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CHARACTERIZATION AND MEASUREMENT OF DIESEL NANO-PARTICLES

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ABSTRACT

Thermo-physical behavior of diesel nano-particles under different conditions has been investigated. Stability in measurement was also attempted depending on the characteristics. Quality of the raw exhaust gas, the dilution ratio and temperature, and the thermal conditioning temperature were considered as the main parameters. Exhaust gas from a medium duty DI diesel engine was used for analysis. Scanning Mobility Particle Sizer was used for measuring the concentration of nano-particles. It was concluded that the concentration of nuclei-mode particles within the size range of 15~30 nm are significantly influenced by the thermal conditioning temperature. However the concentration of accumulation mode particles having the diameter of about 100 nm experience no influence. Thermal conditioning of exhaust gas at a temperature of over 300°C is assumed to be sufficient for stabilizing the nano-particles.

Keywords: Nano-particles, Diesel Engine, Exhaust Gas, Dilution Ratio

1. INTRODUCTION

Nano-particles smaller than 50 nm are called as the nuclei-mode particles and particles larger than 100 nm are called as the accumulation mode particles. The accumulation mode particles possess a higher fraction of the total PM mass whereas the mass of nuclei mode particles is negligible. Conventional gravimetric method cannot detect such a negligible mass accurately though there is higher particle number density. Sometimes the measurement fluctuation exceeds the actual mass. Therefore methods alternative to gravimetric one such as counting particle number is gaining more attention recently [5]

It is generally thought that human body reacts significantly to the diesel nano-particles; especially the small size nuclei-mode particles, which are more dangerous than the accumulation mode particles [1]. Figure 1 shows a schematic representation of how nano-particles interact with human respiratory system [2]. Particles larger than 2.5µm can easily be trapped into the upper airways of the respiratory system. But particles smaller than 2.5µm can easily penetrate deep into the lower airways and can cause respiratory diseases, followed by cardiovascular diseases on long time contamination. Because these particles have wider surface area and are thought to be carcinogenic [1]. Therefore modification of the present mass based particulate matter (PM) regulations received much attention globally. However nano-particles are very unstable, especially the physical structure of nuclei mode particles significantly influenced is © ICME2005

circumferential conditions such as temperature, humidity, and the residence time [3~4]. Thereby questioning the feasibility of the nano-particles measurement under these conditions. However, stable measurement of nano-particles with high accuracy is the most important pre-condition for implementation of any regulation.

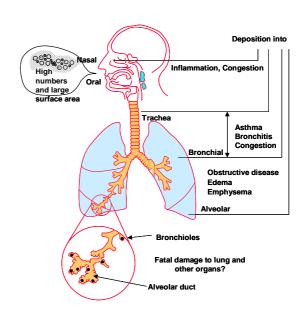


Fig 1. Schematic representation of health effect of nano particles

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As a part of stable measurement of nano-particles the GRPE/PMP has proposed "Thermo-Conditioner" [5]. The thermo-conditioner vaporizes the volatile fractions by re-heating the diluted gas to a certain temperature and cooling down again to room temperature. As a result the measurement fluctuation due to volatile fractions can be avoided. The prime objective of this study is to clarify the effect of thermo-conditioner on nano-particle characteristics under different conditions. Moreover stability in measurement was attempted depending on the characteristics of nano-particles.

2. EXPERIMENTAL SYSTEM AND METHOD

Figure 2 shows the schematic of the experimental system. The engine is a six-cylinder direct injection diesel engine with common rail injection system. Specification of the test engine used in this study is shown in Table 1. Exhaust gas was sampled from three different points; point before the silencer (BS), point before the full dilution tunnel (BDT), and point after the full dilution tunnel (ADT). At the two upstream points such as the point before silencer and the point before dilution tunnel, hot dilutions were performed with a Rotary-Disc Diluter in order to keep the particles concentration within the measurement range of SMPS [4]. But no hot dilution was performed at the point after dilution tunnel as recommended by the GRPE. However as a principal investigating tool Thermo-Conditioner was used at all sampling points.

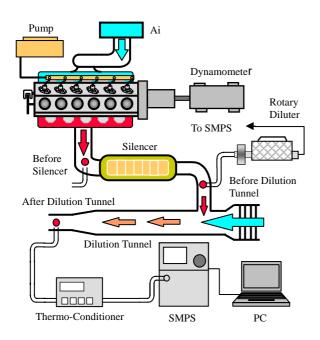


Fig 2. Schematic of the experimental system

Figure 3 shows the rear view photograph of the Thermo-Conditioner. Specification of the ThC used in this study is shown in Table 2. It consists of a main heating tube; temperature of this tube is controllable externally. Sample exhaust gas flows from the right side to left side. The heated sample gas then flows through the heat exchanger for cooling to room temperature which then flows to sensors. The volatile fraction can be

eliminated by heating the diluted gas. However like with hot dilution, the compound remains in the vapor phase upon immediate cooling of the sample to room temperature. The basic principle is described by M. Kasper in detail [6].

SMPS was used for analyzing the particle number concentration. Specification of the SMPS used in this study is shown in Table 3. The engine was operated at three different load conditions depending on the types and concentrations of nano-particles desired. The conditions are mentioned in detail in Table 4. It is confirmed that idling condition can produce a clear bi-modal distribution of nano-particles even when measured at the exhaust manifold [7]. However, at low load condition the exhaust gas is significantly influenced by the cold dilution [8]. Therefore idling and low load conditions have been considered mainly in this study. A low sulfur fuel having the sulfur content of 30 ppm was used. The fuel properties are summarized in Table 5.

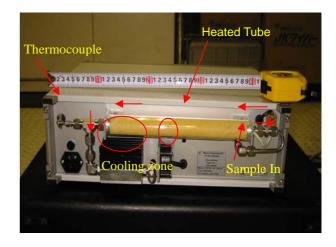


Fig 3. Photograph of the Thermo-Conditioner

Table 1: Specifications of Test Engine

Engine Type	Six Cylinder DI-Diesel
Injection System	Common-rail
Bore x Stroke	114 mm x 130 mm
Swept Volume	7.96 Liter
Cooling system	Water Cooled
Maximum Torque	745 N-m/1600rpm
Maximum Power	191kW/2700rpm

Table 2: Specifications of Thermo-Conditioner

Dimension (mm)	400 x 132 x 448
Flow rate	1 to 5 Liter/min
Heating range	0 to 300°C
Maximum temp	400°C

Table 3: Specifications of SMPS

DMA (Particle separation)
CPC (Counting)
10 to 487 nm
10^2 to 10^7 #/cubic meter
1 Liter/min
4 Liter/min
5 to 40°C

Table 4: Test Conditions

Idling	550 rpm x 0 N-m
Low-load	1200 rpm x 98 N-m
Medium-load	1620 rpm x 460 N-m
High Load	2160 rpm x 600 N-m
ThC Temp. °C	Room, 100, 200, 300, 400
Dilution Ratio	50
Dilution temp. °C	25, 80, 150

Table 5: Fuel Properties

Fuel Type	Diesel
Density @25°C	0.8201 gm/cc
Viscosity @30°C	3.518 mm/s
Distillation point 90%	336.5 °C
Sulfur content	30 ppm

3. RESULTS AND DISCUSSION

3.1 Effect of Sampling Points

Nano-particle number distributions at three different sampling points such as the point before silencer (BS), the point before dilution tunnel (BDT) and the point after dilution tunnel (ADT) for idling condition are shown in Figure 4. At the point before silencer, hot dilution of exhaust gas at 150°C was performed. The engine was operated at idling when both the nuclei and accumulation mode particles are generated. It shows that the distribution trend is almost the same at all sampling points. There is no significant difference in the concentration of accumulation mode particles when the sampling point changes. But the concentration of nuclei mode particles increases when the sampling point shifts to downstream section. Shifting the sampling point to downstream section causes increases in the residence time of exhaust gas in the low temperature dilution air. In the full dilution tunnel both the concentration and temperature of exhaust gas are reduced and the compound passes its dew point. Some volatile fractions and water vapor in exhaust gas condense and nucleates into nano-particles during dilution.

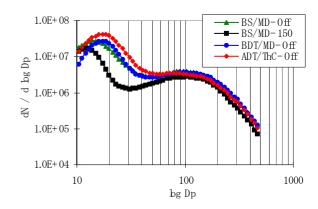


Fig 4. Effect of sampling point on nano-particle number distribution (Idling condition: 550 rpm, 0 N-m)

Comparing the results of with and without hot dilution at the point before silencer it is clear that the concentration of nuclei mode particles within the size range of 15~30 nm are significantly suppressed by hot dilution. Particles at this point may consist of both the solid, semi-volatile and volatile fractions. It is difficult to comment from this results about what type of particles are suppressed by the hot dilution process. To confirm the matter calibration data for each type of particles is necessary. However, the particles formed in the dilution tunnel are characteristically different from the nano-particles. The semi-volatile and volatile fractions may experience some higher effect of hot dilution. A detailed investigation is necessary to confirm the characteristics of both the combustion-generated nano-particles and the nano-particles formed in the dilution tunnel.

Figure 5 shows the particle number distribution at different sampling points for low load condition when both the nuclei mode and accumulation mode particles are generated. It is reported that the dilution process significantly influences the exhaust gas during low load condition [9]. It can be seen from the graph that the concentration of accumulation mode particles does not change when the sampling point and the dilution process change. The results for hot dilution of exhaust gas at 150°C at the points before silencer (BS) and before dilution tunnel (BDT) and thermo-conditioning of exhaust gas at 300°C at the point after dilution tunnel show that there are no significant concentration of nuclei-mode particles within the size range of 15~30 nm. Only the concentration of nuclei mode particles less than 10 nm in diameter increases slightly in the downstream sections and a new peak can be expected in this region. Particles in this region are beyond the measurement limit of SMPS. However, without heat treatment (Hot Dilution and Thermo-Conditioning) a significant number of nuclei-mode particles were detected at the point after dilution tunnel. Therefore it can be assumed that some volatile fractions (HC and H2O) in the exhaust gas condense and nucleate into nano-particles during dilution.

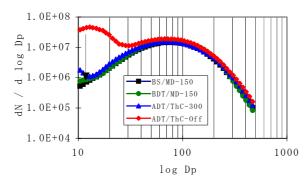


Fig 5. Effect of sampling point on nano-particle number distribution (Low load condition: 1200 rpm, 98 N-m)

3.2 Effect of Thermo-Conditioning

Thermo-conditioning of exhaust gas after dilution is proposed by the GRPE/PMP; therefore variation in the thermo-conditioning temperature logically corresponds to the variation in evaporation condition of the volatile and semi volatile particles condensed during dilution in the full dilution tunnel. However, in this study thermo-conditioner was used before and after dilution in order to investigate it's effect on both the combustion-generated nano-particles and the nano-particles formed in the dilution tunnel.

3.2.1 Before the Silencer

Figure 6 shows the effect of thermo-conditioning temperature on nano-particle number distribution with hot dilution temperature of 150°C. Tests were done with idling operating condition. After exhaust manifold no cold dilution takes place. It means majority of the nuclei-mode particles are combustion generated with some volatile and semi-volatile fractions condensed due to drastic change in temperature across the exhaust valves and up to the sampling point [9]. Moreover as hot dilution is done at 150°C, it is assumed that there is no moisture and most of the volatile particles may be HC having the boiling point sufficiently higher than 150°C. However, specific tests are necessary to confirm the matter.

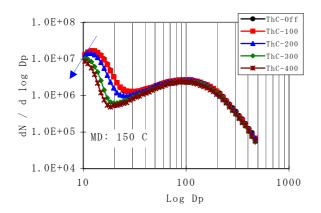


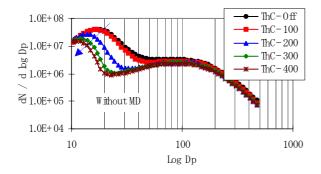
Fig 6. Effect of thermo-conditioning on nano-particle number distribution at a point before silencer with hot dilution at 150°C (Idling condition: 550 rpm, 0 N-m)

The results show that there is no significant effect of thermo-conditioning concentration the on accumulation mode particles. When thermo-conditioning temperature is less than the hot dilution temperature (ThC-Off and ThC-100) there is no change in the concentration of nuclei-mode particles. Thermo-conditioning temperature higher than the hot dilution temperature (ThC-200~300) shows slight decreases in the concentration of nuclei-mode particles. Especially the peak of the nuclei mode particle distribution shifts to the smaller size region. Thermo-conditioning up to 300°C offers significant improvement but further increase in thermo-conditioning temperature does not offer significant improvement. From this result it is concluded that thermo-conditioning at 300°C is sufficient for stabilizing the nano-particles generated during in-cylinder combustion and sudden cooling across the exhaust valve.

3.2.2 After the Dilution Tunnel

Figure 7 shows the effect of thermo-conditioning temperature on nano-particle number distribution at a point after the dilution tunnel. The engine was operated at idling condition. Therefore, nuclei mode particles in this graph include both the combustion-generated particles and the particles formed in the dilution tunnel due to cold dilution. The results show that without thermo-conditioning (black line) thermo-conditioning at 100°C (red concentration of nuclei mode particles within the size range of 15~30 nm is very high. As thermo-conditioning temperature increases, distribution peak shifts to the left and the concentration decreases. However, thermo-conditioning temperature over 300°C shows no more suppression of the nuclei-mode particles. Therefore, thermo-conditioning temperature of 300°C was assumed to be sufficient for stabilizing the nano-particles formed in the dilution tunnel. The concentration of nuclei-mode particles having 10 nm diameters or less does not change. The accumulation mode particles experience no significant influences within this thermo-conditioning temperature range.

The same test was performed at low load condition and the results are shown in Figure 8. It shows that without thermo-conditioning there is significant concentration of nuclei mode particles within the size range of 10~30 nm. However, it is suppressed significantly when thermo-conditioning is done at 100°C. Therefore it is thought that most of the nuclei mode particles in this graph are formed in the dilution tunnel due to condensation of water vapor during cold dilution. Further increases in the thermo-conditioning temperature show decreases in the concentration of nuclei mode particles due to increases in the evaporation of the volatile fractions (HC). However, a detailed chemical analysis is necessary to confirm the assumption. The nuclei mode particles almost disappear and becomes saturated concentration thermo-conditioning temperature of 300°C. Therefore, it is thought that thermo-conditioning can suppress almost all the nuclei mode particles (volatile) formed in the dilution tunnel due to cold dilution.



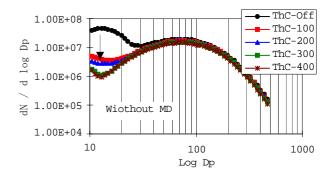


Fig 7. Effect of thermo-conditioning on nano-particle number distribution at a point after full dilution tunnel without hot dilution (Idling condition: 550 rpm, 0 N-m)

Fig 8. Effect of thermo-conditioning on nano-particle at a point after full dilution tunnel without hot dilution (Low Load condition: 1200 rpm, 98 N-m)

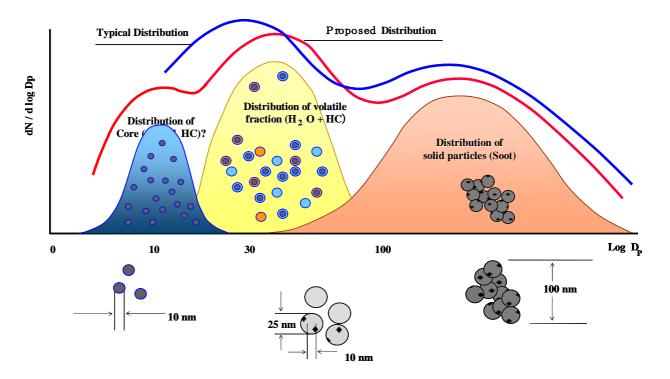


Fig 9. Hypothetical distribution of diesel nano-particles

Comparing Figure 6 and Figure 7, almost similar distribution trend of nano-particles can be seen. It means that hot dilution followed by thermal conditioning of raw exhaust gas (over 300°C) can yield almost similar number distribution of nano-particles like as thermal conditioning of diluted exhaust gas. Therefore sampling of both raw and diluted exhaust gas can be used for thermal conditioning in order to stabilize the nano-particles effectively.

3.3 Classification of Nano-particles

Based on the experimental results diesel nano-particles have been classified into three major groups. These three groups are hypothetically represented in figure 9.

Group-1: D_m = 10 nm (5 nm < D < 20 nm) Particles within the size range of 5~20 nm and a distribution peak at around 10 nm are included in this group. Particles in this group are relatively stable and may not be affected by the thermo-conditioning temperature even up to 400°C. These particles are assumed to be core of nuclei particles, which may be metallic ash, or carbon or heavy HC having the boiling point over 400°C [10].

Group-2: $D_m = 25 \text{ nm} (10 \text{ nm} < D < 50 \text{ nm})$

Particles within the size range of 10~50 nm and a distribution peak at around 25 nm are included in this group. Particles in this group are very unstable and significantly affected by the thermo-conditioning and therefore assumed to be particles, which may or may not consist of a solid core depending on the condition but always consist some volatile fractions. The volatile fractions may be water condensed in the dilution tunnel due to cold dilution and molecular HC having the

boiling point of less than 300°C.

Group-3: $D_m = 75 \text{ nm} (30 \text{ nm} < D < 150 \text{ nm})$

Particles within the size range of 30~150 nm and a distribution peak at around 100 nm are included in this group. Particles in this group are solid particles such as soot or agglomerate of some solid soot. These cannot be affected easily by thermo-conditioning temperature range used in this study.

4. CONCLUSIONS

The potential of thermo-conditioner for stable measurement of nano-particle under different conditions have been investigated and the characteristics of thermo-conditioned particles have been clarified in this study. The following conclusions have been drawn:

- 1. The concentration of nuclei-mode particles within the size range of 15~30nm are significantly influenced by the thermal conditioning temperature while the concentration of accumulation mode particles having the diameter of about 100 nm experience no influence.
- 2. Thermal conditioning of exhaust gas can suppress almost all the volatile and semi-volatile fractions of nano-particles formed during in-cylinder combustion, sudden cooling of exhaust gas across the exhaust valve and during cold dilution in the dilution tunnel. But the effects solid particles are not clear. Thermal conditioning at 300°C is sufficient for stabilizing the nano-particles.

Thermal conditioning of hot diluted and usual cold diluted exhaust gas shows almost similar performance of stabilizing the nano-particles. Therefore sampling from both raw and diluted exhaust gas can be used for thermal conditioning.

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