

Analysis of Oxidative Deterioration of Biodiesel Fuel

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ABSTRACT

Methyl esters of saturated/unsaturated higher aliphatic acids (FAMES) and a FAME of waste cooking oil (WCOME) were heated at 120°C in an air gas flow. The samples were analyzed before and after heating, using six different methods including electrospray ionization mass spectrometry. As a result, the samples after heating were found to contain low molecular weight aliphatic compounds and oligomers of the FAME. Based on the chemical structure of these oxidation products, reaction schemes were proposed for the deterioration of FAMES. In addition, two unsaturated FAMES containing 2,6-di-*t*-butyl-*p*-cresol (BHT) were similarly heated and analyzed to examine the effect of BHT on the oxidation of these FAME.

INTRODUCTION

Biodiesel fuels synthesized from plant oils and animal fats have gathered much attention as a sustainable energy resource that has benefits with regard to air pollution, oil depletion and the greenhouse effect [1,2]. However, it has been well known that biodiesel fuels are more easily oxidized or unstable than conventional diesel fuels, and are therefore easily deteriorated. Therefore, the suppression of oxidation of biodiesel fuel during storage, and the protection of vehicle fuel-delivery system materials or parts from oxidized biodiesel fuel have been major problems [3,4].

Oxidation of biodiesel fuel is divided into two reactions. The first is that where the molecular weight of biodiesel fuel decreases, and the second is that where the molecular weight of the biodiesel fuel increases. Although the analytical methods for the products from the former reaction have already been established, the analytical methods for the products from the latter reaction have not been established. Therefore, the reaction mechanism in which the molecular weight of the biodiesel fuel increases, yielding gum or sludge, has not been clarified so far.

Fang et al. [5] analyzed biodiesel fuels heated under an air atmosphere using Fourier-transform infrared spectrometry (FT-IR) and Fourier-transform nuclear magnetic resonance spectrometry (FT-NMR). Based on the results, they proposed structures for the high molecular weight compounds. However, the fine structure of these high molecular weight compounds has not been clarified, because FT-IR and FT-NMR provide little information regarding the molecular weight or molecular formula.

From this background, we have investigated the oxidation products of biodiesel fuel, and studied the effect of an antioxidant on the oxidation of biodiesel fuel. We addressed a WCOME, which has been the only biodiesel fuel commercialized in Japan.

Firstly, a WCOME and three kinds of methyl esters: methyl palmitate (PME), methyl oleate (OME) and methyl linoleate (LME) were heated under air flow at 120°C, and analyzed using ion chromatography (IC), gas chromatography/mass spectrometry (GC/MS), FT-IR, gel permeation chromatography (GPC), FT-NMR and electrospray ionization mass spectrometry (ESI-MS). Incidentally, PME, OME and LME, which were detected as the main components in the preliminary analysis of the WCOME, were used as reference samples to facilitate the analysis of WCOME. Based on the analytical results, the molecular formulae of the FAME-dimers in each sample are clarified, and the proposed structural formulae of the dimers are elucidated using the molecular dynamics method. Oxidation pathways for the main components in all FAMES are also proposed.

Secondly, two unsaturated FAMES: LME and methyl linolenate (LnME), with or without an antioxidant (2,6-di-*t*-butyl-*p*-cresol: BHT), were similarly heated and analyzed. Based on the analytical results, the effect of BHT on the oxidation of these FAMES is examined, that is, the amount and composition of oxidation products. Finally, the reaction mechanism of BHT in the FAMES is discussed.

EXPERIMENTAL

Sample for Analysis of Oxidation - A WCOME, which was purchased from Revo International Inc., Kyoto, Japan and three FAMEs (PME, OME and LME), which were purchased from Tokyo Kasei Kogyo Co. Ltd., Tokyo, Japan, were used as samples. Table 1 shows the sample code, molecular weight and carbon number and double bond equivalence (DBE) value of the samples. FAMEs are generally expressed by the carbon number of the aliphatic acid moiety and the DBE value of the aliphatic chain. However, in this report, the FAMEs are expressed by the carbon number and DBE value of the entire molecule, because there are both compounds with and without ester-moieties ($\text{CH}_3\text{-(CO)-O-}$) in the oxidation products from these FAMEs.

Table 1. Series-I samples

FAME	Code	MW	Cmn*		Remarks
			m	n	
Methyl palmitate	PME	270.5	17	1	99.5% GC
Methyl oleate	OME	296.5	19	2	99% GC
Methyl linoleate	LME	294.5	19	3	99.5% GC
Methyl ester of waste cooking oil	WCO-ME	-	-	-	Mixture of FAME

*: m denotes carbon number and n denotes the DBE value of entire molecule.

Sample for Analysis of Effect of Antioxidant - LME and LnME were used with various levels (0, 0.01, 0.1, 1 and 10%) of BHT, purchased from Tokyo Kasei Kogyo Co. Ltd., Tokyo, Japan. Table 2 shows the composition of the samples.

Table 2. Series-II samples

Sample	BHT (%)	BHT (mg)	Sample (g)	Sample	BHT (%)	BHT (mg)	Sample (g)
LME-0	0.00	0.00	4.284	LnME-0	0.00	0.00	4.347
LME-0.01	0.01	0.46	4.496	LnME-0.01	0.01	0.46	4.214
LME-0.1	0.10	4.60	4.171	LnME-0.1	0.10	4.60	4.479
LME-1	1.00	46.10	4.440	LnME-1	1.00	46.10	4.514
LME-10	10.00	454.00	4.845	LnME-10	10.00	458.20	4.900

Note. LME and LnME mean methyl linoleate and methyl linolenate, respectively.

Purity of LnME was greater than 70%.

Heating Test - Each sample of series-I (0.5 g) was heated in a vial with inner volume of 10 mL under a flow of 2-3 mL/min of purified air at 120°C for 20 h, as shown in Figure 1. The headspace exported from the sample vial was passed through de-ionized water and chloroform at 23°C. Each sample of series-II was heated in a vial with inner volume of 50 mL under a flow of 8 mL/min of purified air at 120°C for 35 h, using a similar device to that used for the series-I samples.

Analytical Method - The samples of series-I and II were analyzed before and after heating using IC and GC/MS for clarification of low boiling point compounds, and using FT-IR, GPC, FT-NMR and ESI-MS for clarification of high boiling point compounds.

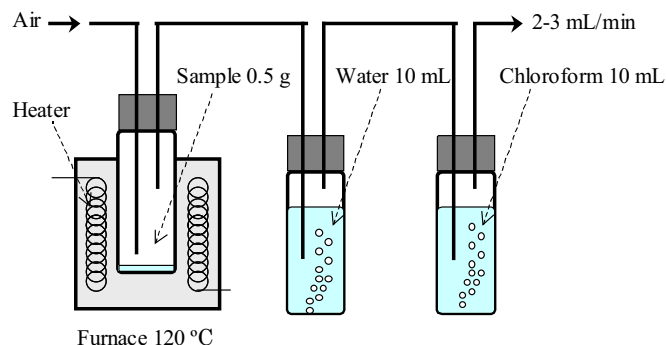


Figure 1. Device for the oxidation test of series-I samples.

Analysis of Low Boiling Point Compounds - The sample was dissolved in chloroform before and after heating at a concentration of 20%, and analyzed using GC/MS to clarify the composition of the low boiling point compounds. The water aerated with the headspace from the sample bottle was directly analyzed using IC.

Analysis of High Boiling Point Compounds - Samples were analyzed by FT-IR before and after heating. The samples were then dissolved in chloroform at a concentration of 30 mg/mL, and separated by GPC. The fractions with molecular weights greater than that of the original FAME were collected and analyzed by FT-NMR and ESI-MS to clarify the composition of these high boiling point compounds.

RESULTS AND DISCUSSIONS

ANALYSIS OF OXIDATION

Results of IC - Figure 2 shows the IC results for the water aerated by the headspace exported from the sample vial. It was found that formic acid and acetic acid were the main acids present. As the number of double bonds of the FAME increases by one, the amount of aliphatic acids increases by more than ten-fold.

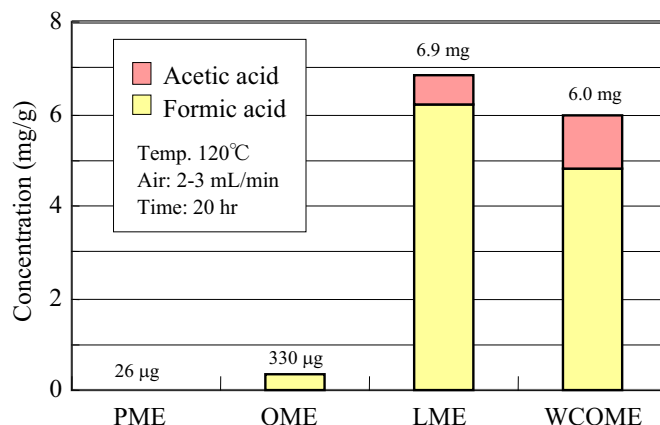


Figure 2. Results of ion chromatography of water aerated with headspace from the series-I samples.

Results of GC/MS - Total ion chromatograms obtained by GC/MS for PME, OME, LME and WCOME after heating are shown in Figure 3. The peaks eluted at the retention time between 14 and 16 min were assigned to PME, OME and LME from their mass spectra. Similarly, the peaks eluted at the retention time before 14 min were assigned to the decomposition products, most of which were yielded from the aliphatic moiety of the FAME. On the other hand, the peaks eluted after 16 min were assigned to the partial oxidation products of FAME. From Figure 3, the amounts of oxidation products produced from the four kinds of FAME, that is the amounts of all compounds except the original FAME, were found to be in the order LME > WCOME > OME >> PME. It was also found that LME yielded many oxidation products including aldehyde-derivatives (CHO-FAME), alcohol-derivatives (OH-FAME), acid-derivatives (COOH-FAME), acids (R-COOH; R: alkyl group) and aldehydes (R-CHO), while OME yielded only a small amount of oxidation products including epoxy-derivatives (Epo-FAME), aldehyde-derivatives (CHO-FAME) and aldehydes (R-CHO). WCOME yielded various FAME-derivatives due to the presence of OME and LME, in addition to alcohols, aldehydes and acids. The peak heights of the substances identified were determined from the mass chromatograms of their typical fragment ions. Their peak heights were classified according to their type and DBE, and plotted

against the carbon number of the molecules in Figures 4 to 7. From these figures, the following findings were made.

PME (C17:1) - As shown in Figure 4, PME yielded a oxo-PME (CO-PME), FAME-derivatives with carbon numbers less than 13 (ketones formed by oxidation at the middle carbon atom of the aliphatic moiety, aldehydes formed by oxidation at the terminal carbon atom in the molecule, and epoxides formed by oxidation at two adjacent carbon atoms), ketones and hydrocarbons with carbon numbers less than 15, and aldehydes and aliphatic acids with carbon numbers less than 11.

OME (C19:2) - As shown in Figure 5, OME yielded an epoxy-OME (Epo-OME), a hydroxy-OME (OH-OME), FAME-derivatives with carbon number less than 11 (aldehydes, alcohols, epoxides), unsaturated aldehydes with carbon numbers 10 and 11, and aldehydes and aliphatic acids with carbon numbers less than 10.

LME (C19:3) - As shown in Figure 6, LME yielded a FAME with carbon number 9, FAME-derivatives with a carbon number of approximately 10 (aldehydes and epoxides), and aldehydes and aliphatic acids with carbon number 6.

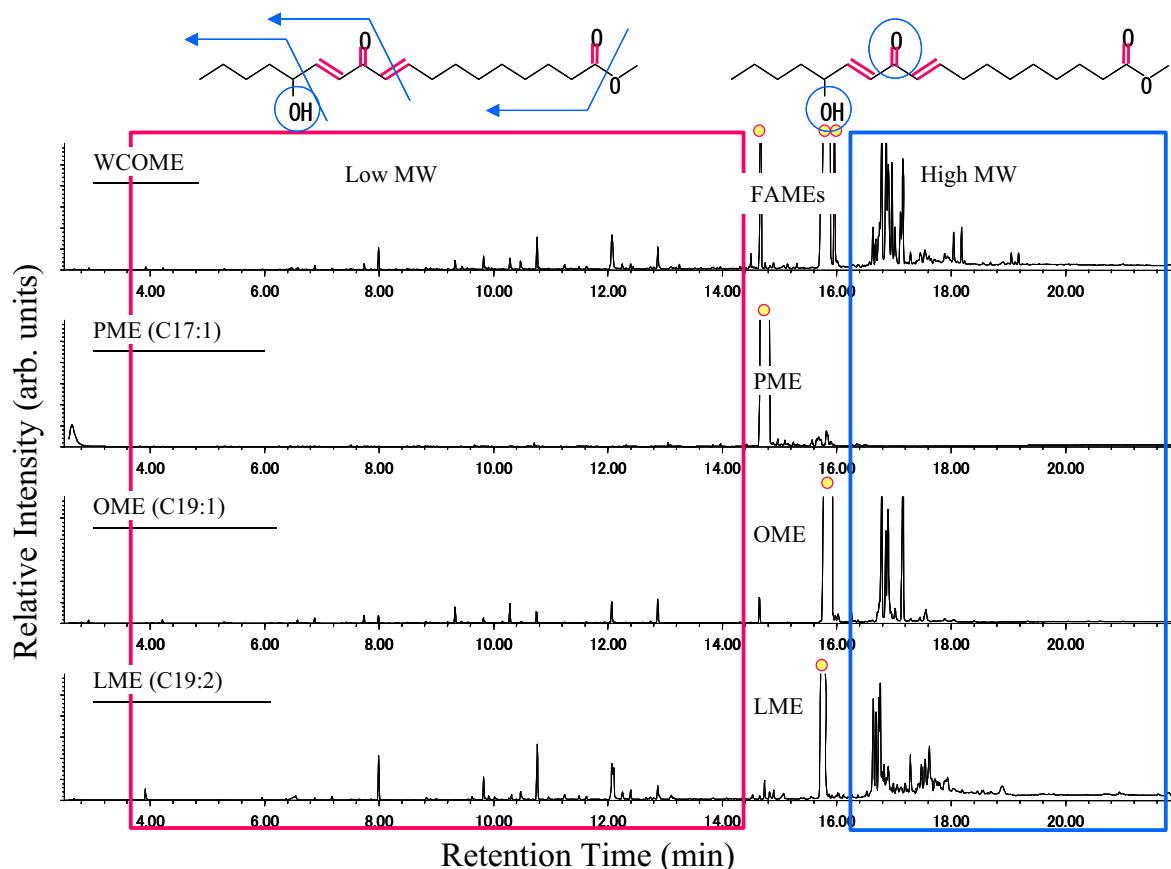


Figure 3. Total ion chromatograms for various FAMEs after heating

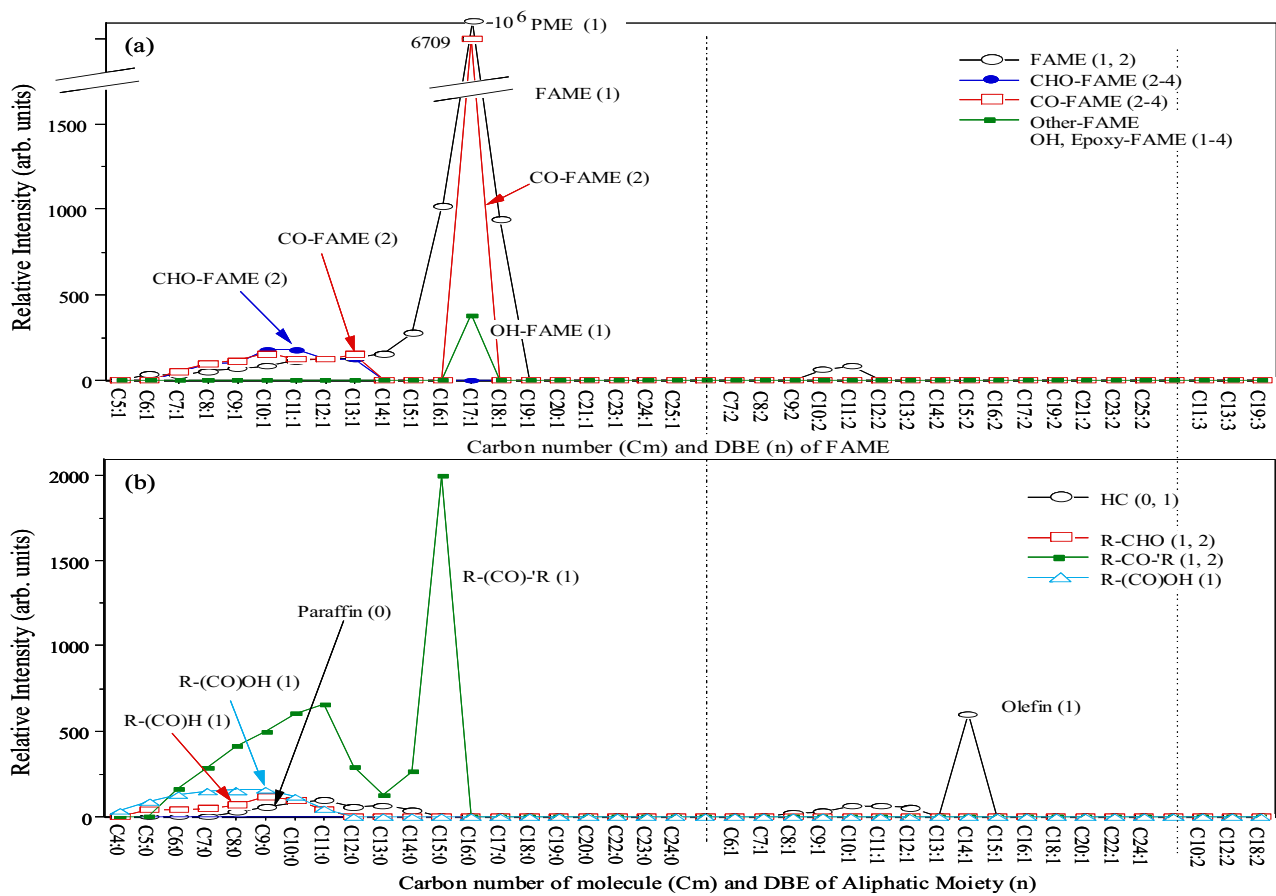


Figure 4. FAMEs and their derivatives (a) and hydrocarbons, alcohols, ketones and aldehydes (b) in PME after heating.

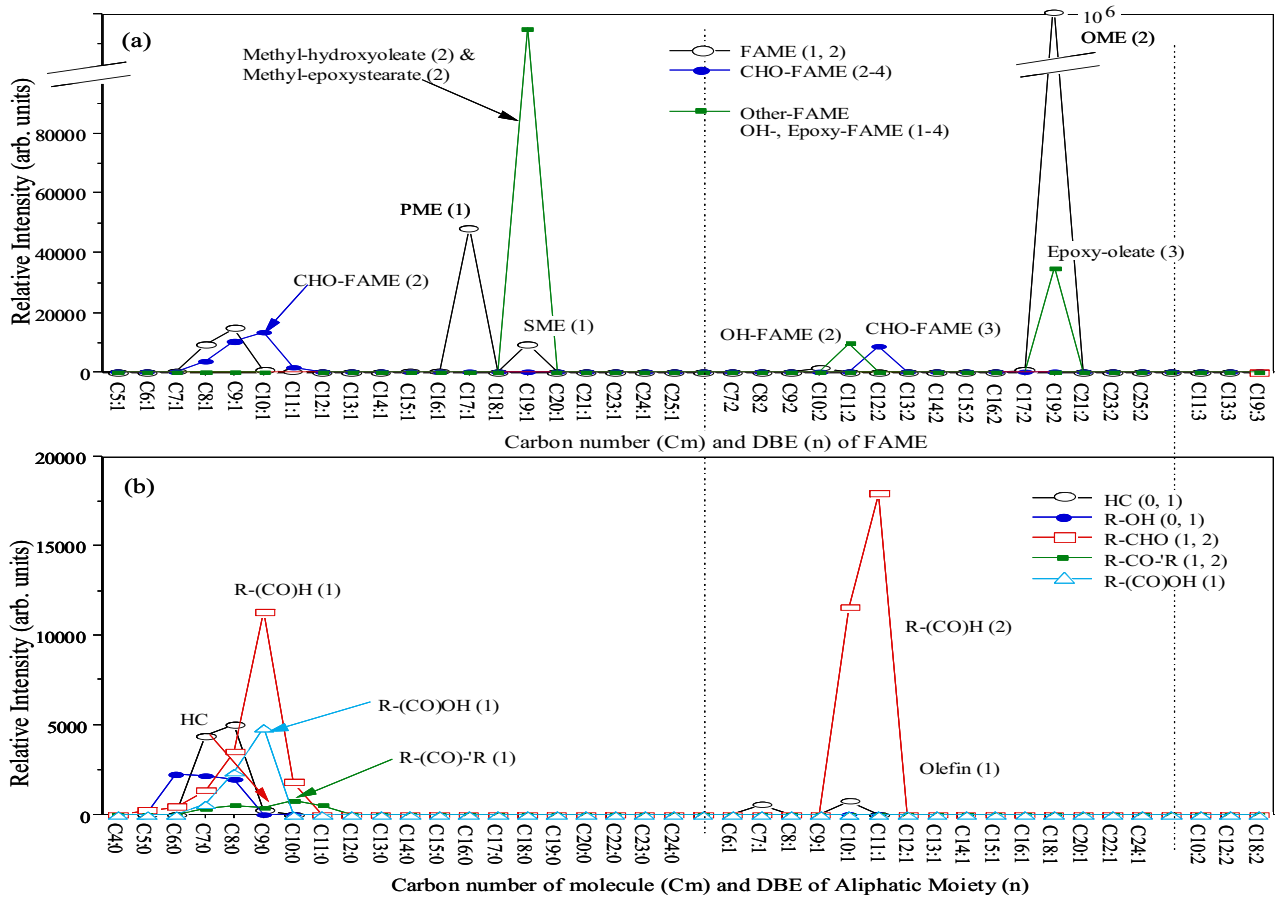


Figure 5. FAMEs and their derivatives (a) and hydrocarbons, alcohols, ketones and aldehydes (b) in OME after heating.