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Size distributions and number concentrations of particles from the DOC and CDPF

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Abstract

Particulate matters (PM) from diesel combustion comprise the major portion of harmful components of air in urban areas. In this study, the effects of DOC and/or CDPF on the size distributions and catalytic reactions of these nano-sized particles were investigated to clarify the exhaust mechanism and to minimize the emission of the nano-sized PM. Parameters of interest in the investigation included sulfur content of the fuels used, air-fuel equivalence ratio, fuel injection pressure, and the engine speed. The number concentration of the particles in diluted exhaust gas was measured by a SMPS in the diametric range of 10-385 nm. The number of nanometer-sized particles increased when the engine was operated at high equivalence ratio with diesel fuel that contained 500 ppm of sulfur. As the sulfur concentration in the fuel increased, the number of the particles smaller than 30 nm increased upon passing DOC and CDPF in the exhaust system of the common-rail diesel engine.

Keywords: Diesel engine; PM (Particulate matters); Nano-sized particle; DOC (Diesel oxidation catalyst); CDPF (Catalyzed diesel particulate filter); SMPS (Scanning mobility particle sizer)

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1. Introduction

Since diesel engines have higher thermal efficiency than gasoline engines, the use of more diesel engines will extend the lifetime of quantity-limited fossil fuel as well as slow down global warming. However, they emit more hazardous pollutants such as NOx and PM (particulate matters) than gasoline engines. Particulate matters are presently regulated in gravitational units such as grams per kilometer or grams per kilowatt-hour. Advanced technologies as high pressure fuel injection, variable geometry turbo-charging, and diesel particulate filters are employed on latest diesel vehicles to meet the strict weight-based legislations. The engines applying these technologies emit far less particulates in weight, but they tend to emit out increased number of ultra-fine particles, which believed to be more harmful to human health than larger particles [1, 2]. In response, society has required a new regulation based on a particle number which is now under active discussion for introduction in the near future.

DOC (diesel oxidation catalyst) can oxidize a large portion of engine-out HC (hydrocarbons), CO (carbon monoxide), and SOF (soluble organic fraction) of PM. But it can also generate PM in the form of sulfates like SO_4 or H_2SO_4 at temperatures over 300℃ [3, 4, 5]. Although sulfur dioxide is an unregulated diesel emission, it plays a critical role in the formation process of nano-sized particles. Sulfur dioxide originates from the sulfur in the fuel and engine lubricating oil and can be oxidized into sulfur trioxide (SO_3), which is a precursor of sulfuric acid responsible for sulfate particle emissions. As ULSD (ultra-low sulfur diesel), ultra low sulfur diesel with less than 30 ppm of sulfur, is distributed in Korea since early 2006, and engine lubricating oils have become an important source of

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SO_2 in diesel engine exhaust. Diesel lube oils typically contain 4,000-10,000 ppm sulfur, primarily as part in their additives. Antiwear additives for example contain zinc, sulfur, calcium, boron, and phosphorus etc. [6].

CDPF (catalyzed diesel particulate filter) or plain DPF (diesel particulate filter) is extremely effective in removing solid particles in the exhaust gas, but CDPF may generate a large number of particulates in nuclei mode during high-load engine operations. Diesel particles leaving the engine are composed primarily of solid-phase carbon material. Both individual (nuclei mode) and agglomerated carbon particles are formed in the combustion chamber. In the exhaust system, depending on the temperature, the particles undergo limited oxidation and further agglomeration. Some particles are deposited on the exhaust system due to thermophoretic forces. Other PM precursors including hydrocarbons, sulfur oxides, and water are present in the hot diesel exhaust gases. Another source of solid material in diesel exhaust is the metal ash compounds that are derived from lubricating oil additives and from engine wear. Nucleation of volatile ash constituents is believed to take place during the expansion stroke in the engine cylinder. The ash nuclei can then agglomerate to form accumulation mode particles [3, 7]. Many recent studies have suggested that nano-sized particles from modern engines are primarily volatile, and are probably formed by homogeneous nucleation of sulfuric acid followed by absorption or heterogeneous nucleation of the heavier hydrocarbons in the SOF. Nano-sized particles smaller than 50 nm in the diesel exhaust are mainly comprised of hydrocarbons and condensates of hydrated sulfuric acid, and nano-sized particles are also generated in the nucleation mode during the cooling process of the exhaust gas by dilution. The amount of nano-sized particles is measured as required by the regulations. A small fraction of nucleation mode particles may be of such solid materials as carbon or metallic ash from lube oil additives. Nucleation mode particles comprise the major portion (about 90%) of the particulate matters in number but only a few percent in mass [3]. It is also known that the lower the temperature, the more SOF contained in the exhaust gas [8, 9]. Number concentration of these nano-sized particles over the size spectrum often shows different characteristics depending on the measurement technique employed, especially the sampling and diluting process, during which the particles may continue to grow [3, 10].

In this study, the effects of DOC and/or CDPF on the size distributions and catalytic reactions of these nano-sized particles are investigated to clarify the exhaust mechanism and to minimize the emission of the nano-sized PM. Parameters of interest in the investigation include the sulfur content of the fuels used, air-fuel equivalence ratio, fuel injection pressure, and the engine speed.

2. Experimental methodology

Engine experiments were conducted on a system consisting of major devices like a single-cylinder diesel engine, exhaust gas diluters, and a SMPS (scanning mobility particle sizer), DOC or CDPF, and a set of exhaust gas analyzer, as illustrated in Fig. 1. The test engine is a common rail type of single-cylinder diesel engine with a 0.5 L swept volume. The DOC of 0.51 L (76 mm in diameter x 110 mm in length) was used. The honeycomb type of monolithic substrate with cell density of 93 cpsc (cell per square centimeter, 600 cpsi) was coated with γ–Al_2O_3 and 3.18 g/L of platinum (Pt). After the CDPF which used about 200 hours at the 4 cylinder CRDI (common rail direct injection) diesel engine, it was modified for single cylinder diesel engine. The reason why used CDPF selected is that it is for the reliability of the experimental data. The CDPF is a cylindrical silicon carbide (SiC) based wall flow filter with a diameter of 51 mm, length of 250 mm, and cell density of 31 cpsc (200 cpsi). An exhaust gas analyzer (Horiba, MEXA-9100DEGR) was also used to measure HC, CO, NOx, CO_2 and O_2 concentrations. Particle size distribution was measured over a range of diameters from 10 to 385 nm by the SMPS. Table 1 shows the specifications of the SMPS and the ejector type diluter. In this study, a part of the exhaust gas and the filtered ambient air were mixed in the ratio of 1:132 by using an ejector type diluter system that we made. The double-staged dilutor had a built-in electric heater in the first stage which allowed the dilution air temperature to be changed when desired. Because the upper concentration limit of CPC (condensation particle counter) is 10^5 particles/cm^3, the diesel engine exhaust that includes the order of 10^7 particles/cm^3 must be diluted under the order of 10^5 particles/cm^3. The measurement range of particle size is determined by sheath flow, sample flow and scanning time. Sheath and sampling flow rates were set to 6 and 0.6 LPM,

Table 1. Specifications of SMPS and ejector type diluter.

SMPS (model : 3080, TSI)	
Description	Specification
Particle size range (L-DMA 3081)	Adjustable : 10 to 1000 nm (10-385 nm range used)
Upper concentration limit (3025A CPC)	10^5 (particles/㎤)
Scanning time	30 to 300 sec
Diluter (ejector type, CNU)	
Diluter	Dilution ratio
1st diluter	1:12 (Temperature range 20-180℃)
2nd diluter	1:11 (TDR 1 : 132)

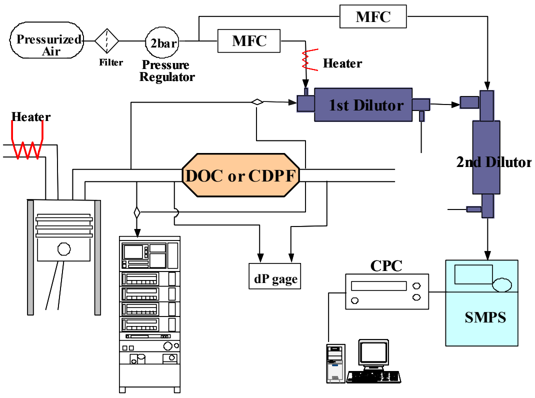

Fig. 1. Schematic diagram of the experimental apparatus.

respectively, and the scanning time was 60 seconds. For an inlet impactor, a cut-point of 499 nm was used. For CPC, a high-flow mode was used to minimize the diffusion loss. The total number concentration (particles/cm^3) for each mode was calculated as the product of the particle number from the SMPS and the dilution ratio.

The test engine was operated with fuels of different sulfur concentrations to investigate the effects of sulfur content in the diesel fuel on the particle size distributions and number concentrations at upstream and downstream of the DOC or CDPF. Two kinds of the test fuels having 12 and 500 ppm of sulfur by weight were used. Engine operating conditions for the DOC experiment are described in Table 2. The sample gas from which the particle size distribution was measured was diluted by the ambient air temperature about 20℃.

Table 2. Test conditions.

Parameters	Description
Engine type	Single cylinder CRDI diesel engine
Sulfur content (ppm)	12, 500
Equivalence ratio (Φ)	0.3, 0.5, 0.8
Engine speed (rpm)	800, 1500, 2200, 3200
Dilution air temperature (℃)	20, 80, 120, 180
Fuel injection pressure (MPa)	65, 100, 135

3. Results and discussion

3.1 Particle size distributions in the DOC

Fig. 2 shows the size distribution of particles in the exhaust gas of the engine operating at 1500, 2200 or 3200 rpm on ULSD fuel with 12 ppm sulfur. Other operating parameters of the engine are as follows: fuel equivalence ratio of 0.5, fuel injection pressure of 100 MPa, and fuel injection timing for maximum brake torque (5°, 9° and 14° BTDC, respectively, for each speed). The vertical axis dN/dlogDp indicates the particle number concentration, as proposed by Kittelson [3]. Fig. 2 shows a general trend of particle size distribution, in which more particles exist in the engine-out exhaust gas as the engine runs faster. The general shape of the particle size distribution remains similar for exhaust samples taken upstream or downstream of the DOC, except for the result for the exhaust sample taken upstream of the DOC at 1500 rpm. In the last case, great numbers of nano-sized particles, the volatile and semi-volatile materials undergoing gas-to-particle conversion as the exhaust cools and dilutes, are believed to form due to the relatively low exhaust gas temperature associated with the engine speed, but nano-sized particles (hydrocarbon precursors) may be adsorbed and oxidized on the DOC. The exhaust gas temperatures were 280℃, 350℃ and 396℃, respectively, for each speed (1500, 2200, 3200 rpm). In the case of 1500 rpm, PM may have been adsorbed on the DOC surface because of low temperature (280 ℃). In the cases of 2200, 3200 rpm, PM was partly oxidized, but the oxidation performance of PM on the DOC was not impressive at these operating conditions of engine.

Fig. 3 shows the influence of the fuel injection pressure on the particle size distributions. The operating parameters of the engine are as follows: fuel injection timing was set to 9° BTDC, the fuel injection

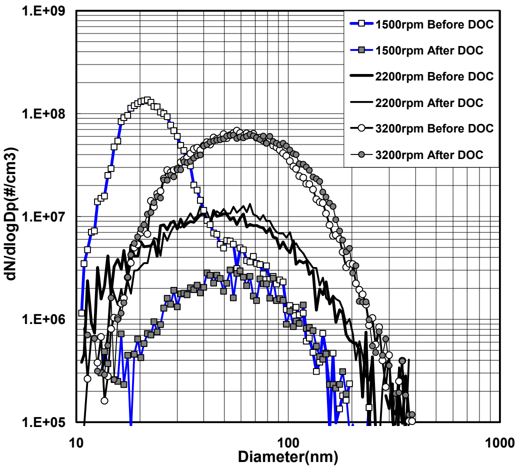

Fig. 2. Size distributions and number concentrations of PM with various engine speeds (Sulfur content = 12 ppm, P_{inj} = 100 MPa, Φ = 0.5).

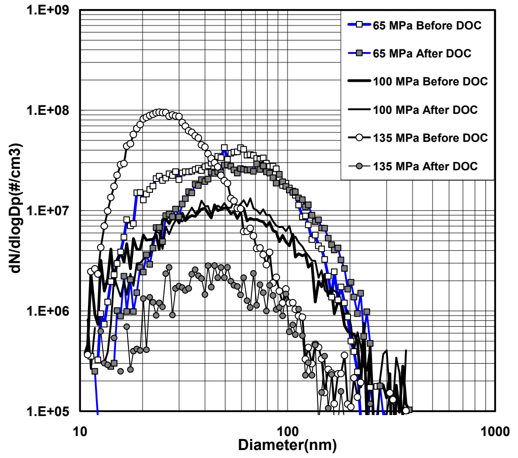

Fig. 3. Size distributions and number concentrations of PM with various fuel injection pressures (Sulfur content = 12 ppm, Engine speed = 2200 rpm, Fuel injection at 9 ° BTDC, Φ = 0.5).

pressures were set to 65, 100, 135 MPa, and the fuel injection durations were 635, 500 and 415 µs, respectively. The exhaust gas temperatures appeared also as 356℃, 375℃ and 321℃ according to the fuel injection pressure. The number of particles in the engine-out exhaust gas tends to decrease as the fuel injection pressure increases from 65 MPa to 100 MPa, but the trend reversed with further increase of the fuel injection pressure (135 MPa). Great numbers of nano-sized particles are observed at the highest pressure condition of 135 MPa [11]. Particulates at downstream of the DOC demonstrate approximately similar shape of distribution curves with less number of particles at higher fuel injection pressures as the nano-sized particles are adsorbed and oxidized on the DOC. High fuel injection pressure of 135 MPa will introduce extra-fine fuel droplets in the engine combustion chamber, and some of these fine fuel droplets can not burn at relatively low engine speed condition. Therefore, the exhaust emission includes relatively many nano-sized PMs.

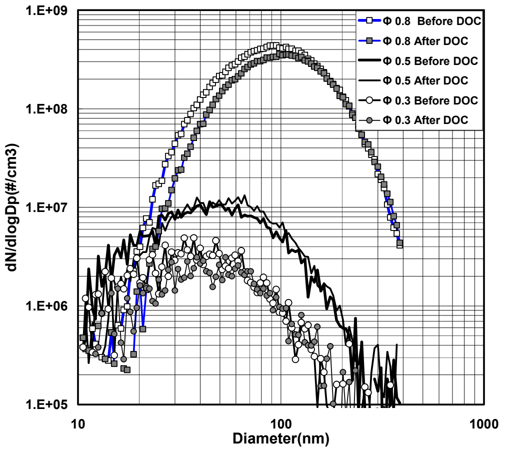

Fig. 4. Size distributions and number concentrations of PM with various equivalence ratios (Sulfur content = 12 ppm, Engine speed = 2200 rpm, P_{inj} = 100 MPa).

Fig. 4 shows the characteristic trend of the PM size distribution as the fuel equivalence ratio varies from 0.3, 0.5 and 0.8. More particles are emitted as the fuel equivalence ratio increases. The peaks of the maximum particle densities appear in different size ranges as the equivalence ratio varies. Namely, most particles are generated in the 30~50 nm, 40~60 nm, and 80~100 nm ranges when the equivalence ratio varies from 0.3 to 0.5 and 0.8. At the equivalence ratio 0.8, the number of particles become very high in the relatively large size range as the engine approaches the smoke limit (full load). But the number of particles of under 20 nm in diameter reduces more than those at the equivalence ratio of 0.3 and 0.5 because of the high exhaust gas temperature (>588℃), so it suppresses the condensation of volatile hydrocarbons into SOF [12].

Fig. 5 compares the size distribution of PM in the engine exhaust gas for fuels of different sulfur contents. The overall shapes of the curves for fuels with different sulfur contents look quite different from each other. In comparison to the ULSD fuel with 12 ppm sulfur, the fuels with 500 ppm sulfur produces an

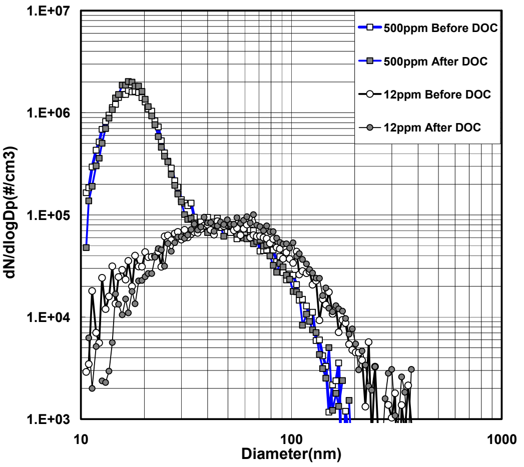

Fig. 5. Size and number distributions of PM for fuels with different sulfur contents (Engine speed = 2200 rpm, Φ = 0.5, P_{inj} = 100 MPa).

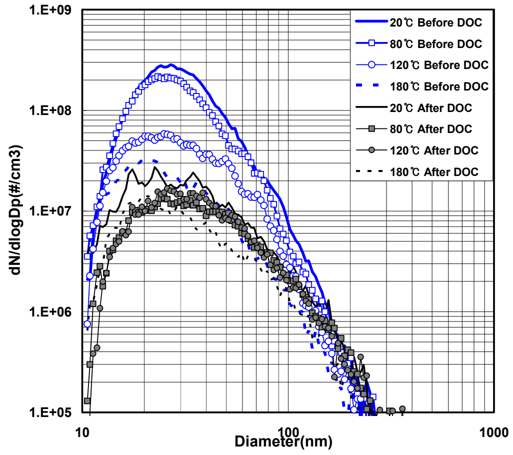

Fig. 6. Size distributions and number concentrations of PM with various temperatures of dilution air (Sulfur content = 12 ppm, Engine speed = 800 rpm, Φ = 0.3, P_{inj} = 65 MPa).

enormous number of 10~30 nm nano-sized particles, presumably due to the condensation of volatile hydrocarbons and sulfates in the engine out emission and sulfates formed on the DOC [12]. The exhaust gas temperature at upstream of the DOC was 350℃. Most of the sulfur in the fuel was oxidized to SO_2, but a small amount (1- 4%) oxidized to SO_3, which rapidly formed sulfuric acid in the presence of water vapor in the exhaust. For the fuel with 500 ppm sulfur, the number of the nano-sized particles increased, probably due to the increased numbers of sulfate and volatile particles. At downstream of the DOC, the number of nano-sized particles reduced in the DOC because of the removal of volatile particles, but sulfate particles increased on the DOC due to the oxidation of SO_2. Hydrocarbon precursors may be destroyed on the DOC, but sulfuric acid will be formed.

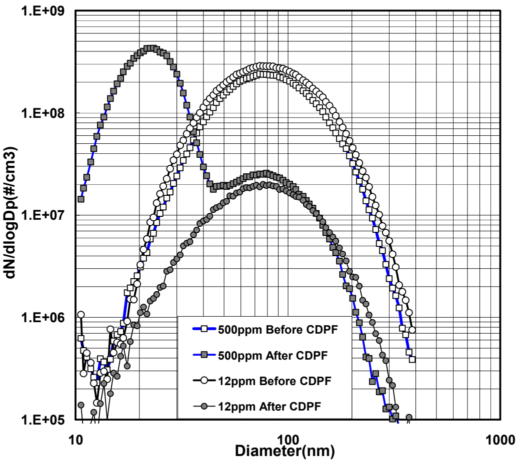

Fig. 7. Size distributions and number concentrations of PM for fuels with different sulfur contents (Engine speed = 2200 rpm, Φ = 0.8, P_{inj} = 135 MPa).

Fig. 6 shows the size distribution of PM emitted by the engine running at 800 rpm at equivalence ratio of 0.3 and fuel injection pressure of 65 MPa. As the dilution air temperature increases, the less number of particles are found in the exhaust gas both at upstream and downstream of the DOC [13, 14]. When the temperature of the diluting air increased, the number of the nano-sized particles decreases in the sample gas due to the reduced condensation of the volatile organic compounds and the moisture in the diluters.

3.2 Particle size distributions in the CDPF

Fig. 7 represents the particle size distribution at the upstream and downstream of CDPF for fuels of different sulfur contents. The data of the CDPF correspond to the result for the continuous regeneration period. The exhaust gas temperature in front of the CDPF ranges from 553℃ to 569℃. With the ULSD fuel with 12 ppm sulfur, the CDPF reduced the number of the particles by 1/10 in all over size distribution. With the engine running on fuel with 500 ppm sulfur, however, the same CDPF significantly increased the number of particles under 40 nm in diameter. These changes in the particle size distributions can be attributed to the more vigorous sulfate formation on the CDPF at high fuel equivalence ratio and exhaust gas temperature environment [8, 15].

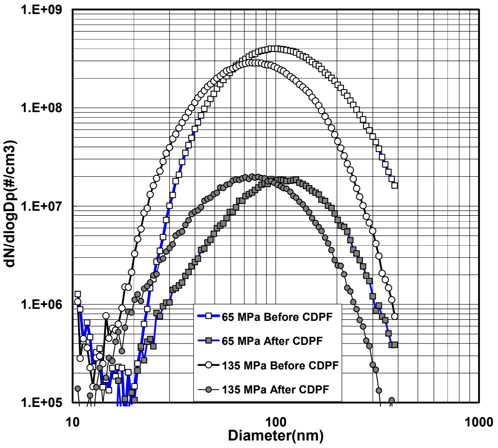

Fig. 8. Size distributions and number concentrations of PM with various fuel injection pressures (Sulfur content = 12 ppm, Engine speed = 2200 rpm, Fuel injection at 5 ° BTDC, $\Phi = 0.8$).

Fig. 8 shows the effect of fuel injection pressure on the particle size distributions at the upstream and downstream of the CDPF. The engine operating conditions are 2200 rpm, equivalence ratio of 0.8, and the ULSD fuel with 12 ppm sulfur. As the fuel injection pressure increases, the number of the nano-sized particles from 10 to 60 nm increases while the number of relatively large particles, over 60 nm in diameter, decreases. The change of the fuel injection pressure does not influence the size distribution of particles under 20 nm in diameter. High pressure fuel injection in diesel engines provides the mixing energy and good spray preparation needed for low PM, but they tend to emit more nano-sized PM. The combination of the ULSD fuel with the CDPF after-treatment system can be an effective method for reducing the concentration of nano-sized PM in the CRDI diesel exhaust gas.

4. Conclusions

A single cylinder diesel engine was used to investigate the characteristics of particle size distribution in the exhaust gas sampled at upstream and downstream of the DOC or/and CDPF as the test conditions were varied. The test engine was run on diesel fuels of different sulfur contents at various speeds and loads. DOC and CDPF in the exhaust stream caused the number of particles under 30 nm in diameter to significantly increase when diesel fuel with 500 ppm sulfur was used, the number of the same particles did not increase so when 12 ppm sulfur diesel was used. When either the engine speed or the equivalence ratio increases, the number of the nucleation mode particles smaller than 50 nm, excluding the volatile and semi-volatile ones formed during the dilution and cooling of the exhaust gas, increased, and more of larger particles tended to come out in the exhaust gas. When the temperature of the diluting air increased, the number of the nano-sized particles decreased in the exhaust gas due to the reduced condensation of the volatile organic compounds and the moisture in the diluters. When the engine ran on fuel with 12 ppm sulfur, the CDPF reduced the number of the particles by 1/10 in all over size distribution. With the engine running on fuel with 500 ppm sulfur, however, the same CDPF significantly increased the number of particles under 40 nm in diameter. As the fuel injection pressure increased, the number of the nano-sized particles of diameter from 10 to 60 nm increased while the number of the relatively large particles decreased. The combination of the ULSD fuel and CDPF-type after-treatment systems can effectively control the concentration of nano-sized particles in the diesel exhaust gas.

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