C to -1°C and 3°C to -4°C, when blended with 2% ethanol and up to -7°C and -11°C when blended with 2% Lubrizol 7671 for NME and RME, respectively. Thus, kerosene and EVA improve the cold flow properties of biodiesel when blended with biodiesel up to 10 and 2%, respectively. Though, lower blends with 2% cristol and Lubrizol 7671 shows better lowering of CFPP of NME and RME. Similar results were reported by Bhale et al. [5] on blending Mahua methyl ester (MME) with these additives. However, blends with ethanol are to be discouraged as it may reduce the overall calorific value and cetane number [4].

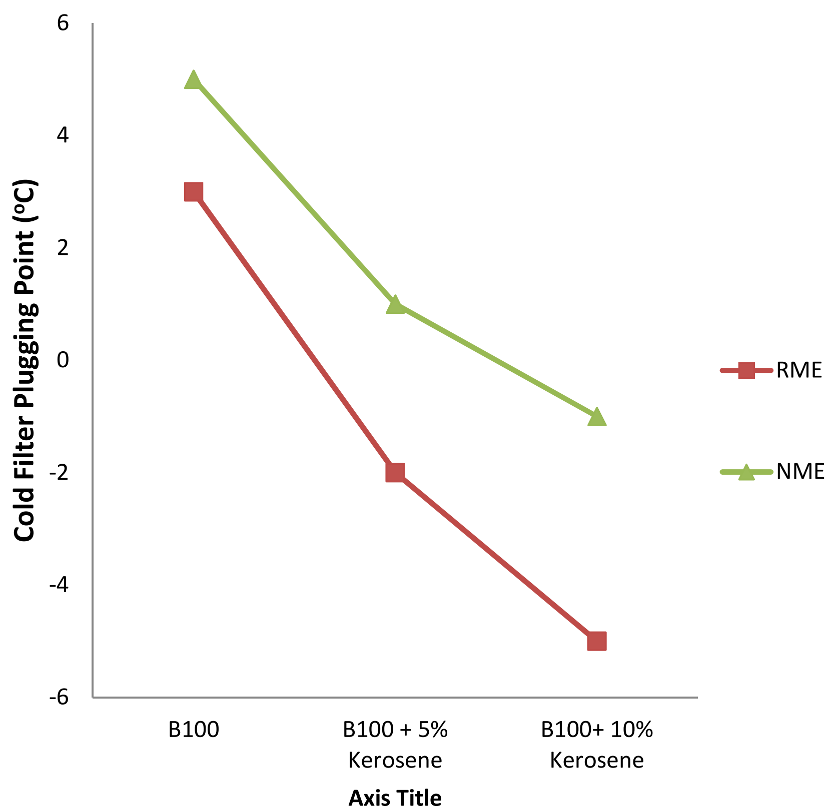

Fig. 2. Effect of kerosene on cfpp of different biodiesel samples

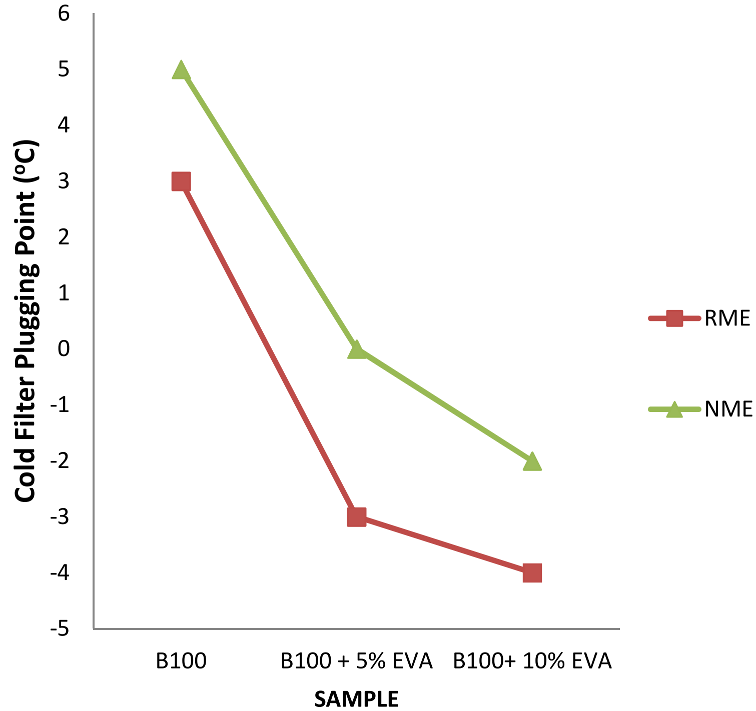

Fig. 3. Effect of EVA on CFPP of different biodiesel samples

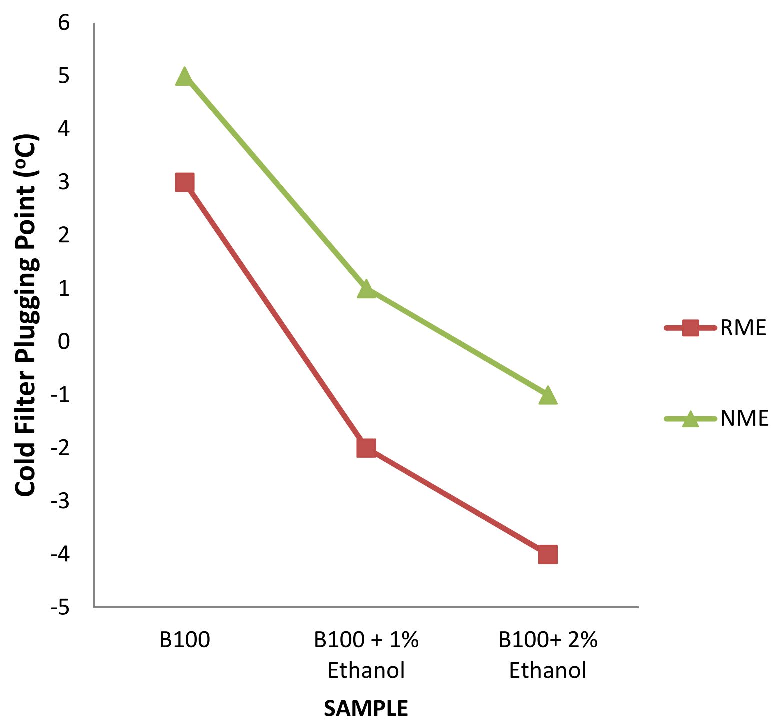

Fig. 4. Effect of ethanol on CFPP of different biodiesel samples

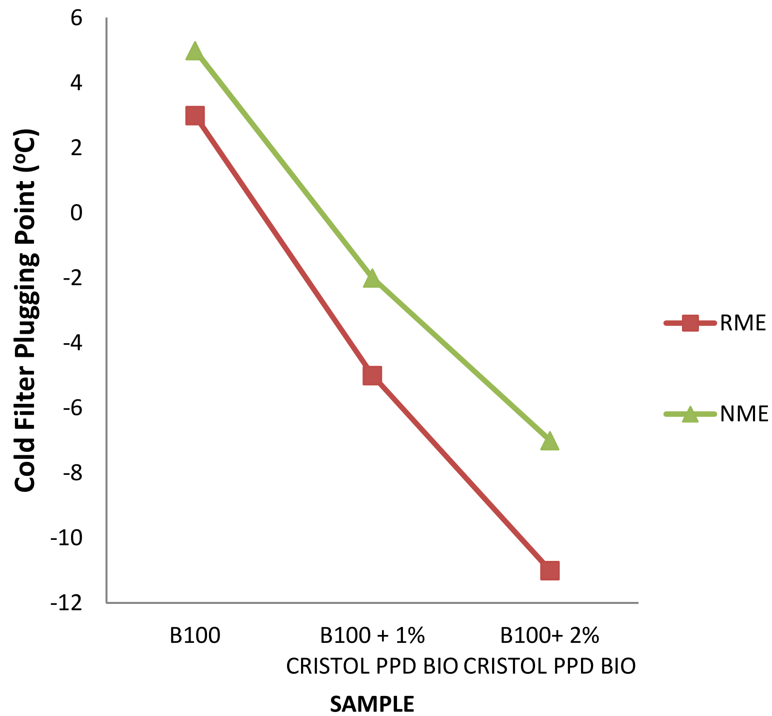

Fig. 5. Effect of Cristol on CFPP of different biodiesel samples

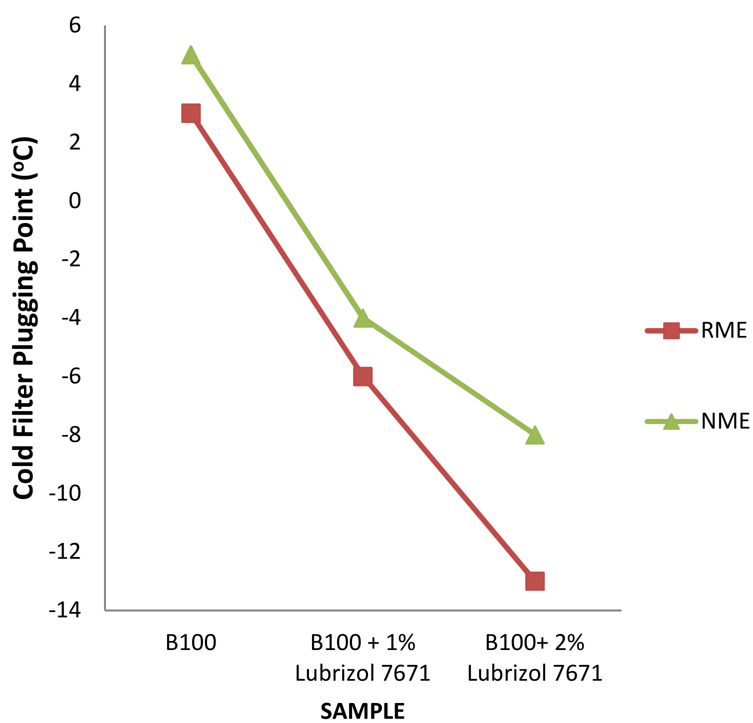

Fig. 6. Effect of lubrizol 7671 on CFPP of different biodiesel samples

4. CONCLUSION

From the results, it was shown that cold filter plugging point decreases with increase in biodiesel concentration in the biodiesel blends. Therefore, the results suggest that with up to 40% substitution of biodiesel in diesel, cold flow properties of biodiesel-diesel blends are as good as neat diesel. The effect of ethanol, kerosene, EVA, cristol and Lubrizol 7671 additive on cold flow behaviour of this biodiesel has been studied. It was observed that kerosene and EVA improve the cold flow properties when blended up to 20%. Though, lower blends 2% with cristol and Lubrizol 7671 shows better lowering of CFPP, NME and RME. This will lead to development of biodiesel as an alternative source of energy to diesel.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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