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Emissions of $PM_{2.5}$-bound Polycyclic Aromatic Hydrocarbons and Metals from a Diesel Generator Fueled with Biodiesel Converted from Used Cooking Oil

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ABSTRACT

To elucidate the characteristics of fine particulate matter pollutant emitted from a diesel engine, a fossil-based diesel fuel (D100) and two blended fuels consisting of D100 and waste cooking oil (WCO) convered biodiesel (W) are tested with a diesel engine generator at loads of 1.5 kW and 3.0 kW. The blended fuels contain 20% and 40% W and are referred to as W20 and W40, respectively. The $PM_{2.5}$ emissions and their polycyclic aromatic hydrocarbon (PAH) and metallic components are investigated. Experimental results show that higher concentrations of $PM_{2.5}$, $PM_{2.5}$-bound ΣPAHs and Σmetals, and ΣBaP_{eq} are generated at the 3.0 kW load, with its greater fuel consumption (FC), than the 1.5 kW load. Additionally, of the three fuels, using W20 emits the lowest concentrations of $PM_{2.5}$, $PM_{2.5}$-bound ΣPAHs, and ΣBaP_{eq}. Specifically, the reduction in ΣBaP_{eq} mainly results from the effective inhibition of HMW-BaP_{eq}. Conversely, when using W40, the $PM_{2.5}$-bound Σmetals significantly decreases, and its composition is strongly affected by the metallic content in the fuel. Although W20 and W40 exhibit higher FC (3.0% more) and brake-specific fuel consumption (BSFC; 3.1% more) than D100, they generate lower concentrations of $PM_{2.5}$ (18.1% less), $PM_{2.5}$-bound ΣPAHs (22.8% less) and Σmetals (22.0% less), and ΣBaP_{eq} (35.0% less) at both engine loads. The emission factors of these pollutants in the engine exhaust are also reduced, particularly at the higher load (3.0 kW). Accordingly, WCO-based biodiesel additives may decrease the $PM_{2.5}$, PAHs, and metals exhausted by diesel engines, thus reducing the BaP_{eq} of these emissions.

Keywords: $PM_{2.5}$; Biodiesel; PAHs; Metals; Generator.

INTRODUCTION

Many researchers are concerned by mobile source air pollution, which causes environmental problems and is associated with adverse health effects. Compared with gasoline engines, diesel engines yield more emissions of pollutants, including soot, black smoke, nitrogen oxides, trace metals (Liati *et al.*, 2015) and harmful components (e.g., polycyclic aromatic hydrocarbons (PAHs) and polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs)) (Cheruiyot *et al.*, 2016; Redfern *et al.*, 2017; Tsai *et al.*, 2018). Diesel PM has a diameter smaller than 1 μm, and thus can be easily inhaled into the respiratory system (Baldauf *et al.*, 2016; Gao and Tian, 2019). Several epidemiological studies have shown that gaseous and particulate air pollutants have a significant and close temporal association with admissions to hospital for stroke or mortality from stroke (Shah *et al.*, 2015), and exposure to fine particulate matter ($PM_{2.5}$) is linked with high symptoms of anxiety, with more recent exposures potentially more relevant than more distant exposures (Power *et al.*, 2015). Research is needed to explore the physicochemical properties of $PM_{2.5}$ in diesel engine exhaust (DEE) and how to reduce those emissions.

Research has demonstrated the presence of carcinogenic PAHs on diesel particles. The formation of PAHs is well known to be due to incomplete combustion and high-pressure processes (Johnson, 2008). The combustion process in the diesel engine chamber produces PAH emissions even if the primary fuels are free of PAHs in their fuel structures

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(Yilmaz and Davis, 2016). Because PAHs are semi-volatile, they may condense on surfaces within the engine, and then damage the engine through 'wetstacking' (Überall *et al.*, 2015). Using biodiesel, or increasing the oxygen content of the fuel, leads to more complete combustion, and helps to inhibit PAH formation (Lin *et al.*, 2017). Thus, the effect of biodiesel blends on the formation of PAHs in exhausts is important to understand from the perspectives of human health, the environment and its influence on engine failure.

The metallic elements on the diesel particles are roughly derived from the addition of lubricating oil containing metals (e.g., Zn, Ca and Mg; Hu *et al.*, 2009; Liati *et al.*, 2015) and engine-component friction emissions (e.g., Fe, Ni, Cu, Cr and Sb; Lim *et al.*, 2007; Sappok *et al.*, 2012). Generally, the diesel particulates have low metallic content, but the metallic particles have small particle size, and can be easily inhaled into the deep part of the respiratory tract. Diesel particles containing heavy metals (e.g., Zn, Cr and Ni) can trigger irreversible damage to the human body. For instance, inhalation of particles containing Ni and V may cause acute cardiac function and short-term mortality (Chen and Lippmann, 2009). Cakmak *et al.* (2014) indicated that metals contained in $PM_{2.5}$ were found to be associated with acute changes in cardiovascular and respiratory physiology. Therefore, as well as organic matter and particulate matter, the metallic content in diesel exhaust also needs to be studied to evaluate the health effects associated with diesel emissions.

Biodiesel is recognized to be one of the ways to successfully reduce diesel engine pollutant emissions (Wang *et al.*, 2016; Lin *et al.*, 2017; Redfern *et al.*, 2017). Biodiesel is environmentally friendly, but has slightly higher fuel consumption (Mwangi *et al.*, 2015; Lin *et al.*, 2017) and levels of trace metals on the particles in the exhausts than standard diesel fuel under the same operating conditions (Shukla *et al.*, 2017). Moreover, some characteristics of biodiesel, such as density, viscosity, and cold flow properties make it unsuitable for direct use in high addition percentages (over 50 vol%) as an alternative fuel (How *et al.*, 2012; Yilmaz and Davis, 2016). However, few researchers have explored the emissions of $PM_{2.5}$ and its compositions in exhausts. Hence, this work investigates the emission characteristics of $PM_{2.5}$ and $PM_{2.5}$-bound PAHs and metals by operating a diesel engine generator with several diesel and waste-cooking-oil-based biodiesel (WCO-biodiesel) blends as fuels.

MATERIALS AND METHODS

Sampling Procedures

Three biodiesel-diesel blends with different mixing ratios of WCO-biodiesel to premium diesel were tested: premium diesel fuel (D100), W20 (20 vol% WCO-biodiesel + 80 vol% D100) and W40. The different blended fuels were tested in a generator at a stable energy output (110V/60Hz, 1800 rpm) under loads of 1.5 kW and 3.0 kW. The diesel engine generator was a four-stroke, water-cooled, single-fuel-injection cylinder (bore = 88.0 mm, stroke = 96.0 mm, Model TF110E and YSG-5SEN) manufactured by Yanmar Co., Ltd. (Japan). The generator had one phase/two wires, an output frequency of 50–60 Hz and a maximum output power of 4 kW. The premium diesel fuel was obtained from the Chinese Petroleum Corporation (Taiwan), and the pure WCO-biodiesel was manufactured by Chant Oil Co., Ltd. (Taiwan). Table 1 shows the characteristics of the tested fuels.

The samples of $PM_{2.5}$ and $PM_{2.5}$-bound PAHs and metals were obtained from the generator exhaust by using $PM_{2.5}$ cyclones equipped with 47 mm quartz fiber filters (2500 QAT-UP; Pall Corp., USA) to separate aerodynamic particle sizes $\leq$ 2.5 μm from the larger particles in the tailpipe stream based on Method 201A (U.S. EPA). The quartz filters were pretreated before being sampled by heating them in a muffle furnace in air for 2.5 h at 900°C. Before and after field sampling, the quartz filters were dried for 24 h in a desiccator at 25 ± 3°C and a relative humidity of 40 ± 5%; they were then weighed on an electronic balance (UXM2; Mettler Toledo) with a precision of 0.1 μg to determine the mass concentration. The $PM_{2.5}$ mass concentration of particles was then calculated by dividing the particle mass by the sampled air volume.

The experiments were conducted 22 times (each sampling time = 60 min) for each combination of parameters. 2 of these 22 samples were taken for metal analysis, and the remaining 20 samples were combined into 1 sample for PAH analysis to satisfy the detection limits of the instrument. Sampling data were obtained after the engine had been run for at least 30 min.

PAH Analysis

The $PM_{2.5}$-bound PAH samples collected from the diesel generator exhausts were extracted by 1:1 (v/v) *n*-hexane/dichloromethane for 24 hr. The extracts were then concentrated, cleaned with a silica column of ~27 cm silica gel particles (size range = 0.04–0.063 mm) under a layer of anhydrous Na_2SO_4 (~1 cm high) and above a support of glass fibers, and re-concentrated by purging with ultra-pure nitrogen to exactly 1.0 mL for the subsequent identification of 16 PAHs by a gas chromatograph/mass selective detector (GC/MSD; 6890N GC with HP 5973 MSD; Agilent Technologies, Inc., USA). The limits of detection (LODs)

Table 1. Fuel properties.

Item	Pure Diesel	Pure WCO-biodiesel
Density (g mL^{-1})	0.84	0.88
Lower calorific vaporization (MJ kg^{-1})	43.5	37.8
Viscosity (mm^2 s^{-1})	3.06	4.08
Carbon (%)	86.3	78.9
Oxygen (%)	n.d.	11.8
Hydrogen (%)	13.3	9.30

for the 16 PAH compounds were 0.023–0.106 ng, and the recovery efficiencies were 83.9–92.6% (average = 86.4%). Additional analysis parameters and procedures of GC/MSD can be found elsewhere (Lin *et al.*, 2012; Chang *et al.*, 2013).

The PAHs were divided into three categories according to the molecular weights of the 16 PAH compounds: low molecular weight (LMW), medium molecular weight (MMW), and high molecular weight (HMW) PAHs. The LMW-PAHs comprised naphthalene (Nap), acenaphthylene (AcPy), acenaphthene (Acp), fluorine (Flu), phenanthrene (PA) and anthracene (Ant), while the MMW-PAHs were fluoranthene (FL), pyrene (Pyr), benzo[*a*]anthracene (BaA) and chrysene (CHR). The HMW-PAHs were benzo[*b*]fluoranthene (BbF), benzo[*k*]fluoranthene (BkF), benzo(*a*)pyrene (BaP), dibenzo[*a*,*h*]anthracene (DBA), indeno[1,2,3,-*cd*]pyrene (IND) and benzo[*ghi*]perylene (Bghip). The carcinogenic factors of the identified PAHs were derived in terms of BaP_{eq}, from the toxic equivalency factors (TEFs) of these compounds (= PAH concentration × TEF). This study adopted the TEFs specified by Nisbet and LaGoy (1992). The carcinogenic potency of Total-PAHs (Total-BaP_{eq}) was assessed by summing the BaP_{eq} concentrations of individual PAH compounds.

Metal Analysis

The $PM_{2.5}$-bound metallic samples obtained from quartz filter papers were extracted with nitric acid solution, and analyzed by inductively coupled plasma mass spectrometry (ICP-MS). The extraction and analysis steps were as follows. Each quartz filter paper was carefully cut into small pieces. Each piece was then placed in a 50 mL screw-cap graphite digestive tube. A 20 mL 10% HNO_3 solution was then added into each tube, and the screw cap was tightened. The locked graphite digestive tubes were extracted for 120 min with an ultrasonic bath, and then heated in a block heater at 80–85°C for 30 min. After cooling, each digested solution was filtered with a cellulose acetate filter (pore size = 0.45 μm) and diluted to a volume of 25 mL using 10% HNO_3 to analyze 21 metals (Na, Mg, Al, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, As, Sr, Mo, Cd, Sn, Sb, Ba and Pb) using ICP-MS (7500a ICP-MS; Agilent Technologies, Inc., USA). The calibration was conducted using multi-element (metallic) standards (certified reference materials (CRMs); Spex, Metuchen, USA) in a 1% (v/v) HNO_3 solution. Every tenth sample was spiked using liquid standards that contained known quantities of the analyzed metallic elements. The CRMs were also employed as quality control standards.

For analyzing elements using ICP-MS measurements, the method detection limits (MDLs) for Na, Mg, Al, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, As, Sr, Mo, Cd, Sn, Sb, Ba and Pb were 6.12, 5.22, 3.16, 19.3, 24.3, 0.36, 0.04, 0.14, 0.03, 2.22, 0.03, 0.31, 5.27, 0.31, 0.20, 0.99, 0.02, 3.15, 0.12, 0.51 and 0.06 μg L^{-1}, respectively. The recovery efficiencies of these 21 metals ranged from 95.2% to 113.8% (average = 106.2%). Both field and laboratory blank samples were prepared and analyzed for each sampling and analysis. All data were corrected from blanks.

RESULTS AND DISCUSSION

Effect of Biodiesel on $PM_{2.5}$ Emission and Engine Performance

The $PM_{2.5}$ levels in exhaust gas from D100, W20 and W40 were 16.3 ± 2.04, 13.8 ± 1.71, and 14.1 ± 2.14 mg Nm^{-3}, respectively, at 1.5 kW load, and 30.2 ± 6.43, 23.2 ± 3.55, and 24.0 ± 3.40 mg Nm^{-3}, respectively, at 3.0 kW load (as shown in Table 2). Obviously, the $PM_{2.5}$ concentrations were higher at 3.0 kW than at 1.5 kW when using D100, W20 or W40, because more fuel was consumed (higher fuel consumption) at 3.0 kW, causing more $PM_{2.5}$ mass emissions at the higher engine load (Tsai *et al.*, 2017). Reductions in $PM_{2.5}$ emissions by using W20 and W40 in comparison to D100 were 14.4% and 14.0%, respectively, at 1.5 kW load, and 22.1% and 20.3%, respectively, at 3.0 kW load. The lower PM levels emitted by W20 and W40 might be due to the higher oxygen content (11.8%) of waste cooking oil derived biodiesel (W100) than that of conventional diesel fuel (Table 1). Therefore, 20% and 40% W100 containing diesel blends (W20 and W40) had significantly higher oxygen content than in D100 (n.d.), further raising the combustion efficiency and lowering PM mass concentrations at the same engine load. Nevertheless, W20 showed the greatest reduction rate among all fuel blends at both engine loads.

The engine generator showed higher FC by using all three fuels at 3.0 kW than at 1.5 kW load, while the opposite trend was found for BSFC (as shown in Table 2). This result indicates that the engine operated at the higher load had higher fuel consumption than at the lower load, but better energy efficiency, resulting in a lower BSFC for the latter. Although, as mentioned above, the generator produced higher $PM_{2.5}$ mass concentrations at 3.0 kW load, it consumed less fuel to produce 1 kWh electricity energy output. Restated, W20 had slightly higher FC (increased by 1.8%) and BSFC (increased by 2.0%), since it had a lower

Table 2. $PM_{2.5}$, FC, and BSFC values from engine generator by using various fuels.

Fuel Performances	Loads	D100	W20	Increases (%)	W40	Increases (%)
$PM_{2.5}$ (mg Nm^{-3})	1.5 kW	16.3 ± 2.04	13.8 ± 1.71	–15.3%	14.1 ± 2.14	–13.5%
(N = 22)	3.0 kW	30.2 ± 6.43	23.2 ± 3.55	–23.2%	24.0 ± 3.40	–20.5%
FC (L h^{-1})	1.5 kW	1.06 ± 0.04	1.07 ± 0.02	+0.94%	1.08 ± 0.04	+1.89%
(N = 22)	3.0 kW	1.54 ± 0.04	1.58 ± 0.05	+2.60%	1.64 ± 0.05	+6.49%
BSFC (L kWh^{-1})	1.5 kW	0.678 ± 0.027	0.691 ± 0.016	+1.92%	0.693 ± 0.028	+2.21%
(N = 22)	3.0 kW	0.542 ± 0.012	0.553 ± 0.017	+2.03%	0.575 ± 0.015	+6.09%

[#] increases in comparison to D100 in percentage (%).

heating value (as shown in Table 1). Fortunately, W20 provided more $PM_{2.5}$ reduction rates (decreased by 19.3%) than general diesel fuel.

Experimental results indicate that biodiesel is not only a potential diesel alternative, but has lower PM emissions than standard diesel, particularly when using 20% biodiesel additive blends (McCormick, 2007; Tsai *et al.*, 2010, 2014). Conversely, too high additive fractions of biodiesels (> 50%) significantly raised the viscosity of fuel, reducing the nebulization efficiency of fuel spray, leading to incomplete combustion and eventually producing more PM emissions (Akasaka *et al.*, 1997; Durbin *et al.*, 2000).

Effects of Biodiesel on $PM_{2.5}$-bound PAHs and BaP_{eq}

Fig. 1 displays emissions of $PM_{2.5}$-bound ΣPAHs, which were mostly dominated by LMW-PAHs (46.0–74.7%, average = 59.6%), followed by MMW-PAHs (17.5–35.2%, average = 27.0%) and HMW-PAHs (7.4–19.5%, average = 13.4%) by using D100, W20 and W40. However, the $PM_{2.5}$-bound ΣBaP_{eq} were almost all contributed by HMW-PAHs (92.5–94.8%, average = 94.0%), with small contributions from MMW-PAHs (3.5–5.3%, average = 4.5%) and LMW-PAHs (0.6–2.5%, average = 1.5%). The biodiesels were reported to have lower ΣPAHs and ΣBaP_{eq} emissions than the conventional diesel, due to higher oxygen content and better combustion condition (Chang *et al.*, 2014; Mwangi *et al.*, 2015). Notably, W40 showed slightly higher $PM_{2.5}$-bound ΣPAHs and ΣBaP_{eq} emissions than W20. This phenomenon was attributed to the incomplete combustion and worse breakup efficiency of fuel spray when using

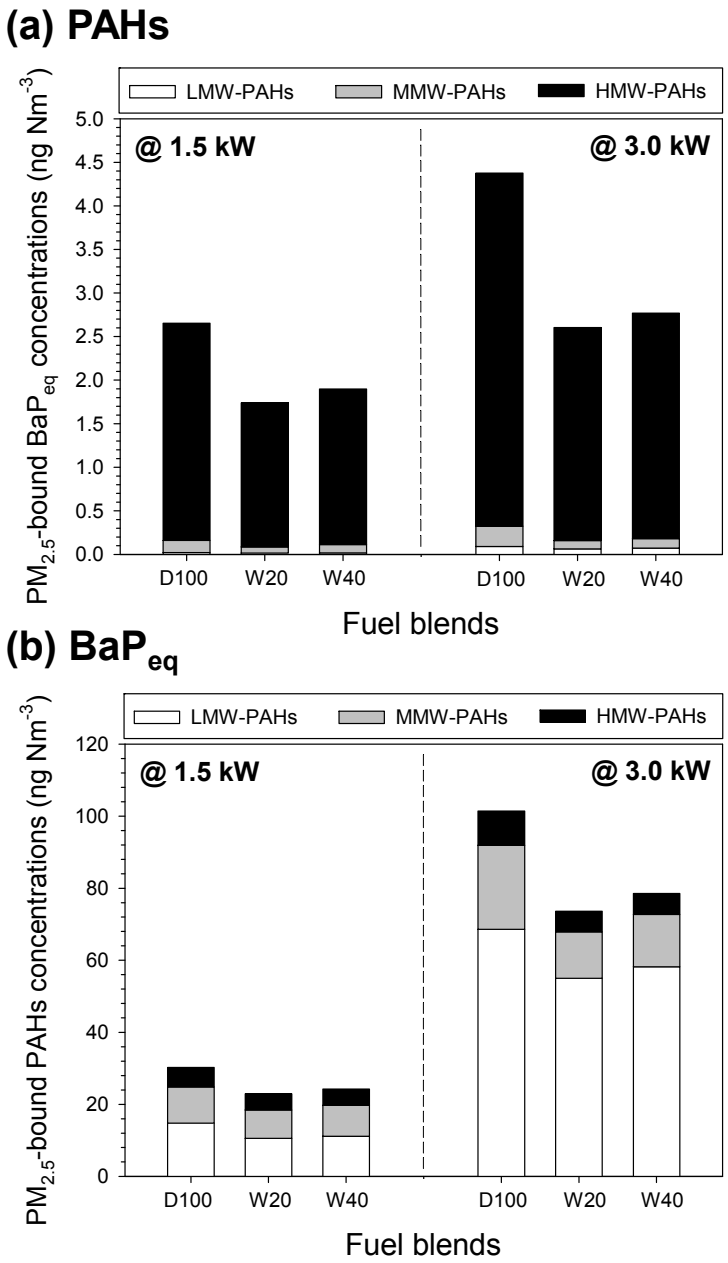

Fig. 1. $PM_{2.5}$-bound (a) PAH and (b) BaP_{eq} concentrations using W20 and W40 vs. using D100 operated at two engine loads.

high additions of biodiesel. Additionally, the higher additive fractions of biodiesels not only diluted the concentration of PAH precursors (C_2H_2 radical) in the combustion area, but also provided more oxidant (O_2) to enhance the combustion reaction and reduce the PAH formations (Chang *et al.*, 2013). Apart from that, biodiesel addition into petroleum diesel could break down HMW-PAHs and MMW-PAHs into LMW-PAHs, which have lower toxic equivalencies, during fuel combustion (Li *et al.*, 2005; Yilmaz *et al.*, 2014).

Fig. 2 depicts the reduction rates of PAHs and BaP_{eq} from using D100 by using W20 and W40. Specifically, the reduction rates of PM-bound LMW-, MMW-, HMW-PAHs, and ΣPAHs by using W20 were 28.5%, 21.2%, 18.2% and 24.2%, respectively, at 1.5 kW load, and were 19.8%, 44.8%, 39.7%, and 27.4%, respectively, at 3.0 kW load. The corresponding reductions by using W40 were 24.6%, 14.8%, 16.1%, and 19.8%, respectively, at 1.5 kW load and were 15.2%, 37.6%, 38.9% and 22.6%, respectively, at 3.0 kW (as shown in Fig. 2(a)). Interestingly, the LMW-PAHs had higher reduction fractions than MMW-PAHs and HMW-PAHs by using W20 and W40 at 1.5 kW, while MMW-PAHs and HMW-PAHs had much higher reduction fractions (2 times) than LMW-PAHs at 3.0 kW. For the emission of toxic equivalency, the reduction rates of PM-bound LMW-BaP_{eq}, MMW-BaP_{eq}, HMW-BaP_{eq} and ΣBaP_{eq} by using W20 were 30.0%, 49.6%, 33.7%, and 34.5%, respectively, at 1.5 kW, and 29.0%, 59.7%, 39.7%, and 40.5%, respectively, at 3.0 kW. The reductions using W40 were 18.5%, 32.6%, 28.3%, and 28.5%, respectively, at 1.5 kW, and 20.1%, 53.3%, 36.2% and 36.8%, respectively, at 3.0 kW (as shown in Fig. 2(b)). MMW-PAHs had a greater reduction factor of $PM_{2.5}$-bound BaP_{eq} (average = 48.8%) than HMW-PAHs (average = 34.5%) and LMW-PAHs (average = 24.4%), while MMW-PAHs had almost double

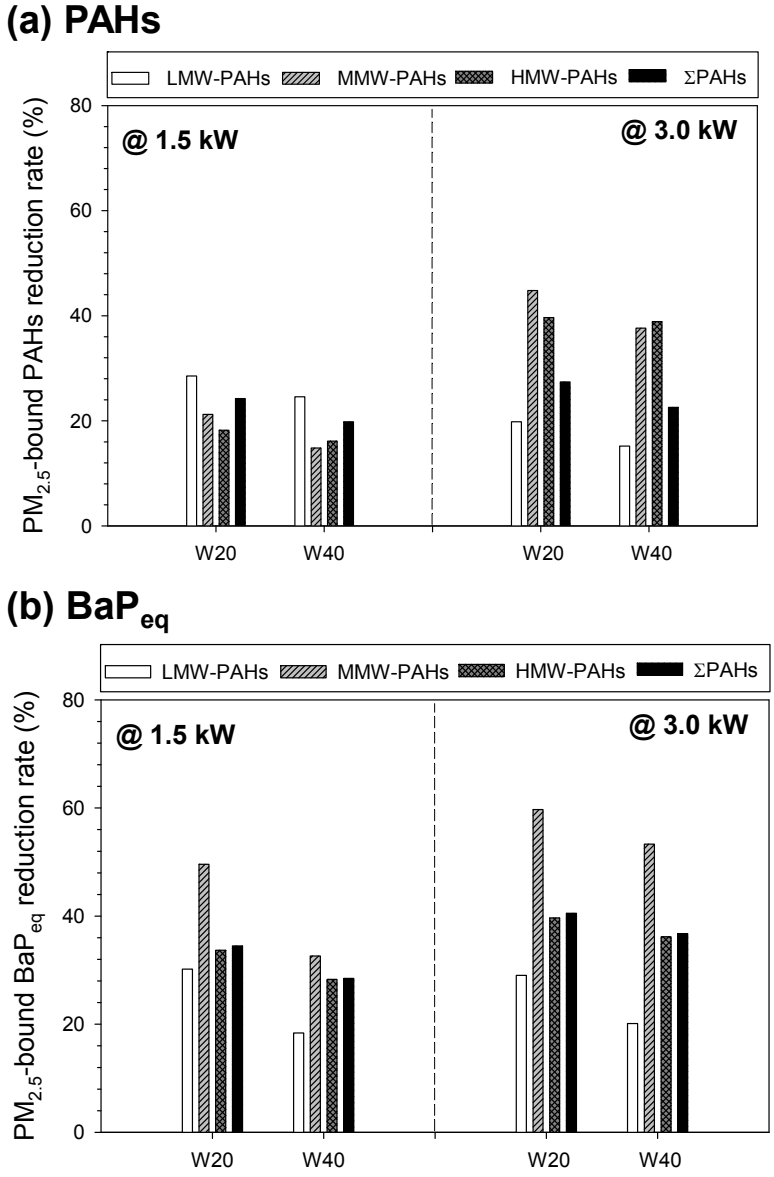

Fig. 2. Reduction fractions of $PM_{2.5}$-bound (a) PAHs and (b) BaP_{eq} using W20 and W40 vs. using D100 operated at two engine loads.

the BaP_{eq} reduction factor of LMW-PAHs. The $PM_{2.5}$-bound ΣPAHs and ΣBaP_{eq} had similar reduction mechanisms to PM. The oxygen contents were significantly higher in W20 and W40 than in D100 (n.d.), which led to increase in combustion efficiency and decreased PM mass concentration at the same engine load. Nevertheless, W20 showed the largest reduction rate among all fuel blends at both engine loads.

Fig. 1 show that the concentrations of ΣPAHs and ΣBaP_{eq} were higher at 3.0 kW than at 1.5 kW when using D100, W20, or W40, owing to higher fuel consumption at the higher engine load (Table 2), increasing PAH emissions. Compared with D100, for the mass concentrations, the decreased amounts of HMW-PAHs in total-PAH reduction on $PM_{2.5}$ in the exhausts were small (13.6–16.2%, average = 14.5%) when using W20 and W40; however, for the toxic equivalency (TEQ) concentrations, the percentages of HMW-BaP_{eq} decrements in total-BaP_{eq} reduction ranged from 90.7–93.4% (average = 91.7%). The reduction of ΣBaP_{eq} concentrations were mainly contributed by HMW-BaP_{eq}. The higher engine load (3.0 kW) had a higher FC and led to more ΣPAHs emission than the lower engine load (1.5 kW). Additionally, the reduction fractions of ΣBaP_{eq} concentration by using both biodiesel-diesel blends were higher at 3.0 kW than at 1.5 kW. Although the use of W20 and W40 slightly increased FC (0.9–6.5%, average = +2.8%) and BSFC (1.9–6.1%, average = +3.2%) as shown in Table 2, the $PM_{2.5}$-bound ΣPAHs and ΣBaP_{eq} were reduced by 19.8–24.7% (average = 22.8%) and 28.3–40.6% (average = 35.0%), respectively, indicating that the additions of biodiesel could effectively reduce the emission of hazardous organic compounds and their toxicity on $PM_{2.5}$ produced from DEEs.

Concentrations of $PM_{2.5}$-bound Metals

This study investigated the effects of D100, W20 and W40 on engine performance at different loading conditions (1.5 kW and 3.0 kW). Fig. 3 shows a description of 21 $PM_{2.5}$-bound metallic components (Na, Mg, Al, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, As, Sr, Mo, Cd, Sn, Sb, Ba and

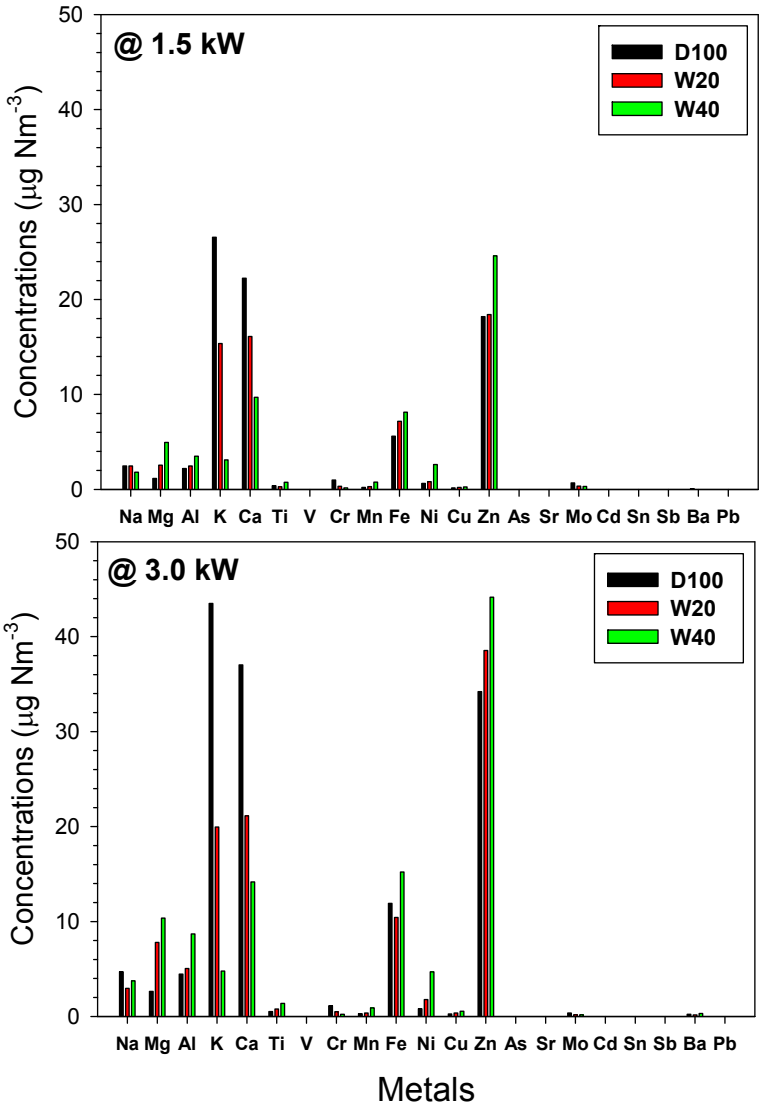

Fig. 3. Emissions of $PM_{2.5}$-bound metallic content using W20 and W40 vs. using D100 operated at two engine loads.

Pb). Fig. 4 illustrates the heavy metal contents in pure conventional diesel, WCO-biodiesel and engine oil. Among these metals, K had the highest concentration, followed by Ca, Zn, Fe, Na and Al, under both loading conditions fueled with D100. The 7 most abundant $PM_{2.5}$-bound metals when using W20 were in the order (descending) of K, Ca, Zn, Fe, Mg, Na and Al at 1.5 kW, and K, Ca, Zn, Fe, Mg, Al and Na at 3.0 kW load. For using W40, the rankings were Zn, Ca, Fe, Mg, Al, K, Ni at 1.5 kW, and Zn, Fe, Ca, Mg, Al, K and Ni at 3.0 kW load. The Σmetal concentrations declined with rising percentage of biodiesel added to the blends of W20 (–20.3%) and W40 (–24.4%) in comparison to that of conventional fuel (D100). Biodiesel can lower the $PM_{2.5}$ emissions from engine combustion, as well as effectively improving the lubricity of biodiesel-diesel blends, and impeding the metallic emission due to wearing between cylinder block, piston and piston ring (Agarwal, 2007). Additionally, the lower metallic contents in pure WCO-biodiesel than pure fossil diesel could directly reduce the $PM_{2.5}$-bound metallic emissions (Fig. 4). The dominant metallic components were Na, Mg, Al, K and Ca in both D100 and W100, while Na, Mg, K, Ca, Fe and Zn dominated in L100. The major components of the metallic profiles in $PM_{2.5}$ (Fig. 3) and fuels (Fig. 4), were Na, Mg, Al, K, Ca, Fe and Zn at both engine loads, showing that the metallic composition for the $PM_{2.5}$ was related to the oil composition.

The above inference was further examined by comparing the metallic distribution patterns on relative concentrations normalized by upper continental crust (UCC; data from Taylor and McLennan, 1985) (Weckwerth, 2001). In Fig. 5, the metallic compositions in $PM_{2.5}$ vs. UCC with the fuel blends of D100, W20 and W40 under two engine loads (1.5 kW and 3.0 kW) are compared. The UCC values of $PM_{2.5}$-bound Na, Mg, Al, K, Ca, Ti, V, Mn, Fe, Sr and Ba were all less than 0.1, while those of Cr, Ni, Cu, Cd, Sb, and Pb were in the range 0.1–10. Additionally, the UCC values of $PM_{2.5}$-bound Zn and Mo were greater than 10. The UCC values of $PM_{2.5}$-bound K and Ca in exhaust by using W20 were close to those using D100, indicating that these metals were probably from the fuel (K) and engine oil (Ca) contents. All three testing fuels (D100, W20 and W40) had similar UCC values of $PM_{2.5}$-bound Na, Al, V, Fe, Zn, Sr, Mo, Cd, Ba and Pb, indicating a high correlation between metallic emissions and wearing of engine parts instead of fuel chemical compositions. Singh *et al.* (2006) indicated that wearing dust could remain in lubricant oil, and become sources of Fe, Cu, Cr, Al, Ni, Zn, Mg, Pb, and Mn emissions.

Emission Factor of $PM_{2.5}$ and Toxicity in the Exhaust of Diesel Engine

Table 3 shows the emission factors (EFs) of $PM_{2.5}$, metallic composition of $PM_{2.5}$, total PAHs and BaP_{eq} in terms of unit fuel consumption (EF_{FC}) and power generation (EF_P). Compared to D100, the EF_{FC} reductions of $PM_{2.5}$ for using W20 and W40 under 1.5 kW engine load were 15.8% and –6.66%, respectively, while the EF_P reduction values were 13.8% and –9.43%, respectively. The EF_{FC} reductions of $PM_{2.5}$-bound metals were 16.4% and 9.68%, respectively, and the EF_P reduction values were 18.1% and 12.4%, respectively. With regard to the $PM_{2.5}$-bound ΣPAHs, the EF_{FC} reductions when using W20 and W40 were 25.4% and 0.57%, respectively, while the EF_P reduction values were 23.6% and –2.30%, respectively. The EF_{FC} reductions of $PM_{2.5}$-bound ΣBaP_{eq} by using W20 and W40 were 35.2% and 11.1%, respectively, while the EF_P reduction values were 34.1% and 8.54%, respectively. Similar or even better EF reductions were also found by using W20 and W40 under 3.0 kW engine load. These experimental results indicate significant reductions of $PM_{2.5}$, $PM_{2.5}$-bound Σmetals, ΣPAHs and ΣBaP_{eq} when using the WCO-biodiesel blends (i.e., W20 and W40). At 1.5 kW, greater reduction was observed for using W20 than for using W40; the

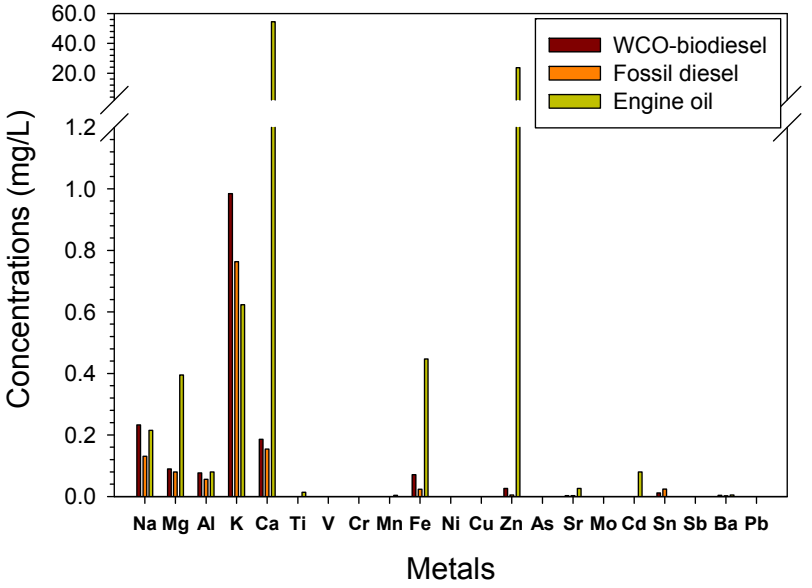

Fig. 4. Metallic compositions in fossil diesel, WCO-biodiesel and engine oil.

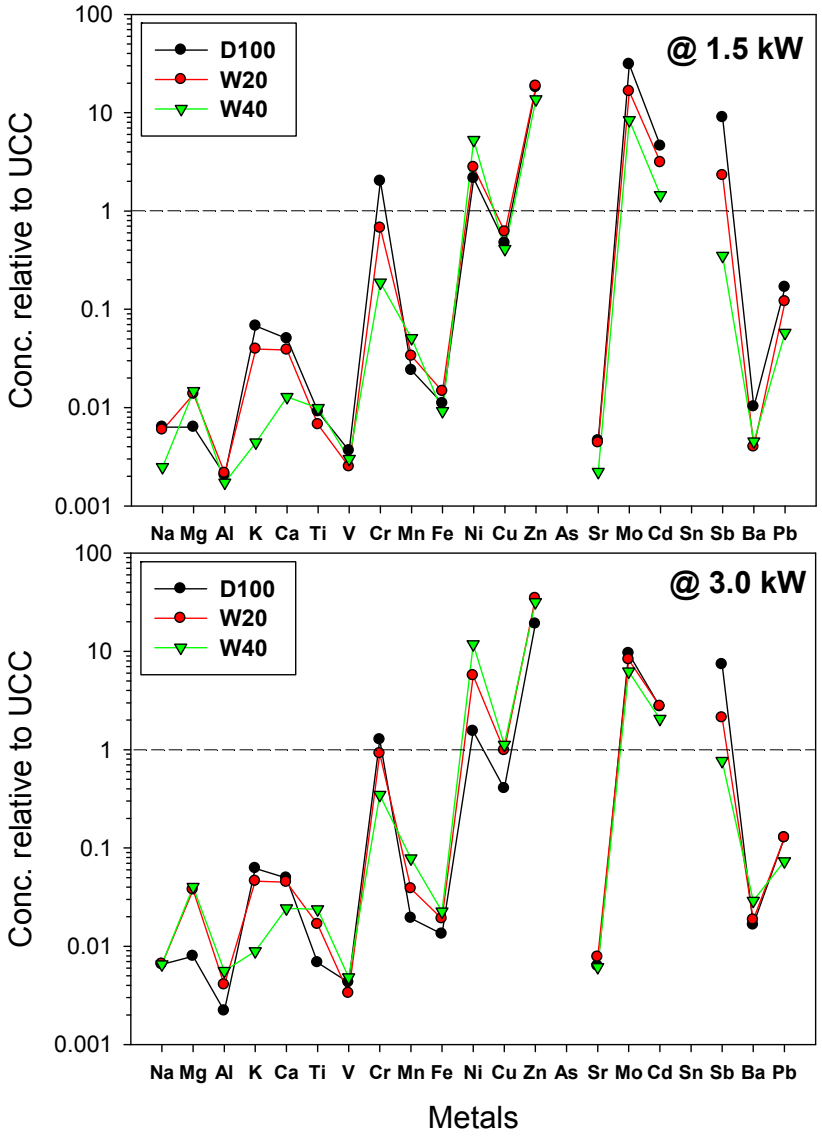

Fig. 5. Comparison between metallic content of $PM_{2.5}$ and upper continental crust.

Table 3. Emission factors of $PM_{2.5}$, $PM_{2.5}$-bound metals, PAHs, and BaP_{eq}.

Emission factors	1.5 kW			3.0 kW		
	D100	W20	W40	D100	W20	W40
Based on fuel consumption						
$PM_{2.5}$ (mg L^{-1}) (N = 22)	1490 ± 197	1250 ± 150	1600 ± 244	2680 ± 566	2220 ± 358	2080 ± 297
$PM_{2.5}$-bound Σmetals (mg L^{-1}) (N = 2)	7.19	6.01	6.49	12.1	9.89	9.17
$PM_{2.5}$-bound ΣPAHs (μg L^{-1}) (N = 1*)	2.78	2.08	2.77	9.04	7.06	6.82
$PM_{2.5}$-bound ΣBaP_{eq} (μg-TEQ L^{-1}) (N = 1*)	0.244	0.158	0.217	0.390	0.250	0.240
Based on power generation						
$PM_{2.5}$ (mg kWh^{-1}) (N = 20)	1010 ± 127	866 ± 99	1110 ± 154	1450 ± 304	1220 ± 178	1190 ± 160
$PM_{2.5}$-bound Σmetals (mg kWh^{-1}) (N = 2)	5.33	4.36	4.67	6.66	5.76	5.39
$PM_{2.5}$-bound ΣPAHs (μg kWh^{-1}) (N = 1*)	1.87	1.43	1.91	4.89	3.89	3.91
$PM_{2.5}$-bound ΣBaP_{eq} (μg-TEQ kWh^{-1}) (N = 1*)	0.164	0.108	0.150	0.211	0.137	0.138

* obtained by 20 filter samples.

opposite trend was observed at 3.0 kW, reflecting better combustion under the high engine load with oxygenated fuel additives. Previous research also indicates that the fuel blends of biodiesel could dilute the aromatic compounds from fossil fuel more easily, which not only oxidized the PAH precursor, but also expressed more complete combustion,

further decreasing toxicity in the exhaust of diesel engine (Chang *et al.*, 2014; Chen *et al.*, 2017; Lin *et al.*, 2017).

Interestingly, the 3.0 kW load had higher EF values of $PM_{2.5}$, Σmetals, ΣPAHs, and ΣBaP_{eq} than the 1.5 kW load irrespective of fuel blends (Table 3). This tendency was different from other studies. It is well known that a diesel engine has a better combustion efficiency and fuel utilization under a higher load, reducing the emission factor for total PM (Chang *et al.*, 2013, 2014). Although the engine operated at the high load helped reduce the total PM in the exhausts, the particulate matter might not be completely destroyed and removed in this process of destruction. Instead, some particles turned into finer particles, and continued to exist in the exhaust gas, increasing the amount of fine particles in the exhaust (Yoon *et al.*, 2011). Therefore, we hypothesize that the increasing amounts of fine particles in the exhausts raised the surface area of the particles, and promoted the condensation of gas-phase PAHs on the particles, thus increasing the $PM_{2.5}$-bound PAHs and BaP_{eq} emission factors at the high engine load in this study. Unlike organic matter, the metallic components (from fuels, engine oil, and engine parts wear) in the exhaust could not be easily oxidized and removed under the general engine combustion. Moreover, this greater surface area also contributed to the condensation of metallic vapor, so the emission factors of the $PM_{2.5}$-bound metals increased as the engine load rose.

CONCLUSIONS

- Of the three tested fuels, using W20 generated the least $PM_{2.5}$, $PM_{2.5}$-bound ΣPAHs, and ΣBaP_{eq}, especially when the engine was operated at a 3.0 kW load.
- Biodiesel-diesel blends instead of D100, the HMW-BaP_{eq} decreased by 90.7–93.4% (average = 91.7%) even though, of all the PAHs, the HMW ones were reduced the least (13.6–16.2%, average = 14.5%) in terms of mass concentration. The decrease in ΣBaP_{eq} was mainly contributed by the HMW-BaP_{eq}.
- Although using W20 and W40 slightly increased the FC (3.0% on average) and BSFC (3.1% on average), the $PM_{2.5}$-bound ΣPAHs and ΣBaP_{eq} decreased by 19.8–24.7% (22.8% on average) and 28.3–40.6% (35.0% on average), respectively, indicating that the addition of biodiesel can effectively reduce hazardous organic compounds in DEE and their associated toxicity.
- At both the 1.5 kW and 3.0 kW engine loads, the least Σmetals were generated when using W40, followed by W20 and D100. Certain metals, however, were emitted at higher concentrations by the blended fuels than the diesel fuel, which was caused by larger mass fractions for these components in the W fuels.
- The UCC values for $PM_{2.5}$-bound K and Ca in the exhaust when using W20 and D100 were close, indicating that these metals possibly originated in the fuel (K) and the engine oil (Ca). All three tested fuels (D100, W20, and W40) exhibited similar UCC values for $PM_{2.5}$-bound Na, Al, V, Fe, Zn, Sr, Mo, Cd, Ba, and Pb; thus, engine wear, rather than fuel composition, was highly correlated with metallic emissions.
- Substituting D100 with W20 and W40 can significantly lower the emission factors for $PM_{2.5}$, $PM_{2.5}$-bound ΣPAHs and Σmetals, and ΣBaP_{eq} at high engine loads (e.g., 3.0 kW).

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