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Increase in ozone due to the use of biodiesel fuel rather than diesel fuel☆

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The consumption of fuel by vehicles emits nitrogen oxides (NO_x) and non-methane hydrocarbons (NMHCs) into the atmosphere, which are important ozone precursors. Ozone is formed as a secondary pollutant via photochemical processes and is not emitted directly into the atmosphere. In this paper, the ozone increase resulting from the use of biodiesel and diesel fuels was investigated, and the different ozone formation trends were experimentally evaluated. Known amounts of exhaust gas from a power generator operated using biodiesel and diesel fuels were added to ambient air. The quality of the ambient air, such as the initial NMHC and NO_x concentrations, and the irradiation intensity have an effect on the ozone levels. When 30 cm^3 of biodiesel fuel exhaust gas (BFEG) or diesel fuel exhausted gas (DFEG) was added to 18 dm^3 of ambient air, the highest ratios of ozone increase from BFEG compared with DFEG in Japan and Vietnam were 31.2 and 42.8%, respectively, and the maximum ozone increases resulting from DFEG and BFEG compared with the ambient air in Japan were 17.4 and 26.4 ppb, respectively. The ozone increase resulting from the use of BFEG was large and significant compared to that from DFEG under all experimental conditions. The ozone concentration increased as the amount of added exhaust gas increased. The ozone increase from the *Jatropha*-BFEG was slightly higher than that from waste cooking oil-BFEG.

1. Introduction

The ozone layer in the stratosphere plays an important protective role; however, tropospheric ozone is a photochemical oxidant. Ozone is a secondary pollutant that is produced from volatile organic compounds (VOCs) and NO_x under sunlight (Orlando et al., 2010). It reacts with some gases, such as NO, NO_2 and alkenes, as well as with some surfaces, leaves, and biological membranes. These reactions can damage living cells and human lungs. Exposure to ozone has been associated with several adverse health effects and decreased lung function (Hadavi et al., 2013). Ozone pollution at the ground level is an environmental concern in the US, Brazil, China, Japan, and other countries.

Understanding the increases in ozone production will help improve predictability and reduce ozone pollution by controlling NO_x and VOCs emissions. A considerable number of studies on the ozone increases resulting from emissions from vehicles, engines and generators operating using various fuels have been conducted; however, most of these studies were conducted using modeling, computer simulations or direct tailpipe measurements (Mellouki et al., 2015; Shin et al., 2016). To assess the ozone formation potential in the atmosphere and the importance of NMHC precursors, the maximum incremental reactivity (MIR), also known as the maximum ozone incremental reactivity (MOIR) was proposed by Carter in the late 1980s (Carter and Atkinson, 1987, 1989). The values for quantifying the relative ground-level ozone impacts of

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VOCs and associated uncertainty classifications have been updated (Carter, 1994, 2010; Carter et al., 1995), and these values have been used to describe the maximum ability of a certain hydrocarbon to produce ozone under specific atmospheric conditions.

The production, emissions, and benefits of biodiesel fuel (BDF) have been the focus of studies for several decades. Currently, the benefits of using biodiesel fuel include its ability to mitigate emissions that cause global warming; its ability to minimize CO, SO_2 and particulate emissions (Basha et al., 2009; Basha and Raja,2012; Guarieiro et al., 2009; Zhu et al., 2010)-; and its use as an alternative to fossil fuels, which are continuously being depleted. Previous studies have shown some negative aspects related to the use of biodiesel, such as increased emissions of low-molecular-weight methyl esters (Thang et al., 2014, 2016) and carbonyl compounds (Chai et al., 2013; Dong et al., 2014; Guarieiro et al., 2009; Schröder et al., 1999), increased ozone formation potential (OFP) (Chai et al., 2013; Gentner et al., 2013; Li et al., 2011) and increased NO_x concentration compared to conventional diesel fuel emission (Dorado et al., 2003; Fernando et al., 2005; Guarieiro et al., 2009; Lin et al., 2006; Ribeiro et al., 2016; Xue et al., 2011). The majority of published reports examine biodiesel production, engine performance and biodiesel emissions. Biodiesel emissions have also been considered when BDFs were used rather than diesel fuel. Scientists are interested in clarifying the characteristic emissions from the use of BDFs, therefore, studies have been conducted on the use of B100 (100% BDFs), various blend ratios, different types of engines and operating modes (Basha et al., 2009; Fontaras et al., 2009; Lopes et al., 2014; Schröder et al., 2013).

BFEG has been demonstrated to increase NO_x and carbonyl compounds, which are important ozone precursors. The highest emission of carbonyl compounds was found from B100 (Chai et al., 2013), and this result was consistent with those of other reports (Cardone et al., 2002; Fontaras et al., 2009; He et al., 2009; Lin et al., 2009). These studies also indicated that formaldehyde, acetaldehyde and acrolein were the most abundant carbonyl compounds under all test conditions. The MIR method was applied to several models to estimate the ozone increase associated with the use of BDFs (Chai et al., 2013; Gentner et al., 2013; Hadavi et al., 2013; Schröder et al., 1999). However, reports on the ozone increase determined experimentally using biodiesel exhaust gas and a diesel fuel engine are not available. An achievement of this study was providing a better understanding of ozone as a secondary pollutant. We focused on the increase in ozone when BDF was used as a substitute for conventional diesel fuel. Sunlight and test chamber experiments were conducted and compared using ambient air and ambient air plus exhaust gas. The impacts of NO_x, NMHC, irradiation intensity and quality of the regional ambient air between Hanoi, Vietnam and Osaka, Japan were evaluated.

2. Experimental

An electric power generator (Yanmar YDG 250 VS with 2.5 kVA, four cylinders and direct injection) was used for the emission test. CO, CO_2, hydrocarbon (HC), and NO_x emissions from biodiesel and diesel fuel were analyzed using a Horiba MEXA 584L. Commercial diesel fuel and *Jatropha* and waste cooking oil (WCO) biodiesel fuels were used for testing. The *Jatropha* and WCO biodiesel fuels and their qualities were reported in our previous study (Thanh et al., 2013). Emission gases were collected in a 1-dm^3 glass vacuum bottle. Known volumes of exhaust were then removed and injected into 18-dm^3 Teflon bags using a MS - CANX00 gastight syringe with a volume of 30-cm^3. The Teflon bags were filled with 18-dm^3 of ambient air that was homogenized before the experiment. The ambient air was collected in a 100-dm^3 Teflon bag prior to homogenization, and the ambient air was then divided into three or four 18-dm^3 Teflon bags. The flow rate was controlled using a mass flow controller (KOFLOC, Model 3660). The 18-dm^3 Teflon bags were purchased from GL Sciences Co. Ltd. The transmittance of the Teflon bags is shown in Fig. 1 of the supporting information. The same volume of exhaust gas was collected from the power generator while using biodiesel or diesel fuel during idle mode and injected into two or three 18-dm^3 Teflon bags. One 18-dm^3 bag was filled with ambient air only.

The experiments were conducted under two irradiation conditions: one experiment was conducted using natural sunlight on the roof of the B5 building, Nakamozu campus, Osaka Prefecture University, and the other experiment was conducted using four UV lamps in a test chamber. In the first experiment, three Teflon bags were exposed to sunlight for 6–8 h after being filled with ambient air and with ambient air plus BFEG and DFEG. The concentrations of ozone and NO_x were analyzed after every two hours of irradiation. In the second experiment, three Teflon bags (the same ones as above) were placed in the test chamber, which had a cubic shape with dimensions of 110 (height) x 91 $\times$ 91 cm for the measurements in Osaka, Japan and dimensions of 105 $\times$ 105 $\times$ 105 cm for the measurements in Vietnam. The interior walls of both test chambers were covered with aluminum tape for effective reflection. Four IZ-SLH UV black lights lamp with wavelengths of 315–400 nm and powers of 21 W were used as the UV source. Ozone and NO_x were detected using a Thermo Fisher Scientific model 49 ozone analyzer and a 42i NO_x analyzer, respectively. The irradiation intensity and meteorology factors in the test chamber were detected using a YK-35UV UV light meter purchased from Lutron Electronic Enterprise Co, Ltd. Three bags were placed on a round wooden plate with a diameter of 40.6 cm that could be rotated 360°. After varying the irradiation time, the concentrations of NO_x and O_3 in the Teflon bag were analyzed. The solar intensity in the summer (August and September) ranged from 2 to 4 mW cm^{-2}, whereas the UV light intensity in the test chamber was only 0.2 $\pm$ 0.02 mW cm^{-2}. The photochemical reaction under natural sunlight occurred very fast and reached its maximum within 2 h; inside the test chamber, the reaction required 24–30 h and 12 h for the Osaka and Hanoi experiments, respectively.

To investigate and explain why the NO_x concentration decreased in the air after the photochemical reaction, two Teflon bags containing ambient air were used: One was placed in the dark, and the other was exposed to UV light. To observe the decrease in NO_x after irradiation, a known concentration of standard NO gas was spiked into both bags. After 36 h, all air samples were filtered using an ADVENTEC glass fiber filter, 90608702 (47 mm i.d. and 0.6 μm pore size) before introduction into the NO_x analyzer. The filter was extracted with 5 cm^3 of Millipore water (resistivity $\geq$ 18.2 MΩ cm) by shaking for 10 min. The extracted solution was then filtered using a 0.5-μm filter, and the nitrate and nitrite concentrations were analyzed using a Dionex ICS-1500 ion chromatograph (IC) (the eluent was a 9 mM Na_2CO_3 solution with a 1-cm^3/min flow rate). To wash the interior wall of the bag, 10 cm^3 of pure water was added to the bag before the air was added. The concentrations of NO_2^- and NO_3^- in the solution were analyzed using IC and the same method mentioned above.

3. Results and discussion

3.1. Primary emission of biodiesel and diesel fuels, ozone formation impacts

Biodiesel fuel is known to reduce HC emissions but increase NO_x emissions. The primary emissions from this study are shown in Fig. 1 and are consistent with those of many previous studies. Much of the literature reports that the use of pure BDFs increases NO_x