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A new alternative paraffinic–palmbiodiesel fuel for reducing polychlorinated dibenzo-p-dioxin/dibenzofuran emissions from heavy-duty diesel engines

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ABSTRACT

Polychlorinated dibenzo-p-dioxin/dibenzofuran (PCDD/F) emissions from heavy-duty diesel engines (HDDEs) fuelled with paraffinic–palmbiodiesel blends have been rarely addressed in the literature. A high-resolution gas chromatograph/high-resolution mass spectrometer (HRGC/HRMS) was used to analyze 17 PCDD/F species. Experimental results indicate that the main species of PCDD/Fs were OCDD (octachlorinated debenzo-p-dioxin) and OCDF (octachlorodibenzofuran), and they accounted for 40–50% of the total PCDD/Fs for all test fuels. Paraffinic–palmbiodiesel blends decreased PCDD/Fs by 86.1–88.9%, toxic PCDD/Fs by 91.9–93.0%, THC (total hydrocarbons) by 13.6–23.3%, CO (carbon monoxide) by 27.2–28.3%, and PM (particulate matter) by 21.3–34.2%. Using biodiesel blends, particularly BP9505 or BP8020, instead of premium diesel fuel (PDF) significantly reduced emissions of both PCDD/Fs and traditional pollutants. Using BP9505 (95 vol% paraffinic fuel + 5 vol% palmbiodiesel) and BP8020 instead of PDF can decrease PCDD/F emissions by 5.93 and 5.99 g I-TEQ year^{-1} in Taiwan, respectively.

1. Introduction

Diesel engines are widely used in heavy-duty buses, trucks, construction machines, and generators, because they have high fuel efficiency, power output, and fuel economy and lower emissions of traditional pollutants than gasoline-powered engines [1,2]. However, emissions of smoke, particulate matter (PM), organic/elemental carbons, sulfur oxide (SOx), polycyclic aromatic hydrocarbons (PAHs), polychlorinated dibenzo-p-dioxin/dibenzofurans (PCDD/Fs), and exhaust odor from HDDE exhausts have long been a concern for the public and environmental researchers [3–12].

Unfortunately, emissions of hydrocarbons and polycyclic aromatic hydrocarbons (PAHs) from diesel vehicles may be consistent with the role of aromatic precursors for PCDD/F formation and the degenerated graphitic soot structure in de novo synthesis [6]. Furthermore, incomplete combustion and chlorine in fuel lead to PCDD/F emissions from vehicular engines [4]. Previous research showed that the most significant emissions from diesel engines are gas-phase PCDD/Fs, and that PCDD/F concentrations decreased with increasing load rate. Furthermore, studies have found that high load and new engines cause lower PCDD/F emissions due to better combustion, with PCDD/F emissions ranging from 0.024 to 0.550 ng I-TEQ L^{-1} due to different steady-state procedures and vehicles [13–16]. Gullett and Ryan [16] found that diesel fuel with low sulfur caused high PCDD/F emissions (0.044 ng I-TEQ L^{-1}) as compared to commercial diesel fuel bought in North Carolina (0.024 ng I-TEQ L^{-1}). In addition, PCDD/F emissions can be reduced from 0.097 to 0.023 ng I-TEQ L^{-1} when a diesel oxidation catalyst is used [17]. The health risk of PCDD/Fs emitted from HDDEs in the areas with relatively high automobile and population density should not be ignored. However, it is still desirable to find an alternative fuel to reduce PCDD/F emissions from HDDEs.

Recently, biodiesel has received significant attention because of the need to reduce emissions from diesel engines without modifying them, as well as in order to reduce the use of fossil fuels. Biodiesel is an oxygenated fuel that can be used in diesel engines to improve combustion efficiency, as well as reducing emissions of total hydrocarbons (THC), carbon monoxide (CO), sulfur oxide (SO_2), PAHs, and carbonyl compounds [9–12,18–28]. Therefore, it is anticipated that biodiesel can reduce PCDD/F emissions, as it has already been shown to reduce those of both HCs and PAHs, and the latter may act as aromatic precursors for the formation of PCDD/Fs and the degenerated graphitic soot structure in de novo synthesis [6]. Palmbiodiesel has a better potential for commercial applications than other biodiesels because it meets the requirements of diesel-engine combustion, and has comparable performance to

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Table 1
Details of the Cummins B5.9-160 HDDE.

Parameters	Test HDDE
Engine model	Cummins
Engine type	B5.9-160
Aspiration	Turbocharged
Intercooler	Water cooler
Injection type	Direct injection
Bore × stroke	102 mm × 120 mm
Displacement	5880 cm^3
Injection sequence	1-5-3-6-2-4
Injection timing	12.3° BTDC[a]
Compression ratio	17.9:1
Idle speed	810 rpm
Max. power	118 kW (at 2400 rpm)
Max. torque	534 N m (at 1600 rpm)

[a] Before top dead center.

other biodiesels such as soybean and rapeseed oils. In addition, palmbiodiesel is cheaper than both soybean-biodiesel and corn-biodiesel [29–30]. In our previous study, the aromatic, paraffin, and naphthene contents in base diesel fuel (premium diesel fuel) were measured using an NMR C^{13} (nuclear magnetic resonance C^{13}), and were found to be 30.8, 45.1, and 24.1 wt%, respectively. However, >99% alkane with 12–16 element carbon has been found in paraffinic fuel [31]. Paraffinic fuel can be synthesized from methane or produced by the reaction of CO and hydrogen (H_2), and thus it is better than premium diesel fuel. Since palmbiodiesel is an oxygenated fuel, it can be blended with paraffinic fuel and used in diesel engines to enhance combustion efficiency. In our previous study, we found that there was no significantly negative influence by using palmbiodiesel-diesel blends and paraffinic–palmbiodiesel blends instead of diesel in diesel engines for 18,000 km [28]. Therefore, palmbiodiesel and paraffinic fuel were selected as alternative fuels in this study.

Pollutant emissions from HDDEs under the US-HDD transient cycle test [32] are representative because engines are tested over a full range of load and speed conditions, including expressway, congested-urban, and uncongested-urban settings. Although PCDD/F emissions from diesel engines have been investigated in the literature, the test loadings are steady-state conditions. Moreover, reductions in PCDD/F emissions from HDDEs fuelled with biodiesel blends under the US-HDD transient cycle have been rarely been reported in the past. Therefore, this study first examined PCDD/F emissions from a HDDE by using palmbiodiesel–diesel blends and paraffinic–palmbiodiesel blends with the US transient cycle. Second, emission factors of PCDD/Fs and traditional pollutants in the exhaust of the HDDE were compared and discussed. Finally, reductions in PCDD/F emissions from a test HDDE fuelled with biodiesel blends were evaluated.

2. Methods and materials

2.1. Test engine and fuels

The Cummins B5.9-160 HDDE (non-catalyst) was used in this study, with details shown in Table 1. The test engine was manufactured in 1994 and is commonly used in Taiwan for regulation test of pollutant emissions. Testing was conducted according to Code of Federal Regulations (CFR) 40 Part 86 Subpart N (the US-HDD Transient Cycle) [32]. A Schenck GS-350 dynamometer was used, while a dilution tunnel and a monitoring system were installed downstream of the diesel-engine's exhaust to supply dilute air and to facilitate continuous measurement of suspended particles (PM and particulate-phase PCDD/F). Gas-phase pollutants (THC, CO, CO_2, NOx and gas-phase PCDD/F) were also collected and measured. In order to decrease the temperature of the original exhaust, clean ambient air was used to dilute it. Active carbon is used for cleaning the inlet ambient air, which is used for diluting the engine exhaust. The sampling system was a CVS (constant volume sampling) one. The volumetric flow rate of clean ambient air was roughly 17 times higher than that of the original exhaust. Thus, the appropriate dilution ratio was approximately 18 to 1. Due to the low PCDD/Fs level, we ran one cycle for one sample and then we mixed 10 samples to get one mixed sample. Totally three mixed samples were taken for each test fuels in this study. The following six test fuels were selected for this study: premium diesel fuel (PDF), B20 (20 vol% palmbiodiesel + 80 vol% PDF), B100 (100 vol% palmbiodiesel), BP9505 (95 vol% paraffinic fuel + 5 vol% palmbiodiesel) and BP8020 (80 vol% paraffinic fuel + 20 vol% palmbiodiesel). Palmbiodiesel was purchased from Gibson Chemical Corporation in Malaysia. Paraffinic fuel was purchased from Gibson Chemical Corporation in Germany.

2.2. Sample collection

A schematic of the sampling equipment is given in Fig. 1. After the original exhaust gas was diluted, suspended particles (PM and particulate-phase PCDD/Fs) and gas-phase pollutants (THC, CO, CO_2, NOx and gas-phase PCDD/Fs) were collected and measured. PCDD/Fs, in both gas- and particulate-phases, were collected using a PCDD/F sampling system at a temperature below 52 °C to avoid desorption of the PCDD/Fs collected on the cartridges. However, the usual temperature of the exhaust in this study was 30–35 °C. The average temperature of the XAD module during testing was 32.4 °C. Gas-phase PCDD/Fs were collected on a three-stage glass cartridge. The mass of XAD-2 resin used for the testing was 150 g. PUF plugs were used as well. Prior to sampling, XAD-2 resin was spiked with PCDD/F surrogate standards pre-labeled with isotopes, including $^{37}C_{l4}$-2,3,7,8-TCDD (tetrachlorodibenzo-p-dioxin), $^{13}C_{12}$-1,2,3,4,7,8-HxCDD (hexachlorinated dibenzo-p-dioxin), $^{13}C_{12}$-2,3,4,7,8-PeCDF (pentachlorinated dibenzofuran), $^{13}C_{12}$-1,2,3,4,7,8-HxCDF (hexachlorinated dibenzofuran) and $^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF (heptachlorinated dibenzofuran). The recoveries of PCDD/F surrogate standards met the criteria within 70–130%. To ensure the free contamination of the collected samples, one trip blank and one field blank were also taken during the field sampling was conducted. The glass cartridges were spiked with a known amount of surrogate standard in the laboratory prior to the field sampling being conducted. Trip blanks and field blanks were below detection limit. Furthermore, we have run tunnel blanks. The PCDD/F concentrations of tunnel blanks were below detection limit. Therefore, it can be assumed that clean ambient air is free of background PCDD/Fs and there is no thermophoretic loss of PCDD/Fs to the tunnel wall during engine testing.

2.3. Analytic method

Each filter sample was weighed again using electronic analytical balance with fully automatic calibration technology (AT200, Mettler, Switzerland) to determine the net mass of the particulate matter (PM) collected. For THC analysis, each sample was analyzed with a flame ionization detector (FID) (Model 404, Rosemount, UK). For CO/CO_2 analysis, each sample was analyzed using a non-dispersive infrared detector (NDIR) (Model 880A, Rosemount, UK). For NOx analysis, each sample was analyzed by chemiluminescent detection (CLD) (Model 404, Rosemount, UK). Analyses of PCDD/F samples followed the U.S. EPA Modified Method 23 and EPA Reference Method T09A. All chemical analyses were conducted at the Super Micro Mass Research and Technology Center at Cheng Shiu University – an accredited laboratory in Taiwan for analyzing PCDD/Fs. Each collected sample was spiked with a