アイドル時に DI ディーゼル機関から排出されるナノ粒子の熱物理的特性について

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Thermo-physical Behavior of Nano-Particles Emitting from DI Diesel Engine at Idling

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Abstract

Thermal and physical behaviors of diesel nano-particles have been clarified under idling condition when bi-modal distributions of particles are generally seen even at the engine exhaust manifold. The dilution ratio, dilution temperature, and thermal conditioning temperature were considered as the parameters. Stability in measurement was also confirmed depending on the characteristics of nano-particles. 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. The concentration of accumulation mode particles having the diameter of about 100 nm experiences no influence. Thermal conditioning of exhaust gas at a temperature of over 300°C is sufficient for stable measurement. Depending on the characteristics a new hypothetical model for diesel nano-particles has been proposed depending on the characteristics.

Keywords: Nano-particles, Thermo-Conditioner, SMPS, Dilution, DI Diesel Engine

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1. INTRODUCTION

According to the typical diesel nano-particle distribution graph developed by D. B. Kittelson [1, 2], nano-particles smaller than 50 nm are defined as the nuclei-mode particles and particles larger than 100 nm are defined as the accumulation mode particles. The accumulation mode particles possess a higher fraction of the total PM mass whereas the nuclei mode particles possess a negligible fraction. Conventional gravimetric mass measurement method cannot detect such a negligible mass of the nuclei-mode particles accurately though there is higher particle number concentration. Sometimes the measurement fluctuation exceeds the actual mass of nuclei-mode particles [3]. Therefore methods alternative to gravimetric one such as counting particle number is gaining more attention recently [4].

It is generally thought that human body reacts significantly to the diesel nano-particles; especially the small size nuclei-mode particles, which may be more dangerous than the accumulation mode particles [5~7]. Particles larger than 2.5μm can easily be trapped into the upper airways of human 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 [8]. 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 and the number concentration of nuclei mode particles is significantly influenced by the circumferential conditions such as temperature, humidity and the residence time. Thereby questioning is 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.

An initiative by the authorities responsible for emission regulation from a number of European countries resulted the Particle Measurement Program PMP under the auspices of the United Nations UNECE WP29/GRPE. As a part of stable measurement of nano-particles the PMP has proposed “Thermo-Conditioner” [9]. The prime objective of thermo-conditioner is to vaporize 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. However it is a newly developed device and performance of this device is yet to be understood sufficiently for many measuring parameters. Especially the characteristics of thermo-conditioned nano-particles are completely unknown. The prime objective of this study is to clarify the thermo-physical characteristics of nano-particle emitting from DI diesel engines at idling condition when a wide variety of particles are produced. Moreover stability in measurement was attempted depending on the characteristics of nano-particles.

2. EXPERIMENTAL SYSTEM AND METHOD

Figure 1 shows the schematic of the experimental system. The engine is an in-line six-cylinder direct injection diesel engine with high-pressure common rail injection system. Specification of the 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 [10]. But no hot dilution was performed at the point after dilution tunnel as recommended by the PMP. However as a principal investigating tool in this study, Thermo-Conditioner was used at all sampling points.

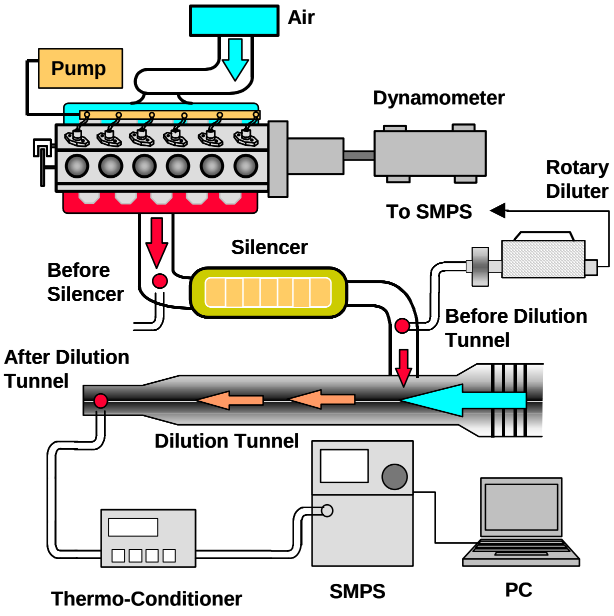

Figure 1: Schematic of the experimental system

Figure 2 shows the schematic of the Thermo-Conditioner (real panel only) used in this study. Specification of the Thermo-Conditioner 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 the left side. The heated sample gas then flows through the heat exchanger for cooling to room temperature which then flows to sensors. Heating of diluted gas results in evaporation of the volatile fractions completely. However the compound remains in the vapor phase even upon immediate cooling of the sample to room temperature. The basic principle of thermo-conditioner is described by M. Kasper in detail [11].

Scanning Mobility Particle Analyzer (SMPS) was used for analyzing the particle number concentration according to their sizes though it can measure the mobility diameter of the particles only by applying some electrical charges on them. Specification of the SMPS used in this study is shown in Table 3. The engine was operated at idling condition (500 rpm and 0 N-m torque, Exhaust gas temperature of 75°C±3 after exhaust manifold). It is confirmed that idling condition can produce a clear bi-modal distribution of nano-particles even when measured at the exhaust manifold [12]. A low sulfur fuel having the sulfur content of 30 ppm was used. The fuel properties are summarized in Table 4.

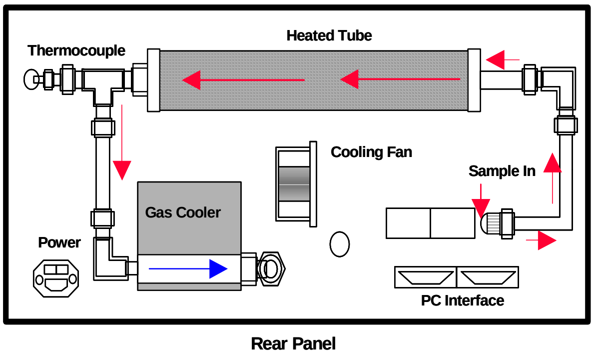

Figure 2: Schematic of the Thermo-Conditioner

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		
Maximum Torque	745 N-m/1600rpm		
Maximum Power	191kW/2700rpm		
Exhaust Emission g/kW-h		Japan ‘98	Test engine
	PM	0.25	0.15*
	NOx	4.50	4.11*

*Results for Japanese D-13 test mode

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 temperature	400°C

Table 3: Specifications of SMPS

Operation mode	DMA (Particle separation) CPC (Counting)
Particles size range	10 to 487 nm
Counting range	10^2 to 10^7 #/cm^3
Sample flow	1 Liter/min
Sheath flow	4 Liter/min
Operating temperature	5 to 40°C

Table 4: 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 3. Shifting the sampling point to downstream section causes increases in the residence time and decreases in the ambient temperature. At the point before silencer, hot dilution of exhaust gas at 150°C was performed. 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.

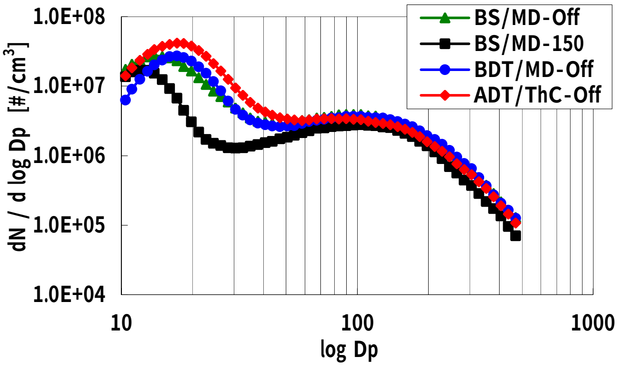

Fig. 3 Effect of sampling point on nano-particle number distribution (Idling: 550 rpm, 0 N-m)

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. Comparing the results of with and without hot dilution at BS, 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 and volatile fractions. It is difficult to comment from this results about what type of particles are suppressed by the hot dilution process.

In order to clarify the effect of temperature on nano-particles, experiments were performed with different exhaust gas temperature at three different sampling points for the same residence time. The results are represented in Figure 4. In order to achieve the required test conditions the engine was initially running at medium load (1620 rpm, 450 N-m) for a certain period of time. Just after achieving the required high exhaust gas temperature, the engine was suddenly triggered to idling condition allowing the exhaust gas temperature to decrease slowly. During this cooling down process seven measurements were performed at each sampling point by SMPS. The temperature variation during this cooling down process is summarized in Table 5.

Table 5: Temperature variation with sampling point and test

Sampling point	Before SL	Before DT	After DT
Test-1	211	90	19.0
Test-2	148	70	17.0
Test-3	108	55	15.5
Test-4	86	48	14.5
Test-5	78	41	13.3
Test-6	75	34	13.0
Test-7	73	32	12.5

Figure 4 shows that there is no significant difference in the distribution of accumulation mode particles when the exhaust gas temperature and residence time change. However the distribution of nucleation mode particles changes significantly with exhaust gas temperature even at a same sampling point. At the points before silencer and before dilution tunnel there were almost mono-modal particle distributions in the first test. However it suddenly changes into bi-modal in the second test with gradual increasing in the peak concentration in the successive tests.

When comparing the results at three different sampling points (combined effect of both exhaust gas temperature and residence time) it was found that a small peak of nucleation mode particles appears at the point after dilution tunnel for the first test, which was not found in the upstream sampling points. This difference in distribution was thought to be due to the difference in the dilution process. Specifically at the tunnel outlet cold dilution of the exhaust gas occurs which is different from the other sampling points where the rotary disk type diluter was used for hot dilution. From this it was concluded that ambient temperature is more influential than the residence time. Once the nucleation occurs at the upstream of the exhaust pipe where a very sharp temperature gradient exists, the particles flow to the low temperature downstream section.

To confirm the total phenomena calibration data for each type of particles (solid and volatile) is necessary. However, the particles formed in the dilution tunnel are characteristically different from the in-cylinder combustion generated nano-particles. 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.

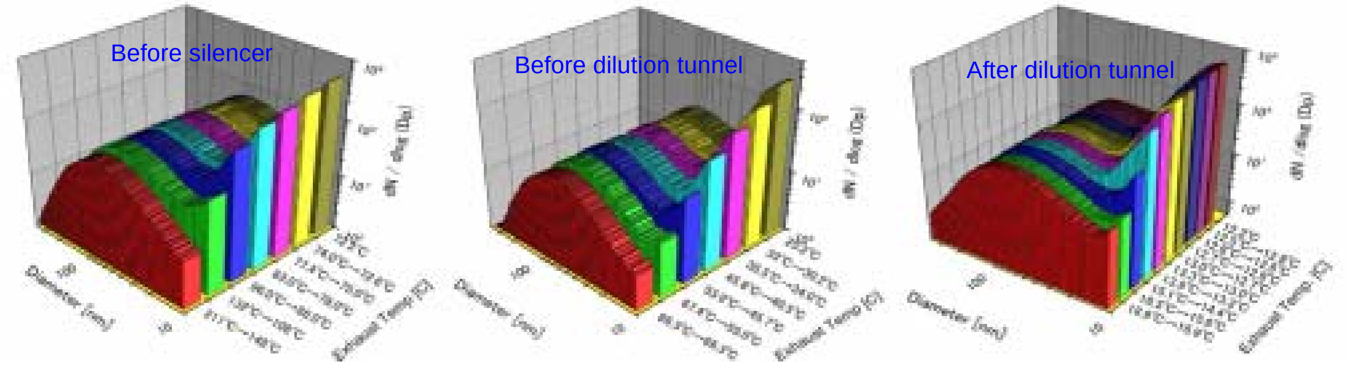

Fig. 4 Influence of exhaust gas temperature on nano-particle distribution

3.2 EFFECT OF HOT DILUTION TEMPERATURE

Nano-particle number distributions at the point BS for different hot dilution temperatures are shown in Figure 5. Dilution temperature was controlled by a rotary-disc type diluter keeping the dilution ratio constant (50). Variation in dilution temperature corresponds to the variation in condensation condition of the volatile fractions in exhaust gas. Tests were done with and without thermal conditioning of exhaust gas.

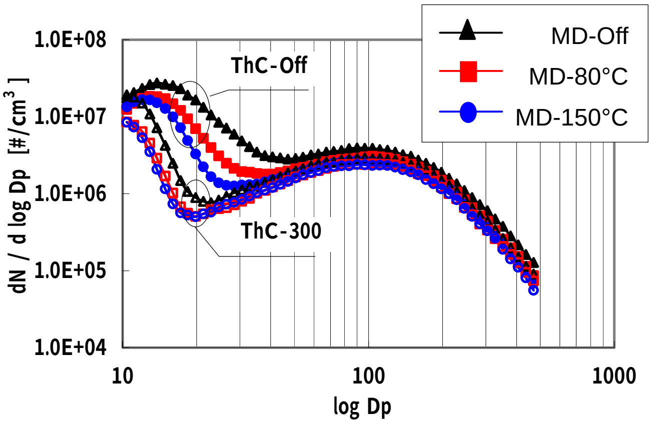

Fig. 5 Effect of dilution temperature on nano-particle number distribution (Idling: 550 rpm, 0 N-m)

The graph shows that hot dilution and thermal conditioning of exhaust gas has insignificant influence on the concentration of accumulation mode particles. Without thermal conditioning (ThC-Off) concentration of nuclei mode particles within the range of 15~30 nm decreases significantly with increases in the hot dilution temperature. When thermal conditioning is done at 300°C (ThC-300) it was found that concentration of nuclei mode particles decreases more but the influence of hot dilution temperature becomes insignificant between the dilution temperatures of 80°C and 150°C. However, concentration of nuclei mode particles of 10 nm in diameter or less does not show significant variations even with hot dilution and or with thermal conditioning.

3.3 EFFECT OF THERMAL CONDITIONING

Thermal conditioning of exhaust gas after dilution is proposed by the PMP; therefore variation in the thermal conditioning temperature logically corresponds to the variation in evaporation condition of the 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.

3.3.1 Before the Silencer

Figure 6 shows the effect of thermal conditioning temperature on nano-particle number distribution with hot dilution temperature of 150°C. After exhaust manifold no cold dilution takes place. It means that majority of the nuclei-mode particles are combustion generated with some volatile fractions condensed due to drastic change in temperature across the exhaust valves and up to the sampling point [13]. 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.

The results show that there is no significant effect of thermal conditioning on the concentration of accumulation mode particles. When the thermal 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. Thermal 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. Thermal conditioning up to 300°C offers significant improvement but further increase in thermal conditioning temperature does not offer significant improvement. From this result it can be 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.

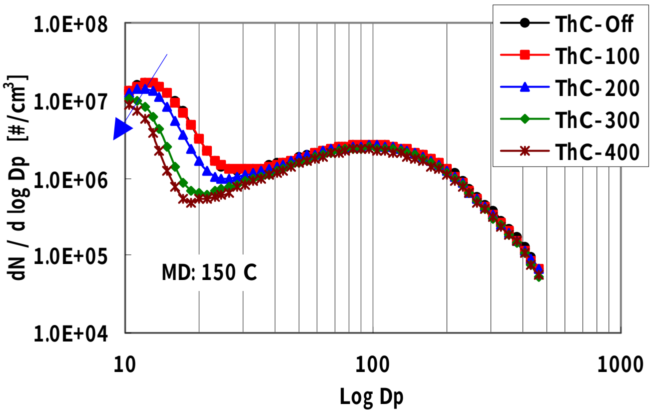

Fig. 6 Effect of thermo-conditioning on nano-particle number distribution at a point before silencer with dilution at 150°C.

3.3.2 After the Dilution Tunnel

Figure 7 shows the effect of thermal conditioning temperature on nano-particle number distribution at a point after the dilution tunnel. The 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 thermal conditioning (black line) and thermal conditioning at 100°C (red line), the concentration of nuclei mode particles within the size range of 15~30 nm is very high. As the thermal conditioning temperature increases, the distribution peak shifts to the left and the concentration decreases. However, thermal conditioning temperature over 300°C shows no more suppression of the nuclei-mode particles. Therefore, thermal 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 thermal conditioning temperature range.

Comparing Figure 5 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.

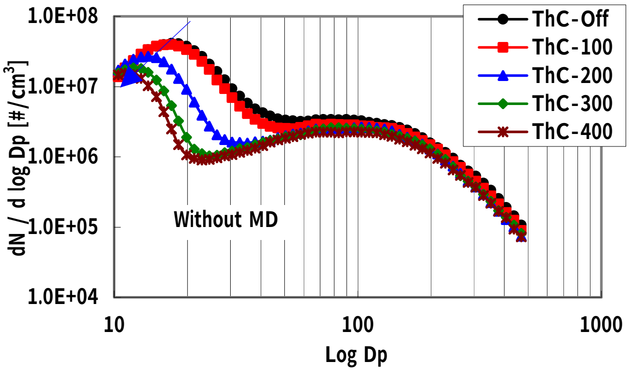

Fig. 7 Effect of thermo-conditioning on nano-particle number distribution at a point after full dilution tunnel without hot dilution (Idling: 550 rpm, 0 N-m)

3.4 GC ANALYSIS

Collection of size-resolved nano-particles emitted from the test engine was attempted by two Electrical Low Pressure Impactors (ELPI). The engine was running at idling condition for total of 10 days at the rate of 7 hours/day. Two ELPIs were used together in order to have sufficient PM mass for GC analysis. An ejector type diluter was used to maintain the sample flow rate and temperature required for ELPI. The chemical compositions of these nano-particles laden on stage-1 and stage-3 were analyzed by gas chromatography (GC).

Figure 8 shows the gas chromatographic results of SOF extracted from the nano-particles laden on 1st and 3rd stages. The basic compositions of SOF included in the accumulation mode particles laden on 3rd stage consist of some unburned hydrocarbon having the carbon number more than 16. The highest spike was appeared near about the carbon number of 20. Similarly, the major compositions of SOF included in the nuclei-mode particles laden in the 1st stage have carbon number higher than the compositions of SOF included in the particles laden in the 3rd stage. From this it can be concluded that the basic compositions of nuclei mode particles have some high boiling point unburned fuel composition having the carbon number higher than 20. The peak was found at about 25. However it is to mention that in the size range of nucleation mode, some solid particles may appear, which can be attributed to metallic ash residues mainly from lubricating oil [14]. Though there is no strong evidence but a motoring test (no firing) performed in the same laboratory shows that about 15% nucleation mode particles appear those can be attributed to lubricating oil.

In case of particles extraction by electrical low-pressure impactor (ELPI), as the particles size becomes smaller, extraction occurs at lower pressures and there is some possibility of evaporation of the low boiling point component. Therefore only some high boiling point component can be detected in chemical analysis. In order to confirm the matter a detail investigation is necessary for different extraction pressures on each stage, which is beyond the scope of this study.

3.5 HYPOTHETICAL MODEL FOR NANO-PARTICLES DISTRIBUTION

Based on the experimental results a hypothetical model for diesel nano-particle distribution has been proposed in this study. According to this model the nano-particles are classified into three major groups. The model is schematically represented in Figure 9.

Group-1: D_m= 10 nm (D < 20 nm)

Particles less than 20 nm in diameter 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 thermal 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.

Group-2: D_m= 25 nm (10 nm < D < 50 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 thermal conditioning and therefore assumed to be particles, which may or may not consist of a solid core depending on the condition but always consists 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 nm (30 nm < D < 150 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.

The three groups of particles proposed in this hypothetical model basically do not contradict with the typical bi-modal distribution of diesel nano-particles. The second group has a tendency to merge with the first group or third group depending on the heat treatment and residence time and shows a bi-modal distribution when measured by conventional CPC or Electrometer. Therefore measurement of only 10 nm and 75 nm particles instead of measuring all the particles can give information about almost all the nano-particles. As a result only a simple instrument with two channels should suffice the nano-particles measurement instead of the costly and complicated multi-channel instruments.

4. CONCLUSIONS

The thermo-physical properties of diesel nano-particles have been investigated and the potential of thermo-conditioner for stable measurement of nano-particle under different conditions 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 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 on solid particles are not clear. Thermal conditioning at 300°C is sufficient for stabilizing the nano-particles.
3. The accumulation mode particles consist of some unburned hydrocarbon having the carbon number more than 16. The highest spike was appeared near about the carbon number of 20. Similarly, the basic compositions of nuclei mode particles have some high boiling point unburned fuel composition having the carbon number higher than 20. The peak was found at about 25.
4. A new hypothetical size distribution model for diesel nano-particles has been proposed depending on the thermo-physical characteristics found in this study.

5. REFERENCES

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6. **ABBREVIATIONS**

MD: Rotary Disc-type diluter temperature
ThC: Thermo-conditioner
HC: Hydrocarbon
PM: Particulate matter
CPC: Condensed Particle Counter
SOF: Soluble Organic Fraction
GC: Gas Chromatograph
ELPI: Electrical Low Pressure Impactor

7. **DEFINATIONS**

Hot Dilution: Dilution of the exhaust gas at a temperature higher than the ambient.
Cold Dilution: Dilution of the exhaust gas at ambient temperature or less.
Thermo-Conditioner: Device used for conditioning of exhaust gas.

PM Deposition on 1st stage of ELPI

(50% Cut off dia. 30 nm)

PM Deposition on 3rd stage of ELPI

(50% Cut off dia. 110 nm)

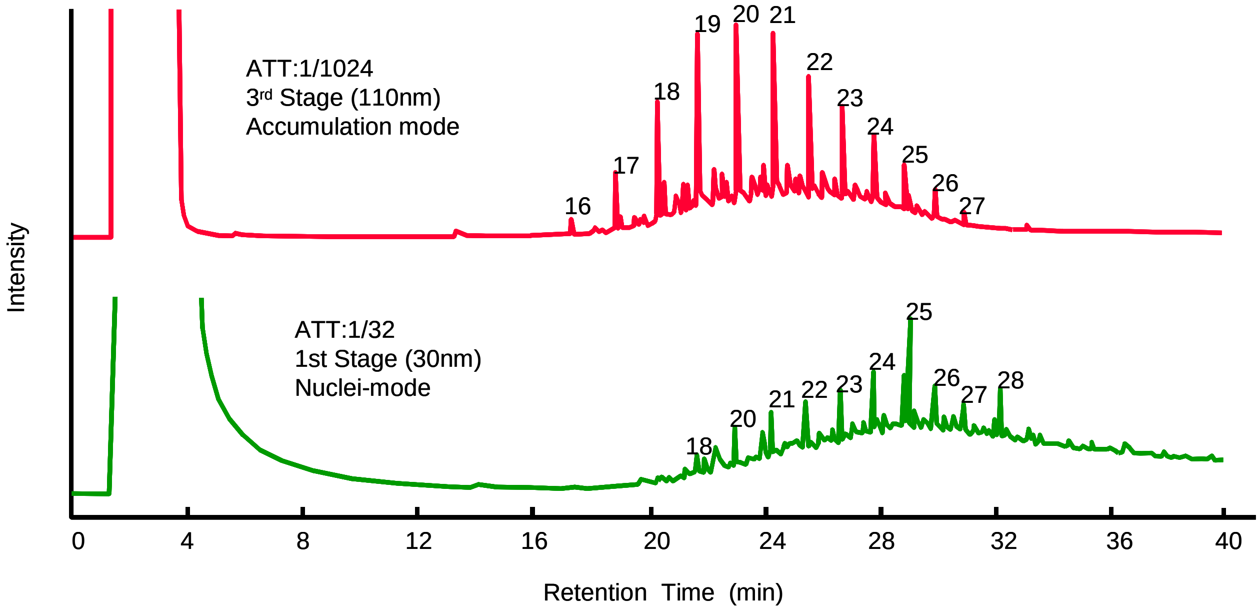

Figure 8: Results of GC Analysis of Size-Resolved Nano-particles

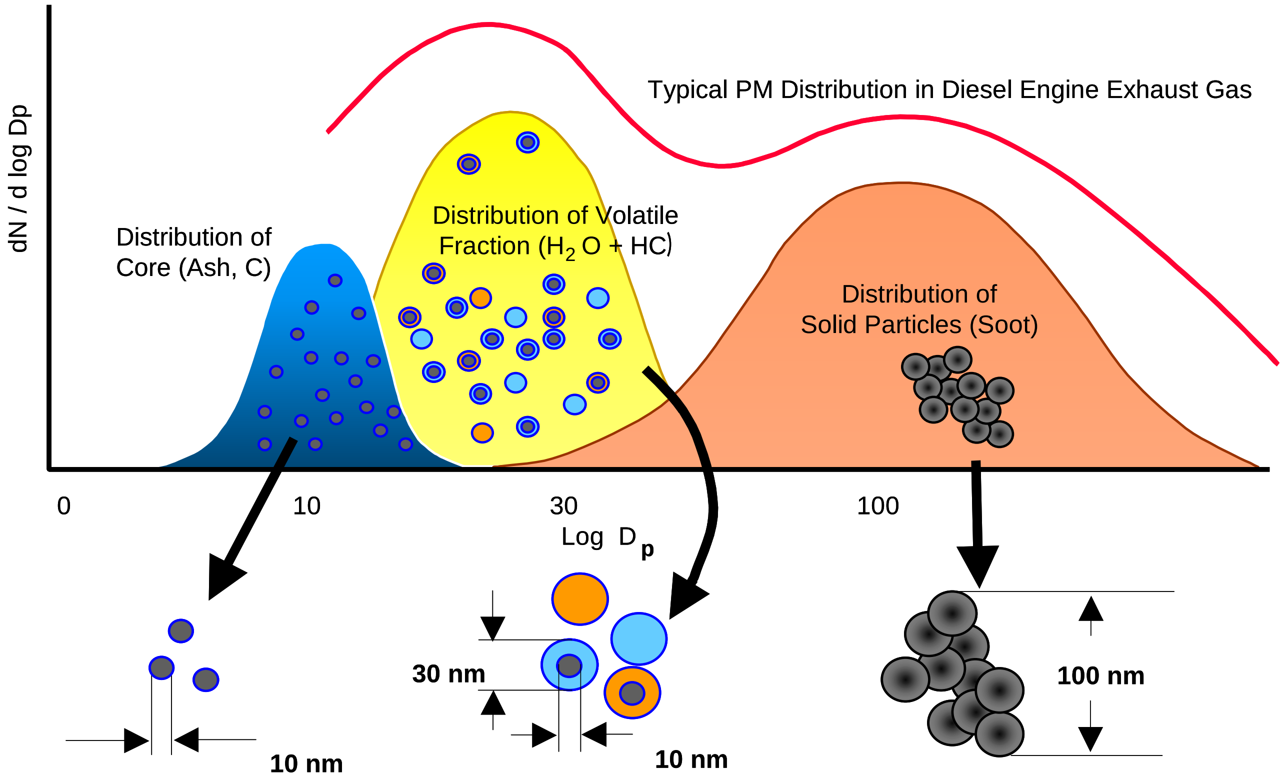

Figure 9: Hypothetical Model for Diesel Nano-particles Distribution