The use of biodiesel blends on a non-road generator and its impacts on ozone formation potentials based on carbonyl emissions

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ABSTRACT

In this study, emissions of carbonyl compounds from the use B50 and B100 were measured with a non-road diesel generator. A total of 25 carbonyl compounds were identified in the exhaust, including 10 with laboratory-synthesized standards. Formaldehyde, acetaldehyde, and acrolein were found as the most abundant carbonyl compounds emitted for both diesel and biodiesel. The sulphur content of diesel fuels and the source of biodiesel fuels were not found to have a significant impact on the emission of carbonyl compounds. The overall maximum incremental reactivity (MIR) was the highest at 0 kW and slightly increased from 25 to 75 kW. The MIR of B100 was the highest, followed by diesel and B50, which is consistent with the emission rates of total carbonyl compounds. This suggests that the use of biodiesel blends may be more beneficial to the environment than using pure biodiesel.

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1. Introduction

Biodiesel fuel is receiving increased acceptance as an alternative to petroleum diesel. The main portion of commercially available biodiesel fuel is manufactured from vegetable oils or (and) animal fats through a transesterification reaction in the presence of a catalyst (typically potassium or sodium hydroxide or methylate) where the viscous triglycerides are transformed into less viscous methyl or ethyl esters (Knothe et al., 2005; Tickell, 2003). Biodiesel is considered to reduce greenhouse gas emission, since the CO_2 released in biodiesel combustion can be absorbed by the oil pro-ducing plants during growth. The European Union (EU) estimated that the typical greenhouse gas emission savings from biodiesel are 36—88%, depending on the feedstock (European Union, 2009). Compared to diesel fuel, studies have shown that using biodiesel fuel reduces criteria atmospheric pollutants such as carbon mon-oxide (CO), particulate matters (PM), hydrocarbons (HCs), and sulphur dioxide (SO_2) (U.S. EPA, 2002; Graboski and McCormick, 1998; Anderson, 2012; Bunger et al., 2012). Since 2010, all heavy duty diesel engines come equipped with emission controls to reduce nitrogen oxides (NO_x) and PM thus mitigating the down-sides of biodiesel usage, which had been known to generate slightly higher NO_x (Graboski and McCormick, 1998). However, the emis-sion of carbonyl compounds from petroleum diesel and biodiesel combustion has not been adequately addressed (Grosjean et al., 2001; Ban-Weiss et al., 2008).

Carbonyl compounds such as formaldehyde, acetaldehyde and acrolein are labelled as motor vehicle air toxics and are known human carcinogens or irritants (Shepson et al., 1986; WHO, 1989, 1991, 1995; IARC, 1995). Five carbonyl compounds (formaldehyde, acetaldehyde, acrolein, propionaldehyde, and butanone) are listed as hazardous air pollutants (HAP) by United States Environmental Protection Agency (USEPA, 2012a). Some aldehydes, such as form-aldehyde, acetaldehyde, acrolein, and some di-aldehydes, have high incremental reactivity for ozone formation (Seinfeld and Pandis, 1998; Carter, 1995), which may result in increased ground level ozone (a regulated air pollutant) and pose problems for areas that are already in ozone non-attainment or on the borderline. The Maximum Incremental Reactivity (MIR) values have been used to describe the maximum ability to produce ozone by a certain hy-drocarbon under specific atmospheric conditions (Carter, 1995).

Various studies have been published on the test results of carbonyl emission from combustion of biodiesel blends (Lin et al., 2009; Liu et al., 2009; Di et al., 2009; Fontaras et al., 2010; Peng et al., 2008; Correa and Arbilla, 2008; Guarieiro et al., 2008; He et al., 2009; Baldassarri et al., 2004; Cardone et al., 2002; Fontaras

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et al., 2009; Karavalakis et al., 2009a, 2009b, 2009c; Ballesteros et al., 2011; Karavalakis et al., 2010; Cahill and Okamoto, 2012; Cosseron et al., 2012; Gomez et al., 2012), to name a few. However, most studies were performed on on-road diesel engines, including passenger cars, heavy-duty trucks and tractors, with very limited reports on non-road engines (generators). Unlike on-road diesel engines, non-road diesel engines tend to be older in age and can use lower quality fuels. While the sulphur content for on-road diesel fuel has reduced to 15 ppm or less since 2006 in U.S., the 500 ppm sulphur fuel can be used on non-road engines until 2014 (USEPA, 2012b).

The existing studies also have reported variations on biodiesel's contribution to carbonyl compounds. Ballesteros et al. (2011) found that total carbonyl emissions from pure animal-fat biodiesel are 101.12–1157.38% higher compared to emission from diesel in all test modes. He et al. have observed the weighted carbonyls emission of biodiesel is almost three times higher than that of diesel (He et al., 2009). On the contrary, Gomez et al. (2012) found reductions in both formaldehyde and acetaldehyde when using B50, B100 soybean biodiesel and B100 beef tallow biodiesel compared to diesel. Karavalakis et al. (2009a) have noticed reduction of carbonyl emissions with the usage of B20. However, in another study, Karavalakis et al. (2010) found significant carbonyl emissions increase from B50. The difference has been reported for both the total carbonyl compounds as well as individual carbonyl compounds. The inconsistency of existing results could be due to various operating conditions, which include engine type, engine age, engine load, fuel sources, fuel composition, and sulphur contents, etc. Meanwhile, the impacts of the resulting ozone formation from biodiesel use were almost not evaluated.

The purpose of this study was to better understand the ozone formation potentials of using biodiesel blends and pure biodiesel. The carbonyl compound emissions from petroleum diesel, biodiesel and its blends on a non-road diesel generator were quantified with both commercially available and laboratory synthesized standards. The impacts of sulphur content and the biodiesel feedstock were evaluated.

2. Materials and methods

2.1. Fuels

Overall, six fuels were tested in this study. Two petroleum diesel fuels obtained from Steve Krebs Oil Company (a BP company) were referred to as low-sulphur diesel (LSD, less than 500 ppm sulphur) and ultra low-sulphur diesel (ULSD, less than 15 ppm sulphur). The average sulphur contents were quantified by a commercial laboratory as 212 and 15 ppm respectively. Two biodiesel fuels used were Nexsol BD-0100 (PC B100) biodiesel fuel purchased from Peter Cremer North America, which was produced from virgin soybean oil and a biodiesel fuel made in the laboratory from waste vegetable oil (WV B100), which was obtained from the University of Cincinnati's cafeteria (Agnew et al., 2009). The two biodiesel fuels were chosen because they are most common ones in U.S. market and they were used to compare the carbonyl compound emissions from different sources of biodiesel fuels. Two petroleum diesel fuels (LSD and ULSD) mixed with PC B100 at a volume ratio of 1:1 (denoted as LS B50 and ULS B50 respectively) were utilized in this study to test the effect of sulphur content on carbonyl compound emissions. As indicated in Table 1, the carbon to hydrogen (C/H) ratios of diesel fuels and biodiesel fuels are very similar (average of 6.03 for biodiesel fuel and average of 6.11 for petroleum diesel fuel). The heating values of biodiesel fuels are approximately 13% lower than those of petroleum diesel fuels due to the higher oxygen content of biodiesel fuel.

The compositional analyses of the two tested biodiesel fuels (listed in Table 2) were performed on gas chromatography/mass spectrometry (GC/MS, Varian Inc., GC model: CP 3800 and MS model: Saturn 2200) with a CP Wax 58 (FFAP) capillary column (Varian Inc., 30 m × 0.32 mm × 0.25 μm). The major components of both biodiesel fuels are C16:0, C18:0, C18:1, and C18:2 methyl esters. The compositions of PC B100 are consistent with the certificate of analysis provided by the vendor, which is an indication that our analytical method is effective. The major methyl esters are unsaturated, which is consistent with another compositional study (Fallen et al., 2011). The waste vegetable oil biodiesel fuel is much higher in C18:1 and lower in C18:2 fractions compared to the soybean biodiesel, which is also reported by another study (Cao et al., 2008). This compositional difference might be due to the different feedstocks as well as the oxidation of the unsaturated fractions.

Table 1
Properties of petroleum diesel fuels and biodiesel fuels.

Properties	Low-sulphur diesel (LS-D)	Ultra low-sulphur diesel (ULS-D)	Biodiesel from soybean oil (PC-BD)	Biodiesel from recycle cooking oil (WV-BD)
Density (g/cm^3)	0.802	0.798	0.880	0.889
Oxygen (wt%)	N.D.	N.D.	8.04	7.96
Carbon (wt%)	85.08	85.24	79.01	78.82
Hydrogen (wt%)	14.10	14.15	12.90	12.92
Sulphur (ppm)	212	15	N.D.	2
C/H ratio	6.03	6.02	6.12	6.10
Heating value (Btu/lb)	19,468	19,612	17,038	16,988

2.2. The non-road diesel engine

The emission test was conducted on a compression-ignition non-road diesel generator (Generac, 1992, Model SD080, model number 92A-03040-S). The generator is direct-injection, turbo-charging, 4 cylinders with a displacement of 4.5 L, rated at 80 kW with a normal engine speed of 1800 revolutions per minute (rpm) and compression ratio 17.5:1, and equipped with a diesel muffler and exhaust sampling stack. The generator has approximately 700 h of work, which is lightly used considering the expected engine life averages of 2500 h at full load for engines of this size (USEPA, 2002). A SIMPLX Merlin 100 load bank simulator was utilized to simulate different operation conditions of the generator, from 0 kW (idle) to 75 kW. The load bank simulator has a 3-wire connection, with airflow of 4000 cubic feet per minute, a capacity of up to 100 kW, a voltage up to 480 V, and a frequency of 60 Hz. When initiating the load bank simulator, the output power was altered while the speed of generator remained at 1800 rpm. Four loads were applied in this study, 0 kW–75 kW with 25 kW increments. The same engine loads and operation procedures were used by other diesel and biodiesel emission tests (Liu et al., 2005; Tzillah, 2009).

2.3. Sample collection

The procedure of sampling carbonyl compounds in the exhaust followed USEPA Method TO-11A (USEPA, 1999) and is briefly described here. Partial exhausted gases from the diesel generator were introduced into a two-foot-long, 5-mm inner diameter copper probe through an ozone scrubber (Sep-Pak, Waters Corporation) by a sampling pump (AirChek 2000, SKC Inc.). The probe was wrapped with an ice pack to cool down the exhaust gas. The temperature of exhaust gas dropped from approximately 204 °C (400 °F) to less than 20 °C (68 °F) after going through the sampling probe. The carbonyl compounds were collected on cartridges coated with 2,4-dinitrophenylhydrazine (DNPH) from Waters Corporation. The sampling flow rates ranged from 0.4 to 0.8 L/min with a sampling time range of 15–30 min. After sampling, the cartridges were capped, wrapped immediately with aluminium foils and stored under low temperature (in an on-site cooler filled with ice, and in a refrigerator upon arrival at the laboratory) until analysis. Under each operating condition, three to five samples were collected for reproducibility. The relative standard deviation (RSD) for each sample set was less than 10%. At least one backup cartridge at each operating condition was tested to determine breakthrough. The breakthrough was found to be less than 10% for all samples. At least one parallel sample was collected under each operation condition to check the distribution of the

Table 2
Compositions of tested biodiesel fuels (relative %).

Methyl ester	Soybean oil	Recycled cooking oil
C10:0	0.02	0
C12:0	0.03	0.02
C14:0	0.46	0.03
C15:0	0.03	0
C16:0	11.34	3.31
C16:1	1.41	0.13
C17:0	0.60	0.76
C17:1	0.16	0.04
C18:0	11.71	2.07
C18:1	46.26	79.10
C18:2	25.26	12.29
C18:3	2.46	2.02
C20:0	0.23	0.22
C22:0	0	0
Saturated	24.42	6.41
C18 portion	85.69	95.48