Emission Characteristics of Particulate Matter and Particle-bound Metals from a Diesel Engine Generator Fueled with Waste Cooking Oil-based Biodiesel Blended with \( n \)-Butanol and Acetone

Jen-Hsiung Tsai\(^1\), Sheng-Lun Lin\(^2,3\), Shui-Jen Chen\(^1\), Ciao-Jhen Guo\(^1\), Kuo-Lin Huang\(^1\), Jia-Twu Lee\(^1\), Kuei-Jyum C. Yeh\(^1\), Juei-Yu Chiu\(^1\), Chih-Chung Lin\(^1\)

\(^1\) Department of Environmental Science and Engineering, National Pingtung University of Science and Technology, Pingtung 91201, 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

ABSTRACT

This study examines the emission properties of particulate matter and particle-bound metals from a diesel engine generator fueled by traditional fossil diesel (D100) with the addition of \( n \)-butanol (B), hydrous \( n \)-butanol (\( B' \)), acetone (A), hydrous acetone (\( A' \)), isopropyl alcohol (I) or waste cooking oil-based biodiesel (W). The fuel blends were B30W20D50 (abbr. B30), B30W20D50 (abbr. B30'), A3I1W20D76 (abbr. A3), A3I1W20D76 (abbr. A3'), B30A3I1W20D46 (abbr. B30'A3) and B30'A3I1W20D46 (abbr. B30'A3') tested at loads of 1.5 kW and 3.0 kW for the diesel engine generator. Experimental results indicate that adding B30, A3 or B30A3 reduces the PM mass concentration in the exhaust at both engine loads compared to using only W20. Additionally, the PM emission concentrations are lower when using B30', A3' and B30'A3' than when using B30, A3 and B30A3, respectively; in other words, replacing pure \( n \)-butanol/acetone with hydrated \( n \)-butanol/acetone in the blends further reduces the PM emission concentrations. However, B30 or B30A3 is more effective than A3 in reducing the PM emissions, irrespective of the water content in the fuel blends. Conversely, using B30, B30', A3, A3', B30A3 or B30'A3' instead of W20 reduces the metal content in the PM emissions at both engine loads. The major metal components in PM are Na, Mg, Al, K, Ca, Fe and Zn, accounting for about 97 wt.% of 21 overall metals. The remaining analyzed metals were dominated by Mn, Ni, Cu, Mo and Ba. Accordingly, adding biodiesel from waste cooking oil and hydrous acetone/\( n \)-butanol to diesel fuel for diesel engine generators reduces the levels of PM and particle-bound metals. The waste hydrous acetone/\( n \)-butanol can be used for recycling purposes during this process.

Keywords: Diesel engine generator; Waste cooking oil-based biodiesel; Acetone; \( n \)-Butanol; Particle-bound metal.

INTRODUCTION

Diesel engine is a major power source of transportation and industrial activities, including on-/off-road vehicles, ships, construction and power utilities. However, researchers have reported significant negative effects of diesel engine emission on human health. Several studies in this decade have focused on the particulate matter (PM) diesel engines and alternative greener fuels, such as emissions from biodiesel. Moreover, the International Agency for Research on Cancer (IARC) classified diesel engine exhaust (DEE) as carcinogenic to humans (Group 1), based on sufficient evidence, in June 2012. Additionally, researchers consider diesel particulate matter (DPM) as a hazardous pollutant to human health and the environment. Conversely, biodiesel is reported as a diesel alternative to improve the combustion efficiency of diesel engines, and reduce emissions of carbon monoxide (CO), unburned hydrocarbon (HC), particulate matter (PM) and polycyclic aromatic hydrocarbons (PAHs) (Lin et al., 2010; Tsai et al., 2010; Xue et al., 2011; Guido et al., 2013; Wu et al., 2016; Redfern et al., 2017), as well as to reduce DPM biotoxicity (Tsai et al., 2011, 2012).

Dwivedi et al. (2006) found that a mixture of 20% biodiesel with 80% diesel had higher emissions of Cr, Fe, Al, Zn and Mg, and lower Pb, Cd, Na and Ni, than 100% diesel in a diesel engine. Certain metals might be originally present in the food ingredients, such as Cu, Fe, Zn and Mn in vegetables (Kawashima and Valente Soares, 2003); Cu, Fe, Zn and Mn in meat (Lombardi-Boccia et al., 2005), and Cu, Zn and Cd in fish (Atta et al., 1997). Additionally,
some metals are released into cooking oil during high-
temperature frying, or from cooking utensils (Kuligowski
and Halperin, 1992). Metals can also be transported into
waste cooking oil (WCO)-based biodiesel following
transesterification. Consequently, combustion of WCO-based
biodiesel potentially produces Fe, Zn, Cu and Mn emissions.
Use of biodiesel in diesel engines has led to Na and K
emissions, since these metals are components of major
alkaline catalysts (KOH or NaOH) in transesterification of
fatty acids. The metal content of PM in diesel engine exhaust
may also be affected by factors including engine operation
parameter, testing cycle, fuel property, fuel chemical
composition and quality and engine wearing level (Wang
et al., 2016).

The fine particles emitted from diesel engines are easily
inhaled through the respiratory system, and thus can
penetrate deeply into the alveolus, be transported to epithelial
mesenchyme and lymph nodes, and eventually accumulate
in organs in the human body via the circulation system
(Kreyling et al., 2012). Some metal components, such as
Cr, Cd, Pb, Ni, Mn, As, Zn and Cu, are poorly biodegradable,
and are toxic to humans because they disrupt bio-metabolism
and change blood composition, although they have fairly
low contributions in PM2.5 mass. Furthermore, these metals
become increasingly concentrated in animal bodies up the
food chain through bioaccumulation or biomagnification,
and are thus especially toxic in the predators at the top of a
food web (Adham et al., 2011; Fang et al., 2013; Abuduwaili
et al., 2015).

Adding 20% WCO-based biodiesel additive, a certain
amount of acetone/butanol, or even a small amount of
water, to diesel fuel reduces PM emission from diesel
generator (DEG) (Tsai et al., 2017). However,
little information is available on whether using such multi-
component fuels in DEG also reduces emissions of particle-
bound metals. Hence, this work adopts traditional fossil
diesel (D) as the base fuel, blended with n-butanol (B),
5 vol.% hydrous n-butanol (B'), acetone (A), 5 vol.%
hydrous acetone (A'), isopropyl alcohol (I) or waste cooking
oil-based biodiesel (W) to investigate the characteristics of
PMs and their bound metals emitted from a DEG operated
at 1.5 kW and 3.0 kW loads.

MATERIALS AND METHODS

Engine System and Sampling

Fig. 1 shows the tested engine generator and stack
sampling system. The diesel engine generator applied in this
study was a four-stroke, single horizontal cylinder engine
produced by Yanmar S. P. Co. The fuels were injected with
2845 psi at BTDC 17.0° CA by a direct injection system,
which was the same for each fuel. The generator loads
were controlled with a variable resistance system comprising
100 parallel bulbs, which was equivalent to the maximum
5 kW load. The DEG was operated at two engine loads, 1.5
and 3.0 kW, both at 110 V with 60 Hz power output, to test
its performances and exhaust during operation.

Testing Fuel Blends

The base fuel in this work was premium diesel fuel
produced by Chinese Petroleum Corporation (CPC),
Taiwan. Waste cooking oil-based biodiesel was provided
by Chant Oil Co., LTD. Analytical-grade acetone, n-butanol
and isopropyl alcohol all had > 99.5% purity, and were
supplied by Sigma-Aldrich, Inc. The premium diesel fuel
(D) was adopted as the base fuel and the control group in

Fig. 1. The testing Diesel Engine Generator (DEG) system in this study.
the current study. WCO-based biodiesel was tested as an additive (20 vol.% fraction) in diesel blend to form W20. n-Butanol was added to W20 to prepare B30/W20D50 (abbr. B30) (30 vol.%) while the 5 vol.% hydrous n-butanol (B′) was used to prepare B′30/W20D50 (abbr. B′30). Acetone was blended with W20 at a concentration of 3 vol.%, to which 1 vol.% isopropyl alcohol was added to stabilize the blend and form A31/W20D76 (abbr. A3). Meanwhile, 30 vol.% of pure/hydrous n-butanol (B′) was used to prepare B′30/W20D50 (abbr. B′30). Acetone was blended with W20 at a concentration of 3 vol.%, to which 1 vol.% isopropyl alcohol was added to stabilize the blend and form A31/W20D76 (abbr. A3). Finally, 30 vol.% of pure/hydrous n-butanol and 3 vol.% of pure or hydrous acetone were added to W20 with 1% isopropyl alcohol to form B30A31/W20D46 (abbr. B30A3) or B′30A′31/W20D46 (abbr. B′30A′3), respectively. The test data for W20 are in our previous study (Lin et al., 2017).

PM Sample Analyses

PM Mass Concentrations

The PM and particle-bound metals were collected on a 47 mm-diameter quartz fiber filter using a stack sampling system (Anderson Auto 5). The PM samples accumulated on the quartz fiber filters were stored and conditioned at 23°C ± 1°C at relative humidity 40 ± 5% in a clean room over 24 h. Each filter was weighed twice with an electronic microbalance (METTLER TOLEDO Model XP2U) before and after sampling to minimize the inner-group error. Each PM mass concentration was calculated by subtracting the filter mass before sampling from the final filter mass (with PM sample), and further divided by the sampling volume (modified by the standard temperature and atmospheric pressure condition, Nm³).

Metal Elements Analysis

The particle-bound metal contents were further measured by the analytical process described in standard method M105 from the Environmental Analysis Laboratory (EAL), Environmental Protection Administration (EPA), Taiwan. The weighed quartz fiber filters with PM sample were placed into 50 mL graphite digestion tubes, soaked with 20 mL nitric acid (HNO₃, 10% purity), and locked with cover. The graphite tubes were treated with 450W ultrasonic waves in a basin for 120 min, and further heated at 80–85°C for 30 min. After the heating process, the sample acid solutions were poured out and sieved using a 0.45 µm sieving plate. The metal contents in the pre-treated sample solution were quantified with an inductively coupled plasma mass spectrometer (ICP-MS, Jobin Yvon ULTIMA 2000). The calibration lines (with absolute error < 10%) were evaluated by using a standard solution. The analytical method had recovery levels in the range 75–125%, which were checked every 10 samples by an extra standard sample solution. Additionally, the methodological blank sample was determined and found to be less than 2 times the method detection limit (MDL). The MDLs of the 21 target metals, namely 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.

RESULTS AND DISCUSSION

PM Mass Concentrations in the DEG Exhaust

Effect of Engine Operation Load

Table 1 shows the PM mass emissions from the tested DEG by using B30, B′30, A3, A′3, B30A3 and B′30A′3 at engine loads of 1.5 kW and 3.0 kW. The PM emission concentrations of using these blends at 1.5 kW were 33.9 ± 4.0, 28.8 ± 1.8, 40.6 ± 3.0, 35.2 ± 2.4, 30.9 ± 5.2 and 30.2 ± 4.3 mg Nm⁻³, respectively, while those at 3.0 kW were 58.7 ± 3.3, 53.9 ± 1.7, 76.3 ± 7.0, 70.2 ± 2.6, 50.8 ± 3.9 and 49.5 ± 2.8 mg Nm⁻³, respectively. For the diesel engine generator fueled with those blends, the PM emission factors based on fuel consumptions were in the range 11.1–15.9 mg L⁻¹ at 1.5 kW and 13.6–22.9 mg L⁻¹ at 3.0 kW. The above result indicates that the DEG fueled with these blends (B30, B′30, A3, A′3, B30A3 and B′30A′3) emitted higher PM mass concentrations and emission

<table>
<thead>
<tr>
<th>Fuels</th>
<th>PM mass concentrations (mg Nm⁻³) (n = 3)</th>
<th>PM emission factors (mg L⁻¹) (n = 3)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1.5 kW</td>
<td>3.0 kW</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>W20</td>
<td>52.3 (± 2.7)</td>
<td>94.7 (± 9.2)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>B30</td>
<td>33.9 (± 4.0)</td>
<td>58.7 (± 3.3)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>B′30</td>
<td>28.8 (± 1.8)</td>
<td>53.9 (± 1.7)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A3</td>
<td>40.6 (± 3.0)</td>
<td>76.3 (± 7.0)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A′3</td>
<td>35.2 (± 2.4)</td>
<td>70.2 (± 2.6)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>B30A3</td>
<td>30.9 (± 5.2)</td>
<td>50.8 (± 3.9)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>B′30A′3</td>
<td>30.2 (± 4.3)</td>
<td>49.5 (± 2.8)</td>
</tr>
</tbody>
</table>

*Table 1. PM mass concentrations and emission factors in DEG exhaust.*

*Cited from Lin et al. (2017).*
factors at 3.0 kW than at 1.5 kW. This phenomenon likely resulted from the higher fuel consumption (FC) for the same fuel blend at 3.0 kW than at 1.5 kW, which increased the PM mass produced in the sample volume of exhaust gas (Tsai et al., 2017). This speculation is observed by Lin et al. (2017), who studied the use of D100, W20 and W40 in a diesel engine.

**Effect of Various Fuel Blends**

Fig. 2 depicts the reduction rates (%) by using B30, B’30, A3, A’3, B30A3 and B’30A’3, in comparison with using W20. These diesel blends reduced the PM emission by 35.1 ± 7.7%, 44.8 ± 3.5%, 22.2 ± 5.7%, 32.7 ± 4.5%, 40.9 ± 9.9%, and 42.1 ± 8.3%, respectively, compared with W20 at 1.5 kW, and 38.0 ± 3.5%, 43.0 ± 1.8%, 19.4 ± 7.3%, 25.8 ± 2.7%, 46.4 ± 4.1% and 47.7 ± 2.9%, respectively, at 3.0 kW. Thus, B30, A3 and B30A3 had lower PM emissions than WCO-based biodiesel additives (i.e., W20). The reduction rate was even better with (5 vol.%) in n-butanol and acetone in fuel blends (i.e., B’30, A’3 and B’30A’3). Blending 30 vol.% anhydrous/hydrous n-butanol with diesel fuels led to greater reductions in PM mass (35.1–44.8%; average: 40.2%) emission than blending 3 vol.% anhydrous/hydrous acetone (19.4–32.7%; average: 25.0%). On average, the diesel blends comprising W20 and both n-butanol and acetone (i.e., B30A3 and B’30A’3) had the greatest PM reductions (40.9–47.7%; average: 44.3%) among all tested fuel blends.

The pure WCO-biodiesel had ~11 wt.% of oxygen, while acetone (C6H6O) and n-butanol (C4H9OH) had higher oxygen contents (27.5 wt.% and 21.6 wt.%, respectively). The oxygen contents of tested fuel blends in this work were listed in Table 2. The significant PM emission reductions at both DEG loads from adding anhydrous n-butanol/acetone into W20 (i.e., B30, A3 and B30A3) could have resulted from the rise in fuel-oxygen content of fuel blend and the supply of additional oxygen radicals to initiate combustion, leading to more complete reaction and thus enhancing the combustion efficiency (Saxena and Maurya, 2016; Yang et al., 2016).

Moreover, water present in the hydrated n-butanol and acetone mixtures B’30, A’3 and B’30A’3 further lowered the PM emissions. This finding could be explained by both physical and chemical mechanisms. Physically, water has a much lower boiling point than either diesel or biodiesel. Therefore, the water tended to evaporate as steam at the very beginning of fuel droplet combustion. The sudden increase in volume of water (liquid to gas) destroyed the outer oil layer, and split each fuel droplet into much smaller ones, thus significantly increasing the specific intake air reaction area while initiating combustion. Therefore, this secondary atomization, called a micro-explosion (Ivanov and Nefedov, 1965), improved the combustion and decreased the PM emission (Tsai et al., 2014a, b). A fraction of water compound in steam are pyrolyzed to form OH•, O•, and H• radicals, which improve the oxidation of the fuel compound rapidly and completely, while the unburned hydrocarbon is also reduced, thus inhibiting PM formation. Consequently, the anhydrous/hydrous oxygenated additives in this study lowered the PM emissions.

**Emissions of Particle-bound Metals**

The average emission concentrations of ΣMetal (sum of

<table>
<thead>
<tr>
<th>Fuel blends</th>
<th>1.5 kW</th>
<th>3.0 kW</th>
</tr>
</thead>
<tbody>
<tr>
<td>B30</td>
<td>0.12</td>
<td>0.14</td>
</tr>
<tr>
<td>B’30</td>
<td>0.13</td>
<td>0.15</td>
</tr>
<tr>
<td>A3</td>
<td>0.14</td>
<td>0.16</td>
</tr>
<tr>
<td>A’3</td>
<td>0.15</td>
<td>0.17</td>
</tr>
<tr>
<td>B30A3</td>
<td>0.16</td>
<td>0.18</td>
</tr>
<tr>
<td>B’30A’3</td>
<td>0.17</td>
<td>0.19</td>
</tr>
</tbody>
</table>

**Table 2. Oxygen contents of fuels.**

<table>
<thead>
<tr>
<th>Oxygen contents (wt%)</th>
<th>Anhydrous fuel blends</th>
<th>Hydrous fuel blends</th>
</tr>
</thead>
<tbody>
<tr>
<td>W20</td>
<td>2.31</td>
<td>–</td>
</tr>
<tr>
<td>B30</td>
<td>8.62</td>
<td>B’30</td>
</tr>
<tr>
<td>A3</td>
<td>3.34</td>
<td>A’3</td>
</tr>
<tr>
<td>B30A3</td>
<td>9.68</td>
<td>B’30A’3</td>
</tr>
</tbody>
</table>

Fig. 2. Reduction rates of PM emissions using various fuels in comparison with W20.
21 particle-bound metals, namely Na, Mg, Al, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, As, Sr, Mo, Cd, Sn, Sb, Ba and Pb) from using B30, B’30, A3, A’3, B30A3 and B’30A’3 were 453 ± 264, 422 ± 75, 443 ± 108, 431 ± 68, 341 ± 103 and 337 ± 41 µg Nm⁻³, respectively, at 1.5 kW load (Table 3).

Additionally, the high ΣMetal levels in exhaust were found to be 1218 ± 116, 1047 ± 67, 1173 ± 139, 1004 ± 234, 869 ± 99, and 853 ± 88 µg Nm⁻³ by using B30, B’30, A3, A’3, B30A3 and B’30A’3, respectively, at 3.0 kW (Table 4). The above results show that B30, B’30, A3, A’3, B30A3, and B’30A’3 all resulted in lower ΣMetal levels than W20.

The metal contents of the pure WCO-based biodiesel (W100), premium diesel fuel (D100), and lubricating oil (L100) were also determined (as presented in Fig. 3).

### Table 3. Particle-bound metal concentrations in DEG exhaust at 1.5 kW Load (µg Nm⁻³) (n = 3).

<table>
<thead>
<tr>
<th>Metals</th>
<th>W20a</th>
<th>B30</th>
<th>B’30</th>
<th>A3</th>
<th>A’3</th>
<th>B30A3</th>
<th>B’30A’3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mean (± SD)</td>
<td>Mean (± SD)</td>
<td>Mean (± SD)</td>
<td>Mean (± SD)</td>
<td>Mean (± SD)</td>
<td>Mean (± SD)</td>
<td>Mean (± SD)</td>
<td></td>
</tr>
<tr>
<td>Na</td>
<td>81.4 (± 7.0)</td>
<td>64.2 (± 16)</td>
<td>74.8 (± 19)</td>
<td>46.2 (± 15)</td>
<td>69.3 (± 13)</td>
<td>39.4 (± 4.7)</td>
<td>35.5 (± 2.6)</td>
</tr>
<tr>
<td>Mg</td>
<td>26.6 (± 4.1)</td>
<td>20.3 (± 6.7)</td>
<td>17.8 (± 14)</td>
<td>17.5 (± 3.5)</td>
<td>19.1 (± 18)</td>
<td>16.2 (± 17)</td>
<td>16.4 (± 3.8)</td>
</tr>
<tr>
<td>Al</td>
<td>20.6 (± 2.3)</td>
<td>19.1 (± 23)</td>
<td>16.9 (± 1.7)</td>
<td>18.0 (± 4.4)</td>
<td>16.4 (± 4.7)</td>
<td>14.4 (± 3.4)</td>
<td>11.7 (± 2.8)</td>
</tr>
<tr>
<td>K</td>
<td>56.1 (± 9.8)</td>
<td>43.4 (± 13)</td>
<td>40.2 (± 22)</td>
<td>45.9 (± 8.3)</td>
<td>45.3 (± 6.8)</td>
<td>40.4 (± 22)</td>
<td>36.1 (± 14)</td>
</tr>
<tr>
<td>Ca</td>
<td>119 (± 12)</td>
<td>148 (± 47)</td>
<td>122 (± 41)</td>
<td>135 (± 50)</td>
<td>120 (± 44)</td>
<td>113 (± 45)</td>
<td>120 (± 27)</td>
</tr>
<tr>
<td>Ti</td>
<td>N.D. (± 0.31)</td>
<td>0.575 (± 0.077)</td>
<td>0.575 (± 0.099)</td>
<td>0.654 (± 0.020)</td>
<td>0.646 (± 0.014)</td>
<td>0.547 (± 0.078)</td>
<td>0.563 (± 0.051)</td>
</tr>
<tr>
<td>V</td>
<td>0.0719 (± 0.0010)</td>
<td>0.0923 (± 0.028)</td>
<td>0.0844 (± 0.056)</td>
<td>0.0801 (± 0.018)</td>
<td>0.0834 (± 0.0098)</td>
<td>0.0865 (± 0.014)</td>
<td>0.0937 (± 0.015)</td>
</tr>
<tr>
<td>Cr</td>
<td>2.03 (± 0.35)</td>
<td>1.65 (± 0.84)</td>
<td>1.73 (± 1.8)</td>
<td>1.83 (± 2.4)</td>
<td>1.74 (± 1.1)</td>
<td>1.48 (± 0.54)</td>
<td>1.20 (± 1.5)</td>
</tr>
<tr>
<td>Mn</td>
<td>4.89 (± 1.3)</td>
<td>1.13 (± 0.55)</td>
<td>1.30 (± 0.47)</td>
<td>1.66 (± 0.18)</td>
<td>1.60 (± 1.3)</td>
<td>1.12 (± 0.10)</td>
<td>0.808 (± 0.10)</td>
</tr>
<tr>
<td>Fe</td>
<td>152 (± 13)</td>
<td>93.5 (± 141)</td>
<td>84.2 (± 39)</td>
<td>105 (± 53)</td>
<td>89.5 (± 24)</td>
<td>63.8 (± 27)</td>
<td>62.7 (± 11)</td>
</tr>
<tr>
<td>Ni</td>
<td>1.30 (± 0.20)</td>
<td>1.03 (± 0.44)</td>
<td>0.578 (± 0.46)</td>
<td>0.81 (± 0.35)</td>
<td>0.623 (± 0.65)</td>
<td>0.136 (± 0.058)</td>
<td>0.249 (± 0.24)</td>
</tr>
<tr>
<td>Cu</td>
<td>1.00 (± 0.050)</td>
<td>4.52 (± 4.4)</td>
<td>6.27 (± 6.1)</td>
<td>3.59 (± 0.95)</td>
<td>5.84 (± 4.7)</td>
<td>1.95 (± 0.65)</td>
<td>1.87 (± 0.20)</td>
</tr>
<tr>
<td>Zn</td>
<td>58.4 (± 3.7)</td>
<td>50.2 (± 15)</td>
<td>50.8 (± 20)</td>
<td>59.7 (± 12)</td>
<td>55.4 (± 3.4)</td>
<td>44.3 (± 15)</td>
<td>44.5 (± 1.6)</td>
</tr>
<tr>
<td>As</td>
<td>N.D.</td>
<td>N.D.</td>
<td>N.D.</td>
<td>N.D.</td>
<td>N.D.</td>
<td>N.D.</td>
<td>N.D.</td>
</tr>
<tr>
<td>Sr</td>
<td>0.499 (± 0.11)</td>
<td>0.455 (± 0.32)</td>
<td>0.488 (± 0.12)</td>
<td>0.612 (± 0.053)</td>
<td>0.579 (± 0.056)</td>
<td>0.597 (± 0.040)</td>
<td>0.491 (± 0.23)</td>
</tr>
<tr>
<td>Mo</td>
<td>0.350 (± 0.040)</td>
<td>0.835 (± 0.38)</td>
<td>0.694 (± 0.77)</td>
<td>0.781 (± 0.11)</td>
<td>0.738 (± 0.10)</td>
<td>0.742 (± 0.16)</td>
<td>0.765 (± 0.18)</td>
</tr>
<tr>
<td>Cd</td>
<td>0.0658 (± 0.024)</td>
<td>0.0608 (± 0.038)</td>
<td>0.0604 (± 0.077)</td>
<td>0.0280 (± 0.077)</td>
<td>0.0368 (± 0.010)</td>
<td>0.0299 (± 0.012)</td>
<td>0.0571 (± 0.031)</td>
</tr>
<tr>
<td>Sn</td>
<td>6.21 (± 0.34)</td>
<td>3.28 (± 0.027)</td>
<td>2.81 (± 0.68)</td>
<td>5.06 (± 0.12)</td>
<td>3.82 (± 1.0)</td>
<td>2.68 (± 0.18)</td>
<td>2.68 (± 0.69)</td>
</tr>
<tr>
<td>Sb</td>
<td>0.132 (± 0.049)</td>
<td>N.D.</td>
<td>N.D.</td>
<td>N.D.</td>
<td>N.D.</td>
<td>N.D.</td>
<td>N.D.</td>
</tr>
<tr>
<td>Ba</td>
<td>0.411 (± 0.062)</td>
<td>0.274 (± 0.21)</td>
<td>0.393 (± 0.23)</td>
<td>0.347 (± 0.206)</td>
<td>0.303 (± 0.045)</td>
<td>0.230 (± 0.016)</td>
<td>0.301 (± 0.022)</td>
</tr>
<tr>
<td>Pb</td>
<td>0.731 (± 0.10)</td>
<td>0.878 (± 0.65)</td>
<td>0.406 (± 0.18)</td>
<td>0.343 (± 0.090)</td>
<td>0.732 (± 0.081)</td>
<td>0.0954 (± 0.038)</td>
<td>0.145 (± 0.023)</td>
</tr>
<tr>
<td>Σmetals</td>
<td>531 (± 28)</td>
<td>453 (± 264)</td>
<td>422 (± 75)</td>
<td>443 (± 108)</td>
<td>431 (± 68)</td>
<td>341 (± 103)</td>
<td>337 (± 41)</td>
</tr>
<tr>
<td>Σmetals content in PM (%)</td>
<td>1.02 (± 0.10)</td>
<td>1.35 (± 0.81)</td>
<td>1.48 (± 0.35)</td>
<td>1.11 (± 0.35)</td>
<td>1.22 (± 0.14)</td>
<td>1.14 (± 0.45)</td>
<td>1.13 (± 0.23)</td>
</tr>
</tbody>
</table>

*aCited from Lin et al. (2017) (2017)
avoid the explosion caused by the high temperature condition in ICP/MS operation, W100, D100, and L100 were heated to 150°C to remove the volatile organic compounds, and were ultrasonically digested prior to the analysis of the 21 metals. The most abundant 7 metals were in the order K > Na > Ca > Mg > Al > Fe > Zn in W100, and K > Na > Ca > Mg > Al > Sn > Fe in D100. Obviously, the sums of the above 7-metal contents in fuels were similar (98.4% of W100 and 98.5% of D100). However, the major metals in lubricating oil were Ca (69.3%) and Zn (30.2%). The measurement results in Tables 3 and 4 indicate that the top 7 predominant particle-bound metals emitted when using W20 followed the order Fe > Ca > Na > Zn > K > Mg > Al, and Ca > Zn > Na > Fe > K > Mg > Cr (while Al...
is the 8th one) at 1.5 kW and 3.0 kW, respectively. The above dominant particle-bound metal compositions were very similar to those (K, Na, Ca, Mg, Fe, and Al) in the unburned W20 (comprising 20% of W100 and 80% of D100). Conversely, the top 7 dominant metals in the emitted PM when using B30, B’30, A3, A’3, B30A3, and B’30A’3 varied with the order Ca > Fe > Zn > Na > K > Mg > Al at 1.5 kW, and Ca > Zn > Fe > Na > K > Mg > Al at 3.0 kW loads. All emission had the metals Na, Mg, Al, K, Ca, Fe and Zn.

The emissions of diesel engine were dominated by unburned black carbon (soot) and small amount of metals (ash) (Liati et al., 2015). For diesel emission, metal might be harmful to human health, although they contribute relatively lower mass fractions. Those particle-bound metals could be linked with the lubricant, fuel, additive and detergent contents. The emission levels of metals generally rise with increasing content in fuels (Wang et al., 2016). The particle-bound metallic pollutants in diesel engine emissions can be formed and released by several pathways: (1) the original metal contents are released by heating, and are adsorbed on the PM surface at a certain temperature and pressure; (2) the nuclei of metal components simultaneously move with PM in the engine exhaust, and coagulate with each other to form metal-containing PM; (3) metals react with oxygen, halogens or organic components to form metallic compounds, which either become residue in the combustion ashes or evaporate as metallic fume; and (4) the metallic fume is further condensed on the colder surface of the PM or fly ashes during treatment of diesel engine emissions (Eddings et al., 1994).

Shah et al. (2014) reported that Fe and Ca were the major particle-bound metallic components in fossil fuel combustion, while Na could be emitted from biodiesel combustion. Additionally, the blend of ultra-low-sulfur diesel and biodiesel caused the particle-bound metals to be dominated by As, Co, Al and Mn in diesel engine emissions, while they shifted to Cr, Cu, Fe, Ba, Zn, Mg, Ni and K when using pure biodiesel (B100). The increased Cu, Fe or Zn content in biodiesel fuel may be from the feedstock used in biodiesel preparation (Betha and Balasubramanian, 2011). The high lubricity of biodiesel decreases the friction of piston rings, cylinder liners, intake/exhaust valves and crank shafts during diesel engine operation, thus lowering Fe emissions. Additionally, the improvement in lubricity also reduces Cr emission, and impedes the wear of gears, compression rings, and cam bearings (Agarwal, 2007). Nevertheless, the use of biodiesel was also reported to reduce Cr, Zn and Al emissions from fossil diesel fuel by improving the lubricity (Wang et al., 2016).

The Σmetals content in PM by using B30, B’30, A3, A’3, B30A3 and B’30A’3 (1.11–1.48%) was greater than by using W20 (1.02%) at 1.5 kW load (Table 3). However, the Σmetals content by using these blends (1.42–2.07%) was roughly lower than by using W20 (1.93%) at 3.0 kW load (Table 4). The above phenomenon may be related to the fact that the addition of pure/hydrous butanol and acetone will slightly restrain the lubrication of the engine oil. Shukla et al. (2017) indicated that biodiesel had worse nebulization of fuel spray than conventional diesel, due to its higher density, viscosity and surface tension. Bigger biodiesel droplets may even penetrate into the cylinder wall, becoming hydrocarbon residues. Moreover, the mechanical friction and wear between the piston ring and cylinder liner may lead to metallic emissions in diesel engine exhaust.

This investigation found that the emitted particle-bound metals by using B30, B’30, A3, A’3, B30A3 or B’30A’3 as the fuel of DEG were predominated (97% in mass) by Na,
Mg, Al, K, Ca, Fe and Zn among the 21 analyzed metals, while Mn, Ni, Cu, Mo and Ba were the main components among the remaining metals. The pure/hydrous n-butanol and acetone additives in W20 could further reduce the metal emissions during DEG operation.

CONCLUSIONS

The main objective of this study was to investigate the effects on particle-bound metal emissions when using W20, pure/hydrous n-butanol or acetone additives as alternatives to conventional diesel in a DEG. The findings of this investigation are summarized as follows.

1. Using B30, A3 or B30A3 reduced the PM emissions in comparison to using W20 at two DEG loads. Additionally, using B30, A3, and B30A3 (n-butanol and/or acetone with 5 vol.% water) instead of pure B/A diesel blends resulted in a higher reduction of PM emissions. The blended fuels (B30/B′30 and B30A3/B′30A3) with higher B/A fractions exhibited lower PM emission levels than those (A3/A′3) with lower ones, regardless of the varying water content in the blended fuels.

2. The application of B30, B′30, A3, A′3, B30A3 and B′30A3 decreased the particle-bound metal emissions at both DEG loads compared with adopting only W20.

3. The dominant metals among the 21 analyzed metals in the PM emissions were Na, Mg, Al, K, Ca, Fe and Zn. The sum of their mass contributed about 97 wt.% of the total metal mass, while Mn, Ni, Cu, Mo and Ba were the main components of the remaining metals. Consequently, the addition of waste cooking oil-based biodiesel and pure/hydrous acetone/n-butanol to traditional diesel is a potential green diesel alternative for DEGs to lower PM and particle-bound metal emissions. The waste hydrous acetone/n-butanol can be adopted for recycling in this operation.

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