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LASER PROBE SIZING ON IN-FLAME PM AND ITS PRECURSOR

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ABSTRACT In this study, sizing techniques of in-flame PM and its precursor were developed on the basis of laser probe methods. Sooting diffusion flames of diesel fuel were used as the test flames. Laser Induced Incandescence (LII) method was employed for the measurement of PM size. Spatial distribution of soot diameter in PM was measured from the data of intensity change of LII signal. It was thought that Polycyclic Aromatic Hydrocarbons (PAHs) were precursor molecules of PM. Spatial distributions of PAHs in the diffusion flame were visualized by a Laser Induced Fluorescence (LIF) method. KrF excimer laser was used for the excitation of PAHs molecules. Emission spectra of PAHs fluorences were analyzed by a spectroscope. Since the peak wavelength of the LIF spectrum of PAHs was a function of the carbon number of PAHs, the molecular size of PAHs could be estimated form the in-flame data of spectrum. Change of molecular size in the diffusion flames was discussed. As the result, final carbon number of PAHs in the flame was about 20-25 and the molecule size of PAHs was less than 1nm. In the meanwhile, soot particle diameter was estimated about several ten nanometers from the data of LII. Thereforre, these results suggested that the PAHs molecule rapidly grew up to the soot particles at nucleation area of PM.

Keywords: PM, PAHs, Soot, Diffusion Flame, Laser probe method, LII, LIF

1. INTRODUCTION
Particulate matter (PM) emission from automotive engines is one of major pollutants. Reduction of PM emission from diesel engine is required for the future development. In order to reduce the PM emission, a lot of studies have been carried out by engine researchers \cite{1-6}, and PM emission level decreases obviously. For reducing more the PM emission from a diesel engine, detail knowledge about chemical and physical processes of PM formation and oxidation is necessary.

In recent years, it was known that the nanometer size PM (nano-PM) was formed in the diesel exhaust emission \cite{7}. Weight ratio of nano-PM in engine emission was very low compared with that of aggregated PM. However, it seemed that considerable number of nano-PM was generated from a diesel engine. Since nano-PM is harmful to human health, new technologies should be established to remove the nano-PM emission.

It was thought that the polycyclic aromatic hydrocarbons (PAHs) were a precursor of nano-PM. Investigations of PAHs behavior in the flame were very important to understand the formation mechanism of nano-PM. PM emission was consisted of coarse and aggregate particles, and nuclei-mode particles of which diameter was less than 50nm. However the detail characteristics about these particles were still unknown. More physically accurate measurement method should be established for the detail analysis of PM formation process.

In this paper, spatial distribution of the soot diameter in the diffusion flame was investigated by using the laser induced incandescence (LII) method \cite{4-10}. Moreover, a molecular size of PAHs was measured by the laser induced fluorescence (LIF) method \cite{11-15}. And the data of soot diameter was compared with that of molecular size for the discussion of soot formation processes.

2. EXPERIMENTAL APPARATUS AND METHOD
Pool combustion equipment was used to make a laminar diffusion flame of liquid fuel. Figure 1 shows the schema of the equipment. This equipment is made up of a fuel tank, a fuel supplying system, a fuel pool and a electric balance. Fuel was supplied from a fuel tank through a float chamber. The float chamber could realize the constant fuel feeding. The flame height was controlled by an adjustment of pool depth. Weight of the equipment was measured by an electric-balance and the fuel flow rate was derived from the weight loss of it.

Figure 2 shows the test flame and the size of fuel pool. In order to enhance the fuel vaporization, a sintered metal was used as shown in the figure. The diameter and height of the sintered metal were 8mm and 20mm, respectively. Flame height \( L_f \) was defined as a distance from the top of sintered metal to the flame tip. Diesel fuel (JIS No.2) was used as a test fuel.

The laser diagnostic system is composed of an excimer laser (Lambda Physik, LPX-150T) and an ICCD camera (La-Vision, FlameStar \textsuperscript{I}). Figure 3 shows the optical arrangement. A narrowband KrF excimer laser (pulse energy 100mJ/pulse) was used for the excitation of PAHs molecules. Wavelength of the excimer laser was tuned on 248.469nm that was an off-resonance wavelength of the OH molecules. The laser light was arranged into a sheet beam (0.5mmx20mm) by an aperture and was introduced into the flame. A 248nm notch filter was used to eliminate the elastic scattering from the molecules and soot particles. LIF signal of PAHs was detected by the ICCD camera. LII signal of soot particles was measured by the same laser diagnostic system. LII signal was also detected by the ICCD camera. In order to separate the PAHs-LIF image and soot-LII image, the temporal resolved method was used \cite{16}. Detail procedure is explained in the following section.
LII signal of soot. Low intensity region exists between PAHs-LIF and soot-LII. Intensity profile on flame axis clearly showed the minimum point around z=12mm. This was a transition region from PAHs to soot. It was considered that soot precursor that had higher molecules existed in it. Similar results had been reported by Vander Wal et al.\textsuperscript{10} and Smyth et al.\textsuperscript{15}. Vander Wal et al. had sampled soot precursor particles in this region and investigated the particle size by transmission electron microscopy (TEM). They observed small particles of approximately 2 to 5nm in size.

In order to investigate the detail characteristics of soot precursor region, it is necessary to separate the PAH-LIF from the soot-LII. Procedure of image separation was explained in Fig.5. Origin of the time was determined by the time of first detection of Rayleigh scattering. Delay time of the camera gate was controlled based on this origin of time. At the early time of laser irradiation (after 120ns from the start of Rayleigh scattering), both signals of PAHs-LIF and soot-LII were observed as shown in Fig.5 (a). The second image (b) was obtained at the timing of 270ns that was corresponding to a late timing after laser irradiation. Since a relaxation time of LIF signal was faster than LII, LIF signal could not observed at this timing. Therefore, LII image could be obtained at 270ns. After adjusting the LII intensity of image (b), the LII image was subtracted from image (a). By this separation method, PAHs-LIF image (d) could be obtained.

3. RESULTS AND DISCUSSION

3.1 Temporal-Resolved LIF Method

Averaged LIF and LII images were derived from more than 20 elemental images because the laser power fluctuated every irradiation. An example of averaged image that contained LIF and LII light emissions is shown in Fig.4. Emission intensity curve on the flame axis is also indicated in the figure. Since the PAHs were formed by the abstraction process of hydrogen from the fuel vapor, it seemed that the high intensity part near the sintered metal was corresponding to the LIF signal of PAHs. And the high intensity area at downstream part was corresponding to the
3.2 Size estimation of PAHs molecules

Figure 6 shows the images of PAHs and soot obtained by using the temporal resolved LIF method. PAHs appeared near the sintered metal and the soot appeared downstream part of the flame. Here, since the intensity of the laser light was strongly attenuated by the soot absorption, symmetric distribution of LII could not be obtained. PAHs-LIF distributed inside the sooting region. In this figure, it was confirmed that the PAH-LIF appeared just on the sintered metal (z=0 mm). This result suggested that the diesel fuel contained the aromatic component and the aromatic rings might be promptly formed in the fuel vapor.

By using a spectroscopy, emission spectra of PAHs-LIF were observed. PAHs had a broadband emission from 300nm to 700nm in wavelength. Generally, since the difference of energy level between the ground state of molecules and electronic excitation state decreases with increasing the molecule size of PAHs, the fluorescence wavelength shifts toward longer wavelengths when the molecule size of PAHs increases. Classification of PAHs size might be performed using the PAHs-LIF spectrum obtained from a flame, because the peak fluorescence wavelengths reflect the molecular size of PAHs.

Figure 7 shows the emission spectra obtained at various heights of test flames. Measurements were performed on the flame axis. A LII spectrum obtained from the sooty part of the flame was also indicated in the figure for the reference. From this figure, it was confirmed that the peak wavelength of the emission spectrum of PAHs-LIF shifted to longer wavelengths with an increase of the flame axis z. A small peak shown in the spectrum at z=13mm was the contribution from the second-order interference from the original Mie scattering. Variations in the spectral profile suggested that the PAHs grew up to the large molecule when the PAHs approached to the sooting region.

Figure 8 presents the relation between the peak wavelengths of PAHs-LIF and carbon number of PAHs. The peak wavelength data were obtained from references. PAHs spectra in the vapor phase were mainly excited by UV laser sources. Figure 8 clearly showed that the peak of PAHs-LIF shifted to longer wavelengths as the carbon number of the PAH increase. For large carbon number (>24), there was no fluorescence data of vapor phase.

The carbon number of PAHs in the test flame was derived using Fig.7 and Fig.8. Results are summarized in Fig.9. The upper part of this figure indicates the relation between carbon number of PAHs and axial height z. Lower figure indicates the axial intensity distribution of PAHs-LIF and soot-LII. Hatching area indicates the transition region from PAHs to soot. This figure showed that the small PAHs molecules changed to the larger molecules along the flame axis z. At z=16mm, fuel vapor was consisted of PAHs molecules which contain approximately 20 to 25 carbon atoms. Coronene (C_{28}H_{13}) might be nominated as an example of PAHs.

![Fig. 6 PAHs-LIF and soot-LII](image)

![Fig. 7 Emission wavelength of PAHs-LIF](image)

![Fig. 8 Relation between carbon number and maximum emission wavelength of PAHs](image)

Figure 10 shows the examples of PAH molecules. Molecular size of PAHs were simply derived from the averaging of longer size and shorter size based on the ring structure of PAHs as shown the figure. For example, molecular size of benzene was estimated about 0.26nm, which is decided from the size of 0.28nmx0.24nm.

Figure11 shows the change of molecular size along the flame axis. Relation between the carbon number of PAHs and axial height z is also indicated in the figure. It was confirmed that the molecular size of PAHs increased with
increasing of z and growth rate of the PAH molecule was low.

![Graph showing the relation between carbon number of PAHs and height](image)

**Fig. 9 Relation between carbon number of PAHs and height**

![Diagram showing molecular size and particle diameter](image)

**Fig. 10 Molecular size and particle diameter**

![Graph showing the molecular diameter of PAHs](image)

**Fig. 11 Molecular diameter of PAHs**

3.3 Soot diameter

Soot diameter was evaluated using the LII technique. Usually, soot particles are heated by the laser irradiation and the temperature of soot becomes several thousand degrees. After finish of laser irradiation, soot temperature decreases by the effect of the heat transfer. LII signal decreases corresponding to the soot temperature. Decreasing rate of LII signal is a function of soot particle diameter. Therefore the soot particle diameter is able to derive the decreasing rate of LII signal. Temporal change of LII signal could be calculated by the Melton’s theory. Figure 12 shows calculated curves of LII signal for various soot diameters. Decreasing rate became large when the soot diameter increased. Images obtained at various delay time of ICCD camera. Figure 13 shows the examples of LII images obtained at various delay. It was confirmed that the LII intensity gradually decreased with the increase of delay time. From these figures, the spatial distribution of soot diameter in the flame was derived.

![Graph showing the relation between LII intensity and elapsed time](image)

**Fig. 12 Relation between LII intensity and elapsed time**

![Images showing Soot-LII images at various delay](image)

**Fig. 13 Soot-LII images at various delay**

Figure 14 shows the result of soot diameter estimated from the LII method. The upper part of the figure indicates the relation between soot diameter and z, and the lower figure indicates the intensities of LIF and LII signals on the flame axis. It was found that the diameter of detected soot particle around z = 13 mm was approximately 30 nm. The diameter increased gradually, and had a maximum diameter around z = 25 mm.

Soot diameter obtained from the LII method was compared with the molecular size of PAHs obtained from the LIF method. Data were summarized in Fig. 15. Molecular size of PAHs is changed from 0.6 nm to 0.8 nm. On the contrary, the measurement diameter of soot at transition region was about 30 nm. This result indicated that the PAHs grew up rapidly from PAHs to the soot particle.
As mentioned above, observed carbon number of PAHs was about 20-26. In order to form the soot particles of 30nm, PAHs molecules numbered 10^4 orders in volume base. Therefore the rapid polymerization occurred during short period.

**Fig. 14 Soot diameter**

**Fig. 15 Molecular size and soot diameter**

4. CONCLUSIONS

PAHs and soot in a diffusion flame of diesel fuel were measured using LIF and LII method. Main results are summarized as follows.

The molecular size of PAHs increased along the flame. At the transition region from PAHs to soot, the size was approximately 0.6-0.8nm. On the contrary, soot diameter obtained from LII method showed the several ten nanometer. This result indicated that the PAHs grew up rapidly from PAHs to the soot particle and rapid polymerization occurred during short period at the nucleation region in the diffusion flame.

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