Journal of Hazardous Materials 185 (2011) 1–7

Contents lists available at ScienceDirect

Journal of Hazardous Materials

journal homepage: www.elsevier.com/locate/jhazmat

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

Yuan-Chung Lin[a,*], Shou-Heng Liu[b], Yan-Min Chen[c], Tzi-Yi Wu[d]

[a] Institute of Environmental Engineering, National Sun Yat-sen University, Kaohsiung 804, Taiwan
[b] Department of Chemical and Materials Engineering, National Kaohsiung University of Applied Sciences, Kaohsiung 807, Taiwan
[c] Sustainable Environment Research Center, National Cheng Kung University, Tainan 701, Taiwan
[d] Department of Chemistry, National Cheng Kung University, Tainan 701, Taiwan

ARTICLE INFO

Article history:
Received 31 March 2010
Received in revised form 25 June 2010
Accepted 18 July 2010
Available online 22 July 2010

Keywords:
PCDD/Fs
Biodiesel
Paraffinic fuel
Exhaust
Diesel engine

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

---

[*] Corresponding author. Tel.: +886 7 5252000x4412; fax: +886 7 5254412.
E-mail address: yclin@faculty.nsysu.edu.tw (Y.-C. Lin).

0304-3894/$ – see front matter © 2010 Published by Elsevier B.V.
doi:10.1016/j.jhazmat.2010.07.071

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 $^{37}C_{14}$-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

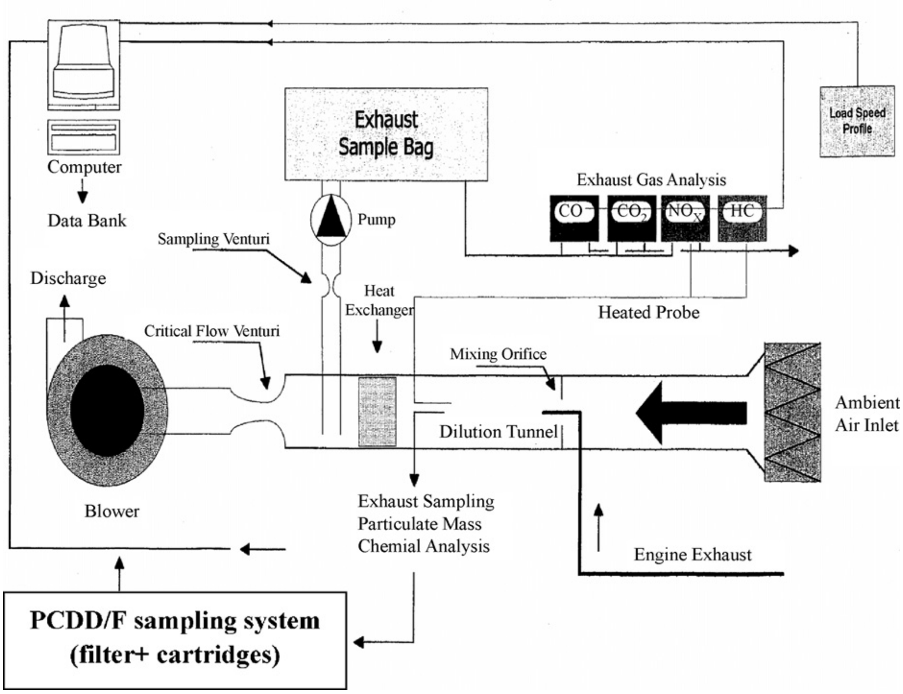

Fig. 1. A schematic of the sampling equipment.

known amount of the internal standard. After being extracted for 24 h, the extract was concentrated, treated with concentrated sulfuric acid, and then subjected to a series of sample cleanup and fractionation procedures. The eluate was concentrated to ∼1 mL, transferred to a vial, and then further concentrated to nearly dryness by using a nitrogen stream. Prior to PCDD/F analysis, the standard solution was added to the sample to ensure the recovery during the analysis. A high-resolution gas chromatograph/high-resolution mass spectrometer (HRGC/HRMS) was used to analyze 17 PCDD/F species. The HRGC (Hewlett Packard 6970 Series gas, CA, USA) was equipped with a DB-5 fused silica capillary column (L = 60 m, ID = 0.25 mm, film thickness = 0.25 μm) (J&W Scientific, CA, USA) and splitless injection. Helium was employed as the carrier gas. The HRMS (Micro Mass Autospec Ultima, Manchester, UK) was equipped with a positive electron impact (EI^+) source. The analyzer mode of selected ion monitoring (SIM) had a resolving power of 10,000. The electron energy and source temperature were at 35 eV and 250 °C, respectively. The toxic equivalent quantity of PCDD/Fs is given by I-TEQ = $\sum X_i I_i$, where I-TEQ denotes the international toxic equivalent quantity, X_i represents the concentration of PCDD/F congeners, and I_i is the international toxic equivalent factor of each PCDD/F congener (I-TEF) [33]. All PCDD/Fs were above the detection limit.

3. Results and discussion

3.1. Fuel specifications

Mean sulfur and total poly-aromatics in PDF were 30 ppmw (parts per million by weight) and 0.5 wt%, respectively. Mean sulfur and total poly-aromatics in B20 were 23 ppmw and 0.4 wt%, respectively. Mean sulfur and total poly-aromatic content in B100, BP9505, and BP8020 were less than the detected limit (10 ppmw and 0.1 wt%, respectively). Lower PAH contents in fuel caused lower PAH emissions in our previous studies [9,34,35], so PAH reductions in diesel-engine emissions are expected with the use of these alternative fuels instead of PDF in HDDEs. Similar results may be expected with regard to SOx emission. Higher density could cause longer liquid penetration for biodiesel. The boiling point, which is important for air–fuel mixing, is generally higher for biodiesel. Higher boiling point may lead to a longer penetration [36]. From the results of viscosity, it shows that all the fuels have permissible viscosities for diesel engines. The viscosity of B100 was 1.54 times higher than that of PDF. High viscosity may influence spray development and droplet atomization as well as injection dynamics. Another important property is the cetane number, which greatly affects the auto-ignition characteristics. Further details of the fuels are given in Table 2.

3.2. Emissions of traditional pollutants

The emission factors of traditional air pollutants in HDDE exhaust are presented in Table 3. Particulate matter (PM) emitted from engines is comprised of three major components: soot formed during combustion, heavy hydrocarbons condensed or absorbed by the soot, and sulfates. The boiling point of a fuel is important for air–fuel mixing. A higher boiling point may also lead to longer penetration, resulting in more fuel impingement and poorer combustion. In addition, and as suggested above, high viscosity may influence spray development and droplet vaporization [36]. The 90% boiling point (T90) and viscosity of PDF were lower than those of B20, B100, BP9505 and BP8020, indicating that in theory PDF evaporated and atomized more easily than the other fuels. However, we found that emissions of THC, CO, and PM for biodiesel blends were lower than those for PDF, and that the CO_2 emissions were higher. The above results suggest that palmbiodiesel, an oxygenated fuel, caused B20, B100, BP9505, and BP8020 to be burn more easily than PDF. Compared with PDF, the mean reductions of THC were 2.51%, 36.6%, 13.6%, and 23.3% for B20, B100, BP9505, and BP8020, respectively. For CO, they were 15.5%, 20.3%, 27.2%, and 28.3%, respectively. For PM, they were 13.8%, 33.5%, 21.3%, and 34.2%, respectively. However, the mean increases of CO_2 were 7.62%, 10.7%, 4.55%, and 4.11% for B20, B100, BP9505, and BP8020, respectively, when compared with PDF. No significant differences were found in NOx emissions.

Table 2
Specifications of the test fuels.

Fuel parameter	PDF[a]	B20[b]	B100[c]	BP9505[d]	BP8020[e]	Analytic method
Density (g mL^{-1} at 15 °C)	0.832	0.833	0.875	0.790	0.802	ASTM[f] D4052
Viscosity (cSt at 40 °C)	2.72	2.88	4.18	3.57	3.42	ASTM D445
Cetane number	56.0	54.8	63.7	>65	>65	ASTM D613
Carbon residue (wt%)	0.06	0.06	0.05	0.05	0.05	ASTM D542
Distillation, T90 (°C)	317	328	335	337	339	ASTM D86
Ash (wt%)	0.001	0.001	0.001	0.001	0.001	ASTM D482
Sulfur content (ppmw)	30	23	ND[g] (<10)	ND (<10)	ND (<10)	ASTM D2622
Poly-aromatic content (wt%)	0.5	0.4	ND (<0.1)	ND (<0.1)	ND (<0.1)	ASTM D6591
Chloride content (ppbw)	275	214	ND (<50)	ND (<50)	ND (<50)	ASTM D4929
Residue (vol%)	0.03	0.02	0.02	0.01	0.02	ASTM D2709
Corrosiveness, 3 h at 50 °C	1a	1a	1a	1a	1a	ASTM D130

[a] Premium diesel fuel as base fuel.
[b] 20% palmbiodiesel + 80% PDF.
[c] 100% palmbiodiesel.
[d] 95% paraffinic fuel + 5% palmbiodiesel.
[e] 80% paraffinic fuel + 20% palmbiodiesel.
[f] American Society for Testing and Materials.
[g] Not detected.

3.3. PCDD/F concentrations and congener profiles in the exhaust of HDDEs

The PCDD/F concentrations in HDDE exhaust are listed in Table 4. PCDD/F emissions from the Cummins B5.9-160 HDDE follow the order of PDF > B20 > B100 > BP8020 > BP9505. Compared with PDF, PCDD/F reductions were (32.9%, 43.0%), (80.3%, 85.1%), (88.9%, 93.0%), and (86.1%, 91.7%) for B20, B100, BP9505, and BP8020, respectively. Previous research indicated that PCDD/F precursors form when organic or inorganic chlorine ions (Cl^-) are present [37]. PCDD/Fs also form due to the reactions between benzene and inorganic Cl^- [29]. In general, PCDD/F formation rates are related to chlorine concentrations [38]. Emissions of HC and PAHs may be consistent with the role of aromatic precursors in the formation of PCDD/Fs [6]. The results in Table 2 show that no PAH and chlorine were present in palmbiodiesel and paraffinic fuel. Moreover, THC was reduced by use of palmbiodiesel/PDF blends and palmbiodiesel/paraffinic fuel blends (Table 3). Thus, PCDD/F reductions may be attributed to no PAH and chlorine being present in palmbiodiesel and paraffinic fuel, but 0.5 wt% and 275 ppbw were found in PDF, respectively. Notably, the ratios of PCDDs/PCDFs were all <1.0 (Table 4), indicating that the main PCDD/Fs emitted from HDDEs were PCDFs not PCDDs. The ratios of toxic PCDDs/PCDFs were all <1.0, indicating the main I-TEQ PCDD/Fs emitted from HDDEs were also PCDFs and not PCDDs. Palmbiodiesel/paraffinic fuel blends thus decreased PCDD/F emissions by 86.1–88.9% and toxic PCDD/F emissions by 91.9–93.0%. Therefore, using biodiesel blends instead of PDF, particularly BP9505 or BP8020, significantly reduced PCDD/F emissions.

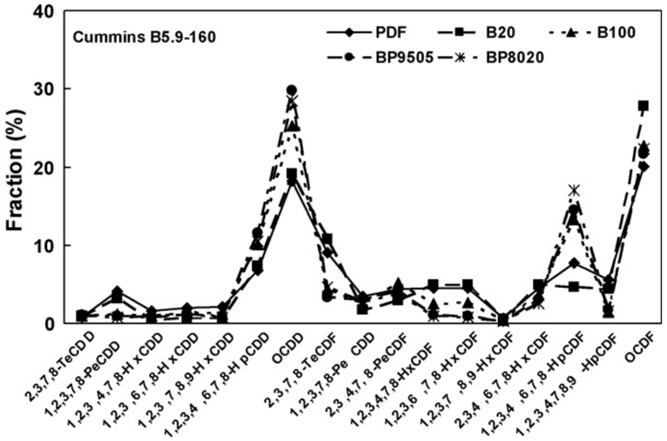

Fig. 2. PCDD/F congener profiles in the exhaust of the Cummins B5.9-160 HDDE.

There are 75 PCDDs and 135 PCDFs differentiated from each other by the number and location of chlorine atom addition. The mixture of PCDD/Fs can be translated into profiles (mass fractions) representing the distribution of individual PCDD/Fs, as shown in Fig. 2, in which the *y* coordinate is the concentration of each congener divided by the sum concentration of the seventeen PCDD/Fs. As can be seen from the figure, the PCDD/F congener patterns were similar. For the Cummins B5.9-160 HDDE, the four predominant species of PDF were OCDF (20.0%), OCDD (18.2%), 2,3,7,8-TeCDF (8.99%), and 1,2,3,4,6,7,8-HpCDF (7.75%). They were OCDF

Table 3
Emission factors of traditional pollutants from the Cummins B5.9-160 HDDE.

Test fuels	Traditional pollutants (g BHP^{-1} h^{-1})									
	THC		CO		CO_2		NOx		PM	
	Mean	SD[a]	Mean	SD	Mean	SD	Mean	SD	Mean	SD
PDF[b]	0.279	0.0159	1.941	0.0581	682	31.1	5.05	0.179	0.114	0.00363
B20[c]	0.272	0.00849	1.641	0.0816	734	22.3	5.02	0.227	0.0983	0.00555
B100[d]	0.177	0.00631	1.547	0.0248	755	31.6	4.95	0.139	0.0758	0.00370
BP9505[e]	0.241	0.00557	1.414	0.0641	713	33.5	4.96	0.241	0.0897	0.00380
BP8020[f]	0.214	0.00195	1.391	0.0485	710	20.6	5.02	0.270	0.0750	0.00368

[a] Standard deviation.
[b] Premium diesel fuel as base fuel.
[c] 20% palmbiodiesel + 80% PDF.
[d] 100% palmbiodiesel.
[e] 95% paraffinic fuel + 5% palmbiodiesel.
[f] 80% paraffinic fuel + 20% palmbiodiesel.

Table 4
PCDD/F concentrations from the Cummins B5.9-160 HDDE.

PCDD/F (pg m^{-3})	Test fuels										I-TEF[a]
	PDF[b]		B20[c]		B100[d]		BP9505[e]		BP8020[f]		
	Mean	SD[g]	Mean	SD	Mean	SD	Mean	SD	Mean	SD	
2,3,7,8-TeCDD	0.304	0.0134	0.225	0.0196	0.0708	0.00382	0.0472	0.00350	0.0503	0.00532	1
1,2,3,7,8-PeCDD	1.53	0.108	0.823	0.0622	0.0936	0.00887	0.0385	0.000930	0.0417	0.00116	0.1
1,2,3,4,7,8-HxCDD	0.596	0.0303	0.148	0.0121	0.0714	0.00636	0.0361	0.00146	0.0462	0.00331	0.5
1,2,3,6,7,8-HxCDD	0.762	0.0359	0.167	0.0125	0.108	0.00607	0.0512	0.00126	0.0593	0.00627	0.05
1,2,3,7,8,9-HxCDD	0.797	0.0486	0.162	0.00929	0.0899	0.00312	0.0386	0.00169	0.0399	0.00170	0.5
1,2,3,4,6,7,8-HpCDD	2.54	0.101	1.84	0.188	0.755	0.0671	0.487	0.0433	0.554	0.0472	0.1
OCDD	6.88	0.306	4.84	0.540	1.88	0.161	1.26	0.0125	1.49	0.130	0.1
2,3,7,8-TeCDF	3.40	0.140	2.73	0.249	0.328	0.0167	0.142	0.0134	0.247	0.0164	0.1
1,2,3,7,8-PeCDF	1.30	0.0383	0.444	0.0464	0.187	0.0153	0.127	0.0142	0.146	0.00733	0.1
2,3,4,7,8-PeCDF	1.67	0.126	0.758	0.0675	0.387	0.0341	0.172	0.0185	0.197	0.0178	0.1
1,2,3,4,7,8-HxCDF	1.73	0.115	1.25	0.106	0.192	0.0104	0.0471	0.00523	0.0483	0.00128	0.1
1,2,3,6,7,8-HxCDF	1.73	0.0764	1.24	0.0647	0.195	0.00779	0.0367	0.00346	0.0391	0.00351	0.1
1,2,3,7,8,9-HxCDF	0.237	0.0121	0.142	0.0146	0.0278	0.00284	0.00962	0.000964	0.0117	0.00119	0.01
2,3,4,6,7,8-HxCDF	1.70	0.103	1.25	0.0492	0.264	0.0201	0.129	0.00849	0.130	0.00663	0.01
1,2,3,4,6,7,8-HpCDF	2.93	0.0953	1.19	0.0928	0.991	0.105	0.609	0.0250	0.895	0.0920	0.01
1,2,3,4,7,8,9-HpCDF	2.11	0.135	1.11	0.101	0.107	0.0100	0.0727	0.00786	0.0811	0.00292	0.001
OCDF	7.58	0.319	7.06	0.382	1.69	0.0701	0.912	0.0627	1.17	0.0261	0.001
PCDDs	13.4	0.561	8.21	0.774	3.07	0.252	1.96	0.0601	2.28	0.149	–
PCDFs	24.4	0.912	17.2	1.03	4.36	0.250	2.26	0.121	2.97	0.145	–
PCDDs/PCDFs	0.550	0.0134	0.478	0.0272	0.703	0.0173	0.866	0.0199	0.769	0.0237	–
Total PCDD/Fs	37.8	1.41	25.4	1.73	7.43	0.501	4.21	0.181	5.25	0.286	–
PCDDs (pg I-TEQ m^{-3})	1.32	0.0686	0.707	0.0451	0.154	0.00989	0.0852	0.00422	0.0927	0.00742	–
PCDFs (pg I-TEQ m^{-3})	1.84	0.0979	1.09	0.0839	0.316	0.0229	0.137	0.0123	0.164	0.0107	–
PCDDs/PCDFs	0.718	0.0251	0.648	0.0153	0.487	0.0223	0.624	0.0430	0.564	0.0340	–
Total PCDD/Fs (pg I-TEQ m^{-3})	3.16	0.157	1.80	0.128	0.470	0.0314	0.222	0.0152	0.257	0.0168	–

[a] Ref. [33].
[b] Premium diesel fuel as base fuel.
[c] 20% palmbiodiesel + 80% PDF.
[d] 100% palmbiodiesel.
[e] 95% paraffinic fuel + 5% palmbiodiesel.
[f] 80% paraffinic fuel + 20% palmbiodiesel.
[g] Standard deviation.

(27.8%), OCDD (19.1%), 2,3,7,8-TeCDF (10.8%), and 1,2,3,4,6,7,8-HpCDD (7.26%) for B20. They were OCDD (25.3%), OCDF (22.7%), 1,2,3,4,6,7,8-HpCDF (13.3%), and 1,2,3,4,6,7,8-HpCDD (10.2%) for B100. They were OCDD (29.8%), OCDF (21.6%), 1,2,3,4,6,7,8-HpCDF (14.5%), and 1,2,3,4,6,7,8-HpCDD (11.6%) for BP9505. Finally, they were OCDD (28.4%), OCDF (22.3%), 1,2,3,4,6,7,8-HpCDF (17.0%), and 1,2,3,4,6,7,8-HpCDD (10.5%) for BP8020. In general, OCDD and OCDF account for 40–50% of total PCDD/Fs. Similar results were found that main species of PCDD/Fs emitted from the diesel engine were OCDD, OCDF, 1,2,3,4,6,7,8-HpCDF, and 1,2,3,4,6,7,8-HpCDD [13,14,39]. However, Gullett and Ryan [16] concluded that main species of PCDD/Fs emitted from heavy-duty diesel vehicles were TCDD and TCDF. The difference may be attributed to test engines and mode.

3.4. *PCDD/F emission factors and annual emissions*

The emission factors of PCDD/Fs were calculated and are shown in Table 5. The PCDD/F emission factors of the Cummins B5.9-160 HDDE fuelled with PDF were 17.2 ng L^{-1} and 1.43 ng I-TEQ L^{-1}. Chang et al. [14] concluded that PCDD/F emission factor of the test HDDE is 0.550 ng I-TEQ L^{-1} when it was tested under 90 km h^{-1}. 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]. Compared with PDF, mean reductions of PCDD/Fs from the exhaust of the Cummins B5.9-160 HDDE were 25.6%, 81.7%, 88.8%, and 86.2% for B20, B100, BP9505, and BP8020, respectively. In addition, compared with PDF, the mean reductions of toxic PCDD/Fs from the exhaust of the Cummins B5.9-160 HDDE were 36.8%, 86.1%, 92.9%, and 91.9% for B20, B100, BP9505, and BP8020, respectively. The results of the experiment indicate that emissions of PCDD/Fs can be reduced dramatically by fuelling HDDEs with BP9505 and BP8020. The annual diesel fuel consumption of diesel-engine vehicles was estimated to be around 4.5×10^9 L in Taiwan in 2009. Based on our sampling results, the PCDD/F emissions from diesel engines were thus 6.44 g I-TEQ year^{-1} ($=1.43 \times (4.5 \times 10^9) \times 10^{-9}$). Therefore, using BP9505 and BP8020 instead of PDF can decrease this by 5.93 and 5.99 g I-TEQ year^{-1}, respectively. Similar trends for mean reductions of PCDD/F emissions in pg BHP^{-1} h^{-1} were found. Compared with PDF, mean reductions of PCDD/Fs from the exhaust of the Cummins B5.9-160 HDDE were 22.1%, 78.4%, 88.1%, and 85.0% for B20, B100, BP9505, and BP8020, respectively. In addition, compared with PDF, mean reductions of toxic PCDD/Fs from the exhaust of the Cummins B5.9-160 HDDE were 33.8%, 83.6%, 92.5%, and 91.2% for B20, B100, BP9505, and BP8020, respectively.

3.5. *Brake specific fuel consumption*

Details of the brake specific fuel consumption (BSFC) for the test fuels are shown in Table 6. Compared with PDF, the mean increases in BSFC were 5.06%, 24.0%, 0.774%, and 5.06% for B20, B100, BP9505 and BP8020, respectively. In addition, the BSFC of B100 was inferior to that of PDF, likely due to the fact that the density and viscosity of B100 are much higher than those of PDF, B20, BP9505 and BP8020, resulting in poor fuel atomization and combustion. Similar results were found with BSFC in L BHP^{-1} h^{-1}. Compared with PDF, the mean increases of BSFC were 4.93%, 17.9%, 6.13%, and 8.99% for B20, B100, BP9505 and BP8020, respectively. However, this was compensated for by the higher density of palmbiodiesel and lower

Table 5
PCDD/F emission factors from the Cummins B5.9-160 HDDE.

PCDD/Fs	Test fuels									
	PDF[a]		B20[b]		B100[c]		BP9505[d]		BP8020[e]	
	Mean	SD[f]	Mean	SD	Mean	SD	Mean	SD	Mean	SD
ng L^{-1}	17.2	0.259	12.8	0.593	3.14	0.112	1.93	0.109	2.37	0.00572
ng I-TEQ L^{-1}	1.43	0.0470	0.904	0.0399	0.199	0.00774	0.101	0.00809	0.116	0.00398
pg $\text{BHP}^{-1}\,\text{h}^{-1}$	4367	159	3404	235	943	63.6	519	22.3	657	35.8
pg I-TEQ $\text{BHP}^{-1}\,\text{h}^{-1}$	364	17.5	241	17.3	59.7	3.98	27.3	1.87	32.2	2.10

[a] Premium diesel fuel as base fuel.
[b] 20% palmbiodiesel + 80% PDF.
[c] 100% palmbiodiesel.
[d] 95% paraffinic fuel + 5% palmbiodiesel.
[e] 80% paraffinic fuel + 20% palmbiodiesel.
[f] Standard deviation.

Table 6
Brake specific fuel consumption (BSFC) for the test fuels.

BSFC	Test fuels									
	PDF[a]		B20[b]		B100[c]		BP9505[d]		BP8020[e]	
	Mean	SD[f]	Mean	SD	Mean	SD	Mean	SD	Mean	SD
g $\text{BHP}^{-1}\,\text{h}^{-1}$	211	5.17	222	6.39	262	8.25	213	2.93	222	7.04
L $\text{BHP}^{-1}\,\text{h}^{-1}$	0.254	0.00621	0.267	0.00767	0.300	0.00942	0.270	0.00371	0.277	0.00877

[a] Premium diesel fuel.
[b] 20% palmbiodiesel + 80% PDF.
[c] 100% palmbiodiesel.
[d] 95% paraffinic fuel + 5% palmbiodiesel.
[e] 80% paraffinic fuel + 20% palmbiodiesel.
[f] Standard deviation.

density of paraffinic fuel in the volumetric injection system. Thus, differences in volumetric consumption between diesel and palmbiodiesel became smaller, but became larger between diesel and paraffinic fuel. Compared with other studies, it was found that the increases in BSFC for B20, BP9505, and BP8020 were lower than those for soybean-biodiesel (18% by Haas et al. [40]; 13.8% by Monyem and Van Gerpen [20]), soapstock-biodiesel (18% by Haas et al, 2001 [40]), brassica-carinate biodiesel (>9% by Cardone et al. [23]), rapeseed-biodiesel (>9% by Cardone et al. [23]), and coconut oil (>40% by Kalam et al. [26]), except for B100.

4. Conclusion

The present paper shows using biodiesel blends instead of PDF, particularly BP9505 or BP8020, significantly reduced emissions of PCDD/Fs and traditional pollutants. Compared with PDF, PCDD/F reductions were (32.9%, 43.0%), (80.3%, 85.1%), (88.9%, 93.0%), and (86.1%, 91.7%) for B20, B100, BP9505, and BP8020, respectively, as there was no PAH or chlorine in the palmbiodiesel and paraffinic fuel. Conclusively, paraffinic–palmbiodiesel blends decreased PCDD/Fs by 86.1–88.9%, toxic PCDD/Fs by 91.9–93.0%, THC by 13.6–23.3%, CO by 27.2–28.3%, and PM by 21.3–34.2%, respectively. In addition, using BP9505 and BP8020 instead of PDF could decrease PCDD/F emissions by 5.93 and 5.99 g I-TEQ year^{-1} in Taiwan, respectively. In our previous study, we found that there was no significant difference in unusual operations and damage from deposits inside the chamber and the inferior condition of engine oil for 18,000 km [28]. However, further investigation of long term use of palmbiodiesel-diesel blends and paraffinic–palmbiodiesel blends instead of diesel in diesel engines is desired.

Acknowledgments

The authors gratefully acknowledge the contributions from Mr. S.H. Gua, Refining and Manufacturing Research Center, CPC Corporation, for heavy-duty diesel-engine operation, and the team of Super Micro Mass Research & Technology Center at Cheng Shiu University, for PCDD/F analysis.

References

[1] P.T. Williams, M.K. Abbass, G.E. Andrews, Diesel particulate emission: the role of unburned fuel, Combust. Flame 75 (1989) 1–24.

[2] K.P. Schinder, Integrated Diesel European Action (IDEA): study of diesel combustion. SAE Paper No. 920591, 1992.

[3] J.H. Tsai, S.J. Chen, K.L. Huang, Y.C. Lin, W.J. Lee, C.C. Lin, W.Y. Lin, PM, Carbon, and PAH emissions from a diesel generator fuelled with soy-biodiesel blends, J. Hazard. Mater. (2010), doi:10.1016/j.jhazmat.2010.02.085.

[4] K. Ballschmiter, H. Buchert, R. Niemczyk, A. Munder, M. Swerev, Automobile exhausts vs. municipal waste incineration as sources of the polychloro-dibenzodioxins (PCDD) and furans (PCDF) found in the environment, Chemosphere 15 (1986) 901–915.

[5] W.J. Lee, Y.F. Wang, T.C. Lin, Y.Y. Chen, W.C. Lin, C.C. Ku, J.T. Cheng, PAH characteristics in the ambient air of traffic-source, Sci. Total Environ. 159 (1995) 185–200.

[6] H. Huang, A. Buekens, On the mechanisms of dioxin formation in combustion processes, Chemosphere 31 (1995) 4099–4117.

[7] R.M. Harrison, D.J.T. Smith, L. Luhana, Source apportionment of atmospheric polynuclear aromatic hydrocarbons collected from an urban location in Birmingham, UK, Environ. Sci. Technol. 30 (1996) 825–832.

[8] H.H. Yang, C.F. Chiang, W.J. Lee, K.P. Hwang, M.F. Wu, Size distribution and dry deposition of road dust PAHs, Environ. Int. 25 (1999) 585–597.

[9] Y.C. Lin, W.J. Lee, H.C. Hou, PAH emissions and energy efficiency of palm-biodiesel blends fueled on diesel generator, Atmos. Environ. 40 (2006) 3930–3940.

[10] Y.C. Lin, W.J. Lee, H.R. Chao, S.L. Wang, T.C. Tsou, G.P. Chang-Chien, Approach for energy saving and pollution reducing by fueling diesel engines with emulsified biosolution/biodiesel/diesel blends, Environ. Sci. Technol. 42 (2008) 3849–3855.

[11] Y.C. Lin, C.H. Tsai, C.R. Yang, C.H. Wu, T.Y. Wu, G.P. Chang-Chien, Effects on aerosol size distribution of polycyclic aromatic hydrocarbons from the heavy-duty diesel generator fueled with feedstock palm-biodiesel blends, Atmos. Environ. 42 (2008) 6679–6688.

[12] T.J. Nestrick, L.L. Lamparski, W.B. Crummett, Thermolytic surface-reaction of benzene and iron (III) chloride to form chlorinated dibenzo-p-dioxins and dibenzofurnas, Chemosphere 16 (1987) 777–790.

[13] K.S. Kim, K.H. Hong, Y.H. Ko, K.D. Yoon, M.G. Kim, Emission characteristics of PCDD/Fs in diesel engine with variable load rate, Chemosphere 53 (2003) 601–607.

[14] M.B. Chang, S.H. Chang, Y.W. Chen, H.C. Hsu, Dioxin emission factors for automobiles from tunnel air sampling in Northern Taiwan, Sci. Total Environ. 325 (2004) 129–138.

[15] J.V. Ryan, B.K. Gullett, On-road emission sampling of a heavy-duty diesel vehicle for polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans, Environ. Sci. Technol. 34 (2000) 4483–4489.

[16] B.K. Gullett, J.V. Ryan, On-road emissions of PCDDs and PCDFs from heavy duty diesel vehicles, Environ. Sci. Technol. 36 (2002) 3036–3040.

[17] P.H. Dyke, M. Sutton, D. Wood, J. Marshall, Investigations on the effect of chlorine in lubricating oil and the presence of a diesel oxidation catalyst on PCDD/F releases from an internal combustion engine, Chemosphere 67 (2007) 1275–1286.

[18] W.G. Wang, D.W. Lyons, N.N. Clark, M. Gautam, Emissions from nine heavy trucks fueled by diesel and biodiesel blend without engine modification, Environ. Sci. Technol. 34 (2000) 933–939.

[19] C.A. Sharp, S.A. Howell, J. Jobe, The effect of biodiesel fuels on transient emissions from modern diesel engines, part I. Regulated emissions and performance. SAE Paper No. 2000-01-1967, 2000.

[20] A. Monyem, J.H. Van Gerpen, The effect of biodiesel oxidation on engine performance and emission, Biomass Bioenerg. 20 (2001) 317–325.

[21] G. Antolin, F.V. Tinaut, Y. Briceno, V. Castano, C. Perez, A.I. Ramírez, Optimisation of biodiesel production by sunflower oil transesterification, Bioresour. Technol. 83 (2002) 111–114.

[22] T. Beer, T. Grant, D. Williams, H. Watson, Fuel-cycle greenhouse gas emissions from alternative fuels in Australian heavy vehicles, Atmos. Environ. 36 (2002) 753–763.

[23] M. Cardone, M.V. Prati, V. Rocco, M. Seggiani, A. Senature, S. Vitolo, Brassica carinata as an alternative oil crop for the production of biodiesel in Italy: engine performance and regulated and unregulated exhaust emission, Environ. Sci. Technol. 36 (2002) 4656–4662.

[24] T.D. Durbin, J.M. Norbeck, Effects of biodiesel blends and arco EC-diesel on emissions from light heavy-duty diesel vehicles, Environ. Sci. Technol. 36 (2002) 1686–1691.

[25] M.P. Dorado, E. Ballesteros, J.M. Arnal, J. Gomez, F.J. Lopez, Exhaust emission from a diesel engine with transesterified waste olive oil, Fuel 82 (2003) 1311–1315.

[26] M.A. Kalam, M. Husnawan, H.H. Masjuki, Exhaust emission and combustion evaluation of coconut oil-powered indirect diesel engine, Renew. Energy 28 (2003) 2405–2415.

[27] S. Kalligeros, F. Zannikos, S. Strournas, E. Lois, G. Anastopoulos, C.H. Teas, F. Sakellarppoulos, An investigation of using biodiesel/marine diesel blends on the performance of a stationary diesel engine, Biomass Bioenerg. 24 (2003) 141–149.

[28] Y.C. Lin, W.J. Lee, T.S. Wu, C.T. Wang, Comparison of PAH and regulated harmful matter emissions from biodiesel blends and paraffinic fuel blends on engine accumulated mileage test, Fuel 85 (2006) 2516–2523.

[29] P. Wibulswas, S. Chirachakhrit, U. Keochung, J. Tlansuman, Combustion of blends between plant oils and diesel oil, Renew. Energy 16 (1999) 1098–1101.

[30] M.A. Kalam, H.H. Masjuki, Biodiesel from palmoil-an analysis of its properties and potential, Biomass Bioenerg. 23 (2002) 471–479.

[31] Y.C. Lin, T.Y. Wu, W.C. Ou-Yang, C.B. Chen, Reducing emissions of carbonyl compounds and regulated harmful matters from a heavy-duty diesel engine fueled with paraffinic/biodiesel blends at one low load steady-state condition, Atmos. Environ. 43 (2009) 2642–2647.

[32] Code of Federal Regulations (CFR) 40 Part 86 Subpart N, pp. 1342–1384.

[33] NATO/CCMS, Scientific basis for the development of the international toxicity equivalency factor (I-TEF) method of risk assessment for complex mixtures of dioxins and related compounds. Report No. 178, 1988.

[34] Y.C. Lin, W.J. Lee, C.B. Chen, Characterization of polycyclic aromatic hydrocarbons from the diesel engine by adding light cycle oil to premium diesel fuel, J. Air Waste Manage. 56 (2006) 752–758.

[35] Y.C. Lin, W.J. Lee, H.W. Li, C.B. Chen, G.C. Fang, P.J. Tsai, Impact of using fishing boat fuel with high poly-aromatic content on the emission of polycyclic aromatic hydrocarbons from the diesel engine, Atmos. Environ. 40 (2006) 1601–1609.

[36] J.E. Dec, R.M. Green, D.T. Daly. The influence of fuel volatility on the liquid-phase fuel penetration in a heavy-duty D.I. diesel engine. SAE Paper No. 980510, 1998.

[37] G.G. Choudhry, O. Hutzinger, Mechanistic Aspects of the Thermal Formation of Halogenated Organic Compounds Including Polychlorinated Dibenzo-p-dioxins, Gordon and Breach, New York, 1983.

[38] K.R. Bruce, L.O. Beach, B.K. Gullett, The role of gas-phase Cl_2 in the formation of PCDD/PCDF during waste combustion, Waste Manage. 11 (1991) 97–102.

[39] M. Oehme, S. Larssen, E.M. Brrvik, Emission factors of PCDD and PCDF for road vehicle obtained by tunnel experiment, Chemosphere 23 (1991) 1699–1708.

[40] M.J. Haas, K.M. Scott, T.L. Alleman, R.L. Mccormick, Engine performance of biodiesel fuel prepared from soybean soapstock: a high quality renewable fuel produced from a waste feedstock, Energy Fuels 15 (2001) 1207–1212.