Low molecular weight methyl ester in diesel/waste cooking oil biodiesel blend exhausted gas

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Letter to the editor

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1. Introduction

The utilization of biodiesel fuel (BDF) is well known as an eco-friendly and biodegradable method for reducing pollutants and particulate matter including SO_2, CO, and hydrocarbons. The BDF is an alternative fuel used to fulfill the energy demands of the world, as fossil fuels are gradually being depleted each day [1–3]. However, we have found a new pollutant group, a low molecular weight methyl ester (LMW-ME) with one carbon–carbon double bond [$C_nH_{2n-2}O_2$] between C_4 and C_9, in exhaust gas from a diesel electric power generator that uses waste cooking oil BDF. The concentration of this LMW-ME group increased as the BDF ratio increased, and it was not detected in diesel emissions. In addition, the most dominant compound found in the exhaust gas was methyl acrylate (C_4), of which toxicity is 15 and 3 times higher that of xylene and benzene, respectively. We report here about this new pollutant group generated by a BDF-utilizing diesel engine.

2. Equipment, materials and methods

2.1. Equipment and materials

A diesel electric power generator, model Yanmar YDG 250 VS with 2.5 kVA, four cylinders, and a direction inject mode, was used for testing. GCMS Agilent 5975 and HP-INOWAX 19091N-133 capillary columns were used to detect LMW-ME. Diesel fuel (B0) and BDF blends of 5% (B5), 25% (B25), 50% (B50), 75% (B75) and 100% (B100) of waste cooking oil BDF in diesel were used for this study, and the engine loads used in the experiment were either 0%, 50% or 75%. The composition of the specific BDF used is shown in Table S1 in the supporting information.

LMW-ME standard solutions C_4, C_5, C_6, C_8 and C_9 were purchased from Sigma–Aldrich, and C_7 and C_9 were purchased from Tokyo Chemical Industry Co., Ltd. A reagent-grade CS_2 solvent was purchased from Wako Co., Ltd.

2.2. Sampling and analytical method

Exhaust gas was diluted 20 times with clean air to prevent water deposition and to decrease the gas temperature [4]. The schematic of the experimental system is described in Fig. S1 in the supporting information. The diluted air was then introduced into a glass tube packed with 0.35 g carbopack B (40–100 mesh) to absorb LMW-ME at a rate of 0.5 L min^{-1} for 30 min. LMW-ME was then desorbed by 1 cm^3 of CS_2 for 1 h. A total of 1 mm^3 of the extracted solutions was injected into a GCMS.

3. Results and discussion

Biodiesel is composed of fatty acid methyl esters (FAME), some of which have at least one double bond at the C_{10} position; examples include methyl palmitoate ($C_{17}H_{32}O_2$), methyl oleate ($C_{19}H_{36}O_2$), methyl linoleate ($C_{19}H_{34}O_2$) and methyl linolenate ($C_{19}H_{32}O_2$). Under thermal cracking, cleavage will preferentially occur at the bond adjacent to the double bond; thus, the C_9 and C_{11} positions will be cleaved first. The carbon chain with the methyl ester radical will be produced by the smaller carbon number methyl ester [5], which starts from $C_9H_{16}0_2$ [$CH_2{=}CH{-}(CH_2)_5COOCH_3$]. The carbon chain without the methyl ester radical will produce alkane and alkene. In theoretical combustion, BDF will be cleaved and decompose into CO_2 and H_2O, but the combustion process in the engine is incomplete. Therefore, the LMW-ME, hydrocarbon, and carbonyl species will be produced and emitted in the exhaust gas. In this study, $C_4H_6O_2$ [$CH_2{=}CH{-}COOCH_3$] was observed with the highest LMW-ME concentration. This result is consistent with the results reported by Matthew et al. [6], who concluded that C_4 and C_5 are the most intense peaks in the exhaust gas using B20 and B100; however, they did not quantify and explain more in detail. The ratios of each LMW-ME concentration depend on the fuel mixture and combustion time. The mechanism and kinetics of each LMW-ME formation will be studied in future works. Fig. 1 shows the concentration of each LMW-ME at different loads and diesel/BDF ratios ranging from B0 to B100 (mean concentration of 4 samples). The concentration of C_8 is irregular and higher than that of C_6 and C_7. While their physical properties are similar, the substance that has the higher carbon number also has a higher boiling point and lower vapor pressure. This result will be investigated and clarified in more detail in future studies.

Fig. 2 shows the total LMW-ME concentration at different load and diesel/BDF blend ratios (mean concentration of 3 samples). The concentration of LMW-ME increased with increasing BDF ratios up to B100 because the source of LMW-ME is BDF. However, the LMW-ME concentration decreased with increasing load because temperature and combustion efficiency increase with increasing load. The variation in exhausted gas temperature is shown in Fig. S5 in the supporting information. The total LMW-ME ranged from 0 mg m^{-3} (B0) to 16.7 ± 1.8 mg m^{-3} (B100 at 75% load). We reported new pollutant compounds generated by BDF. Furthermore, it should be noted that of the seven LMW-ME compounds, the highest in concentration was C_4, which had an LD_{50} value of 277 mg kg^{-1} in rats via oral testing [7]. This toxicity is 15 and 3 times higher than that of xylene (LD_{50} = 4300 mg kg^{-1}) and benzene (LD_{50} = 930 mg kg^{-1}), respectively. It is important that the mechanism and conditions of production of LMW-ME are clarified in future studies. In addition, investigation into the measurement and evaluation of their toxicity using various types of BDF is needed.

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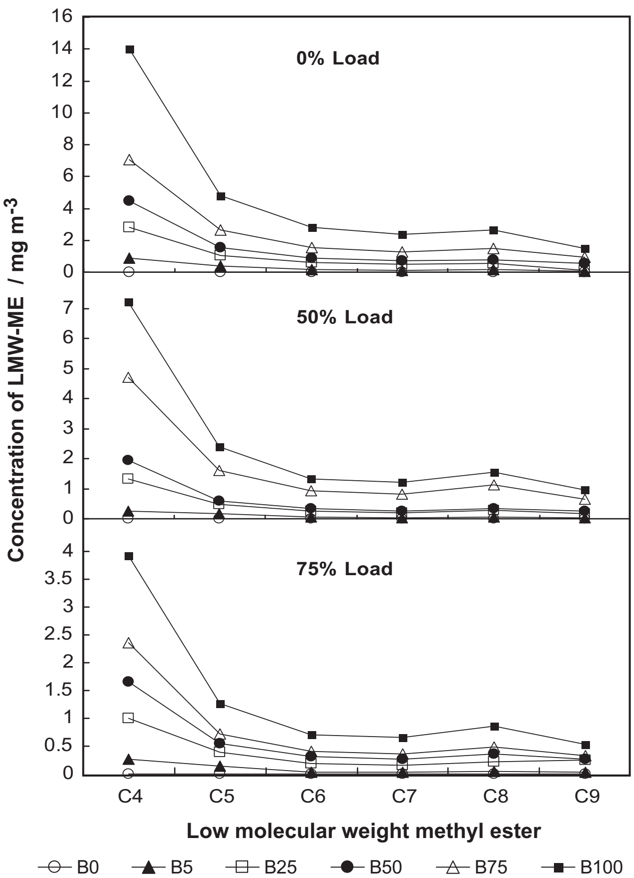

Fig. 1. The concentration of each LMW-ME at different loads and diesel/BDF blend ratios ranging from B0 to B100.

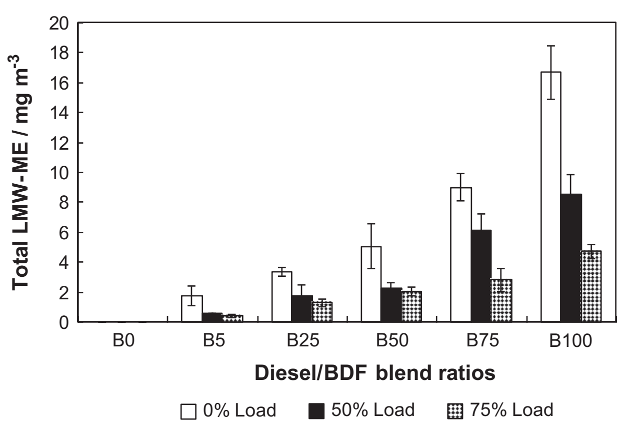

Fig. 2. Total LMW-ME concentrations at different loads (0%, 50% and 75%) and diesel/BDF blend ratios.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.fuel.2013.06.054.

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