

Effect of Additives in Various Biodiesels and Their Blends on Cold Flow Properties, Oxidation Stability and Diesel Exhaust Emissions

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ABSTRACT

The objective of this study was to obtain an improved understanding of the effects of the simultaneous use of cold flow improver (CFI) and antioxidant on the cold flow properties, oxidation stability and diesel exhaust emissions of various biodiesels and biodiesel blends. Cold flow properties were evaluated by assessing the cloud point (CP) and pour point (PP) values, as well as from the results of the cold soak filtration test (CSFT). Oxidation stability was also determined by measuring the peroxide induction period (IP). The neat biodiesels (B100) derived from soybean oil(SME), *Jatropha curcus* oil(JME), rice bran oil(RBME), palm oil(PME) and waste cooking oil(WME), and biodiesel blends with JIS No.2 diesel fuel were tested. A CFI and antioxidant specially designed for use in biodiesel fuels were employed during the work. The experimental data demonstrated that the addition of antioxidant had no effect on either the CP or PP values. The CSFT time value increases with increasing biodiesel content in biodiesel blends, although the addition of the CFI has little effect on the CSFT value. On the other hand, the CSFT results, however, were increased by antioxidant addition and also by increasing the CFI content in the SME(B100). The CSFT value was found to be well correlated with both CP and PP results in the case of the palm oil biodiesel. The IP value of SME(B100) is elevated with increasing CFI addition when an amine-based type antioxidant is added. We also determined that the addition of CFI and antioxidant reduces the extent of initial combustion due to premix combustion of DI diesel engines, which results in slightly decreased total unburned hydrocarbon (THC) and particulate matter (PM) emissions in exhaust at high engine loads.

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INTRODUCTION

Biodiesel is composed of fatty acid methyl esters (FAMES) produced from a wide variety of feedstocks, including vegetable oils such as soybean, palm and rapeseed oils, animal fats and waste cooking oils such as used frying oils. Biodiesel has become a valuable commodity and has been employed as an alternative to diesel fuel [1]. Formulations which contain a large concentration of saturated FAMES are highly resistant to oxidation and displaying better ignition properties but have a disadvantage since they exhibit a tendency to crystallize. Conversely, biodiesel formulations with a high concentration of unsaturated FAMES readily deteriorate through oxidation but have improved cold flow properties.

The transesterification process by which FAMES are made from plant oils or animal fats results in small residual concentrations of some compounds, including saturated monoglycerides and sterol glucosides, and these minor contaminants are suspected to cause precipitation above the cloud point (CP) [2-3]. Lopes *et al.* [2] reported that the presence of these contaminants had a moderate effect on the CP, a negligible effect on the pour point (PP) but a significant influence on the cold soak filtration test (CSFT) performance. Dunn [3] reported that increasing the monoglyceride content of biodiesel from 0.10 to 1.0 mass% increased both the CP and the freezing point (FP), and also noted that the cold filter plugging point (CFPP) was more sensitive than either CP or FP to variations in monoglyceride content below 0.10 mass%, though it was not affected by increasing the monoglyceride concentration above 0.50 mass%.

There are two primary means of improving the cold flow properties of biodiesel and biodiesel blends: (i) the addition of cold flow improver (CFI) and (ii) winterization of the biodiesel component. Several investigators have studied one or more of the cold flow properties of biodiesel and biodiesel blends based on different types of vegetable oils. Dunn *et al.* [4] also investigated the effects of 12 CFIs on CP, PP, low temperature flow test (LTFT) and CFPP. Their results showed that these additives significantly improved the PP, but did not greatly affect the CP. Shrestha *et al.* [5] measured the effects of four additives on the CP and PP of No. 2 diesel and B5, B20 and B100. Four types of biodiesel were used in the experiments: soy methyl ester (SME), mustard ethyl ester (MEE), mustard methyl ester (MME) and used vegetable oil methyl ester (UVME). The CFI additives tested had no effect on the CP but a significant effect on the PP, particularly for blends containing 20% (B20) biodiesel content or lower. They observed that the additives generally worked better with ethyl esters than with methyl esters and that a higher percentage of diesel in the blend resulted in better CFI additive effectiveness.

The winterization of biodiesel involves removing the saturated methyl esters by inducing crystallization via cooling, followed by separation of the high melting temperature components by filtration. This process tends to result in low yields [6], however, and therefore the addition of CFI is more common. Dry (or melt) fractionation is based on crystallization of biodiesel from a molten state without the use of a solvent, and is the simplest, least expensive and most common process of separating high- and low-melting FAMES. Dunn *et al.* [7-8] showed that dry fractionation of SME decreased its CP from 0 °C to -20 °C and its LTFT from 0 °C to -16 °C, values that are comparable to the properties of low sulfur No. 2 petrodiesel. The PP and CFPP of the SME were also significantly reduced by dry fractionation. Its PP from -2 °C to -21 °C and its CFPP from -2 °C to -19 °C were reduced.

In general, the oxidative deterioration of oils and fats, including edible oils, may be roughly classified as either autooxidation or thermal oxidation. The auto-oxidation of oils and fats exposed to air at ambient temperatures is a slow process, brought about by the formation and accumulation of hydroperoxide species in the material, and antioxidants meant to retard this process have been investigated and reviewed by many researchers [9,10, 11]. Antioxidants are chemicals meant to inhibit the oxidation processes of unsaturated FAMES, and typically fall into one of two categories: chain breakers and hydroperoxide decomposers. The BIOTAB project [9] evaluated 20 phenolic antioxidants, added to FAMES at a level of 1000 ppm, and found that none of the tocopherol additives provided any benefit. The two best performing additives were pyrogallol (PY) and propyl gallate (PG), although t-butyl hydroquinone (TBHQ) also performed well. Yamane *et al.* [10] reported that a mixture of amine and phenolic antioxidants produces a synergistic effect superior to the effect of either component on its own. Mittelbach *et al.*

[11] reported that the efficiency and the required amount of each antioxidant strongly depend on the feedstock and technology used for production of the biodiesel to which the antioxidant is added.

There have been several studies concerned with the influence of antioxidants on engine performance and emissions. Hess *et al.* [12,13] reported that the addition of butylated hydroanisole (BHA) to B20 works to reduce the effects of the "prompt" NO_x formed during the combustion process. However, the extent to which the addition of antioxidants meant to enhance the oxidation stability of biodiesels affects combustion characteristics and exhaust emissions in diesel engines are still unknown, and this requires further work, since ensuring the stability of biodiesel is necessary to increase its market share in future. Ryu [14] reported that the combustion characteristics and exhaust emissions of a diesel engine were not influenced by the addition of TBHQ antioxidant to the biodiesel fuel used in the engine. The brake specific fuel consumption (BSFC) of biodiesel fuel containing TBHQ was seen to decrease more than that of biodiesel fuels without antioxidants, but no trends were observed according to the type or amount of antioxidant. Antioxidants were also found to have few effects on the exhaust emissions of a diesel engine running on biodiesel. Conversely, combustion of an oxidized biodiesel increased combustion pressure and temperatures, resulting in elevated nitrogen oxides (NO_x) emissions, although CO emissions and smoke were decreased and there was no change in the fuel consumption rate [15].

Many biodiesel CFIs and antioxidants are available to reduce the pour point and to increase oxidation stability, but the influence of the simultaneous use of such additives on the filter plugging temperature and oxidation stability is not clear. The main objective of our study was therefore to clarify the effects of the simultaneous use of CFI and antioxidant additives on a variety of biodiesel and biodiesel blends with different fatty acid compositions, derived from soybean oil, *Jatropha curcus* oil, rice bran oil, palm oil and waste cooking oil. Specifically, the cold flow properties, oxidation stability and diesel exhaust emissions resulting from the biodiesel with CFI and antioxidant additives were investigated. The cold flow properties were evaluated by assessing the CP and PP and by performing the CSFT. The oxidation stability was assessed by measuring the peroxide induction period (IP). A direct injection (DI) diesel engine was employed in this study, fueled by neat biodiesel incorporating CFI and antioxidant additives, to investigate engine performance and exhaust emissions.

EXPERIMENTAL PROCEDURE

Materials

Five biodiesels were investigated in this work: soybean oil methyl ester (SME), *Jatropha curcus* oil methyl ester (JME), rice bran oil methyl ester (RBME), palm oil methyl ester (PME) and waste cooking oil methyl ester (WME).



Documents

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SME and RBME were produced from refined soybean and refined rice bran cooking oils and JME was obtained from degummed crude *Jatropha curcus* oil. These oils were transesterified in a batch process unit in authors' laboratory, utilizing an alkali catalyst. PME was imported from Thailand and WME was purchased from a commercial producer in Japan. Ultra-low sulfur (<10 ppm) JIS No. 2 diesel fuel was used to make the biodiesel blends. Figure 1 shows the four fatty acid methyl ester compositions used in the five biodiesel test specimens examined in this work, and Table 1 provides the main specifications for five biodiesels.

The CFI used was a prototype compound termed LX3135 and provided by the ADEKA Co., Ltd. (Tokyo, Japan). The antioxidant used was amine-based type compound termed Ecotive and a commercially available phenol-based compound, butylated hydroxytoluene (BHT), was also used for reference. Both antioxidants were provided by the Seiko Chemical Co., Ltd. (Saitama, Japan) [10]. LX3135 and Ecotive are both products specifically designed for application in biodiesel.

Main property of LX3135 is as follows: kinematic viscosity of 131mm²/s@40°C, acid value of 6.9mgKOH/g, molecular weight of 21000g/mol, and Ecotive is as follows: density of 0.98-1.02g/cm³, ash content of 0.3mass-%, liquid of dark brown.

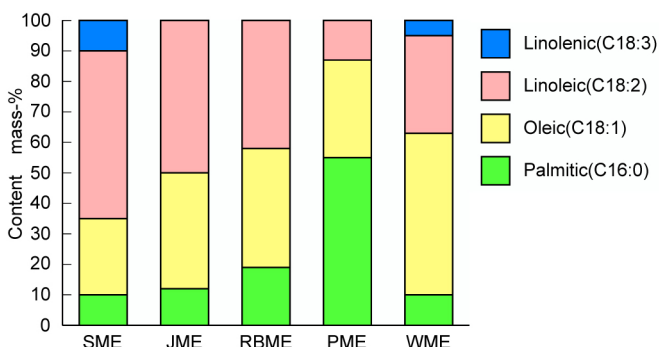


Figure 1. Composition of fatty acid methyl esters in five biodiesels

Table 1. Main specification of five biodiesels

	SME	JME	RBME	PME	WME
Density @15°C g/cm ³	0.882	0.881	0.883	0.876	0.884
Kinematic viscosity@40°C mm ² /s	4.75	4.27	4.88	4.76	4.20
Acid value mgKOH/g	0.26	0.36	0.28	0.25	0.27
Carbon residue@100% mass-%	0.016	0.023	0.036	0.004	0.024
KF water content mass-ppm	984	310	301	323	101
Lower calorific value MJ/kg	37.0	35.2	35.8	35.4	36.4

Experiment and Methods

The cold flow performances of the five biodiesels(B100) with added CFI were evaluated by measuring the CP, PP and CSFT value of each. The SME blend with JIS No.2 diesel fuel added CFI and the PME blend with JIS No.2 diesel fuel added CFI were also tested for cold flow performance by measuring their CP, PP and CSFT values. B5, B20, B50 and B70 blends were selected and 1 mass% of CFI was added in the blends. The oxidation stability and cold flow performance of SME with antioxidant and CFI was evaluated by assessing its IP, CP and PP and by performing the CSFT.

Both CP and PP values were measured using a Tanaka MPC-102A CP/PP tester which determines both the cloud point (in accordance with ASTM D2500) and the pour point (in accordance with ASTM D6749) at 1 °C intervals in a single automated test. The CSFT was determined using a method in accordance with ASTM D7501-09b which involves cooling a 300 ml sample of neat biodiesel (B100) to 4.4 °C (40 °F) for 16 hours, after which the sample is warmed to between 20 and 22 °C. The B100 is then filtered through a 47 mm diameter glass fiber filter with 0.7 micron pores under a 585 torr partial vacuum and the time required for filtration is recorded. The CSFT is currently approved under the ASTM D6751-12 standard specification for biodiesel fuel blend stock (B100) intended for middle distillate fuels. In this research, the CSFT was also applied to the biodiesel blends. For the measurement of CP, PP, and CSFT values, the average of three time of measurement was adopted.

The oxidation stability of each biodiesel was evaluated by its IP value, ascertained using an automated oil and fat stability test apparatus (679 type, Metrohm-Shibata, Japan), equivalent to the Rancimat test in the European characteristic analysis standard EN14112. This measurement was run three times and its average data was adopted.

The influences of CFI and antioxidant addition on the combustion and exhaust emission characteristics of the DI diesel engine were evaluated by rate of heat release analysis (ROHR) and brake specific fuel consumption (BSFC) and by measuring exhaust particulate matter (PM), NO_x, total unburned hydrocarbons (THC), carbon monoxide (CO) and opacity. Figure 2 shows the experimental set-up of the engine bench test. The experiments were carried out using a single cylinder, horizontal-type, four-stroke-cycle DI diesel engine (NFD170, Yanmar Co., Japan) which was naturally aspirated and water-cooled. The engine was attached to a direct current dynamometer as a load carrier. Table 2 shows the main specifications of the test engine and the injection systems. The engine was operated at a speed of 1800 r/min and a fixed cooling water temperature of 80 °C. Fuel was injected at a fixed static injection timing of 17 deg. before top dead centre (BTDC) using a PFR-1AW injection pump. The nozzle opening pressure was set at 20 MPa and the cylinder pressure was measured by piezo-type pressure transducers (6053C, Kistler Co., Austria). The nozzle needle lift was measured by eddy-current sensor (PU-05, AEC, Japan). Each set of data