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Influence of Waste Cooking Oil Biodiesel on the Particulate Emissions and Particle Volatility of a DI Diesel Engine

Tian Lu[1,2], C.S. Cheung[2*], Zhen Huang[1]

[1] *Combustion and Environmental Technology Center, School of Environmental Science and Engineering, Shanghai Jiao Tong University, Shanghai 200240, China*
[2] *Department of Mechanical Engineering, The Hong Kong Polytechnic University, Hung Hom, Kowloon, Hong Kong*

ABSTRACT

The effect of biodiesel produced from waste cooking oil on the particulate emissions of a direct injection (DI) diesel engine was investigated experimentally and the results were compared with two diesel fuels, namely, an ultra low sulfur diesel fuel with less than 10-ppm-wt of sulfur (ULSD) and a low sulfur diesel fuel with 400-ppm-wt of sulfur (LSD). For each fuel, the number and mass based particle emissions, as well as the particle volatility, were evaluated and compared. The particulate mass emissions were measured with a tapered element oscillating balance (TEOM) and further divided into different size bins using a micro-orifice uniform deposition impactor (MOUDI). The particle number concentration and size distribution were measured with a scanning mobility particle sizer (SMPS). The size-segregated samples collected with the MOUDI were further analyzed with a thermogravimetric analyzer (TGA) to obtain the mass of volatile substances in each size bin. The SMPS was further connected in series with a thermodenuder (TD) to obtain the number concentration and size distribution of non-volatile particles, and hence the number concentration and size distribution of the volatile particles. The results indicate that the biodiesel could effectively reduce the particle mass and number concentrations, including the volatile substances, in all the measured size range, compared with LSD. Compared with ULSD, there is also a reduction in the particle mass and number concentrations, however, a higher concentration of volatile substances was found with the use of biodiesel, which should be a concern in the application of this fuel.

Keywords: Diesel particle; Particle volatility; Biodiesel.

INTRODUCTION

Diesel particulates are composed of soot aggregates and volatile substances which include hydrocarbons and sulfate. Volatile substances have complex composition, some of which are toxic and carcinogenic. Therefore, it is important to analyze the volatility of diesel particles because it is an indication of the toxicity of these particles (Giechaskiel *et al*., 2009; Chuang *et al.*, 2010; Ning and Sioutas, 2010; Wu *et al.*, 2010; Tsai *et al.*, 2011). There are different methods for investigating particle volatility. Maricq *et al.* (2002) used a scanning mobility particle sizer (SMPS) and a thermal denuder (TD) to investigate the particulate emissions of a diesel engine fueled with a diesel fuel containing 350 ppm-wt sulfur. They found that most of the nuclei mode particles could be adsorbed by the TD. Rönkkö *et al.* (2007) compared the particle number-size distribution using a nano-SMPS and a TD and found that the nucleation mode particles have a non-volatile core with volatile species condensed on it. Kwon *et al.* (2003) and Sakurai *et al.* (2003) investigated the volatility of diesel particles using a tandem differential mobility analyzer (TDMA) and found that the volatility was size-dependent. Filter-based methods have also been used to investigate the volatile substance in diesel particles. These methods include thermal-gravimetric analysis, thermal optical carbon analysis and Soxhlet extraction (Kerminen *et al.*, 1997; Ning *et al.*, 2004; Collura *et al.*, 2005; Shen *et al*., 2009; Mustafi *et al.*, 2010).

Former investigations on particle volatile mainly focused on the effects of fuel sulfur content, which have been well reported (Maricq *et al*., 2002; Vaaraslahti *et al*., 2004; Ristovski *et al*., 2006; Rönkkö *et al*., 2007) and induced the tightening up of diesel sulfur content. In China, the national standard of diesel fuel follows the standard EN590. The limit of sulfur content in EN590 and its execution date in Europe and China are listed in Table 1. In China the current maximum sulfur content is limited to about 350 ppm-wt and will be further reduced, while in Europe, it has been limited to less than 10 ppm-wt. Over the past decade, using biodiesel as an alternate diesel fuel has drawn increasing

[*] Corresponding author. Tel.: +852 2766 7819;
Fax: +852 2365 4703
E-mail address: mmcsc@polyu.edu.hk

Table 1. Diesel fuel sulfur content in Euro Standards and execution date in Europe and China.

Diesel fuel standard		Euro I	Euro II	Euro III	Euro IV	Euro V
Sulfur content (mg/kg)		< 2000	< 500	< 350	< 50	< 10
Execution date	Europe*	1993	1996	2001	2006	2009
	China**	2000	2003	2010	-	-

* http://en.wikipedia.org/wiki/EN_590
** http://www.chinagb.org

interest due to its biodegradable and nontoxic properties and using biodiesel can significantly reduce particulate emissions and overall life-cycle CO_2 emission from the engine (Lapuerta *et al*., 2008). However, research on volatility of particles generated from the combustion of biodiesel, in particular biodiesel produced from waste cooking oil, is rare (Jung *et al*., 2006; Heikkilä *et al*., 2009; Surawski *et al*., 2011a, b).

In this study, we investigated the effect of a biodiesel produced from waste cooking oil on the particle number/ mass-size distributions and the volatility of the particles in the exhaust of a diesel engine. We used a SMPS and a TD to investigate the number-size distributions of the volatile substances, and used a thermal-gravimetric analyzer to investigate the mass-size distributions of the volatile substances in the particles collected with a micro-orifice uniform deposition impactor (MOUDI), and the two results were compared. Investigation on both mass-based and number-based particle volatility is rarely reported in the literature. Two diesel fuels with different sulfur contents of 10-ppm-wt sulfur and 400-ppm-wt sulfur were used for comparison.

EXPERIMENTAL METHODS

The study was performed on a naturally-aspirated, water cooled, 4-cylinder direct-injection diesel engine (ISUZU 4HF1). The specifications of the engine are shown in Table 2. The engine was connected to an eddy-current dynamometer and a control system was used for adjusting its speed and torque. The major properties of the three fuels are given in Table 3. ULSD is widely used in Europe while the properties of the LSD are similar to the diesel fuel available in China. The biodiesel used in this study was produced from waste cooking oil by Dynamic Progress Ltd. and its properties are in compliance with the standard EN14214.

The schematic of the experimental system is shown in Fig. 1. The study was conducted at a steady engine speed of 1800 r/min and at five engine loads, corresponding to the brake mean effective pressures (BMEP) of 0.08, 0.2, 0.38, 0.55 and 0.7 MPa. To ensure the repeatability and comparability of the measurements, particulate samples were collected after the cooling water and lubricating oil temperature reached their corresponding steady values. Moreover, for minimizing cross contamination of different fuels, the engine was allowed to operate with the new fuel for thirty minutes to clean the fuel system.

Table 2. Specifications of the test engine.

Model	ISUZU 4HF1
Type	In-line 4-cylinder
Maximum power	88 kW/3200 rev/min
Maximum torque	285 Nm /1800 rev/min
Bore × stroke	112 mm × 110 mm
Displacement	4334/cc
Compression ratio	19.0:1
Fuel injection timing (BTDC)	8°
Injection pump type	Bosch in-line type
Injection nozzle	Hole type (with 5 orifices)

Particle number concentration and size distribution was measured with a scanning mobility particle sizer (SMPS TSI Model 3934) for the size range of 10–486 nm. For each test condition, the SMPS scan was repeated 4 times. Before passing through the SMPS, the engine exhaust gas was diluted with a two-stage dilution unit (Dekati Ltd.). The transfer line from the exhaust to the diluter was heated at 170°C. The first stage was heated to keep the dilution air at 150°C to avoid condensation of volatile substances. The second diluter was directly connected to the first diluter and the diluted gas was maintained at about 25°C for direct coupling to the SMPS which counts particle concentrations on volume basis. The dilution ratio was determined from the measured CO_2 concentrations of background air, undiluted exhaust gas and diluted exhaust gas. CO_2 concentrations were measured with a non-dispersive infra-red analyzer (NDIR, CAI 300). The dilution ratio for the SMPS varied from 67.5 to 89.6, depending on the actual operating conditions. The dilution process will induce some variation of the particle size distribution in the exhaust gas, especially the nucleation mode particles which are sensitive to the dilution conditions (Shi and Harrison, 1999).

Particulate mass concentration was measured with a tapered element oscillating microbalance (TEOM, Series 1105, Rupprecht & Patashnick Co., Inc.). The engine exhaust gas passed through the TEOM with the first stage dilution and the sampling temperature was around 52°C. The dilution ratio for the TEOM was one-eighth of that for the SMPS. Classified particulate samples were also collected using a micro-orifice uniform deposition impactor (MOUDI-110R, MSP Corporation) with 10 cut-point sizes of 10, 5.6, 3.2, 1.8, 1.0, 0.56, 0.32, 0.18, 0.1 and 0.056 μm for investigating the particle mass-size distributions. The sampling conditions are the same for the MOUDI and the TEOM, both have one-stage dilution. 47mm quartz filters (Whatman Corporation) were used as impaction substrate for the MOUDI to collect particulate samples. The quartz filters were prebaked at 500°C for 4 hours to remove any carbon contamination. Before and after sampling, the quartz filters in the MOUDI were allowed at least 24 hours equilibration in a controlled

Table 3. Properties of test fuels.

	ULSD	Biodiesel	LSD
Cetane number	52	51	51
Lower heating value, MJ/kg	42.5	37.5	42.5
Density (kg/m^3) @20°C	840	871	834
Viscosity (mPa s)@40°C	2.4	4.6	3.03
Heat of evaporation (KJ/Kg)	250–290	300	280
Carbon content (%wt)	86.6	77.1	87.4
Oxygen content (%wt)	0	10.8	0
Hydrogen content (%wt)	13.4	12.1	12.6
Sulfur content (mg/kg)	< 10	< 10	400

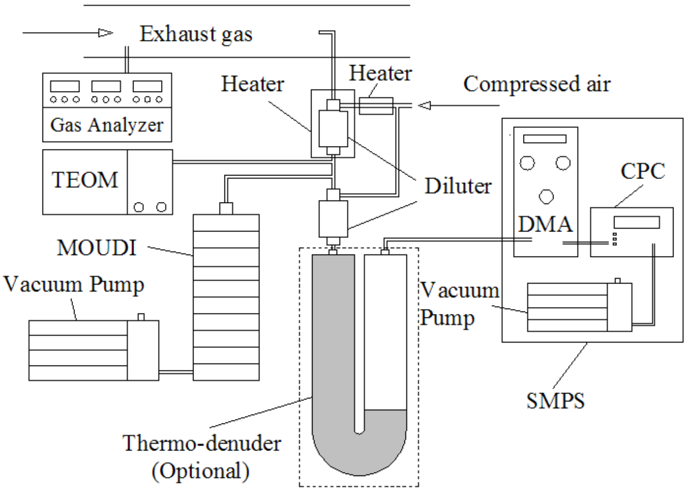

Fig. 1. Schematic diagram of the experimental setup.

environment with a temperature of 21–22°C and relative humidity of 40–45% and then weighed with a microbalance (Mettler-Toledo XS105). Previous studies indicated that for motor vehicles, 80–90% of the particulate mass fraction is within the fine-particle size range (Kerminen *et al*., 1997; Chien *et al*., 2009; Zhang *et al*., 2009). Therefore, in this study, despite particles in all size bins were collected, only those less than 1.8 µm were weighed and analyzed.

Two methods were used to investigate particle volatility, namely, a mass-based method and a number-based method. The former method involves the thermogravimetry analysis (TGA) of filter samples collected with the MOUDI. TGA was conducted using the Netzch-STA 449 TGA/DSC (thermogravimetric analyzer/differential scanning calorimetry) with Al_2O_3 crucible. The particulate samples were firstly heated in an argon environment with a heating rate of 10°C per minute to 400°C, and then held at 400°C for 10 minutes. The mass loss in the argon environment was taken as the mass of the volatile substances. The remaining part was heated at an air environment with a heating rate of 10°C per minutes to 800°C. The mass loss at the air environment was taken as the mass of the non-volatile substances. Similar approach had been used by Boehman *et al*. (2005) and Mustafi *et al*. (2010) to distinguish the volatile and non-volatile fractions of diesel particles. The number-based method was conducted by comparing the SMPS measurements with and without the Dekati thermo-denuder (TD). The TD consists of a heated section followed by an adsorber section where the vaporized compounds are adsorbed in activated charcoal. In this study, the particle number-size distributions obtained after the TD have been corrected for diffusion losses using the measured diesel particle number concentration with the TD set at 25°C (Surawski *et al*., 2011b).

For the particle number and mass concentrations, the average values were presented. The standard errors were determined following the method of Kline and McClintock (1953). In order to ensure that the results are repeatable within the experimental uncertainties, for each test condition, the tests were repeated twice. In this study, the maximum standard errors are 2.5% for particle mass concentration using TEOM, 1.7% for particle number concentration, 2.3% for particle geometric mean diameter, and 4.5% for the volatile mass fraction determined with the TGA.

RESULTS AND DISCUSSIONS

Particle Mass Concentrations and Size Distribution

The total particulate mass concentration for each fuel and at each engine load was measured with the TEOM. The variation of brake specific particulate matter (BSPM) with engine load is shown in Fig. 2. For each fuel, the minimum BSPM appears at some intermediate engine loads which can be attributed to the lower brake thermal efficiency at

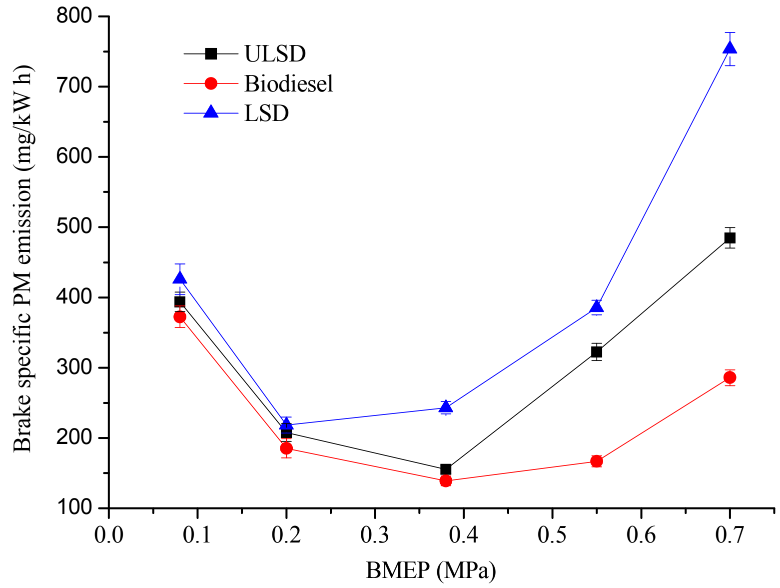

Fig. 2. Effect of fuel type and engine load on brake specific particulate emission.

low engine load and the higher particulate emissions at high engine load. At high engine load, the increase in fuel burned in the diffusion mode leads to a rapid increase in the particulate mass concentration in the engine exhaust gas and hence a corresponding increase in the BSPM.

For the three fuels, the biodiesel and LSD generate the lowest and highest BSPM, respectively. The BSPM of biodiesel is 229.8 mg/kWh, on average of the five engine loads, which is 26.5% and 43.3% lower than BSPM of ULSD and LSD, respectively. The effectiveness of biodiesel on reducing particulate emission has been reported in the literature (Corporan *et al*., 2005; Tsolakis, 2006; Lapuerta *et al*., 2008). In general, there are three reasons leading to the lower particulate emission with biodiesel. Firstly, the advanced fuel ignition associated with biodiesel provides a longer time for soot oxidation. Secondly, the oxygen content of biodiesel enables more complete combustion and promotes the oxidation of the already formed soot. Thirdly, the absence of aromatics in biodiesel leads to a reduction in soot formation. Therefore, in this study, the engine fueled with biodiesel has lower particulate emission than fueled with the two diesel fuels. On the other hand, the lower aromatics content and the lower sulfur content are reasons for the lower particulate emission of ULSD, compared with LSD. Ullman *et al*. (1994) found a 3–5% particulate reduction for a 100 ppm-wt reduction in fuel sulfur on a heavy-duty diesel engine tested under a transient drive cycle.

The particulate emission at the engine load of 0.7 MPa was chosen for the investigation of particulate mass-size distribution using the MOUDI. The BSPM at different size bins are shown in Fig. 3 while the mass median diameters (MMD) and their geometric standard deviations of the diesel particulate are listed in Table 4. For each fuel, the mass-size distribution of the particles exhibits a peak BSPM at the size bin of 100–180 nm. The brake specific emissions of $PM_{1.8}$ are 198.8, 399.6 and 576.4 mg/kWh for the biodiesel, ULSD and LSD, respectively. Effect of the biodiesel on reducing particulate emission in comparison with the ULSD and LSD, is in line with results obtained with the TEOM. As shown in Fig. 3, biodiesel could reduce BSPM in all the size bins, while the MMD of biodiesel particles is less than those of the ULSD and LSD, which indicates that the biodiesel particles contain a larger proportion of small-size particles and the reduction on particulate emission arises from the reduction of the large-size particles. The same reasons which cause a larger reduction of particulate emissions with biodiesel, compared with the two diesel fuels, also lead to a larger reduction in particle MMD (Mathis *et al*., 2005; Tsolakis, 2006). Moreover, the reduction in particulate mass concentration may also suppress particle coagulation and hence reduce the MMD.

Mass-Based Investigation of Particle Volatility

Mass-based particle volatility was investigated with the TGA to evaluate the mass fraction of volatile and non-volatile substances in the particulate samples collected on filter papers installed inside the MOUDI. The brake specific emissions of volatile and non-volatile substances at different size bins are shown in Fig. 3 for the engine load of 0.7 MPa, and the MMD and geometric standard deviation for the non-volatile substances are listed in Table 4. For $PM_{1.8}$, the brake specific emissions of volatility substances are 64.2, 55.2 and 132.6 mg/kWh for biodiesel, ULSD and LSD, respectively, indicating that using biodiesel, the emission of volatile substances could reduce, compared with LSD, but could increase, compared with ULSD. However, in terms of mass fraction, biodiesel particles contain 32.2% volatile substances which is larger than 13.8 and 23.0% for ULSD and LSD particles, respectively. Chang *et al*. (1998) suggested that due to its lower volatility (higher boiling point), unburned biodiesel fuel should be more likely to condense and adsorb on the soot particles, leading to higher volatile fraction on these particles. Ballesteros *et al*. (2008)

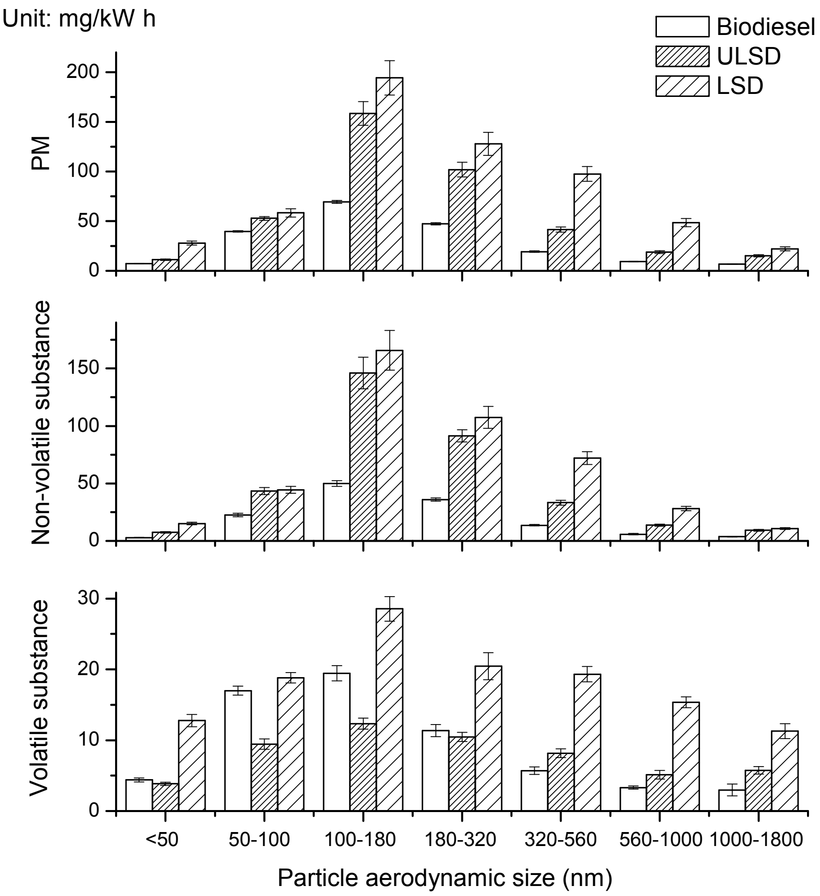

Fig. 3. Effect of fuel type on the mass-size distribution of particulate matter (PM), volatile substances and non-volatile substances at 0.7 MPa.

Table 4. Mass median diameter (MMD) and geometric standard deviation (σ) of particulate matter (PM) and non-volatile substance sampled at 0.7 MPa.

	PM		Non-volatile substance	
	MMD	σ	MMD	σ
ULSD	191.19	2.15	180.82	1.97
Biodiesel	176.40	2.22	170.31	2.04
LSD	225.00	2.28	219.59	2.08

attributed the higher volatile fraction in biodiesel particles to their higher surface/volume ratio. The higher surface/volume ratio implies an increment in the active surface in which the hydrocarbons can be adsorbed and causes a rise in the volatile fraction. Moreover, oxygenated fuels like biodiesel have significant effect on the reduction of soot. On the other hand biodiesel might also lead to a reduction in hydrocarbon emissions which might reduce the volatile fraction. Further analysis shows that, with biodiesel, the non-volatile substances in $PM_{1.8}$ decrease by 69.7 and 60.9%, compared with LSD and ULSD, respectively, while for volatile substances, the corresponding reductions are 51.6% and –16.3%. It indicates more effective reduction on non-volatile substances than volatile substances. The LSD particles contain a larger percentage of volatile substances than the ULSD particles. Liu *et al.* (2005) suggested that higher fuel sulfur content results in higher concentration of nucleated sulfuric acid particles, which provides larger amount of sites for the condensation of volatile organic compounds.

The size resolved particle volatility is compared among the three fuels in Fig. 3. For particles with aerodynamic size less than 180 nm, the brake specific emissions of volatile substance are 40.9 and 25.7 mg/kWh, respectively, for biodiesel and ULSD, while for particles with aerodynamic size between 180–1800 nm, the corresponding values are 23.4 and 29.5 mg/kWh. It indicates that the higher brake specific emission of volatile substances from biodiesel is mainly in the smaller size bins. Fig. 3 also shows that the brake specific emission of volatile substances from LSD is larger than those from biodiesel and ULSD in all the size bins.

Fig. 4 shows the mass fraction of volatile substances at different aerodynamic size bins for the three fuels at the engine load of 0.7 MPa. For each fuel, the mass fraction of volatile substances first decreases with the particle size and then increases. The decrease of volatile fraction with particle size in the small-size range (for particles less than 100 nm in diameter) has been found by Kwon *et al.* (2003) who conducted an experimental investigation on particulate emissions of a medium-sized diesel truck mounted on a chassis dynamometer. It is known that nucleation mode

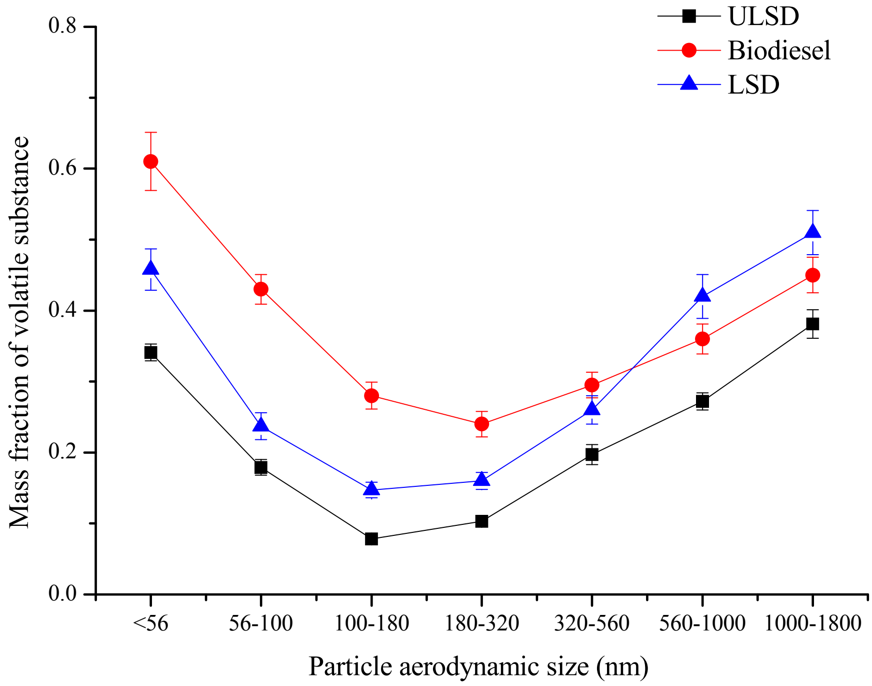

Fig. 4. Effect of fuel type on mass-fraction of volatile substances in difference size bins at 0.7 MPa).

particles with diameter less than 50 nm are mostly formed from volatile hydrocarbon or sulfuric acid in the dilution process, thus these particles contain a higher mass fraction of volatile substances. On the other hand, particles with much larger size have fractal-like structure which provides more pores and intra-particle cavities for the condensation and adsorption of volatile substances (Kerminen *et al.*, 1997; Ristovski *et al.*, 2006), leading to an increase of the volatile fraction in these particles. Similar result was also found by Kerminen *et al.* (1997) and Zhang *et al.* (2009) who used low-pressure impactor in their investigations. In this study, for the three fuels, biodiesel particles contain the highest mass fraction of volatile substances in the small-size range. In the large-size range, LSD particles exhibit stronger volatility because the larger amount of large-size LSD particles promotes the adsorption and condensation of volatile substances.

Particle Number Concentration, Size Distribution and Volatility

Number-based particle concentration, size distribution and volatility were investigated using the SMPS and the TD, with the TD set to 275°C. The particles measured with the SMPS alone contain both non-volatile and volatile substances while those measured with the SMPS and the TD contain non-volatile substances only with the volatile substances being adsorbed in the TD. Typical number concentration and size distributions measured with and without the TD are shown in Fig. 5 for the engine load of 0.38 MPa, while the influence of engine load and fuel on particle geometrical mean diameter (GMD) is shown in Fig. 6. The number concentrations measured with the SMPS can be converted into brake specific particle number concentrations (BSPN) and the results are shown in Fig. 7 for different engine loads, with and without the TD.

Fig. 5 shows that the LSD and biodiesel, respectively, generate the highest and the lowest number of particles, both with and without the TD. The difference among the different fuels is mainly due to difference in particles larger than 50 nm in diameter. Number-based particle volatility was investigated using the SMPS measurements, with and without the TD. Basically, particles measured with the SMPS with the TD are non-volatile ones. As shown in Fig. 5, the loss of particles associated with the TD is mainly concentrated on particles which are less than 100 nm in size, especially for the biodiesel and ULSD. With the TD, some of the particles may be completely adsorbed if they are completely composed of volatile substances, while some of them may shrink in size to form particles with diameter less than 10 nm (Rönkkö *et al.*, 2007). In this study, particles below 10 nm could not be measured because the SMPS measurement was set to 10–486 nm. However, particles above 100 nm in size are less affected by the TD. Alander *et al.* (2004) suggested that accumulation mode particles mostly exist in the form of primary particle agglomerates and the volatile substances may be collected in pores and intra-particle cavities between the primary particles. Thus the mobility size of the accumulation mode particles is not significantly influenced by the removal of the volatile substances.

Fig. 6 shows that the GMD increases with engine load for each fuel which is a consequence of the increase in mass of fuel burned in the diffusion combustion mode at high engine load (Tsolakis, 2006; Zhu *et al.*, 2010; Srivastava1 *et al.*, 2011). The high fuel/air ratio and local temperature associated with high engine load also promote particle formation. Moreover, at high engine load, the time available for soot oxidation after the end of the diffusion combustion

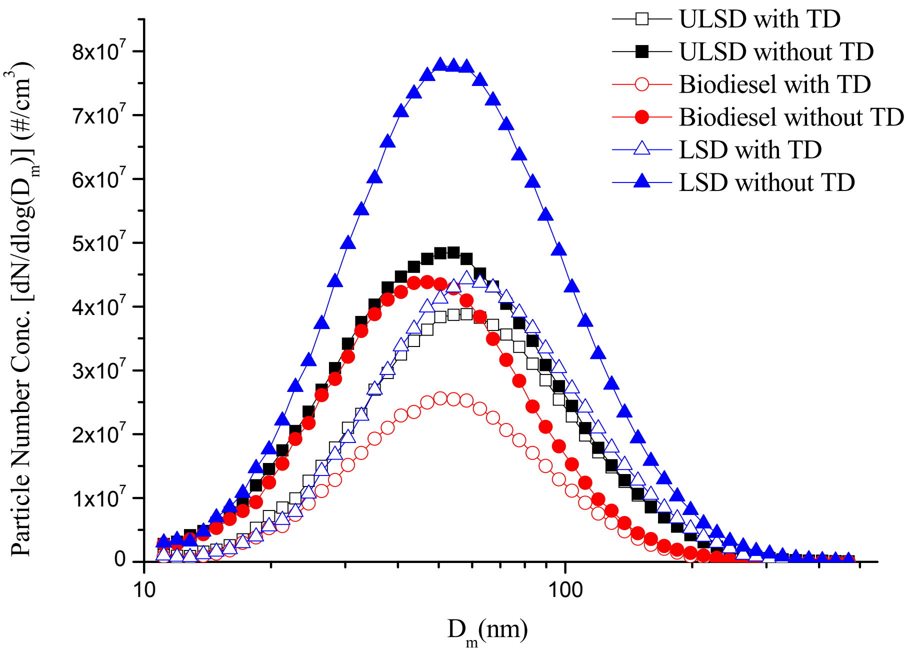

Fig. 5. Effect of fuel type and TD on particle number-size distribution at 0.38 MPa. D_m: mobility particle diameter.

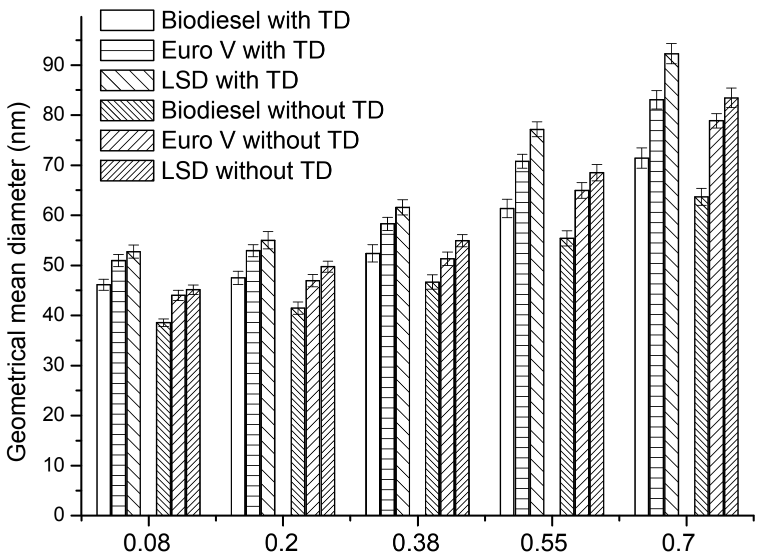

Fig. 6. Particle geometrical mean diameter (GMD) with and without TD.

period is shorter, leading to the formation of a larger number of particles (Tsolakis, 2006). With more particles being formed, they tend to coagulate to form larger particles. Furthermore, during the dilution and cooling of the exhaust gas, the volatile substances could condense on the surface of the existing particles to form larger ones (Bagley *et al*., 1998; Schneider *et al*., 2005). This effect is more significant at high engine load when the exhaust gas temperature is higher (Ning *et al*., 2004). Fig. 6 also shows that, with the TD, there is an increase in the GMD of the particles. On average of the different engine loads, the GMDs increased by 13.5, 12.3 and 10.4% for the biodiesel, LSD and ULSD, respectively, which could be attributed to the higher level of volatility in the small size particles. Biodiesel has a higher level of volatility in the small size particles, hence, the adsorption of the smaller particles lead to a larger increase in GMD, after passing through the TD, compared with the two diesel fuels.

Fig. 7 shows that in general, with and without the TD, for each fuel, the BSPN firstly decreases with the increase of engine load and then increases, which is similar to the results of the mass-based BSPM (Fig. 2). A comparison on the results, obtained without the TD, shows that the BSPN is the highest for LSD and the lowest for biodiesel, for all the engine loads. On average of the five engine loads, with biodiesel, the BSPN is decreased by 19% and 47%, compared with ULSD and LSD, respectively. Besides a reduction in BSPN, there is also a corresponding reduction in the GMD.

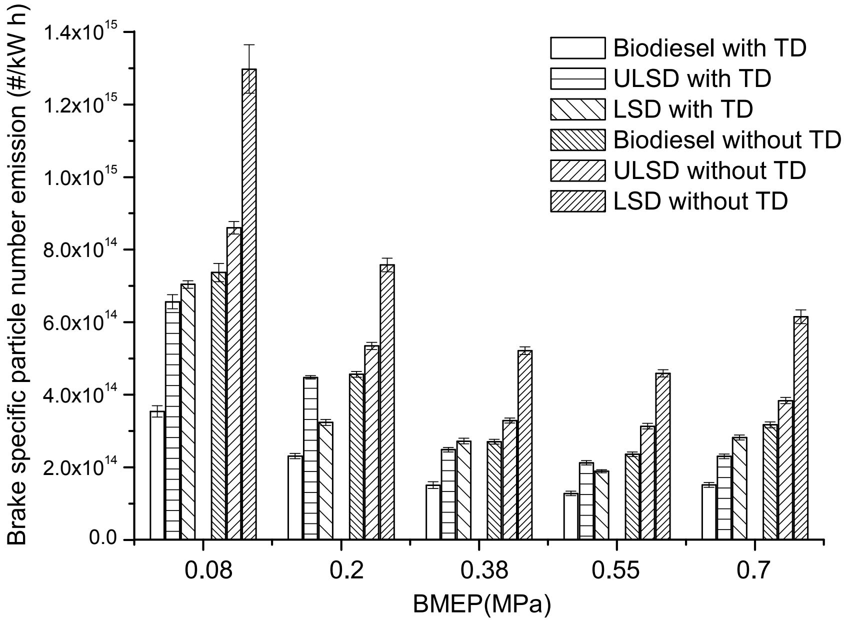

Fig. 7. Brake specific particle number emission with and without TD.

For the biodiesel, the explanations for its lower BSPM and MMD could also be applied to explain the lower BSPN and GMD.

Fig. 7 shows both the BSPN obtained with and without the TD. If the BSPN obtained without the TD is considered as a combination of non-volatile and volatile particles, and the BSPN obtained with the TD represents the non-volatile particles, the difference between them can be used as an indication of the BSPN of volatile particles. The BSPN thus obtained is presented in Fig. 8(a) while Fig. 8(b) shows the fraction of the BSPN of volatile particles in the BSPN obtained without the TD. As shown in Fig. 8(a), for each fuel, the BSPN of volatile particles firstly decreases with the increase of engine load and then increases, which is consistent with the trend of BSPN in Fig. 7. Fig. 8(a) shows that the biodiesel particles contain a higher BSPN of volatile particles than the ULSD particles at almost all engine loads while the LSD particles contain the highest level of volatile particles, which is in line with the results obtained in the mass-based investigation on volatile particles. On average of the five engine loads, the BSPNs of volatile particles are 2.00×10^{14}, 1.25×10^{14}, and 3.76×10^{14} #/kW h for biodiesel, ULSD and LSD respectively. However, the volatile particles occupy 52.3%, 40.0% and 58.7% in the total particle emissions at the engine load 0.7 MPa, for the biodiesel, ULSD and LSD, respectively, which is larger than the corresponding reduction in the mass fraction of volatile substances especial for the biodiesel and LSD. One of the reasons is that a portion of the volatile substances exists as nanoparticles which contribute significantly to number concentration reduction but much less to the mass concentration reduction.

In regard to the number-fraction of volatile particles, as shown in Fig. 8(b), the minimum percentage of volatile particles occurs at the intermediate engine load for the biodiesel and ULSD. For example, for biodiesel, there is 44.2% volatile particle in total BSPN at 0.38 MPa, while the corresponding percentages at 0.08 and 0.7 MPa are 51.9% and 52.3%, respectively. However, for the LSD, the percentage of volatile particles exhibits monotonic increase with engine load. At low engine load, due to lower in-cylinder gas temperature, there is a larger amount of unburned hydrocarbon and lubricating oil in the exhaust gas which could be converted to volatile particles or condense on existing soot agglomerates (Ning *et al.*, 2004; Ristovski *et al.*, 2006; Mustafi *et al.*, 2010), leading to an increase in particle volatility. The increase in volatility under high engine load is uncommon but has also been observed by Meyer and Ristovski (2007) through a VH-TDMA (volatilization and humidification tandem differential mobility analyzer) investigation on emissions from a six-cylinder diesel engine fueled with commercial 500-ppm-wt sulfur diesel fuel. Meyer and Ristovski (2007) suggested that ternary nucleation involving sulfuric acid, water and ammonia might be the dominant mechanism for production of volatile substances at high engine load. Therefore, in this study, the ternary nucleation might be one of the dominant mechanisms for the formation of volatile substances when the engine is fueled with the LSD.

Particle Number Concentration and Volatility in Different Size Groups

Nanoparticles (< 50 nm) are more hazardous to human health (Peters *et al.*, 1997; Somers *et al.*, 2004). Thus, the particles are classified into three groups: < 50, 50–100 and > 100 nm, for further analysis. The effect of fuel type and engine load on the BSPN and fraction of the particles in each of the three size groups is shown in Fig. 9. Compared with ULSD, the BSPN of biodiesel is at similar level for particles < 50 nm but lower for the larger particles, indicating that the reduction of BSPN associated with the biodiesel is concentrated on large size particles. In comparison with

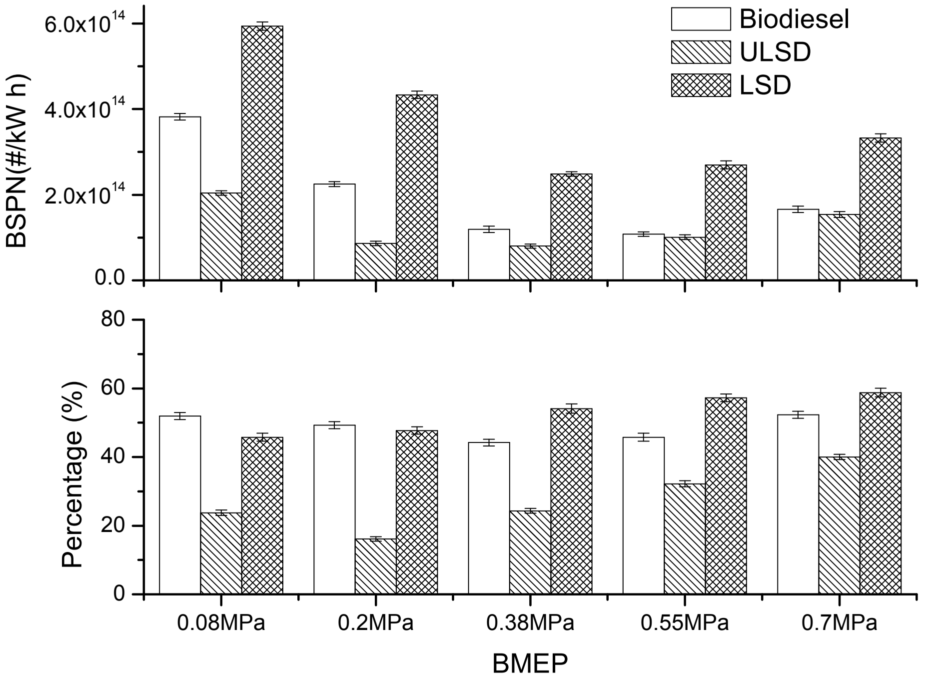

Fig. 8 Effect of fuel type and engine load on (a) BSPN of volatile particles and (b) number-fraction distribution of volatile particles

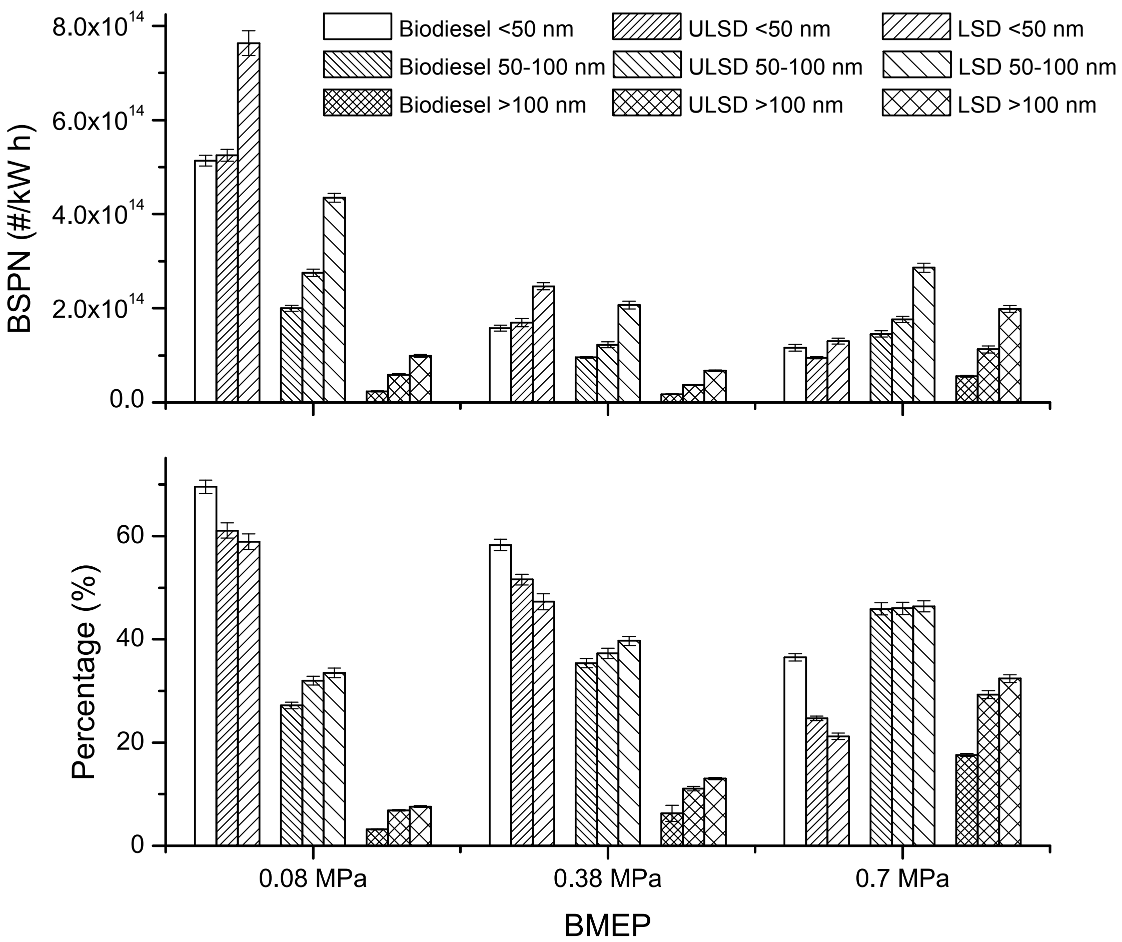

Fig. 9. Effect of fuel type and engine load on (a) BSPN (without TD) and (b) number-fraction distribution in different size groups

LSD, biodiesel and ULSD could lead to reduction of BSPN in all size groups, and LSD has the lowest fraction of small size particles while biodiesel has the highest.

The volatility of particles in different size groups is also investigated. For different size groups, the BSPN of volatile particles and their percentage in the total volatile particles are shown in Fig. 10. On average of the five engine loads, in the size group of < 50 nm, the BSPNs of volatile particles are 1.38×10^{14}, 8.64×10^{13} and 2.02×10^{14} #/kW h for biodiesel, ULSD and LSD respectively. The results indicate that the biodiesel could reduce the volatile particles in the small size range, compared with LSD but leads to an increase, compared with ULSD. The number-fractions of volatile particles in the size group of < 50 nm are 57.6, 35.7 and 59.5% for biodiesel, ULSD and LSD, respectively. The number fraction of volatile particles is similar between biodiesel and LSD in this size range. While for the size group of > 100 nm, the number-fractions of volatile substances are 31.3, 15.2 and 42.9%, for biodiesel, ULSD and LSD, respectively. LSD particles exhibit obviously higher number-fraction of volatile substances than those from the biodiesel and ULSD. The higher volatility of the LSD particles in the large-size range is in line with the mass-based results. However, there might be different mechanisms leading to these results as a consequence of the different methods used to assess the mass-based and number-based volatile fractions. In the mass-based case, it is assessed based on the loss of adsorption and condensed volatile substances upon heating in the TGA. In the number-based method, the volatile substances are adsorbed in the TD instead of being adsorbed or condensed on the soot particles, leading to a reduction of particle sizes and reflected in the change of BSPN, in particular for the LSD which generates a larger amount of large-size particles. Both the number-based and mass-based results show that the volatile substances in the LSD particles are distributed over a wider range of size than the biodiesel and ULSD particles.

CONCLUSIONS

In this study, the particulate emissions from a DI diesel engine fueled with a waste cooking oil biodiesel and two diesel fuels were investigated. The results indicate that the biodiesel could effectively reduce the particle mass and number concentrations, compared with the ULSD and LSD. Both the mass-size and number-size distributions indicate that the biodiesel could reduce particle number and mass emission in all the size ranges, compared with LSD, while reduction mainly concentrate in large size particles, compared with ULSD.

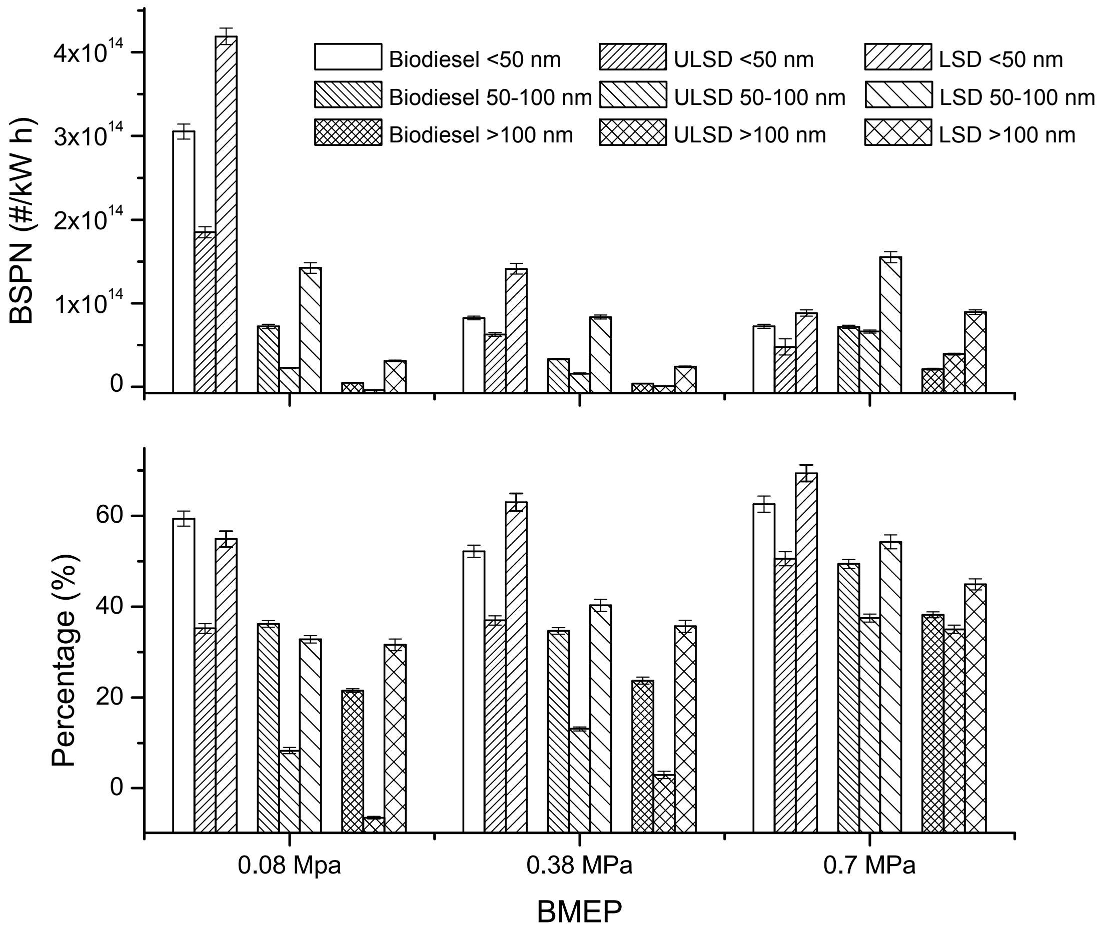

Fig. 10. Effect of fuel type and engine load on (a) BSPN of volatile particles and (b) number-fraction distribution of volatile particles in different size groups

With regard to brake specific emission of volatile substances, both the number and mass-based measurements indicate that the biodiesel could obviously reduce the emission rate of volatile substances in all the size ranges, compared with LSD. However, compared with ULSD, there is an increase in the volatile substances in the biodiesel particles and the increase in volatile substances concentrates in the small size range. In term of mass fraction of volatile substances in total particle emissions, for each fuel, the mass fraction first decreases with particle size for the small-size particles, which then increases with particle size for the large-size particles. In the small-size range, biodiesel particles contain the highest mass-fraction of volatile substances, while in the large-size range, the LSD particles contain the highest mass-fraction of volatile substances. Similar results are also found in the number-fraction of volatile particles. Moreover, number-based measurements show that the volatile fraction of biodiesel and ULSD particles first decreases with engine load and then increases, while the LSD particles exhibit increasing volatility with engine load. The different size distribution characteristics and load effect could be attributed to the different formation mechanisms of volatile substance in the use of different fuels.

Thus it can be concluded that the application of biodiesel as a replacement of LSD could effectively reduce particle emissions, both in mass and in number, including the volatile substance in all the size ranges. However, in comparison with ULSD, the usage of biodiesel could increase the emission of volatile substances, especial in the small size range, which should be a major concern in the application of biodiesel to replace ULSD, because nano-size particles are known to cause more damage to human health than the micron-size particles.

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REFERENCE

Alander, T.J.A., Leskinen, A.P., Raunemaa, T.M. and Rantanen, L. (2004). Characterization of Diesel Particles: Effects of Fuel Reformulation, Exhaust Aftertreatment, and Engine Operation on Particle Carbon Composition and Volatility. *Environ. Sci. Technol.* 38: 2707–2714.

Bagley, S.T., Gratz, L.D., Johnson, J.H. and McDonald, J.F. (1998). Effects of an Oxidation Catalytic Converter and a Biodiesel Fuel on the Chemical, Mutagenic, and Particle Size Characteristics of Emissions from a Diesel Engine. *Environ. Sci. Technol.* 9: 1184–1191.

Ballesteros, R., Hernández, J.J., Lyons, L.L., Cabañas, B. and Tapia, A. (2008). Speciation of the Semivolatile Hydrocarbon Engine Emissions from Sunflower Biodiesel. *Fuel* 87: 1835–1843.

Boehman, A.L., Song, J. and Alam, M. (2005). Impact of Biodiesel Blending on Diesel Soot and the Regeneration of Particulate Filters. *Energy Fuels* 19: 1857–1864.

Chang, D.Y. and Van Gerpen, J.H. (1998). Determination of Particulate and Unburned Hydrocarbon Emissions from Diesel Engines Fueled with Biodiesel. *SAE Technical Paper* 982527, doi: 10.4271/982527.

Chien, S.M., Huang Y.J., and Chuang S. C. (2009). Effects of Biodiesel Blending on Particulate and Polycyclic Aromatic Hydrocarbon Emissions in Nano/Ultrafine/Fine/Coarse Ranges from Diesel Engine. *Aerosol Air Qual. Res.* 9: 18–31.

Chuang, S.C., Chen, S.J., Huang, K.L. Wu, E.M.Y., Chang-Chien, G.P., and Wang, L.C. (2010). Gas/Particle Partitioning of Dioxins in Exhaust Gases from Automobiles. *Aerosol Air Qual. Res.* 10: 489–496.

Collura, S., Chaoui, N., Azambre, B., Finqueneisel, G., Heintz, O., Krzton, A., Koch, A. and Weber, J.V. (2005). Influence of the Soluble Organic Fraction on the Thermal Behaviour, Texture and Surface Chemistry of Diesel Exhaust Soot. *Carbon* 43: 605–613.

Corporan, E., Reich, R., Monroig, O., DeWitt, M.J., Larson, V., Aulich, T., Mann, M. and Seames, W. (2005). Impacts of Biodiesel on Pollutant Emissions of a JP-8-fueled Turbine engine. *J. Air Waste Manage. Assoc*. 55: 940–949.

Giechaskiel, B., Alfoeldy, B. and Drossinos, Y. (2009). A Metric for Health Effects Studies of Diesel Exhaust Particles. *J. Aerosol Sci.* 40: 639–651.

Heikkilä, J., Virtanen, A., Rönkkö, T., Keskinen, J., Aakko-saksa, P. and Murtonen, T. (2009). Nanoparticle Emissions from a Heavy-duty Engine Running on Alternative Diesel Fuels. *Environ. Sci. Technol.* 43: 9501–9506.

Jung, H., Kittelson, D.B. and Zachariah, M.R. (2006). Characteristics of SME Biodiesel-fueled Diesel Particle Emissions and the Kinetics of Oxidation. *Environ. Sci. Technol.* 40: 4949–4955.

Kerminen, V.M., Makela, T.E., Ojanen, C.H., Hillamo, R.E., Vilhunen, J.K., Rantanen, L., Havers, N., Bohlen, A. and Klockow, D. (1997). Characterization of the Particulate Phase in the Exhaust from a Diesel Car. *Environ. Sci. Technol.* 31: 1883–1889.

Kline, S.J. and McClintock, F.A. (1953). Describing Uncertainties in Single Sample Experiments. *Mech. Eng.* 75: 3–8.

Kwon, S.B., Lee, K.W., Saito, K., Shinozaki, O. and Seto, T. (2003). Size-dependent Volatility of Diesel Nanoparticles: Chassis Dynamometer Experiments. *Environ. Sci. Technol.* 37: 1794–1802.

Lapuerta, M., Armas, O. and Rodríguez-Fernández, J. (2008). Effect of Biodiesel Fuels on Diesel Engine Emissions. *Prog. Energy Combust. Sci.* 34: 198–223.

Liu, Z.F., Lu, M.M., Birch, M.E., Keener, T.C., Khang, S.J. and Liang, F.Y. (2005). Variations of the Particulate Carbon Distribution from a Non-road Diesel Generator. *Environ. Sci. Technol.* 39: 7840–7844.

Maricq, M.M., Chase, R.E., Xu, N. and Laing, P.M. (2002). The effects of the Catalytic Converter and Fuel Sulfur Level on Motor Vehicle Particulate Matter Emissions: Light Duty Diesel Vehicles. *Environ. Sci. Technol.* 36: 283–289.

Mathis, U., Mohr, M., Kaegi, R., Bertola, A. and Boulouchos,

K. (2005). Influence of Diesel Engine Combustion Parameters on Primary Soot Particle Diameter. *Environ. Sci. Technol.* 39: 1887–1892.

Meyer, N.K., and Ristovski, Z.D. (2007). Ternary Nucleation as a Mechanism for the Production of Diesel Nanoparticles: Experimental Analysis of the Volatile and Hygroscopic Properties of Diesel Exhaust using the Volatilization and Humidification Tandem Differential Mobility Analyzer. *Environ. Sci. Technol.* 41: 7309–7314.

Mustafi, N.N., Raine, R.R. and James, B. (2010). Characterization of Exhaust Particulates from a Dual Fuel Engine by TGA, XPS, and Raman Techniques. *Aerosol Sci. Technol.* 44: 954–963.

Ning, Z., Cheung, C.S. and Liu, S.X. (2004). Experimental Investigation of the Effect of Exhaust Gas Cooling on Diesel Particulate. *J. Aerosol Sci.* 35: 333–345.

Ning, Z. and Sioutas, C. (2010). Atmospheric Processes Influencing Aerosols Generated by Combustion and the Inference of Their Impact on Public Exposure: a Review. *Aerosol Air Qual. Res.* 10: 43–58.

Peters, A., Wichmann, H.E., Tuch, T., Heinrich, J. and Heyder, J. (1997). Respiratory Effects are Associated with the Number of Ultra Fine Particles. *Am. J. Respir. Crit. Care Med.* 155: 1376–1383.

Ristovski, Z.D., Jayaratne, E.R., Lim, M., Ayoko, G.A. and Morawska, L. (2006). Influence of Diesel Fuel Sulfur on Nanoparticle Emissions from City Buses. *Environ. Sci. Technol.* 40: 1314–1320.

Rönkkö, T., Virtanen, A., Kannosto, J., Keskinen, J., Lappi, M. and Pirjola, L. (2007). Nucleation Mode Particles with a Nonvolatile Core in the Exhaust of a Heavy Duty Diesel Vehicle. *Environ. Sci. Technol.* 41: 6384–6389.

Sakurai, H., Park, K., McMurry, P.H., Zarling, D.D., Kittelson, D.B. and Ziemann, P.J. (2003). Size-Dependent Mixing Characteristics of Volatile and Nonvolatile Components in Diesel Exhaust Aerosols. *Environ. Sci. Technol.* 37: 5487–5495.

Schneider, J., Hock, N., Weimer, S., Borrmann, S., Kirchner, U., Vogt, R., and Scheer, V. (2005). Nucleation Particles in Diesel Exhaust: Composition Inferred from in Situ Mass Spectrometric Analysis. *Environ. Sci. Technol.* 39: 6153–6161.

Shen, Z.X., Cao, J.J., Tong, Z., Liu, S.X., Reddy, L.S.S., Han, Y.M., Zhang, T. and Zhou, J. (2009). Chemical Characteristics of Submicron Particles in Winter in Xi'an. *Aerosol Air Qual. Res.* 9: 80–93.

Shi, J.P. and Harrision, R.M. (1999). Investigation of Ultrafine Particle Formation during Diesel Exhaust Dilution. *Environ. Sci. Technol.* 33: 3730–3736.

Somers, C.M., McCarry, B.E., Malek, F. and Quinn, J.S. (2004). Reduction of Particulate Air Pollution Lowers the Risk of Heritable Mutations in Mice. *Science* 304: 1008–1010.

Srivastava1, D.K., Agarwal, A.K. and Gupta, T. (2011). Effect of Engine Load on Size and Number Distribution of Particulate Matter Emitted from a Direct Injection Compression Ignition Engine. *Aerosol Air Qual. Res.* 11: 915–920.

Surawski, N., Miljevic, B., Ayoko, G., Eltahir, S., Stevanovic, S., Fairfull-Smith, K., Bottle, S.E. and Ristovski, Z.D. (2011a). A Physicochemical Characterization of Particulate Emissions from a Compression Ignition Engine: the Influence of Biodiesel Feedstock. *Environ. Sci. Technol.* 45: 10337–10343.

Surawski, N.C., Miljevic, B., Ayoko, G.A., Roberts, B.A., Elbagir, S., Fairfull-Smith, K.E., Bottle, S.E. and Ristovski, Z.D. (2011b). Physicochemical Characterization of Particulate Emissions from a Compression Ignition Engine Employing Two Injection Technologies and Three Fuels. *Environ. Sci. Technol.* 45: 5498–5505.

Tsai, J.H., Huang K.L. and Chiu C.H. (2011). Particle-Bound PAHs and Particle-Extract-Induced Cytotoxicity of Emission from a Diesel-Generator Fuelled with Soy-Biodiesel. *Aerosol Air Qual. Res.* 11: 822–836.

Tsolakis, A. (2006). Effects on Particle Size Distribution from the Diesel Engine Operating on RME-biodiesel with EGR. *Energy Fuels* 20: 1418-1424.

Ullman, T.L., Spreen, K.B. and Mason, R.L. (1994). Effects of Cetane Number, Cetane Improver, Aromatics, and Oxygenates on 1994 Heavy-Duty Diesel Engine Emissions. *SAE Technical Paper* 941020, doi: 10.4271/941020.

Vaaraslahti, K., Virtanen, A., Ristimäki, J. and Keskinen, J. (2004). Nucleation Mode Formation in Heavy-duty Diesel Exhaust with and without a Particulate Filter. *Environ. Sci. Technol.* 38: 4884–4890.

Wu, S.P., Wang, X.H., Yan, J.M., Zhang, M.M. and Hong, H.S. (2010). Diurnal Variations of Particle-Bound PAHs at a Traffic Site in Xiamen, China. *Aerosol Air Qual. Res.* 10**:** 497–506.

Zhang, J., He, K.B., Ge, Y.S. and Shi, X.Y. (2009). Influence of Fuel Sulfur on the Characterization of PM_{10} from a Diesel Engine. *Fuel* 88: 504–510

Zhu, L., Cheung, C.S., Zhang, W.G. and Huang, Z. (2010). Influence of Methanol–biodiesel Blends on the Particulate Emissions of a Direct Injection Diesel Engine. *Aerosol Sci. Technol.* 44: 362–369.

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