

Effect of Bio Diesel Fuel on Sludge Prevention Performance of Engine Oil

Daichi SHIMOKOJI*

Yosuke OKUYAMA*

Masashi MARUYAMA*

ABSTRACT

The research discussed in this paper clarified the effect of biodiesel fuel (BDF) on two effective sludge generation indexes of engine oil, the base number (BN) and the oxidation induction time (OIT). The results of laboratory tests of oil deterioration using an engine oil mixed with BDF showed that BDF, which contains a large number of unsaturated bonds, accelerates sludge generation of engine oil.

1. Introduction

The use of bio diesel fuel (BDF) as an alternative fuel that effectively addresses crude oil depletion and CO₂ reduction is expanding around the world. BDF is a mixture of diesel oil with fatty acid methyl esters (FAME) obtained by transesterification of animal and vegetable oils with methanol. The use of BDF has already advanced in Europe and the United States. The main FAME used in Europe is rapeseed methyl ester (RME), and in the U.S. it is soybean methyl ester (SME).

Although BDF is useful, there are many concerns about its fuel stability. The acids generated by BDF and the oxidation products from BDF deposits have been reported to affect fuel systems by clogging fuel filters, forming injector deposits, causing corrosion of materials, and the like^{(1), (2)}.

As controls on exhaust gases have become more stringent, it has become common to install diesel particulate filters (DPF) in diesel vehicles. DPF-equipped vehicles perform a main fuel injection, followed by a post-injection, to regenerate the DPF. As a result of this multi-stage injection, fuel tends to become intermixed with the engine oil. Consequently, the engine oil is also affected, and it is important to ascertain that effect in order to determine when the engine oil should be changed.

The present research investigated the influence of BDF on engine oil properties mainly in terms of the effect on sludge prevention performance.

2. Engine Oil Sludge Generation Indexes

It was previously reported that the remaining amounts of anti-oxidation performance and cleaning performance in engine oil provide valid sludge generation indexes for engine oil^{(3), (4)}.

It is known that the amount of remaining cleaning performance can be evaluated by the engine oil base number (BN)⁽⁵⁾. Figure 1 illustrates the relationship between BN and sludge with photographs of piston interiors showing the results from tests of engine oil deterioration in actual engines.

The fall of the BN results when the detergent used as an engine oil additive is neutralized and consumed by heat and the nitric acid that is generated by the NO_x gas in the blow-by gas. It was confirmed that, as shown in Fig. 1, a fall in the BN is accompanied by a reduction in cleaning performance and the formation and progressive accumulation of sludge. Maintaining the BN is therefore crucial in limiting the formation of sludge.

Meanwhile, it is known that the remaining amount of anti-oxidation performance can be evaluated from the oxidation induction time (OIT) using a high pressure differential scanning calorimeter (HPDSC)⁽⁶⁾. Figure 2 shows the relationship between the OIT and the generated content of nPB insolubles⁽⁷⁾ in sludge-producing and non-producing vehicles.

Reduction in the OIT results when the anti-oxidant used as an additive in engine oil undergoes a radical

* Automobile R&D Center

reaction with heat, NO_x gas, and unburned fuel. As shown in Fig. 2, sludge is not generated when there is remaining OIT. Maintaining the OIT is therefore important in preventing the generation of sludge.

It is apparent from the above that BN and OIT are valid indexes of sludge generation in engine oil.

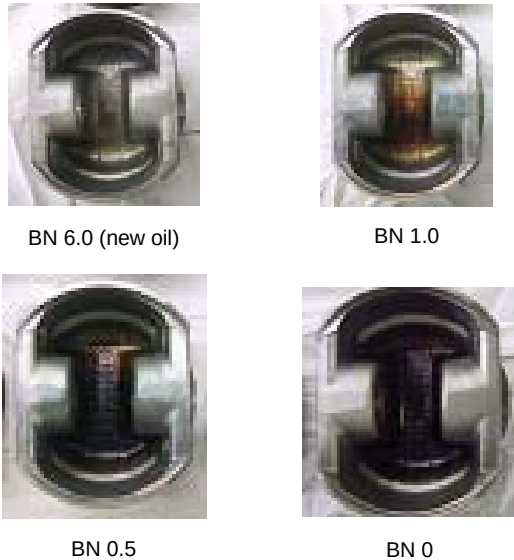


Fig. 1 Relationship between BN and deposits

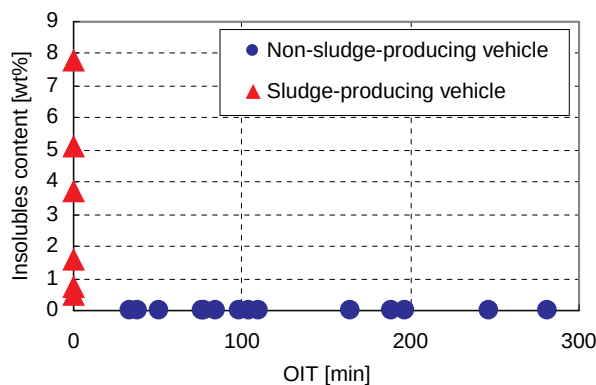


Fig. 2 Relationship between OIT and nPB insolubles

3. Effect on Engine Oil Sludge Prevention Performance

A NO_x bubbling test was conducted in order to study the effects on engine oil sludge prevention in BDF in a diluted state. Figure 3 shows a schematic diagram of the device⁽³⁾. The NO_x bubbling test is a laboratory test that simulates the deterioration of engine oil in the crankcase as a result of heat and NO_x being blown through it. Honda genuine oil combined with the types of BDF

Table 1 Properties of fuel for NO_x bubbling test

Items	Diesel	RME10	RME100	SME20	SME100
FAME in diesel (%)	0	10	100	20	100
Kinematic viscosity (40°C, mm ² /s)	2.721	2.792	4.452	2.833	4.137
Sulfur (ppm)	3	3	<3	3	<3
Density (15°C, mgKOH/g)	0.8356	0.8322	0.8831	0.8377	0.8831
Acid number (mgKOH/g)	0.01	0.03	0.1	0.06	0.17
Oxidation stability (hr) *	24.0<	18.6	7.8	2.9	1.1

* Rancimat

shown in Table 1 in a 10 wt% mixture of each was used for the test oil. The test measured the rate of reduction in the BN and OIT over time. The rate of reduction in the BN and OIT are shown in Figs. 4 and 5, respectively.

The BN and OIT reduction rates with the RME10 mix showed no difference from the mixture containing diesel oil. With the BDF mix, however, which has greater FAME content, the reduction tended to accelerate, indicating a marked effect. When BDF of equal concentrations was used, mixed with RME100 and with SME100, the rate of reduction was greater when mixed with SME100. This indicates that differences in the rate of reduction can occur with different BDF base materials.

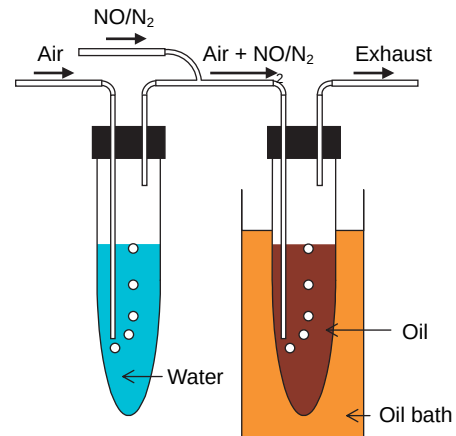


Fig. 3 NO_x bubbling device

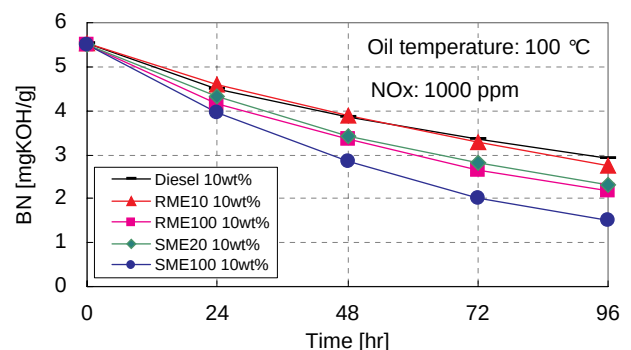


Fig. 4 BN reduction rate of BDF/oil mixture

determine whether the line of superposition of the reduction effects of the various FAMES coincided with the mode of reduction in actual mixtures with BDF. Table 2 shows the ratios of the individual FAMES that are mixed in the oil when the BDF in Table 1 is a 10 wt% mixture with engine oil. As one example, the BN reduction effect in a 10 wt% mixture with methyl linolenate is shown in Fig. 7, and the reduction effect of a 5 wt% mixture can be approximated by the roughly intermediate curve shown in Fig. 9. A similar method was used to create the estimated reduction curves for the corresponding amounts of each FAME present in the oil for 10 wt% mixtures of RME100 and SME100. The results for BN and OIT when those curves are superposed are shown in Figs. 10 and 11. There was a reliable correspondence between the superposition lines and the modes of RME100 and SME100 reduction. Therefore, the difference in the rate of reduction attributable to the difference in base materials is due to the percentage composition of FAMES with different numbers of unsaturated bonds.

4.3. Detailed Analysis of FAME Oxidation Products

Conceivable reduction factors that accelerate the lowering of BN and OIT include the involvement of acids and substances with radical properties. With the NO_x bubbling test, however, it is challenging to analyze and identify the reduction factors in the deteriorated oil, which is a complex chemical mixture. An attempt was therefore

Table 2 FAME rate at BDF 10 wt% mixture in engine oil

Items	Diesel	RME10	RME100	SME20	SME100
Methyl linolenate (wt%)	0.00	0.09	6.16	0.15	2.37
Methyl linoleate (wt%)	0.00	0.20	1.98	1.07	5.37
Methyl oleate (wt%)	0.00	0.62	0.85	0.47	0.75

made to estimate the BN and OIT reduction factors by forcing oxidation of the individual FAME constituents at a constant temperature under blown air, and observing the resulting products after the test.

Figures 12 and 13 show the results of analysis of low molecular weight products by means of ion chromatography (IC) and GC-MS. The IC analysis results indicate the production of lower fatty acids. However, acids were formed in the largest quantities with methyl oleate, which is counter to the effect on BN reduction shown in Fig. 7. This is probably because the rate of acid formation in engine oil mixtures is different from that in FAMES alone. The results of GC-MS analysis confirm the production of several aldehydes.

Figure 14 shows the results of analysis of high molecular weight products by means of gel permeation chromatography (GPC). The molecular weight distribution results after testing confirm the production of higher molecular weight substance than FAME. High molecular weight products occurred in the largest quantities with

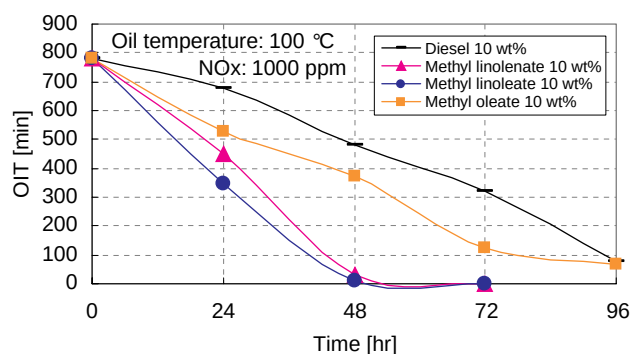


Fig. 8 OIT reduction rate of FAME/oil mixture

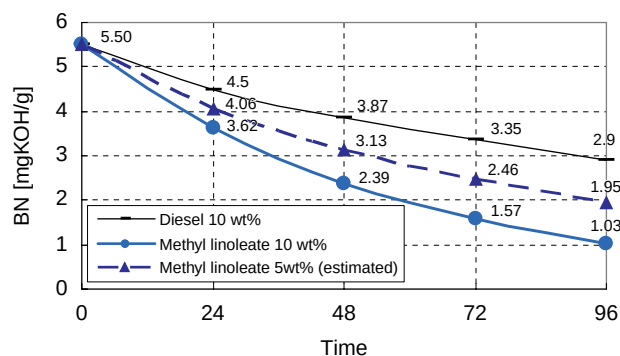


Fig. 9 Example of estimated reduction curve

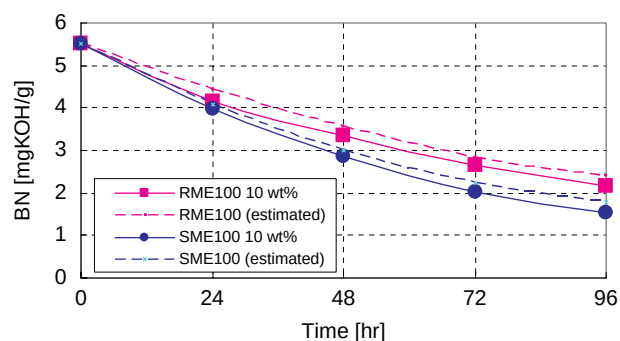


Fig. 10 Estimated BN reduction curve

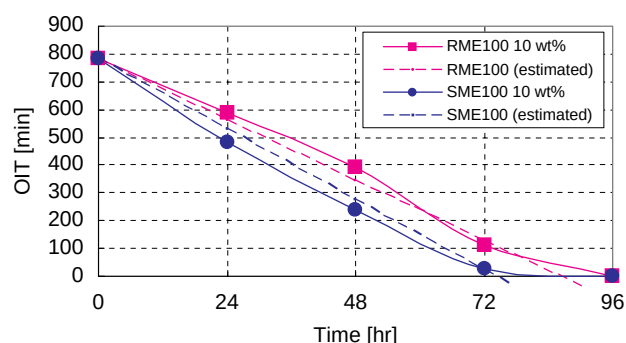


Fig. 11 Estimated OIT reduction curve

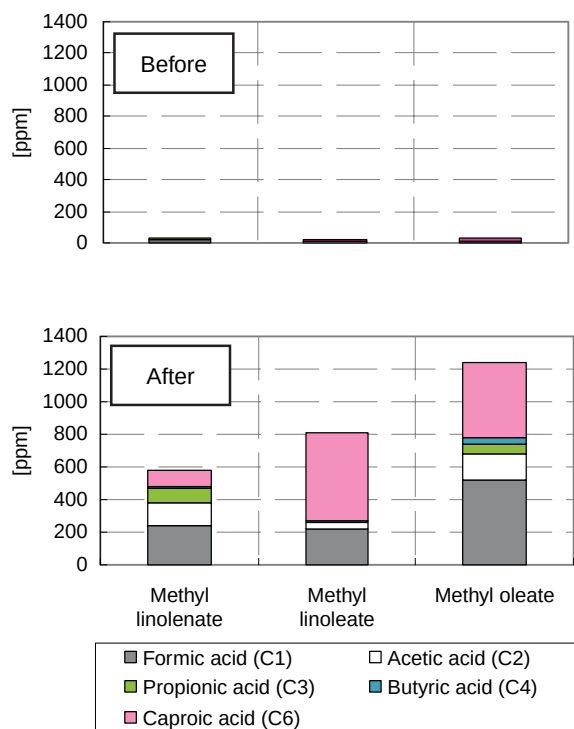


Fig. 12 Results of IC analysis after FAME oxidation test

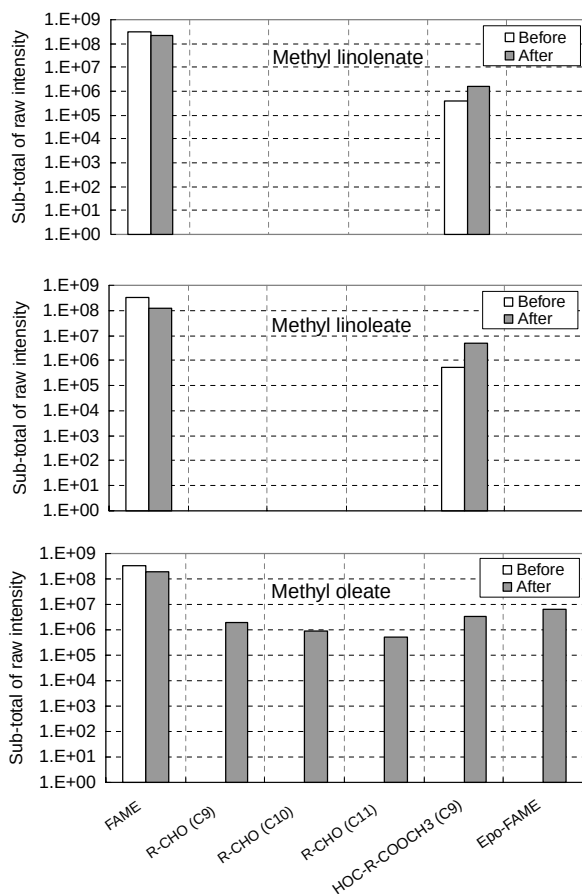


Fig. 13 Results of GC-MS analysis after FAME oxidation test

methyl linoleate. These high molecular weight products were then further separated and refined using high performance liquid chromatography (HPLC) and analyzed by means of atmospheric pressure chemical ionization mass spectrometry (APCI-MS). The results confirmed their mass to be equivalent to a dyad in each FAME. It is conjectured that these high molecular weight products are dimers resulting from polymerization reactions.

4.4. FAME Oxide Production Mechanism

It is known that FAME chemical reactions are generally started by methylene hydrogen elimination reactions near unsaturated bonds. Methylene hydrogens

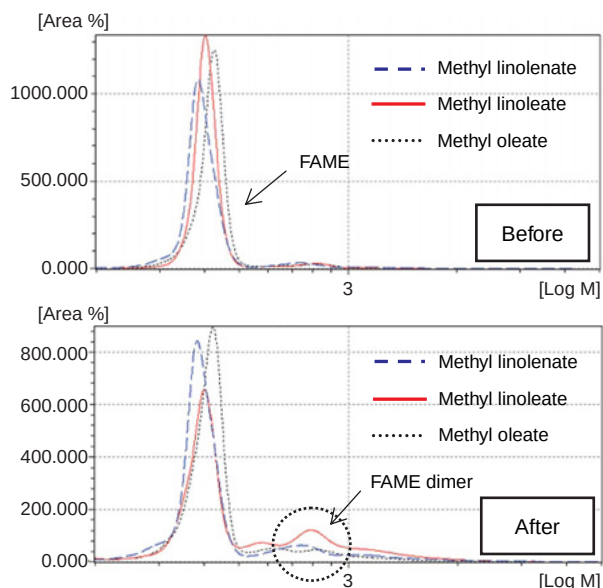
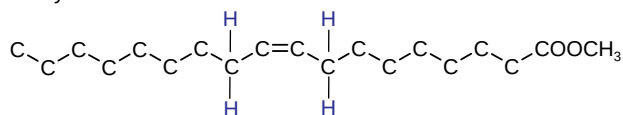
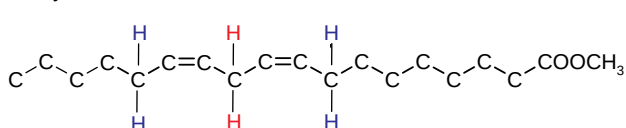


Fig. 14 Results of GPC analysis after FAME oxidation test

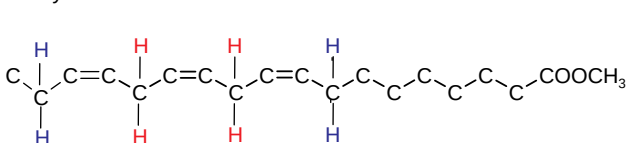
Methyl oleate



Methyl linoleate



Methyl linolenate



H: Allyl H: Bis-allyl

Fig. 15 Model of chemical structure of FAME

that bond to carbon atoms near unsaturated bonds, as shown in Fig. 15, are termed allyl hydrogens, while methylene hydrogens that bond to carbon atoms between unsaturated bonds are termed bis-allyl hydrogens. These hydrogens produce highly chemically reactive free radicals on carbon by elimination reactions. It has also been reported that the bis-allyl hydrogens undergo elimination reactions at a rate 100 times greater than the allyl hydrogens⁽⁸⁾. Methyl linolenate and methyl linoleate with numerous unsaturated bonds that can have bis-allyl hydrogens are highly chemically reactive.

Figure 16 shows the oxide production mechanism in FAMES that are the main constituent of RME and SME. FAMES produce free radical intermediates through hydrogen elimination reactions. Free radical intermediates proceed selectively to oxidation reactions or polymerization reactions. The oxidation reactions result in the carbon chains splitting and producing lower fatty acids. The polymerization reactions also result in the dyads acting as cross-links to produce dimers.

In the FAME oxidation test in section 4.3, methyl oleate generated the greatest quantities of acids, a result that is counter to the influence on BN reduction. The highly chemically reactive methyl linolenate and methyl

linoleate should produce greater quantities of acids. They formed acids in small quantities, however, and formed dimers in large quantities. It is conjectured that FAME in mixture with engine oil is less likely to collide with the

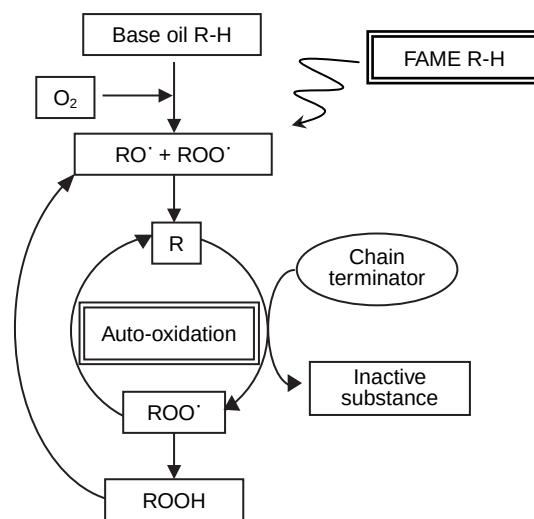


Fig. 17 Mechanism of engine oil auto-oxidation and terminal reaction with FAME mixture

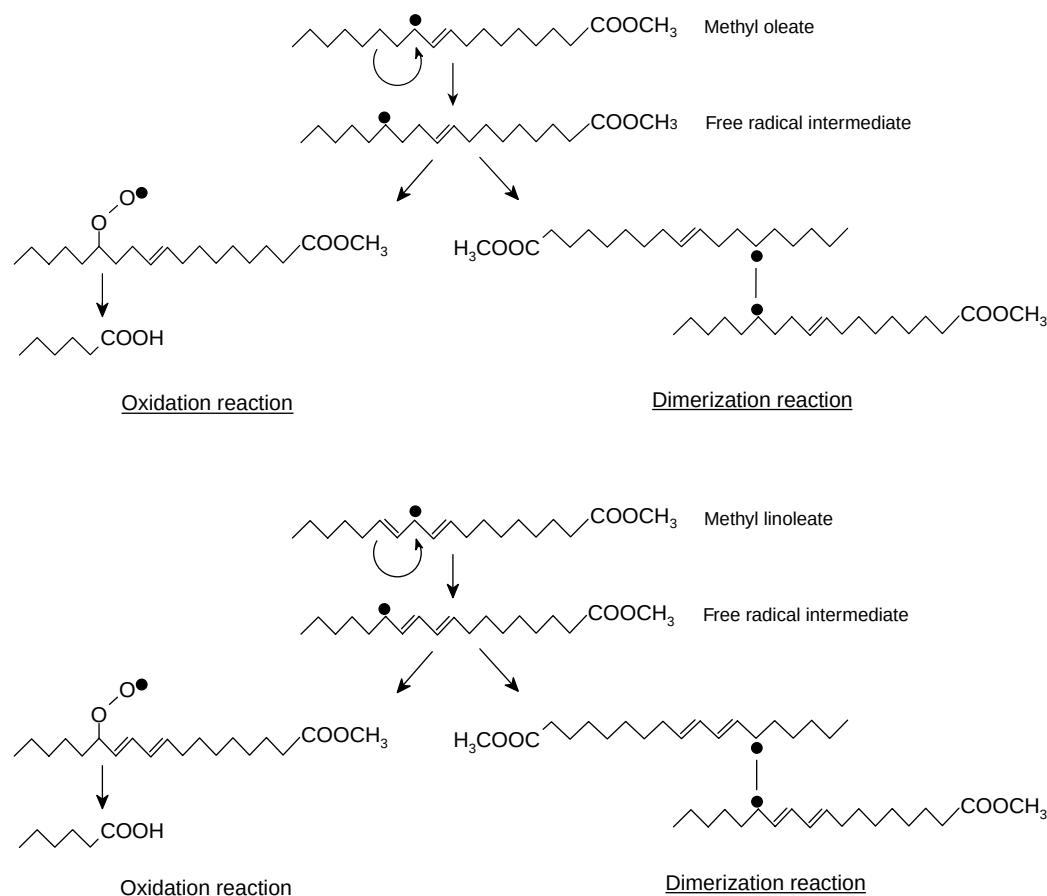


Fig. 16 Mechanism of generation of FAME oxidation compound

counterpart molecules required for a polymerization reaction since the engine oil would intervene, so that the oxidation reaction, rather than the polymerization reaction, is more likely to be selected.

4.5. BN and OIT Reduction Factors due to FAME

The above investigation suggests that the BN reduction factors are the lower fatty acids that are oxidation products of the FAME radical intermediates. It also appears that the OIT reduction factors are ROO radicals (ROO $\cdot$) that are generated in the course of producing the lower fatty acids. As shown in Fig. 17, once RO radicals (RO $\cdot$) and ROO radicals (ROO $\cdot$) are generated, the base oil of engine oil undergoes a chain of oxidation reactions. Antioxidants are known to be additives that function to stop these oxidation reactions and render the RO $\cdot$ and ROO $\cdot$ inactive⁽⁹⁾. Antioxidants function by means of a mechanism called chain termination to render the RO $\cdot$ and ROO $\cdot$ inactive. In a BDF mixture, however, ROO $\cdot$ is produced by the FAME as well as by the base oil for engine oil, and this promotes the consumption of antioxidant. It is conjectured that, as a result, OIT reduction tends to accelerate when in a BDF mixture.

5. Conclusion

Investigation of the effects that bio diesel fuel has on BN and OIT, which are engine oil sludge generation indexes, yielded the following findings:

- (1) Mixture with BDF results in the BN and OIT falling, so that sludge prevention performance is reduced.
- (2) The rate of reduction in sludge prevention performance is greater when BDFs include more unsaturated bonds.
- (3) It is thought that BN reduction factors are lower fatty acids, and OIT reduction factors are ROO radicals (ROO $\cdot$) that are formed during the production of lower fatty acids. These are factors accelerating the generation of engine oil sludge from BDF.

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■ Author ■



Daichi SHIMOKOJI



Yosuke OKUYAMA



Masashi MARUYAMA