

Effect of Biodiesel Blends on Ultrafine Particle Number Concentration from Diesel Passenger Car under Real-World Driving Conditions

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Abstract. Based on a suit of on board test system, this paper conducted Real-World tests by means of a diesel passenger car with low-sulfur diesel and biodiesel processed by waste cooking oil on Real-World roads in Shanghai city and investigated the characteristics of ultrafine particle number concentration based on vehicle specific power (VSP). Experimental result shows that: 1) the passenger car with low-sulfur diesel and biodiesel blends emits the lowest number and mass emission rates in VSP bin [0]. Biodiesel blends can reduce the number and the reducing percentage depends on the blend ratios. 2) The car fueled biodiesel blends can reduce total particle number concentration. In higher VSP bins, the percentage of nucleation mode number concentration weighs more as the biodiesel blend ratio increase. 3) Biodiesel can reduce the geometric mean diameter of number distinctly. The average values of geometric mean diameters of number of BD0 to BD100 are 113.5, 102.4, 61.1, 64.7, 52.1, 39.3 nm in sequence.

Keywords: Biodiesel, ultrafine particle number, real-world, vehicle specific power.

1. Introduction

In 2013, severe hazy weather had happened many times in north and south of China. Researchers most familiar with these studies have speculated that one of the main haze pollutants is fine particles which contain both primary particles coming from direct emissions of all kinds of pollution sources and secondary particles deriving from the gaseous precursor through the process of condensation or complex chemical changes [1]. Due to the complexity of the physical dimension, chemical composition, temporal-spatial distribution, component source, etc., atmospheric ultrafine particles are acknowledged to be the most complex atmospheric pollutants [2]. At present, particle number and mass concentration are the main monitoring index and evaluation criterion for environmental administration, meanwhile particle geometric mean diameter can be better to evaluate the peak value and particle size distribution which determines many important physical and chemical properties of the particle itself and environmental effect relevant to atmospheric lifetime, activity of cloud condensation nuclei and extinction effect of which play a significant role on atmospheric environment [3].

Motor vehicle emissions, especially the particulate emissions from diesel vehicles have become the main sources of atmospheric pollution. The aerodynamic diameter (D_p) of particles can be classified as fine ($D_p < 2.5 \mu\text{m}$), ultrafine ($D_p < 0.10 \mu\text{m}$) and nanoparticles ($D_p < 0.05 \mu\text{m}$) [4]. The D_p of diesel vehicles particulate emissions are mostly less than $1 \mu\text{m}$. There are three typical particle modes of diesel vehicles [5]: nucleation, accumulation and coarse modes. With the diameter of 50 nm as boundary, these particles can be divided into two typical particle modes, nucleation and accumulation mode, which are difference in terms of physical dimensions, formation mechanism and chemical component. Nucleation mode particles, mainly in liquid phase, typically range in diameter from 3 to 50 nm and consist of volatile organic compounds, sulfate, metallic and carbonaceous compounds. The nucleation mode particles are formed during exhaust gas dilution

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and cooling [6]. For diesel vehicles aerosol, the nucleation mode typically contains less few percent of the particle mass but a high percent of the particle number [7], [8]. The accumulation mode ranges in diameter size from roughly 50 to 500 nm and its compositions primarily contain carbonaceous agglomerates and adsorbed materials. The coarse mode consists of particles larger than 1 μm and contains certain a few percent of the particle mass [9]. For instance, nanoparticles can spread to the entire respiratory system by means of pulmonary ventilation and generate deposits further in blood circulation. The smaller the particle size, the higher the deposition rate in human body.

At present, China is not only confronted with grim problem of environmental pollution, but also suffering from severe crisis of energy shortage. In order to reduce the environmental pollution caused by fossil fuels and alleviate the present situation of the shortage of oil resources, the government of China follows the path of diversified energy structure and actively develops clean renewable automobile fuels, which is one of the important ways to realize energy-saving and emission reduction for diesel vehicles. Biodiesel is a perfect clean renewable fuel for diesel vehicles [10], [11]. Various studies on chemical and physical properties of biodiesel have suggested that biodiesel with a high level of cetane number and oxygen content may have excellent characteristics to the benefit of ignition quality and reducing particulate emissions. Many researchers have found that particulate matter (PM), hydrocarbons (HCs) and carbon monoxide (CO) are reduced through the use of biodiesel. However, NO_x emissions are increased [12]. Biodiesel can greatly reduce the greenhouse gas emissions based on life cycle analysis conclusion [13]. However, there's little research on fine particle number concentration of biodiesel passenger car under Real-World driving conditions.

The aim of this paper is to research the ultrafine particle number concentration from diesel passenger car with biodiesel blends based on vehicle specific power (VSP) on real-world driving conditions in Shanghai city. VSP originally reported by Jimenez-Palacios in his PhD has been used as a proxy variable for power demand or engine load. VSP is defined as the engine power output per unit mass of the vehicle and is expressed as the function of speed, acceleration, and road grade [14]. In the physical sense, VSP takes into account four kinds of needed power, addition of kinetic energy and potential energy, overcoming the rolling friction and air resistance [15]. VSP is adopted to be the core parameter of driving condition in MOVES mode which had substituted for MOBILE as the U.S. EPA's next-generation vehicle emissions model. To use the models to analyze the effect of different traffic conditions on emissions, certain types of model inputs are required, which creates the need to better characterize the driving pattern by using the VSP [16]. The detailed derivation procedures of VSP could be found in Jimenez-Palacios's doctoral thesis [17]. In order to investigate a typical light-duty vehicle, this paper applied the following simplified expression [15], [16] to calculate VSP (eq.1).

$$\text{VSP} = v \cdot [1.1a + 9.81 \cdot \text{grade} (\%) + 0.132] + 0.000302 v^3 \quad (1)$$

In eq.1 v = vehicle speed in the unit of m/s; a = vehicle acceleration in the unit of m/s^2 ; and grade (%) = vehicle vertical rise divided by the slope length, which is generally assumed to be 0.

The paper is to investigate ultrafine particle number concentration of diesel car with biodiesel blends based on VSP on Real-World driving conditions in Shanghai city. The particle number emission rate and geometric mean particle size can scientifically reflect the difference between diesel and biodiesel blends and would support basic particle emissions data of the passenger car on real-world for atmospheric environmental research and monitoring departments.

2. Materials and Methods

2.1. Testing Fuels

The testing fuels used for the tests were commercially available low sulfur diesel fuel (refer to Euro IV standard, BD0) and waste cooking oil based biodiesel. Blends of biodiesel with low sulfur diesel (5% (BD5), 10% (BD10), 20% (BD20), 50% (BD50) and 100% (BD100) by volume) were tested. The major fuel properties of the testing fuels are shown in Table 1.

Table 1: Properties of testing fuels

Properties	BD0	BD5	BD10	BD20	BD50	BD100
Density @20°C [Kg/m ³]	822.0	824.7	827.4	832.9	849.2	876.3
Low heating value[MJ/Kg]	38.0	37.8	37.5	37.0	35.5	32.9
Cetane number [-]	51.2	51.7	52.1	53.1	55.8	60.4
Sulphur content [mg/kg]	15	19	22	29	51	87
Kinematic viscosity @40°C [mm ² /s]	3.35	3.40	3.46	3.56	3.87	4.39
Aromatic hydrocarbon[% mass]	3.0	3.6	4.1	5.3	8.7	14.4
Carbon [% mass]	85.5	85.0	84.6	83.7	80.9	76.3
Hydrogen [% mass]	13.9	13.8	13.7	13.6	13.0	12.1
Oxygen [% mass]	-	1.1	1.7	2.8	6.1	11.6

2.2. Test Vehicle

The test vehicle was a light duty in-use diesel passenger car, mileage traveled was 21 390 km. The test car weighted 1 435 kg totally and was equipped with turbo-charged diesel engine with electric pump nozzle and EGR. A suit of diesel oxidation catalytic converter (DOC) was equipped on the diesel engine as after-treatment.

2.3. Measurement System

The on-board measurement system mainly consisted of engine exhaust particle sizer spectrometry (EEPS 3090, TSI Inc.), exhaust flowmeter, Global Position System (GPS) and controlling computers. EEPS 3090 has a total of 32 channels between 5.6 and 560 nanometer. It's able to give data every 0.1 second and can offer two main advantages: a) its ability to give data every 0.1 second, a necessary feature to characterize the transient particle size distribution graph; and b) a size range suitable for emission measurement in modern diesel engines [18]. In order to simulate the real physiochemical process of the exhaust particle emissions in the atmosphere, the particle number sampling system was made of two parts: primary and secondary dilution devices. The primary dilution device was a MD19-2E rotating disk dilutor (Matter Engineering AG). A polyporous stainless steel pipe (approximately 50 mm length) inserted the exhaust flowmeter was sampled particles in the exhaust emissions. A copper pipe (approximately 200 mm length, 8mm in outer diameter) was connected the stainless steel pipe and rotating disk dilutor. Particle losses inside the short sampling tube (upstream of the sampling device) were calculated at 2% for 10 nm particles and zero for 100 nm particles. In this study the 10 cavity disk was used. According to the manufacturer's calibration, the dilution ratio was controlled in the 200:1. The temperature was set to 120°C for both the dilutor body and dilution air in order to evaporate volatile particles and reduce the partial pressures of the gas phase species to prevent re-condensation at the dilutor exit. As secondary dilution device, the glass rotor flowmeter added air to EEPS and the controlled dilution ratio was 2.5:1, and the dilution air was purified by an HEPA filter. So the total dilution ratio was 500:1. Before measure the particle size distribution, EEPS was calibrated by clean air which was purified by an HEPA filter. Once the calibration was done and the heat temperature reached up to 120°C, EEPS can introduce dilute gas and start to analyze particle size distribution. A suit of GPS was installed in the car to log the transient speed and the geographical position including longitude, latitude and height.

2.4. Test Route

In order to keep consistent with Shanghai vehicles typical driving road condition [19], three typical roads were selected in Shanghai city, which included urban arterial road, residential street and elevated road. The total distance of the route was 35 km and the speed of the car was limited at the prescribed speed. The tests were completed continuously in 6 days.

2.5. Method of VSP Binning

The VSP interval between -20 and 20 kW/ton covers the most operating modes in the city road network [19]. To choose the VSP bins, the paper investigated the VSP bins distribution before the result discussion. The VSP in Chinese cities was divided into 10 bins according to the analysis in previous sections and the

authors' relevant studies [20]. For the purpose of reducing both the aggregation errors and computational complexity [21], the work divided the $[-20,-2)$ as a VSP bin, and $(10, 20]$ as a VSP bin. Table 3 shows the detailed division of VSP bins.

Table 2: Intervals of VSP bins

VSP(kW/ton)	-20	-2	0	2	4	6	10	20
Interval	$[-20,-2)$	$[-2,0)$	0	$(0,2]$	$(2,4]$	$(4,6]$	$(6,10]$	$(10,20]$

3. Results and Discussion

3.1. Particle Number Emissions Rate

Fig.1 shows fine particle number emissions rate (ER) of from diesel passenger car with biodiesel blends based on different VSP bins. In the range of $VSP \geq 0$ kW/ton, particle number ER of each test fuel rises with the VSP increase, as shown in Fig.1. With the VSP increase, the car was often in high speed or harsh acceleration modes which lead to the engine in much higher load and unstable conditions. Thereby, the air-fuel ratio fluctuated frequently and combustion in the combustor is unstable. These cause the increase of particle number ER. The particle number ER of biodiesel blends is lower than that of BD0. There are two possible reasons. Firstly, oxygen content of biodiesel fuel restrains carbonaceous particle production contributing to the increment of accumulation mode particles. Secondly, the car was equipped with DOC which would oxidate those major liquid particles and SOF (soluble organic fraction) caused by increased viscosity and lower volatility of biodiesel blends. However the reduction rates of particle number ER aren't accord with the blend ratios of biodiesel. For instance, the particle number ERs of BD10 and BD20 have close character, while both the ERs are much lower than that of BD5. The number ER of BD100 at $VSP=0$ kW/ton is apparently higher than those of moderate blend ratios of biodiesel. While the $VSP > 0$ kW/ton, the number ERs of BD100 and BD50 are approximate and lower than those of other biodiesel blends. The possible cause is that increased oxygen content and higher cetane number of the biodiesel make the combustion easier in the engine combustion chamber, meanwhile increased viscosity and lower volatility of biodiesel could lead to that evaporation and air mixing in combustor is slower and worse comparing with diesel fuel instead. Therefore, some specific physicochemical properties of biodiesel blends play a leading impact on the particle emissions on specific VSP bins. During the VSP bin $(0, 2]$, the particle number ER of BD0 rises significantly while increases gradually in the VSP range $(2, 20]$. The similar sharp increase of biodiesel blends turn up during VSP $(0, 4]$. When the $VSP > 4$ kW/ton, the particle number ERs of BD20, BD50, BD100 show a change of slightly lower first and then increase slowly.

By analyzing the definition of VSP, it's not hard to understand that negative VSP is always associated with braking mode. As shown in Fig.1, the particle number ERs of test fuels increase sharp first and then keep stable as the VSP reducing in negative ranges. The emissions trend above mentioned are consistent with that of gaseous emissions. During decelerating condition, the particle number ER of the car give a peak value, and specifically, the peak is much higher in high speed-decelerating condition. The load and speed of diesel engine reduce when the car is in decelerating condition and then reduction of fuel injection quantity and lag effect of the turbocharger lead to increase the excess air coefficient in the combustion chamber. Instant increase of excess air coefficient attributable to the mixed zone increase and some fuel can't be ignited before emitting out of the engine. On the other side, the excess air cools down the combustion chamber which leads to flame quenching of much more mixed fuel. Thereby, these reasons mentioned above result in sharp increase of unburned hydrocarbon which increase nucleation mode particles. Five proportions of biodiesel blends are difference in particle number ER. This's because of the differences of physicochemical property result in the particle differences in physical dimensions and chemical components.

3.2. Particle Number Concentrations

Fig.2 (a-d) shows particle number concentrations of the fuels in VSP bins. During $VSP \geq 0$ kW/ton, the total number concentrations of most of the test fuels rise gradually with the VSP increase. As Fig.2a shown, the total number concentrations of BD0 and BD5 are relatively higher and appear significantly growing as

the VSP increase. While the total number concentration of higher biodiesel blends ratio is much lower and the increasing trend isn't obvious. During VSP bins above zero, shown in Fig.2b, the nucleation mode number concentration of BD0, BD5 and BD10 rise first and then decline. The peak values of nucleation mode appear in the VSP bin (4, 6] and decrease in sequence, 9.9×10^7 , 8.1×10^7 and 7.6×10^7 $\#/cm^3$. The nucleation mode number concentrations of BD20, BD50 and BD100 appear peak and valley values in succession in the bins, (2, 4] and (4, 6] and then rise gradually to varying degrees. It's worth noting that the nucleation mode number concentrations of BD0 to BD100 first drop and then rise in each VSP bin. When the VSP is positive, the nucleation mode number concentration of BD20 is the lowest while that of BD10 is the lowest in negative VSP bins.

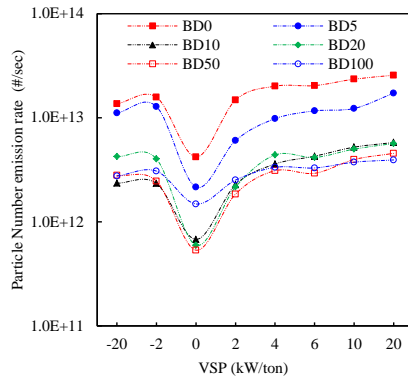


Fig. 1: Particle number ERs

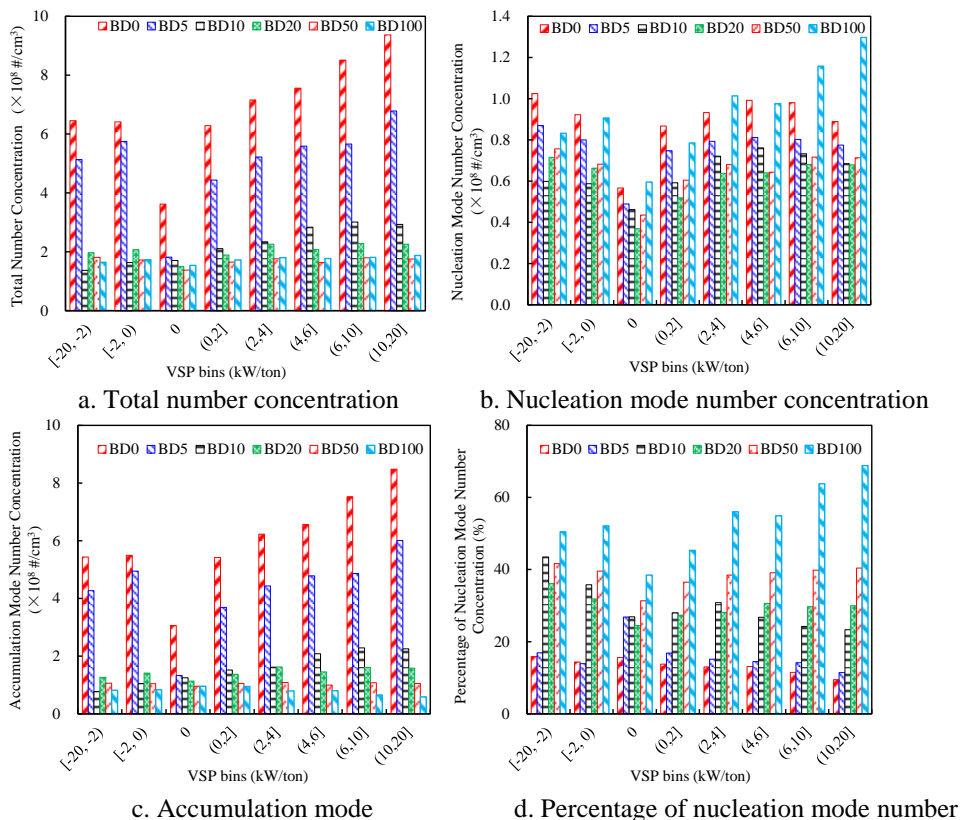


Fig. 2: Particle number concentration

As shown in Fig.2c, in the positive VSP bins, the accumulation mode particle number concentrations of BD0 to BD100 are dropping in successively in each positive VSP bin. In positive VSPs, as the VSP increase, the accumulation mode particle number concentrations of BD0 and BD5 rise obviously. There's only slight increase trend of the accumulation mode number concentration of BD10. However, the concentrations of BD20 and BD50 basically keep stable while that of BD100 drops as the VSP increase. In each positive VSP

bin, the accumulation mode number concentrations lessening successively as the biodiesel blend ratios increase. Compared to the accumulation mode number concentrations of the VSP bin [0], those of negative VSPs are much higher. BD10 appears to reduce the accumulation mode particles signally.

Fig. 2d shows the percentage of nucleation mode number concentration in each VSP bin. The percentages of nucleation mode number concentration of BD0 to BD100 show the same change trend of increase generally in each VSP bin. The percentage of nucleation mode number concentration of BD100 ranges from 38.5% to 68.8%. As to BD10, BD20 and BD50, the percentages are much higher and more changeable in negative VSP bins than that in the positive bins. The car fueled with BD0 shows minor and stable percentage of nucleation mode number concentration, ranging from 9.5% to 16.9%. A phenomenon is observed that BD0 and lower biodiesel blend ratio, such as BD5 and BD10, could reduce the percentage of nucleation mode number concentration as the VSP increase.

According to Fig. 2 (a-d), in VSP interval [0, 20], accumulation mode particles dominate in the increasing number concentration from BD0 and BD5 as the VSP increase. In higher VSP bin, the percentages of both the fuels rise to 80%. As biodiesel blend ratios increase, the total particle number concentrations become lower and more stable while the percentage of nucleation mode number concentration get much higher. This characteristic is more obvious in the higher VSP bin. Biodiesel blends are able to reduce the total particle number concentration, specially, the accumulation mode particle. While the biodiesel blends increase the nucleation particle number emission. In negative VSP bins, the percentages of nucleation mode concentration of biodiesel blends rise obviously. The decelerating modes of the car increase the nucleation mode particles emission. As explained in 3.1part, it's due to increased oxygen content, cetane number and viscosity which contribute to decrease accumulation mode but increase nucleation mode particles.

3.3. Particle Geometric Mean Diameter

Table 3: Particle geometric mean diameter of number (Unit: nm)

VSP(kW/ton)	-20	-2	0	2	4	6	10	20
BD0	113.4	115.4	96.5	110.5	114.6	112.2	118.3	127.2
BD5	103.0	111.7	63.5	97.3	104.2	108.7	109.4	121.3
BD10	43.2	52.3	63.6	62.5	60.4	66.2	69.6	70.8
BD20	56.8	62.0	69.7	66.7	67.3	64.1	65.6	65.5
BD50	48.3	50.3	59.6	53.5	51.7	50.9	50.1	50.3
BD100	41.1	40.0	52.9	45.5	37.0	37.1	32.0	29.3

Particle geometric mean diameter not only reflects the range of particle concentration, but also represents the particle number size distribution. Table3 shows the particle geometric mean diameter. In VSP bins, biodiesel blends can decrease the geometric mean diameters of number and mass, but the degree of decreasing and changing are different with each other. As shown in Table3, in VSP bin [0], the geometric mean diameters of number of BD0 and BD5 appear valley value, 96.5 and 63.5 nm, while BD10 to BD100 rise peaks, 63.6, 69.3, 59.6 and 52.9 nm. In positive VSP bins, the geometric mean diameters of number of BD0 and BD5 give a rising trend in general while those of BD20 to BD100 decrease as the VSP increase. In negative VSP bins, the geometric mean diameters of number of BD0 and BD5 rise and then drop while those of the other biodiesel blends reduce as the VSP decreasing. Biodiesel can reduce the geometric mean diameter of number distinctly. The average values of geometric mean diameters of number of BD0 to BD100 are 113.5, 102.4, 61.1, 64.7, 52.1, 39.3 nm in sequence.

4. Conclusions

Based on a suit of on board test system, this paper investigated ultrafine particle number concentration from diesel passenger car with biodiesel blends based on vehicle specific power (VSP) on real-world. Experimental result shows that: 1) the passenger car with low-sulfur diesel and biodiesel blends emits the lowest number emission rate in VSP bin [0]. The number emission rates rise to varying degrees as the VSP

bin increase or decrease. Biodiesel blends can reduce the number rates and the reducing percentage depends on the blend ratios. 3) Biodiesel blends can reduce total particle number and mass concentration from the car. In higher VSP bins, the percentage of nucleation mode number concentration weighs more as the biodiesel blend ratio increase. In VSP bin [10, 20], the percentage of nucleation mode number concentration between BD0 to BD100 is in the range of 11.4% to 68.9%. 4) Biodiesel can reduce the geometric mean diameter of number distinctly. The average values of geometric mean diameters of number of BD0 to BD100 are 113.5, 102.4, 61.1, 64.7, 52.1, 39.3 nm in sequence.

5. Acknowledgments

This work was supported by National 863 Project (2008AA11A169) and Shanghai science and Technology Commission project (10231201902). The authors gratefully acknowledge all members of On-Board test team.

6. References

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