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Effect of antioxidants on the oxidative stability and combustion characteristics of biodiesel fuels in an indirect-injection (IDI) diesel engine[†]

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Abstract

Biodiesel fuels that consist of saturated and unsaturated long-chain fatty acid alkyl esters are an alternative diesel fuel produced from vegetable oils or animal fats. However, autoxidation of biodiesel fuels during storage is easily caused by air, reducing fuel quality by adversely affecting its properties such as kinematic viscosity and acid value. One approach to improve the resistance of biodiesel fuels to autoxidation is to mix them with antioxidants. This study investigated the effectiveness of five such antioxidants in mixtures with biodiesel fuels produced by three biodiesel manufacturers: butylated hydroxytoluene (BHT), butylated hydroxyanisole (BHA), tert-butylhydroquinone (TBHQ), propyl gallate (PrG) and α-tocopherol. An engine test was also performed to investigate the combustion characteristics of biodiesel fuel with antioxidants in an indirect-injection (IDI) diesel engine. Oxidation stability was determined using Rancimat equipment. The results showed that TBHQ, BHA, and BHT were the most effective and α-tocopherol was the least effective in increasing the oxidation stability of biodiesel. The combustion characteristics and exhaust emissions in diesel engine were not influenced by the addition of antioxidants in biodiesel fuel. This study recommends TBHQ and PrG to be used for safeguarding biodiesel fuel from the effects of autoxidation during storage.

Keywords**:** Biodiesel fuel; Oxidative stability; Antioxidant; Vegetable oil; Storage; Exhaust emissions

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1. Introduction

Biodiesel fuels, which consist of mono fatty acid methyl esters without high-molecular-weight glycerin, are made from vegetable oils (including used edible frying oil, rapeseed oil, and soybean oil) or animal fats via a transesterification reaction with alcohol. Biodiesel has great potential as an alternative fuel for compression ignition engines, and one of its great advantages is that it is similar to diesel fuel. Biodiesel is easy to handle because its boiling point is higher than that of diesel and it is an environment-friendly fuel with low smoke emissions because it contains 10% oxygen. In addition, biodiesel has a higher specific gravity and higher kinematic viscosity than diesel; the higher cetane number of biodiesel can shorten the ignition delay, reducing the NO_x emissions during the initial combustion process. Biodiesel also emits lower levels of hydrocarbons (HC), CO, particulate matter (PM), polycyclic aromatic hydrocarbons (PAH), SO_2, and smoke than diesel [1-5].

With its good lubrication properties, biodiesel is also used as an additive to improve the lubricity of petroleum fuels [6, 7]. As it consists of free fatty acids or monoacylglycerols, it has better lubricity than petrodiesel, which is composed of HC only, because of the polarity-imparting O atoms. Consequently, adding biodiesel to ultralow-sulfur diesel with low lubricity improves the lubricity of low-sulfur petrodiesel compared with that of low biodiesel blends [8].

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Nevertheless, biodiesel still has many disadvantages related to their long-term thermal stability and low-temperature flow properties. Maintaining their quality is especially difficult because of their low cold filter plugging point during long-term storage. Air causes autoxidation of biodiesel during storage, reducing fuel quality by adversely affecting its properties such as kinematic viscosity and acid value. Recently, several studies have examined its oxidation stability to solve long-term storage problems [9-12]. Studies on the deterioration of various biodiesels under different storage conditions have also been conducted, including those made of methyl esters of rapeseed oil, used edible frying oil, and palm oil [13-15]. Upon storage, the kinematic viscosity, peroxide value, and acid value all increased.

One approach to improve the resistance of biodiesels to autoxidation is by adding antioxidants, while another is to mix them with diesel fuels. Worldwide, the storage stability of biodiesel is generally six months. Testing the oxidation stability of fats and oils for the period of circulation and managing the quality of the fats and oils are achieved using natural and synthetic antioxidants.

Studies have investigated the effects of different antioxidants on various biodiesels such as those made of palm oil and soybean oil esters [16, 17]. The antioxidants inhibit the oxidation of distilled palm oil methyl esters. However, it is unknown how the addition of antioxidants to enhance the oxidation stability of biodiesels affects the combustion characteristics and exhaust emissions in diesel engines.

Ensuring the stability of biodiesels is necessary to increase their market. Furthermore, developing antioxidants suitable for a variety of regional biodiesels is needed because the oxidation characteristics of biodiesels depend on the properties of the raw materials used to make them.

This study investigates the oxidation stability of biodiesels made from used edible frying oils and soybeans using the Rancimat test, as recommended in European normalization (EN) 14214. The effects of antioxidants in biodiesels on engine performance, combustion characteristics, and exhaust emissions are also studied.

2. Experimental apparatus and method

2.1 Test fuels

Biodiesel can be produced by both batch and continuous process systems. Batch processing is the classic method for producing alcohol esters using a large stirred tank reactor. The system is first charged with vegetable oil, followed by the catalyst and methyl alcohol. The system is agitated during the reaction. The stirring is then stopped, and the reaction mixture is made to settle in the reactor to allow the initial separation of the esters and glycerol. Next, the alcohol is removed from both the glycerol and ester streams using an evaporator or flash unit. Finally, the esters are neutralized, are washed gently using warm water, and are dried.

Continuous process systems produce biodiesel continuously using constantly stirred tank reactors in a series. The first tank reactor is larger to allow for a longer residence time and greater extent of reaction. After the initial product glycerol is decanted, the reaction in the second tank reactor is rapidly completed to

Table 1. Properties of biodiesel fuel.

Test item		Test method	Limit	Test results			
				SDOB	SDXB	SDXC	UDOB
Fatty acid methyl ester(wt.%)		EN 14103	96.5 <	98.6	96.9	98.5	98.8
Flash point(PM, ℃)		ASTM D93	120 <	182	182	178	180
Kinematic viscosity (40℃, mm^2/s)		ASTM D445	1.9 ~ 5.0	4.164	4.17	4.2	4.155
Carbon residue(wt.%)		ASTM D4530	< 0.1	< 0.01	0.01	< 0.1	0.01
Sulfur content(mg/kg)		ASTM D5453	< 10	< 1	0.00	< 1	1
Ash(wt.%)		ASTM D482	< 0.01	0.001	0.00	< 0.01	< 0.001
Copper strip corrosion (50℃,3 h)		ASTM D130	< 1	1	1A	1	1
Density(15℃, kg/m^3)		ASTM D4052	860 ~ 900	886	0.885	885	883.6
Water and sediment (vol.%)		ASTM D1796	< 0.05	< 0.01	0.086	< 0.01	< 0.005
Acid value(mg KOH/g)		EN 14104	< 0.50	0.31	0.39	0.27	0.4
Total glycerine(wt.%)		EN 14105	< 0.24	< 0.01	0.212	0.03	0.025
Oxidation stability (110℃, h)		EN 14112	6 <	1.36	3.4	3.66	2.46
Methanol(wt.%)		EN 14110	< 0.2	-	0	-	0.00
Alkali metal(mg/kg)	(Na + K)	EN 14108	< 5	< 1	0.2	< 1	< 0.1
	(Ca + Mg)	EN 14109	< 5	< 1	0	< 1	0.5
Phosphorus(mg/kg)		EN 14107	< 10	< 1	0	< 1	0.1
Pour point(℃)		ASTM D97	-	-1.0	-2.0	-1.0	0
CFPP(℃)		ASTM D6371	-	-3.0	-2.0	-2.0	-1.0
Low heating value(MJ/kg)		ASTM D 240	-	40.566	40.395	40.307	40.001

Table 2. Properties of antioxidants.

Items	Molecular weight	Chemical structure	Production company	Type
α -Tocoperol	430.71	$C_{29}H_{50}O_2$	Kanto Chemical Co., INC., Japan	Natural
Butylated hydroxyanisole (BHA)	180.25	$C_{11}H_{16}O_2$	Sigma, USA	Synthetic
Tert-Butylhydroquinone (TBHQ)	166.22	$C_{10}H_{14}O_2$	ACROS ORGANICS, Belgium	Synthetic
butylated hydroxytoluene (BHT)	220.35	$C_{15}H_{24}O$	JUNSEI, Japan	Synthetic
propyl gallate (PrG)	212.2	$C_{10}H_{12}O_2$	ACROS ORGANICS, Belgium	Synthetic

over 98%. Solid catalysts are commonly used for continuous reaction systems.

This study investigated the oxidation stability of four types of biodiesel produced in Korea. Table 1 summarizes the properties of the four biodiesels. SDOB and SDXB (both produced by Company B) are produced from soybean oil via batch production process with and without distillation processing, respectively. SDXC (produced by Company G) is made from soybean oil via a continuous production system without distillation processing. UDOB (produced by company E) is from used edible frying oils via batch production process with distillation processing.

As shown in Table 1, the oxidation stability of all four biodiesels failed to meet the 6 h quality requirement for oxidation stability, making it necessary to add antioxidants to the biodiesels to satisfy the quality specification for oxidation stability.

We evaluated the effect of the five antioxidants on the oxidation stability of the biodiesels (Table 2): the synthetic antioxidants tert-butylhydroquinone (TBHQ), butylated hydroxyanisole (BHA), butylated hydroxytoluene (BHT), and propyl gallate (PrG), and the natural antioxidant α-tocopherol. The quantity of antioxidant added was 0, 100, 300, 500, 1000, and 2000 ppm by weight for all four fuels tested. After determining that the antioxidants were soluble in biodiesel, the test fuels were sampled to examine their oxidation stability.

2.2 Test of oxidation stability

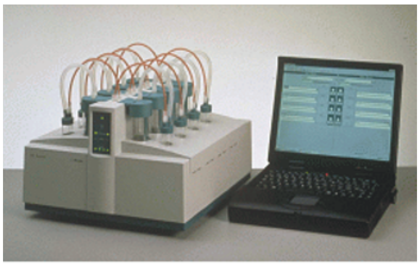

Photo 1. 743 Rancimat.

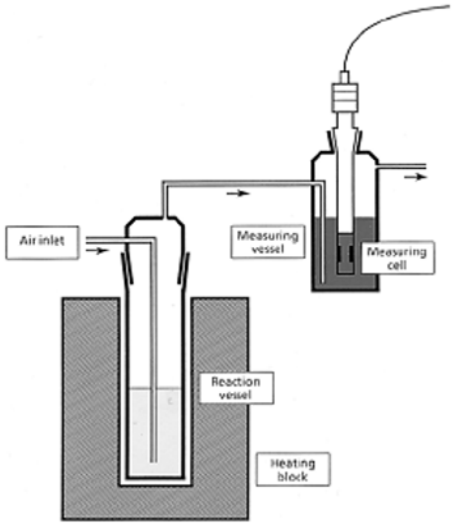

Fig. 1. Principle of oil aging in the Rancimat.

A Model 743 Rancimat (Metrohm, Herisau, Switzerland) was used to measure the thermal oxidation stability. Over time, oxygen breaks down fats (oxidation) and volatile acids are formed, affecting the consistency and taste of a product. The 743 Rancimat accelerates this process by exposing the sample to elevated temperatures while pumping air into it. The induction time, calculated automatically, is usually a few hours instead of weeks or months, and the time correlates to the years of shelf life of a product. The Rancimat oxidative stability method allows us to test the effectiveness of antioxidants, determine a product's shelf life, and test the stability of new ingredients.

The oxidation stability of the four biodiesels was evaluated with a Rancimat 743 applying the accelerated oxidation test (Rancimat test) specified in EN 14214 [18]. Each biodiesel sample was heated to 110°C with airflow of 10 L/h passing through it. The air is passed through the sample and then through an aqueous solution and the conductivity of the water is then measured. After a given heating time, the conductivity of the water trap increases rapidly with the formation of volatile acidic organic compounds, following the total consumption of the antioxidants in the heated oil. Photo 1 shows the 743 Rancimat tester and Fig. 1 outlines the principle of oil aging in the Rancimat.

2.3 Engine test

We used an unmodified, water-cooled, 4-cylinder, 4-stroke, commercial indirect-injection (IDI) diesel engine to evaluate the effect of antioxidants in biodiesel on the performance and exhaust emissions of the diesel engine. The test engine had a compression ratio of 22, a displacement of 2607 cc, and a swirl chamber. It was started using a starter motor and it was controlled manually with an eddy current engine dynamometer (W130; Schenck, Darmstadt, Germany). The specifications of the test engine are given in Table 3.

The test engine was operated at 80 ± 2°C with cooling water under all experimental conditions. After completing the test work for a selected fuel, the fuel filter and engine oil were replaced with new ones to prevent them from effecting on the next test.

The experiments were conducted with SDOB fuel at an engine speed of 1500 rpm and engine loads of 0%, 25%, 50%, 75%, 90%, and 100%. To investigate exhaust emissions with SDOB, a full flow-type opacimeter (OP-110; EplusT, Seoul, Korea) and exhaust gas analyzer (HG-550; Heshbon, Chungnam, Korea) using an electrochemical cell type detector were installed 500 mm down the exhaust pipe from the exhaust manifold. The fuel consumption rate was measured with a 150 cc measuring gauge and a stop-watch.

Table 3. Specifications of the test engine.

Item	Specification
Engine model	HD D4BB
Number of cylinder	4
Bore × stroke	91.1 × 100(mm)
Displacement	2607 (cm^3)
Compression ratio	22
Combustion chamber	Swirl chamber
Coolant temperature	80 ± 2℃
Injection type	In-direct injection
Injection pressure	150 bar

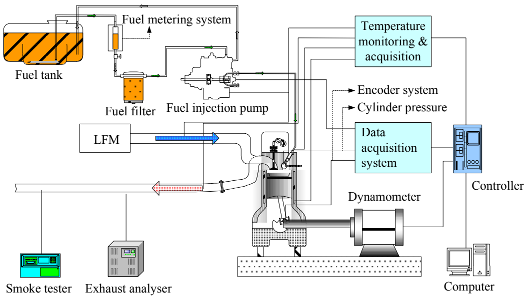

Fig. 2. Schematic diagram of the experimental apparatus.

To analyze the combustion characteristics of the diesel engine with SDOB, an integrated circuit piezoelectric (ICP) pressure sensor (model 112B10; PCB Piezotronics, Depew, NY, USA) was mounted on the pre-chamber of the fourth cylinder, and the pressure data generated from the sensor were sent to a data acquisition system via a pressure transducer (5011; Kistler, Winterthur, Switzerland).

Fig. 2 shows a schematic diagram of the experimental apparatus.

3. Results and discussion

3.1 Effect of antioxidants on the oxidative stability of biodiesel fuels

Fig. 3 shows the effect of antioxidants on the oxidation stability of biodiesel fuels. Using the natural antioxidant α-tocopherol in SDOB, no difference was observed in the oxidation stability as the amount of antioxidant increased. BHA and BHT were better antioxidants than α-tocopherol for SDOB. With BHA and BHT, the oxidation stability of SDOB increased with the amount added. However, only at a level of 1,000 ppm did BHA and BHT improve the oxidation stability to meet the specification. PrG and TBHQ enhanced the oxidation stability of SDOB and required smaller amounts compared with α-tocopherol, BHA, and BHT. TBHQ performed the best, and at a dosage of 2,000 ppm, the SDOB resisted oxidation for more than 40 h. The efficiency of the antioxidants on the oxidation stability of SDOB in this study was in the order TBHQ > PrG > BHA > BHT > α-tocopherol.

For SDXB, no difference was detected in the oxidation stability with increasing amounts of α-tocopherol. As in the case of SDOB, BHA and BHT increased the oxidation stability of SDXB as the amount added increased, but the oxidation stability only reached the 6 h quality standard at a dosage of 1,000 ppm. PrG had better antioxidant properties than BHA and BHT; at a dosage of 300 ppm, PrG satisfied

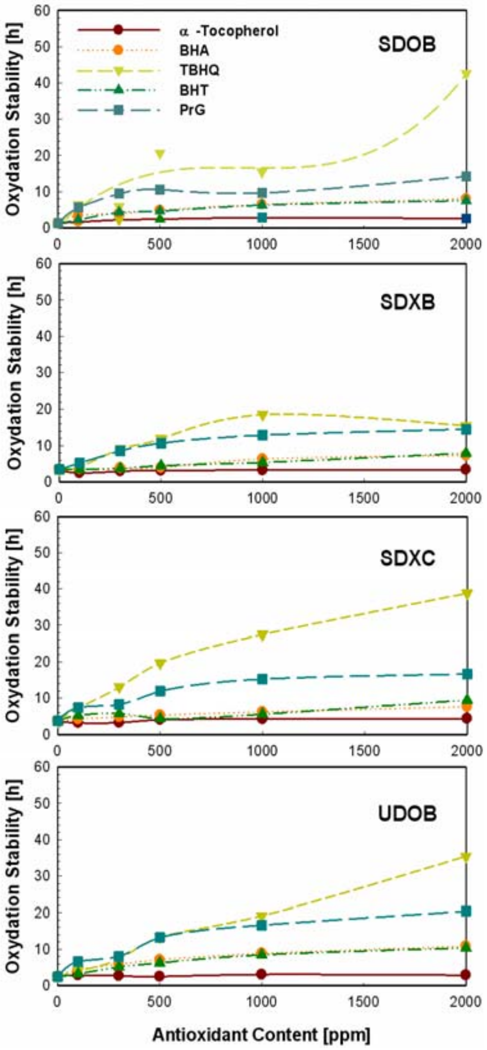

Fig. 3. Effect of antioxidant loading on oxidation stability of biodiesel fuels.

the standard, and the oxidation stability of SDXB increased slowly with the increase in the amount of additive from a dosage of 500 ppm. TBHQ significantly enhanced the oxidation stability of SDXB at a dosage of 300 ppm, although it was less effective for SDXB (undistilled) than for SDOB (distilled). The efficiency of the antioxidants on the oxidation stability of SDXB was in this order TBHQ > PrG > BHA = BHT > α-tocopherol.

Like the results for SDOB, the efficacy of the antioxidants on the oxidation stability of SDXC was in the order TBHQ > PrG > BHA > BHT > α-tocopherol. The effects of the antioxidants on the oxidation stability of UDOB, which is produced from used edible frying oils using a distillation process, were similar to the cases of SDOB and SDXC, although BHA and BHT improved the oxidation stability of UDOB to the 6 h quality standard at a dosage of 500 ppm.

The results of this study showed that α-tocopherol could not be used as an antioxidant to improve the oxidative stability of biodiesel, while TBHQ, PrG, BHA, and BHT could be used effectively. The efficiency of the antioxidants on the oxidation stability of biodiesel produced in Korea was in the order TBHQ > PrG > BHA > BHT.

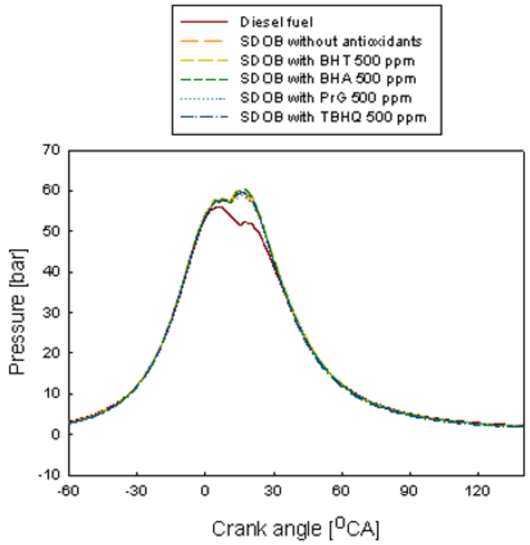

Fig. 4. Cylinder pressure at 1,500 rpm of engine speed and 75% of engine load.

3.2 Effect of antioxidants on combustion characteristics

Fig. 4 shows the cylinder pressure profiles of the diesel fuel and SDOB with or without 500 ppm of antioxidants at an engine speed of 1,500 rpm and engine load of 75%. The peak combustion pressure of the biodiesel fuel was higher than that of diesel. The oxygen in the biodiesel was believed to accelerate the combustion actively and rapidly, although the heating value of the biodiesel was lower than that of diesel. No difference was observed in the combustion pressure profiles with antioxidants in biodiesel.

Fig. 5 shows the effect of antioxidants on the brake-specific fuel consumption (BSFC) of SDOB containing 300, 500, 1000, and 2000 ppm of the 5 antioxidants, respectively. The BSFC of SDOB with or without antioxidants was higher than that of diesel

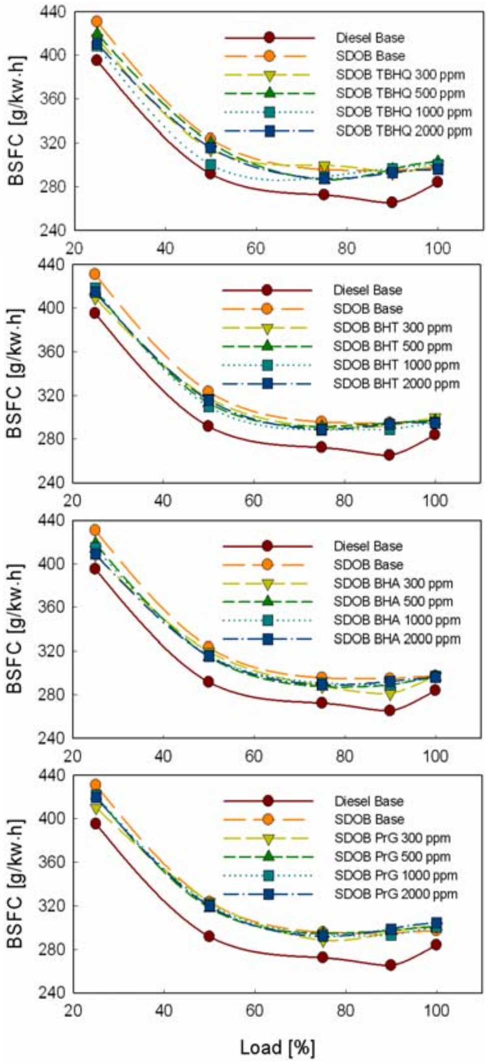

Fig. 5. BSFC of SDOB with antioxidants at 1,500 rpm of engine speed.

fuel. The BSFC of SDOB with antioxidants was less than that of SDOB without antioxidants, but no specific trends were detected according to the type or amount of antioxidants.

3.3 Effect of antioxidants on exhaust emissions

Fig. 6 shows the characteristics of the exhaust emissions of SDOB containing the antioxidant TBHQ at an engine speed of 1,500 rpm. Smoke and HC emissions were lower than those acquired with diesel at an intermediate load or more, but no differences were seen between SDOB with or without antioxidants. With biodiesel, the NO_x emissions were slightly higher than those with diesel. All of the biodiesels showed the traditional trade-off between smoke and NOx, although no significant correlations were observed with the quantity of antioxidants added. The CO emissions in biodiesel exhaust were lower than those with diesel fuel up to a 75% load but ex-

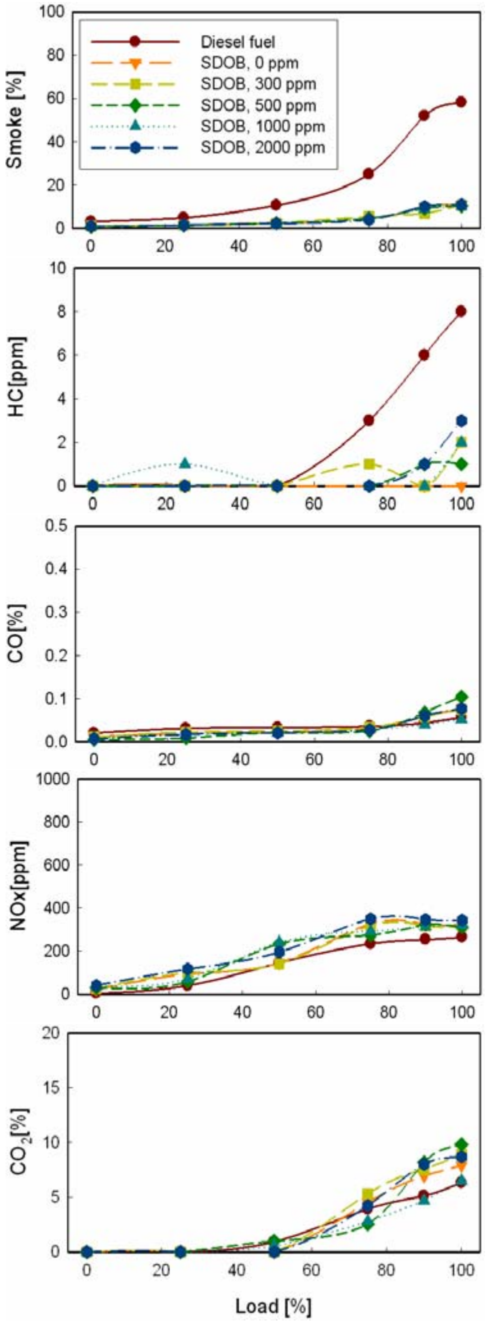

Fig. 6. Exhaust emissions versus engine load with TBHQ.

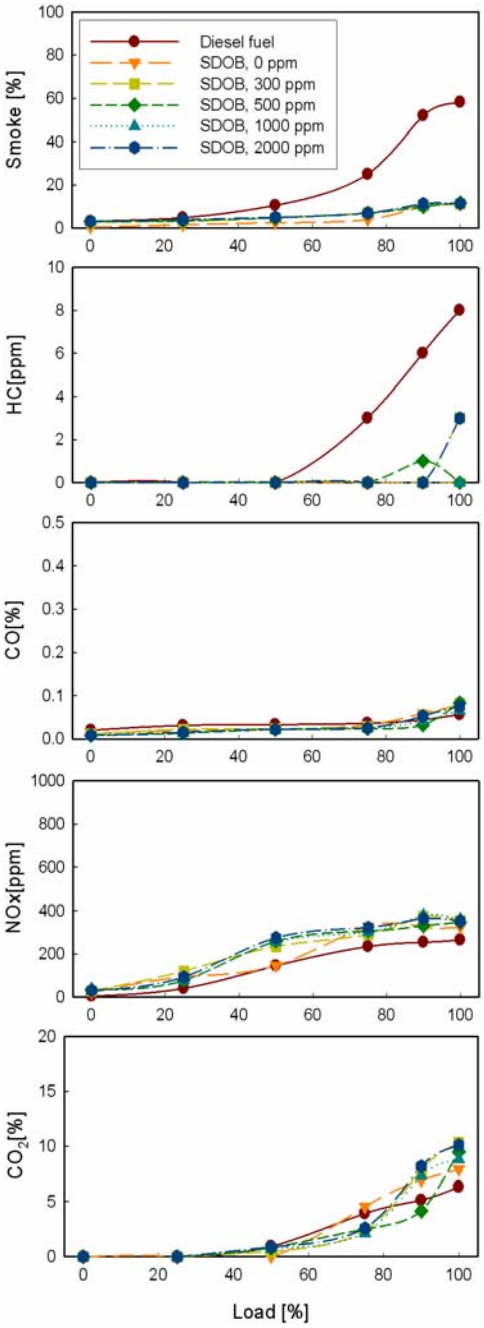

Fig. 7. Exhaust emissions versus engine load with BHT.

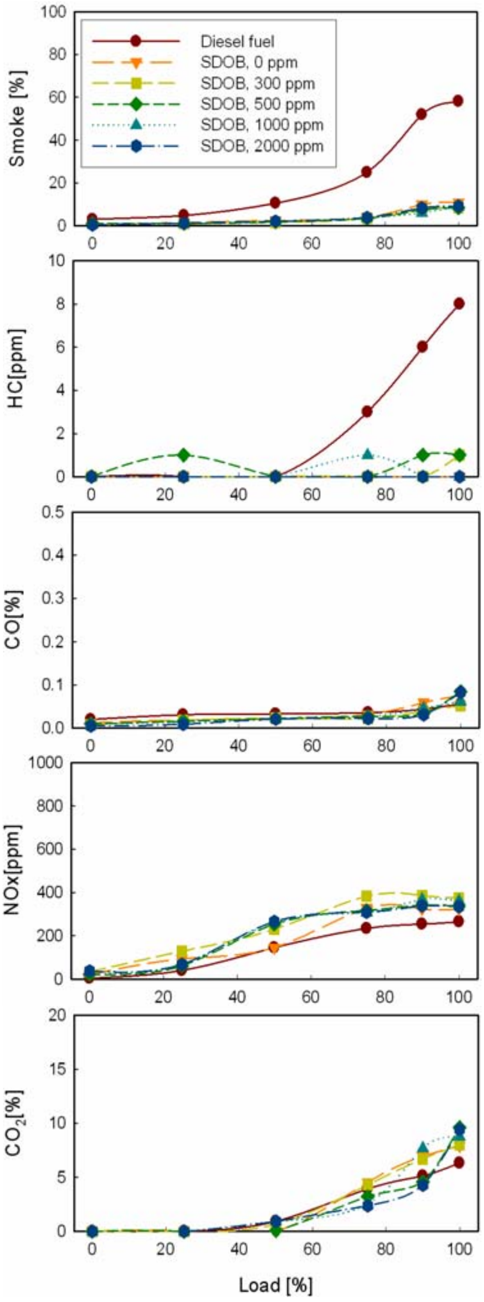

Fig. 8. Exhaust emissions versus engine load with BHA.

ceeded those of diesel at loads of 90% and 100%. The amount of TBHQ added had no effect on the CO exhaust characteristics.

Figs. 7-9 show the characteristics of the exhaust emissions of SDOB containing the antioxidants BHT, BHA, and PrG at an engine speed of 1,500 rpm. As in the case of using TBHQ, the smoke and HC emissions with SDOB containing the BHT, BHA, and PrG were lower than those with diesel at an intermediate load or more, but no differences were seen between SDOB with or without antioxidants. The NO_x emissions with biodiesel fuels were also slightly higher than those with diesel fuel, but no special relation

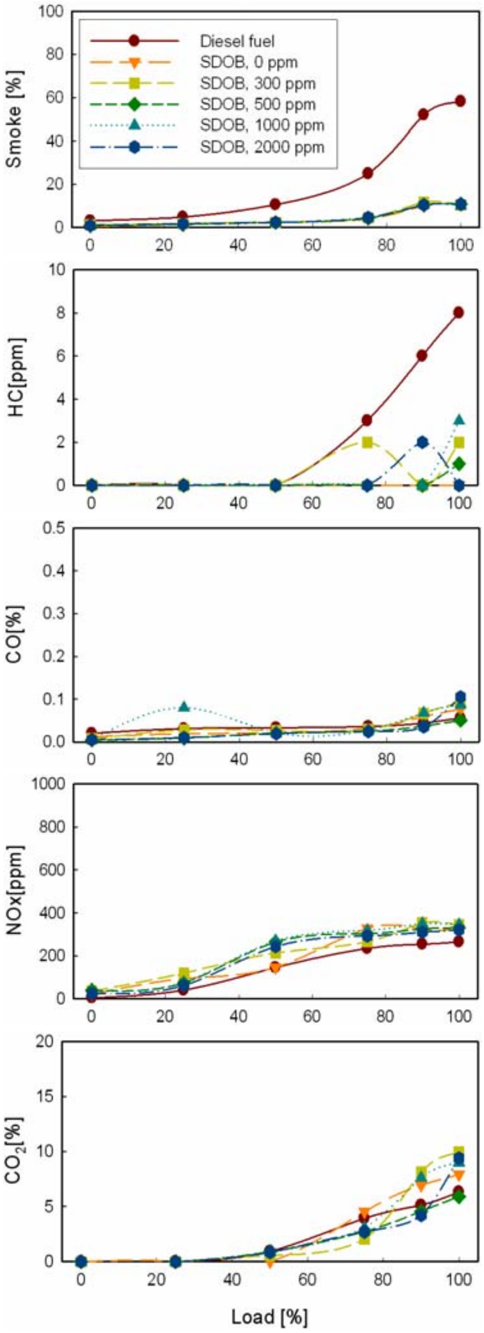

Fig. 9. Exhaust emissions versus engine load with PrG.

ships were observed according to the amount and type of antioxidants added. The CO_2 emissions in biodiesel with or without antioxidants were higher than those with diesel fuel at higher load conditions. This was due to the exact combustion of biodiesel fuels containing about 10% oxygen in fuel exact combustion. However the amount of antioxidants added had no effect on the CO_2 exhaust characteristics.

4. Conclusion

This study investigated the effects of antioxidants on the oxidation stability of four biodiesel fuels and examined the combustion characteristics and the exhaust emissions of a diesel engine using SDOB. The data gathered indicated the following.

1) The natural antioxidant α-tocopherol had no effect on the oxidative stability of biodiesel, although it is very soluble in biodiesel.

2) BHA enhanced the oxidative stability of biodiesel. The oxidation stability of UDOB produced from used edible frying oils satisfied the 6 h quality standard with 500 ppm or more of BHA, while the oxidation stability of SDOB, SDXB, and SDXC was satisfied with 1,000 ppm or more BHA. BHT had effects similar to those of BHA, but the quality standard was satisfied with a dosage of 1000 ppm in SDOB, 1000 ppm or more in SDXB and SDXC, and 500 ppm in UDOB.

3) TBHQ offered the best oxidation stability for all the biodiesels. The oxidative stability of SDOB and SDXC attained the 6 h quality standard with 100 ppm TBHQ, while the oxidative stability of SDXB and UDOB met the specification with 300 ppm TBHQ. PrG was the next-best performing antioxidant, and the specification was met using 300 ppm PrG in SDOB and SDXB and 100 ppm PrG in SDXC and UDOB.

4) The synthetic antioxidants TBHQ and PrG were more effective than the natural antioxidant α-tocopherol in terms of their ability to enhance the oxidation stability of biodiesel. The efficiency of the antioxidants investigated in this study was in the order TBHQ > PrG > BHA > BHT > α-tocopherol.

5) The BSFC of SDOB with antioxidants was lower than that of SDOB without antioxidants, but no trends were observed according to the type or amount of antioxidant.

6) The smoke and HC emissions with SDOB were lower than those with diesel under an intermediate load or more. However, no differences were seen in the emission levels between SDOB with or without antioxidants. Antioxidants had little effect on the exhaust emissions of a diesel engine running on biodiesel.

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