Generation of Model Diesel Particles by Spark Discharge and Hydrocarbon Condensation

Hakjoon Kim*
Environmental System Research Center, Environmental and Energy Research Div., KIMM, 171 Jang-dong, Yuseong gu, Daejeon 305-343, Korea
Jinho Kim, Youngjoo Choi, Hyenchul Oh, Jungbum Chu, Sangsoo Kim
Aerosol and Particle Technology Laboratory, ME3061 Department of M. E., KAIST, Guseong dong, Yuseong gu, Daejeon 305-701, Korea

This study was conducted in order to generate model particles which were similar to particles in diesel emission. Spark discharge was used for carbon agglomerates and hydrocarbon condensation for particles that consist of carbon agglomerates and hydrocarbon. The size of the carbon agglomerates, whose mean size were 30 and 70 nm, ranged between 15 and 200 nm, and the total number concentration of the particles ranged from 3 to 5×10^7#/cm^3 as the controllable variables in spark discharge generator changed. The result of the hydrocarbon condensation experiment showed that the final sizes of the particles enlarged by condensation did not depend on the initial sizes, but the maximum condensational growth of carbon agglomerates by dodecane ($C_{12}H_{26}$) condensation was 112 times the initial size of 40 nm, while the size of the agglomerates by benzene (C_6H_6) was 3.25 times its initial size.

Key Words : Model Diesel Particles, Spark Discharge, Carbon Agglomerates, Hydrocarbon, Condensation, Benzene, Dodecane

Nomenclature

NC : Number concentration
TNC : Total number concentration
GSD : Geometrical standard deviation
DC : Direct current
RC : Resistor-capacitor

1. Introduction

Currently, diesel vehicles are growing in popularity in the world due to their higher fuel efficiency and reduced CO_2 emissions compared to gasoline vehicles. However, the regulations on emissions are becoming stricter because of the harmful effects of diesel exhaust on the environment and human health as well. Diesel particles are of particular concern among diesel exhaust because they cause serious respiratory diseases.

In a typical size distribution of diesel particles, most of the large particles which are included in the accumulation mode are the diesel soot particles while small particles in the nucleation mode are liquid phase particles (Walker, 2004). The former consist of carbon soot particles that various hydrocarbons condense on (Kittelson, 1997), but the latter is mainly composed of hydrocarbons (Tobias et al., 2001). With increasing concerns and studies about the diesel particles, a simple method of model particle generation to mimic diesel particles without elaborate engine set up in laboratories is necessary for several studies, such as experiments on particle removal, human health, and filter traps.

Many researchers have researched the generation of the carbon particles. Hogan (1985) sus-

* Corresponding Author,
E-mail : diayolk@kimm.re.kr
TEL : +82-42-868-7775; **FAX** : +82-42-868-7284
Environmental System Research Center, Environmental and Energy Research Div., KIMM, 171 Jang-dong, Yuseong gu, Daejeon 305-343, Korea. (Manuscript **Received** March 15, 2006; **Revised** August 21, 2006)

pended India ink particles in distilled water to generate carbon particles. Prenni et al. (2000) used a fluidized bed generator to generate carbon particles whose count mean diameters were 0.1 to 0.3 micronmeter, and the TNC was more than 10^5#/cm^3. Furthermore, Sunderland (Sunderland and Faeth, 1996) generated soot particle by using hydrocarbon and an air diffusion flame to understand soot formation. However, it is difficult for these generation methods to control the size and NC of the particles.

As a simple and easily controllable method, we used a spark discharge method for carbon particle generation and produced model particles of diesel particles by condensation with hydrocarbon on the carbon particles.

The condensation with hydrocarbons on carbon particles is the growth mechanism of diesel particles in diesel exhaust pipes. In generating the model particles, we also investigate condensational characteristics of carbon particles during the condensation process with different hydrocarbons. This study will help us understand how different hydrocarbons affect the growth of carbon particles.

2. Experiments

2.1 Generation of carbon particles

Figure 1 shows the schematic diagram of a spark discharge generator of carbon particles. This generator produces particles using the heat from sparks when electrical energy is discharged sporadically between two carbon electrodes (Schwyn et al., 1988). The electrical energy is stored in a capacitor in an RC circuit, and then the energy is discharged between the electrodes with a periodic frequency when the energy reaches the energy storage limit. This charge and discharge continue with sparks. Heat from the sparks evaporates part of the carbon electrodes, and the vaporized carbons are cooled by N_2 gas.

Due to the rapid cooling by N_2, carbon vapors become carbon particles, which are shown in Fig 1, after the vapors undergo nucleation, condensation, and coagulation processes.

Carbon rods (99% purity) with a 6.3 mm diameter were used, and a micrometer was connected to the rods to change the distance between them. At top and bottom sides of the generator, acrylic windows which were inserted to monitor spark frequency, were connected with PMT (Photomultiplier, PDS-1, DongWoo Opron Inc, Kor) and Ocilloscope (Dual digital oscilloscope, MDL-9400, Lecroy). As a carrier gas, N_2 gas was used to make sure no chemical reaction with carbon vapors. In the RC circuit, a 500 kΩ resistance, a 0.0025 μF capacitor, and a high voltage power supply (KSC 1303, Korea switching Inc, Kor) were used to generate stable sparks.

Fig. 2 shows the schematic diagram for the experiment of carbon particle generation.The physical characteristics of the carbon particles from spark discharge, such as size and NC, were controlled by the spark frequency, the flow rates of carrier gas, and clean air (Helsper and Mölter, 1993). Furthermore, the spark frequency was also changed by the distance between the two carbon

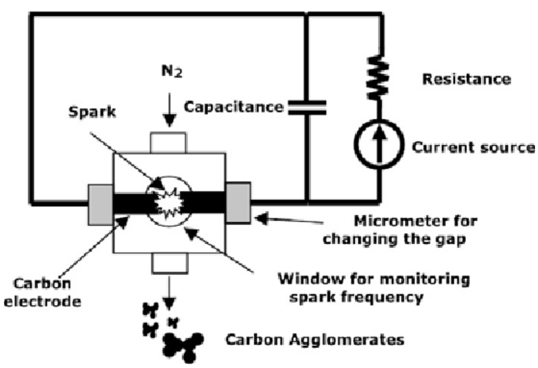


Fig. 1 Schematic diagram of a spark discharge generator

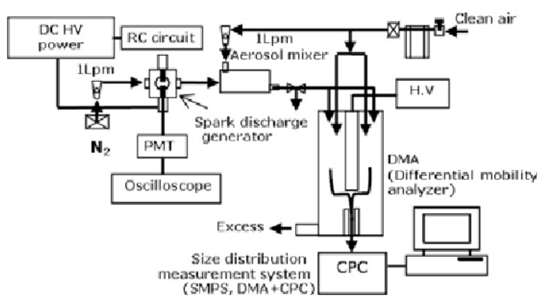


Fig. 2 Experimental set up for the generation of carbon agglomerates by spark discharge

rods, current of the DC power supply, and capacity of the capacitor (Horvath and Gangl, 2003).

To keep constant flow rates in the measurement equipments, the rod distance and the current of the power supply were varied to control the amount of carbon vapor.

As shown in Fig. 2, 1 lpm N_2 gas constantly flowed into the generator. The breakdown voltages that were necessary for stable sparks between the two carbon rods at specific distances were decided by changing voltage and current of the DC power supply in the current source. When the rod distances were 0.5, 1 and 2 mm, the voltages for the stable sparks were decided, respectively, and then at the voltages, the current of DC power supply increased for faster spark frequencies. To prevent further coagulation among carbon particles, the clean air of 1 lpm was mixed with the carbon particles in a mixer and the changes in size distributions of carbon particles were measured with SMPS (Scanning Mobility Particle Sizer, DMA (Differential Mobility Analyzers, TSI model 3071, USA) and CPC (Condensation Particle Counter, TSI model 3022A)) in changing the rod distances and frequencies. The carbon particles were sampled on a 300 mesh copper carbon TEM grid (Electron Microscopy Sciences, USA) in a thermophoresis sampler for SEM analysis.

2.2 Generation of model particles

2.2.1 Experimental apparatuses for condensation

The electrical heating plate in the heater described in Fig. 3 evaporated hydrocarbons, and a temperature controller (TZ4ST, Autonics Inc, Kor) was used to produce the constant amount of hydrocarbon vapors.

Carbon particles and hydrocarbon vapors moved through a tube in a cooler, which was made of stainless steel (Fig. 4), where condensation with hydrocarbons on carbon particles took place. It was cooled by four thermoelectic modules (Ace Tech Inc, Kor) and four electrical fans. A thermocouple inserted to the inside of cooler was connected to a 16 channel thermo couple monitor

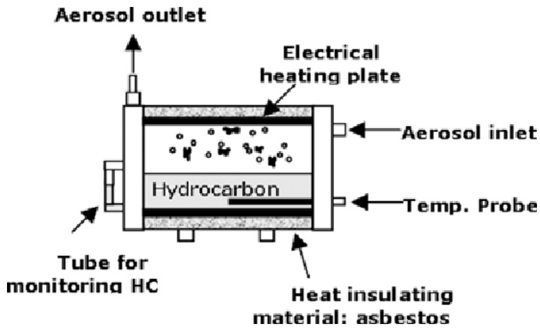


Fig. 3 Electrical heater for evaporating hydrocarbons

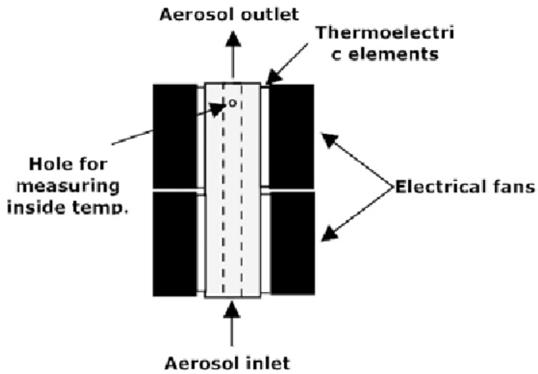


Fig. 4 Electrical cooler for condensation

(Model SR630, Stanford research system Inc, USA) to measure the temperature of the flow inside the cooler.

2.2.2 Condensational growth of carbon particles

Fig. 5 shows the experimental setup for the condensation of carbon particles by hydrocarbons. The carbon particles from the spark discharge generator were mixed with clean air at the ratio of 1 to 1 lpm. The first DMA (Differential Mobility Analyzer, TSI model 3071, USA) classified carbon particles to monodisperse particles in order to investigate the initial size effect of the carbon particles on condensational growth.

The particles that had specific sizes, such as 40 and 80 nm, passed through the heater, where hydrocarbons evaporated, and the cooler, in which the condensation of the particles with hydrocarbons took place, and then they moved into size measurement devices.

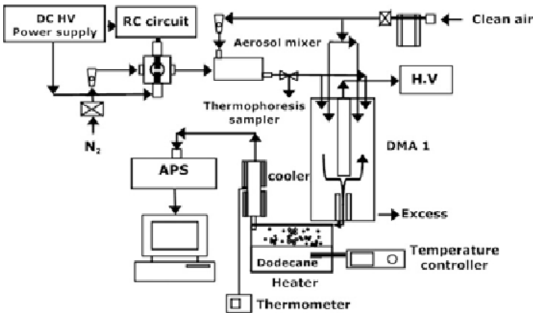


Fig. 5 Experimental set up for the condensation of carbon agglomerates by hydrocarbons

To understand influences by different hydrocarbons on the condensational growth, two hydrocarbons, benzene (C_6H_6) and dodecane ($C_{12}H_{16}$), were chosen. These two hydrocarbons are from diesel exhaust, and benzene is included in C1-C6, which are high during the cold start of a diesel engine (Raihan et al., 2001), and dodecane is an alkane contributing to most of diesel nano particle mass and is included in C10-C25, which are rich in diesel fuel (Tobias et al., 2001). We used an APS (Aerodynamic particle sizer, Model 3321, TSI, USA) and SMPS for size distribution measurement after the condensation. The reason for using two different measurement devices, APS for dodecane and SMPS for benzene, was that the size growth by condensation was much different according to the kind of hydrocarbon.

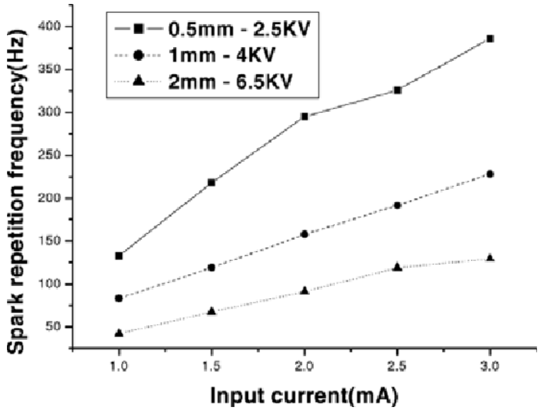


Fig. 6 Conditions of parameters in the spark discharge generator

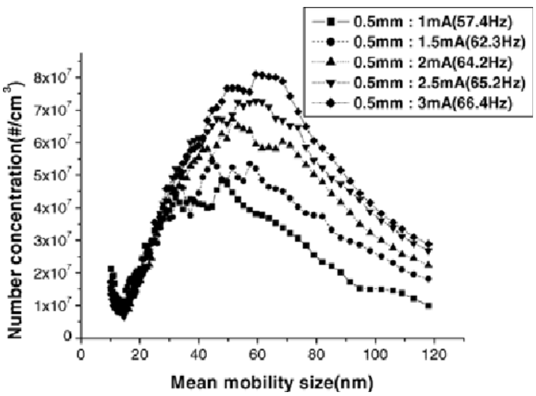


Fig. 7 Changes in size distribution by spark repetition frequencies

3. Result and Discussion

3.1 Carbon particle generation

Several experiments were conducted at different carbon rod distances and spark frequencies to understand their effects on the physical characteristics of carbon particles from the spark discharge generator.

Fig. 6 describes how distances between two carbon electrodes and current of the DC power supply affect spark frequencies in the generator. At rod distances such as 0.5, 1 and 2 mm, the voltages of the DC power supply for stable sparks were 2.5, 4 and 6.5 KV, respectively. The spark frequency increased from 42.22 to 386 Hz as the rod distance is increased and the current is increased. As shown in Fig. 7, the peak size of the particles increased, and the size distribution became broader as spark frequency increased.

At a constant distance, increasing frequency contributed to an increase in the amount of carbon vapor from the carbon rods, so the increased vapor made more particles and induced more collisions between particles. This resulted in a size increase of the particles, and, in all three cases at different rod distances, the trend of graph was the same as in Fig. 7. The particle size ranged from a 15 to 200 nanometers.

Additional results of carbon particle generation are shown in Figs. 8 and 9. As the rod distances and spark frequencies increased, the mean sizes and TNC of the carbon particles increased. This

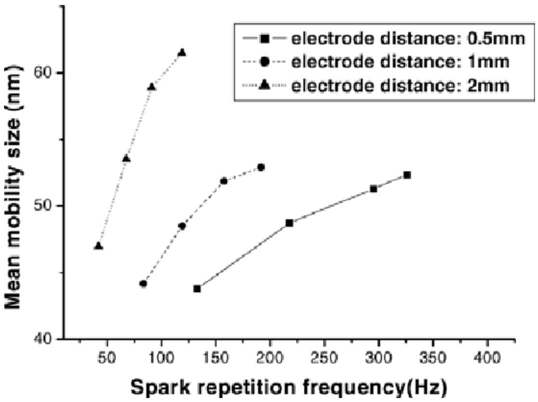


Fig. 8 Changes in mean size by spark repetition frequencies & rod distances

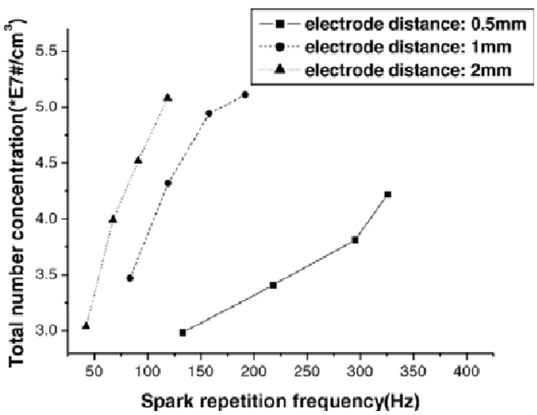
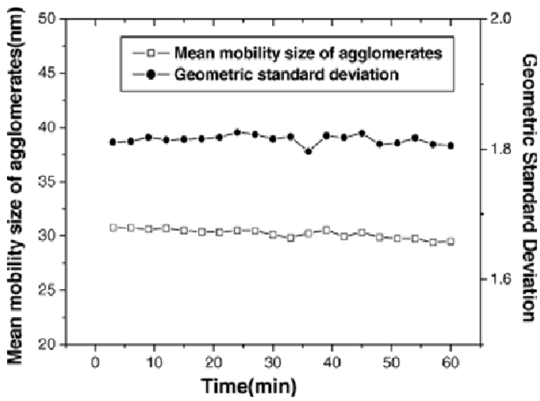
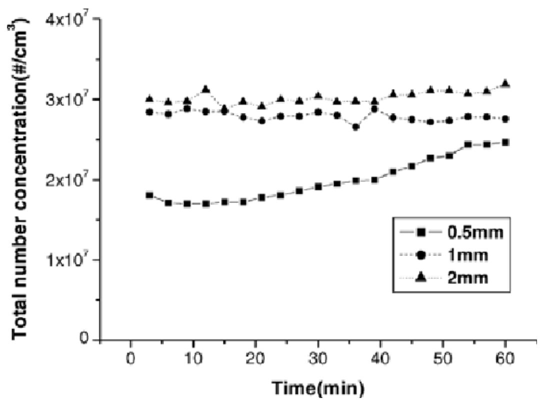


Fig. 9 Changes in TNC by spark repetition frequencies & rod distances



(a) Distance: 1 mm, Input voltage/current: 4 KV/1 mA (Mean mobility size, GSD)



(b) TNCs of three cases (0.5, 1, and 2 mm with 1 mA input current)

Fig. 10 Stability of the generator for one hour

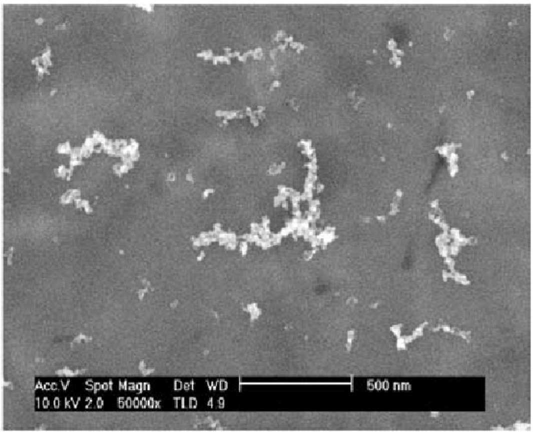
increase resulted from an increase in the amount of carbon vapor from sparks, and in Figs. 8 and 9, widening the rod distances also tended to increase the mean sizes and TNCs. Since the voltage to generate stable sparks increased as the rod distance became wider, the discharged electrical energy also increased. This was attributable to the increase in the mean sizes and TNCs.

The mean sizes of the carbon particles ranged from about 30 to 70 nm, and the TNC was 3–5 $\times 10^7$#/cm^3. The mean diameters were similar to the mean diameter (60–100 nm) of diesel carbon particles (Burtscher, 2005). The results showed that the mean size and TNC from the spark discharge generator could be adjusted to mimic particles in diesel emissions by controlling the rod distances and spark frequencies.

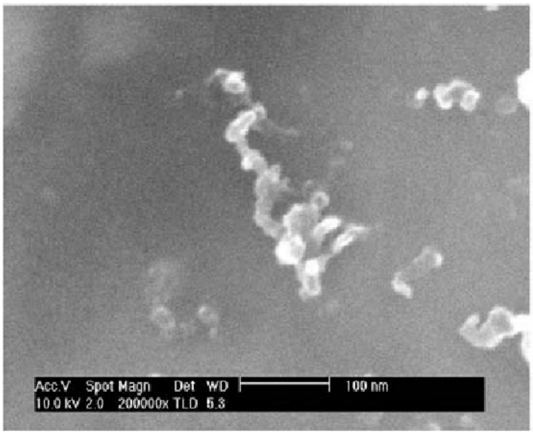
The result of the stability test of the generator for one hour is shown in Fig. 10. With 1 mA current, the mean sizes, geometric standard deviation, and TNC of the carbon particles remained constant for one hour, and the most stable generation was achieved at a 1 mm of rod distance and a 1 mA of current.

This result indicated that at least for one hour the generator could produce carbon particles which had constant physical characteristics.

Fig. 11 shows the SEM images of the carbon particles from the spark discharge generator. All particles were grape-like carbon agglomerates, and this result was also confirmed by the fact that the geometry and sizes of carbon particles from spark discharge were similar to diesel soot par-



(a) 50000X



(b) 200000X

Fig. 11 SEM images of carbon particles with different magnifications

ticles from combustion (Evans et al., 0000).

3.2 Generation of model diesel particle

To generate carbon particles that were surrounded by hydrocarbons, condensation with hydrocarbons on carbon particles was used. It is necessary to understand the effect of the amount of hydrocarbon vapor and the kinds of hydrocarbons on the condensational growth of carbon particles. Fig. 12 shows changes in size distributions of 40 nm carbon particles after condensation with benzene heated at different temperatures. As the heating temperature increased from 45℃ to 60℃, which meant that amount of benzene vapor increased, the size distributions after the condensation moved to a larger size range. This was due to the size increase by condensation with benzene vapor on the carbon particles.

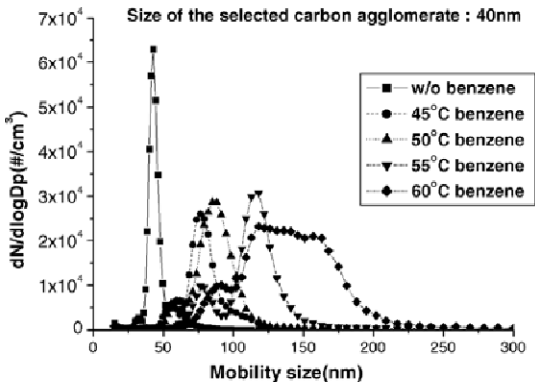


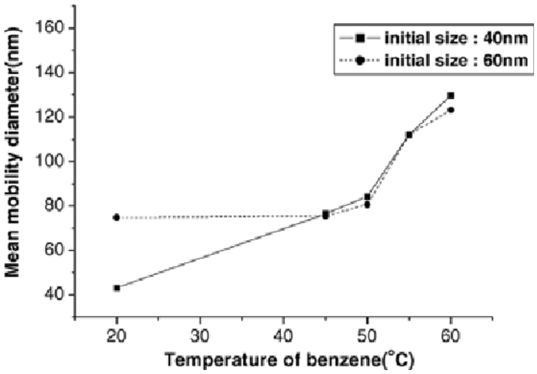
Fig. 12 Changes in size distributions by the heating temperatures of benzene after condensation

It was expected that most of evaporated benzene was eliminated by a wall loss because theoretical ratios of concentrations of benzene that was used for particle growth to those of benzene that was vaporized in the evaporator were 2.2×10^{-4}, 1.63×10^{-3}, 9.06×10^{-3} and 1.1×10^{-2}.

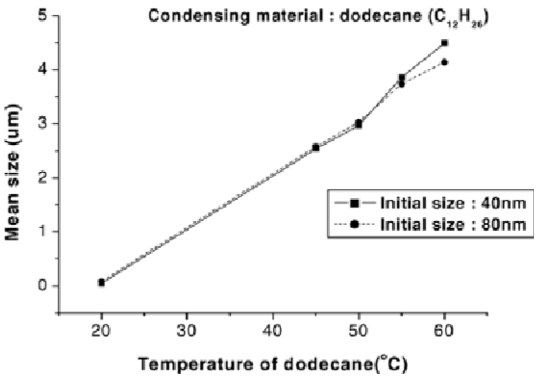
The results of condensational growth by different hydrocarbons and with different initial sizes were described in Fig. 13. Regardless of the initial sizes of carbon particles, the final sizes of particles after condensation were the same. Since the rate of droplet growth depends on the droplet size, which means smaller particles grow faster than larger particles, theoretically, the particles whose sizes are initially different could grow to nearly monodisperse droplet sizes (Heidenreich and Ebert, 1995).

However, the maximum size increase after condensation with different hydrocarbons, such as benzene and dodecane, differed significantly. Compared to the a) and b) graphs in Fig 13, the maximum size increase with benzene was about three times that of the initial size, 40 nm, while that with dodecane was approximately 100 times.

This was the reason that SMPS (measurement size range: 10–359 nm) for benzene and APS (measurement size range: 0.5–20 μm) for dodecane were used to measure size distributions after the condensation. Since the rate of condensation-



(a) In the case of benzene



(b) In the case of dodecane

Fig. 13 Changes in size distributions by the temperature of different hydrocarbons after condensation

al growth is very sensitive to the supersaturation ratio (Brown, 1981), the maximum increase is highly affected by vapor pressure in the cooler when the hydrocarbons are cooled down.

When the temperature of the two hydrocarbons decreases from 60℃ to 15℃, the supersaturation ratio of dodecane is 28.9, and that of benzene is only 6.7. Therefore, the size increase of carbon particles by condensation with dodecane was larger than that with benzene.

4. Conclusion

Summarizing the results of the experiments, the following conclusions can be drawn ;

(1) The size of the carbon agglomerates, whose mean sizes were 30 to 70 nm, ranged between a 15 and 200, and the TNCs of the particles were in the range of 3-5$\times 10^7$#/cm^3 as the controllable variables in the spark discharge generator changed.

(2) SEM images showed that their primary particles were a few tens, and their physical sizes and shapes were the same as those of the diesel soot particles

(3) In the case of the condensation with benzene, the final particles after carbon agglomerates grew by a few times and could be similar particles to diesel particulate matter, which has carbon particles and hydrocarbon around it.

(4) In the case with dodecane, the final particles after carbon agglomerates were enlarged by more than 100 times, were hydrocarbon particles, which were composed of dodecanes whose volume fraction in a particle was 10^6.

These particles were mostly liquid phase particles that were similar to diesel nano particles that consist of liquid phase hydrocarbons.

Therefore, with spark discharge and hydrocarbon condensation, we can produce model particles that have similar characteristics of particles in diesel emissions without engine setup.

Acknowledgements

This study was supported by the Ministry of Commerce, Industry and Energy.

References

Anthony J. Prenni, Ronald L. Siefert, Timothy B. Onasch, Margaret A. Tolbert and Paul J. DeMott, 2000, "Design and Characterization of a Fluidized bed Aerosol Generator : A Source for Dry, Submicrometer Aerosol," *Aerosol Science and Technology*, Vol. 32, pp. 465～481.

Burtscher, H., 2005, "Physical Characterization of Particulate Emissions from Diesel Engines : a Review," *J. Aerosol Sci*., Vol. 36, No. 7, pp. 896～932.

David B. Kittelson, 1997, "Engine and Nanoparticles : A Review," *J. Aerosol Sci*., Vol. 29, No. 5/6, pp. 575～588.

Douglas E. Evans, Roy M. Harrison and Jon G. Ayres, 0000, "The Generation and Characterization of Elemental Carbon Aerosols for Human Challenge Studies," *J. Aerosol Sci*., Vol. 34, No. 8, pp. 1023～1041.

Heidenreich, S. and Ebert, R., 1995, "Condensational Droplet Growth as a Preconditioning Technique for the Separation of Submicron Particles from Gases," *Chemical Engineering and Processing*, Vol. 34, pp. 235～244.

Helsper, C. and Mölter, W., 1993, "Investigations of a New Aerosol Generator for the Production of Carbon Aggregate Particles," *Atmospheric Environment*, Vol. 27 (A), No. 8, pp. 1271～1275.

Herbert J. Tobias, Derer E. Beving and Paul J. Ziemann, 2001, "Chemical analysis of Diesel Engine Nanoparticles Using a Nano-DMA/Thermal Desorption Particle Beam Mass Spectrometer," *Environ. Sci. Technol*, Vol. 35, No. 11, pp. 2233～2243.

Hogan, A., Ahmed, N., Black, J. and Barnard, S., 1985, "Some Physical Properties of a Black Aerosol," *Journal of Aerosol Science*, Vol. 16, pp. 391～397.

Horvath, H. and Gangl, M., 2003, "A Low-Voltage Spark Generator for Production of Carbon Particles," *J. Aerosol Sci*., Vol. 34, No. 11, pp. 1581～1588.

James T. Brown, Jr., 1981, "Condensational Enlargement as a Supp. Lement to Particle Control Technologies," *Environmental International*, Vol. 6, pp. 365～369.

Khandoker Abu Raihan, Fumito Takimoto, Hideyuki Ogawa and Noboru Miyamoto, 2001, "Time-resolved Behavior of Unburned Hydrocarbon Components in Diesel Exhaust Under Transient Operations," *SAE Paper*, 2001-01-1259.

Schwyn, S., Garwin, E. and Schmidt-ott, A., 1988, "Aerosol Generation by spark Discharge," *J. Aersol Sci*., Vol. 19, No. 5, pp. 639～642.

Sunderland, P. B. and Faeth, G. M., 1996, "Soot Formation in Hydrocarbon/Air Laminar Jet Diffusion Flames," *Combustion and flame*, Vol. 108, pp. 132～146.

Walker, A. P., 2004, "Controlling Particulate Emissions from Diesel Vehicles," *Topics in Catalysis*, Vol. 28, No. 1-4, pp. 165～170.