Characterization of Diesel Soot Particles

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The characteristics of diesel soot particles sampled from diesel exhaust of a common-rail turbo-charged diesel engine are quantified by optical diagnostics. The radius of gyration representing the soot aggregates size is measured by the angular distribution of scattering intensity, while the specific extinction is measured by a two-wavelength extinction method. The refractive index of diesel soot is discussed using these data as well as the soot aggregates scattering theory. Lastly, the two-colour method is re-examined and the physical meaning of the apparent emissivity of luminous flames is explained clearly based on the scattering theory.

Keywords: Diesel engine, PM emission, soot aggregate, Characterization, Two-color method

1. INTRODUCTION

The diesel particulate in diluted diesel exhaust comprises of elementary carbon particles and secondary particles that are created from volatile hydrocarbons during the dilution processes in the atmosphere. The measured size distribution of the secondary particles varies significantly depending on the dilution conditions, and the effects of these liquid particles on human respiratory organs are still unclear. On the other hand, it is reported that the ultra-fine solid particles pass rapidly from the lung into the blood stream [1]. For this reason, the characterization of the elementary carbon particles is one of the primary issues in diesel emissions measurements.

Fig.1 is a TEM (Transmission Electron Micrograph) photograph of a diesel soot aggregate sampled from a 3-litre common rail, turbo-charged diesel engine (Isuzu-4JX), which meets EURO-III emissions standard. As the picture shows, the soot aggregates has a chain-like geometry and is composed of a number of elementary primary carbon particles. The pdf of the number of primary particles is represented by the log normal distribution. According to published data, the mode of the distribution varies depending on the engine operating condition and the type of engine, while the standard deviation remains almost constant irrespective of the condition and engine type. Since the standard deviation doesn't change much even if the mode of the distribution shifts, the simplest way to characterize the soot particle size is to express it with an average size of the soot aggregates, i.e. the average radius of gyration, $\overline{R}_g$. Fractal dimension, D_f, and the diameter of primary particles, d_p as well as $\overline{R}_g$ have been investigated by analyzing TEM photographs [2,3]. Among those, D_f is measurable only by TEM analysis, but $\overline{R}_g$ and d_p can be measured by a scattering technique and LII (Laser Induced Incandescence) techniques, respectively [4].

The present paper will report first the measurements of $\overline{R}_g$ by a scattering method and discuss the results comparing them with published TEM data.

Optical diagnostics of diesel particulates such as extinction, LII and photo-acoustic methods make use of light absorption and emission, and then the emissivity of soot, which is a function of the refractive index, is the most important optical parameter in these diagnostics. In spite of this, the nature of the refractive index of diesel soot particles is not well understood. The second part of this paper will deal with the refractive index of diesel soot particles based on the experimental data obtained in the present study.

The two-color method is a well-known optical tool to measure the diesel flame temperature and soot concentration focusing on the radiation from the luminous flame. The author will re-examine and discuss the two-color method making use of the soot aggregates scattering theory.

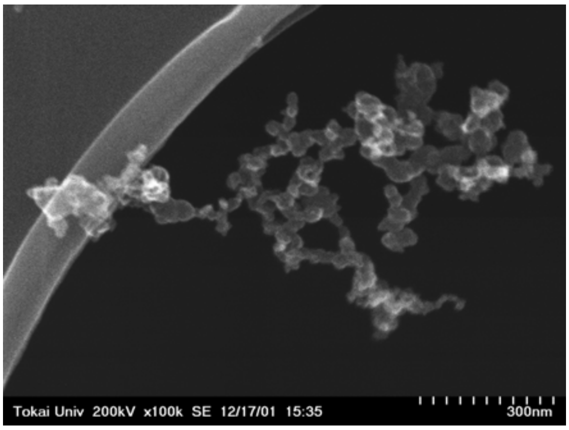

Fig.1 Typical TEM photograph of a diesel soot aggregate

2. MEASUREMENT OF AVERAGE RADIUS OF GYRATION BY A SCATTERING METHOD

2.1 Experimental setup and procedures

When vertically polarized laser beam irradiates a cloud of soot aggregates suspended in exhaust, the angular pattern of scattered light from a small volume in the cloud varies depending on the mean aggregate size present in the volume.

The non-dimensional scattering intensity, $I^A / \overline{n_p^2}$, is expressed as a function of $q^2 \overline{R_g^2}$ as given below [5].

$$q^2 \overline{R_g^2} \le 1 \qquad \frac{I^A}{\overline{n_p}^2} \approx c_1 \exp\left(-c_2 \frac{q^2 \overline{R_g^2}}{3} \right) \qquad (1)$$

where $c_1 = c_2 = 1$. $\overline{n_p}$ is the average number of primary particles per aggregate. q is a function of wavelength, λ , and scattering angle, θ , on v-v plane and is given by $q = 4\pi \sin(\theta/2)/\lambda$.

The radius of gyration is defined by the next equation.

$$\overline{R_g^2} = \frac{\sum R_{gi}^2 dN_{ai}}{\sum dN_{ai}} \qquad R_{gi}^2 = \sum r_j^2 \qquad (2)$$

where r_j is the distance from the center of gravity of an aggregate and dN_{ai} is the number of aggregates with R_{gi}.

Fig. 2 shows a schema of the experimental setup for scattering measurement. The gas sample is lead through a sample line heated at 200 ℃ to a nozzle with 3 mm diameter held vertically in a 24 liter clean chamber. A vertically polarized light beam from an Ar cw laser (514.5 nm) passes a lens of 150 mm focal length to form a thin laser beam of 0.02 mm diameter at the focal point. The thin beam illuminates soot particles across the sooty jet at about 5 mm above the nozzle exit. The scattered light from the measurement volume at an angle, θ ,is imaged by a collection lens of 40.6 mm focal length to a plane with a pinhole of 0.4 mm diameter, which define the length of the measurement volume. The scattered light through the pinhole passes a polarization film, laser filer and is detected by a silicon-diode photo-sensor (Hamamatsu photonics-S2281-01).

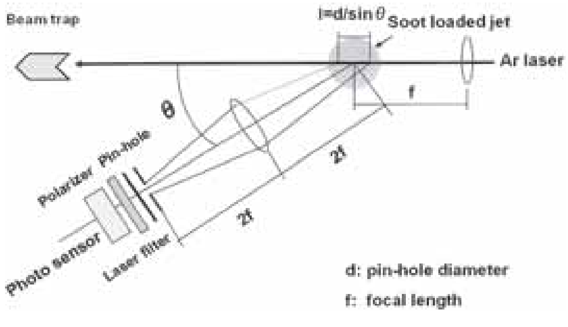

Fig. 2 Schematic optical layout of scattering measurement

A 3-litre common rail, turbo-charged diesel engine (Isuzu-4JX), which meets EURO-III emissions standard was used as a smoke emitter in the experiments. The engine was run at steady operating conditions to provide data for determining the radius of gyration in the scattering measurement and the specific extinction in the light extinction measurement.

2.2 Results and discussion

The angular distribution of normalized scattering intensity, $I(\theta)/I(30)$, was measured at various loads at 1500 rpm. Fig.3 shows selected angular distributions of normalized scattering intensity, $I(\theta)/I(30)$, obtained at three engine loads of 30, 90 and 150 Nm at 1500 rpm. The angular distributions are found to fit the theoretical curves for 80 nm to 120 nm. Fig.4 shows the data plot of the radius of gyration against the soot mass concentration at normal condition. It is seen that the size of the aggregates spans from 80 to 120 nm and increases slightly with the increase in soot mass concentration probably due to the enhanced agglomeration.

The data obtained are compared with published data [2,3], which are based on TEM photo analysis as shown in Table 1. Lee et al. sampled soot aggregates directly from exhaust of modern diesel engines using the thermopheritic sampling devices and investigated the morphology of the sampled particles. It is worth noting that the values of average radius of gyration by Lee et al. are very close to the data in the present study. The average diameter of primary particles in the present study is 33 nm ±5 nm, and a bit larger than those by lee et al. The LII technique was developed aiming primarily at measuring soot mass concentration, but at the same time it can measure in principle the primary particle diameter from the temperature decay curves of incandescent primary particles. However, the values of the primary particle diameters given in the table [6,7] are slightly smaller than those obtained by TEM analysis. This is probably due to the uncertain physical properties such as the refractive index of soot at high temperatures and the heat transfer coefficient for the small particles in the exhaust gases, which are all included in the equation to calculate the primary particle diameter.

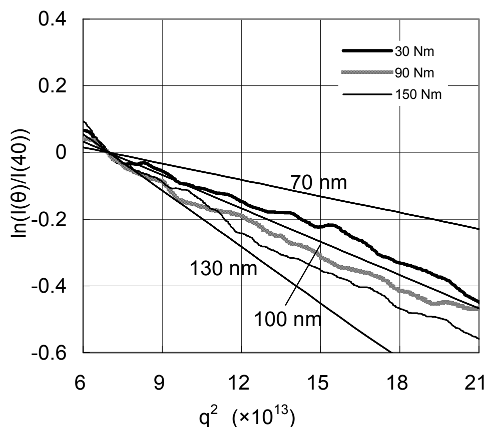

Fig. 3 Angular distributions of scattering intensity obtained at three engine torques at 1500 rpm

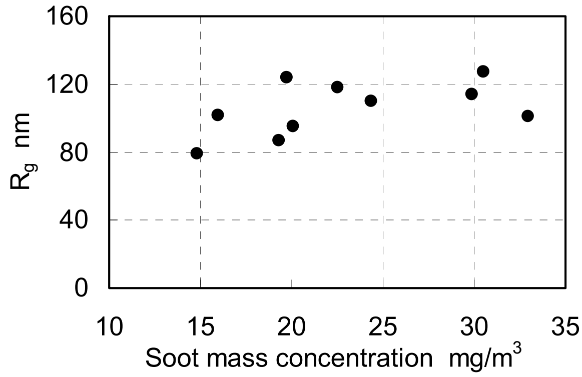

Fig.4 Variation of average radius of gyration with soot mass concentration in exhaust

Table 1 Selected values of morphological characteristics of diesel soot particles

	D_p nm	Rg nm	Reference
1	29-34	90-110	Lee et al (2001)
2	19-33	84-120	Lee et al (2003)
3	24-30*	-	Schraml et al (2000)
4	33	80-120**	Present work (2005)

* LII method
** scattering method
Source
1 75 Hp single cyl. DI
2 1.7 L Common-rail TIDI
3 6.8 L Common-rail TIDI
4 3.0 L Common-rail TIDI

2. REFRACTIVE INDEX OF DIESEL SOOT

3.1 Previous work

The refractive index of soot is an important electro-magnetic property in most of the optical diagnostics used for the studies of soot formation and extinction in flames and exhaust. A number of papers concerning the refractive indices have been published so far. Table 2 presents the selected values of the refractive index, which have been widely used in various optical diagnostics [6,7]. Values of E(m) are also listed in the table as it is a function of the refractive index m included in the specific absorption coefficient in the extinction method. The refractive indices in the table are all obtained for soot collected from various types of steady flames, and there are scatterings in the data depending on the type of fuels and burners used in experiments. It is unfortunate to have no data available in optical diagnostics of diesel soot particles in spite of its current importance in characterizing diesel soot.

In this chapter, the author will discuss a new approach on how to investigate the refractive index of diesel soot particles.

3.2 Experimental

First, the specific extinction σ_{ext} for diesel soot sampled from raw exhaust was measured. When a collimated light beam irradiates a cloud of soot particles in exhaust, the transmitted light attenuates based on the Bouguer-Lambert law.

Table 2 Selected values of refractive index and function E(m)

	λ nm	n	k	E (m)	Reference
1	650	1.55	0.55	0.259	Dalzell & Sarofim (1969)
2	300～600	1.90	0.35	0.125	Chippett & Gray (1978)
3	630	1.55	0.78	0.358	Dobbins & Mulholland (1994)
4	635	?	?	0.53	Present work (2005)

Source
1 Propane soot, Reflectance measurements of soot pallet
2 Acetylene premixed flame, Filteration
3 Diesel smoke, Alberta Sweet cruid oil, TEM analysis
4 Diesel smoke, (carbonaceous particles), JIS NO.2 Diesel fuel, Extinction and gravimetric measurements

$$\ln \tau = -\sigma_{ext} c_m L \qquad (3)$$

where τ is the transmittance, σ_{ext} is the specific extinction, c_m is the mass concentration of soot particles at measurement conditions, and L is the optical length. The specific extinction can be calculated directly from measured values of soot mass concentration c_m and transmittance τ.

Fig. 5 is a schematic diagram of the experimental setup for extinction measurement. The diesel exhaust was sampled from the main exhaust at a distance of 1.6 m from the turbocharger exit and lead to a measurement tube 0.80 m long through a flexible conditioning tube 2.5 m long at a constant flow rate of 27 litre/min. Two diode laser beams with wavelengths of 635 nm (10 mW) and 780 nm (30 mW) are co-axially aligned and illuminated the gas sample in the measurement tube through two quartz windows attached to both sides of the tube. The intensities of the two transmitted laser beams are detected by two silicon photo-diodes (Hamamatsu photonics-S2281-01), respectively.

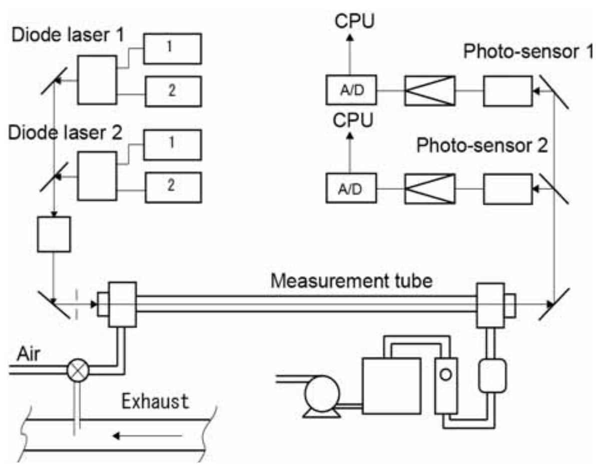

Fig. 5 Schema of experimental setup for extinction measurement

The soot mass concentration at normal condition, c_{mN} , was measured by a gravimetric method. A raw gas stream is lead through a sample line heated at 200 ℃ to a filter holder, and a mass of about 2 mg is collected on a quartz fibre filter with 47 mm diameter (Pallflex TX40HI20) at each run. The sample is then evacuated for an hour in an oven at an absolute pressure of 0.15 at and a temperature of 300℃ to remove SOF (Soluble Organic Fraction) from the sample.

The specific extinction remained approximately constant at an average value of 9.7 m^2/g at 635 nm and 7.6 m^2/g at 780 nm, respectively, regardless of engine load at 1500 rpm. Table 3 includes the specific extinctions for diesel soot in the present work and found in literatures [7-9]. The σ_{abs} of Japar obtained at 514.5 nm was converted to σ_{abs} at 635 nm assuming that σ_{abs} is inversely proportional to wavelength as eq.(5) shows. The specific extinction obtained here is a bit higher but close to the reported values despite the different instruments and gravimetric measurement methods.

Table 3 Selected values of specific extinction of diesel soot

	λ nm	σ_{abs} m^2/g	σ_{ext} m^2/g	Reference
1	514.5 635	8.9±0.5 7.2±0.4*		Japar et al (1981)
2	550 635	9.05±1.13 7.83±0.98		Scherrer et al (1982)
3	630		7.8±1.2	Dobbins et al (1994)
4	635	8.4±0.5**	9.7±0.5	Present work (2005)

* converted by calcuration to value at 635 nm

** calcurated from σ_{ext} by estimating σ_{sca}

Comments

1 2.3L Opel engine,Laser spectrophone at 514.5 nm. Zefluor filter (47mm) and Soxhlet extraction (16 hours)

2 1.5L IDI and 3.6L DI engines, integrating plate absorption measurment. Pallflex TX40HI20-WW teflon coated glass fiber filter and vacum volatilization at 1 kPa and 175℃ for 24 hours

3 Diesel exhaust, L=1m for extinction measurement, Alberta Sweet cruid oil. TEOM without SOF separation

4 3.0L common-rail turbo-intercooled DI engine, L=0.8m for extinction measurement, JIS NO,2 Diesel fuel. Pallflex TX40HI20-WW teflon coated glass fiber filter and vacum volatilization at 15 kPa and 300℃ for 1 hour

3.3 Function E(m) obtained from the specific extinction data

The specific extinction of soot aggregates, σ_{ext} , comprises of the specific absorption, σ_{abs} , and the specific scattering, σ_{sca} , as given by Eq. (4)

$$\begin{aligned}\sigma_{ext} &= \sigma_{abs} + \sigma_{sca} \\ &= \sigma_{abs}\left(1 + \overline{\rho}_{sa}\right)\end{aligned} \qquad (4)$$

$$\sigma_{abs} = \frac{6\pi}{\lambda\rho_p} E(m) \qquad (5)$$

$$E(m) = \mathrm{Im}\left(\frac{m^2 - 1}{m^2 + 2}\right)$$

where $m = n + ik$ is the refractive index of soot, and ρ_p is the density of soot. The ratio of scattering to absorption, $\overline{\rho}_{sa}$, is given by the soot aggregate scattering theory as follows [7].

$$\overline{\rho}_{sa} = C\alpha_p^3\left(\frac{\overline{R}_g}{d_p}\right)^{D_f}\left\{1 + \frac{16}{3D_f}\alpha_p^2\left(\frac{\overline{R}_g}{d_p}\right)^{2/D_f}\right\}^{-D_f/2} \qquad (6)$$

$$C = \frac{2}{3}\frac{F(m)}{E(m)} f_n k_f$$

$$\alpha_p = \frac{\pi d_p}{\lambda} \qquad F(m) = \left|\frac{m^2 - 1}{m^2 + 2}\right|^2$$

f_n is the moment ratio specific to the pdf of aggregate size distribution, k_f a pre-factor representing the aggregate shape. If $\overline{\rho}_{sa}$ is known, σ_{abs} , which is a function of refractive index, can be separated from the measured specific extinction, σ_{ext} .

In calculating $\overline{\rho}_{sa}$, we need to know three values in eq.(6), $\overline{R}_g$, d_p and constant C. $\overline{R}_g = 100$ nm and 33 nm were employed from the data in this study. $D_f = 1.75$ was selected from a literature as the most common value [10].

It is hard to independently estimate three parameters, $F(m)/E(m)$, f_n and k_f in constant C, and the author proposed a novel approach to determine constant C [11]. Here the refractive index was assumed constant in visible wavelength range based on ref. [12]. This assumption allows to calculate constant, C , from a measurable parameter, $\ln\tau_2/\ln\tau_1$. The two-wavelength extinction measurements provided an average value of 0.781 for $\ln\tau_2/\ln\tau_1$, and we finally obtain $C = 6.5$. $\overline{\rho}_{sa1}$ and $\overline{\rho}_{sa2}$ thus determined are 0.158 at 635 nm and 0.091 at 780 nm respectively.

Fig.6 presents the effect of scattering $1 + \overline{\rho}_{sa}$ as a function of wavelength, showing that the scattering is not negligible in the visible wavelength but marginal in the infrared wavelength.

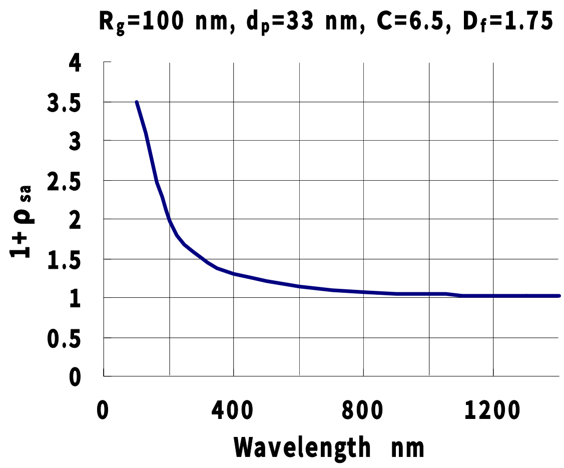

Fig.6 Effect of scattering, ,$1 + \overline{\rho}_{sa}$, on extinction as a function of wavelength

3.4 Refractive index

Now the specific absorption, σ_{abs}, can be calculated from $\overline{\rho}_{sa}$ and σ_{ext} obtained in the previous section. Assuming $\rho_p = 1.86$ g/cm³ , we obtain $E(m) = 0.53$ using eq.(5). As seen in Table 2, the values of $E(m)$ proposed by Dobbins et al. [7], and Dalzell and Sarofim [6] are both smaller than 0.53 acquired in the present study. The author calculated E(m) using many refractive indices available and found that no refractive indices give E(m) obtained in this study. The reasons for this difference are not clear at this time, but the specific extinctions of diesel soot in Table 3 are surely higher than those for soot measured for flames under atmospheric pressure.

4. RE-EXAMINATION OF THE TWO=COLOR METHOD

4.1 Explanation of α=1.39

In the two-color method, the monochromatic emissivity of the flame ε_λ is given by an empirical equation, which Hottel and Broughton obtained in their optical pyrometer experiment of several flames placed in a raw [13]. The emissivity they proposed is given by the following equation.

$$\varepsilon_\lambda = 1 - \exp\left(-\frac{KL}{\lambda^\alpha}\right) \tag{7}$$

where $\alpha = 1.39$, and KL factor represents the soot concentration and optical length L.

There arose a question whether this equation holds for diesel flames, and Matsui and Kamimoto sampled soot on a quartz window attached to the cylinder head of a 0.78 liter single cylinder DI diesel engine running at a steady condition [14].

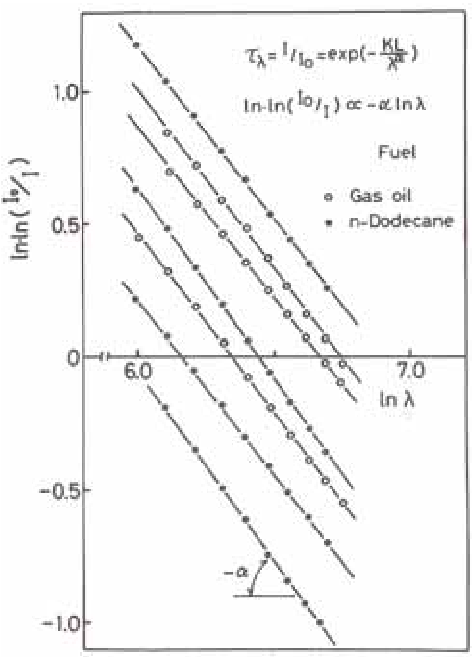

Fig. 7 Spectroscopic analysis of diesel soot layer deposited on an optical window placed in the combustion chamber (I_0: incident light intensity, I; transmitted light intensity, τ_λ: transmittance) Ref.[14]

Fig.7 shows the spectroscopic analysis of the diesel soot layer deposited on the optical window. As seen in the figure, the average gradient of all the straight lines with different amounts of soot deposit was 1.38, which agrees well to α=1.39.

Senftleben and Benedict, and Yagi applied Mie's theory to explain the number 1.38, but the results are not satisfactory because the soot aggregates are not obviously spherical [15]. The author applied the soot aggregates scattering theory to calculate the relationship between ln σ_{ext} and $\ln\lambda$ using $\overline{R}_g = 100$ and d_p =33 nm. Fig.8 shows the result of calculation. As expected, the average gradient of the curve in the visible wavelength range is 1.41 that shows a good agreement to 1.39 proposed by Hottel and Broughton. If only absorption dominates in extinction, α should be unity as Eq.(5) shows, but we obtained 1.41 using $\overline{\rho}_{sa}$ that represents the effect of scattering. It was concluded from this result that when considering the emissivity of soot aggregates in visible wavelength range, we have to take into account the effect of scattering.

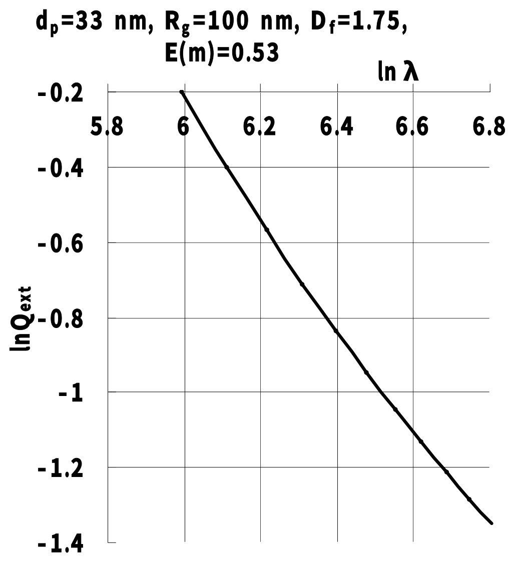

Fig.8 Calculated relationship between ln σ_{ext} and ln λ, showing the gradient of 1.41 in visible wavelength range
(d_p=33 nm, R_g=100 nm, C=6.5, D_f=1.75, E(m)=0.53)

4.2 Further discussion of α

Let's discuss further the Hottel and Broughton's equation considering the original meaning of the radiation from lamps lined in a row. They measured the apparent temperatures using an optical pyrometer by changing the number of lamps as shown in Fig.9. The total radiation intensity $I_{t\lambda}$ can be expressed by the next equation.

$$I_{t\lambda} = I_{b\lambda}\varepsilon(1 + \tau + \tau^2 + \tau^3 + ... + \tau^{n-1})$$

$$= I_{b\lambda}\varepsilon\frac{1-\tau^n}{1-\tau} \tag{8}$$

Where $I_{b\lambda}$ is the monochromatic radiation intensity of blackbody at temperature T and n is the number of lamps. ε and τ are the emissivity and transmittance of the flame in each lamp, respectively. Since $\varepsilon = 1 - \tau$, Eq.(8) is rewritten as follows.

$$1-\tau^{n} = 1-\exp(-\sigma_{ext} c_m L) = 1-\exp(-KL/\lambda^{\alpha}) \quad (9)$$

Where l is the thickness of each flame, and $nl = L$. This equation is equivalent to the Hottel and Broughton's emissivity equation, and now it is clear that the equation means $1-\tau^{n}$ in which τ depends not only absorption but also scattering, although they mentioned nothing about scattering. According to this understanding, we might be better to call the Hottel and Broughton's semi-empirical equation not as "emissivity " but as "apparent emissivity" because it includes the effect of scattering.

From the relationship given in Eq.(9), it became possible to calculate soot mass concentration c_m from KL factor if we assume an appropriate flame thickness L. Fig. 10 shows the relationship between them at conditions given in the legend.

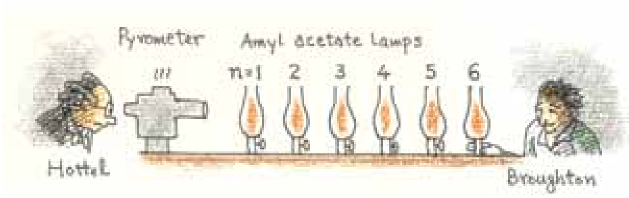

Fig.9 Optical arrangement of Hottel and Broughton's experiment using lamps and an optical pyrometer

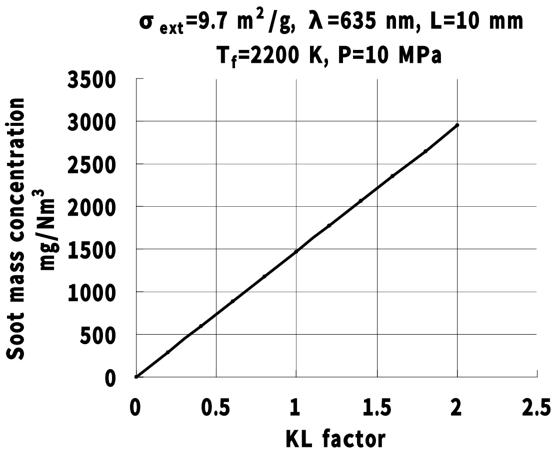

Fig.10 Relationship between KL factor and soot mass concentration c_m

5. CONCLUSION

The physical and optical properties of diesel soot particles were characterized by taking into account the effect of scattering on extinction. The specific extinction obtained experimentally was compared with those in published reports, and found larger by around 10%. The specific extinction was then separated using the soot aggregate scattering theory into specific scattering and absorption. The function E(m) derived from the specific absorption was found too large for any of the refractive complex indexes to account for.

The emissivity of the luminous flame used in the two-colour method was re-examined using the soot aggregate scattering theory and experimental data acquired in the present work. The wavelength dependency of a semi-empirical expression for the emissivity, which was proposed by Hottel and Broughton in 1932, was successfully elucidated by the theory. That is, when considering the emissivity of soot aggregates in visible wavelength range, we have to take into account the effect of scattering.

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