Morphological Study of the Particulate Matter from a Light-Duty Diesel Engine

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Abstract

In this investigation, the morphological characteristics of diesel particulates were revealed through accurate analyses of dimensions and fractal geometry. Diesel particulates were collected from a 1.7-L light-duty compression-ignition direct-injection diesel engine under various engine operating conditions by using a thermophoretic sampling system. The samples were analyzed by using a high-resolution transmission electron microscope and customized digital image processing/data acquisition systems. The analyses showed that the mean primary particle diameter ranged from 19.4 to 32.5 nm through a range of operating conditions: 675 (idling) to 4000 rpm and 0–100% load. Particle size was significantly affected by the operating conditions, such as exhaust gas recirculation (EGR) rate, engine speed and load, air/fuel ratio, and temperature. Larger primary particles were produced at higher EGR rates, lower air/fuel ratios, and lower exhaust temperatures. The fractal properties of diesel particulates were also measured. From this analysis, it was confirmed that the formation of diesel particulates is controlled by a diffusion-limited growth mechanism. A database of the morphology and fractal geometry of diesel particulates will be available for the design of efficient diesel particulate control systems.

Introduction

Compression-ignition direct-injection (CIDI) diesel engines are inherently more energy-efficient than spark-ignition gasoline engines. As uncertainty in the oil supply looms and concern over global warming grows, diesel engines are considered a promising power source among existing transportation technologies that can alleviate the nation's dependence on imported oil and reduce the production of greenhouse gases such as carbon dioxide (CO_2). Nevertheless, the use of diesel engines is controversial, mainly because of the health and environmental effects associated with particulate emissions. Epidemiological studies have shown a correlation between exposure to particulate emissions and daily morbidity and mortality [1–3]. The Environmental Protect Agency has already imposed restrictions on diesel particulate emissions. Future regulations and emission standards will be far more stringent.

In this challenging environment, numerous investigators have performed creative work to control diesel particulate emissions by improving combustion processes and developing aftertreatment systems or different fuel properties. To meet upcoming standards, however, a better understanding of complex particulate formation and destruction mechanisms is necessary. A new approach, accurate analyses of the physical and fractal properties of diesel particulates, has been developed.

Engine researchers have generally used commercial particle sampling and measurement systems, such as the electrical aerosol analyzer (EAA), scanning mobility particle sizer (SMPS), and impactor, to analyze the size distributions of diesel particulates. Both EAA and SMPS measure the mobility-equivalent diameter of charged particles, defined as the diameter of a spherical particle representing the same electrical mobility [4–9]. For measurements, however, a high degree of air dilution of the exhaust stream is often needed, and the physical and chemical properties of diesel particulates are very sensitive to dilution ratios and schemes [10].

Laser diagnostics has also been used to measure diesel particle sizes. In principle, laser-induced

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incandescence measures particle sizes by detecting the radiation emitted from laser-excited particles [11]. In this technique, however, investigators need to compromise with an assumption of mono-dispersed spherical particles. High-power laser emission to particles in the measurement volume could change their morphology and internal structures. Application to internal combustion engines also requires an excessive amount of air to dilute exhaust streams.

Carpenter and Johnson [12] analyzed the physical characteristics of diesel particulates by using microscopy. They sampled particulate matter from a naturally aspirated heavy-duty direct-injection diesel engine with an Anderson impactor. They found that primary particle diameters ranged from 7 to 120 nm under the experimental conditions used. However, the use of an impactor can change particulate morphology and size because particulates accumulate on the collecting plates during long sampling times. This measurement system is also limited in measuring relatively small particles.

Lee et al. [13–15] introduced a direct thermophoretic sampling technique for internal combustion engines, which collects diesel particulates directly from high-temperature undiluted exhaust streams. Detailed morphology and microstructures were analyzed for particulates sampled from a heavy-duty single-cylinder direct-injection diesel engine under various engine operating conditions. Rapid collection of particulates from the exhaust manifold can prevent possible nucleation and growth of particulates and condensation of volatile species, which could occur in other measurement systems during dilution processes. No changes in morphological properties were observed during sampling and analysis.

The objective of this study is to better understand the formation and destruction mechanisms of particulates in a light-duty diesel engine. We analyzed particle size, structure, and fractal geometry by using the direct thermophoretic sampling technique, transmission electron microscopy (TEM), and an image processing/data acquisition system. The results were compared with previous experimental data obtained with a heavy-duty diesel engine [13–15]. Finally, we provided a database of the morphology and geometry of light-duty diesel particulates for the design of efficient particulate control systems.

Experimental Description

Experiments were performed on a light-duty 1.7-L CIDI diesel engine (see Table 1). California low-sulfur commercial 2-D diesel fuel, HF-328, was used. For particulate sampling, the thermophoretic device was installed on a rigid platform near the exhaust manifold. A custom-designed sampling chamber was connected to the exhaust manifold through a stainless steel shutter valve. The release of exhaust emissions from the engine to the sampling chamber was controlled manually at each experiment. A TEM copper grid was attached in a grid holder on the tip of the air cylinder rod, which was controlled by a solenoid valve and an electronic sampling controller. The sampler collects particulates from the exhaust stream flowing through the sampling chamber in an optimized residence time.

Table 1. OM668 Engine Specifications

Type	Diesel, 4-stroke cycle
Number of Cylinders	4
Bore Size	80 mm
Stroke	84 mm
Displacement	1689 cm^3
Compression Ratio	19:1
Air induction	Turbocharged, intercooled
Valves per Cylinder	4
Maximum Power	66 kW @ 4200 rpm
Maximum Torque	180 Nm @ 1600-3200 rpm
Maximum Speed	4800 rpm
Fuel-Injection Type	Common-rail, direction injection
Rotating Inertia	0.148 kg-m^2

Diesel particulates were sampled at engine speeds of 675 (idling), 1000, 2500, and 4000 rpm with various loading conditions from 0% to 100%. Engine exhaust temperatures, exhaust gas recirculation (EGR) rates, and air/fuel equivalence ratios were monitored to maintain constant values during each sampling experiment. The engine was warmed up at 2500 rpm/45 Nm for about 30 minutes before experiments. During that period, the exhaust temperature and pressure were checked to ensure experimental reproducibility. The engine was stabilized for another 10 minutes at each sampling condition. Particulates were then collected on the sampling grid by thermophoresis effects, which are driven by the temperature gradient generated between the hot exhaust stream and the near-room temperature of the sampling grid surface. The residence time of the sampling probe in the exhaust stream was optimized to both provide a sufficient amount of particles to be analyzed and avoid possible particle overlapping on samples.

The TEM grid samples were observed and photographed by a Philips CM30 TEM. The micrographs were then digitized with a high-resolution closed-coupled device (CCD) camera and an image processing/data acquisition system to analyze detailed morphological properties, such as the primary particle diameter d_p, radius of gyration R_g, and fractal dimension D_f. Detailed descriptions of this analysis technique can be found in Lee et al. [16] and Guenç et al. [17].

Results and Discussion

Table 2 shows the results of the morphological analysis. For each experiment, the exhaust temperature, EGR rate, and air/fuel equivalence ratio were recorded to observe their effects on particulate properties. In qualitative observation of particulate morphology in the TEM images, diesel particulates appeared to consist of an agglomeration of numerous spherical primary particles. These aggregate particles represented a stretched chain-like shape at large, independent of engine rpm and load. The particles, in which tens to hundreds of primary particles were clustered around each other, were distributed in a wide range of size − tens of nanometers to a few microns. At low load, many particles appeared to be nebulous in morphology, where boundaries between primary particles were not clear. These amorphous soot particles may contain a significant amount of soluble organic compounds. Further investigations into chemical composition and internal structure are needed to validate these observations.

The size distributions of primary particles were measured by using a digital image processing/data acquisition system under various engine operating conditions. For each condition, more than 200 primary particles were randomly selected from different aggregates to determine an average diameter of the primary particles. Table 2 shows the results. In most cases, the size distribution of primary particles represented a typical Gaussian distribution, as shown in Figure 1.

As shown in Table 2, average primary particle diameters were measured to be between 19.4 and 34.2 nm for all engine conditions used. These values were smaller than those reported in our previous study (28.5–34.4 nm), which were obtained for a heavy-duty single-cylinder diesel engine [13–15]. Figure 2 shows these particle diameters as a function of engine load. At low load, primary particle diameters appeared to be sensitive to engine speed, depending on the operation of the EGR system. The primary particle sizes at both 1000 and 2500 rpm were larger than those at 4000 rpm.

Exhaust gas recirculation is commonly used to reduce diesel nitrogen oxide (NO_x) emissions. Our EGR system can supply exhaust gas to the intake manifold at different rates, depending on operating conditions. EGR reduces NO_x emissions by lowering the combustion temperature according to thermal NO_x formation mechanism. However, EGR produces a high level of particulate emissions. In this study, the EGR rate was defined as

$$EGR = \frac{[CO_2]_{man} - [CO_2]_{bkg}}{[CO_2]_{exh} - [CO_2]_{bkg}} \cdot 100\% \qquad (1)$$

where $[CO_2]_{bkg}$ is the background CO_2 concentration, $[CO_2]_{man}$ the CO_2 concentration in the intake manifold, and $[CO_2]_{exh}$ the CO_2 concentration in the exhaust manifold. The EGR rate at each engine condition is shown in Figure 2 as a percentage. The EGR rates of less than 2% resulted from normal leakage in the control valve while the EGR valve was closed. A higher EGR rate implies that more exhaust gases are introduced into the combustion chamber. As described above, the average primary particle diameters at 1000 and 2500 rpm were larger than those at 4000 rpm, when the EGR system was turned off. It is very likely that EGR increases primary particle size under most engine operating modes. Low combustion temperatures caused by high EGR rates will reduce particulate oxidation in the combustion chamber.

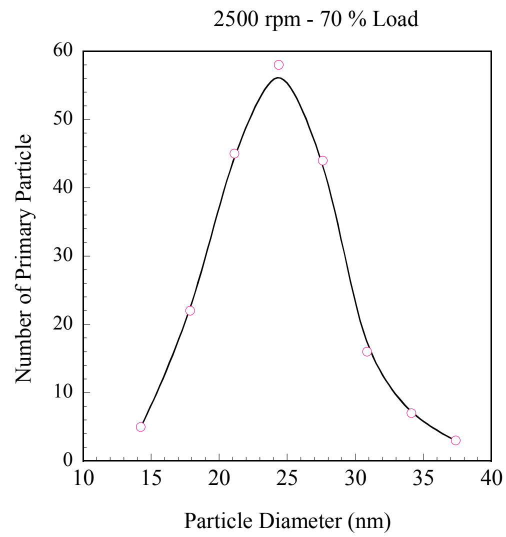

Figure 1. Primary Particle Size Distribution

In a comparison of data at 1000 and 2500 rpm in the region where the EGR system was operated (approximately up to 60% load), the primary particle diameters at 2500 rpm appeared to be relatively larger even when the air/fuel equivalence ratios and EGR rates were comparable. In the particulate formation mechanism, primary particles experience a series of chemical and thermal processes in which precursor particles nucleate, grow through coagulation (collision + coalescence) with other primary particles, and oxidize to reduce the hydrogen/carbon (H/C) ratio. A major factor in controlling these processes is the combustion temperature. Higher combustion temperature enhances both particle nucleation and oxidation. Thus, the existence of a primary particle in the combustion field depends on competition of those two events. In our engine, exhaust temperatures were measured to be 212.9 and 348.9°C at 1000 rpm/25% load and 2500 rpm/25% load, respectively. At 50% load under the same engine speed, the corresponding temperatures increased to 300.5 and 468.6°C. Under these operating conditions, combustion temperatures are higher at higher engine speeds and loads. Therefore, it is likely that enhanced particle nucleation and growth due to high combustion temperatures exceed the oxidation of diesel particulates at 2500 rpm. Furthermore, the residence time available for oxidation should decrease at higher engine speeds. In fact, Pung et al. [19] reported that diesel particulates form rapidly during the initial stage of combustion, and then oxidation takes place.

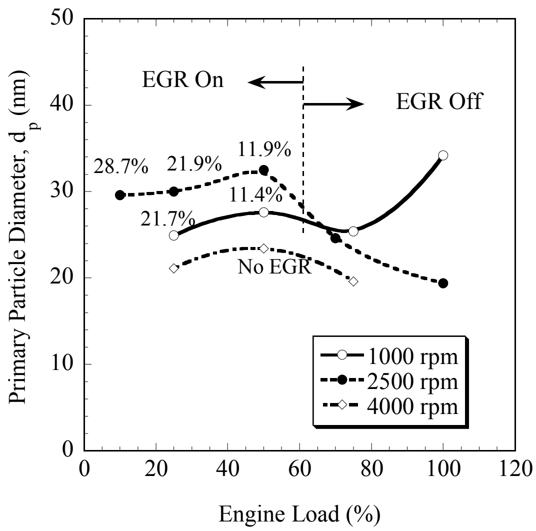

Figure 2. Primary Particle Size as a Function of Engine Load

Our previous study [13–15] showed that primary particle size decreases at high engine load because of particle oxidation in the high-temperature environment. A similar trend was observed in Figure 2. Particle size remained fairly constant at low load and decreased as load (or combustion temperature) increased, except in the case of 1000 rpm/100% load. Figure 3 shows primary particle size as a function of exhaust temperature. The size distribution at 1000 rpm shows a local peak at 100% load (exhaust temperature of 458.8°C) in contrast to other distributions. Increasing size at maximum load can be supported by the following observations: the baseline tests on our engine showed a rapid increase in total particulate emissions at this condition, particle oxidation is enhanced above a temperature of 550–600°C [20], and particle formation significantly increases only in a narrow bandwidth of equivalence ratios [21]. At 1000 rpm/100% load, the combustion temperature should relatively be low to oxidize the particulates formed at a significantly fuel-rich condition (an air/fuel equivalent ratio of 0.99 at 1000 rpm/100% load).

In our previous study performed with a 75-hp heavy-duty single-cylinder, direct-injection diesel engine [13–15], primary particle sizes were comparable to the data reported here although the current data show several smaller sizes, especially at high loading conditions. Primary particle sizes for the heavy-duty diesel engine were distributed in a range of 28.5–34.4 nm, while the current data fall between 19.4 and 34.2 nm. The smaller sizes reported here seem to be caused by enhanced oxidation due to higher temperatures at maximum load, even if a difference in fuel composition may be effective.

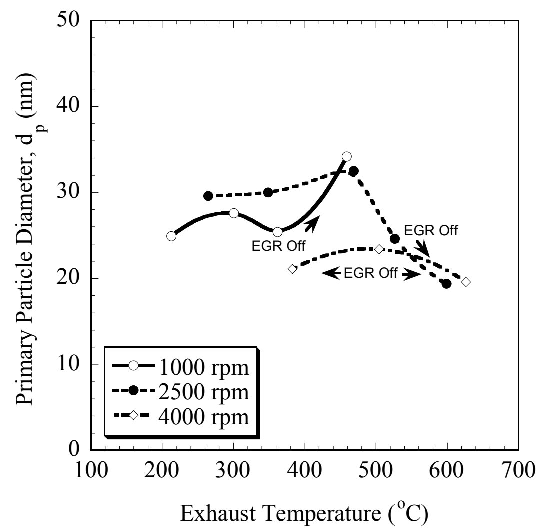

Figure 3. Primary Particle Size as a Function of Exhaust Temperature

The fractal geometry characteristics of diesel particulates, such as radius of gyration R_g and fractal dimension D_f, were also measured in this study. The measurement of fractal dimension is essential in understanding the agglomeration and growth mechanisms of diesel particulates. The fractal dimension D_f is defined as

$$n = k_f \left(\frac{R_g}{d_p} \right)^{D_f} \tag{2}$$

where n is the total number of primary particles within an aggregate particle, k_f a prefactor, R_g the radius of gyration of an aggregate, and d_p the average primary particle diameter. The number of primary particles n is determined by the following relationship [22]:

$$n = \left(\frac{A_a}{A_p} \right)^{1.09} \tag{3}$$

where A_a is the projected area of an aggregate and A_p the average projected area of primary particles.

The radius of gyration of a single aggregate particle is measured by the following equation:

$$R_g = \sqrt{\frac{1}{n}\sum_{i=1}^{N} r_i^2} \tag{4}$$

where r_i is the distance between the center of an individual primary particle and the centroid of the associated aggregate. By plotting ln(n) versus ln(R_g/d_p), the fractal dimension D_f can be obtained by evaluating the slope of linear regression line.

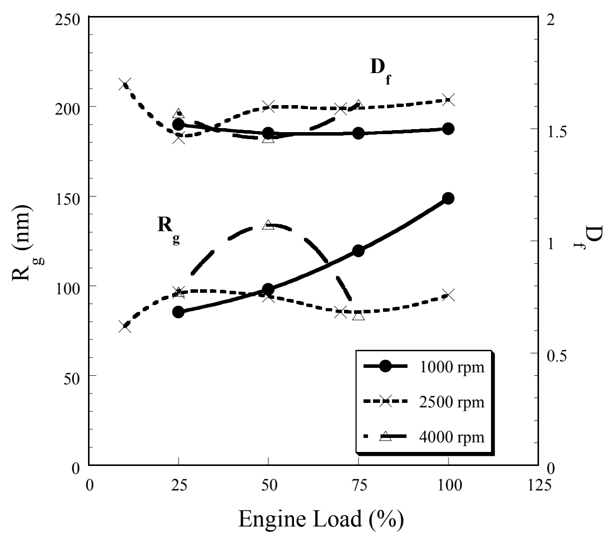

Figure 4. Distributions of the Radius of Gyration (R_g) and Fractal Dimension (D_f) as a Function of Engine Load

Figure 4 displays the radii of gyration R_g and fractal dimensions D_f as a function of engine load. The magnitudes of D_f appear to be distributed in the range of 1.46 to 1.70. These values are slightly lower than those measured for heavy-duty diesel particulates in our previous study [13–15]. This result implies that more chain-like particulates were produced in the light-duty diesel engine, which confirms that the diesel particulates analyzed here were formed under the diffusion-limited particle growth mechanism. The magnitude of radius of gyration R_g was distributed in the range of 83.7–148.7 nm. As seen in Figure 4, the engine load has a greater influence on particulate sizes (i.e., the radii of gyration of aggregate particles), than engine rpm does.

Conclusions

A thermophoretic sampling apparatus was used to sample diesel particulates directly from the exhaust stream of a light-duty turbo-charged CIDI diesel engine at various engine speed and load conditions. The morphology and fractal geometry of diesel particulates were analyzed with a TEM and high-resolution digital image processing/data acquisition system. A detailed database of the morphology and dimensions of light-duty diesel particulates was created.

Analyses showed that the mean values of primary particle diameter fell between 19.4 and 32.5 nm under a range of engine conditions from 675 (idling) to 4000 rpm and 0– 100% load. The primary particle size was significantly affected by engine operating conditions, such as engine speed and load, EGR mode, and air/fuel equivalence ratio. In the high-load region (>60%), the primary particle sizes at 2500 and 4000 rpm decreased with engine load because of high-temperature particle oxidation. At 1000 rpm, however, it is likely that the fuel-rich condition is responsible for the increasing primary particle size. Use of EGR significantly increased primary particle sizes under most engine speed and load conditions. In the low-load region (<60%), when a similar EGR mode was used at 2500 and 1000 rpm, the larger primary particle sizes measured at 2500 rpm were influenced by the effects of particle nucleation and growth exceeding oxidation.

The fractal dimensions of diesel particulates were measured at a range of 1.5–1.7, which is comparable with those of heavy-duty diesel particulates (1.8~1.9). This result confirmed that the formation of light-duty diesel particulates we analyzed here was controlled by a diffusion-limited growth mechanism.

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Table 2. Engine Operating Conditions and Measurements of Diesel Particulate Dimensions

Engine RPM	Engine Torque (Nm)	Engine Load (%)	Exhaust Temperature (^oC)	EGR Rate (%)	Air/Fuel Equivalence Ratio	d_p (nm)	R_g (nm)	D_f
675	0	0	N/A	0	N/A	28.6	N/A	N/A
1000	31	25	212.9	21.7	1.66	24.9	85.4	1.52
1000	62	50	300.5	11.4	1.58	27.6	98.0	1.48
1000	93	75	362.0	0.5	1.08	25.4	119.5	1.48
1000	124	100	458.8	0.3	0.99	34.2	148.7	1.50
2500	18.8	10	264.3	28.7	2.65	29.6	77.4	1.70
2500	47	25	348.5	21.9	1.79	30.0	96.3	1.46
2500	94	50	468.6	11.9	1.60	32.5	94.2	1.60
2500	131.6	70	526.2	1.0	1.67	24.6	85.5	159
2500	188	100	598.7	0.5	1.24	19.4	95.0	1.63
4000	40	25	382.8	0	2.48	21.1	96.7	1.57
4000	79	50	504.4	0	1.69	23.4	134.1	1.46
4000	118.5	75	626.3	0	1.39	19.6	83.7	1.61