Influences of Waste Cooking Oil-Based Biodiesel Blends on PAH and PCDD/F Emissions from Diesel Engines in Durability Testing Cycle

Farran Mack Redfern[1], Sheng-Lun Lin[2,3*], Lin-Chi Wang[2*], Shun-I Shih[4**]

[1] Department of Environmental Engineering, National Cheng Kung University, Tainan 70101, Taiwan
[2] Department of Civil Engineering and Geomatics, Cheng Shiu University, Kaohsiung 83347, Taiwan
[3] Super Micro Mass Research and Technology Center, Cheng Shiu University, Kaohsiung 83347, Taiwan
[4] Department of Environmental Engineering, Kun Shan University, Tainan 71003, Taiwan

ABSTRACT

In this study, the 60,000-km durability tests were performed on two diesel engines (EURO IV and EURO II) by using B10 (10% waste cooking oil + 90% diesel) and B8 (8% waste cooking oil + 92% diesel), respectively, to determine the impacts on the emissions of polycyclic aromatic hydrocarbons (PAHs) and polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs). The above emissions were measured per 20,000-km testing intervals. The highest total PAH mass concentrations were 38.2 and 25.6 µg Nm^{-3} before durability test by operating the EURO IV and II engines, respectively, and decreased 51–55% after 60,000-km operation. The dominant congeners of PAH emissions were naphthalene (> 45%), pyrene, and phenanthrene, which belonged to the LM-PAHs. The total PAH BaP_{eq} had different emission trends between the two engines during the durability tests. The highest level was 2.17 µg BaP_{eq} Nm^{-3} from EURO II engine before the test and reduced 84% after a 60,000-km cycle, when the total-BaP_{eq} emissions of EURO IV tended to increase from 0.0894 to 0.154 µg BaP_{eq} Nm^{-3} after the same test. The most dominant congener to the toxicity emissions was benzo(a)pyrene (~70%). Additionally, the PCDD/F emissions were tested in EURO IV engine by using B10. The PCDD/F concentrations of mass and toxicity approached the highest levels, 167 ng Nm^{-3} and 3.69 pg WHO-TEQ Nm^{-3}, after 60,000-km and 20,000-km running cycles, respectively. The main dominant congeners were *O*CDD (> 50%) for mass, 2,3,7,8-*Te*CDD (> 35%) and 1,2,3,7,8-*Pe*CDD (> 18%) for toxicity. Consequently, the use of WCO-biodiesel might reduce the PAH mass and toxicity emissions in older engine but had no significant effect in PAH and PCDD/F emissions during the deterioration of a newer engine.

Keywords: Biodiesel; Polycyclic aromatic hydrocarbons; Polychlorinated dibenzo-*p*-dioxins and dibenzofurans; Durability test.

INTRODUCTION

Diesel Engines and Their Emissions

As the fossil fuel crisis is getting more and more global attention, the demand for alternative fuel or green energy is becoming even stronger than before. Diesel engines were reported as one major mobile emission sources of pollutants, including carbon monoxide (CO), total hydrocarbons (HC), nitrogen oxides (NO_x), and particulate matter (PM).

Additionally, several toxic chemicals, such as polycyclic aromatic hydrocarbons (PAHs), polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs), and brominated persistent organic compounds, are also found in diesel engine operation (Lloyd and Cackette, 2001; Shah *et al.*, 2005; Lin *et al.*, 2010; Laroo *et al.*, 2012; Mwangi *et al.*, 2015b; Chen *et al.*, 2017). These emissions are well known to pose higher risk of human health (Scheepers, 2015).

PAHs and PCDD/Fs are semi-volatile species and classified as persistent organic pollutants (POPs). They are recognized as two of the potentially toxic pollutants emitted from heavy-duty diesel vehicles to the atmosphere (Chang *et al.*, 2014a; Mwangi *et al.*, 2015b). Considering that PAH compounds and PCDD/Fs are known human carcinogens, the carcinogenic potencies of PAH emissions and PCDD/Fs especially from anthropogenic mobile emission sources, including diesel engine have drawn considerable attention for researchers (Cheruiyot *et al.*, 2016; Chen *et al.*, 2017). Diesel engines have higher PM emissions, which provide large surface area and carbon sources to adsorb and generate the organic

---

* Corresponding author.
 Tel.: +886-7-735-8800 ext. 2605; Fax: +886-7-733-2204
 E-mail address: cbmsgml@gmail.com
 Tel.: +886-7-7351275; Fax: +886-7-733-2204 (L.C. Wang)
 E-mail address: lcwang@csu.edu.tw
** Corresponding author.
 Tel.: +886-6-2050110; Fax: +886-6-2050540
 E-mail address: ssi10@mail.ksu.edu.tw

compounds and lead to PAH emissions (Wichmann, 2007; Laroo *et al.*, 2011; Cheruiyot *et al.*, 2015). Additionally, the PCDD/F emission inventories of various regions indicated that the diesel heavy-duty trucks became one of the dominant sources, which poses a key concern due to its proximity to residential areas (Cheruiyot *et al.*, 2016).

Biodiesel Development, Application, and Their Emissions

There are numerous studies focusing on the biodiesel as one of the most promising alternatives of diesel. They were produced from animal fats or vegetable oils by transesterification reaction and could mitigate the increase in greenhouse gas emissions (Yang *et al.*, 2007; Lee *et al.*, 2011; Williams *et al.*, 2011; Mwangi *et al.*, 2015a; Scheepers, 2015). Several advantages by using biodiesels have been reported. The higher oxygen content of biodiesels than petroleum diesel can produce more complete combustion and lower the emissions of CO, PM, HC and persistent organic pollutants (Raheman and Ghadge, 2007; Özener *et al.*, 2014). Additionally, the lower sulfur and almost no aromatic compositions could reduce the SO_2 and POP emissions from the diesel engine and further reduce the potential of secondary fine particle formation (Tsai *et al.*, 2015). The safety of storage and transport could also be enhanced by the higher flash point of biodiesel than that of fossil fuel (Li *et al.*, 2016; de Mello *et al.*, 2017).

However, the food demand, land use change, excessive water and energy demand, and secondary waste water treatment became the serious challenges of the first-generation of biodiesel produced from energy crops (Demirbas, 2008; Pimentel *et al.*, 2009; Lin *et al.*, 2011). In densely populated countries, such as Taiwan, the waste-cooking oil (WCO) is considered as the most promising feedstocks of biodiesel production, which does not need farming and huge extra water supply, as well as recycling the waste from human daily activity. However, WCO contain five times higher chlorine content than those in the conventional diesel due to the sauces used during food preparation (Chang *et al.*, 2014a; Tsai *et al.*, 2016). The higher chlorine might be responsible for causing more PCDD/F emissions from WCO combustion. Fortunately, Chang *et al.* (2014) conducted the research of WCO-based biodiesel and found the lower POP (PAHs, PCDD/Fs, PCBs, PBDEs, PBDD/Fs) emissions. The more complete combustion of WCO spray with higher oxygen and lower aromatic contents were the reasons of POP reduction (Chang *et al.*, 2014a).

During application, the viscosity of biodiesel is so high it generates some problems. For example, deposits and obstruction, injector chocking, piston ring sticking and poor atomization are very common when using biodiesel (Ramadhas *et al.*, 2005). Moreover, higher viscosity may have bad influence on spray properties and cause incomplete combustion (Muralidharan and Vasudevan, 2011). Therefore, it is like a trade-off problem between higher oxygen content and higher viscosity. It should be investigated which property is dominant in what specific situation by durability tests.

Durability Test and Deterioration of Diesel Engine

The emissions from diesel engines depend on several factors such as fuel content, engine type, loads, speed, mileage, availability of catalysts and operational conditions like temperature, pressure, injection timing, humidity, and exhaust gas recirculation (Cheruiyot *et al.*, 2015). In the aspect of emission control, the deterioration of diesel engine is the most comprehensive analysis to express the fuel suitability for a real-scale engine. The engine durability tests then took place for testing petroleum diesel and biodiesel in the previous studies.

Engine wear and friction are the major problems after a long-term operation. The wear usually occurs on the sliding units, including cylinder liner, cam, bearing, tappet, crankshaft, pistons and pins, valves, and guides…etc. The fuel itself acted as the lubricant for the above components, when the biodiesels were reported to have better lubricity than the petroleum diesel. There were oxygen containing trace compounds, such as esters and fatty acids adsorb on rubbing surface to reduce the adhesion and limit the friction and wear formation (Haseeb *et al.*, 2010). Many studies focused on the engine wear by long-term operation with static engine or field trail tests. The biodiesel blends (B20 to B100) were reported to have similar or even 30% less wear as compared to petroleum diesel after the durability tests (2–4 years, 200–500 h, or 30,000–200,000 km), because the unsaturated molecule could have better lubricity than the saturated ones (Clark *et al.*, 1984; Kalam and Masjuki, 2002; Agarwai *et al.*, 2003; Fraer *et al.*, 2005; Proc *et al.*, 2006; Agarwal *et al.*, 2008). On the other hand, the biodiesels might lose their proven lubricity by auto-oxidation and corrosiveness for material degradation (Fazal *et al.*, 2011). Therefore, the lubricity of biodiesel blends could be the competitive results by the above opposite effects. For the deterioration in diesel engine emission, Hsieh *et al.* (2011) reported higher PCDD/F concentrations with greater mileage of diesel engine. Yang *et al.* (2007) also reported that total PAH concentrations and their BaP_{eq} emissions could be reduced by using B20, when HC, CO, PM, and particulate phase PAH emissions increased with accumulated mileage. The higher viscosity could be the reason that led to several durability issues, such as deposition formation, carbonization of injector tip, fuel filter plugging (Saxena and Maurya, 2016) and cause the increasing emissions.

Despite a good number of researches on biodiesel as an alternative fuel that has been widely investigated in diesel engines, there have been limited studies on PAH and PCDD/F emissions comparing accumulated mileage test involving different generations of engines, especially for the use of WCO-based biodiesel blends. Therefore, in this present study we will examine the PAH and PCDD/F emissions from a diesel engine by a series of durability tests. The objective of the study was to determine the long-term effects in terms of engine performances and emissions by using WCO-based biodiesel blends.

EXPERIMENTAL SECTION

Fuel Property

Two WCO-based biodiesel blends were tested in this study: B8 (8% WCO-based biodiesel + 92% pure petroleum

diesel) and B10 (10% WCO-based biodiesel + 90% pure petroleum diesel). The test fuels met the requirements of CNS 1471 (Chinese National Standards, CNS), provided by CPC corporation, Taiwan. The fuel properties were provided in Table 2. B8 was tested in Mitsubishi 4M40-0A (EURO II) while B10 was used in Mitsubishi 4M42-4AT2 (EURO IV). Based on the fuel important properties considered in the test, B8 has Cetane Index of 54 and viscosity (40°C) of 3.12 cSt, while B10 has 50.2 and 3.15 cSt for Cetane Index and viscosity (40°C), respectively. For the aspect of energy density, both two fuel blends had only < 1% lower heating values (42.76 MJ kg^{-1} for B8 and 42.64 MJ kg^{-1} for B10) than that of the petroleum diesel (42.98 MJ kg^{-1}). The oxygen contents of B8 and B10 were 1.03% and 1.17%, respectively, much higher than pure diesel and potentially provide more complete combustion.

Engine, Durability Test and Sampling Procedure

The Mitsubishi 4M42-4AT2 (EURO IV) engine and Mitsubishi 4M40-0A (EURO II) engine were used in this study. The specifications of two test engines were shown in Table 1. In durability test, the test procedure divided into four steps: start, warm-up, accumulation and shutdown. The engine was started with the speed of 800 rpm for 4 min, then the engine's speed was tuned up from 1,500 to 2,000 during a 9-min warm up. Subsequently, the engine was continuously run at 3700 rpm for 13 h per day and accumulated the test hours (or mileages). The sampling was conducted at 0, 125, 250, 375, and 500 hours. The accumulation duration can be converted to real life mileage accumulation and replicate on-road conditions based on fuel consumption rate. The

accumulation durations of 0, 125, 250, 375, and 500 hr are approximated to 0, 20,000, 40,000, 60,000, and 80,000 km respectively. The detail was provided in our previous study (Yang *et al.*, 2007).

At every selected accumulated mileage, the exhaust gas samples were collected from the test engines by an isokinetic sampling system, which was specified by the U.S. EPA, modified Method 5 (USEPA, 2001) for PAH and PCDD/F analyses. A heated sampling probe (120 ± 14°C) was employed to collect both PAH and PCDD/F samples simultaneously. The target pollutants in particulate phase were collected with a glass fiber filter. Subsequently, a cooler was equipped to lower the exhaust temperature to less than 5°C before a two-stage glass cartridge set. The gaseous POPs were then collected by the cartridges. Specifically, each cartridge was packed with a 5.0 cm thickness (approximately, 20 g) of XAD-2 resin sandwiched between two 2.5 cm-thick polyurethane foam plugs. The same procedure was also applied in the durability test.

Analytical Processes

The PAH and PCDD/F samples were analysed in accordance with the US EPA modified Method 23 and were carried out in the Super Micro Mass Research and Technology Center in Cheng Shiu University, Taiwan.

PAH Analysis

The samples for PAH were extracted with a Soxhlet extractor using a mixture of *n*-hexane and dichloromethane (v:v = 1:1; each 250 mL) for 24 hours. The extracts were then concentrated by gently purging a stream of ultra-pure

Table 1. Fuel property/specification.

Fuel Properties	B8	B10
Physical Properties		
Cetane Index	54	50.2
Density, 15°C	839.6	839.7
Viscosity, 40°C	3.124	3.153
Lower Heating Values (kcal)	10213	10185
Chemical Composition		
S	7	0.5
C	85.46	84.99
H	13.36	13.09
O	1.03	1.17
MF	$CH_{1.88}O_{0.009}$	$CH_{1.85}O_{0.01}$

Table 2. Specifications of tested diesel engine.

Item	Mitsubishi 4M42-4AT2 (EURO IV)	Mitsubishi 4M40-0A (EURO II)
Configuration	In-line 4-cylinder/4 Stroke	In-line 4-cylinder/4 Stroke
Air intake	Turbocharged with intercooler	Turbo-charging type
Compression ratio	17	21
Type of fuel injection system	Common Rail	Distributor type
Injection type	Direct injection	Distributor type fuel injection pump
Fuel injection pressure	1600 bar max	147 bar
Displacement	2977 c.c.	2835 c.c.
Max torque	294 Nm @1700 rpm	195 Nm @2000rpm
Max power	92 kW @3200 rpm	69.1 kW @4000rpm

Nitrogen followed by passing through a silica gel column to be cleaned. The effluents were then re-concentrated to precisely 1 mL and moved to vial. There were 16 USEPA priority PAHs detected with gas chromatography/mass spectrometry (GC/MS) (HP 5890A/5972) equipped with a capillary column (HP Ultra 2, 50 m × 0.32 mm × 0.17 μm). The detailed PAH analytical procedures can be found in our previous studies (Wang *et al.*, 2007; Wang *et al.*, 2009). Sixteen PAHs were grouped based on their molecular weights: low molecular weight (LM-PAHs) were two-and three-ringed PAHs including naphthalene (Nap), acenaphthylene (AcPy), acenaphthene (Acp), fluorene (Flu), phenanthrene (PA), anthracene (Ant); middle molecular weight (MM-PAHs) were four-ringed PAHs including fluoranthene (FL), pyrene (Pyr), benzo(a)anthracene (BaA), chrysene (CHR); high molecular weight (HM-PAHs) were five-, six- and seven-ringed PAHs including benzo(b)fluoranthene (BbF), benzo(k)fluoranthene (BkF), benzo(a)pyrene (BaP), indeno (1,2,3,-cd)pyrene (IND), dibenzo(a,h)anthracene (DBA), and benzo(ghi)perylene (BghiP) (Cheruiyot *et al.*, 2015).

PCDD/F Analysis

After the aforementioned PAH analysis, the sample solutions were subsequently analyzed for 17 PCDD/Fs. The solutions were pre-treated with the concentrated sulfuric acid, followed by a series of sample clean-up procedures, including a multi-layered silica and alumina columns. Finally, the activated carbon columns were eluted by 40 mL toluene before instrumental analysis. A high-resolution gas chromatograph (HRGC), combined with a high-resolution mass spectrometer (HRMS), was used to measure PCDD/Fs. The HRGC (Hewlett Packard 6970 Series) is gas chromatograph equipped with a DB-5 (J&W Scientific, CA, USA) fused silica capillary column (60 m, 0.25 mm ID, 0.25 mm film thickness), splitless injection, and an initial oven temperature of 150°C. The HRMS (Micromass Autospec Ultima, UK) is a mass spectrometer with a positive electron impact (EI+) source using the selected ion monitoring (SIM) as the analyzer mode operating at a resolving power of 10000. The electron energy was fixed at 35 eV, and the operational temperature was set to 250°C. The operating details of HRGC/HRMS and the procedure for measuring of PCDD/Fs are given in our previous works (Wang *et al.*, 2003a, b; Wang *et al.*, 2010).

Quality Assurance and Quality Control (QA/QC)

Before the sampling, the glass fiber filters were placed in an oven at 450°C for 8 h to remove all organic compounds. The cleaned filters were kept in a desiccator for at least 8 h to maintain their fixed humidity levels prior and after the sampling. For PAHs, a breakthrough test was conducted with a three-stage glass cartridge in preliminary sampling work. The results showed the mass of 16 individual PAHs in the third stage was only 0.582–4.07% that in the total three stages. The two-stage glass cartridges deployed in this study should thus ensure a 95% collection efficiency. For PCDD/Fs, the respective surrogate standards (13C-labeled PCDD/Fs) were spiked into the cartridges and their

recoveries were used to analyze the breakthroughs of POPs in the study samples. Before each diesel engine test, a leak check was carried out between the inlet of the filter holder and the outlet of the flow meter (Chang *et al.*, 2014b). For all compound analyses, they went through the pretreatment procedures where both the internal and recovery standards were added to the sample. All procedures including the recovery of precision and recovery (PAR), surrogate, and internal labeled standards for both PAH and PCDD/Fs all complied with the relevant standards.

RESULTS AND DISCUSSION

Emission Differences of 2 Test Engines

All experimental conditions for EURO IV and II engines as well as for B10 and B8 in this study were controlled. It is important to compare the emission differences of the two engines, because the results can be used to check whether the differences of emission results are attributed to the fuel or to engine differences. In this study, the two engines were fuelled with B10 and B8, respectively, when the emissions of PAHs and PCDD/Fs were compared to verify the emission differences of the two engines at the beginning (0 km) and the end (80,000 km for only EURO IV for PAHs) and (60,000 km for EURO II for both PAHs and PCDD/Fs) of mileage accumulation.

PAHs Emission from Diesel Engines
Euro IV Engine

The concentration of 16 PAHs emitted from Mitsubishi 4M42-4AT2 (EURO IV) engine fuelled with B10 were listed in Tables 3 and 5, respectively. For EURO IV, the total PAHs concentrations were 38.2, 33.2, 26.2, 18.8 and 14.4 μg Nm^{-3} for 0, 20,000, 40,000, 60,000, and 80,000 km. The highest concentration of 38.2 μg Nm^{-3} was emitted at 0 km and then decreased to the lowest of 14.4 μg Nm^{-3} at 80,000 km, representing a reduction of 62%. Both the LM-PAH and MM-PAH concentrations had a reduction of 64 and 44%, respectively, whereas HM-PAHs have an increase of 113% at 80,000 km, compared to 0 km. The respective PAH congener profile fraction was shown in Fig. 1. The profile show Naphthalene as the most dominant congener (> 75%) followed by Pyrene, and Phenanthrene (each contributed > 5%); the 3 congeners all belong to the LM-PAHs.

The present study applies toxic equivalency factors (TEFs) for the 16 selected PAHs to assess the carcinogenic potencies for B10 and B8. The TEFs are useful for the comparison of the carcinogenic potency of individual PAHs in reference to the carcinogenicity of BaP (Nisbet and LaGoy, 1992). Consequently, the total BaP$_{eq}$ represents the carcinogenic potency of the total PAH mass concentrations (Yang *et al.*, 2017). The BaP$_{eq}$ of 16 PAHs emitted from Mitsubishi 4M42-4AT2 (EURO IV) engine fuelled with B10 were listed in Table 3. The total BaP$_{eq}$ were 0.0894, 0.104, 0.125, 0.154, and 0.161 μg BaP$_{eq}$ Nm^{-3} for 0, 20,000, 40,000, 60,000, and 80,000 km, respectively. The lowest PAH BaP$_{eq}$ of 0.0894 μg BaP$_{eq}$ Nm^{-3} was emitted at 0 km, then it continued to increasing until 80,000 km, exhibiting an increase of 80%. The BaP$_{eq}$ for LM-PAHs showed a decrease of 52%,
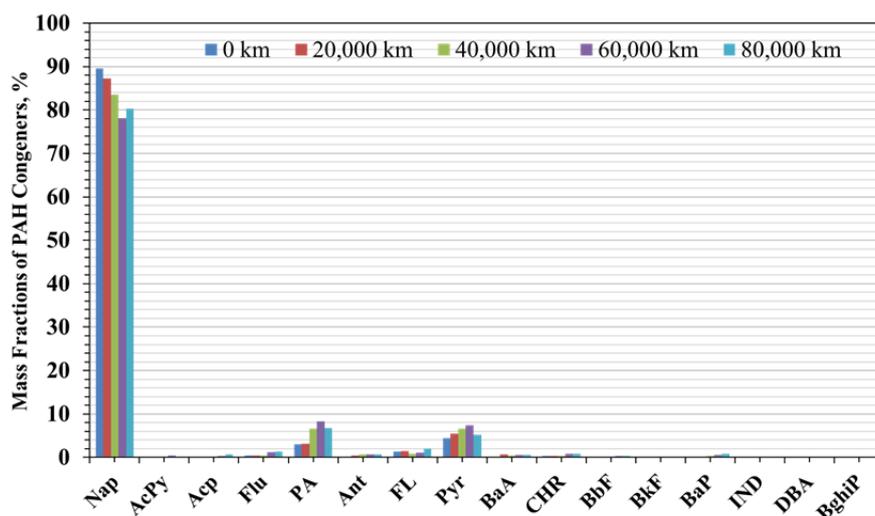
Fig. 1. Mass fractions of PAH congeners in the emission of EURO IV engine by using B10.

Table 3. PAH mass and BaP$_{eq}$ concentrations emitted from EURO IV diesel engine fueled with B10.

PAHs	Rings	0 hr (0 km)	125 hr (20,000 km)	*Increase %*	250 hr (40,000 km)	*Increase %*	375 hr (60,000 km)	*Increase %*	500 hr (80,000 km)	*Increase %*
Nap	2	34.2	29.0	− 15	21.9	− 36	14.7	− 57	11.5	− 66
AcPy	3	0.0610	0.0570	− 7	0.0110	− 82	0.0847	+ 39	0.0110	− 82
Acp	3	0.0439	0.0504	+ 15	0.0193	− 56	0.0626	+ 43	0.100	+ 128
Flu	4	0.167	0.161	− 4	0.128	+ 23	0.217	+ 30	0.191	+ 14
PA	3	1.14	1.04	− 9	1.73	+ 52	1.55	+ 36	0.968	− 15
Ant	3	0.0889	0.157	+ 77	0.189	+111	0.118	+ 33	0.0919	+ 3
FL	4	0.513	0.486	− 5	0.201	− 61	0.194	− 62	0.293	− 43
Pyr	4	1.67	1.81	+ 8	1.74	+ 4	1.40	− 16	0.754	− 55
BaA	4	0.0877	0.210	+139	0.0990	+ 13	0.110	+ 25	0.0784	− 11
CHR	4	0.105	0.113	+ 8	0.0835	− 20	0.163	+ 55	0.112	+ 7
BbF	5	0.0392	0.0444	+ 13	0.00924	− 76	0.0552	+ 4	0.0362	− 8
BkF	5	0.0191	0.0329	+ 72	0.00987	− 48	0.0364	+ 91	0.0222	+ 16
BaP	5	0.0253	0.0304	+ 20	0.0749	+196	0.103	+307	0.114	+ 351
IND	6	0.00909	0.00909	+ 0	0.00909	+ 0	0.00909	+ 0	0.0284	+ 212
DBA	5	0.00874	0.00874	+ 0	0.00874	+ 0	0.00874	+ 0	0.0139	+ 59
BghiP	6	0.00901	0.0126	+ 40	0.00901	+ 0	0.00901	+ 0	0.0189	+ 110
∑LM-PAHs	2–3	35.5	30.3	− 15	23.8	− 32	16.5	+ 54	12.7	− 64
∑MM-PAHs	4	2.54	2.78	+ 9	2.25	− 11	2.08	− 18	1.43	− 44
∑HM-PAHs	5–7	0.110	0.138	+ 25	0.121	+ 10	0.222	+102	0.234	+112
Total PAHs **(µg Nm^{-3})**	**2–7**	**38.2**	**33.2**	**− 13**	**26.2**	**− 31**	**18.8**	**− 51**	**14.4**	**− 62**
∑LM-BaP$_{eq}$	2–3	0.0363	0.0317	− 13	0.0255	− 30	0.0175	− 52	**0.0135**	− 63
∑MM-BaP$_{eq}$	4	0.0122	0.0245	+101	0.0128	+ 5	0.0144	+ 18	**0.0102**	− 16
∑HM-BaP$_{eq}$	5–7	0.0409	0.0479	+ 17	0.0865	+112	0.122	+192	**0.137**	+235
Total BaP$_{eq}$ **(µg BaP$_{eq}$ Nm^{-3})**	**2–7**	**0.0894**	**0.104**	**+ 16**	**0.125**	**+ 40**	**0.154**	**+ 72**	**0.161**	**+ 80**

(+) increase; (−) decrease.

whereas MM-PAHs and HM-PAHs had 18% and 192% increase, respectively, at 80,000 km compared to 0 km. Benzo(a)pyrene was the dominant congener contributing between 28.3% (0 km) to ~71.0% (80,000 km) to the toxicity followed by Naphthalene ranged between ~38.3% (0 km) to 7.2% (80,000 km), Benzo(a)anthracene, and Dibenzo(a,h)anthracene. All the 4 dominant congeners belong to HM-PAHs except Naphthalene which is a LM-PAH.

The above result showed the PAH emissions of mass could be inhibited by B10 even in the long-term durability test, since the most dominant Naphthalene could be reduced by more complete combustion provided by fuel oxygen and higher Cetane Index than petroleum diesel. However, the higher-ring PAHs, which have higher toxicity, were

not obviously decreased, because the HM-PAH emissions of petroleum diesel were originally low, and could not be strongly reduced by enhancing the combustion.

The PCDD/F emission concentrations from EURO IV diesel engine fuelled with B10 were also investigated in the current study, with the results listed in Table 4. The levels were 116, 149, 90, and 167 ng Nm^{-3} for the accumulated mileages of 0, 20,000, 40,000, 60,000 km, respectively. The trend did not show a continuously increase or decrease concentration with mileage accumulation, and produced the highest PCDD/F concentration of 167 ng Nm^{-3} emitted at

60,000 km, representing an 44% increase compared to 0 km. The PCDD/Fs congener profile fraction was shown in Fig 2. The dominant congener was OCDD contributing > 50% followed by OCDF (> 20%), 1,2,3,4,6,7,8-HpCDF and 1,2,3,4,6,7,8-HpCDD for all accumulated mileages.

The corresponding PCDD/F WHO-TEQ concentrations based on the total mass concentrations and toxic equivalency factors (TEFs) of PCDD/Fs were 2.51, 3.69, 2.66, and 1.50 ng WHO-TEQ Nm^{-3} for 0, 20,000, 40,000, and 60,000 km, respectively. The highest toxicity level was 3.69 ng WHO-TEQ Nm^{-3} recorded at 20,000 km. The toxicity trend showed

Table 4. PCDD/F concentrations and toxicities emitted from EURO IV diesel engine fueled with B10.

PCDD/Fs (pg Nm^{-3})	WHO-TEF	0 hr (0 km)	*Increase %*	125 hr (20,000 km)	*Increase %*	250 hr (40,000 km)	*Increase %*	375 hr (60,000 km)	*Increase %*
2,3,7,8-*Te*CDD	1	1.18	Base	1.36	*+ 15*	1.24	*+ 5*	0.829	*– 30*
1,2,3,7,8-*Pe*CDD	1	0.483	Base	1.19	*+ 15*	0.523	*+ 8*	ND	*– 100*
1,2,3,4,7,8-*Hx*CDD	0.1	0.321	Base	ND	*– 100*	ND	*– 100*	ND	*– 100*
1,2,3,6,7,8-*Hx*CDD	0.1	0.621	Base	0.909	*+ 46*	ND	*– 100*	ND	*– 100*
1,2,3,7,8,9-*Hx*CDD	0.1	0.802	Base	1.09	*+ 29*	1.86	*+132*	1.38	*+ 72*
1,2,3,4,6,7,8-*Hp*CDD	0.01	6.56	Base	5.54	*– 16*	5.54	*– 16*	10.0	*+ 52*
*O*CDD	0.0003	63.2	Base	88.5	*+ 40*	46.5	*– 26*	88.7	*+ 40*
2,3,7,8-*Te*CDF	0.1	0.341	Base	0.815	*+139*	0.706	*+107*	ND	*– 100*
1,2,3,7,8-*Pe*CDF	0.03	0.816	Base	2.30	*+182*	1.74	*+113*	1.97	*+141*
2,3,4,7,8-*Pe*CDF	0.3	0.642	Base	0.783	*+ 22*	0.647	*+ 1*	ND	*– 100*
1,2,3,4,7,8-*Hx*CDF	0.1	0.576	Base	0.639	*+ 11*	0.642	*+ 11*	ND	*– 100*
1,2,3,6,7,8-*Hx*CDF	0.1	0.563	Base	0.540	*– 4*	0.464	*– 18*	0.501	*– 11*
2,3,4,6,7,8-*Hx*CDF	0.1	0.519	Base	0.549	*+ 6*	ND	*– 100*	ND	*– 100*
1,2,3,7,8,9-*Hx*CDF	0.1	0.815	Base	2.05	*+152*	1.63	*+ 10*	1.87	*+129*
1,2,3,4,6,7,8-*Hp*CDF	0.01	7.83	Base	7.77	*– 1*	4.50	*– 43*	9.00	*+ 15*
1,2,3,4,7,8,9-*Hp*CDF	0.01	0.546	Base	0.926	*+ 70*	0.355	*– 35*	ND	*– 100*
*O*CDF	0.0003	30.6	Base	34.3	*+ 12*	23.6	*– 23*	52.5	*+ 72*
∑PCDDs	-	73.2	Base	98.6	*+ 3*	55.6	*– 24*	101	*+ 38*
∑PCDFs	-	43.2	Base	50.7	*+ 17*	34.3	*– 21*	65.9	*+ 52*
Total PCDD/Fs (pg Nm^{-3})	-	**116**	**Base**	**149**	*+ 28*	**90.0**	*– 22*	**167**	*+ 44*
Total WHO-TEQ (pg WHO-TEQ Nm^{-3})	-	*2.51*	**Base**	*3.69*	*+ 47*	*2.66*	*+ 6*	*1.50*	*– 40*

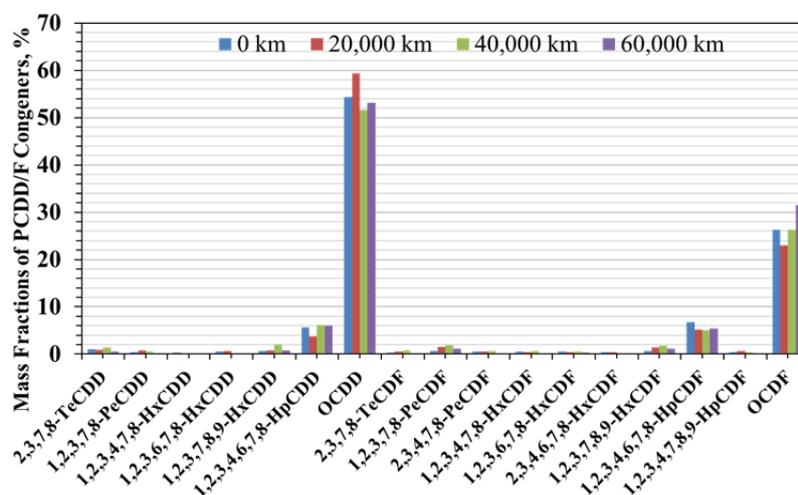(+) increase; (–) decrease.

Fig. 2. Mass fractions of PCDD/F congeners in the emission of EURO IV engine by using B10.

an initial increase of 47% at 20,000 km, and then decreased to 1.5 ng WHO-TEQ Nm^{-3}, showing a 40% reduction, compared to 0 km. For the PCDD/F WHO-TEQ Nm^{-3} congener profile fraction, the two most dominant congeners were 2,3,7,8-TeCDD (> 35%) and 1,2,3,7,8-PeCDD (> 18%). Our results of PAH and PCDD/F emissions from EURO IV engine fuelled with B10 were supported by the previous study (Chang *et al.*, 2014a).

Euro II Engine

With regards to EURO II, the respective levels of PAHs emitted at 0, 20,000, 40,000, and 60,000 km were 25.6, 19.7, 17.2, and 11.4 µg Nm^{-3} as shown in Table 5. The highest level of 25.6 µg Nm^{-3} was emitted at 0 km and then dropped until it reached the lowest level of 11.4 µg Nm^{-3} at 60,000 km; a reduction of 55%. The levels for LM-, MM-, and HM-PAHs all showed a similar pattern; a decrease of 51, 62, and 51% at 60,000 km, respectively, compared to 0 km. The respective PAH congener profile fraction was shown in Fig. 3. The dominant PAH species were Naphthalene contributing more than 45%, followed by Pyrene, Fluoranthene, and Phenathrene. The dominant congeners all belong to the LM-PAHs except Fluoranthene, a MM-PAH. This typical pattern was also reported in a study that analyzed the relative risk associated with PAH emissions from diesel exhaust and highlighting the importance of naphthalene as a dominant specie (Shah *et al.*, 2005). This

was concluded based on the level of the emission rate of naphthalene in comparison to other congeners. Lee *et al.* (2011) also reported LM-PAHs as dominant congeners of total-PAH masses.

Mwangi *et al.* (2015) investigated PAH emissions from a diesel engine using base diesel and fuel blends and observed a notable drop of 22.0–59.5% in PAH emissions when fuel blends were used. Yang *et al.* (2007) used a fuel blend of B20 (80% diesel + 20% methyl ester derived from waste cooking oil) to operate Mitsubishi (4M40-2AT1) diesel engine, and they observed a PAH emission reduction of 23.7%.

Biodiesel is known to have higher oxygen content and due to the increase in methanol, it may improve the combustion performance and promote the breakdown of benzene hence reducing benzene emissions (Cheung *et al.*, 2009). Chang *et al.* (2014a) suggested that the use of WCO-based was responsible for reducing the precursors of the PAHs and enhanced more complete combustion in the diesel engine. In another study, Lee *et al.* (2011) observed a negative correlation between the biodiesel blends and the total PAHs emissions and total BaP_{eq}. They suggested several factors causing this phenomenon including the enhanced combustion efficiency, improved PAH oxidization of forming precursors due to increased oxygenation, dilution effect which reduces fuel PAH content, and absence of aromatic content in the biodiesel (Chang *et al.*, 2014a).

Table 5. PAH mass and BaP_{eq} concentrations emitted from EURO II diesel engine fueled with B8.

| PAHs (µg Nm^{-3})	Rings	0 hr (0 km)	Increase %	125 hr (20,000 km)	Increase %	250 hr (40,000 km)	Increase %	375 hr (60,000 km)	Increase %
Nap	2	12.3	*Base*	12.3	*+ 0*	12.1	*− 2*	6.19	*− 50*
AcPy	3	0.0649	*Base*	0.0608	*− 6*	0.0315	*− 51*	0.0217	*− 67*
Acp	3	0.0570	*Base*	0.0581	*+ 2*	0.0263	*− 54*	0.0182	*− 68*
Flu	4	0.179	*Base*	0.179	*+ 0*	0.0831	*− 54*	0.0400	*− 78*
PA	3	1.41	*Base*	0.901	*− 36*	0.680	*− 52*	0.584	*− 59*
Ant	3	0.137	*Base*	0.108	*− 21*	0.0598	*− 56*	0.0459	*− 66*
FL	4	3.41	*Base*	1.71	*− 50*	1.12	*− 67*	1.17	*− 66*
Pyr	4	4.98	*Base*	2.66	*− 47*	1.86	*− 63*	2.00	*− 60*
BaA	4	0.541	*Base*	0.266	*− 51*	0.177	*− 67*	0.205	*− 62*
CHR	4	0.694	*Base*	0.350	*− 50*	0.250	*− 64*	0.275	*− 60*
BbF	5	0.674	*Base*	0.363	*− 46*	0.270	*− 60*	0.303	*− 55*
BkF	5	0.140	*Base*	0.0866	*− 38*	0.0685	*− 51*	0.0845	*− 40*
BaP	5	0.568	*Base*	0.327	*− 42*	0.249	*− 56*	0.262	*− 54*
IND	6	0.145	*Base*	0.100	*− 31*	0.0634	*− 56*	0.0773	*− 47*
DBA	5	0.0161	*Base*	0.0300	*+ 86*	0.00893	*− 45*	0.00965	*− 40*
BghiP	6	0.274	*Base*	0.197	*− 28*	0.139	*− 49*	0.161	*− 41*
∑LM-PAHs	2–3	13.9	*Base*	13.4	*− 4*	12.9	*− 7*	6.86	*− 51*
∑MM-PAHs	4	9.81	*Base*	5.17	*− 47*	3.49	*− 64*	3.69	*− 62*
∑HM-PAHs	5–7	1.82	*Base*	1.10	*− 40*	0.799	*− 56*	0.897	*− 51*
Total PAHs (µg Nm^{-3})	**2–7**	**25.6**	***Base***	**19.7**	***− 23***	**17.2**	***− 33***	**11.4**	***− 55***
∑LM-BaP_{eq}	2–3	1.42	*Base*	0.0144	*− 99*	0.0134	*− 99*	0.00727	*− 100*
∑MM-BaP_{eq}	4	0.0696	*Base*	0.0347	*− 50*	0.0232	*− 67*	0.0265	*− 62*
∑HM-BaP_{eq}	5–7	0.683	*Base*	0.414	*+ 48*	0.300	*− 56*	0.319	*− 53*
Total BaP_{eq} (µg BaP_{eq} Nm^{-3})	**2–7**	**2.17**	***Base***	**0.463**	***− 79***	**0.337**	***− 84***	**0.353**	***− 84***

(+) increase; (–) decrease.
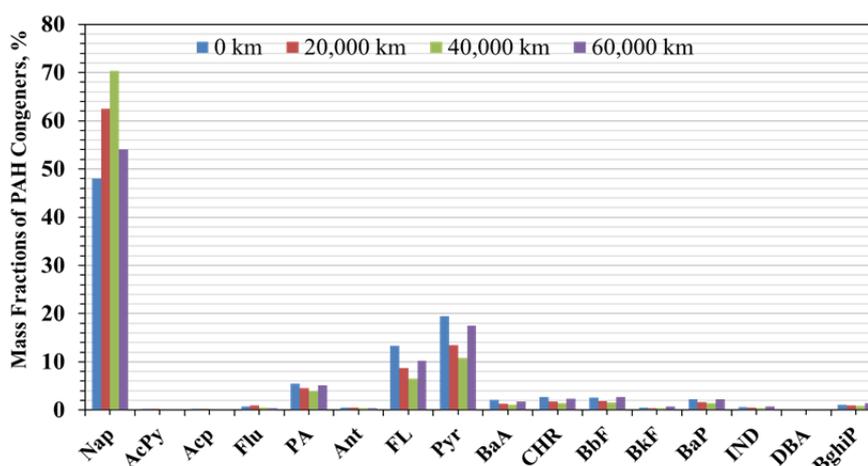
Fig. 3. Mass fractions of PAH congeners in the emission of EURO II engine by using B8.

Furthermore, studies have reported that fuel at optimum conditions enhances chemical reactions of unsaturated hydrocarbons, which are precursors responsible for PAH emissions that may reduce total PAH emissions (Inal and Senkan, 2002; Cheruiyot *et al.*, 2015).

For EURO II, the total BaP_{eq} were 2.17, 0.463, 0.337, and 0.353 µg BaP_{eq} Nm^{-3} for 0, 20,000, 40,000, and 60,000 km, respectively, as shown in Table 5. The BaP_{eq} started with the highest level of 2.17 µg BaP_{eq} Nm^{-3} at 0 km, and then significantly dropped to 0.463 µg BaP_{eq} Nm^{-3} (78.7%) at 20,000 km. It then continued with a gentle decrease until it reached the lowest level of 0.353 µg BaP_{eq} Nm^{-3} at 60,000 km, 23.75% reduced compared to 20,000 km, showing an overall reduction of 84%. The LM-, MM-, and HM-PAHs all showed a similar pattern with their highest levels of 1.42, 0.0696, and 0.683 µg BaP_{eq} Nm^{-3} at 0 km, respectively, and then all decreased having 99.5, 61.9, and 53.3% reduction at 60,000 km, respectively, compared to 0 km. With respect to PAH BaP_{eq}, the dominant congeners were Benzo(a)pyrene (70.6–74.1%) followed by Benzo(b)fluoranthene (7.8–8.8%), and Benzo(a)anthracene (5.3–7.0%), representing the HM- and MM-PAHs.

The PAH emissions from EURO II engine fuelled with B8 had a different trend in BaP_{eq} concentration during durability test. The reductions by using WCO-based biodiesel blends in all PAH species were found more significantly in the engine with higher mileage. This might be resulted from not only the inhibition of PAH formation during engine combustion, but also have cleaning effect to the wear and friction area to reduce the carbonates and particle on the surface of engine units and further reduce the MM- and HM-PAHs. Therefore, the WCO-based biodiesel blends were observed to reduce the PAH emissions more effectively in the older engine model.

CONCLUSION

The 80,000- and 60,000-km durability tests for EURO IV and II engines by using 10% and 8% additions of WCO, respectively, in diesel fuels, showed varied results on PAH and PCDD/F concentration and toxicity emissions. The highest total PAH mass concentrations were found to be 38.2 and 25.6 µg Nm^{-3} before the test by using EURO IV and II engines, respectively, and decreased 62 and 55% after 80,000- and 60,000-km operation, respectively. The dominant congeners of PAH emissions were naphthalene (> 45%), pyrene, and phenanthrene, which belong to the LM-PAHs. The total PAH BaP_{eq} had different emission trends between the two engines during the durability tests. The highest level was 2.17 µg BaP_{eq} Nm^{-3} from EURO II engine before test and reduced 84% after a 60,000-km cycle, when the total-BaP_{eq} emissions of EURO IV tended to increase from 0.0894 to 0.161 µg BaP_{eq} Nm^{-3} (80% increase) after the 80,000-km testing cycle. The most dominant congener contributing to the toxicity emissions of engines was benzo(a)pyrene (~70%), which had higher molecular weight and tend to be in particulate phase (Lee *et al.*, 2011). Additionally, the PCDD/F emissions were tested in EURO IV engine by using B10. The PCDD/F concentrations of mass and toxicity approached the highest levels, 167 ng Nm^{-3} and 3.69 pg WHO-TEQ Nm^{-3}, after 60,000-km and 20,000-km running cycles, respectively. The main dominant congeners were *O*CDD (> 50%) for mass, 2,3,7,8-*Te*CDD (> 35%) and 1,2,3,7,8-*Pe*CDD (> 18%) for toxicity. Consequently, the use of WCO-biodiesel might reduce the PAH mass and toxicity emissions in older engine (EURO II) but showed no significant effect in PAH and PCDD/F emission during the deterioration of a newer engine (EURO IV).

REFERENCE

Agarwai, A.K., Bijwe, J. and Das, L.M. (2003). Wear assessment in a biodiesel fueled compression ignition engine. *J. Eng. Gas Turbines Power* 125: 820–826.

Agarwal, A.K., Srivastava, D.K., Dwivedi, G., Kawatra, G., Kumar, M.R.P., Bhardwaj, O.P., Abraham, M. and

Jaura, A. (2008). Field trial of biodiesel (B100) and diesel fuelled common rail direct injection Euro-III compliant sports utility vehicles in India condition. *SAE Technical Paper* 2008-28-0077.

Chang, Y.C., Lee, W.J., Wang, L.C., Yang, H.H., Cheng, M.T., Lu, J.H., Tsai, Y.I. and Young, L.H. (2014a). Effects of waste cooking oil-based biodiesel on the toxic organic pollutant emissions from a diesel engine. *Appl. Energy* 113: 631–638.

Chang, Y.C., Lee, W.J., Yang, H.H., Wang, L.C., Lu, J.H., Tsai, Y.I., Cheng, M.T., Young, L.H. and Chiang, C.J. (2014b). Reducing emissions of persistent organic pollutants from a diesel engine by fueling with water-containing butanol diesel blends. *Environ. Sci. Technol.* 48: 6010–6018.

Chen, C.Y., Lee, W.J., Wang, L.C., Chang, Y.C., Yang, H.H., Young, L.H., Lu, J.H., Tsai, Y.I., Cheng, M.T. and Mwangi, J.K. (2017). Impact of high soot-loaded and regenerated diesel particulate filters on the emissions of persistent organic pollutants from a diesel engine fueled with waste cooking oil-based biodiesel. *Appl. Energy* 191: 35–43.

Cheruiyot, N.K., Lee, W.J., Mwangi, J.K., Wang, L.C., Lin, N.H., Lin, Y.C., Cao, J.J., Zhang, R.J. and Chang-Chien, G.P. (2015). An overview: Polycyclic aromatic hydrocarbon emissions from the stationary and mobile sources and in the ambient air. *Aerosol Air Qual. Res.* 15: 2730–2762.

Cheruiyot, N.K., Lee, W.J., Yan, P., Mwangi, J.K., Wang, L.C., Gao, X., Lin, N.H. and Chang-Chien, G.P. (2016). An overview of PCDD/F inventories and emission factors from stationary and mobile sources: What we know and what is missing. *Aerosol Air Qual. Res.* 16: 2965–2988.

Cheung, C.S., Zhu, L. and Huang, Z. (2009). Regulated and unregulated emissions from a diesel engine fueled with biodiesel and biodiesel blended with methanol. *Atmos. Environ.* 43: 4865–4872.

Clark, S.J., Wagner, L., Schrock, M.D. and Piennaar, P.G. (1984). Methyl and ethyl soybean esters as renewable fuels for diesel-engines. *J. Am. Oil Chem. Soc.* 61: 1632–1638.

de Mello, M., Young, A., Villardi, H., Pessoa, F. and Salgado, A. (2017). Biodiesel production by the methylic-alkaline and ethylic-enzymatic routes: Discussion of some environmental aspects. *J. Cleaner Prod.* 144: 347–357.

Demirbas, A. (2008). Biofuels sources, biofuel policy, biofuel economy and global biofuel projections. *Energy Convers. Manage.* 49: 2106–2116.

Fazal, M.A., Haseeb, A.S.M.A. and Masjuki, H.H. (2011). Biodiesel feasibility study: An evaluation of material compatibility; performance; emission and engine durability. *Renewable Sustainable Energy Rev.* 15: 1314–1324.

Fraer, R., Dinh, H., Proc, K., McCormick, R.L., Chandler, K. and Buchholz, B. (2005). Operating experience and teardown analysis for engines operating on biodiesel blends (B20). *SAE Technical Paper* 2005-01-3641

Haseeb, A., Sia, S.Y., Fazal, M.A. and Masjuki, H.H. (2010).

Effect of temperature on tribological properties of palm biodiesel. *Energy* 35: 1460–1464.

Hsieh, L.T., Wu, E.M.Y., Wang, L.C., Chang-Chien, G.P. and Yeh, Y.F. (2011). Reduction of toxic pollutants emitted from heavy-duty diesel vehicles by deploying diesel particulate filters. *Aerosol Air Qual. Res.* 11: 709–715.

Inal, F. and Senkan, S.M. (2002). Effects of oxygenate additives on polycyclic aromatic hydrocarbons(PAHs) and soot formation. *Combust. Sci. Technol.* 174: 1–19.

Kalam, M.A. and Masjuki, H.H. (2002). Biodiesel from palmoil - An analysis of its properties and potential. *Biomass Bioenergy* 23: 471–479.

Laroo, C.A., Schenk, C.R., Sanchez, L.J. and McDonald, J. (2011). Emissions of PCDD/Fs, PCBs, and PAHs from a modern diesel engine equipped with catalyzed emission control systems. *Environ. Sci. Technol.* 45: 6420–6428.

Laroo, C.A., Schenk, C.R., Sanchez, L.J., McDonald, J. and Smith, P.L. (2012). Emissions of PCDD/Fs, PCBs, and PAHs from legacy on-road heavy-duty diesel engines. *Chemosphere* 89: 1287–1294.

Lee, W.J., Liu, Y.C., Mwangi, F.K., Chen, W.H., Lin, S.L., Fukushima, Y., Liao, C.N. and Wang, L.C. (2011). Assessment of energy performance and air pollutant emissions in a diesel engine generator fueled with water-containing ethanol–biodiesel–diesel blend of fuels. *Energy* 36: 5591–5599.

Li, W., Zhao, X.H., Ji, Y.H., Peng, H., Li, Y.F., Liu, L. and Han, X. (2016). An investigation on environmentally friendly biodiesel-based invert emulsion drilling fluid. *J. Pet. Explor. Prod. Technol.* 6: 505–517.

Lin, L., Zhou, C.S., Vittayapadung, S., Shen, X.Q. and Dong, M.D. (2011). Opportunities and challenges for biodiesel fuel. *Appl. Energy* 88: 1020–1031.

Lin, S.L., Lee, W.J., Lee, C.F. and Chen, S.J. (2010). Energy savings and emission reduction of nitrogen oxides, particulate matter, and polycyclic aromatic hydrocarbons by adding water-containing acetone and neat soybean oil to a diesel-fueled engine generator. *Energy Fuels* 24: 4522–4533.

Lloyd, A.C. and Cackette, T.A. (2001). Diesel engines: Environmental impact and control. *J. Air Waste Manage. Assoc.* 51: 809–847.

Muralidharan, K. and Vasudevan, D. (2011). Performance, emission and combustion characteristics of a variable compression ratio engine using methyl esters of waste cooking oil and diesel blends. *Appl. Energy* 88: 3959–3968.

Mwangi, J.K., Lee, W.J., Whang, L.M., Wu, T.S., Chen, W.H., Chang, J.S., Chen, C.Y. and Chen, C.L. (2015a). Microalgae oil: Algae cultivation and harvest, algae residue torrefaction and diesel engine emissions tests. *Aerosol Air Qual. Res.* 15: 81–98.

Mwangi, J.K., Lee, W.J., Wang, L.C., Cheruyiot, N.K., Chen, C.Y. and Redfern, F. (2015b). An overview: Emission of brominated persistent organic compounds in the diesel engine exhaust. *Earozoru Kenkyu* 30: 254–260.

Nisbet, I.C.T. and LaGoy, P.K. (1992). Toxic equivalency factors (TEFs) for polycyclic aromatic hydrocarbons

(PAHs). *Regul. Toxicol. Pharm.* 16: 290–300.

Özener, O., Yüksek, L., Ergenç, A.T. and Özkan, M. (2014). Effects of soybean biodiesel on a DI diesel engine performance, emission and combustion characteristics. *Fuel* 115: 875–883.

Pimentel, D., Marklein, A., Toth, M.A., Karpoff, M.N., Paul, G.S., McCormack, R., Kyriazis, J. and Krueger, T. (2009). Food versus biofuels: Environmental and economic costs. *Hum. Ecol.* 37: 1–12.

Proc, K., Barnitt, R., Hayes, R.R., Ratcliff, M., McCormick, R.L., Ha, L. and Fang, H.L. (2006). 100,000-mile evaluation of transit buses operated on biodiesel blends (B20). *SAE Technical Paper* 2006-01-3253.

Raheman, H. and Ghadge, S.V. (2007). Performance of compression ignition engine with mahua (Madhuca indica) biodiesel. *Fuel* 86: 2568–2573.

Ramadhas, A.S., Jayaraj, S. and Muraleedharan, C. (2005). Biodiesel production from high FFA rubber seed oil. *Fuel* 84: 335–340.

Saxena, M.R. and Maurya, R.K. (2016). Effect of butanol blends on nano particle emissions from a stationary conventional diesel engine. *Aerosol Air Qual. Res.* 16: 2255–2266.

Scheepers, P.T.J. (2015). Health Implications of Combustion Engine Exhaust, In *Environmental Indicators*, Armon, R.H. and Hänninen, O. (Eds.), Springer Netherlands, Dordrecht, pp. 899–924.

Shah, S.D., Ogunyoku, T.A., Miller, J.W. and Cocker, D.R. (2005). On-road emission rates of PAH and *n*-Alkane compounds from heavy-duty diesel vehicles. *Environ. Sci. Technol.* 39: 5276–5284.

Tsai, J.H., Chen, S.J., Huang, K.L., Chaung, H.C., Lin, W.Y., Lin, C.C., Wu, T.Y., Yang, C.H. and Chiu, J.Y. (2015). Biological toxicities of exhausts from a diesel-generator fueled with water-containing acetone/butanol and waste-edible-oil-biodiesel blends. *Aerosol Air Qual. Res.* 15: 2668–2675.

Tsai, J.H., Chen, S.J., Huang, K.L., Chang-Chien, G.P., Lin, W.Y., Feng, C.W., Syu, J.Y. and Huang, H.T. (2016). Characteristics of persistent organic pollutant emissions from a diesel-engine generator fueled using blends of waste cooking oil-based biodiesel and fossil diesel. *Aerosol Air Qual. Res.* 16: 2048–2058.

USEPA (2001). Modified Method 5. Determination of Particulate Emission from Stationary Sources. Code of Federal Regulations, Title 40, Part 60, Appendix A.

Wang, L.C., Lee, W.J., Lee, W.S., Chang-Chien, G.P. and Tsai, P.J. (2003a). Characterizing the emissions of polychlorinated dibenzo-*p*-dioxins and dibenzofurans from crematories and their impacts to the surrounding environment. *Environ. Sci. Technol.* 37: 62–67.

Wang, L.C., Lee, W.J., Lee, W.S., Chang-Chien, G.P. and Tsai, P.J. (2003b). Effect of chlorine content in feeding wastes of incineration on the emission of polychlorinated dibenzo-*p*-dioxins/dibenzofurans. *Sci. Total Environ.* 302: 185–198.

Wang, L.C., Wang, I.C., Chang, J.E., Lai, S.O. and Chang-Chien, G.P. (2007). Emission of polycyclic aromatic hydrocarbons (PAHs) from the liquid injection incineration of petrochemical industrial wastewater. *J. Hazard. Mater.* 148: 296–302.

Wang, L.C., Lin, L.F. and Lai, S.O. (2009). Emissions of polycyclic aromatic hydrocarbons from fluidized and fixed bed incinerators disposing petrochemical industrial biological sludge. *J. Hazard. Mater.* 168: 438–444.

Wang, M.S., Chen, S.J., Huang, K.L., Lai, Y.C., Chang-Chien, G.P., Tsai, J.H., Lin, W.Y., Chang, K.C. and Lee, J.T. (2010). Determination of levels of persistent organic pollutants (PCDD/Fs, PBDD/Fs, PBDEs, PCBs, and PBBs) in atmosphere near a municipal solid waste incinerator. *Chemosphere* 80: 1220–1226.

Wichmann, H.E. (2007). Diesel Exhaust Particles. *Inhalation Toxicol.* 19: 241–244.

Williams, A., McCormick, R., Luecke, J., Brezny, R., Geisselmann, A., Voss, K., Hallstrom, K., Leustek, M., Parsons, J. and Abi-Akar, H. (2011). Impact of biodiesel impurities on the performance and durability of DOC, DPF and SCR technologies. *SAE Int. J. Fuels Lubr.* 4: 110–124.

Yang, H.H., Chien, S.M., Lo, M.Y., Lan, J.C.W., Lu, W.C. and Ku, Y.Y. (2007). Effects of biodiesel on emissions of regulated air pollutants and polycyclic aromatic hydrocarbons under engine durability testing. *Atmos. Environ.* 41: 7232–7240.

Yang, T.T., Hsu, C.Y., Chen, Y.C., Young, L.H., Huang, C.H. and Ku, C.H. (2017). Characteristics, sources, and health risks of atmospheric $PM_{2.5}$-bound polycyclic aromatic hydrocarbons in Hsinchu, Taiwan. *Aerosol Air Qual. Res.* 17: 563–573.