Investigation of the Effects of Biodiesel Blend on Particulate-Phase Exhaust Emissions from a Light Duty Diesel Vehicle

B. Wang, W. H. Or, S.C. Lee, Y.C. Leung, B. Organ

Abstract—This study presents an investigation of diesel vehicle particulate-phase emissions with neat ultralow sulphur diesel (B0, ULSD) and 5% waste cooking oil-based biodiesel blend (B5) in Hong Kong. A Euro VI light duty diesel vehicle was tested under transient (New European Driving Cycle (NEDC)), steady-state and idling on a chassis dynamometer. Chemical analyses including organic carbon (OC), elemental carbon (EC), as well as 30 polycyclic aromatic hydrocarbons (PAHs) and 10 oxygenated PAHs (oxy-PAHs) were conducted. The OC fuel-based emission factors (EFs) for B0 ranged from 2.86 ± 0.33 to 7.19 ± 1.51 mg/kg, and those for B5 ranged from 4.31 ± 0.64 to 15.36 ± 3.77 mg/kg, respectively. The EFs of EC were low for both fuel blends (0.25 mg/kg or below). With B5, the EFs of total PAHs were decreased as compared to B0. Specifically, B5 reduced total PAH emissions by 50.2%, 30.7%, and 15.2% over NEDC, steady-state and idling, respectively. It was found that when B5 was used, PAHs and oxy-PAHs with lower molecular weight (2 to 3 rings) were reduced whereas PAHs/oxy-PAHs with medium or high molecular weight (4 to 7 rings) were increased. Our study suggests the necessity of taking atmospheric and health factors into account for biodiesel application as an alternative motor fuel.

Keywords—Biodiesel, OC/EC, PAHs, vehicular emission.

I. INTRODUCTION

DIESEL vehicle exhaust is the major source of ambient aerosols on street-level pollution and will cause severe adverse health effects [1]. In 2016, licensed diesel commercial vehicles constituted around 18% of the total vehicle in Hong Kong yet they were accountable for 93% of road transport fine suspended particulates ($PM_{2.5}$) emissions [2]. Biodiesel, an oxygenated diesel made from vegetable oils, animal fats or waste cooking oil through the transesterification reaction, has been promoted as a sustainable alternative to diesel. Biodiesel contains less sulfur and aromatic compounds but higher oxygen content than diesel, and is more prone to oxidation during long-term storage [3]. As a result, the exhaust emissions from biodiesel or its blends might be different than that from diesel fuel.

Several studies have reported that the application of biodiesel blends resulted in lower particulate matter (PM) emissions compared to diesel fuel [4]-[7]. The chemical composition of the emitted PM from biodiesels or their blends might be very different to diesel fuel due to the difference in oxygen aromatic content. However, information about chemical composition of the PM emission such as EC, OC, particulate-phase PAHs, and oxy-PAHs is scarce. Some studies reported a reduction in EC emissions from using biodiesel, as biodiesel could prevent soot formation by reducing fuel-rich zone and enhance soot oxidation [6], [8]-[10]. On the other hand, OC emissions have been reported to be increased [8], [10], [11] or decreased [11] due to the difference in fuel chemical composition, physical properties, as well as engine speed and loading.

PAHs are identified as one of the major toxic air pollutants and there is sufficient evidence that PAH-enriched diesel exhaust is a cause of lung cancer [12]. The carcinogenic effect of diesel exhaust exposure is mainly by the inhalation of particles, on which carcinogens such as PAHs may absorb [13]. Several studies reported that vehicular emissions, especially diesel vehicles, are the most important sources of PAHs in urban areas [14], [15]. Reference [16] pointed out that most of the oxy-PAHs found in diesel exhaust particles are toxic and mutagenic. Biodiesel may promote the formation of oxy-PAHs for its higher oxygen content, enhanced combustion processes, and induced oxidation [17], [18]. Some studies indicated that fuel type has a significant effect on EFs, toxicity, and composition of PAHs and oxy-PAHs from vehicle engines [18]-[20]. However, there is little and inconsistent information on PAH emissions from engine with biodiesel/biodiesel blends. With different types of biodiesel, the total PAHs emission are reported to be reduced [9], [20] or increased [4], [21]. These contradictory results raise concern on the effect of biodiesel on PAH and oxy-PAH exhaust emissions from diesel vehicles.

The objective of this study is to compare the effects of biodiesel blends (i.e., B0 and B5) on the PM emissions and chemical composition including OC, EC, PAHs, and oxy-PAHs from a light duty diesel vehicle over different driving conditions on a chassis dynamometer.

II. METHODOLOGY

A. Fleet, Fuel and Instrumentation Set-Up Overview

A Euro-VI light duty diesel vehicle (Euro VI-LDV, H1, Hyundai) was tested with B0 (ULSD) and biodiesel blend B5 (5% biodiesel blended with 95% diesel, by volume) fuels. The tested LDV was registered in 2019 and has a pre-test odometer reading of 77 km. It has a diesel particulate filter (DPF) and exhaust gas recirculation (EGR) as exhaust aftertreatment

B. Wang is with the Faculty of Science and Technology, Technological and Higher Education Institute of Hong Kong, Hong Kong, (corresponding author, phone: +852-2176-1465; e-mail: beiwang@thei.edu.hk).

World Academy of Science, Engineering and Technology
International Journal of Transport and Vehicle Engineering
Vol:15, No:5, 2021

system.

The neat biodiesel (B100) was manufactured from the waste-derived feedstock, including locally recycled waste cooking oil (WCO) and grease trap oil, by Dynamic Progress Int. Ltd. Table I lists the physicochemical properties of the neat biodiesel and the neat diesel.

The exhaust emission tests were performed at Jockey Club Heavy Vehicle Emissions Testing and Research Centre (JCEC) in Hong Kong. The vehicle was driven on a Mustang chassis dynamometer with a 48'' single roller. A 50% loading was added by increasing the roller resistance of the dynamometer to simulate the real driving condition. The tailpipe of the vehicle was connected to the constant volume sampler (CVS) and dilution tunnel system, from which the exhaust emission was measured and sampled. The volumetric flow rate, the static pressure and the temperature in the dilution tunnel were operated at 0.3 m/s, -1.87 kPa and 30 °C, respectively. Fig. 1 presents the schematic set-up of the vehicle testing. This paper presents the experiment and findings of selected particulate emissions (OC, EC, PAHs and oxy- PAHs), while the other measurements are presented in a separate paper.

TABLE I
THE PROPERTIES OF THE TESTED FUELS [22], [23]

|		Biodiesel (B100)	ULSD (B0)
Fuel standard		EN14214:2012	Euro V diesel
Physical properties			
Cetane Index		51	52
Heat of evaporation	(kJ kg^{-1})	300	250–290
Lower heating value	(MJ kg^{-1})	37.5	42.5
Density at 20 °C	(kg m^{-3})	871	840
Vapor point at 25 °C	(mmHg)	< 2	NA
Viscosity at 40 °C	(mPa•s)	4.6	2.4
Chemical properties			
Carbon content	(wt%)	77.1	86.6
Hydrogen content	(wt%)	12.1	13.4
Oxygen content	(wt%)	10.8	0
Sulphur content	(mg kg^{-1})	<10	<10
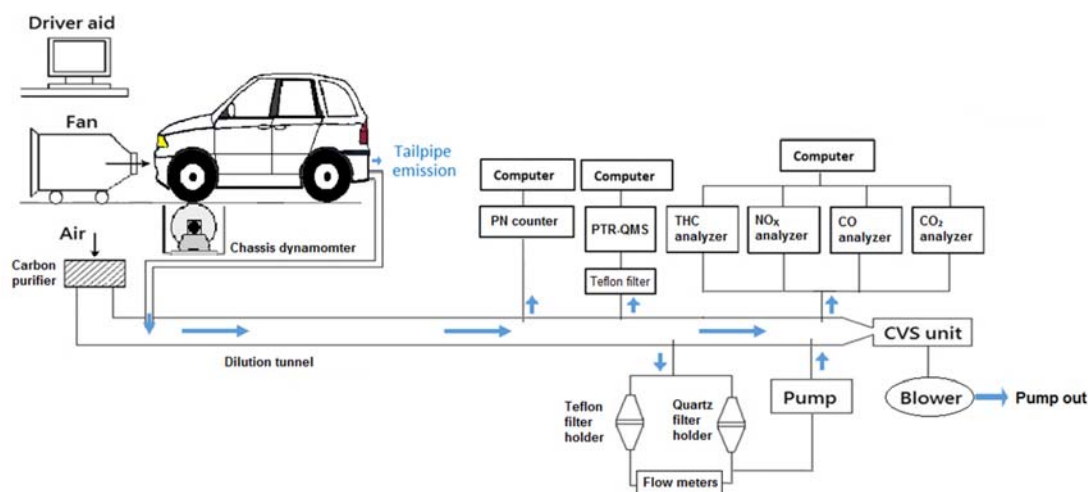
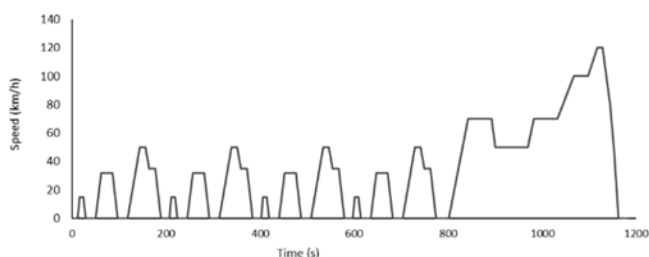Fig. 1 The set-up of the vehicle test on the chassis dynamometer

Fig. 2 The driving speeds of the Ne NEDC tests in the chassis dynamometer experiments

B. Driving Cycles

Three driving conditions including transient, steady-state and idling were conducted for the emission tests of B0 and B5 fuels, respectively. Three trials were performed for each combination of driving cycle and fuel blend. For the transient test, NEDC test was performed to simulate dynamic conditions in urban and extra-urban areas (Fig. 2). For the steady-state test, a constant speed of 50 km/h was set to match the speed limit for the majority of local urban roads. The driving speed was initially accelerated for 30s to attain this constant speed. For the idling test, the vehicle was stationary on the dynamometer while the engine was on. The duration of one NEDC test was run for 1180 s, those of steady and idling tests were run for 1200 s.

C. PM Sample Collection

Particulate emission was collected by a pre-baked quart filter (Whatman, USA) and a Teflon filter (Whatman, USA) simultaneously for each trial. The average flow rate of the exhaust onto the filters was maintained at about 47 L/min over each test. The masses of PM (PM$_{2.5}$) on both types of filters were determined by an electronic microbalance (MC5, Sartorius, Germany) with a readability of 0.001 mg. The filters were conditioned in a humidity- and temperature-controlled chamber (i.e., relative humidity = 45%; temperature = 22 °C) for at least 24 h before weighing. Each filter was weighed at least twice before and after sample collection. The weighing result was accepted only if the difference of the two consecutive

World Academy of Science, Engineering and Technology
International Journal of Transport and Vehicle Engineering
Vol:15, No:5, 2021

weightings was less than 0.01% of the filter weight. The filters were then sealed in zip-zap bags and stored at –20 °C for subsequent chemical analyses. Operational blanks and laboratory control blanks were prepared and processed simultaneously with the field samples, and were used to correct filter data.

D. Chemical Analysis

Each quartz filter was cut exactly in half with a specially designed chopper for OC/EC and PAHs/oxy-PAHs analyses. The OC/EC analysis was conducted using the Desert Research Institute (DRI) Model 2001 Thermal/Optical Carbon Analyzer following the Interagency Monitoring of Protected Visual Environments (IMPROVE)-A protocol [24]. The frictions of OC and EC (OC1, OC2, OC3, OC4, EC1, EC2 and EC3) were obtained in non-oxidizing (Helium; for OC) and subsequently oxidizing atmospheres (Helium with 2% oxygen; for EC). The four fractions of OC were produced at 120, 250, 450, and 550 °C, respectively; while the three fractions of EC were produced at 550, 700 and 800 °C, respectively. During the volatilization of OC, some OC may pyrolytically convert to EC. This was corrected by monitoring the change of reflectance using a helium-neon laser. The data recording and processing was done with the DRICarb software analysis package. OC is defined as OC1+OC2+OC3+OC4+OP; EC is defined as EC1+EC2+EC3.

The particulate samples on another half portion of each quartz filter were used for PAHs and oxy-PAHs analysis. The samples were analyzed using the thermal desorption-gas chromatography/mass spectrometer (TD-GC/MS) method [25]. Internal standard was spiked onto the filters. The filter strips were transferred into a TD tube, which was placed into the GC injection port at 50 ºC. The temperature of the injection port was set to 275 ºC in splitless mode after the input of the tube and the closure of the septum cap. The initial temperature of the GC oven was 30 ºC, then it was increased to first 120 ºC, and then 310 ºC. The mass spectrometer was operated in electron impact ionization mode, and the detector scanned from 50 to 550 amu. Species were identified by comparing the mass spectrum and chromatographic peaks retention time with the standards. The detailed experimental procedure was described by [25]. 30 PAHs and 10 oxy-PAHs were targeted in this study. The PAHs included in this study are Naphthalene (NAP, 2-ring), 1-Methylnaphthalene (1-NAP, 2-ring), 2-Methylnaphthalene (2-NAP, 2-ring), 2,6-Dimethylnaphthalene (2,6-NAP, 2-ring), Acenaphthylene (ACY, 3-ring), Acenaphthene (ACE, 3-ring), Fluorene (FL, 3-ring), Anthracene (ANT, 3-ring), Phenanthrene (PA, 3-ring), 9-Methylanthracene (9-ANT, 3-ring), Retene (RET, 3-ring), Pyrene (PYR, 4-ring), Fluoranthene (FLA, 4-ring), Methylfluoranthene (Mt-FLA, 4-ring), Benzo[a]anthracene (BaA, 4-ring), Chrysene (CHR, 4-ring), Methylchrysene (Mt-CHR, 4-ring), Cyclopenta[c,d]pyrene (CPcdPYR, 5-ring), Benzo[a]fluoranthene (BaF, 5-ring), Benzo[a]pyrene (BaP, 5-ring), Benzo[b]fluoranthene (BbF, 5-ring), Benzo[e]pyrene (BeP, 5-ring), Benzo[k]fluoranthene (BkF, 5-ring), Perylene (Per, 5-ring), Picene (PIC, 5-ring), Dibenzo[a,h]anthracene (DBA, 5-ring), Indeno[1,2,3-c,d]pyrene (IND, 6-ring),

Benzo[g,h,i]perylene (BghiP, 6-ring), Dibenzo[a,e]pyrene (DBP, 6-ring), and Coronene (COR, 7-ring). The oxy-PAHs included in this study are 1-Naphthaldehyde (1-NAD, 2-ring), 1,4-Naphthoquinone (1,4-NQ, 2-ring), 1-Acenaphthenone (1-ACP, 3-ring), 9-Fluorenone (9-FLO, 3-ring), 9,10-Anthraquinone (9,10-ANQ, 3-ring), 1,8-Naphthalic anhydride (1,8-NAPAyd, 4-ring), 5,12-Naphthacenequinone (5,12-NACQ, 4-ring), Benzo[a]anthracene-7,12-dione (BaA7,12-dio, 4-ring), 1,4-Chrysenequinone (1,4-CRQ, 4-ring), and 6H-Benzo[c,d]pyrene-6-one (6H-BcdP-6-one, 5-ring).

E. Calculation of EFs

A fuel-based EF approach was employed to show the amount of pollutant emitted in the exhaust per kilogram of fuel consumed during each driving cycle. The fuel consumption for a driving test was calculated by (1), considering that 1 mole of carbon atom in fuel produces 1 mole of CO_2 as diesel engines have high combustion efficiency and have CO_2 as the major combustion product.

$$\frac{V_f \times \rho_f \times \omega_f}{MW_C} = \frac{M_{CO_2}}{MW_{CO_2}} \tag{1}$$

In (1), V_f [L] is the volume of fuel consumed in, ρ_f [kg/L] is the density of B0 (i.e., 0.83) or B5 (i.e., 0.8325) fuel, ω_f is the mass fraction of carbon in B0 (i.e., 0.87) or B5 (i.e., 0.86), M_{CO_2} [g] is the background corrected mass of CO_2 produced in each trial of driving test, MW_C and MW_{CO_2} are the molecular mass of carbon and CO_2 [g/mol], respectively. The EFs of OC, EC, and individual PAH, oxy-PAH species were calculated by dividing the amount of that compound by the amount of fuel consumed for each driving cycle.

III. RESULTS AND DISCUSSION

A. OC and EC

The EFs of OC ((from 2.86 to 15.36 mg/kg) and EC (from 0.01 to 0.25 mg/kg)) from the exhaust particulate samples in all driving conditions fueled with both B0 and B5 were low. This may attribute to the high effectiveness of DPF to remove particulate emissions from the vehicular exhaust [26]. In this study, the EC emissions were close to detection limit with both B0 and B5 under all driving conditions. For some trials/ samples, the EC emissions were even below the detection limit. As a result, the average EFs EC were very low and the majority of carbon fractions measured was OC.

Fig. 3 compares the EFs of OC and EC over different driving conditions fueled with B0 and B5. The OC EFs for B0 ranged from 2.86 ± 0.33 to 7.19 ± 1.51 mg/kg, and those for B5 ranged from 4.31 ± 0.64 to 15.36 ± 3.77 mg/kg, respectively. For both fuel blends, the highest EFs of OC were observed in idling cycle. Previous studies have also reported higher OC emissions in idling condition and explained this with higher fuel consumption or lower temperature in cylinder due to fuel lean condition [27], [28]. The EFs at NEDC were the lowest for both fuel blends, yet the differences between that with steady-state test were mild. OC emissions in each driving cycle when using

World Academy of Science, Engineering and Technology
International Journal of Transport and Vehicle Engineering
Vol:15, No:5, 2021

B5 were higher that B0 in each corresponding cycle. Compared with B0, B5 rocketed OC EFs by more than double during idling, and increased OC EFs by 50.6% and 39.5%, respectively, during NEDC and steady test. On the other hand, the EC emissions did not show an increase pattern across all driving cycles. The effects of the application of B5 fuel on EC were from - 80% to + 816%. The unburnt biodiesel has lower volatility and may facilitate nucleation and condensation of particles during the cool down of the exhaust in the tailpipe and result in a higher OC emission, especially in low load situation with a low fuel/air ratio [8]. The increase in OC observed in this study is in accordance with the previous studies [8], [29]. The increment of OC in steady test with the substitution of B5 is statistically significant (Student's t-test, $p < 0.05$). References [8] and [29] both reported a decrease in EC when biodiesel was used. While this study reported a change in EC performance in both positive and negative directions in different driving cycles with a large percentage of change, the differences for EC among fuels were statistically insignificant and the OC or EC emissions remained very low.
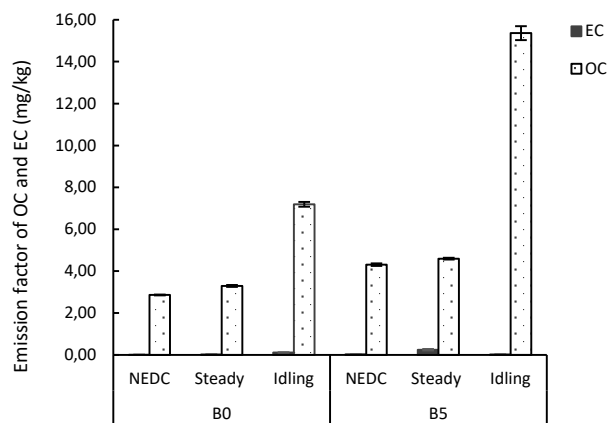

Fig. 3 EFs of OC and EC for B0 and B5 over NEDC, steady state and idling tests

B. PAHs

Among the 30 PAHs and 10 oxy-PAHs being quantified, two PAHs, Retene and Picene, were below detection limits. Fig. 4 presents the total PAH EFs under different fuel blends and driving conditions. In general replacing B0 by B5 resulted in a reduction of total PAHs. The total PAH EFs were 58.9 to 137.9 µg/kg when using B5, which was reduced by 50.2%, 30.7% and 15.2% over NEDC, steady state and idling, respectively, compared to the neat ULSD. Similar to the case of OC emission, the vehicle at idling tests generated the highest EFs of PAHs and oxy-PAHs for both fuel blend. The effect of B5 blend on total PAH EFs over NEDC was statistically significant (Student's t-test, $p < 0.05$).

Tables II and III present the averaged EFs of the PAHs and the oxy-PAHs, respectively, for the 2 blends over NEDC, steady-state and idling tests. Among all quantified particle-phase PAHs, the EFs of total PAHs were predominantly attributed to naphthalene (NAP), acenaphthylene (ACY), acenaphthene (ACE), fluorene (FL), as well as other low

molecular weight (LMW-, 2- to 3-ring) PAHs. These four dominant species accounted for around 70% of the total PAHs in particulate exhaust from B0. Compared with the neat ULSD, the use of B5 reduced total EFs of these dominant PAHs by 61.1%, 47.7% and 28.4%, over NEDC, steady-state and idling, respectively. Overall, the adoption of B5 reduced EFs of LMW-PAHs by 59.1%, 44.7% and 27.7%, over NEDC, steady-state and idling, respectively, in comparison with B0. On the other hand, medium molecular weight (MMW-, 4-ring) and high molecular weight (HMW-, 5- to 7-ring) PAHs showed an increasing trend for most driving conditions with the substitution of biodiesel blend. The use of B5 reduced the EFs of MMW-PAHs by 31.1% over NEDC, but increased it by 5.2% over steady-state and 33.9% over idling, respectively. The application of B5 increased the EFs of HMW-PAHs by 12.7%, 71.4%, and 113%, over NEDC, idling, steady-state, respectively.
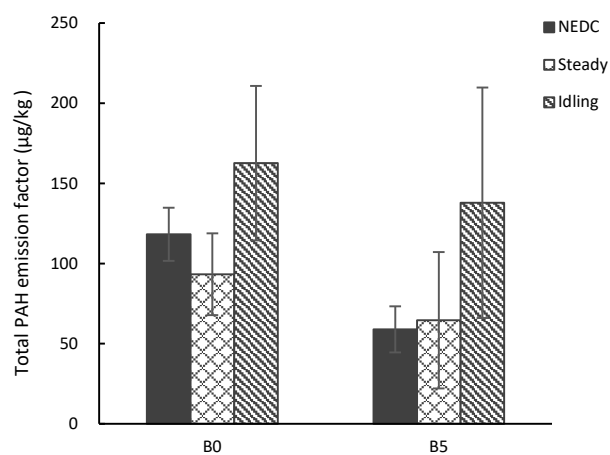

Fig. 4 EFs of total PAH for B0 and B5 over NEDC, steady and idling tests

Oxy-PAHs accounted for a small fraction of the total PAHs (2.6% for B0 and 3.6% for B5 on average). The EFs of oxy-PAHs were 2.2 to 4.3 µg/kg when using B5, which were increased by 12.1% over steady-state but were reduced by 27.0% and 3.8% over NEDC and idling, respectively, when compared to B0. 1,4-Naphthoquinone (1,4-NQ, 2-ring) was the dominant oxy-PAH species in B0 and accounted for almost half of the total EFs of oxy-PAHs. It was reduced substantially under all driving conditions and contributed to the overall reduction in oxy-PAHs emission with the application of B5. 7 of the other 9 PAHs (all oxy-PAHs with 3 to 4 rings) were increased under all driving conditions. Grouping by number of rings using B5 resulted in a reduction in EFs of 2- to 3-ring oxy-PAHs but an increment in *EF*s of 4- and 5-ring oxy-PAHs.

C. PAHs Comparison with Previous Studies

This study observed a reduction of total particle phase PAHs and particularly LMW-PAHs by addition of WCO-based biodiesel, which is in line with previous study [8], [17]. It was suggested that the emission of LMW-PAHs was originated from condensation of unburnt diesel or lubricating oil, or

World Academy of Science, Engineering and Technology
International Journal of Transport and Vehicle Engineering
Vol:15, No:5, 2021

pyrolysis from incomplete fuel combustion [8], [30], [31]. The higher oxygen content in biodiesel blend induces a higher oxidation rate and more complete fuel combustion. Hence, the EFs of total PAHs and LMW-PAHs declined under all driving conditions with inclusion of B5 fuel [8], [17], [30].

TABLE II
SUMMARY OF FUEL-BASED EFs OF PAHs WITH ULSD (B0) AND BIODIESEL BLEND (B5) FUELS OVER NEDC, STEADY-STATE AND IDLING TESTS

PAHs	Fuel-based EFs (µg/kg)											
	NEDC				Steady				Idling			
	B0		B5		B0		B5		B0		B5	
NAP	22.69 ± 0.52		15.12 ± 3.71		18.66 ± 4.45		16.86 ± 11.93		40.17 ± 22.17		39.04 ± 17.69	
1-NAP	2.66 ± 0.43		2.24 ± 0.29 *		2.09 ± 0.74		2.22 ± 1.47		4.23 ± 3.28		4.13 ± 2.03	
2-NAP	2.59 ± 0.14		2.29 ± 0.69		1.87 ± 0.13		2.41 ± 1.70		4.07 ± 2.88		5.01 ± 3.73	
2,6-NAP	1.89 ± 0.71		1.75 ± 0.26		1.50 ± 0.91		1.73 ± 1.01		2.54 ± 1.22		3.04 ± 1.22	
ACY	15.42 ± 3.10		6.41 ± 1.74		13.70 ± 6.32		6.61 ± 4.42		21.80 ± 6.50		16.82 ± 9.78	
ACE	18.70 ± 5.28		5.99 ± 1.71 *		15.48 ± 5.35		6.04 ± 4.07		24.83 ± 4.81		18.75 ± 14.57	
FL	23.08 ± 5.28		3.54 ± 1.47 *		16.51 ± 8.11		4.17 ± 2.76		31.69 ± 4.98		10.18 ± 5.74 *	
ANT	4.03 ± 0.58		0.79 ± 0.26 *		3.37 ± 0.94		0.98 ± 0.70 *		4.37 ± 2.24		1.44 ± 0.79	
PA	3.64 ± 0.66		0.80 ± 0.32 *		2.96 ± 0.81		1.07 ± 0.78 *		3.45 ± 0.93		1.38 ± 0.70*	
9-ANT	1.97 ± 0.12		0.64 ± 0.23 *		1.28 ± 0.37		0.68 ± 0.45		2.58 ± 1.31		1.20 ± 0.70	
RET	<LOD		<LOD		<LOD		<LOD		<LOD		<LOD	
PYR	2.67 ± 0.49		0.91 ± 0.39 *		1.91 ± 0.46		0.98 ± 0.70		2.48 ± 1.01		1.72 ± 0.97	
FLA	1.94 ± 0.36		1.12 ± 0.37		1.28 ± 0.82		1.52 ± 1.15		1.96 ± 0.47		2.62 ± 1.21	
Mt-FLA	0.94 ± 0.06		0.80 ± 0.22		0.63 ± 0.25		0.81 ± 0.61		1.27 ± 0.67		1.62 ± 1.06	
BaA	1.18 ± 0.55		0.90 ± 0.15		1.00 ± 0.53		0.98 ± 0.62		1.06 ± 0.12		1.79 ± 0.79	
CHR	1.53 ± 0.50		1.74 ± 0.25		1.12 ± 0.41		1.81 ± 1.31		1.32 ± 0.16		2.93 ± 1.62	
Mt-CHR	0.32 ± 0.06		0.45 ± 0.11		0.23 ± 0.09		0.40 ± 0.19		0.51 ± 0.24		0.83 ± 0.37	
CPcdPYR	0.72 ± 0.28		1.09 ± 0.38		0.46 ± 0.13		1.50 ± 1.22		1.05 ± 0.39		2.19 ± 1.52	
BaF	0.37 ± 0.06		0.56 ± 0.12		0.29 ± 0.09		0.51 ± 0.35		0.31 ± 0.09		0.94 ± 0.54	
BaP	0.64 ± 0.07		0.82 ± 0.15		0.51 ± 0.05		0.87 ± 0.58		0.64 ± 0.30		1.32 ± 0.61	
BbF	0.85 ± 0.10		0.46 ± 0.13		0.65 ± 0.14		0.56 ± 0.40		0.85 ± 0.21		0.91 ± 0.53	
BeP	0.28 ± 0.03		0.32 ± 0.04		0.24 ± 0.04		0.38 ± 0.27		0.31 ± 0.12		0.56 ± 0.22	
BkF	1.03 ± 0.23		0.54 ± 0.19		0.69 ± 0.30		0.58 ± 0.41		0.80 ± 0.23		0.89 ± 0.45	
PER	0.22 ± 0.01		0.24 ± 0.06		0.18 ± 0.04		0.26 ± 0.15		0.21 ± 0.06		0.40 ± 0.15	
PIC	<LOD		<LOD		<LOD		<LOD		<LOD		<LOD	
DBA	1.58 ± 0.38		1.83 ± 0.50		1.22 ± 0.37		1.96 ± 1.27		1.50 ± 0.32		3.69 ± 1.56	
IND	1.07 ± 0.05		1.93 ± 0.64		0.83 ± 0.12		2.28 ± 1.46		1.09 ± 0.30		3.68 ± 1.55	
BghiP	0.66 ± 0.17		0.84 ± 0.08		0.51 ± 0.25		1.04 ± 0.63		0.66 ± 0.24		1.37 ± 0.43 *	
DBP	1.88 ± 0.32		1.72 ± 0.63		1.30 ± 0.33		2.00 ± 1.33		1.80 ± 0.27		3.94 ± 2.02	
COR	0.57 ± 0.11		0.83 ± 0.17		0.49 ± 0.21		0.83 ± 0.53		0.59 ± 0.33		1.19 ± 0.32 *	
ΣPAHs	115.16 ± 16.22		56.68 ± 13.84*		90.97 ± 24.92		62.03 ± 40.75		158.17 ± 46.48		133.61 ± 69.65	

Values are mean ± S.D. The symbol asterisk (*) indicates significant difference in the effect of B5 on total emissions factors over the driving tests (Student's t-test, $p < 0.05$). LOD: below limit of detection.

The increased emissions in HMW-PAHs are in accordance with [18]. The elevated fractions of HMW-PAHs were attributed to the combustion reaction through pyrosynthesis of the fuel fragments in the diesel engine and the unsaturated components in biodiesel [30], [32].

In accordance with previous studies, the EFs from LMW-PAHs are higher than that for HMW-PAHs [8], [20], [21], [31]. However, the composition of individual compounds varied among different studies. For example, NAP was the most abundant particle PAH species in this study and [33], but other studies (e.g. [8], [20], [33]) reported a rather smaller proportion of particle phase NAP. This may be attributed to the partitioning of compounds with high volatility between particulate and vapor phases or the vapor phase NAP being absorbed on quartz filters.

While previous studies suggested that biodiesel may enhance the formation of oxy-PAHs, this study noticed a reduction in oxy-PAHs over NEDC and idling [17], [34]. The contradiction may attribute to the dominant 2-ring oxy-PAHs, 1,4-NQ, as the emissions of other oxy-PAHs were generally higher when using B5, while 1,4-NQ were greatly reduced. In [17], 1,4-NQ was not the most dominant species and it was increased with the biodiesel content. The study [35] used a passenger car with Euro II standard without DPF equipment and did not test 1,4-NQ. The disagreement in oxy-PAHs results may be attributed from different engine types, fuels, and PAHs being examined. Nevertheless, this study showed that there is a higher proportion of oxy-PAHs in PAH composition and a promotion of 4- and 5-ring oxy-PAHs when biodiesel blend was used.

World Academy of Science, Engineering and Technology
International Journal of Transport and Vehicle Engineering
Vol:15, No:5, 2021

TABLE III
SUMMARY OF FUEL-BASED EFs OF oxy-PAHs, TOTAL PAHs WITH ULSD (B0) AND BIODIESEL BLEND (B5) FUELS OVER NEDC, STEADY-STATE AND IDLING
TESTS

Oxy-PAHs	Fuel-based EFs (µg/kg)																	
	NEDC						Steady						Idling					
	B0			B5			B0			B5			B0			B5		
1-NAD	0.37	±	0.03	0.36	±	0.10	0.27	±	0.07	0.42	±	0.26	0.57	±	0.28	0.64	±	0.30
1,4-NQ	1.51	±	0.13	0.43	±	0.14 *	1.15	±	0.60	0.54	±	0.42	2.13	±	1.02	0.74	±	0.40
1-ACP	0.24	±	0.06	0.29	±	0.11	0.16	±	0.04	0.30	±	0.26	0.30	±	0.11	0.51	±	0.39
9-FLO	0.18	±	0.04	0.20	±	0.07	0.10	±	0.00	0.25	±	0.18	0.22	±	0.09	0.40	±	0.26
9,10-ANQ	0.14	±	0.01	0.21	±	0.05	0.14	±	0.05	0.25	±	0.15	0.30	±	0.10	0.44	±	0.20
1,8-NAPAyd	0.20	±	0.04	0.21	±	0.07	0.15	±	0.03	0.27	±	0.17	0.32	±	0.09	0.42	±	0.21
5,12-NACQ	0.09	±	0.02	0.12	±	0.03	0.07	±	0.03	0.12	±	0.09	0.12	±	0.04	0.28	±	0.26
BaA7,12-dio	0.14	±	0.02	0.25	±	0.09	0.10	±	0.03	0.26	±	0.17	0.20	±	0.10	0.49	±	0.33
1,4-CRQ	0.08	±	0.01	0.09	±	0.01	0.06	±	0.03	0.10	±	0.07	0.13	±	0.08	0.20	±	0.13
6H-BcdP-6-one	0.12	±	0.03	0.09	±	0.02	0.09	±	0.03	0.08	±	0.05	0.15	±	0.05	0.16	±	0.09
Σ oxy-PAHs	3.07	±	0.38	2.24	±	0.60	2.31	±	0.76	2.59	±	1.78	4.44	±	1.74	4.27	±	2.51
Total PAHs	118.23	±	16.59	58.92	±	14.40 *	93.27	±	25.50	64.62	±	42.52	162.61	±	48.21	137.88	±	71.86

Values are mean ± S.D. The symbol asterisk (*) indicates significant difference in the effect of B5 on total emissions factors over the driving tests (Student's t-test, $p < 0.05$). LOD: below limit of detection.

IV. CONCLUSION

The current study compares the particulate emissions from a Euro VI-LDV using B0 and B5 WCO-based biodiesel blend. The OC/EC analysis showed a domination of OC over EC among all driving cycles and fuel blends. The EFs of OC were increased by 30%, 23% and 111% during NEDC, steady, and idling test, respectively, when B5 was used compared with B0. The EFs of EC were very low and did not show a clear pattern of change when B0 was replaced by B5.

The PAHs/oxy-PAHs analysis revealed that the B5 blend reduced emissions of total particulate phase PAHs under all driving conditions B5 fuel reduced. The EFs were reduced by 50%, 31%, and 15% under NEDC, steady and idling test, respectively. The reduction in total PAHs EFs was mostly due to the drop of LMW-ring PAH. MMW- and HMW-PAHs, as well as oxy-PAHs, were generally increased when using B5. Although using B5 WCO-based biodiesel blend could be more sustainable, our results raise concern of atmospheric and health issues, as the OC emissions were higher than using B0 and there was a shift in PAHs composition.

REFERENCES

[1] U.S. Environmental Protection Agency (EPA). "Health assessment document for diesel engine exhaust", Prepared by the National Center for Environmental Assessment, Washington, DC, for the Office of Transportation and Air Quality; EPA/600/8-90/057F. Available from: National Technical Information Service, Springfield, VA; PB2002-107661, and <http://www.epa.gov/ncea>, 2002.
[2] Panel on Environmental Affairs, Legislative Council of the Hong Kong Special Administrative Region of the People's Republic of China, "Administration's paper on progress on improving roadside air quality", Available from: <https://www.legco.gov.hk/yr18-19/english/panels/ea/papers/ea20181219cb1-319-4-e.pdf>, Dec. 2018.
[3] G. Knothe, and L. F. Razon, "Biodiesel fuels", Prog. Energ. Compust. vol. 58, pp. 36-59, Jan. 2017.
[4] E. Bakeas, G. Karavalakis, G. Fontaras, and S. Stournas, "An experimental study on the impact of biodiesel origin on the regulated and PAH emissions from a Euro 4 light-duty vehicle", Fuel, vol. 90, no. 11, pp. 3200-3208, Nov. 2011.
[5] G. Karavalakis, K. C. Johnson, M. Hajbabaei, and T. D. Durbin, "Application of low-level biodiesel blends on heavy-duty (diesel) engines: Feedstock implications on NOₓ and particulate emissions" Fuel

vol. 181, pp. 259-268, Oct. 2016.
[6] M. Lapuerta, O. Armas, and J. Rodriguez-Fernandez, "Effect of biodiesel fuels on diesel engine emissions", Prog. Energ. Compust. vol. 34, no. 2, pp. 198-223., Apr. 2019
[7] K. Na, S. Biswas, W. Robertson, K. Sahay, R. Okamoto, A. Mitchell, and S. Lemieux, "Impact of biodiesel and renewable fuels on emissions of regulated pollutants and greenhouse gases on a 2000 heavy duty diesel truck", Atmos. Environ., vol. 107, pp. 307 -314, Apr. 2015.
[8] T. Lu, Z. Huang, C. S. Cheung, & J. Ma, (2012). "Size distribution of EC, OC and particle-phase PAHs emissions from a diesel engine fueled with three fuels", Sci, Total Environ, vol. 438, pp. 33-41, Nov. 2012.
[9] J. H. Tsai, S. J. Chen, K. L. Huang, Y. C. Lin, W. J. Lee, C. C. Lin, and W. Y. Lin, "PM, carbon, and PAH emissions from a diesel generator fueled with soy-biodiesel blends", J. Hazard. Mater., vol. 179, no. 1-3, pp. 237-243, July 2010.
[10] H. Zhang, K. T. Magara-Gomez, M. R. Olson, T. Okuda, K. A. Walz, J. J. Schauer, and M. J. Kleeman, "Atmospheric impacts of black carbon emission reductions through the strategic use of biodiesel in California", Sci, Total Environ, vol. 538, pp. 412-422, Dec. 2015.
[11] J. Zhang, K. He, X. Shi, and Y. Zhao, "Effect of SME biodiesel blend on PM₂.₅ emission from a heavy-duty engine", Atmos. Environ., vol. 43, no. 15, pp. 2442-2448, May 2009.
[12] IARC, "Diesel and Gasoline Engine Exhausts and Some Nitroarenes Monographs on the Evaluation of Carcinogenic Risks to Humans", Lyon, France, Vol. 105, 2012.
[13] P. T. J. Scheepers, and P. P. Bos, "Combustion of diesel fuel from a toxicological perspective: II. Toxicity", Int. Arch. Occ. Env. Hea., vol. 64, no. 3, pp. 163-177. Sept. 1992.
[14] F. Chen, W. Hu, and Q. Zhong, "Emissions of particle-phase polycyclic aromatic hydrocarbons (PAHs) in the Fu Gui-shan tunnel of Nanjing, China", Atmos. Res., vol. 124, 53–60, Apr. 2013.
[15] H. Z. Shen, S. Tao, R. Wang, B. Wang, G. F. Shen, W. Li, S. S. Su, Y. Huang, X. L. Wang, W. X. Liu, B. G. Li, and K. Sun, "Global time trends in PAH emissions from motor vehicles", Atmos. Environ., vol. 45, no. 12, pp. 2067–2073, Apr. 2011.
[16] M. Maria del Rosario Sienra, "Oxygenated polycyclic aromatic hydrocarbons in urban air particulate matter", Atmos. Environ., vol. 40, no. 13, pp. 2374-2384, Apr. 2006.
[17] C. Guan, C. S. Cheung, X. Li, and Z. Huang, "Effects of oxygenated fuels on the particle-phase compounds emitted from a diesel engine". Atmos. Pollut. Res., vol. 8, no. 2, pp. 209-220, Mar. 2017.
[18] I. Sadiktsis, I. (2016). "Traffic related air pollution with emphasis on particle associated polycyclic aromatic hydrocarbons", Available from: <https://su.diva-portal.org/smash/get/diva2:917324/FULLTEXT01.pdf>, 2016.
[19] R. Abrantes, J. V. Assuncao, C. R. Pesquero, R. E. Bruns, and R. B. Nobrega, "Emission of polycyclic aromatic hydrocarbons from gasohol and ethanol vehicles", Atmos. Res., vol. 43, no. 3, pp. 648–654, Jan. 2009.
[20] C. He, Y. Ge, J. Tan, K. You, X. Han, and J. Wang, "Characteristics of

World Academy of Science, Engineering and Technology
International Journal of Transport and Vehicle Engineering
Vol:15, No:5, 2021

polycyclic aromatic hydrocarbons emissions of diesel engine fueled with biodiesel and diesel", *Fuel* vol. 89, no. 8, pp. 2040-2046, Aug. 2010.

[21] G. Karavalakis, V. Boutsika, S. Stournas, and E. Bakeas, "Biodiesel emissions profile in modern diesel vehicles. Part 2: Effect of biodiesel origin on carbonyl, PAH, nitro-PAH and oxy-PAH emissions", *Sci, Total Environ*, vol. 409, no. 4, pp. 738-747, Jan. 15.

[22] Dynamic Progress International Limited, "Material Safety Data Sheet for B100 Biodiesel", Available from <http://www.dynamic-progress.com.hk/products_services.php?action=details&nid=9>, 2012.

[23] X. J. Man, C. S. Cheung, Z. Ning, L. Wei, and Z. H. Huang, "Influence of engine load and speed on regulated and unregulated emissions of a diesel engine fueled with diesel fuel blended with waste cooking oil biodiesel", *Fuel,* vol. 180, pp. 41-49, Sept. 15.

[24] J. C. Chow, J. G. Watson, L. W. A. Chen, M. C. O. Chang, N. E. Robinson, D. Trimble, and S. Kohl, "The IMPROVE_A temperature protocol for thermal/optical carbon analysis: Maintaining consistency with a long-term database", *Japca. J. Air Wate MA.*, vol. 57, no. 9, pp. 1014-1023, 2007.

[25] S. S. H. Ho, J. Z. Yu, J. C. Chow, B. Zielinska, J. G. Watson, E. H. L. Sit, and J. J. Schauer, "Evaluation of an in-injection port thermal desorption-gas chromatography/mass spectrometry method for analysis of non-polar organic compounds in ambient aerosol samples", *J. Chromatog. A*, vol. 1200, no. 2, pp. 217-227, July 2008.

[26] K. Shibata, K. Enya, N. Ishikawa, and K. Sakamoto, "EC/OC and PAHs Emissions from a Modern Diesel Engine with DPF Regeneration Fueled by 10% RME Biodiesel". *Aerosol Air Qual. Res*, vol. 19, no. 8, pp. 1765-1774, July 2019.

[27] M. P. Fraser, K. Lakshmanan, S. G. Fritz, and B. Ubanwa, "Variation in composition of fine particulate emissions from heavy-duty diesel vehicles", *J. Geophysic. Res.*, vol. 107, no. D21, pp. 8346, Nov. 2002.

[28] S. D. Shah, D. R. Cocker, J. W. Miller, and J. M. Norbeck, "Emission rates of particulate matter and elemental and organic carbon from in-use diesel engines", *Environ. Sci. Technol.*, vol. 38, no. 9, pp. 2544-2550, May 2004.

[29] J. Zhang, K. He, X. Shi, and Y. Zhao, "Comparison of Particle Emissions from an Engine Operating on Biodiesel and Petroleum Diesel", *Fuel,* vol. 90, no. 6, pp. 2089-2097, June 2011.

[30] R. Ballesteros, J. J. Hernández, and L. L. Lyons, "An experimental study of the influence of biofuel origin on particle-associated PAH emissions", *Atmos. Environ.*, vol. 44, no. 7, pp. 930-938, Mar. 2010.

[31] C. V. de Souza, and S. M. Corrêa, "Polycyclic aromatic hydrocarbons in diesel emission, diesel fuel and lubricant oil", *Fuel*, vol. 185, pp. 925-931, Dec. 2016.

[32] K. L. Cheung, L. Ntziachristos, T. Tzamkiozis, J. J. Schauer, Z. Samaras, K. F. Moore, and C. Sioutas, "Emissions of particulate trace elements, metals, and organic species from gasoline, diesel, and biodiesel passenger vehicles and their relation to oxidative potential", *Aerosol Sci. Tech.*, vol. 44, no. 7, pp. 501-513, June. 2010.

[33] De Abrantes, R., De Assunção, J. V., and R. Pesquero, C., "Emission of polycyclic aromatic hydrocarbons from light-duty diesel vehicles exhaust", *Atmos. Environ.*, vol. 38, no. 11, pp. 1631-238, Feb. 1640.

[34] L. Huang, S. V. Bohac, S. M. Chernyak, and S. A. Batterman, "Effects of fuels, engine load and exhaust after-treatment on diesel engine SVOC emissions and development of SVOC profiles for receptor modeling", *Atmos. Environ (1994).,* vol. 102, pp. 228-238, Feb. 2015.

[35] G. Karavalakis, G. Fontaras, D. Ampatzoglou, M. Kousoulidou, S. Stournas, Z. Samaras, and E. Bakeas, "Effects of low concentration biodiesel blends application on modern passenger cars. Part 3: Impact on PAH, nitro-PAH, and oxy-PAH emissions", *Environ. Pollut.*, vol. 158, no. 5, pp. 1584-1594, May 2010.