Emissions of Polycyclic Aromatic Hydrocarbons and Particle-Bound Metals from a Diesel Engine Generator Fueled with Waste Cooking Oil-Based Biodiesel Blends

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ABSTRACT

This study investigates the emission of a heavy-duty diesel engine generator fueled with waste cooking oil (WCO)-based biodiesel blends (W) and operated at 1.5 and 3.0 kW loads. A brand of pure fossil diesel was adopted as the base fuel, with 20% and 40% WCO-based biodiesel added into the based fuel to form W20 and W40 blends, respectively. The emission characteristics of PM, metals and PAHs were analyzed. Experimental results indicate that alternative WCO-based fuels had slightly higher fuel consumption rates (FCR) and brake specific fuel consumptions (BSFC) than conventional diesel (0.6–4.1% for FCR and 1.0–7.6% for BSFC), and similar engine thermal efficiency. The PM emissions reductions when using W20 and W40 were 19% and 6.5%, respectively, at 1.5 kW, and 27% and 19%, respectively, at 3.0 kW. The emissions of particle-bound metals were 13.6–13.8% lower when using W20 than using conventional diesel, but 12.0–12.3% higher when using W40. The metal contents of PM rose with the addition of WCO-based biodiesel. The metal elements of PM were dominated (> 90% mass) by Na, Mg, Al, K, Ca, Fe and Zn, while the major trace metals were Mn, Cu, Sr and Pb. The use of WCO-based biodiesel blends reduced the emissions of total-PAHs (44.0% in average) and total-BaPeq (80.2% in average). The mass reductions of MMW- and HMW-PAHs using W20 and W40 were more significant at 3.0 kW than at 1.5 kW, while the reduction of LMW-PAHs was greater at 1.5 kW than at 3.0 kW. Thus, the reduction in total-BaPeq was greater at the higher engine load. Accordingly, we conclude that the WCO-based biodiesel is a potential candidate of cleaner alternative energy sources.

Keywords: Polycyclic aromatic hydrocarbons; Particle bound metals; Waste cooking oil; Biodiesel; Diesel engine generator.

INTRODUCTION

Diesel engines are widely adopted in large-scale equipment, ships and buses due to their greater dependability, higher torque output and lower fuel costs than gasoline engines. However, diesel engine emissions (e.g., particulate matter (PM), nitrogen oxides (NOx), hydrocarbon (HC), carbon monoxide (CO), and toxic air pollutants) cause serious environmental pollution, and are harmful to human health. Diesel particulate matter (DPM) is a component of diesel exhaust produced mainly by incomplete combustion of carbon particles (Alves et al., 2015; Cheng et al., 2015), soot, trace metals (Lin et al., 2005; Haseeb et al., 2011) and toxic organic pollutants (Tsai et al., 2016), such as polycyclic aromatic hydrocarbons (PAHs) (Jin et al., 2014), polychlorinated dibenzo-p-dioxins (PCDDs), and polychlorinated dibenzofurans (PCDFs) (Mwangi et al., 2015a), polychlorinated biphenyls (PCBs), polybrominated dibenzo-p-dioxins (PBDDs), polybrominated dibenzofurans (PBDDs) and polybrominated diphenyl ethers (PBDEs) (Chang et al., 2014). Studies have shown that exposure to diesel exhaust endanger human health by increasing the risk of cardiovascular and respiratory conditions, as well as lung cancer (Benbrahim-Tallaa et al., 2012; Tang et al., 2016). Diesel engines are commonly known as a major source of ambient PAH emissions in some urban areas and cities (Lin et al., 2008; Shi et al., 2009; Cheruuiyot et al., 2015). Therefore, reducing diesel engine pollution emissions is an important issue for study, and is of concern in many countries. The use of biodiesel as fuel can easily reduce diesel engine emissions.

Biodiesel is one of the most promising and clean alternative fuels that are generated from renewable resources, and can be employed directly in diesel engines without any
modification owing to its biodegradability, high oxygen content (~10 wt%) and high cetane number (Kameda et al., 2007; Refaat, 2009). Many studies have confirmed that the use of an appropriate proportion (~20 vol%) of biodiesel can lower the diesel engine emissions of PM, gas pollutants (HC, CO and CO₂), PAHs and other pollutants (McCormick, 2007; Wu et al., 2009; Lin et al., 2010; Tsai et al., 2010; Lin et al., 2012). The conflict between food and bioenergy can be avoided by converting non-edible greases (e.g., waste cooking oil, WCO) into biofuels, and is presently feasible. However, some poor-quality aluminum, copper or stainless cooking utensils with may result in the presence of toxic metallic elements (Ni, Cr, Fe) (Kamerud et al., 2013; Bassioni et al., 2015) in the recycled WCO. According to Health Canada, cooking a meal in an aluminum pan can add about 1–2 mg aluminium (the WHO acceptable daily intake is 50 mg day⁻¹) to food (Diamond, 2005). Bassioni et al. (2012) concluded that aluminium foil is not appropriate for cooking, especially with acidic food. Excessive consumption of food baked with aluminium foil may carry a serious health risk. Therefore, the emission of particulate toxic metals from the combustion of WCO-biodiesels needs to be investigated.

Several recent studies have found that as well as PAHs, diesel engines may produce other toxic organic compounds (e.g., PCDD/Fs, PCBs and PBDEs) that are harmful to humans in the fuel oil combustion process (precursor or de novo reaction) (Laroo et al., 2011; Pekarek et al., 2001; Chang et al., 2014; Tsai et al., 2016). Investigations on the use of biodiesels as alternative fuels of diesel engines generally focus on the emission reductions of traditional gaseous pollutants, total PM, carbon species and PAHs (Dorado et al., 2003; Agarwal and Agarwal, 2007; Cheng et al., 2015; Mwangi et al., 2015a). The emission of particulate toxic metals from non-road diesel generators fuelled with WCO-biodiesel blends has seldom been explored. This work investigated the emissions of 21 particle-bound metals (Na, Mg, Al, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, As, Sr, Mo, Cd, Sn, Sb, Ba and Pb) and 16 US-EPA PAH (particle- and gas-phase) compounds from a small generator fuelled with WCO-biodiesel blends under 1.5 and 3.0 kW loads. Additionally, fuel consumption and energy efficiency using different WCO-biodiesel blends were also examined at various generator bearing power loads.

**MATERIALS AND METHODS**

**Sampling Methods**

This study adopted three biodiesel-diesel blends with different mixing ratios of WCO-biodiesel to premium diesel: premium diesel fuel (D100), W20 (20 vol% WCO-biodiesel + 80 vol% D100) and W40. Different blended fuels were tested in a generator at a stable energy output (110 V/60 Hz, 1800 rpm) under loads of 1.5 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), manufactured by YANMAR Ltd., Japan (Model: TF110E &YSG-5SEN). The generator had one phase/two wires, an output frequency of 50/60 Hz and a maximum output power of 4 kW.

An auto-detector flow sampling system, equipped with a quartz fiber filter (2500 QAT-UP, 47 mm; Pall Corporation, New York, USA), was installed downstream of the diesel generator exhaust to measure the emitted concentrations of particle-bound PAH samples. Gas-phase PAHs emissions were accumulated using two connected glass cartridges filled with XAD-2 resin. Additionally, the particle-bound metal samples were collected by a Teflon filter (47 mm; 2.0 µm; Pall Corporation) under the same operating parameters. The experiments were performed three times (each sampling time = 30 min) for each combination of parameters. 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. Further details of the fuel compositions and sampling programs can be found elsewhere (Tsai et al., 2015b, 2016).

**PAH Analysis**

The gas-/particle-phase PAH samples accumulated from the diesel-generator exhausts were extracted using 1:1 (v/v) n-hexane/dichloromethane for 24 hr. The extracts were then concentrated, cleaned by a silica column of ~27 cm silica gel particles (size range = 0.04–0.063 mm) under a layer of anhydrous Na₂SO₄ (~1 cm high) and above a support of glass fibers, and reconstituted 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; model: GC 6890N/HP 5973). The limits of detection (LODs) 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).

According to the molecular weights of 16 PAH compounds, the PAHs were divided into three categories: low molecular weight (LMW)-, medium molecular weight (MMW)-, and high molecular weight (HMW)-PAHs. The LMW-PAHs included 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 the group of benzo[h]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo(a)pyrene (BaP), dibenzo[a,h]anthracene (DBA), indeno[1,2,3-cd]pyrene (IND), and benzo[g,h,i]perylene (BghiP). The carcinogenic factors of the identified PAHs were calculated in terms of BaPequiv from the toxic equivalence factors (TEFs) of these compounds (PAH concentration × TEF). In this study, the TEFs that were specified by Nisbet and LaGoy (1992) were used. The carcinogenic potency of Total-PAHs (Total-BaPeq) was evaluated by summing the BaPequiv concentrations of individual PAH compounds.

**Metal Analysis**

In this study, the particle-bound metal samples gathered from Teflon filter paper were extracted by nitric acid solution, and analyzed with inductively coupled plasma mass spectrometry (ICP-MS). The extraction and analysis steps were as follows. Each Teflon filter paper was carefully...
cut into small pieces. Each piece was then placed in a screw-cap 50mL graphite digestive tube. A 20 mL 10% HNO₃ solution was then added into each tube, and the screw cap was tightened. The locked graphite digestive tubes were extracted for 120 minutes with an ultrasonic bath, and then heated in a block heater at 80–85°C for 30 minutes. After cooling, each digested solution was filtered by a cellulose acetate filter (pore size 0.45 µm) and diluted to a volume of 25 mL using 10% HNO₃ for the analysis of 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 inductively coupled plasma-mass spectrometry (ICP-MS) (Agilent 7500a ICP-MS; Agilent Technologies Inc.). The calibration was performed using multi-element (metal) standards (certified reference materials (CRMs); Spex, Metuchen, USA) in a 1% (v/v) HNO₃ solution. Every tenth sample was spiked using the liquid standards that contained known amounts of the metal elements that were analyzed. The CRMs were also used as quality control standards.

For the analyses of elements using ICP-MS measurements, the method detection limits (MDL) 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, 0.09, 0.02, 3.15, 0.12, 0.51 and 0.06 µg L⁻¹, respectively. The recovery efficiencies of 21 metals were 95.2–113.8% (average = 106.2%). Both field and laboratory blank samples were prepared and analyzed for each sampling and analysis. All data were corrected according to blanks.

RESULTS AND DISCUSSION

Engine Performance

The engine performance is the first consideration when developing new alternative fuels, because conventional engines and their related apparatus are generally only run with conventional diesel fuel. Therefore, this work reports the fuel consumption rate (FCR), brake specific fuel consumption (BSFC), and brake thermal efficiency (BTE). The FCRs were measured by a scaled cylinder, and evaluated as described in the experimental section. The FCRs using D100, W20, and W40 were 1.07 ± 0.02, 1.08 ± 0.01, and 1.11 ± 0.013 L hr⁻¹, respectively (Table 1). The FCR levels using W20 and W40 were 0.60–1.69% and 3.95–4.13% higher than that of D100, respectively. To eliminate the effect of unstable electricity generation among the tests of various fuel blends, the BSFCs (L kWh⁻¹) were then determined by Eq. (1) as follows.

$$\text{BSFC} (\text{L kWh}^{-1}) = \frac{\text{FCR}}{P_e} \times 100\%$$  \hspace{1cm} (1)

where FCR denotes the fuel consumption rate (L h⁻¹), and $P_e$ represents the averaging electricity power output (kW) during each sampling period.

The BSFCs using D100 were 0.714 ± 0.012 L kWh⁻¹ and 0.495 ± 0.019 L kWh⁻¹ at 1.5 and 3.0 kW engine load, respectively, and rose by 1.01–2.38% and 3.64–7.56% when using W20 and W40, respectively (Table 1). The higher additive ratio of WCO-based biodiesel might further reduce the heating value of the fuel blend, increasing the BSFC. However, either FCR or BSFC could directly measure the combustion efficiency or emission potential, since they had different input energies (LHVs of fuels). Therefore, this study represents the overall energy transfer efficiencies for using different fuel blends by the BTE (Eq. (2)).

$$\text{BTE} (%) = \frac{3.6}{\text{BSFC} \times d_f \times \text{LHV}_f} \times 100\%$$  \hspace{1cm} (2)

where $d_f$ and $\text{LHV}_f$ represent the density (kg L⁻¹) and lower heating value (MJ kg⁻¹) of each fuel blend, respectively.

The BTEs fell when D100 (14.1% ± 0.2%) was replaced by W20 (13.9% ± 0.1%) and W40 (13.5% ± 0.1%), representing 1.42% and 4.26% reduction, respectively, at 1.5 kW engine load. Additionally, the differences of BTEs among the three diesel blends were all below 0.01%, while more fuel were injected during each stroke at 3.0 kW engine load. Notably, the reductions in BTE when replacing D100 with W40 were smaller than the increases in BSFC, revealing that the oxygen and non-aromatic compounds in WCO-based biodiesel blends partially balance the lower heating value of biodiesel blends. Some previous studies even indicate that the oxygenated additives in diesel could improve the thermal efficiency of engines and reduce the BSFC (Yoshimoto et al., 1999; Lin et al., 2006; Lin et al., 2010; Mwangi et al., 2015a; Tsai et al., 2015a). However, the higher viscosity was the second drawback of WCO-based biofuel for energy performance, since the more viscous fuel pray would lower the break down and vaporization processes before the combustion and eventually led to more incompletely combustion and consume fore fuels. Fortunately, both W20 had W40 had a similar overall energy performance to the original diesel fuel. The emissions of regulated and toxic pollutants thus became the major consideration of the alternatives.

| Table 1. Fuel consumption and engine performance using WCO-based biodiesel blends at various loads. |
|---------------------------------------------------------------|
| **Fuel Performances** | **Loads** | **D100** | **W20** | **W40** |
|-----------------------|-----------|----------|---------|---------|
| **FCR (L hr⁻¹)**      | 1.5 kW    | 1.07 ± 0.02 | 1.08 ± 0.01 | 1.11 ± 0.01 |
|                       | (n = 3)   |           | +1.69%   | +4.13%   |
|                       | 3.0 kW    | 1.49 ± 0.04 | 1.50 ± 0.02 | 1.55 ± 0.01 |
|                       | (n = 3)   |           | +0.60%   | +3.95%   |
| **BSFC (L kWh⁻¹)**    | 1.5 kW    | 0.714 ± 0.012 | 0.731 ± 0.005 | 0.768 ± 0.007 |
|                       | (n = 3)   |           | +2.38%   | +7.56%   |
|                       | 3.0 kW    | 0.495 ± 0.019 | 0.500 ± 0.009 | 0.513 ± 0.006 |
|                       | (n = 3)   |           | +1.01%   | +3.64%   |
| **BTE (%)**           | 1.5 kW    | 14.1% ± 0.2% | 13.9% ± 0.1% | 13.5% ± 0.1% |
|                       | (n = 3)   |           | −1.42%   | −4.26%   |
|                       | 3.0 kW    | 20.3% ± 0.8% | 20.3% ± 0.4% | between ± 0.01% |

D: diesel; W: waste cooking oil-based biodiesel.
PM Emissions

The PM concentrations in engine exhaust ranged from 60.2–69.1 mg Nm\(^{-3}\), 49.5–54.8 mg Nm\(^{-3}\), and 58.4–62.7 mg Nm\(^{-3}\), and averaged 64.9 ± 4.47 mg Nm\(^{-3}\), 52.3 ± 2.66 mg Nm\(^{-3}\), and 60.7 ± 2.21 mg Nm\(^{-3}\) using D100, W20 and W40, respectively, at 1.5 kW (as shown in Fig. 1). Additionally, the high PM levels were found to be 124–133 mg Nm\(^{-3}\) (average: 129 ± 4.52 mg Nm\(^{-3}\)), 85.3–104 mg Nm\(^{-3}\) (average: 94.7 ± 9.17 mg Nm\(^{-3}\)) and 98.0–111 mg Nm\(^{-3}\) (average: 104 ± 6.40 mg Nm\(^{-3}\)) using D100, W20 and W40, respectively, at 3.0 kW. The above results show significant PM emission reductions of 19% and 6.5% at 1.5 kW, and 27% and 19% at 3.0 kW, using W20 and W40, respectively. These emission improvements could result from the higher fuel-oxygen content for WCO-based biodiesel (11.8%) compared to D100 (<0.2%), leading to more complete combustion (Lin et al., 2006; Lin et al., 2010; Chang et al., 2014; Tsai et al., 2015a, 2016). The nanoparticles emission concentration and their total area were also reported to be reduced by oxygenated fuel additives (Saxena and Maurya, 2016). Yang et al. (2016) further indicated that the use of oxygenated diesel blends could affect the nanostructure and pyrolysis of PM, which was easier to oxidize and advantageous for diesel particulate filter regeneration. Additionally, as biodiesel has a higher cetane index than fossil diesel, it shortens the ignition delay, leading to an earlier start of combustion reaction (Musculus, 2002; Lin and Lin, 2011). However, biodiesel had a higher viscosity than D100, inhibiting the nebulization of fuel spray. Therefore, the use of biodiesel reduces the PM emission, with W20 achieving the lowest value and increased again with W40, which has higher viscosity and worse spray combustion than W20 in this investigation. Conversely, a higher engine operation load increased the PM emission concentration, which could be attributed to more fuel mass being injected into the cylinder, and then combusted to produce more products (PM). These rises could be partially inhibited by using W20 and W40, as shown in Fig. 1.

Particle-Bound Metals

The concentrations of total particle-bound metals with D100 were 616 ± 43.2 µg Nm\(^{-3}\) to 2,104 ± 54.5 µg Nm\(^{-3}\) in the engine exhaust, and 13.6–13.8% lower at 531 ± 27.8 µg Nm\(^{-3}\) to 1,817 ± 45.0 µg Nm\(^{-3}\) when using W20 (Table 2). This reduction of metal emission could be attributed to the PM emission reductions, since W20 had a higher fuel oxygen content, while its viscosity was not significantly increased to inhibit the vaporization of fuel spray. However, the metal emission concentrations increased (by 12.0–12.3%) (692 ± 50.7 to 2356 ± 385 µg Nm\(^{-3}\)) when the generator was fuelled with W40, probably because the crude waste cooking oils had a higher metal content than the regular diesel (leading to 7.36–17.7% and 20.0–39.0% higher metal content in PM by using W20 and W40 (Table 2), respectively, than using D100). Therefore, W40 had higher overall particle-bound metal emissions than D100, but higher PM emission concentration.

The metal elements in the PM sample were dominated (over 90% mass of total metals) by Na, Mg, Al, K, Ca, Fe, and Zn. The major contents of the remaining trace metals were Mn, Cu, Sr and Pb (Fig. 2). Several previous studies support our findings. Kerminen et al. (1997) collected the particles emitted from a lab-diesel engine, and found similar results to this study (dominant metals: Na, Mg, Al, K, Ca,
Fe and Zn). Norbeck et al. (1998) also concluded that the major metals on diesel-PM were Zn, Fe, Ca, Pb and Ba, contributing 0.3% of the total PM mass. Yang et al. (1998) also reported that the major metals in PM from diesel exhaust were Fe, Al, Ca, Na, Cr, Ba, Ni, Mg and K, while the Fe and Al contributed 77 mg g$^{-1}$ and 48 mg g$^{-1}$ in PM. The trace metals Mn, Zn, Cu, Pb, Cd, V and Sr were mainly contributed by Mn (5.2 mg g$^{-1}$), Zn (3.7 mg g$^{-1}$), Cu (2.4 mg g$^{-1}$) and Pb (1.8 mg g$^{-1}$). Additionally, Valavanidis et al. (2006) found that diesel vehicles emitted much greater Cu, Pb, V, Cr, and Zn content than gas engines.

The above metal compositions in the fine particle from diesel engine emissions could be associated with the lubricant contents (Zn, Ca and Mg), additives of catalyst and the friction products of engine units (Fe, Ni, Cu, Cr and Sd) (Pacyna, 1996; Sappok et al., 2012). Specifically, Fe emission could be from the friction of cylinder liners, piston rings, valves and crank shafts (Haseeb et al., 2011). Cr was emitted from the wear of compression rings, gears and cam bearings (Agarwal and Dhar, 2010). Pb, Al and Cu, could be from the coating material (Agarwal and Dhar, 2010), wear of pistons (Wander et al., 2011) and wear of bearings (Haseeb et al., 2011), respectively. Hu et al. (2009) and Liati et al. (2015) indicated that the vehicle lubricant contents could cause Ca, Zn, Mg, P and B emissions.

The atmospheric metal pollutants were emitted from natural and anthropogenic sources, transported by air movement and deposited by gravity, or washed out by rainfall to the near-ground environment. Wang et al. (2003) found that the overall annual emissions of crustal metallic elements (Al, Ca, Fe, Mg and Si) and non-natural elements (Ag, Ba, Cd, Cr, Cu, Mn, Mo, Ni, Pb, Sr, Ti, V, Zn, As and Hg) from diesel vehicles were 269 ton yr$^{-1}$ and 58.7 ton yr$^{-1}$, respectively. These annual emissions were significantly higher than those from coal power plants (90.1 ton yr$^{-1}$ and 1.66 ton yr$^{-1}$), coke production plants (60.5 ton yr$^{-1}$ and 3.74 ton yr$^{-1}$) and electric arc furnaces (2.06 ton yr$^{-1}$ and 0.173 ton yr$^{-1}$).
PAH Emissions and Toxicities in the Exhaust of Diesel Engine

Figs. 3(A) and 3(B) show the total-PAHs and BaP toxicity equivalent (BaPeq) concentrations of WCO-based biodiesel blends. The total-PAH mass concentrations for using W20 and W40 were 152–221 µg Nm$^{-3}$ and 167–228 µg Nm$^{-3}$, respectively, at two engine loads, representing about 45.6–46.0% and 40.6–43.8% reductions (as shown in Fig. 4(A)), respectively, in comparison to those for using D100. At the two engine loads, the total-BaPeq concentrations for using W20 and W40 were 0.418–0.451 µg BaPeq Nm$^{-3}$ and 0.462–0.534 µg BaPeq Nm$^{-3}$, respectively (about 74.9–88.5% and 70.3–87.3% reductions when compared with using D100) (Fig. 4(B)). This phenomenon was also likely associated with more complete combustion provided by fuel oxygen in W20 and W40, and the fair viscosity of W20 to the fuel injection system. The above findings are supported by some researches (Chang et al., 2014; Mwangi et al., 2015a; Tsai et al., 2015a, 2016). The emissions of total-PAHs and total-BaPeq were higher at the higher load (3.0 kW) than the lower one (1.5 kW) by using all fuel blends, because the PAH contents in fuels were positively correlated with the FCR and BSFC. Since, the reduction of total-PAH concentrations was more significant at 1.5 kW (40.6–46.0%), while the total-BaPeq levels decreased more obviously at 3.0 kW (87.3–88.5%). This opposite trend contributes to the different compositions of PAH congeners. However, compared with W20, W40 had more PAH emission from the generator was observed at two loads. This phenomenon is possibly associated with W40 had a higher viscosity than W20, reducing the nebulization of fuel spray, which adversely affects fuel combustion and also could result in resynthesis of PAHs during combustion (Lin et al., 2006; Tsai et al., 2010).

Figs. 5 and 6 illustrate the mass and BaP eq concentration of PAH congeners at 1.5 and 3.0 kW loads, respectively. The congener mass and BaP eq fractions (profiles) were computed from the mass and BaP eq of individual PAH congener divided by total-PAH and total-BaP eq, respectively (Figs. 7 and 8 in percentages). The mass fractions of LMW-PAHs (Nap, AcPy, Acp, Flu, PA, and Ant) were 86–94% at two loads and dominated by 2-ring Nap (62.7–72.9%; average: 67.1%), 3-ring PA (5.9–8.9%; average: 7.7%), and Acp (3.9–7.5%; average: 5.5%); while the mass contribution of 5-ring BaP, which has much higher toxicity, was only 0.2% on average. The BaPeq had different congener profiles from the mass. The most contributive congener in toxicity was BaP (16.9–70.9%; average: 36.1%), followed by Nap (7.3–40.3%; average: 22.8%) and BbF (9.4–13.1%; average: 11.4%).

For the congener reductions by using WCO-based biodiesel blends, the greatest mass reductions occurred in Nap (24–30%; average: 27%), while the most toxic BaP was reduced slightly (0.3–0.6%; average: 0.5%). Among the investigated PAH species, BaP exhibited the greatest BaP eq reduction, ranging 49–69% (average 59%), while Nap only reduced the BaP eq level by 2.7–4.7% (3.7% in average). To further clarify the reason of BaP eq reduction by using W20 and W40, the mass and BaP eq concentrations of congeners with similar ring numbers and molecular weights were assigned to three groups, namely low-molecular-weight PAHs (LMW-PAHs), medium-molecular-weight PAHs (MMW-PAHs) and high-molecular-weight-PAHs (HMW-PAHs). The order of mass contribution in term of different molecular weight-PAHs was LMW-PAHs > MMW-PAHs > HMW-PAHs, while the order of BaP eq contribution was HMW- > LMW- > MMW-PAHs. Furthermore, the mass reductions of MMW- and HMW-PAHs by using W20 and W40 were more significant at 3.0 kW than at 1.5 kW, while the reduction of LMW-PAHs was greater at 1.5 kW than at 3.0 kW. Since the MMW- and HMW-PAHs had much higher toxicities than LMW-PAHs, the total-BaP eq reductions were then along with the tendencies of MMW- and HMW-PAHs and leaded to the aforementioned opposite trends to mass reduction in term of engine loads. Previous studies indicated that the use of biodiesels not only dilutes the aromatic compounds released from the fossil fuel and oxidizes the PAH precursor (C$_2$H$_2$), but also provides more rapid and complete combustion to degrade the levels of MMW- and HMW-PAHs to LMW-PAHs, further reducing the total-BaP eq in the diesel engine exhaust (Agarwal, 2007;
Fig. 4. Reduction rates of LMW-, MMW-, and HMW-PAHs in terms of (A) mass and (B) BaP eq concentrations using WCO-based biodiesel blends at two engine loads.

Fig. 5. Mass concentrations of PAH congeners using various diesel blends at (A) 1.5 kW and (B) 3.0 kW engine loads.

Mwangi et al., 2015a). The WCO-based biodiesel blends were also been reported as a greener fuel for POP reduction in both internal combustion engine and incinerators since they could enhance the oxidation of hydrocarbons and further inhibit the reformation of POPs from C2H2 precursor (Tsai et al., 2015b, 2016; Chen et al., 2017).

Emission Factors of PAHs
Table 3 shows the emission factors (EFs) of BaP eq in term of unit fuel consumption and power generation by
using D100, W20 and W40 at the two engine loads. The EFs of D100, W20 and W40 were 1.30 µg-BaPeq L⁻¹, 0.290 µg-BaPeq L⁻¹, and 0.335 µg-BaPeq L⁻¹, (corresponding to 0.931 µg-BaP eq kWh⁻¹, 0.212 µg-BaP eq kWh⁻¹, and 0.257 µg-BaP eq kWh⁻¹), respectively, at 1.5 kW load. The EF reductions were 77.7% and 74.2% in term of fuel

![Fig. 6. BaP eq concentrations of PAH congeners using various diesel blends at (A) 1.5 kW and (B) 3.0 kW engine loads.](image)

![Fig. 7. Mass fractions of PAH congeners using various diesel blends at (A) 1.5 kW and (B) 3.0 kW engine loads.](image)

![Fig. 8. BaPeq fractions of PAH congeners using various diesel blends at (A) 1.5 kW and (B) 3.0 kW engine loads.](image)
Table 3. PAH emission factors in terms of fuel consumption and power generation.

| Fuel  | PAH Emission Factors | Activities | Increases (%) |
|-------|----------------------|------------|---------------|
| D100  |                      |            |               |
| 1.5 kW| 1.30 µg-BaP eq L⁻¹   | Fuel consumption | Based fuel   |
|       | 0.931 µg-BaP eq kWh⁻¹| Power generation | Based fuel   |
| 3.0 kW| 1.53 µg-BaP eq L⁻¹   | Fuel consumption | Based fuel   |
|       | 0.755 µg-BaP eq kWh⁻¹| Power generation | Based fuel   |
| W20   |                      |            |               |
| 1.5 kW| 0.290 µg-BaP eq L⁻¹  | Fuel consumption | –77.7        |
|       | 0.212 µg-BaP eq kWh⁻¹| Power generation | –77.2        |
| 3.0 kW| 0.173 µg-BaP eq L⁻¹  | Fuel consumption | –88.7        |
|       | 0.087 µg-BaP eq kWh⁻¹| Power generation | –88.5        |
| W40   |                      |            |               |
| 1.5 kW| 0.335 µg-BaP eq L⁻¹  | Fuel consumption | –74.2        |
|       | 0.257 µg-BaP eq kWh⁻¹| Power generation | –72.4        |
| 3.0 kW| 0.187 µg-BaP eq L⁻¹  | Fuel consumption | –87.8        |
|       | 0.096 µg-BaP eq kWh⁻¹| Power generation | –87.3        |

consumption, and 77.2% and 72.4% for the EF per power generation using W20 and W40, respectively. At 3.0 kW engine load, the EFs of D100, W20 and W40 were 1.53 µg-BaP eq L⁻¹, 0.173 µg-BaP eq L⁻¹, and 0.187 µg-BaP eq L⁻¹ (or 0.755 µg-BaP eq kWh⁻¹, 0.087 µg-BaP eq kWh⁻¹, and 0.096 µg-BaP eq kWh⁻¹), respectively. The EF reductions corresponded to 88.7% and 87.8% in terms of fuel consumption, and 88.5% and 87.3% by power generation by W20 and W40, respectively. Nevertheless, the reductions in EFs using WCO-based biodiesel blends were greater at the higher engine load, which again reflected a better combustion condition of oxygenated fuel additives.

CONCLUSIONS

This study focuses on the use of WCO-based biodiesel blends in a HDDE with operation loads of 1.5 and 3.0 kW. The energy performance, PM, particle-bound metals and PAHs in the exhaust gas were investigated. The fuel consumption rate and BSFC were slightly higher (0.6–4.1% for FCR and 1.0–7.6% for BSFC) using alternative WCO-based fuels than using conventional diesel, but their engine thermal efficiencies were similar. The use of W20 and W40 achieved PM emission reductions of 19% and 6.5%, respectively, at 1.5 kW and 27% and 19%, respectively, at 3.0 kW. The higher engine load resulted in a higher PM emission. The emission concentrations of particle-bound metals were reduced by 13.6–13.8% when using W20, but increased by 12.0–12.3% when using W40. The metal contents of PM rose with the addition of WCO-based biodiesel to the petroleum diesel. The metal elements in PM were dominated (> 90% mass) by Na, Mg, Al, K, Ca, Fe and Zn. The major trace metals were Mn, Cu, Sr and Pb. The uses of W20 and W40 could effectively reduce the emissions of total-PAHs (average 44.0%) and total-BaP eq (average 80.2%). The mass reductions of MMW- and HMW-PAHs by using W20 and W40 were more significant at 3.0 kW than at 1.5 kW, while the reduction of LMW-PAHs at 1.5 kW was more than that at 3.0 kW. Thus, the total-BaP eq were more reduced at the higher engine load. Nevertheless, the annual consumption of diesel fuel in Taiwan was reported by 16.7 ML, meaning the annual emissions of PAH toxicity were around 2.17–2.56 g BaP eq. Those annual emissions could be further reduced by 1.69–2.27 g BaP eq if we replace the diesel fuel by W20. This result provides a more healthy and sustainable fuel usage in both academic and practical aspects. In conclusion, the WCO-based biodiesel blends are good candidates of cleaner alternative fuels for diesel engine generators.

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