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Determination of the morphology of soot aggregates using the relative optical density method for the analysis of TEM images

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Abstract

The morphology of soot aggregates formed in a laminar coflow ethylene diffusion flame was studied by using the techniques of extractive thermophoretic sampling and subsequent image analysis of transmission electron microscopy (TEM) micrographs. A new image-analysis method, the relative optical density (ROD) method, is described in this paper and was used to obtain the morphological properties of soot aggregates. With this new method, the number of primary particles in each individual aggregate is determined by not only the projected area but also the optical density distribution within the projected area of the aggregate. As such, it attempts to address the three-dimensional nature of the aggregates. This method also calculates an overlap coefficient for each object in the TEM image that can be used to identify non-soot-aggregate structures. Unlike the conventional statistical method for fractal-like aggregate structure determination, ROD is independent of empirical constants based on correlations or numerical simulations. Using this new method, the parameters describing the morphology of soot aggregates generated in a laminar coflow ethylene diffusion flame, such as the geometric mean of the number of primary particles per aggregate, the fractal dimension, and the probability distribution function of aggregate size, were determined. ROD was found to be an accurate and reliable TEM image analysis method for studying the morphology of soot aggregates.

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Keywords: Relative optical density; Soot morphology; Thermophoretic sampling; TEM

1. Introduction

Research on the morphology of the soot aggregates generated in hydrocarbon/air combustion systems is very important for understanding the processes of soot formation, growth, and oxidation.

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Soot aggregates using image analysis

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June 2005

A flame was studied by using
analysis of transmission electron
density (ROD) method, is
not aggregates. With this new
not only the projected area
such, it attempts to address
coefficient for each object
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empirical constants based on
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morphology of the soot ag-
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Various soot diagnostic techniques have been developed in combustion research to aid this understanding. Nonintrusive methods, such as LII (laser-induced incandescence) [1–5] and LS/E (laser scattering and extinction) [6–9], although attractive, still suffer significant uncertainties in their models and parameter determinations [10,11]. For example, knowledge of the soot morphology is required to accurately model the soot cooling in LII [12]. On the other hand, the soot morphological properties inferred from laser elastic scattering are sensitive to the soot refractive index at the laser wavelength, which is in general subject to significant uncertainty [11]. The commonly used intrusive method, i.e., extractive thermophoretic sampling (TS) technique with subsequent scanning electron microscopy (SEM) or transmission electron microscopy (TEM) imaging and analysis, is considered to be a reliable *ex situ* visual method for determining the soot morphology.

Soot morphology investigation using thermophoretic sampling techniques and subsequent TEM analysis was first developed by Dobbins and Megaridis [13], and was later adopted widely [14–22]. In this method, soot particles in the flame deposit on a probe through thermophoresis driven by temperature gradients between the probe and the flame during the probe's exposure to high temperatures. Subsequently, the soot sampled on the probe is imaged with TEM or SEM techniques. Both SEM and TEM characterization techniques can provide clear images of soot aggregates. Fig. 1 shows typical TEM images of soot aggregates sampled from a laminar coflow ethylene diffusion flame described below.

A careful statistical analysis of a large population of soot aggregates from TEM or SEM images typically yields important parameters related to soot morphology. The distribution of the number of primary particles per aggregate, N , is important in describing the morphology of soot aggregates, and can be derived from the statistics of a large population of soot aggregates. Key parameters, such as N_g (the geometric mean of N), σ_{2g} (the geometric standard deviation of N), D_f (the mass fractal dimension), and others can be obtained from this distribution.

Since TEM and SEM generally provide two-dimensional projected images, a statistical equation is typically utilized to relate N of each aggregate to its projected area and the mean primary particle diameter through [15]

$$N_i = k_a (A_i / A_p)^\alpha, \quad (1)$$

where N_i is the number of primary particles in the aggregate, A_i the projected area of the aggregate, $A_p = \pi \bar{d}_p^2 / 4$ the projected area of a single primary particle with the mean primary particle diameter, $\bar{d}_p$, k_a the projected area constant, and α the projected

area exponent. Several values of k_a and α have been reported [23–26]. Statistically, this method may be accurate when considering the average of a large number of aggregates. However, for an individual aggregate, it is very difficult to evaluate the accuracy of this method, due to the variations in the aggregate's structure and its orientation on the mesh. Additionally, non-soot-aggregate structures, which are often found in TEM images, may erroneously be included as soot aggregates in the image analysis. For example, the object indicated with the arrow in Fig. 2a is clearly not a valid soot aggregate generated by the flame. It is possible that such carbon objects originated from the carbon film on the TEM grid. In automated image processing, it is very difficult for the software to distinguish these unwanted structures in the image from the “true” aggregates. It is also impractical to identify and remove those unwanted structures among thousands of aggregates in the TEM images by visual judgment. Thus, without a reliable and efficient means to identify and remove these “false” aggregates in the statistics, the results are likely to be contaminated or have larger statistical error, leading to considerable inaccuracy of the parameters of the soot morphology.

Although TEM images show a two-dimensional representation of soot aggregates, they do provide some information on the aggregates' third dimension. As seen in Fig. 1, the gray level variation from pixel to pixel in an object can be discerned. Our approach is to develop a method that relates this gray level variation to the local thickness of the object in the direction perpendicular to the plane of the image, thus providing a measure of the third dimension. When there are overlapping particles in this direction, the overlapped area is darker than the nonoverlapping region. If we consider the fundamental characteristics of digital TEM imaging, we can relate the local gray level in the TEM images to the local thickness of the object in the third dimension. Through a carefully selected calibration, the local thickness can be quantified. Integration of the local thickness across the projected area of each aggregate can be used to estimate the volume of the aggregate and thus the number of primary particles in the aggregate.

Although the concept of gray level variation difference within images of soot aggregates obtained by TEM has been noted previously by Cai et al. [27], it was not used in a quantitative way since at that time the gray level resolution was poor and the image processing technology was underdeveloped. With improvements to TEM and developments in digital imaging and image processing technologies, it is now possible to formulate a quantitative relationship between the gray level of an object and its thickness in the third dimension. This relationship does not ap-

Fig. 1. Typical TEM images of soot aggregates sampled from an ethylene/air diffusion laminar flame.

Fig. 2. A typical non-soot-aggregate structure (a) and a single soot particle (b) in TEM images.

in TEM images.

in TEM images.

ply to SEM where surface reflection-based images are produced. Although possible, this method would be more difficult to apply to film-based TEM photos due to a nonlinear relationship between the gray level of film and the electron beam intensity, and the need for film processing and digitization.

In this paper, with the help of high-quality digital TEM images and advanced digital image processing techniques, we introduced a new TEM image analysis method that makes use of the gray level distribution recorded in TEM images of soot aggregates to more accurately determine parameters describing the morphology of soot. As this method utilizes the optical density (defined below) of pixels in the soot aggregate relative to that of the background pixels in TEM images, it has been labeled the relative optical density (ROD) method.

2. Formulation of the relative optical density method

When a monochromatic light wave travels through a homogeneous and amorphous medium, light intensity decreases exponentially with the distance traveled by the light in the medium according to the Lambert–Beer–Bouguer law [28],

$$I_{\text{out}} = I_0 \exp(-\delta l), \quad (2)$$

where I_{out} is the intensity of the optical wave leaving the medium, I_0 the incident wave intensity, δ the absorption coefficient, and l the distance propagated by the optical wave through the medium. Because δ is a constant for homogeneous and amorphous media, the length of the medium can be described as

$$l \propto -\log(I_{\text{out}}/I_0). \quad (3)$$

In deriving Eq. (3) from Eq. (2), the relationship $\log(x) = \ln(x) \log(e)$ was used. In TEM, the electron wave intensity attenuation also follows Lambert–Beer–Bouguer law, but the absorption coefficient in Eq. (2) should be replaced by the scattering cross section which is a function of the atomic number [29]. In addition, the gray level of the image of an object recorded by TEM is proportional to the intensity of the electron wave arriving at the response surface of the CCD camera employed as the TEM detector. With a carefully calibrated CCD camera, the proportionality can be made linear. In the TEM imaging procedure, electron waves travel through soot aggregates and the supporting carbon film, resulting in a range of gray levels generated on the projection image, as illustrated in Fig. 3. A quantitative relationship between the pixel intensity (gray level) in a TEM image

Fig. 3. Schematic of the TEM imaging process with electron wave traveling through soot particles and the supporting carbon film.

and the thickness of soot in the direction perpendicular to the imaging plane can be established with the following assumptions:

1. the internal structure of all soot aggregates is homogeneous and amorphous;
2. the intensity of the electron beam transmitted through the thickest point of the aggregate is within the dynamic response range of the TEM detector;
3. within each individual TEM image, the thickness of the supporting carbon film remains uniform everywhere.

Although primary particles are found to contain a large number ($\sim 10^4$) of crystallite structures with high-resolution TEM, the random arrangement of crystallites ([17] and references therein) within the soot particles results in an average amorphous response to an electron beam in low-resolution TEM images, such as those used in this study. Detailed investigation of gray level distributions within single soot particles on TEM images was performed to verify this conjecture. A survey of gray level intensities within all of the TEM images indicated that all pixels were within the dynamic response of the detector. Finally, the thickness uniformity of the supporting carbon film of the grid was confirmed by measurements of the background gray level distributions of all TEM images from the same grid.

To simplify the discussion, the electron beam is considered to be a light beam from this point forward. We define the optical density of each pixel in a TEM image as

$$D(x, y) = -\log \left[\frac{I(x, y) - I_{\text{dark}}}{I_{\text{incident}} - I_{\text{dark}}} \right], \quad (4)$$

where $D(x, y)$ is the optical density at pixel (x, y) , $I(x, y)$ the intensity at the same pixel, I_{dark} the intensity generated when no electron beam goes through the material, and I_{incident} the intensity of the incident electron beam before it travels through the soot aggregates and the supporting carbon film. I_{incident} is assumed to be uniform within the imaging area. For the TEM images investigated in this study, $I_{\text{dark}} = 0$, and the following theoretical development is limited to such images.

There is a background optical density, $D_{\text{background}}$, which includes light attenuation of all the optics in TEM and the supporting carbon film of the TEM grid. $D_{\text{background}}$ can be obtained from the pixel intensity in areas without soot aggregates in the TEM image.

$$D_{\text{background}} = -\log(I_{\text{background}}/I_{\text{incident}}), \quad (5)$$

where $I_{\text{background}}$ is the intensity of the background. In our TEM images, $I_{\text{background}}$ is uniform ($< \pm 3\%$ variation) within the imaging area. By defining a relative optical density, D_{relative} , of each pixel in the image in comparison to $D_{\text{background}}$.

$$\begin{aligned} D_{\text{relative}}(x, y) &= D(x, y) - D_{\text{background}} \\ &= -\log(I(x, y)/I_{\text{background}}), \end{aligned} \quad (6)$$

where the incident electron beam intensities were canceled, we obtain the following relationship based on Eqs. (3) and (6)

$$I_{\text{soot}} \propto D_{\text{relative}}(x, y), \quad (7)$$

where I_{soot} is the thickness of the soot aggregate in the third dimension at pixel (x, y) under consideration. With Eq. (7), the volume of each soot aggregate can be related to the relative optical density as

$$\begin{aligned} V_i &= \int_{A_i} I_{\text{soot}} dA = C \int_{A_i} D_{\text{relative}}(x, y) dA \\ &= C \overline{D_{\text{relative}}} A_i, \end{aligned} \quad (8)$$

where V_i is the volume of each individual aggregate, C the calibration constant relating I_{soot} and D_{relative} , and $\overline{D_{\text{relative}}}$ the projected area-averaged relative optical density of the object. Commercially available imaging processing software is capable of providing the projected area, the mean optical density, and some two-dimensional geometric properties of each object in a TEM image. Unfortunately, for most soot aggregates, V_i is difficult to obtain from the two-dimensional image. However, if we can identify an object in the TEM image for which we know a priori its 3-D shape (hence its volume), we can establish a quantitative relationship between the volume of the object and its projected-area-averaged optical density based on Eq. (8), i.e., determine the calibration constant. Isolated single spherical soot primary particles

are clearly the simplest reference objects for this purpose. A typical isolated single soot primary particle in the TEM image is shown in Fig. 2b, as indicated by the arrow. It should be noted that the chosen single reference soot particle in the TEM image can have a different diameter from the mean diameter of the primary soot particles constituting soot aggregates, without affecting the value of the calibration constant C . Once a representative single soot particle is chosen as a reference object, we need to make the following two assumptions to establish the quantitative relationship between the mean optical density and the volume of the particle:

1. the selected isolated single soot primary particle is spherical in shape;
2. the mass density and the cross section for electron scattering of the selected isolated single primary soot particle are the same as those in aggregates.

Based on the above assumptions, the volume of the selected isolated single soot particle is estimated from its projected area in the TEM image. Subsequently the calibration constant C can be obtained by relating the reference single particle's volume to its relative optical density, using Eq. (8). Then, C is applied to the other aggregates to calculate their individual volumes. The number of primary particles in each aggregate is obtained by dividing its volume by the volume of a mean primary particle. According to this derivation procedure, the number of primary particles in each individual soot aggregate, N_i , can be calculated as

$$N_i = C \frac{6 \overline{D_{i,\text{relative}}} A_i}{\pi \overline{d_p}^3} = 8 \frac{\overline{D_{i,\text{relative}}}}{\overline{D_{\text{ref,relative}}}} \frac{A_i \sqrt{A_{\text{ref}}}}{\pi^{1.5} \overline{d_p}^3}, \quad (9)$$

where A_{ref} and $\overline{D_{\text{ref,relative}}}$ are the measured projected area and the mean relative optical density of the reference particle, and $\overline{D_{i,\text{relative}}}$ the mean relative optical density of the aggregate. $\overline{d_p}$ is the mean primary particle diameter which is measured from the TEM images.

Further, for each object in the TEM image, we can define a maximum projected area for the same number of primary particles

$$A_{\text{max},i} = N_i \pi \overline{d_p}^2 / 4, \quad (10)$$

where N_i is determined from Eq. (9). An overlap coefficient, ϕ , of each object in the TEM image, defined as

$$\phi_i = A_{\text{max},i} / A_i, \quad (11)$$

can be used to quantify the level of overlapping of primary particles within each soot aggregate and also as

reference objects for this purpose. A single soot primary particle is shown in Fig. 2b, as indicated. It is noted that the chosen single particle in the TEM image can have a mean diameter of the primary soot aggregates, without the calibration constant C . A single soot particle is chosen as a reference to make the following two quantitative relationships between optical density and the volume of

a single soot primary particle and the cross section for electron scattering. The selected isolated single primary particles are the same as those in aggregate images.

Assumptions, the volume of the primary soot particle is estimated from the TEM image. Subsequently the volume can be obtained by relating the optical density to its relative optical density. Then, C is applied to the reference images to calculate their individual volumes. The volume of each primary particle in each aggregate is calculated by the volume of a primary particle by the volume of an aggregate. According to this derivation, the volume of primary particles in each image, V_i , can be calculated as

$$V_i = \frac{\overline{D_{i,\text{relative}}}}{\overline{D_{\text{ref},\text{relative}}}} \frac{A_i \sqrt{A_{\text{ref}}}}{\pi 1.5 \overline{d_p}^3}, \quad (9)$$

where $\overline{D_{i,\text{relative}}}$ are the measured projected relative optical density of the primary particle, $\overline{D_{\text{ref},\text{relative}}}$ the mean relative optical density of the reference soot aggregate, $\overline{d_p}$ is the mean primary particle diameter which is measured from the reference soot aggregate.

In the TEM image, we can calculate the projected area for the same number of primary particles.

(10)

From Eq. (9). An overlap coefficient, ϕ , is defined in the TEM image, defined

(11)

The level of overlapping of primary particles in a soot aggregate and also as

a criterion to determine if an object in the TEM image is an unwanted or false aggregate. For a "genuine" soot aggregate, it is expected that its overlap coefficient should be greater than or equal to 1. An object in the TEM image should not be a valid soot aggregate structure if its overlap coefficient, ϕ , is less than 1. This scenario occurs for objects that have a lower mean relative optical density, i.e., "bright" appearance in the TEM images, such as the object identified with an arrow in Fig. 2a. This overlap coefficient provides a useful and efficient way to identify and remove these nonaggregate objects in the TEM image. Previously, one relied upon visual inspection and arbitrary judgment to identify the nonaggregate structures in TEM images. The visual approach is time consuming and subject to human bias.

3. Experimental procedure, TEM imaging, and image processing

To verify the feasibility of ROD for analyzing TEM images of soot aggregates, an experimental study was carried out to thermophoretically sample soot particles from an atmospheric pressure coflow laminar ethylene/air laminar flame. The burner for generating the flame has been described previously in detail [30,31]. Briefly, the burner consists of a central fuel tube with a 10.9-mm inner diameter surrounded by an annular air nozzle of 100 mm in diameter. The ethylene flow rate was 3.23 cm³/s, and the air flow rate was 4733 cm³/s, resulting in a visible flame height of about 64 mm. The burner was similar to that used in Refs. [6,13,15] which reported a higher fuel flow rate and a lower air flow rate that resulted in a visible flame height of 88 mm. The sampling location was 42 mm above the exit of the fuel tube and at the flame centerline. At this height, the annular structure of soot merges to form a radially uniform distribution of soot in the centerline region. The flame structure at this height should be comparable to that at roughly 58 mm height in the flame investigated by Köylü et al. [15], the results from which are used for comparison of soot parameters.

The thermophoretic sampling (TS) instrumentation of the present experiment was similar to those used by Dobbins and Megaridis [13] and Köylü et al. [15]. Our sampling probe consists of a circular carbon-coated copper TEM grid (Electron Microscopy Sciences, Cat. No. CF200-Cu, 3 mm diameter) and a grid holder. The holder is a folded stainless-steel sheet with a 3-mm hole at one end for the grid. The probe's insertion, exposure, and withdrawal were controlled by a double-acting pneumatic cylinder system, with which the sampling time dura-

tion is adjustable. In this study, the sampling time in the flame was set to 25 ms.

After the sampling process, the TEM grids were imaged with a Philips CM20 transmission electron microscope. An UltraScan 1000 CCD camera (Gatan Inc.) coupled to the microscope generated digital TEM images for analysis. Each TEM image typically contained dozens of soot aggregates. The images were subsequently analyzed using commercial image processing software (Media Cybernetics, Image Pro Plus 4.5.1). The image processing software is capable of automatically identifying each object against the background and, at the same time, providing measurements of its geometric properties, such as the projected area, the maximum and minimum caliper lengths, and the mean optical density in the projected area. The images were processed with median filtering to remove impulse noise. During the object identification procedure, the threshold of the smallest projected area to be identified was set to the projected area of one primary particle, A_p (based on the mean primary particle diameter). Objects with smaller projected areas were ignored.

For each sampling grid, the TEM settings were kept identical. When the TEM images were processed using ROD, the mean background optical density of each image was obtained individually, although the variation from image to image was minimal ($< \pm 3\%$), which supported our previous assumption of the uniformity of supporting carbon film within each grid. The background intensity of each image was determined by the image processing software. To minimize the error during the selection of reference single soot particles, we applied the following criteria: the reference-isolated single soot primary particles were identified not only visually but also by a geometric parameter, the aspect ratio of the maximum and the minimum caliper lengths (within 10% of unity). For each sampling grid, several reference soot particles were selected. A calibration constant was calculated for each individual reference soot particle. Then, an algebraic mean value of the calibration constant was adopted in the analysis of each specimen.

4. Results and discussion

4.1. The number of primary particles per aggregate

Four typical TEM images of soot aggregates thermophoretically sampled from the centerline at an axial height of 42 mm above the burner exit in the coflow ethylene/air diffusion laminar flame are shown in Fig. 1. It is clear that most of soot aggregates show high contrast relative to the background and have

Fig. 4. Probability distribution of the number of primary particles per aggregate, and the fitting curves (lognormal and double-lognormal).

clearly identifiable boundaries in the image. In addition, most of the primary particles that constitute soot aggregates appear spherical in shape. This indicates that at this flame height mature soot particles are more prevalent than precursor particles [13].

In total, 62 TEM images with approximately 50–100 aggregates in each image were processed, resulting in a total of 4544 objects identified by the image processing software. Primary particle diameters, $\bar{d}_p$, were measured previously [32], from which mean primary particle diameter $\bar{d}_p = 29$ nm was adopted for this study. The number of primary particles per aggregate, N_i , of each object was calculated using ROD. For each object, the overlap coefficient defined in Eq. (11), ϕ , was also calculated. Ideally, $\phi \geq 1$ should be adopted as the cutoff to eliminate the nonaggregate objects with a lower relative optical density. In practice, this criterion was reevaluated due to the diversity of the morphology of the sampled soot. From the statistical histogram of ϕ and inspections of appearance of some questionable “objects” whose ϕ were close to 1, a threshold of $\phi > 0.8$ was adopted in this study. After filtering, 3415 aggregates/single particles were retained, i.e., nearly a quarter of the total objects in the TEM images were found to be unwanted non-soot-aggregate structures. The statistical distribution of N for these 3415 qualified aggregates/single particles was obtained and is shown in Fig. 4 (open circles).

A widely accepted assumption is that the population distribution of N is lognormal and can be described by two parameters, N_g and σ_{2g} [14],

$$\text{PDF}(N) = \frac{\exp\left[-\left(\frac{\ln(N) - \ln(N_g)}{20.5 \ln(\sigma_{2g})}\right)^2\right]}{N \ln(\sigma_{2g}) (2\pi)^{0.5}}, \quad (12)$$

where PDF(N) is the probability distribution function of N , N_g the geometric mean of N , and σ_{2g} the geometric standard deviation. Several results of N_g , σ_{2g} and arithmetic mean of N , $\bar{N}$, have been reported in the literature for different flame conditions [14,15]. This lognormal distribution model was adopted to describe the probability distribution of N in this study. Since the lower limit of N for real soot is 1 instead of 0, and the upper limit is not infinity, Eq. (12) was scaled by a proportionality coefficient to ensure that the integral of the scaled PDF(N) from 1 to maximum N equals 1, to be consistent with the normalization of the TEM statistical results. The application of the proportionality coefficient ensures that the integral of the scaled PDF(N) within the statistical range (from 1 to the maximum value of N in the TEM analysis) is equal to 1. A similar correction was conducted in the fitting when a lower cutoff of $N > 5$ was employed (see below). As shown in Fig. 4 (open circles and dash-dot line), it was found that the lognormal fit does not coincide well with the data when all of the aggregates/single particles are taken into account. The lognormal fitting result for $N \geq 1$ was $N_g = 26.08$ and $\sigma_{2g} = 8.06$. Considering that a threshold of several primary particles has been used in past studies [14,15,25,26], a cutoff of $N > 5$ was adopted to fit the lognormal probability density function of N (shown as a dashed line in Fig. 4). By ignoring very small N

Fig. 5. Least-square fit of Eq. (15) to N and $L/\bar{d}_p$ to determine k_L and D_f for the soot particles sampled in the laminar ethylene diffusion flame.

(less than 5), the lognormal distribution provides a better fit to the measurement with $N_g = 31.36$ and $\sigma_{2g} = 5.08$. However, the quality of fit remains poor for large N (more than several hundred).

We also applied a double-lognormal model [32],

$$\text{PDF}(N) = a \frac{\exp\left[-\left(\frac{\ln(N) - \ln(N_{g1})}{2^{0.5} \ln(\sigma_{2g1})}\right)^2\right]}{N \ln(\sigma_{2g1}) (2\pi)^{0.5}} + (1-a) \frac{\exp\left[-\left(\frac{\ln(N) - \ln(N_{g2})}{2^{0.5} \ln(\sigma_{2g2})}\right)^2\right]}{N \ln(\sigma_{2g2}) (2\pi)^{0.5}}, \quad (13)$$

to fit the distribution of N . In Eq. (13), a is the weight factor ($0 < a < 1$), N_{g1} the first geometric mean of N , σ_{2g1} the first geometric standard deviation, N_{g2} the second geometric mean of N , and σ_{2g2} the second geometric standard deviation. As before, a similar proportionality coefficient was applied to this model. As shown in Fig. 4 (solid line), the double-lognormal provides the best fit to the data. The cutoff of $N > 5$ was not applied in this case. The fitting results are $a = 0.85$, $N_{g1} = 35.87$, $\sigma_{2g1} = 3.58$, $N_{g2} = 2.27$, and $\sigma_{2g2} = 2.00$.

We also calculated the arithmetic mean of N , $\bar{N}$, which was $\bar{N} = 66.9$ for $N > 1$ and was $\bar{N} = 79.5$ for $N > 5$. This result is somewhat larger than that obtained from the conventional statistical method based on Eq. (1) for the same TEM images [32], but is close to that of Köylü et al. [15] ($\bar{N} = 80$ – 90) at the comparable height in a similar flame using similar techniques (TS/TEM).

4.2. Fractal description of soot aggregates

It is well known that soot aggregates generated from hydrocarbon/air flame consist of various shapes and sizes that can be conveniently characterized using the mass fractal concept, which implies the following statistical relationship [15,24–26]

$$N = k_f (2R_g/\bar{d}_p)^{D_f}, \quad (14)$$

where D_f is the mass fractal dimension, R_g is the radius of gyration of an aggregate, and k_f is the fractal prefactor based on R_g . For most aggregates in TEM images, R_g is very difficult to obtain due to the two-dimensional nature of these photographs. Instead, the following alternative equation is often used for the determination of the fractal dimension [24]

$$N = k_L (L/\bar{d}_p)^{D_f}, \quad (15)$$

where L is the projected maximum caliper length of the aggregate, and k_L the fractal prefactor based on L . Köylü et al. [24] also demonstrated the approximate relationship between k_L and k_f :

$$k_f/k_L = ((D_f + 2)/D_f)^{D_f/2}. \quad (16)$$

This provides a method to recover parameters describing the 3-D soot structure. Parameters D_f and k_L can be obtained from a least-square fit of Eq. (15) to $\log(N)$ and $\log(L/\bar{d}_p)$ for all the aggregates, as shown in Fig. 5. Then k_f can be obtained from Eq. (16).

Based on N calculated from ROD and L determined from the TEM images, D_f , k_L , and k_f were calculated. With a threshold of $N \geq 3$, we found that $D_f = 1.77$ with a standard deviation of 0.009, $k_L = 1.27$ with a standard deviation of 0.011, and $k_f = 2.48$ for our experimental condition. These values compare very well with the values reported in Ref. [24] with $D_f = 1.7 \pm 0.15$ and $k_f = 2.4 \pm 0.4$. The reason to adopt the $N \geq 3$ threshold is that only soot aggregates with at least three primary particles can have a variable fractal dimension resulting from different arrangements of the particles.

4.3. Remarks on ROD

As shown in Eq. (1), the accuracy of the conventional statistical method greatly depends on the selection of k_a and α . Strictly speaking, k_a and α should be dependent on the morphology of the soot aggregates to be analyzed. For a soot sample with *unknown* morphology, the selection of appropriate values of k_a and α is difficult since they are typically determined using soot of *known* morphology obtained from numerical simulations [25,26,33] or experimental samplings [14,25,34]. Numerical simulations generally involve the generation of a population of aggregates with specified fractal parameters, such as D_f , k_f , whereas the statistical analyses of actual soot aggregates rely on a small number of selected soot aggregates. Consequently, there is a distinct lack of universality in the values of k_a and α . The use of inaccurate values of k_a and α could lead to errors in the estimation of N , which could propagate to other parameters describing the morphology of the soot aggregates under consideration.

Using ROD, the above error source does not exist because a priori empirical constants are not required in the analysis. The key step in ROD is the selection of the reference-isolated single soot primary particles in the TEM images. This is the only step in ROD that is subjective, relying upon the operator's judgment to a certain extent. The selection of "poor" reference single particles may lead to considerable inaccuracy in estimating N . Ideally ROD should be used to calculate N based on the qualified reference single soot particles selected in the same TEM image. However, this ideal procedure is not always practical since qualified reference single soot particles may not exist in every TEM image to be analyzed. Therefore, we have to consider the TEM images of one specimen grid as an ensemble. As such, it is assumed that qualified reference single soot particles selected from some images can also be used in the analysis of other images that do not contain reference particles. This assumption should be valid based on the considerations that the TEM parameter setup for each specimen grid

was kept identical during the imaging process. This assumption is further supported by the fact that the ranges of the optical density and the background optical density of all the images from any specific specimen grid show little variation. To reduce stochastic errors, several reference soot particles were selected from each specimen grid under the criteria noted previously. In total, only about 10–15 qualified reference single soot particles were selected from around 2000 objects of soot aggregate/single particle for each specimen. As a result of such a careful selection of the reference single soot particles, the calibration constants among the selected reference particles have only a 10% standard deviation and 5% standard error from the mean value.

5. Conclusion

A new image-analysis method, the relative optical density method, was introduced and developed for deriving accurate parameters describing the morphology of soot particles based on their TEM images. This method was successfully demonstrated in the investigation of the morphology and fractal structure of a large population of soot aggregates thermophoretically sampled from the centerline of a coflow ethylene/air laminar diffusion flame. The following conclusions can be drawn based on the results of the present study:

1. The relative optical density method has proven to be a reasonable and reliable TEM image processing method for soot morphology investigation. This method is independent of empirical or numerically simulated constants employed by other methods. In order to estimate the number of primary particles within individual aggregates, the relative optical density method resolves not only their projected area, as the conventional statistical method does, but also their relative optical density in the TEM images which is related to their thickness in the direction perpendicular to the plane of the image.
2. An overlap coefficient was introduced to help identify and remove non-soot-aggregate objects in the TEM images.
3. The distribution of the number of primary particles within individual aggregates was studied using the relative optical density. Attempts were made to fit the results to a lognormal and a double-lognormal probability density function. The double-lognormal PDF provides the best fit to the measured data. The arithmetic mean value of the number of primary particles per aggregate

the imaging process. This is supported by the fact that the density and the background images from any specific specification. To reduce stochastic soot particles were selected under the criteria noted previously. 10–15 qualified reference particles were selected from around 2000 particles. A careful selection of the reference particles, the calibration constants, the reference particles have only a 5% standard error from

method, the relative optical density was introduced and developed for parameters describing the morphology of soot particles. This was demonstrated in the investigation of the morphology and fractal structure of soot aggregates thermophoretically on the centerline of a coflow ethylbenzene flame. The following conclusions were based on the results of the

optical density method has proven to be a reliable TEM image processing method for morphology investigation. The method is independent of empirical or numerical constants employed by other methods. To estimate the number of primary particles in individual aggregates, the optical density method resolves not only the size of individual aggregates, but also their relative optical density, which is related to the direction perpendicular to the

method was introduced to help identify non-soot-aggregate objects

The number of primary particles in partial aggregates was studied by optical density. Attempts were made to fit to a lognormal and a probability density function. The PDF provides the best fit to the data. The arithmetic mean value of the number of primary particles per aggregate

is in good agreement with that reported in the literature for similar flames.

4. Parameters describing the fractal structure of soot particles were also obtained based on the relative optical density method. The results are within the same range of the values reported in the literature for similar flames.

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