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Comparison of particle emissions from an engine operating on biodiesel and petroleum diesel

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ABSTRACT

Biodiesel is an alternative fuel with growing usage in the transportation sector. To compare biodiesel and petroleum diesel effects on particle emissions, engine dynamometer tests were performed on a Euro II engine with three test fuels: petroleum diesel (D), biodiesel made from soy bean oil (BS) and biodiesel made from waste cooking oil (BW). $PM_{2.5}$ samples were collected on Teflon and quartz filters with a Model 130 High-Flow Impactor (MSP Corp). Organic (OC) and elemental (EC) carbon fractions of $PM_{2.5}$ were quantified by a thermal-optical reflectance analysis method and particle size distributions were measured with an electrical low pressure impactor (ELPI). In addition, the gaseous pollutants were measured by an AMA4000 (AVL Corp). The biodiesels were found to produce 19–37% less and 23–133% more $PM_{2.5}$ compared to the petroleum diesel at higher and lower engine loads respectively. On the basis of the carbon analysis results, the biodiesel application increased the $PM_{2.5}$ OC emissions by 12–190% and decreased the $PM_{2.5}$ EC emissions by 53–80%, depending on the fuel and engine operation parameters. Therefore OC/EC was increased by three to eight times with biodiesel application. The geometrical mean diameter of particles from biodiesels and petroleum diesel had consistent trends with load and speed transition. In all the conditions, there is a shift of the particles towards smaller geometric mean diameter for the biodiesel made from waste oil.

1. Introduction

Biodiesel is one kind of alternative fuel with great developing potential. In China, the total crude oil consumption was 322 million tons in 2006, of which 145 million tons were imported [1]. Therefore, the exploration of alternative energy such as ethanol, biodiesel and gas-to-liquid (GTL) are becoming more and more critical. Biodiesel, which is manufactured from transesterification of vegetable oils or animal fats, can be used without any engine modification. Compared to petroleum diesel, biodiesel has the characteristics of renewability, lower volatility and viscosity. The quality of petroleum diesel and biodiesel, such as cetane number and flash point, could meet the same norm. According to the Mid- and Long-Term Development Plan for Renewable Energy, the consumption of biodiesel in China will reach 2.0 million tons in 2020 [2].

Particle emissions from diesel vehicles received concern in the past years due to adverse effects on human health, urban visibility and global climate [3]. The diesel particles consist of agglomerates of primary carbon particles and condensed organic compounds, sulfate and metallic ash [4]. Most diesel particles are inspirable for a mean diameter of 60–100 nm [5]. These diesel exhaust fine particles contribute mostly to the PAHs collected in urban atmosphere [6]. The particles demonstrated mutagenicity and carcinogenicity in biologic studies [7,8]. For the diesel exhaust, the chronic exposure and its possible relationship to lung cancer has been reported [8,9]. Personal exposures to the diesel exhaust particles have been assessed and predicted [10,11]. Moreover, some epidemiologic research has found elevated cardiovascular and respiratory morbidity and mortality with short-term and long-term diesel particles exposure [12–15].

The biodiesel or biodiesel blend emissions from diesel engine have been investigated by many researchers. However, most of the studies focused on the conventional pollutants (particle mass and gas phase pollutants such as THC, NO_x and CO). Many studies noted strong reduction in particle emissions [16,17] and smoke opacity [18] as a result of biodiesel fuel combustion. A small number of scientists found increased particle emissions by using biodiesel [19]. The effect of biodiesel on particle emissions could be influenced by engine operating conditions, such as load [20].

A few studies investigated the OC and EC emissions and particle size distribution, but in these studies only one kind of biodiesel was chosen to compare with the petroleum diesel. With biodiesel combustion, EC emissions were found decreased significantly while OC emissions remained at the same level [21]. OC/EC ratio was discovered to be increased by applying biodiesel instead of

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diesel [22]. The effect of biodiesel on particle size distribution is still under debate: Jung et al. [16] reported particle number of nucleation mode increased and that of accumulation mode decreased at 75% load when biodiesel, soy methyl ester was applied; Krahl et al. [23] reported lower particle number concentration with biodiesel rapeseed oil methyl ester. If we can have characterization of particle emissions from multiple kinds of biodiesel, it would provide support information for policy development related to biodiesel selection.

The effect of biodiesel on OC and EC emissions needs to be addressed since it is important for source apportionment studies [24,25]. Moreover, the impact of biodiesel combustion on particle size needs to be investigated, for the particle size distribution, especially the nanoparticles emitted from diesel engines were recognized as an important factor in human health study [26].

In order to explore the impact of different biodiesels on particle composition and size distribution, two biodiesels (BS and BW) were chosen in this study to compare with the petroleum diesel. Both biodiesels selected here are products from stable companies with a certain amount of customers. Emissions from a typical Chinese engine were tested on a dynamometer under two sets of selected operating conditions. $PM_{2.5}$ mass, OC and EC emissions as well as PM size distributions were obtained.

2. Experimental setup and measurement

2.1. Engine and fuels

A four-cylinder direct injection diesel engine equipped with an in-line injection pump was used for the experiments. This engine is commonly used in Chinese trucks (China First Automobile Group Wuxi Diesel Engine Works 4CK) and complied with the emission standard of National Standard in China (Phase II), which is equivalent to the Euro II emission standard in terms of PM and gaseous pollutant emission levels. It had four-stroke cycle and a 4.752 L displacement, with a peak power output of 117 kw at 2300 rpm and a peak torque output of 580 Nm at 1400 rpm. In the experiment, engine speed and load was controlled by the Schenck DYNAS HT350 dynamometer. In addition, the cylinder pressure and heat release curve of this engine fueled with petroleum diesel is presented in the Supplementary information.

In this test, the petroleum diesel (D) was purchased from a gas station in Beijing, China; biodiesel made from soybeam oil (BS) was produced by Xi'an Blue Sky Biological Engineering CO., LTD; and biodiesel made from waste oil (BW) was produced by Hebei Wuan Zhenghe Bioenergy CO. Some fuel properties are presented in Table 1.

2.2. Test conditions and sampling

The procedure for diesel engine emissions sampling is shown in Fig. 1. A portion of exhaust gas was transferred to the gaseous pollutants detecting device and dilution systems for filter and real-time sampling. The gaseous pollutants concentration was determined by the AMA4000 from AVL: THC was detected by flame ionization detector (FID); CO and CO_2 were measured by non-dispersive infrared analyzer; and O_2 was monitored by paramagnetic O_2 analyzer. CO_2 concentrations in exhaust gas, diluted gas and background atmosphere were measured to obtain the dilution rate. The method to calculate the dilution rate is defined as Eq. (1):

$$\mathrm{DR} = \frac{(C_E - C_B) - (C_D - C_B)}{(C_D - C_B)} \quad (1)$$

where DR is the dilution rate, C_E is CO_2 concentration in exhaust gas, C_D is CO_2 concentration after dilution and C_B is CO_2 concentration in background atmosphere.

In order to get $PM_{2.5}$ sample at stable engine conditions, smoke was monitored by AVL 439 opacimeter to check the conditions. Smoke was sampled three times in every condition. Only when the error of smoke was less than 5.0%, particles would be collected. The error bars based on sample to sample variation for THC, NO_x and CO were 2.0%, 12% and 5.1% respectively.

2.2.1. Filter sampling

Particles in dilute exhaust gas were collected by Model 130 High-Flow Impactor (MSP Corp) in the filter sampling system. The dilution system (1) was a two-stage dilution system: the first stage was an injection dilution tunnel by Dekati Ltd. (Finland); the second stage was a self-designed dilution tunnel according to the national standard in China (Limits and measurement methods for exhaust pollutants from compression ignition and gas fueled positive ignition engines of vehicles (III, IV, V)). The dilution ratio was in the range of 7–10. The Model 130 High-Flow Impactor is a low-pressure-drop cascade impactor (six cascade stages with cutpoints of 0.26, 0.44, 0.77, 1.4, 2.5 and 10 μm) with 100 L/min flow rate. In this test, only $PM_{2.5}$ stage was used to collect particles. As portrayed in Fig. 1, Teflon filters (Shanghai Plastics Research Institute) and quartz filters (PALL #2500QAT2U) were used for particle collection and measurements.

For the filter sampling, four engine conditions were chosen from the 13-mode test cycle (ECE R49). The four modes were 1400 rpm, 50% load; 1400 rpm, 100% load; 2300 rpm, 25% load and 2300 rpm, 75% load, corresponding to modes 4, 6, 11 and 9 of ECE R49.

2.2.2. Real-time sampling

In the real-time sampling system, the dilution system (2) was composed of two stages which are all injection dilution tunnel

Table 1
Fuel properties of the petroleum diesel (D), biodiesel made from soy bean oil (BS) and biodiesel made from waste oil (BW).

Fuel property	D	BS	BW	Method	Corresponding to ASTM
Sulfur content, ppm	80[a]	160[a]	130[a]	GB/T 380	ASTM D4294
Kinemetic viscosity at 20 °C (10^{-6} m^2/s)	4.4[a]	6.9[a]	8.4[a]	GB/T 265	ASTM D445
Cetane number	⩾51	55[b]	–	GB/T 386	ASTM D6890
Flash point (closed cup) °C	⩾55	130[b]	–	GB/T 261	ASTM D7215
Aromatics, mass%	⩽11	–	–	SH/T 0606	ASTM D6591
Acid number, mg KOH/g	–	3.52[b]	–	GB/T 14489	ASTM D664
Density, kg/m^{-3}	820–845	875[b]	–	GB/T 1884-1885	ASTM D1298/ 4052
Cloud point, °C	–	−1[b]	–	GB/T 6986	ASTM D2500
Distillation temperature, °C	T50 ⩽ 300	–	–	GB/T 6536	ASTM D6751
	T90 ⩽ 355	–	–		
	T95 ⩽ 365	–	–		

[a] Fuel properties were provided by Xi'an Blue Sky Biological Engineering CO., LTD.
[b] Fuel properties were measured by Research Institute of Petroleum Processing in China.

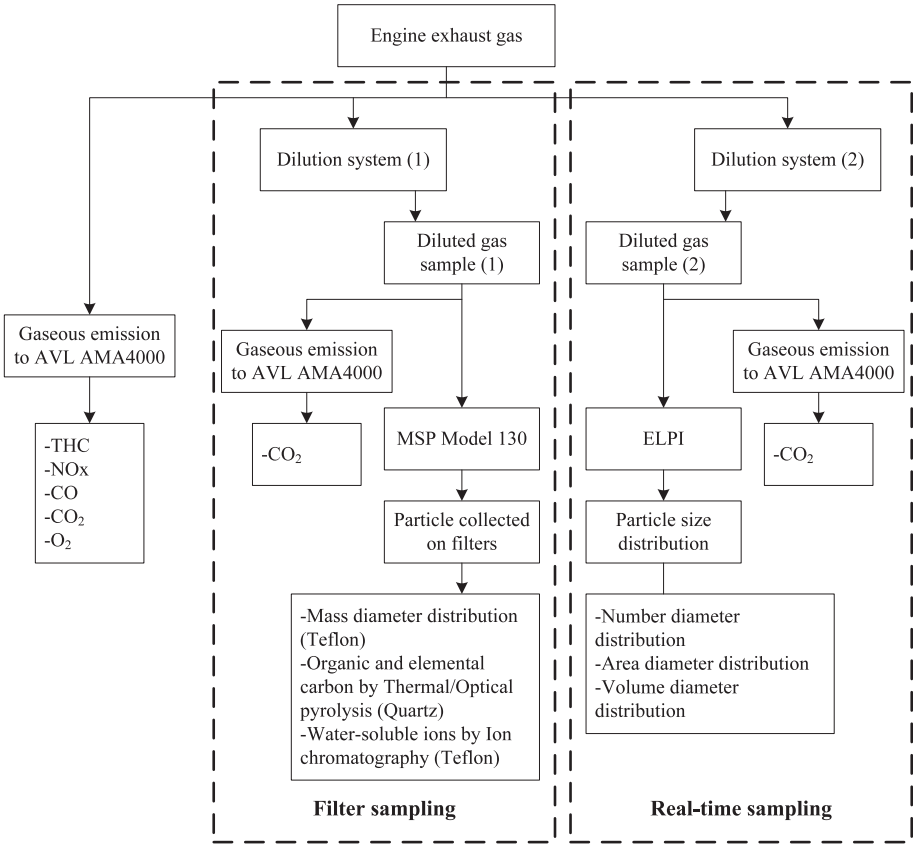

Fig. 1. Engine exhausts sampling procedure.

by Dekati Ltd. The dilution ratio was in the range of 50–90. Particle emissions after dilution were measured by ELPI (Dekati Ltd.). The ELPI has cutpoints at 0.028, 0.056, 0.095, 0.16, 0.26, 0.38, 0.61, 0.95, 1.60, 2.39, 4.00, 6.68, and 9.92 μm for stage 1 to stage 13 with operating flow rate of 9.89 L/min. In the real-time sampling, the engine conditions were chosen, which were 10%, 25%, 50%, 75% and 100% load at engine speeds of 1400 rpm and 2300 rpm.

2.3. Particle physical and chemical measurement

The particle mass was determined by weighting the filters before and after sampling. Teflon filters were weighed on a Mettler AE 240, model Toledo A6 balance of sensitivity 0.01 mg (0.1 mg accuracy). All the filters were conditioned for 24 h at about 40% RH and 25 °C in an air-conditioned room before weighting.

OC and EC were measured by a Thermal/Optical Carbon Analyzer (DRI, Model 2001) [27]. The IMPROVE temperature protocol was used to define the carbon fractions [28]. The quartz filter was heated stepwise to temperatures of 120 °C, 250 °C, 450 °C, and 550 °C in a pure helium environment to determine OC1, OC2, OC3 and OC4 respectively. Then the environment was shifted to 2% O_2/98% He, and the filter continuously heated stepwise to 550 °C, 700 °C and 800 °C to determine EC1, EC2 and EC3 respectively. In order to minimize the background carbon level, the quartz filters were baked at 450 °C for 4 h. An example of the temperature and the FID (Flame Ionization Detector) which was used to reflect the carbon signal is shown in Fig. 2.

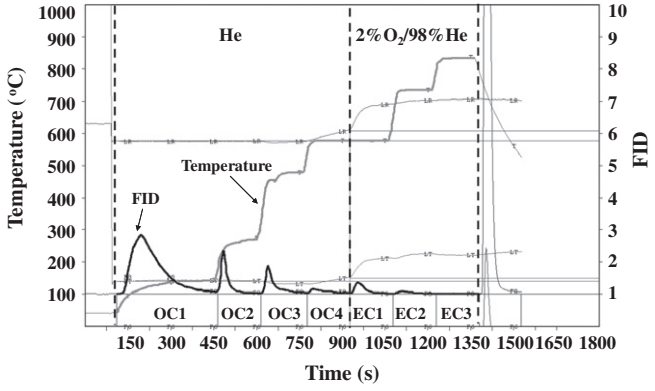

Fig. 2. Example of the temperature profile for IMPROVE protocol operated by Thermal/Optical Carbon Analyzer.

3. Results

3.1. $PM_{2.5}$ and gaseous pollutants emissions

Since the calorific value of biodiesel is lower than that of petroleum diesel, in this test the fuel consumption rate of two biodiesels were both 7% higher than that of petroleum diesel. The emission rates of $PM_{2.5}$, HC, NO_x and CO from D, BS and BW are listed in Table 2. For the petroleum diesel, the $PM_{2.5}$ emission rate increased as speed and load increased. For the biodiesel, $PM_{2.5}$ emission rate decreased with load increase under high engine speed. Under low engine loads, biodiesel application increased $PM_{2.5}$ emissions compared to petroleum diesel. Under high loads, biodiesel application decreased $PM_{2.5}$ emissions. The peak $PM_{2.5}$ emission rates for biodiesels and petroleum diesel were obtained at 2300 rpm, 25% load and 2300 rpm, 75% load, respectively.

Table 2
Emission rate of $PM_{2.5}$, HC, NO_x and CO.

Fuel	Speed (rpm)	Load (%)	Emission rate (mg/min)			
			$PM_{2.5}$	THC	NO_x	CO
D	1400	50	24.9	300	4466	445
	1400	100	84.2	328	6972	3148
	2300	25	121.0	787	2197	2327
	2300	75	201.4	924	6100	2070
BS	1400	50	58.1	218	5272	430
	1400	100	68.5	382	8011	1816
	2300	25	148.4	381	2607	2460
	2300	75	126.3	683	7179	1827
BW	1400	50	53.0	251	5118	389
	1400	100	65.2	386	8119	1788
	2300	25	204.4	330	2438	1991
	2300	75	137.6	656	7227	1879

In this test, the gaseous pollutant emissions from BS and BW were consistent. Compared with petroleum diesel, biodiesel application decreased THC and CO emission by 30% and 21% respectively, but increased NO_x emission by 16%. The reduction of THC and CO are explained by the increase in oxygen content in biodiesel which contributes to complete oxidation [29]. NO_x emissions would be increased by advanced combustion process with higher viscosity, density and oxygen content of biodiesel [30,31].

3.2. $PM_{2.5}$ carbon emissions

OC and EC contributed more than 80% of the $PM_{2.5}$ emission. The fuel-based OC emission factor in $PM_{2.5}$ is shown in Fig. 3a. The OC emission factor of all three fuels decreased as the load increased. Biodiesel increased OC emissions under every lower load operation condition. Compared with petroleum diesel, biodiesel application increased the OC emission factor by 80–190% under low load, and increased OC by approximately 23% under high load. Between the two kinds of biodiesel, at 2300 rpm, 75% load, the OC emission factor by using BW was 36% higher than that of BS. At all the other three conditions, the difference of OC emission factor of BW and BS was within 5–12%.

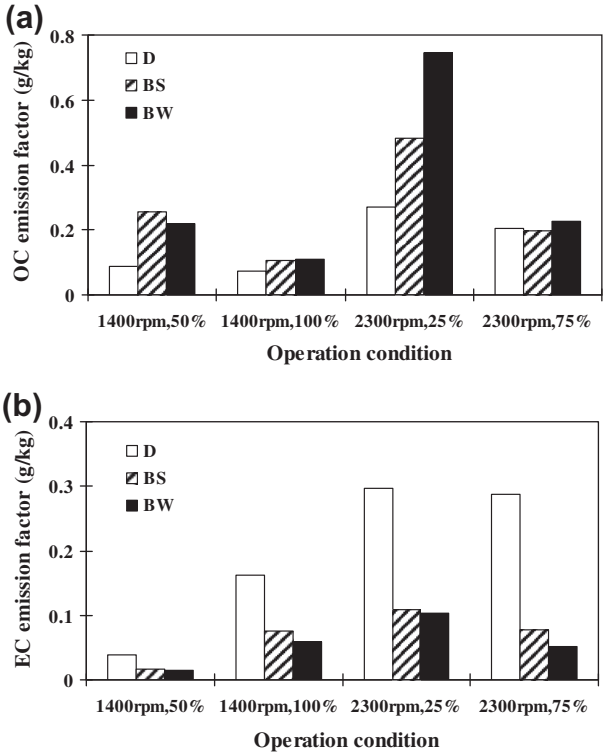

Fig. 3. Fuel-based emission factor of OC and EC at different operation conditions.

The EC emission factor in $PM_{2.5}$ was depicted in Fig. 3b. This value for all the fuels at 1400 rpm increased as the load increased while at 2300 rpm this value decreased as the load increased. The impact of biodiesel usage on EC was opposite to that of OC. EC emission factor was decreased significantly: 65% on average with biodiesel use when compared with petroleum diesel. The lowest EC emission factor was obtained at 1400 rpm, 50% load with biodiesel.

The OC1–OC4 and EC1–EC3 emission rate as well as OC/EC in $PM_{2.5}$ is presented in Fig. 4. In Fig. 4a, OC1 was increased by 260% and 160% with BS and BW when compared to petroleum diesel respectively. BS and BW usage decreased the EC emission rate by 53% and 58% respectively when compared to petroleum diesel. EC1 is the majority fraction in EC, which decreased 54% and 65% by BS and BW respectively.

In Fig. 4b, OC/EC of biodiesel decreased significantly when load was increased from 50% to 100%. Compared to petroleum diesel, BS and BW increased OC by 47% and 54%, and decreased EC by 52% and 62% respectively. Compared to petroleum diesel OC emissions, BS increased OC1 the most by 9.4 mg/min while BW increased OC4 the most by 6.5 mg/min. In the EC emissions, EC2 decreased the most with biodiesel: compared to petroleum diesel emission rate, the emission rate of EC2 by BS and BW was decreased by 21.6 mg/min and 22.8 mg/min which were 93% and 98% respectively.

In Fig. 4c, the OC/EC for all three kinds of fuel at 2300 rpm, 25% load was higher when compared to 1400 rpm, 100% load. In the carbon fractions, OC1 increased the most by comparing biodiesel with petroleum diesel: with BS, OC1 increased by 47.5 mg/min (126%); with BW, OC1 increased by 83.9 mg/min (223%).

In Fig. 4d, the OC emission rate did not increase significantly by using biodiesel, but EC decreased 73% and 80% by using BS and BW respectively. Since the combustion condition became better with increasing load, the EC decrease with use of biodiesel became more obvious.

3.3. Particle size distribution

3.3.1. Number concentration

Fig. 5 presents the particle size distribution under the four steady conditions. The error bar of sample to sample measurement result was less than 5%. Under 1400 rpm, 50% load, number concentration of the smallest particles (0.04 μm) was the highest for all three kinds of fuels. The concentration was BW = BS > D. Under 2300 rpm, the concentration peak was at about 0.1 μm, where the value of three fuels was close. In these four conditions, BS had higher number concentration with particle size of 0.3–2 μm. The biodiesel, especially the biodiesel made of waste oil, may induce higher particle number concentration with smaller diameter.

3.3.2. Specific number concentration

The specific number concentration is defined as particle number concentration per unit power output. The specific number concentration of D, BS and BW at 1400 rpm was presented in Figs. 6–8 respectively.

In Fig. 6, for the 0.04 μm particle, the highest specific number concentration was 2.3×10^5 1/kW h at 25% load, followed by 2.0×10^5 1/kW h at 10% load. Concentration of 0.04 μm particle decreased when the load increased from 25% to 100%. For the other particles, the specific number concentration at 50%, 75% and 100% was at the same level. Generally the specific concentration

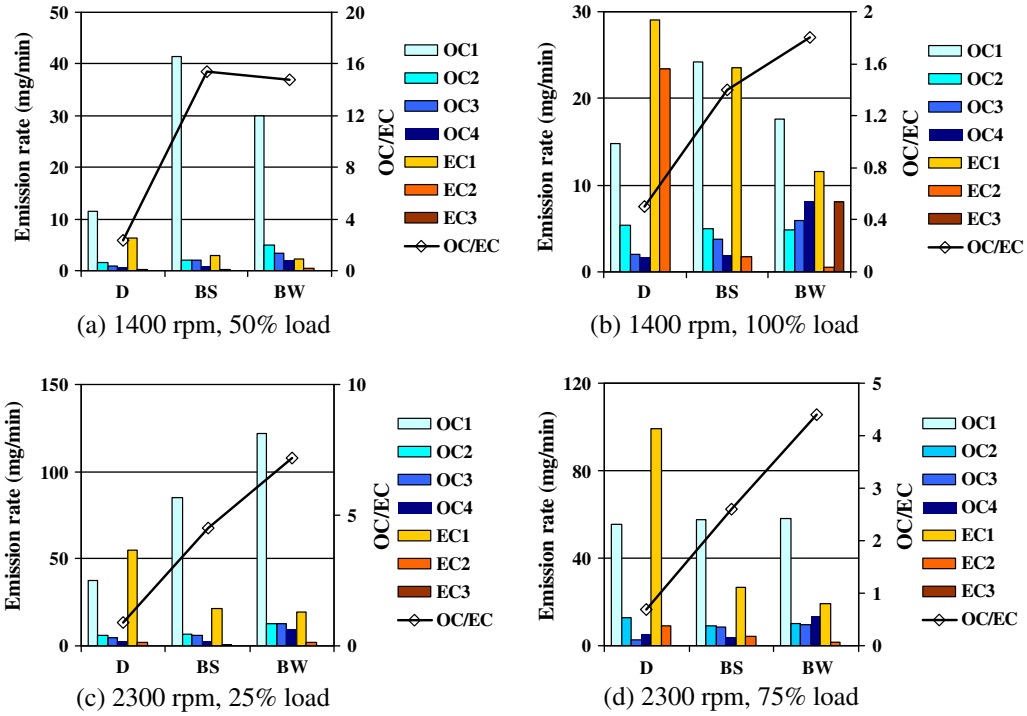

Fig. 4. $PM_{2.5}$ OC1–OC4, EC1–EC3 emission rate and OC/EC ratio.

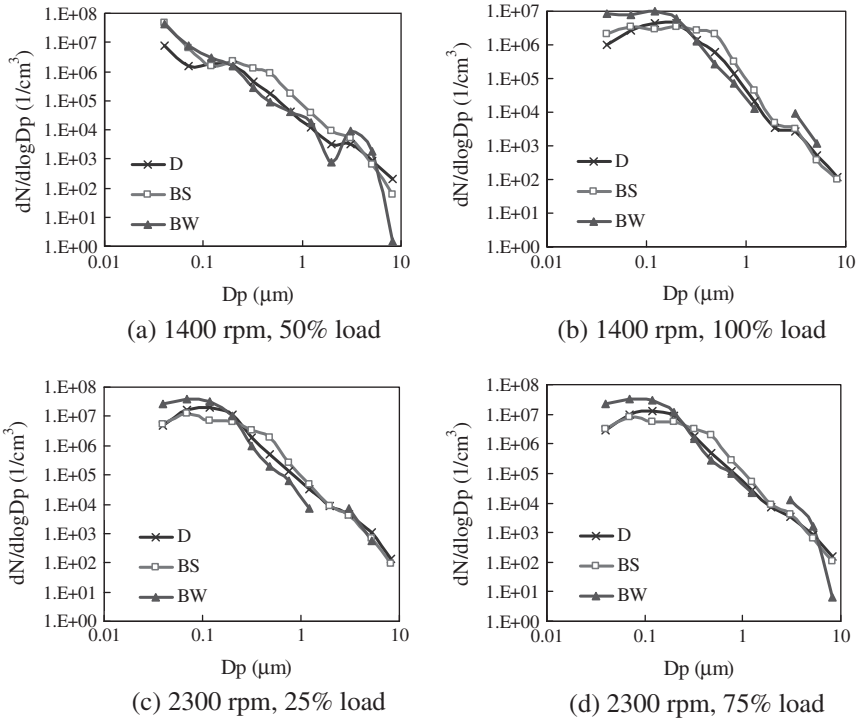

Fig. 5. Particle number concentration under four conditions.

decreased along with increasing particle size. The nuclei mode (0.005–0.05 μm) particles consist of volatile organic compounds that could be adsorbed by particles in the accumulation mode (0.1–0.3 μm), thus reduction in nuclei particle concentration would occur in the atmosphere [26].

The specific number concentration of BS is shown in Fig. 7. The concentration was consistent at 10% and 25% load. At 100% load, the concentration of particles between 0.04 and 0.20 μm did not vary significantly.

The specific number concentration of particles with BW use is shown in Fig. 8. The concentration of particles at 50% load was lower than that of 25% and 75%. The concentration at 100% load was the lowest. For BW, the specific number concentration decreased as the particle diameter increased.

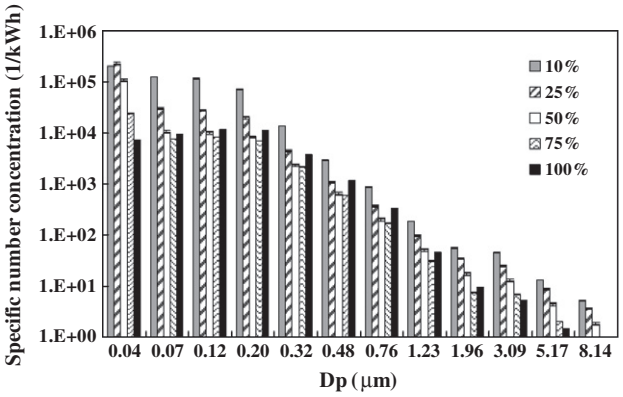

Fig. 6. Specific number concentration of petroleum diesel at 1400 rpm.

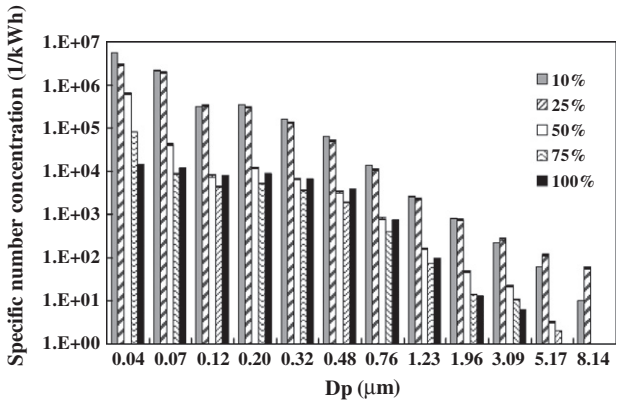

Fig. 7. Specific number concentration of BS at 1400 rpm.

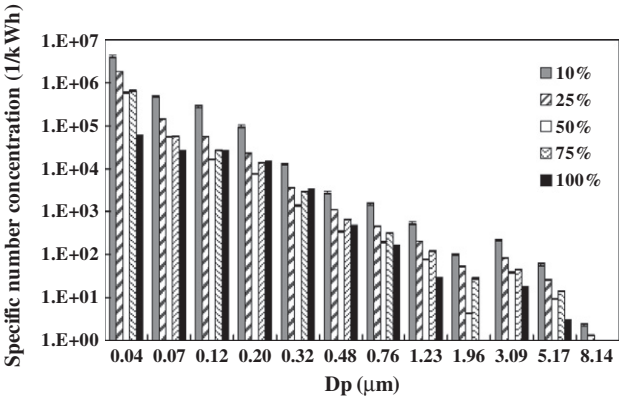

Fig. 8. Specific number concentration of BW at 1400 rpm.

3.3.3. Geometric mean diameter

In order to portray the particle diameter distribution under various conditions, geometric mean diameter was calculated by Eq. (2):

$$D_g = \exp\left(\frac{\sum n_i \ln d_i}{N}\right) \quad (2)$$

where n_i is the number of particles in the ith diameter range; d_i is the cut diameter of the ith diameter range; and N is the total particle number.

The result of D_g of fuels under various conditions is shown in Fig. 9. Not only the diameter of peak particle number concentration but also the distribution of particles was reflected by D_g. Several results could be concluded from the variation of D_g. First, the range of

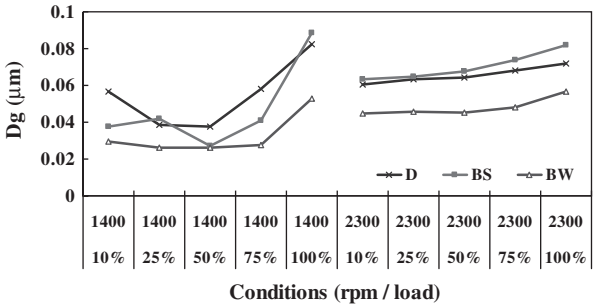

Fig. 9. Geometric mean diameter of three kinds of fuel.

D_g from the three fuels at 1400 rpm was relatively larger than that of 2300 rpm. At 1400 rpm, D_g varied from 0.03 μm to 0.09 μm. At 2300 rpm, D_g range was narrower, from 0.05 μm to 0.08 μm. Second, at 1400 rpm, D_g of all three kinds of fuel first decreased then increased when the load increased; at 2300 rpm, D_g increased as the load increased. Except the condition of 100% load, D_g at higher speed was larger than that of lower speed. Third, BW had the lowest D_g under all conditions, which was caused by the domination of smaller particle diameter.

4. Discussion

4.1. $PM_{2.5}$ mass emissions

Application of both BS and BW decreased $PM_{2.5}$ emissions by approximately 20% and 35% at 1400 rpm, 100% load and 2300 rpm, 75% load respectively when compared with petroleum diesel. A similar trend has been reported by other researchers. Haas et al. [32] obtained 53% of particle reduction by applying biodiesel prepared from soybean soapstock. Compared to petroleum diesel, a 53–69% PM emission reduction was found when applying five different biodiesels (cottonseed methyl ester, soybean methyl ester, rapeseed methyl ester, palm oil methyl ester and waste oil methyl ester) on a Euro III standard, direct injection engine [33]. Kado and Kuzmicky [34] tested particle emissions by substituting petroleum diesel with four kinds of biodiesels which were derived from plant and animal feedstocks. A particle emissions decrease of approximately 70% was found for all four undiluted biodiesels by using a 6-cylinder 4-stroke engine. An even higher particle emissions reduction was found: biodiesel reduced 91% of particles compared with ultra low sulfur diesel (sulfur content <50 ppm) [35].

In this test, biodiesels increased and decreased $PM_{2.5}$ emissions at low and high load respectively. The effect of biodiesel on $PM_{2.5}$ emissions is due to characteristics of biodiesel, such as higher oxygen content and higher viscosity, as already evidenced in past results. Leung et al. [36] tested biodiesel on a single-cylinder engine and reported higher PM emissions reduction compared to petroleum diesel at higher load. The $PM_{2.5}$ mass emission reduction could be explained as the effect of higher oxygen content of the biodiesel: oxidation was improved in locally rich fuel combustion zone; the production of soot precursor species was lowered [37]. The effect of biodiesel on PM at different loads was discussed: at high load, oxygen in biodiesel is the control factor for there are more locally rich regions and oxygen is more effective; at low load, the viscosity would become the primary factor because of worse vaporization and atomization at lower temperature [33].

4.2. OC and EC emissions

In this test, biodiesel application increased OC emissions especially under low load and decreased EC emissions significantly,

thus increased OC/EC ratio by three to eight times. The OC/EC ratio from primary emissions is needed in determining the contribution of secondary organic aerosol to total ambient atmospheric OC concentration [38–40]. Lonati et al. [39] also claimed lack of primary OC/EC in vehicle emissions in quantifying the traffic contribution to ambient $PM_{2.5}$ concentration.

The trend increase and decrease of OC and EC respectively is in accordance with the previous studies. Cheung et al. [21] observed the use of biodiesel in a diesel passenger car led to an increase in OC emissions and a decrease in EC emissions of 70–85% in several driving cycles which was comparable with the result of 65% in this test. Moreover, compared with petroleum diesel, a 126% OC increase and a 45% EC decrease was reported [41]. The EC production during combustion could be disrupted by the oxygen in the biodiesel ester atoms [21]. Thus biodiesel is supposed to have lower EC emissions. Bennett et al. [41] reported OC/EC ratio of 0.5 from B83 (83% biodiesel) combustion which was lower than the OC/EC in this test. It could be influenced by several factors: smaller engine (2.4 L compare with 4.8 L displacement in our study); different fuel (B83 compared with B100, 100% biodiesel in our study); different temperature of dilution tunnel; sampling bias caused by semivolatile compounds; different biodiesel ratio (100% in our test); different methods measuring OC and EC (NIOSH method 5040 [42] by Bennett et al. [41] and DRI IMPROVE method in this test).

Between the two biodiesels, the OC emission factor of BW was much higher than that of BS at 2300 rpm, 75% load. The emissions could probably be influenced by the physical properties (e.g., viscosity) of each kind of biodiesel which can affect the jet formation and dispersion of the fuel in the cylinder. Compared to BS, the higher viscosity of BW could lead to an advanced start of injection in this in-line injection pump of this test engine [43]. This could lead to degradation of the spray and combustion quality at low load conditions [44] which would cause incomplete combustion with higher OC emissions.

In the exhaust, EC is not a single compound, in which EC1 and EC2 + EC3 were operationally defined as char-EC (formed directly from the fuel by pyrolysis) and soot-EC (formed via gas-to-particle conversion) respectively, corresponding to the carbon fractions detected at different temperature [45]. In most of the cases, EC1 contributed approximately 90% of the EC mass, while EC3 was not detected except for BW at 1400 rpm, 100% load. It is indicated that around 90% of the EC emitted by this diesel engine might be pyrolysis char.

The OC and EC fractions, especially OC1, EC1 and their fraction in particle mass could be used to identify the characteristic of the source and is applied in source apportionment studies [46,47]. At 1400 rpm, 50% load, compared to petroleum diesel, OC1 was increased with biodiesel due to higher viscosity which has been discussed. At this condition, higher NO_x concentration of biodiesel indicated higher combustion temperature, which enhanced the combustion of the pyrolysis EC (EC1). Thus EC1 was decreased with biodiesel. At 1400 rpm, 100% load, the EC2 emission rate of petroleum diesel was higher than under any other conditions. The EC2 could be black carbon with heterogeneous material that did not oxidize at 550 °C [47]. Since this condition has the lowest air to fuel ratio, EC2 (soot particles) with graphitic, rigid and high aromatic structure may be triggered by intense aromatic radicals in the gas phase with petroleum diesel [47,48]. The EC3 of BW could be black carbon residues (from BW made from waste oil) which could not be burnt up in this low air to fuel ratio condition.

OC sampling artifacts associated with semivolatile compounds include negative artifact and positive artifact which are caused by evaporation of particle-associated organics from the filter surface and adsorption of gas-phase organics onto the filter respectively [49]. Since quartz filters have a large total surface area, positive artifact (overestimation of OC) could be the dominant problem. Bennett et al. [41] used an extra backup quartz filter to collect the gas-phase organic compounds from diesel engine exhaust. Particulate OC was determined by subtracting the amount of OC detected on the backup quartz filter from the OC detected on the front quartz filter. In this test, no backup filter was applied and therefore OC may have been overestimated. The dilution air in this test was not heated and it may possibly increase condensation and nucleation of the volatile compounds [50]. With theses reasons, the resultant of OC measurement could be artificially high, which needs improvement in future studies.

4.3. Particle number concentration

BS and BW had different effects on the particle number concentration. At the engine speed of 1400 rpm, both BS and BW increased the particle number. The total number concentration with BS use was approximately 5.2 and 2.2 times that of petroleum diesel at 50% and 100% load, and 4.8 and 3.0 times for BW respectively. At the engine speed of 2300 rpm, the BS decreased 29% and 20% of particle number compared to petroleum diesel at 25% and 75% load, but BW increased 3.7 and 8.4 times that of petroleum diesel respectively.

Some other researchers have reported an increase in particle number concentration with biodiesel. The increase of particle number by biodiesel at 1400 rpm in this test was comparable with the result of Di et al. [51] with a B80 blend (v/v: 20%/80% for petroleum diesel and biodiesel) and petroleum diesel combustion at 0.2 MPa Brake Mean Effective Pressure (BMEP). An increase in particle number (<0.091 μm) during rapeseed methyl ester (RME) combustion compared to petroleum diesel was also observed on an engine with exhaust gas recirculation (EGR) [52].

Still there were a number of studies indicating that particle number concentration decreases with biodiesel use. Lower number concentration of biodiesel blend (83% biodiesel) was observed by Bennett et al. [41] on a diesel engine. Comparing biodiesel with petroleum diesel, Jung et al. [16] also reported lower particle number concentration (38% decreases) and smaller geometric mean diameter (from 80 nm to 62 nm). It was comparable with the result in this test, which was around 20 nm reduction of D_g with BW use.

The effect of biodiesel on particle number concentration could be affected by higher oxygen content and higher viscosity. Soot formation was initiated by fuel-rich premixed ignition and lack of sufficient oxygen to burn the fuel completely [53]. The ester structure of biodiesel could reduce the production of soot precursor species [52]. Higher viscosity of biodiesel will increase the fuel injection pressure in the in-line pump which can lead to better fuel atomization [37,52]. On the other hand, however, higher viscosity would decrease the injection velocity and thus induce inferior performance in atomization compared to the petroleum diesel [54]. Moreover, higher cetane number, surface tension and density of biodiesel could also affect the particle number emission by influencing the spray characteristics [52,54]. To solve those problems, further studies are thus needed for better application of biodiesel in the future.

4.4. Impact of sulfur content

In this study, besides the influence of biodiesel, the effect of the sulfur on the particle emissions is still unknown, because the sulfur content of biodiesel is much higher than that of petroleum diesel. Sulfur content was reported to have an impact on diesel particle emissions, including particle mass, OC, EC and particle size distribution. For the diesel fuel, higher sulfur content usually induced higher particle mass and number concentration. Higher overall mean TSP emission and higher nanoparticles concentration from a bus operated with 500 ppm sulfur diesel than that of 50 ppm

sulfur diesel was reported by Ristovski et al. [55]. Higher particle mass with higher sulfur content fuel at most engine conditions was also reported by Zhang et al. [56,57]. Higher 10–480 nm particle number concentration was found in diesel engine exhaust operated with higher sulfur content [58]. In addition, higher sulfur content diesel could induce particle emissions with lower OC/EC ratio. Alander et al. [58] reported OC decreased 10–55% and EC almost unchanged when comparing 27 ppm with 430 ppm sulfur diesel. Lower OC/EC ratio was also reported [56,57]. However, there is no literature on particle emissions from the same kind of biodiesel with different sulfur content.

In our study, if the sulfur level in petroleum diesel in this test would be 150 ppm, which is a mid point of the sulfur content of the two biodiesels, the particle emissions of the diesel may be calculated from results in the previous study [56,57]. Based on our current study and previous study [56] on the same engine with 50 ppm and 100 ppm petroleum diesel, assume the particle emissions changed linearly as sulfur content increased, $PM_{2.5}$, OC and EC mass can be calculated. Using the engine condition 2300 rpm, 75% as an example, the emission rate of $PM_{2.5}$, OC and EC mass could be 290 mg/min, 128 mg/min and 120 mg/min respectively. In other words, the biodiesel could have reduced 53–57% $PM_{2.5}$, 28–38% OC and 74–83% EC if the three kinds of fuel have the sulfur content around 150 ppm. Compared to the result in our current study, this assumption indicates that biodiesel may be able to decrease the OC emissions and may have a more obvious effect on $PM_{2.5}$ and EC decrease.

5. Conclusions

This study evaluated $PM_{2.5}$, OC, EC mass and particle size distribution from engine exhaust of two biodiesels and one petroleum diesel. The results showed that all of these particles emission characteristics varied significantly with engine condition. Biodiesel emissions were shown to be cleaner than petroleum diesel at higher engine load (100% and 75%) due to a decrease in $PM_{2.5}$ mass emission rate. More OC (except comparable OC emission at 2300 rpm, 75% load) and less EC was emitted from biodiesels combustion. Particle number concentration in the exhaust, especially particles smaller than 0.1 μm, was shown to increase with BW (biodiesel made from waste oil) combustion.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.fuel.2011.01.039.

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