42 Accelerated Oxidation Process in Biodiesel and Its Effect on Diesel Combustion and Emission Characteristics

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This paper describes the experimental study on the effect of biodiesel oxidation on diesel combustion and emissions. The biodiesel fuel made from the soybean-oil was deliberately oxidized. The progress of oxidation was evaluated by measuring peroxide value, acid value, kinematic viscosity. The auto-ignition characteristics were analyzed based on the constant-volume combustion method. Engine bench tests were carried out using a single-cylinder engine. Obtained results show that the progress of oxidation increases both viscosity and cetane number. The use of oxidized biodiesel increases the combustion pressure and temperature, resulting in increasing NOx emission. However, CO and smoke is decreased without loss of fuel consumption rate.

Keywords : diesel engine, combustion, emission, biodiesel, oxidation, hydroperoxide, polymer

1. Introduction

Fatty acid methyl ester (FAME), generally referred to as biodiesel, is an alternative diesel fuel derived from a vegetable oil or an animal fat. Recently, there has been considerable interest in biodiesel because of its renewability and its lower level of pollutant emissions such as CO, unburned hydrocarbons and smoke compared to fossil fuels(1-3). It is compatible with conventional diesel fuel and already comprises a commercial fuel in Europe.

One drawback of biodiesel is that it is more prone to oxidation than fossil diesel fuels. Recent interest has focused on the oxidative stability of biodiesel(4)(5). The BIOSTAB project report(4) discusses stability determination methods, the influence of storage conditions on the quality of pure and blended biodiesel, the definition of a minimum level of natural and synthetic antioxidants and the determination of the effects of fuel stability during utilization of biodiesel as an automotive diesel fuel and as a heating fuel. Recently, the influence of unsaturated fatty acid methyl ester composition on oxidation was reported by the authors of this paper(5). However, the auto-oxidation schemes of fatty acid methyl esters are not currently understood.

The oxidation reaction of a lipid is the subject of intense research. The details of its mechanism are being revealed as follows(6). The oxidation reaction is initiated by the loss of the hydrogen atom adjacent to the double bond in the unsaturated molecule, which becomes a free radical. The free radical reacts with oxygen and takes a hydrogen atom away from another lipid molecule, thus forming hydroperoxide, which is the unstable primary product of the oxidation process. Some of the hydroperoxides polymerize with each other to form dimers and polymers, and some are decomposed to yield volatile breakdown products such as acids and aldehydes.

In all, the oxidation process of biodiesel produces hydroperoxides, aldehydes, ketones and acids that change the fuel properties. A few studies report the impact of oxidation products(7)(8) on engine performance and emissions. No research has yet been conducted to determine the maximum degree of oxidation allowable for fuel to be used in diesel engines.

The objective of the present study is to determine the effect of biodiesel oxidation on diesel engine combustion and exhaust emissions. The biodiesel fuel made from edible soybean oil was deliberately oxidized while monitoring the chemical properties in order to evaluate the progress of oxidation. Then, the auto-ignition characteristics of the oxidized fuels were analyzed based on the constant-volume combustion method, and engine bench tests were carried out using a single-cylinder test engine.

2. Experimental method

2.1 Fuel preparation

The tested biodiesel fuel was made from edible soybean oil through the trans-esterification process catalyzed by potassium hydroxide. Table 1 shows the main properties of the original fuel. This biodiesel was deliberately oxidized in a 20-L stainless steel container. The fuel was heated to 100°C while air bubbles were

Table 1 Fuel specifications

Density	0.88 g/cm^3
Kinematic viscosity (30°C)	5.2mm^2/s
Lower calorific value	36.7 MJ/kg
Distillation temperature	
10%	333°C
50%	338°C
90%	356°C
Flash point	174°C
Carbon	78.4 wt%
Hydrogen	12.0 wt%
Oxygen	11.1 wt%
Sulfur	<0.0001wt%

pumped into the fuel at the rate of 20 L/min. The moisture in the pumped air was eliminated by a molecular sieve.

To characterize the progress of oxidation, the peroxide value (POV), acid value (AV), induction period of the peroxide (IP), and kinematic viscosity were measured throughout the oxidation treatment. The measurement method for each index is shown below.

(a) Peroxide value: POV

POV is the content of the hydroperoxide, and it is calculated based on iodometry. If potassium iodide is mixed into the oil, which includes the hydroperoxides (expressed as ROOH), iodine is isolated due to the following reaction.

$$\mathrm{ROOH + 2KI \rightarrow ROH + I_2 + K_2O}$$

POV is defined as the milli-equivalent of the amount of sodium thiosulfate consumed to titrate the isolated iodine in a sample of 1 kg(8). Measurements were carried out using the automatic titrater (Metrohm Titrino 794).

(b)Acid value: AV

In oil chemistry, AV is measured to evaluate the contents of the free fatty-acid isolated from the triglyceride in the oil. AV is defined as the milligrams of potassium hydroxide consumed to neutralize the free fatty acids in a 1-g sample. Since the biodiesel fuel, however, consists of fatty acid methyl ester, it is hardly possible that free fatty acids are formed due to oxidation. So, the AV of biodiesel fuel represents the quantity of low-grade organic acids, which are the decomposed products from hydroperoxides. In the present work, AV is measured by using the simple oil test kit (Shibata Science).

(c) Induction period of peroxide: IP

IP is the oxidation stability of oil and fats. IP is adopted as the biodiesel fuel standard in Europe (EN14112). IP is determined as the time of the rapid increase in the conductivity of water, which traps the volatiles formed during oxidation. IP is measured by using a Rancimat tester (Metrohm Type 679).

(d) Kinematic viscosity

Kinematic viscosity of biodiesel fuel is measured by using capillary glass tube (Shibata Science)

2.3 Test engine

To examine the effect of fuel oxidation on engine performance and exhaust emissions, a single-cylinder water-cooled DI-diesel engine (YANMAR NFD-170) was used. The main specifications are shown in Table 2.

Fig.1 shows the experimental layout. The cylinder pressure was measured by a strain-gage transducer (KYOWA PE-200KWS), the fuel-injection pressure by a piezoelectric transducer (AVL QL61D), and the nozzle needle lift by a hole-effect transducer. The signals of all the above were input into the engine combustion analyzer (ONOSOKKI DS-9100) to calculate the rate of heat release, and so on.

Table 2 Engine specifications

Engine type	Direct injection diesel engine, single cylinder, water cooled
Bore x Stroke	102 mm x 105 mm
Displacement volume	0.857 liters
Compression ratio	17.8 : 1
Chamber shape	Toroidal
Fuel injection system	PFR-1 (plunger diameter=9mm)
Injection nozzle	DLLA150P224

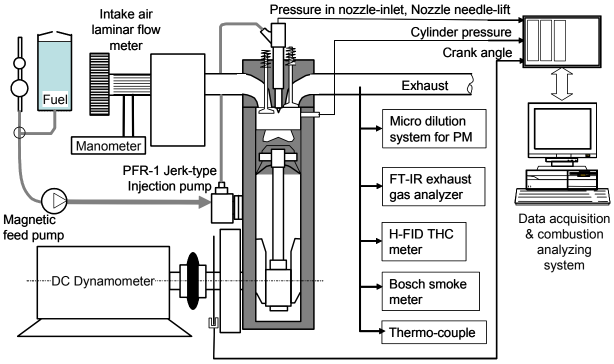


Fig.1 Experimental setup

Gaseous pollutant emissions such as nitrogen oxides are measured by an FT-IR analyzer (HORIBA MEXA4000FT). A Bosch smoke tester (ZEXEL DSM-10) was used for smoke measurement. A micro-dilution tunnel system (F-techno MIT-2000) was used to determine the particulate matter emissions.

3. Result and discussions

3.1 Change in fuel qualities

Fig.2 shows the temporal variation of the POV, AV, kinematic viscosity and IP of the test fuel during the oxidation process. Fig.3 shows the change of the fuel color. A remarkable increase in POV is observed at around 6 hours after the start of the procedure, and POV reaches the maximum value of about 800 meq/kg at 18 hours. Then, it gradually decreases a little. At the same time as the increase in POV, the fuel color changes from light yellow to brown. But a few hours later, it reverts to its original yellow color. Such temporary fuel color is presumably related to the concentration of intermediate products or free radicals in the oxidation process.

The kinematic viscosity begins to increase together with POV, but it continues to increase, unlike POV. Finally, it reaches 11 $\mathrm{mm^2/s}$ at 24 hours, which is about two times as large as that of unoxidized fuel. It is likely that the increase in the viscosity represents the polymerization of the hydroperoxides.

A significant increase in AV is observed 5 hours after the increase in POV. In the present experiment, it is possible that the increase in AV represents the accumulation of low-grade organic

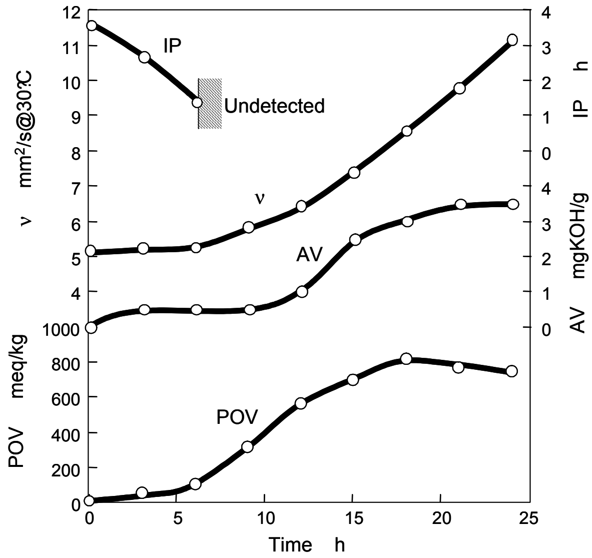


Fig.2 Changes of POV, AV, kinematic viscosity and IP during the thermal oxidation process

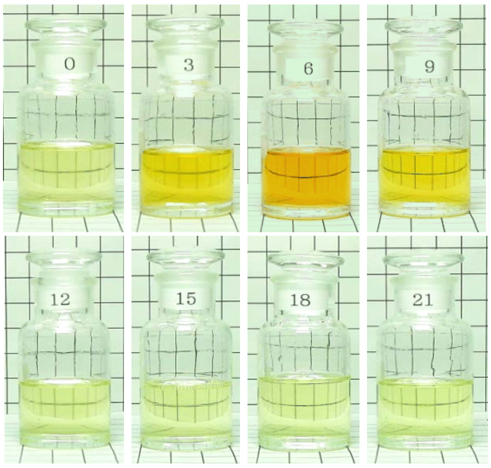


Fig.3 Change of fuel color due to thermal oxidation (The number in each photo shows a elapsed time)

acids decomposed from the hydroperoxides, which are the primary products of the oxidation. The existence of the time lag between the two curves agrees well with this assumption.

3.2 Auto-ignition characteristics

The auto-ignition characteristics of oxidized biodiesel have been examined by using the fuel combustion analyzer (Fueltech FIA-100). Auto-ignition takes place by injecting the test fuel into the constant-volume vessel containing the heated air with the temperature of 400°C and pressure of 2 MPa. The combustion pressure is recorded to calculate various auto-ignition characteristics. Fig.4 shows the combustion pressure for three test fuels with different POVs. The measurements were repeated ten times for each fuel. Fig.5 shows the variation of the ignition delay time, main combustion period and FIA-Cetane number with POV. The ignition timing is defined as the time when the chamber pressure exceeds the initial value by 0.1 MPa. The main combustion period is the time from ignition to the excess of the cumulative heat release over 95%. The FIA-Cetane number is calculated using the already known relation between the Cetane number and the ignition delay time. In Fig.5, it is shown that, as POV increases, the ignition delay decreases, resulting in an increase in the FIA-Cetane number from 40 to 70. Also, the run-to-run variation in the course of pressure becomes smaller, as shown in Fig.4.

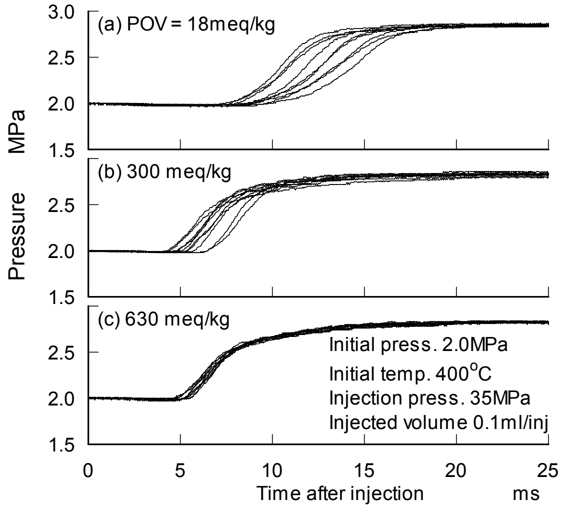


Fig.4 Combustion pressure in the constant-volume vessel

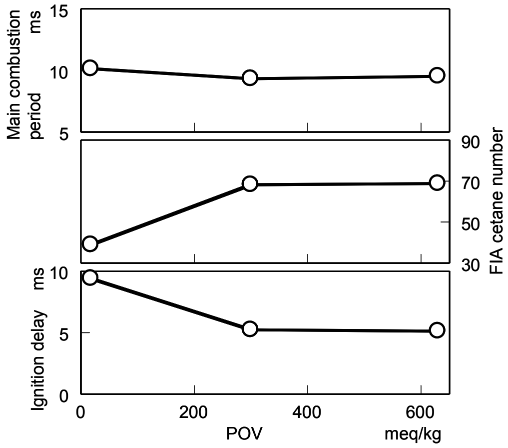


Fig.5 Change of ignition delay, Cetane number by FIA and main combustion period against POV

Generally, a short ignition delay decreases the amount of ignitable mixture formed before ignition, hence decreasing the initial combustion rate and producing the long combustion period. On the contrary, the present experimental results show that, though the ignition delay is shortened by the oxidation treatment of the fuel, the main combustion period does not change or it is shorter. This is probably because the hydroperoxide or low-grade acid or aldehyde produced by the oxidation treatment acts as the accelerator for the combustion.

3.3 Engine performance and exhaust emissions

Engine tests were carried out by using oxidized fuel, which

Table 3 Characteristics of test fuel

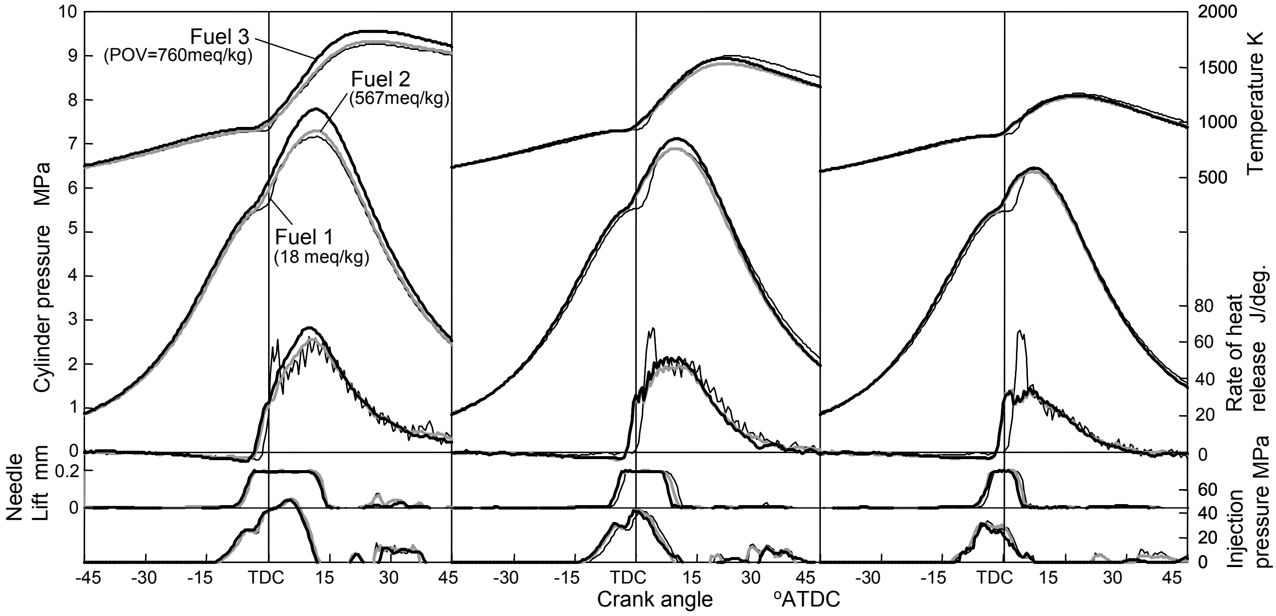
	Fuel 1	Fuel 2	Fuel 3
POV [meq/kg]	18	567	748
kinematic viscosity [mm^2/s@30°C]	5.2	6.4	11.2
AV [mgKOH/g]	0	1	3.5
IP [hour]	3.6	N.A.	N.A.

has high ignitability compared to original test fuel. The characteristics of the test fuels are shown in Table 3. Fuel 1 is the unoxidized biodiesel. The oxidation treatment was applied to Fuel 1 for 12 and 24 hours to obtain Fuel 2 and Fuel 3, respectively. The engine speed was maintained at 1800 rpm, and the static fuel-injection timing was fixed at 17° BTDC (before top dead center).

Fig.6 shows the crank angle histories of the cylinder pressure, average gas temperature, rate of heat release, fuel-injection pressure and nozzle needle lift for the different BMEP (different break mean effective pressure). As shown in the combustibility test, the ignition delay of biodiesel is shortened by the oxidation. The same tendency was observed in the engine test. The times of the start of the heat release for Fuel 2 and Fuel 3, immediately after the nozzle needle lift reaches a maximum, are both several degrees earlier than that for Fuel 1. The short ignition delay reduces the amount of pre-mixture formation. Therefore, the rapid heat release rate in the initial combustion stage due to pre-mix combustion was not observed for Fuel 2 and Fuel 3, while it was clearly observed for Fuel 1, especially in a low load condition. As a result, the rate of the pressure rise for Fuel 2 and Fuel 3 becomes lower than that for Fuel 1.

Fig.7 shows the effect of BMEP on the brake specific fuel consumption BSFC (break specific fuel consumption), NOx (nitrogen oxide) emission, CO (carbon monoxide) emission CO, PM (particulate matter), SOF (soluble organic fraction) included in the PM, and smoke density. The gaseous emission level for Fuel 3 is different from those for the other fuels. As for the BMEP from 0.6 to 0.8 MPa, the NOx emission for Fuel 3 is obviously larger than that for the others. The possible reason for the increase in NOx is that the cylinder pressure and temperature after TDC are raised by the early ignition and large combustibility due to the long oxidation treatment, as shown in Fig.6, hence promoting the thermal NOx formation. The high combustion temperature should also promote the oxidation reaction of CO, so that the CO emission decreases with increasing POV, as shown in Fig.7. As the result, the high cylinder pressure in the expansion stroke and high combustion efficiency of Fuel 3 can reduce BSFC successfully for BMEP from 0.6 to 0.8 MPa.

Though the initial heat release rate of the oxidized fuel is smaller than that of the original, there is little difference in the following heat release curve in the diffusion flame period, and the heat release can be finished at nearly the same timing. Therefore, the smoke density in the exhaust is not increased by the oxidized fuel. It is somewhat decreased by the long oxidation



(a) BMEP = 0.79 MPa (b) BMEP = 0.58 MPa (c) BMEP = 0.28 MPa

Fig.6 Crank angle history of in-cylinder temperature, pressure, rate of heat release, needle lift and injection pressure

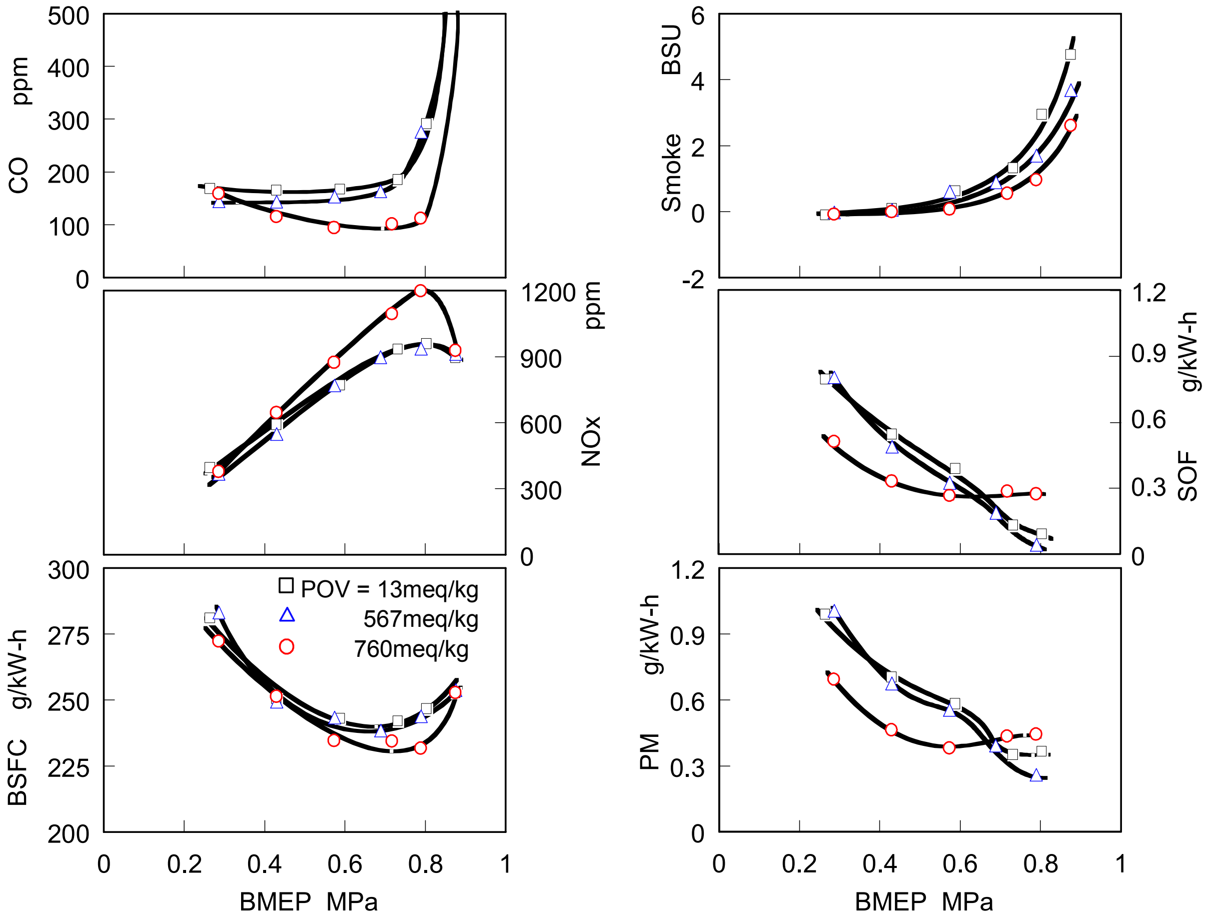


Fig.7 Fuel consumption and emission characteristics

treatment in the high load condition. PM for Fuel 3 also shows a lower level than that for the others in the low load condition. However, it shows the highest level in the high load condition. This change is due to the increase of soluble organic fractions. Fuel 3 should contain the largest amount of hydroperoxide polymers with a high boiling point, which may increase SOF emissions in the high load condition.

Generally, a large viscosity of a diesel fuel yields a large droplet size of fuel spray, which decreases the combustion rate and increases the unburned pollutant emission because of insufficient fuel-air mixing. The present results, however, show that favorable combustion can be obtained by the use of oxidized biodiesel in spite of its high viscosity. This fact suggests that the improvement of the chemical properties of the fuel due to the presence of hydroperoxides or organic acids surpasses the negative effect of the poor spray property.

4. Conclusions

This study described the effect of the oxidation of biodiesel fuel on auto-ignition characteristics, engine performance and emissions. The results show that the progress of oxidation causes an increase in viscosity due to polymer production and an increase in the Cetane number. Also, the use of oxidized biodiesel increases the maximum combustion pressure and temperature, resulting in increasing NOx emissions. However, unburned emissions of CO and smoke can be decreased while maintaining the same fuel consumption rate as the unoxidized fuel.

These results suggest that oxidized biodiesel may be used as a low emission fuel with favorable auto-ignition characteristics, if the polymers can be removed to suppress the increase in fuel viscosity.

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