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Characteristics of Exhaust Emissions of a Diesel Generator Fueled with Water-Containing Butanol and Waste-Edible-Oil-Biodiesel Blends

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ABSTRACT

In recent years, the development of alternative energies has attracted much interest owing to the depletion of crude oil reserves and increasing oil prices. Many efforts have been made to use biodiesel as an alternative fuel in diesel engines. This study examines the particulate matter (PM), particulate carbon (EC and OC), and polycyclic aromatic hydrocarbons (PAHs) that are emitted from a generator using biodieselhols, which comprise 10–50 vol% pure (or dehydrated) butanol (denoted as B) or 10–40 vol% water-containing butanol (2% and 5% water content, denoted as B' and B", respectively), 20 vol% waste-edible-oil-biodiesel (WEO-biodiesel, denoted as W20), and 30–80 vol% conventional diesel. The experimental results reveal that water-containing and -free butanol-added WEO-biodiesel yielded 21.7–56.3% less PM, 28.7–63.8% less PM-EC, 11.8–48.7% less PM-OC, 23.5–59.2% less total-PAHs, and 37.0–55.3% less total-BaP_{eq} than fossil diesel (D100). The greatest reductions were achieved using the blended fuels with 30% added butanol (W20B30, W20B'30, and W20P2B"30). The use of 5% water-containing butanol reduced total-PAHs emission more than did the use of 2% water-containing butanol.

Keywords: Water-containing butanol; Biodiesel; PM; Carbon; PAH.

INTRODUCTION

In recent years, rapid industrial development and urbanization have caused continuous growth in energy consumption. Increasing crude oil prices, limited resources, and growing environmental concern have strongly motivated the development of viable and clean alternative fuels. Emissions (soot, black carbon, sulfur oxides, and nitrogen oxides) from a diesel engine are well known to exceed those from a gasoline engine. In June 2012, the International Agency for Research on Cancer (IARC, WHO) officially recognized diesel engine exhaust as a human carcinogen (Group 1), and diesel engine exhaust has been a concern in many countries owing to its adverse health effects (Chen *et al.*, 2013a; Popovicheva, *et al.*, 2014). Several studies have demonstrated that adding an oxygen agent, such as ethanol, acetone, or biodiesel, to pure petroleum diesel improves combustion efficiency and reduces the emissions of CO, HC, PM, and PAHs (Lin *et al.*, 2010; Tsai *et al.*, 2010; Lin *et al.*, 2012; Lu *et al.*, 2013).

Biodiesel is one of the most promising, clean, alternative fuels that are generated from renewable resources. However, biodiesel has a higher viscosity and cetane number than conventional fossil diesel. Blends with an excessively high percentage of biodiesel are unfavorable for engine operation. Therefore, "biodieselhol" (which is a blend of biodiesel, solvent, and fossil diesel) with an oxygen agent, such as can be formed by adding ethanol, butanol or acetone to pure petroleum diesel, has a lower viscosity than biodiesel, provides better engine fuel combustion efficiency, and causes lower PM emissions (Chang *et al.*, 2014a; Tsai *et al.*, 2014a, b). Chang *et al.* (2014b) studied water-containing acetone–butanol–ethanol (ABE) solution, which they tested as a biodiesel-diesel blend additive to reduce NO_x emissions from diesel engines. They found that the use of ABE–biodiesel–blends could simultaneously reduce PM, NO_x, and PAH by 4.30–30.7%, 10.9–63.1%, and 26.7–67.6%, respectively.

Bio-alcohols such as methanol, ethanol, propanol and butanol typically contain less carbon and sulfur but more oxygen than traditional fossil-based fuels. Among these bio-alcohols, butanol is the best additive for biodieselhols because it is economically feasible, renewable, and environmental-friendly, and can be generated from agricultural-waste cellulose (such as in rice straw, corn stover and sugar cane

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refuse) (Dogan, 2011; Jin *et al.*, 2011). Butanol has a lower volatility and auto-ignition temperature than methanol and ethanol, so it can be ignited more easily when burned in diesel engines (Sarathy *et al.*, 2009). It is also less corrosive and can be blended with diesel fuel without phase separation. Sukjit *et al.* (2012) studied the effects of adding ethanol and butanol to diesel fuel and concluded that butanol produced less CO, THC and soot in emissions than did ethanol.

Huge amounts of surplus waste-edible-oil (WEO) are available globally. The Energy Information Administration (EIA) estimates that 1.4 million tons of WEO are generated per year in the United States (Chhetri *et al.*, 2008), where approximately 9 pounds of WEO are generated per person per year (Radich, 2006). The EU countries produce approximately 0.7–1 million tons year^{-1} of WEO (Jacobson *et al.*, 2008), and the UK and Canada generate 200,000 and 150,000 tons year^{-1} (Chhetri *et al.*, 2008), respectively. Taiwan produces approximately 77,000–94,000 tons of WEO annually, causing a serious environmental problem (Taiwan EAP, 2007). Additionally, most agricultural waste, a huge amount (approximately six million tons) of which is produced in Taiwan annually, is treated by open-field burning, which often significantly degrades air quality (Chang *et al.*, 2013a; Huang *et al.*, 2013). The technology for producing bio-alcohols (such as bio-butanol) by the hydrolytic fermentation of agricultural-waste cellulose is available. Therefore, biodiesel that is manufactured from WEO and the bio-butanol that is obtained by the hydrolytic fermentation of agricultural-waste cellulose can be used as alternatives to diesel fuel to reduce environmental degradation.

To prevent competition between the food and bioenergy sectors, the conversion of non-edible greases into biofuels is now strongly encouraged. The conversion of recycled waste-edible-oil (WEO) into biodiesels and the fermentation of saccharides from hydrolyzed agricultural/wood waste cellulose to bio-alcohols are feasible technology. Therefore, in this investigation, conventional diesel (D100), D100+WEO-biodiesel (W)+butanol (B), D100+W+2% vol water-containing butanol (B'), and D100+W+5% vol water-containing butanol (B") were tested as fuels and their effects on the PM, particulate EC/OC, and PAHs emitted by a generator at a 3 kW load are studied.

MATERIALS AND METHODS

Sampling Methods and Fuel Compositions

A four-stroke, water-cooled, single fuel-injection cylinder diesel-engine generator, manufactured by YANMAR Ltd., Japan (Model: TF110E&YSG-5SEN), was utilized to examine exhaust pollutant emissions. The generator was one-phase/two-wire, with an output frequency of 50/60 Hz and a maximum output power of 4 kW. An auto-detector flow sampling system, that included one 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 suspended particles and particulate-phase PAHs. Gas-phase PAHs were collected by two connected cartridges that were filled with ~35–40 g of XAD-16 resin which was sandwiched by two polyurethane foam plugs. Further details of the sampling programs can be found elsewhere (Tsai *et al.*, 2010; Tsai *et al.*, 2011).

The premium diesel fuel was obtained from the Chinese Petroleum Corporation, Taiwan; the WEO-biodiesel was manufactured by the Taiwan NJC Corp.; the tested butanol and isopropyl alcohol solvents were supplied by Merck Ltd. (Taiwan). Table 1 presents the properties of the tested fuels. Deionized (DI) water was added to pure butanol to form 2 and 5 vol% water-containing butanols (B' and B"), and while 2% isopropyl alcohol (IPA) was used as a co-solvent to stabilize the water content in the B" fuel blends. Table 2 presents the compositions of the fuel blends that were tested in this investigation.

Carbon Analysis

The carbon contents (elemental carbon (EC) and total carbon (TC)) of the particles that were collected using quartz filters were determine using a total organic carbon analyzer (TOC-5000A; Shimadzu Corp., Japan), which included a suspended solid measuring (SSM) instrument. To measure carbon contents, the samples were placed in a sample boat, and were then manually placed in a 900°C burner that was filled with oxygen to ensure complete combustion. After CO_2 and H_2O had formed, the H_2O was removed using a draining device, and the CO_2 content was determined using a non-dispersive infrared (NDIR) gas analyzer. Finally, data were processed and calculations were made to obtain the carbon content of the sample. However, the OC content was not directly obtained using the TOC analyzer. Therefore, one quarter of each filter was heated in an oven at 350°C for 100 min to expel the OC, before being placed in an elemental analyzer to determine the EC content. Another quarter of each filter was fed directly into the elemental analyzer without pre-treatment to measure the TC content (Lin, 2002). The OC value was obtained by subtracting the EC content from the TC content: OC = TC – EC.

PAH Analysis

In this investigation, the data on 21 PAH compounds yielded a Total-PAH value for emission from the diesel generator. The carcinogenic factors of the identified PAHs were calculated in terms of BaP_{eq}, from the toxic equivalence factors (TEFs) of these compounds (PAH concentration × TEF). In this study, the TEFs that were specified by Malcolm and Dobson (1994) were used. The carcinogenic potency of Total-PAHs (Total-BaP_{eq}) was evaluated by summing the BaP_{eq} concentrations of individual PAH compounds.

The *Soxhlet* extraction method was used to extract the PAHs from the paper filters and the glass sleeves that were used in sampling. Each collected sample was extracted in a Soxhlet extractor using a mixed solvent (n-hexane and dichloromethane 1:1 vol/vol, 750 mL each) for 24 h. Following extraction, the extract was concentrated to 2 mL using highly pure nitrogen gas; it was then poured into a purification tube that contained pretreated silica gel (which had been dried at 105°C for 8 h and then activated with distilled water for 24 h) and n-hexane, which removed moisture and any highly polar substances. The purified solution was then concentrated to 1 mL using a stream of

Table 1. Specification of tested fuels.

Properties	Regular Diesel	WEO-biodiesel	Butanol	IPA
Chemical formula	$C_{14}H_{28.33}$	$C_{19.54}H_{38.37}O_2$	C_4H_9OH	C_3H_8O
Cetane number	52	56	17	–
Density at 15°C (g cm^{-3})	0.828	0.881	0.790	0.786
Kinematic viscosity at 40°C (cSt)	2.80	4.52	2.22	–
Lower heating value (MJ kg^{-1})	43.31	37.65	32.2	30.90
Total aromatics (wt%)	23.3	–	–	–
C (wt%)	85.57	76.92	64.78	60.00
H (wt%)	14.43	12.59	13.63	13.33
O (wt%)	–	10.49	21.59	26.67

Table 2. Compositions of tested fuel blends.

Fuel blends	Regular Diesel (vol.%)	WEO-biodiesel (vol.%)	Butanol (vol.%)	Water (vol.%)	IPA (vol.%)
D100	100	–	–	–	–
W20	80	20	–	–	–
W20B10	70	20	10	–	–
W20B20	60	20	20	–	–
W20B30	50	20	30	–	–
W20B40	40	20	40	–	–
W20B50	30	20	50	–	–
W20B'10	70	20	9.8	0.2	–
W20B'20	60	20	19.6	0.4	–
W20B'30	50	20	29.4	0.6	–
W20B'40	40	20	39.2	0.8	–
W20P2B"10	68	20	9.5	0.5	2.0
W20P2B"20	58	20	19.0	1.0	2.0
W20P2B"30	48	20	28.5	1.5	2.0
W20P2B"40	38	20	38.0	2.0	2.0

gaseous nitrogen and then stored in brown sample vials for the subsequent identification of 21 PAHs using a gas chromatograph/mass selective detector (GC/MSD; model: GC 6890N/HP 5973). The PAHs were analyzed using a method that can be found elsewhere (Lee *et al.*, 2011; Lin *et al.*, 2012; Chang *et al.*, 2013b).

RESULTS AND DISCUSSION

PM Emission

Fig. 1 presents the PM concentrations that were emitted from the generator at a 3 kW load, using biodieselhols, which comprised 10–50 vol% pure (or dehydrated) butanol, 10–40 vol% water-containing butanol (2% and 5% water content), 20 vol% WEO-biodiesel, and 30–80 vol% petro-diesel, as fuels. The use of biodieselhols in the generator reduced the concentration PM that was emitted in the engine exhaust, independently of the percentage of butanol added. Adding 10–50% pure or dehydrated butanol to the fuel to form W20B10, W20B20, W20B30, W20B40, and W20B50, reduced the emitted PM concentration by 21.8%, 31.8%, 48.8%, 44.1%, and 34.6%, respectively, from that emitted using D100, for an average reduction of 36.2%. Using the blended fuels with 10–40% butanol that contained 2% water, W20B'10, W20B'20, W20B'30, and W20B'40, reduced the emitted PM concentration by 26.1%, 34.2%, 47.9%, and 39.9%, respectively, for an average of 37.0%. Using blended fuels with 10–40% butanol that contained 5% water, W20P2B"10, W20P2B"20, W20P2B"30, and W20P2B"40, respectively, reduced PM emission by 44.9%, 51.7%, 56.4%, and 49.8% (average = 50.7%). With respect to the blends with pure or dehydrated butanol (W20B10, W20B20, W20B30, and W20B40), the PM reductions achieved using fuels with 2%-water-containing butanol, W20B'10, W20B'20, W20B'30, and W20B'40, were 5.43%, 3.46%, –1.84%, and –7.59%, respectively, while those achieved using fuels with 5%-water-containing butanol, W20P2B"10, W20P2B"20, W20P2B"30, and W20P2B"40, were 29.6%, 29.1%, 14.7%, and 10.1%, respectively.

The results, consistent with those earlier studies (Ribeiro *et al.*, 2007; Basha*et al.*, 2009; Shukla *et al.*, 2014), demonstrate that increasing the oxygen content in diesel (such as by adding biodiesel, ethanol, acetoacid esters, dicarboxylic acid esters, or ethylene glycol monoacetate) improved the combustion efficiency of petro-fuel and so reduced the emission of pollutants. When the percentages of butanol or water-containing butanol added were 10–30%, the emitted PM concentration decreased as the added percentage of water-free or -containing butanol increased. However, as the addition percentage of butanol or water-containing butanol rose above 30%, the PM concentration increased. This phenomenon is attributable to the fact that the cetane number and viscosity of butanol are both lower than those of

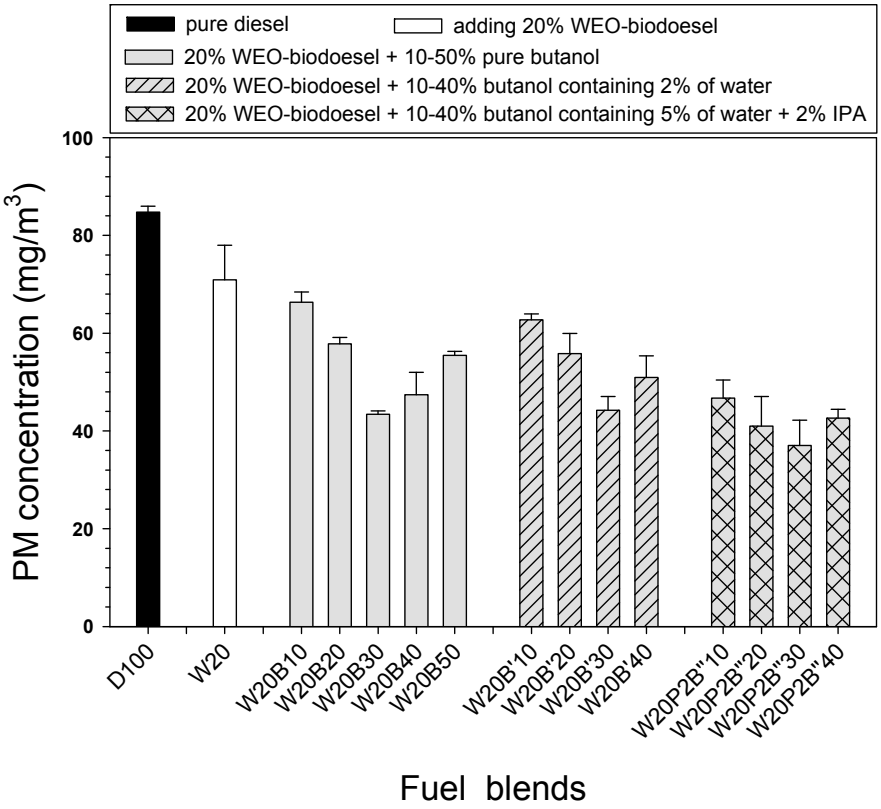

Fig. 1. PM emissions from diesel-engine generator that is fueled with biodieselhol blends under 3 kW load.

conventional diesel. Therefore, for biodieselhols that contain > 30% (40 or 50%) butanol or water-containing butanol, the excessively low viscosity causes more fuel to be injected into the engine from the nozzle at a given pressure, causing fuel-rich combustion (Yilmaz and Donaldson, 2007). Additionally, biodieselhols with excessively low cetane numbers typically exhibit unfavorable conditions for combustion.

Adding 2% or 5% waster-containing-butanol biodieselhols effectively lowers PM emissions by the generator below those obtained using pure butanol. As the water content of butanol increased from 2% to 5%, the PM emission concentration further fell by approximately 20% (which is the average of 25.5%, 26.5%, 16.3%, and 16.5% at various fuel compositions). When the water-containing butanol was added to petro-diesel, the jetted/atomized fuel formed water-in-oil (W/O) emulsions (Chang *et al.*, 2013b) and caused micro-explosions and secondary atomization in the high-temperature combustion chamber, ensuring complete combustion and further reducing PM emission (Lee *et al.*, 2011; Tsai *et al.*, 2014a). This PM emission is attributed to the lower aromatic content of the tested biodiesel and alcohol (Chang *et al.*, 2014a), because aromatic compounds are precursors for soot (McEnally and Pfefferle, 2011).

Particulate Carbon Emission

Fig. 2 displays the concentrations of PM-EC and PM-OC that are emitted from the generator using biodieselhols under a 3 kW load. The mean emitted PM-EC and PM-OC concentrations using D100 were 34.5 ± 2.58 and 34.7 ± 2.03 mg m^{-3}, respectively. Using W20 reduced emitted PM-EC and PM-OC concentrations by 19.1% and 13.8% below those emitted using D100, respectively, whereas using dehydrated-butanol biodieselhols, reduced PM-EC and PM-OC emissions by 28.7–53.6% and 11.8–38.9%, respectively. Using 2%-water-containing-butanol biodieselhols reduced emitted PM-EC and PM-OC concentrations by 28.7–53.6% and 11.8–38.9%, respectively, while using 5%-water-containing-butanol biodieselhols yielded corresponding reductions of 51.9–63.8% and 38.0–48.7%, respectively.

The above results reveal that using pure-butanol/water-containing-butanol biodieselhols effectively suppresses the formation and emission of PM-EC and PM-OC from the engine at 3 kW load, relative to those obtained with D100. Additionally, as the amount of water in the added butanol increased from 2% to 5%, the PM-EC and PM-OC emission concentrations were reduced by a further 22.7–32.2% and 13.7–26.6%, respectively. This finding suggests that the higher oxygen and lower carbon contents (Table 1) of the butanol–diesel blends provided higher combustion efficiency and, further, a stronger oxidation reaction. Some researchers (Dogan, 2011; Chen *et al.*, 2013b; Sukjit*et al.*, 2013) have also found that inserting oxygen-containing additives (such as butanol or acetone) increases the oxygen content of fuel and results in more complete combustion, but reduces the emissions of PM and soot. Additionally, the hydroxyl radicals (OH•) that are formed by the combustion of alcohol in engines may oxidize soot precursors and black carbon particles, and convert hydrogen atoms to molecular hydrogen (Frenklach and Yuan, 1987; Wu *et al.*, 2006). The consequent reduction in the number hydrogen atoms can slow the

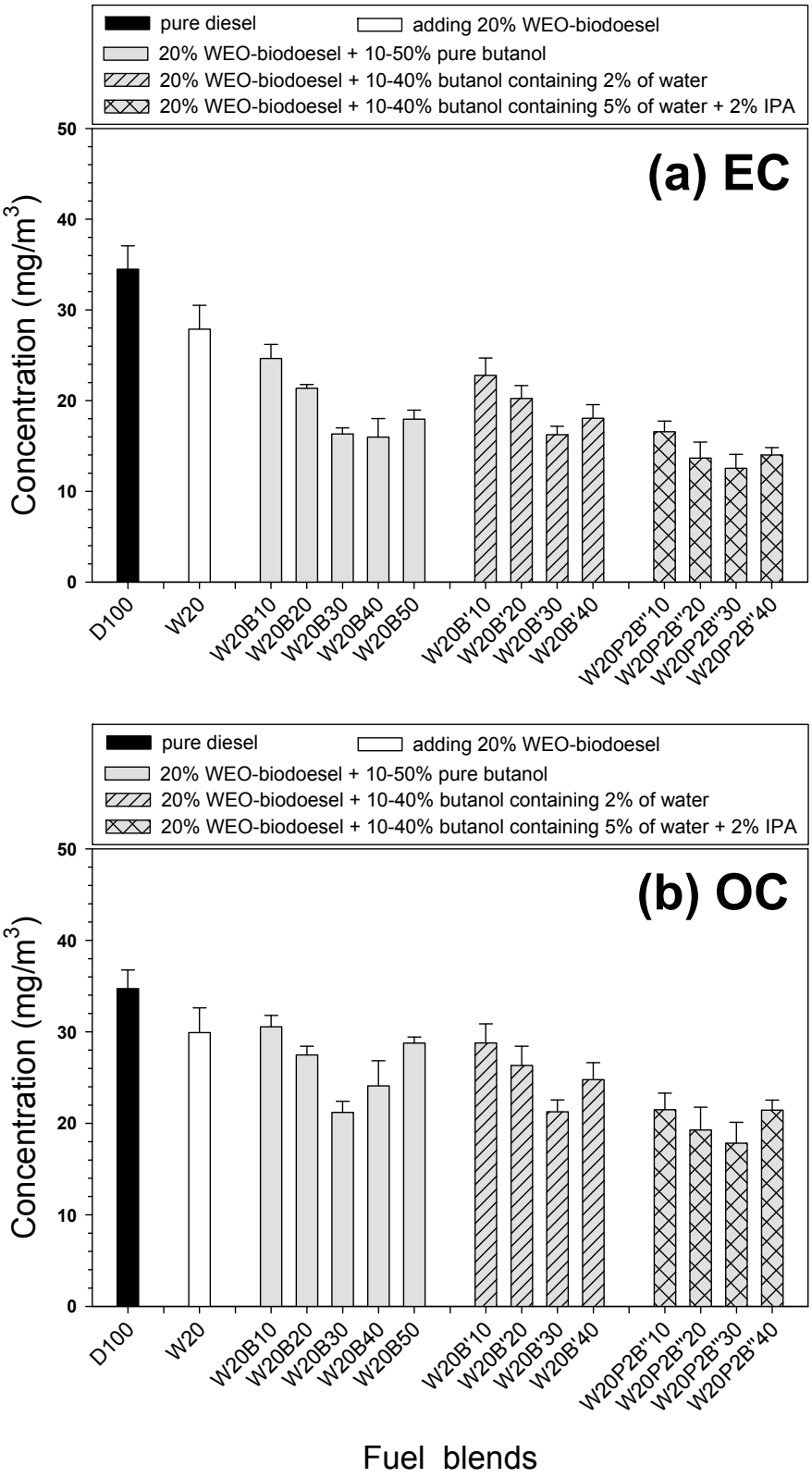

Fig. 2. Concentrations of EC and OC from diesel-engine generator that is fueled with biodieselhol blends under 3 kW load.

propagation of aromatic rings and growth of soot (Frenklach and Yuan, 1987; Wu *et al.*, 2006). In this investigation, small amounts of water in the butanol solution caused micro-explosions and ensured more complete combustion (Chang *et al.*, 2014b), resulting in lower PM and soot emissions.

PAH Emissions

Table 3 presents the concentrations of 21 PAHs (2–7 rings)

Table 3. Concentrations of PAHs with corresponding BaP_{eq} emitted from generator with pure-butanol biodieselhols as fuel.

PAHs	PAHs Concentrations (μg m^{-3}) (n = 3)							TEF*
	D100	W20	W20B10	W20B20	W20B30	W20B40	W20B50	
Nap	36.6 (± 3.6)	29.8 (± 5.6)	34.3 (± 3.4)	27.5 (± 7.26)	21.3 (± 1.6)	27.0 (± 5.3)	30.2 (± 5.2)	0.001
AcPy	3.90 (± 2.28)	3.97 (± 2.37)	3.45 (± 0.71)	3.23 (± 0.44)	2.55 (± 1.24)	2.37 (± 1.23)	2.47 (± 0.39)	0.001
Acp	2.20 (± 1.10)	2.25 (± 1.02)	2.50 (± 0.54)	2.8 (± 0.89)	1.81 (± 0.31)	1.10 (± 0.43)	1.02 (± 0.14)	0.001
Flu	1.55 (± 0.97)	4.28 (± 3.78)	1.10 (± 0.42)	1.02 (± 0.07)	0.57 (± 0.18)	1.42 (± 0.56)	1.19 (± 0.09)	0.001
PA	14.1 (± 3.9)	9.92 (± 3.68)	6.19 (± 0.96)	5.98 (± 1.67)	3.91 (± 0.42)	4.47 (± 1.24)	5.73 (± 1.46)	0.001
Ant	1.02 (± 0.48)	1.28 (± 0.79)	0.49 (± 0.12)	0.59 (± 0.10)	0.45 (± 0.03)	0.77 (± 0.32)	0.68 (± 0.11)	0.01
FL	4.87 (± 1.16)	2.57 (± 0.85)	2.00 (± 0.34)	1.34 (± 0.38)	0.69 (± 0.32)	1.18 (± 0.37)	0.99 (± 0.39)	0.001
Pyr	2.82 (± 0.41)	2.46 (± 0.63)	2.23 (± 0.07)	1.50 (± 0.3)	1.36 (± 0.36)	1.06 (± 0.55)	1.54 (± 0.15)	0.001
BaA	0.58 (± 0.05)	0.52 (± 0.11)	0.51 (± 0.04)	0.45 (± 0.06)	0.42 (± 0.01)	0.19 (± 0.01)	0.20 (± 0.01)	0.1
CHR	0.25 (± 0.07)	0.37 (± 0.21)	0.18 (± 0.10)	0.15 (± 0.03)	0.12 (± 0.04)	0.25 (± 0.00)	0.25 (± 0.01)	0.01
CYC	0.32 (± 0.05)	0.47 (± 0.13)	0.14 (± 0.08)	0.11 (± 0.06)	0.08 (± 0.05)	0.13 (± 0.03)	0.16 (± 0.11)	0.1
BbF	0.86 (± 0.34)	0.57 (± 0.23)	0.4 (± 0.08)	0.30 (± 0.17)	0.27 (± 0.02)	0.35 (± 0.13)	0.33 (± 0.18)	0.1
BkF	0.40 (± 0.19)	0.57 (± 0.13)	0.23 (± 0.02)	0.22 (± 0.05)	0.32 (± 0.23)	0.58 (± 0.52)	0.23 (± 0.03)	0.1
BeP	0.51 (± 0.39)	0.79 (± 0.36)	0.47 (± 0.05)	0.23 (± 0.03)	0.32 (± 0.14)	0.87 (± 0.72)	1.34 (± 0.63)	0.01
BaP	0.72 (± 0.21)	0.55 (± 0.02)	0.44 (± 0.08)	0.39 (± 0.30)	0.37 (± 0.05)	0.25 (± 0.04)	0.29 (± 0.14)	1
PER	0.57 (± 0.21)	0.43 (± 0.12)	0.18 (± 0.10)	0.26 (± 0.11)	0.07 (± 0.08)	0.41 (± 0.12)	0.47 (± 0.13)	0.001
IND	0.47 (± 0.19)	0.13 (± 0.09)	0.43 (± 0.35)	0.29 (± 0.15)	0.39 (± 0.04)	0.21 (± 0.12)	0.22 (± 0.06)	0.1
DBA	0.38 (± 0.05)	0.31 (± 0.18)	0.23 (± 0.13)	0.24 (± 0.06)	0.18 (± 0.07)	0.29 (± 0.13)	0.31 (± 0.19)	1
BbC	0.94 (± 0.2)	0.35 (± 0.12)	0.38 (± 0.10)	0.39 (± 0.11)	0.41 (± 0.18)	0.21 (± 0.10)	0.32 (± 0.22)	–
BghiP	0.49 (± 0.33)	0.46 (± 0.25)	0.33 (± 0.18)	0.29 (± 0.11)	0.24 (± 0.04)	0.07 (± 0.05)	0.11 (± 0.07)	0.01
COR	0.19 (± 0.07)	0.24 (± 0.21)	0.30 (± 0.37)	0.21 (± 0.05)	0.07 (± 0.02)	0.02 (± 0.00)	0.02 (± 0.00)	0.001
LMW-PAH	59.4 (± 7.0)	51.5 (± 14.9)	48.0 (± 5.5)	41.1 (± 9.6)	30.6 (± 3.1)	37.1 (± 8.9)	41.3 (± 7.4)	
MMW-PAH	8.27 (± 1.54)	5.87 (± 1.78)	4.55 (± 0.44)	3.10 (± 0.76)	2.25 (± 0.59)	2.61 (± 0.76)	2.94 (± 0.61)	
HMW-PAH	6.10 (± 1.61)	4.91 (± 1.36)	3.89 (± 1.16)	3.26 (± 0.81)	3.06 (± 0.4)	3.45 (± 0.92)	3.85 (± 0.89)	
Total-PAH	73.8 (± 9.7)	62.3 (± 17.5)	56.5 (± 7.01)	47.4 (± 10.9)	35.9 (± 3.27)	43.2 (± 10.6)	48.1 (± 8.33)	
Total-BaP_{eq}	1.44 (± 0.17)	1.16 (± 0.25)	0.91 (± 0.15)	0.83 (± 0.31)	0.74 (± 0.12)	0.76 (± 0.16)	0.79 (± 0.34)	

*: cited Malcolm and Dobson, 1994; –: No TEF has been suggested.

Table 3. (*continued*).

PAHs	PAHs Concentrations (μg m^{-3}) (n = 3)								TEF*
	W20B'10	W20B'20	W20B'30	W20B'40	W20P2B"10	W20P2B"20	W20P2B"30	W20P2B"40	
Nap	24.5 (± 3.4)	24.2 (± 1.7)	18.1 (± 2.3)	21.6 (± 12.5)	22.2 (± 11.9)	20.3 (± 6.3)	18.5 (± 11.6)	19.7 (± 9.8)	0.001
AcPy	2.46 (± 0.61)	2.19 (± 0.37)	2.05 (± 0.69)	2.03 (± 0.43)	1.47 (± 0.95)	1.72 (± 0.53)	1.99 (± 2.62)	2.2 (± 1.29)	0.001
Acp	1.35 (± 0.43)	0.8 (± 0.09)	0.69 (± 0.09)	0.65 (± 0.21)	0.64 (± 0.34)	0.63 (± 0.22)	0.54 (± 0.67)	0.38 (± 0.23)	0.001
Flu	1.9 (± 0.64)	0.90 (± 0.34)	0.66 (± 0.08)	1.66 (± 0.34)	1.84 (± 0.59)	1.01 (± 0.41)	0.65 (± 0.27)	2.47 (± 1.86)	0.001
PA	8.21 (± 2.29)	5.59 (± 1.88)	3.21 (± 0.31)	3.58 (± 0.10)	3.71 (± 3.17)	2.76 (± 2.03)	2.92 (± 0.88)	3.13 (± 0.61)	0.001
Ant	1.25 (± 0.62)	0.69 (± 0.17)	0.44 (± 0.02)	0.81 (± 0.24)	0.70 (± 0.31)	0.74 (± 0.28)	0.27 (± 0.04)	0.64 (± 0.22)	0.01
FL	1.76 (± 1.87)	0.95 (± 0.41)	0.84 (± 0.04)	1.24 (± 1.09)	1.27 (± 0.39)	0.84 (± 0.01)	0.72 (± 0.18)	0.68 (± 0.23)	0.001
Pyr	1.65 (± 0.48)	1.53 (± 0.36)	1.32 (± 0.03)	1.74 (± 0.50)	1.79 (± 0.36)	1.70 (± 0.42)	1.20 (± 0.16)	1.75 (± 0.36)	0.001
BaA	0.25 (± 0.01)	0.20 (± 0.01)	0.18 (± 0.00)	0.16 (± 0.19)	0.38 (± 0.13)	0.19 (± 0.03)	0.22 (± 0.10)	0.20 (± 0.13)	0.1
CHR	0.28 (± 0.00)	0.25 (± 0.00)	0.24 (± 0.00)	0.15 (± 0.04)	0.19 (± 0.02)	0.18 (± 0.04)	0.17 (± 0.09)	0.27 (± 0.13)	0.01
CYC	0.10 (± 0.03)	0.05 (± 0.01)	0.08 (± 0.03)	0.11 (± 0.02)	0.27 (± 0.08)	0.20 (± 0.11)	0.28 (± 0.27)	0.23 (± 0.02)	0.1
BbF	0.51 (± 0.07)	0.57 (± 0.15)	0.57 (± 0.14)	0.58 (± 0.28)	0.19 (± 0.01)	0.35 (± 0.07)	0.36 (± 0.18)	0.55 (± 0.16)	0.1
BkF	0.29 (± 0.07)	0.13 (± 0.01)	0.14 (± 0.05)	0.40 (± 0.10)	0.39 (± 0.15)	0.32 (± 0.10)	0.26 (± 0.09)	0.52 (± 0.37)	0.1
BeP	0.42 (± 0.15)	0.36 (± 0.05)	0.28 (± 0.06)	0.83 (± 0.15)	0.59 (± 0.07)	0.58 (± 0.17)	0.73 (± 0.13)	0.56 (± 0.32)	0.01
BaP	0.34 (± 0.07)	0.28 (± 0.03)	0.25 (± 0.05)	0.20 (± 0.01)	0.35 (± 0.12)	0.37 (± 0.04)	0.34 (± 0.25)	0.44 (± 0.18)	1
PER	0.42 (± 0.06)	0.42 (± 0.05)	0.37 (± 0.02)	0.50 (± 0.18)	0.57 (± 0.22)	0.61 (± 0.19)	0.33 (± 0.11)	0.69 (± 0.17)	0.001
IND	0.37 (± 0.16)	0.17 (± 0.03)	0.15 (± 0.06)	0.38 (± 0.28)	0.26 (± 0.10)	0.30 (± 0.19)	0.33 (± 0.05)	0.36 (± 0.10)	0.1
DBA	0.33 (± 0.05)	0.31 (± 0.09)	0.23 (± 0.06)	0.26 (± 0.03)	0.34 (± 0.17)	0.32 (± 0.17)	0.18 (± 0.01)	0.27 (± 0.02)	1
BbC	0.48 (± 0.16)	0.21 (± 0.08)	0.19 (± 0.08)	0.24 (± 0.06)	0.48 (± 0.05)	0.53 (± 0.35)	0.54 (± 0.19)	0.69 (± 0.20)	–
BghiP	0.39 (± 0.11)	0.07 (± 0.04)	0.06 (± 0.03)	0.24 (± 0.04)	0.39 (± 0.04)	0.30 (± 0.14)	0.23 (± 0.03)	0.31 (± 0.07)	0.01
COR	0.02 (± 0.00)	0.02 (± 0.00)	0.02 (± 0.00)	0.07 (± 0.00)	0.07 (± 0.00)	0.07 (± 0.00)	0.07 (± 0.00)	0.08 (± 0.01)	0.001
LMW-PAH	39.7 (± 7.5)	34.3 (± 4.5)	25.2 (± 3.2)	30.3 (± 12.0)	30.6 (± 16.1)	27.2 (± 5.0)	24.9 (± 15.4)	28.6 (± 11.5)	
MMW-PAH	3.79 (± 2.32)	2.79 (± 0.78)	2.48 (± 0.01)	3.24 (± 1.52)	3.52 (± 0.81)	2.92 (± 0.27)	2.37 (± 0.13)	2.93 (± 0.64)	
HMW-PAH	3.83 (± 0.09)	2.75 (± 0.11)	2.43 (± 0.46)	3.84 (± 0.44)	3.99 (± 0.4)	3.93 (± 0.83)	3.59 (± 0.15)	4.65 (± 0.64)	
Total-PAH	47.3 (± 9.72)	39.9 (± 5.12)	30.1 (± 3.68)	37.4 (± 12.7)	38.1 (± 16.8)	34.1 (± 4.77)	30.8 (± 15.1)	36.1 (± 10.8)	
Total-BaP_{eq}	0.91 (± 0.08)	0.76 (± 0.06)	0.64 (± 0.08)	0.68 (± 0.06)	0.88 (± 0.21)	0.87 (± 0.24)	0.69 (± 0.21)	0.96 (± 0.17)	

*: cited Malcolm and Dobson, 1994; –: No TEF has been suggested.

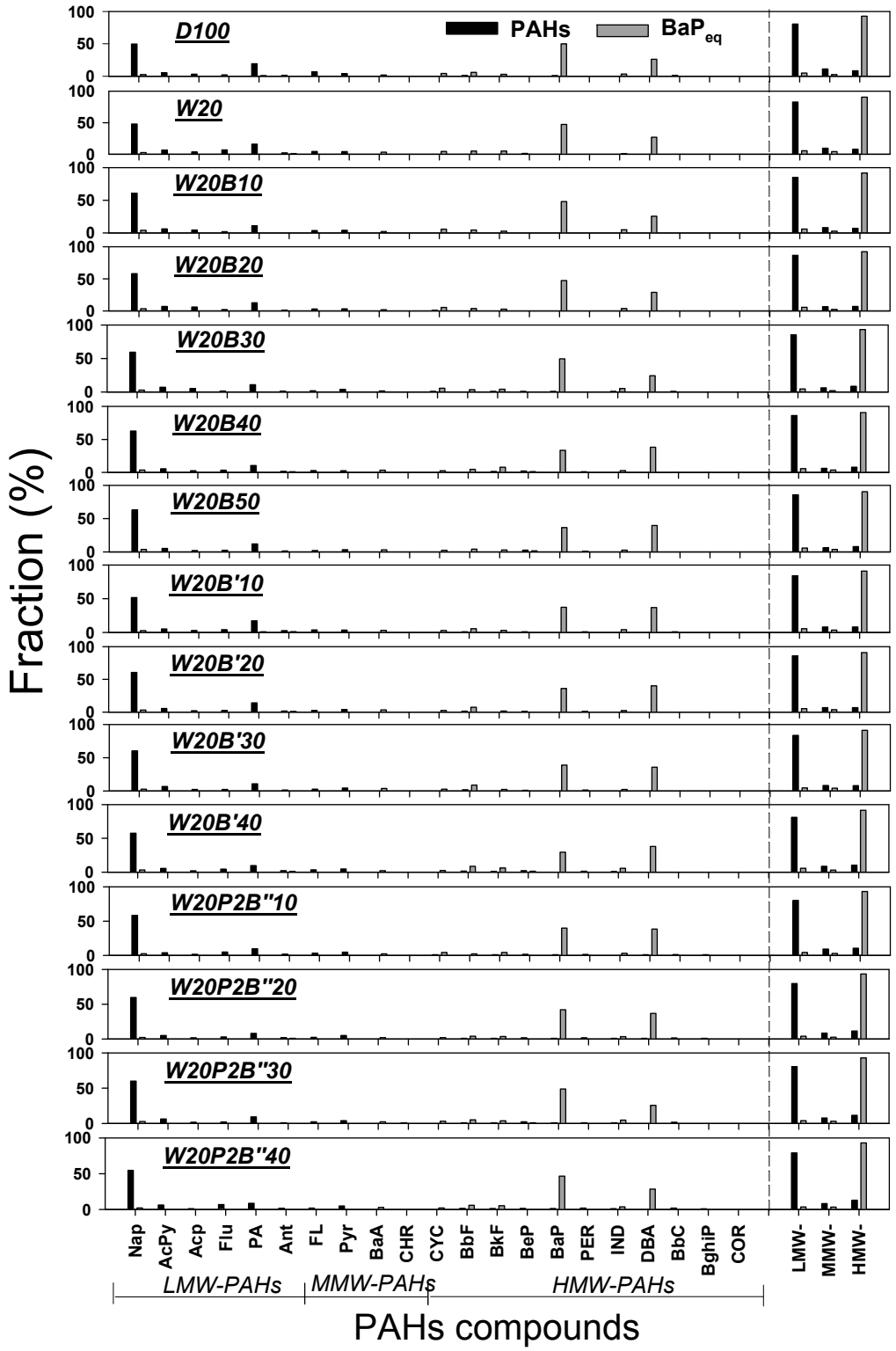

Fig. 3. Characteristic profiles of PAHs and BaP_{eq} emitted from diesel-engine generator that is fueled with biodieselhol blends under 3 kW load.

and BaP_{eq} that were emitted from a generator using pure-butanol/water-containing-butanol biodieselhols under a 3 kW load. The use of W20 and pure-butanol/water-containing-butanol biodieselhols reduced the emitted concentrations of LMW-, MMW-, HMW-, and Total-PAHs as well as Total-BaP_{eq} below those obtained when D100 was used. When the amount of added pure-butanol/water-containing-butanol was at least 30%, the reductions of emitted PAHs and BaP_{eq} increased as the percentage added increased. The largest reductions of PAHs and BaP_{eq} were observed

when the blended fuels contained 30%-pure-butanol/water-containing-butanol (W20B30, W20B'30, and W20P2B"30). Then, the emission reductions were 51.4% for Total-PAHs and 48.4% for Total-BaP_{eq} using W20B30, 59.2% for Total-PAHs and 55.3% for Total-BaP_{eq} using W20B'30, and 58.3% for Total-PAHs and 52.0% for Total-BaP_{eq} using W20P2B"30. The reductions of emitted PAH and BaP_{eq} concentrations that were achieved using biodieselhols that included water (2% or 5%)-containing butanol exceeded those achieved using biodieselhols that contained dehydrated butanol, except in the case of BaP_{eq} when W20P2B"40 was used. A probable explanation is that adding water-containing butanol to petro-diesel formed a water-in-oil (W/O) emulsion and caused micro-explosions and secondary atomization (Garo *et al.*, 2004; Mura *et al.*, 2012), which promoted combustion and further reduced emitted Total-PAHs and Total-BaP_{eq} concentrations. The reduction of PAH emissions is attributed mostly to the lack of aromatic content in the biodiesel (Chang *et al.*, 2014a). Similar results have been observed using various vegetable-based biodiesels (Macor *et al.*, 2011). Previous investigations have shown that the extra oxygen that is provided by biodiesel promotes the complete oxidation of aromatic rings and their precursors (C2 radicals) (Song *et al.*, 2011).

Table 3 also reveals that the emitted Total-PAHs and Total-BaP_{eq} concentrations slightly increased with the percentages of added butanol/water-containing butanol over 30% (W20B40, W20B50, W20P2B'40, and W20P2B"40), because the butanol is less viscous than conventional petro-diesel, so the biodieselhols caused the injection of more fuel into the engine from the nozzle at a given pressure, causing fuel-rich combustion, which favored the formation of PAHs. Can *et al.* (2004) explained that even though the high oxygen content of the fuel increased combustion efficiency, most of this oxygen reduced the gross heating value of the fuel, and thereby reduced the combustion temperature, retarding the oxidation reaction.

Fig. 3 shows characteristic profiles of PAHs and BaP_{eq} that were emitted from the generator using biodieselhols as fuel under a 3 kW load. When D100, W20, or dehydrated/water-containing butanol was used, two-ring Nap was the dominant (47.9–62.8%) species of emitted PAH, followed by three-ring PA (8.11–19.1%) and three-ring AcPy (3.87–7.11%). The fractions of five-ring BaP (with the highest toxic-equivalency (TEF = 1.0) among all of the PAH species herein) and DBA were less than 1% (BaP: 0.53–1.23% and DBA: 0.41–0.94%). LMW-PAHs were responsible for more than 80% of the Total-PAHs concentration; restated, MMW- and HMW-PAHs were together responsible for less than 20%. The concentrations of five-ring BaP and DBA were relatively low (0.53–1.23% and 0.41–0.94%, respectively), but among the 21 PAHs, BaP and DBA were the two with the highest concentrations (33.4–49.8% and 25.5–40.2%, respectively) in Total-BaP_{eq}. The concentration of Nap in Total-BaP_{eq} was very low (only 2.06–3.81%), but Nap had the highest concentration in Total-PAHs. HMW-PAHs (90.3–93.5%) represented more than 90% of Total-BaP_{eq}, followed by LMW-PAHs (3.59–5.98%) and MMW-PAHs (2.00–4.24%).

Table 4. Summary of the relative biodiesel researches.

Fuel blends	Comparison with regular diesel					References
	PM	PAHs	NO_x	CO	HC	
5–25% *n*-butanol + 0.5–1% water	→	→	→	←	–	Lin *et al.*, 2010
10% biodiesel + 5–10% water-containing ethanol	→	→	→	←	–	Lee *et al.*, 2011
10–100% palm-biodiesel	→	–	–	←	→	Ng *et al.*, 2012
20% acetone-butanol-ethanol (ABE) solution + 0.5% water	→	→	→	←	–	Chang *et al.*, 2013
25% water-containing ABE solution + 50% biodiesel	→	→	→	–	–	Chang *et al.*, 2014
20% waste-edible-oil-biodiesel + 30% butanol containing 2% of water	→	→	–	–	–	This study

↓: Decrease; ↑: Increase.

CONCLUSIONS

This study demonstrated the potential of using water-containing butanol blended with biodiesel as a clean and green fuel for diesel engines. Table 4 summaries the effects of the oxygenate fuels in diesel on pollutant emissions from previous studies. In contrast to these effects, a similar trend was observed that using W20B'30 could effectively decreased exhaust emissions from a small diesel-generator. Accordingly, the following conclusions can be derived.

(1) The use of WEO-biodiesel–butanol–diesel blends reduced emitted PM, particulate EC/OC, and PAHs concentrations below those obtained using D100. In the presence/absence of water, adding 10–30% butanol reduced the concentrations of emitted PM, particulate EC/OC, and total-PAHs to an extent that increased with the percentage of butanol.
(2) Adding water-containing butanol, except W20B'30 and W20B'40, reduced emitted PM and particulate EC/OC concentrations by more than did adding water-free butanol.
(3) Using water-containing butanol reduced the emitted concentrations of LMW-PAHs more than did adding water-free butanol. However, addition certain percentages of water-containing butanol increased the emitted concentrations of MMW- and HMW-PAHs, but the concentrations of total-PAHs fell at all percentages of water-containing butanol.
(4) Using water-containing butanol (W20B'20, W20B'30, W20B'40, W20P2B"10, and W20P2B"30) reduced the emitted concentration of total-BaP_{eq}. Using 5% water-containing butanol reduced total-PAHs emissions more than did using 2% water-containing butanol.

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