VOL. 11, NO. 6, MARCH 2016 ISSN 1819-6608
ARPN Journal of Engineering and Applied Sciences

www.arpnjournals.com

COMMERCIAL AND SYNTHESIZED ADDITIVES FOR BIODIESEL FUEL: A REVIEW

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ABSTRACT

In this paper a classification and analysing of commercial and synthesized additives used with biodiesel by different researchers was conducted. Biodiesel is widely accepted as an alternative fuel comparable to petroleum diesel in compression ignition engines. It is relatively poor cold flow property is a characteristic which limits its application. Here, fuel additives become the most viable choice not only to decrease this drawback but also to produce specified products that meet international and regional standards. This article covers a deep and through literature review of the effect of different additives on biodiesel properties, engine performance, and emission characteristics. The additives usage in biodiesel is inseparable both for improving the cold flow properties and for better engine performance and emission control. It can be concluded from the literature that specific additives for biodiesel remain at their infancy. Further research is needed to develop biodiesel specific additives.

Keywords: biodiesel, commercial additives, fuel properties, engine performance, emission.

INTRODUCTION

Biodiesel is a renewable and environmental friendly alternative diesel fuel for diesel engine (Demirbas 2007; Lam *et al.* 2009). It is an oxygenated fuel which contains 10–15% oxygen (Krahl *et al.* 2003; Ali *et al*. 2012) by weight, and is a sulphur-free fuel. These facts lead biodiesel to complete combustion and less exhaust emissions than diesel fuel. Biodiesel has a higher viscosity, density, pour point, flash point and cetane number than diesel fuel. Furthermore, the energy content or the net calorific value of biodiesel is about 12% less than that of diesel fuel on a mass basis, causing lower engine speed and power (Atabani *et al.* 2012; Syed and Gopal 2012; Ali, Yusaf, *et al*. 2014). The use of biodiesel instead of the conventional diesel fuel significantly reduces exhaust emissions such as carbon dioxide (CO_2), (Edward *et al.* 2007; Agarwal 2007) particulate matter (PM), carbon monoxide (CO), sulphur oxides (SO_X), and unburned hydrocarbons (HC) (Canakci *et al.* 2009; Carraretto et al. 2004). On the other hand, biodiesel has a higher nitrogen oxide (NO_X) emissions than diesel fuel (Robbins *et al.* 2011; Hoekman *et al.* 2011). The main disadvantages of biodiesel are injector coking, engine compatibility, and high price (Demirbas 2008). The effects of oxidative degradation caused by contact with ambient air (auto oxidation) during long-term storage present a legitimate concern in terms of maintaining the quality of biodiesel fuel.

Biodiesel is defined as alkyl esters of fatty acids, obtained by the transesterification of oils or fats, from plants or animals, with short-chain alcohols such as methanol and ethanol (Ali and Mamat 2013). It has an engine performance comparable to that with conventional diesel and could be used pure or blended with diesel (Pinto *et al*. 2005; Ali *et al*. 2013). Biodiesel is nonflammable, nonexplosive, biodegradable, and nontoxic. Besides, its use provides a reduction of many harmful exhaust emissions. A nearly complete absence of sulphur oxide (SOx) emissions, particulate and soot, and a reduction in polycyclic aromatic hydrocarbons emissions can be achieved. However, there are some technical problems associated with the use of biodiesel fuels (Ali *et al.* 2015). The use of some of them includes an increase in nitrogen oxide (NOx) exhaust emissions, which have stringent environmental regulations, and relatively poor low temperature flow properties compared to diesel. Another problem is the oxidation stability of biodiesel. The esters of unsaturated fatty acids are unstable with respect to light, catalytic systems and atmospheric oxygen. Since diesel fuels from fossil oil have good oxidation stability, automobile companies have not considered fuel degradation when developing diesel engines and vehicles. It is one of the key issues in using vegetable-oil based fuels, and attention is given to the stability of biodiesel during storage and use. These problems could be circumvented by using additives. The selection of additives for the biodiesel fuel depends on economic feasibility, toxicity, Fuel blending property, Additive solubility, flash point of the blend, viscosity of the blend, solubility of water in the resultant blend, and water partitioning of the additive (Ali, Mamat, *et al.* 2014). At present, concern about environmental regulations has been the major reason to look for alternative fuels. The use of biodiesel has presented a promising alternative in the world. It is not only a renewable energy source, but it can also reduce the dependence on imported oil and support agricultural subsidies in certain regions. The growing interest in this renewable fuel can be illustrated by the number of articles published and patents registered in this area during the past few decades.

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A number of additives have been tried by different researchers for improving the performance and also reducing emissions from diesel engines. The objective of this study to developed data base for the used additives with biodiesel under certain categories and discuss their suitability for each type of biodiesel according to their properties.

BIODIESEL FUEL ADDITIVES

Solid metallic-based additives

Many studies have been undertaken on various types of additives in both petroleum blends and pure biodiesel, to improve either the combustion properties or the emission of a compression ignition engine, through improving the biodiesel properties. Some metal-based additives are reported to be effective in improving diesel engine performance working on biodiesel.

Effect organic based synthetic Mg additive was studied (Metin *et al*. 2010) with chicken fat based biodiesel in a single cylinder direct injection diesel engine. For this purpose, a magnesium based additive was synthesized stoichiometrically. The additive was doped into the biodiesel blend by 12 µmol Mg. Engine tests were carried out with diesel fuel (EN 590) and a blend of 10% chicken fat biodiesel and diesel fuel (B10) at full load operating conditions and different engine speeds from 1800 to 3000 RPM. The results showed that, the engine torque was not changed significantly with the addition of 10% chicken fat biodiesel, while the specific fuel consumption increased by 5.2%. In-cylinder peak pressure slightly rose and the start of combustion was earlier. CO and smoke emissions decreased by 13% and 9% respectively, but NO_X emission increased by 5%. The study includes the effect of magnesium based additive on the biodiesel physical properties pour point, viscosity and flash point of chicken fat methyl ester which is non corrosive in nature and has a higher cetane number, but has certain disadvantages such as a higher freezing point, high viscosity and a high flash point. They identified that increase in additive concentrations from 0 to 16 µmol/l resulted in lower freezing point, viscosity and flash point. A dosage of 16µmol/l Mg into the chicken fat methyl ester caused a 7 ^oC pour point decrease, viscosity decreased from 5.184 to 4.812 and the flash point was decreased from 129 ^oC to 122 ^oC. They concluded that these improvements support the idea that the catalytic cracking effect of the additive results in smaller chains of hydrocarbons.

The properties of biodiesel from pomace oil improved by adding Synthetic manganese additive (Caynak *et al*. 2009). The test conducted by doping the additive with the methyl esters of pomace oil at a ratio of 12µmol/l oil methyl ester. They found that led to a 20.37% decrease in viscosity, 7 ^oC fall in the flash point and reduced the pour point from 0 ^oC to -15 ^oC. Test blend of pomace oil methyl ester at the ratio of 25% and 75% diesel fuel with 12 µmol/l manganese additive in diesel engine show that the maximum effect of the new fuel blend and diesel fuel on engine performance was obtained at 1400 RPM. There was no significant difference in the torque and power values of diesel fuel and test fuels. Maximum torque point of engine was obtained at 1400 RPM for diesel fuel and B25 which were 184.7 NM and 181.7 NM, respectively. The maximum engine power for diesel fuel and B25 were 39.9 (kW) and 39.8 (kW), respectively at 2400 RPM. According to diesel fuel values, the maximum decreasing ratio was 2.19% at 1200 RPM. An average reduction of the values was 1.54%. The reduction ratios were lower at higher speeds of the engine.

Metallic base additives Ni, Mn, Mg, Mo (Keskin *et al.* 2007; Keskin *et al.* 2008) Influence the properties of biodiesel production from tall oil. Each metallic fuel additive was added at the rate of 8µmol/l and 12µmol/l to make mixtures of 60% tall oil methyl ester/40% diesel fuel (TE60) for preparing test fuels. The results of the study showed that metallic fuel additives improved the properties of biodiesel fuels, such as pour point and viscosity values. The minimum values of the pour point and viscosity in this research were -23 ^oC, 4.3 cSt. respectively, (by addition of 12µmol/l Mn to TE60), while the minimum value of the flash point was 79 ^oC (by addition of 12µmol/l Ni to TE60). The engine specific fuel consumption of biodiesel fuels increased by 6.00%, however, in comparison with 60% tall oil methyl ester/40% diesel fuel (TE60), it showed a trend of decreasing with adding of additives. Exhaust emission profile of biodiesel fuels improved. CO emissions and smoke opacity decreased up to 64.28%, 30.91%, 56.42%, and 30.43%, respectively. They also observed low NOx emission in general for the biodiesel fuels.

Waste animal fat biodiesel characteristics were improved (Metin *et al*. 2009) by synthesized nickel and magnesium additives. In this study the effects of organic based Ni and Mg additives on the methyl ester pour point were specified. Organic based metal compounds were synthesized by reacting abietic acid in the tall oil resinic acid with NiO and MgO compounds in order to improve the animal fat methyl ester characteristics. A reduction of the pour point was achieved by adding organic based nickel and magnesium compounds to biodiesel at a ratio of 12 µmol/l oil methyl ester. The maximum effect of the new fuel blend on the engine performance was reached at 2200 RPM of engine torque. The lowest specific fuel consumptions were obtained at 2200 RPM for both fuels.

The combination of MgO as a metal based additive with palm-polyol as oxygenated additive (Husnawan *et al*. 2009) for improving the engine performance and emission characteristics. Blended palm biodiesel with additive shows a good result for exhaust emission (HC, NOx and CO) as compared with conventional diesel fuel and biodiesel diesel blends without additive. Another study (Kannan *et al*. 2011) investigated the use of ferric chloride ($FeCl_3$) as a fuel borne catalyst (FBC) for waste cooking palm oil based biodiesel. The metal based additive was added to biodiesel

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at a dosage of 20 µmol/L. Experiments were conducted to study the effect of ferric chloride added to biodiesel on the performance of a direct injection diesel engine operated at a constant speed of 1500 RPM at different operating conditions. The results revealed that the FBC added biodiesel resulted in a decreased brake specific fuel consumption (BSFC) of 8.6% whiles the brake thermal efficiency increased by 6.3%. Also FBC added biodiesel showed lower nitric oxide (NO) emission and slightly higher carbon dioxide (CO_2) emission as compared to diesel. Carbon monoxide (CO), total hydrocarbon (THC) and smoke emission of FBC added biodiesel decreased by 52.6%, 26.6% and 6.9% respectively compared to biodiesel without FBC at an optimal operating condition of 280 bar injection pressure and 25.5° BTDC injection timing.

Commercial additives

The utilization of additives (pour point depressants, anti-gel additives or cold flow improvers) (Chuang-Wei *et al*. 2004) reported as one of the primary solutions to minimize bulk flow and fuel filter block problems; that enhance the impact of crystal morphology. Four cold flow improver additives were tested at 0.1–2% in B80, B90, and B100 blends to evaluate the cold flow properties of biodiesel. Two additives significantly decreased the pour point of soybean biodiesel blends, but all the four additives had little effect on cloud points. A mixture of 0.2% additive, 79.8% biodiesel, and 20% kerosene reduced the pour point of B100 by 27 °C. According to this study a treatment with chemical additives is the most convenient and economical way of improving the low temperature properties of diesel fuels. This technology is also very attractive in biodiesel industries. They observed that the chemical additives are generally referred to as pour point depressants, flow improvers or wax modifiers and most additives promote the formation of small (10-100mm) needle shaped crystals. These crystals experience significantly reduced growth and agglomeration rates as temperature decreases below the cloud point. However, the rate of nucleation is promoted and causes the formation of a large quantity of the relatively small and more compact crystals. Although most of these crystals will be caught in fuel filters, the cake layer formed on the filter surface is considerably more permeable to fuel flow.

Another study (Labeckas and Slavinskas 2005) investigated the influence of fuel additives on the performance of direct-injection diesel engine and exhaust emissions when operating on shale oil. Tests were conducted by them with a naturally aspirated four stroke, four cylinders, water cooled, direct injection diesel engine when running on shale oil that has been treated with multi-functional fuel additives viz. Marisol FT (Sweden) and SO-2E (Estonia). The purpose of their research was to evaluate the effectiveness of the fuel additives Marisol FT (Sweden) and SO-2E (Estonia) as well as to verify their ability to increase energy conversion and reduce brake specific fuel consumption, contamination and smoke opacity of the exhausts when fuelling the diesel engine with shale oil. The test results showed that the application of these additives could be a very efficient means to improve diesel engine performance on shale oil, especially when operating in the light load range. The identified brake specific fuel consumption at light loads and speeds of 1400-2000 RPM reduces by 18.3-11.0% due to the application of the Marisol FT. The additive SO-2E also produced nearly the same effect. The total NO_X emission from the fully loaded diesel engine fuelled with the treated shale oil reduced by 29.1% (SO-2E) and 23.0% (Marisol FT). Their test results showed that the CO emission at rated power increased by 16.3% (SO-2E) and 48.0% (Marisol FT), whereas the smoke opacity of the exhausts increased by 35% and over 2 times, respectively. However, the test results were complicated and ambiguous on the effect of the fuel additives on the HC emission.

An evaluation of the cold flow properties of Mahua methyl ester (Mahua biodiesel) (Bhale *et al.* 2009) with and without pour point depressants towards the objectives of identifying the pumping and injecting of these biodiesel in CI engines under cold climates was carried out. The effect of a commercial additive on the cold flow behaviour of this biodiesel was studied. A considerable reduction in pour point was noticed by using these cold flow improvers. To enhance the cold weather functionality of biodiesel fuel, the effect of a commercial additive from Lubrizol (Lubrizol 7671) with the amount of 0.5%, 1%, 1.5% 2%, 2.5%, 3%, 3.5% and 4% was also studied.

CONCLUSIONS

Additives used to improve the properties of biodiesel may further improve combustion performance of biodiesel engine. An additive used to improve ignition and combustion performances of biodiesel is advantageous to power recovery of biodiesel engine, thus it will promote economy, and meanwhile this will also improve engine power. Most of the reviewed studies have focused on the effect of biodiesel additives on engine characteristics. However, the relation between the fuel property change with additives and the influence on engine performance remains unclear. The metal-based additives may be effective to reduce PM emissions of biodiesel due to catalyst effect. Furthermore, it seems to be useful to improve NOx emissions of biodiesel. However, the comprehensive assessments on other emissions and engine performances are required in the future. Metal based additives reduce CO emissions but with less efficiency to improve HC and CO_2 emissions for biodiesel than the others emissions. On the other hand, the effect of commercial additive was limited in improving the oxidation stability and low temperature flow properties of biodiesel fuels which are less favorable than the mineral diesel fuel.

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ACKNOWLEDGEMENTS

The authors would like to acknowledge to University Malaysia Pahang for the financial support under AEC Research Grand RDU 1403149.

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