Quantification of the Physical and Optical Properties of Combustion-Generated Fractal Aggregates

by

Charles D. Litton\textsuperscript{1} and Inoka Eranda Perera\textsuperscript{1}

National Institute for Occupational Safety and Health, 626 Cochrans Mill Road, Po Box 18070
Pittsburgh, PA 15236

Combustion-generated carbonaceous aerosols are generally in the form of fractal aggregates (FA’s) with shapes that vary from long chain-like structures to much more compact, almost spherical structures, depending upon the mode or stoichiometry of the combustion process. Typically, as combustion moves from fuel-lean to fuel-rich, aggregate morphologies change from the former to the latter. Accompanying this change in morphology is a change in the chemistry of the aggregates as the percent of carbon in the aggregates also decreases. These combined changes produce radically different scattering and absorption signatures that define their radiative transfer properties. To improve our ability to predict how these optical properties change, experiments were conducted to measure both the physical and optical properties of these aggregates for both flaming and non-flaming modes of combustion. Using the aggregate property data from these experiments, numerical calculations were then performed using both the discrete dipole approximation (DDA) and the Rayleigh-Debye-Gans (RDG) approximation to generate their characteristic scattering and absorption signatures. This paper presents the experimental results, the comparison of the modeling results with the experimental results and discusses those parameters most important to obtain agreement between the modeling and the experiments.

1. Introduction

Combustion processes generate aerosols as a natural by-product with varying sizes, morphologies, and chemical compositions that depend not only upon the combustible solid, liquid or gas but also upon the mode of combustion, such as flaming or non-flaming, or the stoichiometry of the combustion process, ranging from oxygen-rich to fuel-rich. These aerosols are generally in the shape of fractals or fractal-like aggregates, with individual aggregates containing 10’s to 100’s of smaller primary particles connected in some random fashion. In general, for over-ventilated, or oxygen-rich, combustion, these aggregates appear as elongated, chain-like structures with characteristic fractal, or Hausdorff, dimensions, \( D_f \), in the range of 1.6 to 1.9. For aggregates that are produced from non-flaming or fuel-rich combustion, the structure is more compact and clumped with fractal dimensions typically in the range of 2.1 to 2.3. Knowledge of the structure, the size and the chemistry of these aggregates once expelled into the atmosphere is important in the subsequent assessment of their radiative transfer properties and also their potential to produce adverse health effects. In addition, the ability to predict or estimate the most relevant aggregate properties of these aerosols using approximations that agree well not only with experimental data but also with more detailed theoretical calculations is important in understanding the resulting impacts of these aerosols. In particular, The Rayleigh-Debye-Gans (RDG) approximation is routinely used to assess the angular distributions of scattered light and the mass scattering, mass extinction, and mass absorption coefficients for fractal aggregates (1-5).

The question naturally arises as to the accuracy of the RDG approximation and the ranges of validity relevant to size and morphology of the fractal aggregates. In order to address this
question, experimental data were acquired for a range of fractal aggregate properties. Detailed numerical calculations of the scattering, extinction and absorption of a typical fractal aggregate were made as a function of size, morphology and chemistry (via the refractive index) using DDSCAT, an algorithm using the discrete dipole approximation (DDA) developed and maintained by Professor Bruce Draine at Princeton University (2). The results of the DDA computations that best fit the experimental data were then compared to the RDG predictions using the same experimental data to assess the validity of this approximations and, if necessary, to adjust constant parameters within the RDG approximation to yield better agreement with the more detailed calculations and with the experimental data. This paper presents the most important results of this study.

2. Theory and Experiment

The experiments are described in detail elsewhere (6,7), but briefly, combustible materials were allowed to burn or smolder in a small combustion chamber and the smoke that was generated flowed into a rectangular smoke chamber where two small mixing fans produced a homogeneous aerosol distribution. Samples were then flowed from the smoke chamber to various instruments for continuous recording of data. The data acquired included angular intensity data at four forward scattering angles (15º, 22½º, 30º, and 45º) and two backward scattering angles (135º and 150º) and at monochromatic wavelengths of 635 nm and 532 nm; total scattering efficiency at a wavelength of 520 nm and light extinction at a wavelength of 532 nm; total mass concentration of aerosol; and the output of a calibrated ionization chamber that allows for the determination of number mean diameter and aerosol number concentrations. In addition, filter samples were taken for correlation with the continuous aerosol mass measurements and additional filter samples obtained for subsequent analysis using a Scanning Electron Microscope (SEM) and Transmission Electron Microscope (TEM).

The angular intensity data were used to derive the radius of gyration, $R_g$, from the forward angle scattering measurements and the fractal dimension, $D_f$, from the 45º and two backward angle scattering measurements using the standard approximations. For the calibrated ionization chamber, the relevant equations are described elsewhere for the determination of number mean diameter, $d_g$, and number concentration of the aggregate aerosols, $N$ (8). Using the measured aerosol mass concentration, the average mass of an aggregate particle, $M_a$, can then be obtained from the simple relationship

$$M_a = 1 \times 10^{-9} \frac{M}{N} \quad (1)$$

Where $M$ is the mass concentration in mg/m$^3$ and $N$ is the number concentration in particles/cm$^3$.

The mass of an aggregate containing $n_p$ primary particles, each with diameter, $d_p$, can also be expressed as

$$M_a = n_p \rho_p \left(\frac{\pi d_p^3}{6}\right) \quad (2)$$

For smoke (or soot) aggregates, the applicable fractal power law is

$$n_p = k_f (R_g/d_p)^{D_f} \quad (3)$$
where $k_f$ is the prefactor with a value of approximately 6.45

Substituting the expression for $n_p$ (Eq. (3)) into Eq. (2), and rearranging, the following equation for $d_p$ results

$$d_p = \left(\frac{6}{\pi}(M_a/(k_f \rho_p R_g D_f^3))\right)^{1/(3-D_f)} \quad (4)$$

Since all other variables appearing in Eq. 4 are known, then the primary particle diameter can be calculated in essentially real time. Determination of these parameter values is important for subsequent use in the DDA computations and in the RDG approximations.

For the RDG approximations, the following equations define the mass absorption, mass scattering and mass extinction coefficients.

$$\Sigma_{abs} = 6\pi E_m/\lambda \rho_p \quad (5)$$

$$\sigma_{sca} = (4\pi n_2(x_p)^3 F_m/\lambda \rho_p n_1)[1+(4/3D_f)k^2(R_g^2)^{D_f}/16(x_p)^2]^{D_f/2} \quad (6)$$

where $E_m$ is the imaginary component of $(m^2-1)/(m^2+2) = \text{Im}[(m^2-1)/(m^2+2)]$

$F_m$ is the square of the absolute value of $(m^2-1)/(m^2+2) = |(m^2-1)/(m^2+2)|^2$

$m$ is the complex index of refraction, $m = n + ik_e$

$x_p$ is the size parameter $= \pi d_p / \lambda$, where $d_p$ is the diameter of a primary particle and $k$ is the wave vector $= 2\pi/\lambda$

$\rho_p$ is the density of a primary particle, taken to be 1.86 g/cm$^3$ and $n_1$ and $n_2$ are the first and second moments of the aggregate size distribution.

In the case of large aggregates, $n_2 \to (n_p)^2$ and $n_1 \to n_p$ and with $k^2(R_g^2)^2 \gg 1$, Equation 16 reduces to

$$\sigma_{sca} = \left[4\pi(x_p)^3 k_f E_m/\lambda \rho_p \right][3D_f/16(x_p)^2]^{D_f/2} \quad (7)$$

The mass extinction coefficient, $\sigma_{ext}$, is the sum of the mass absorption and mass scattering coefficients, or

$$\sigma_{ext} = \sigma_{sca} + \sigma_{abs} \quad (8)$$

The expressions used to estimate the RDG angular intensity distributions are described in detail in the literature and in the interest of brevity will not be presented here (9,10).

For the DDA calculations using the DDSCAT algorithm, a fractal aggregate consisting of 74 primary spherical particles was used. For input to DDSCAT, the coordinates of the center of each primary particle are specified, along with the radius of the primary particle, an index of refraction for the primary particles, the wavelength of incident electromagnetic radiation (EMR), and the volume equivalent radius, $a_{eq}$, of the aggregate. The algorithm then computes the intensity of scattered EMR for a multitude of different orientations of the aggregate with the incident beam and averages the scattered intensities over these multiple orientations to generate an average angular intensity distribution. DDSCAT also calculates the scattering, absorption, and extinction efficiencies for the aggregate for a given set of input conditions. For the base
fractal aggregate, the primary particle radius is taken to be 0.50 units with the result that the primary particles barely touch each other at only a single point producing a chain-like aggregate with a fractal dimension of $D_f = 1.70$. By increasing the radius of each sphere while holding the coordinates of each sphere’s center constant, the primary particles begin to overlap producing an aggregate that is more compact and less chain-like.

To determine the impact of the overlap on the morphology and volume equivalent radius of the aggregate, the coordinates of the 74 primary particles were entered into an AutoCad three dimensional space and the radius of each primary particle increased. AutoCad then produces the resultant image of the aggregate to show how its morphology has changed, but more than that, subroutines in Autocad allow for the determination of the volume equivalent radius, surface equivalent radius and radius of gyration for the new overlapped particles that can be used as input into DDSCAT. To estimate the impact of overlap on the resultant fractal dimension, the data of Oh and Sorensen was used that relates the increase in fractal dimension to the overlap, where the overlap, $\beta$, is defined as the ratio of an increased primary particle radius to the base primary particle radius. Typical AutoCad drawings are shown below in Fig. 1.

\[
\begin{align*}
\beta &= 1.0 \\
\beta &= 2.0
\end{align*}
\]

![AutoCad drawings of the base fractal aggregate (\(\beta = 1\)) compared to the fractal aggregate with an overlap of \(\beta = 2\).

For comparison, the two images below are data obtained for aggregates produced from the flaming combustion of Pittsburgh seam coal (1A) and for an aggregate produced from non-flaming combustion of Douglas Fir wood chips (1B). The similarities between the AutoCad generated fractal and the actual TEM and SEM images are clearly evident and provide reasonable assurance that the DDA calculations do indeed reflect the reality of the fractal aggregates observed.
Figure 2. TEM image of an aggregate generated from flaming combustion (1A) and an SEM image of an aggregate generated during non-flaming combustion (1B).

3. Results and Discussion

In order to utilize the data obtained to assess the reliability both of the DDA calculations and the RDG approximations, the average values of the relevant aggregate properties were obtained from data from all of the flaming combustion experiments and, similarly, from data from all of the non-flaming combustion experiments. The results are presented below in Table 1.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Aerosol Source</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Flaming</td>
</tr>
<tr>
<td>( R_g ) (nm)</td>
<td>253</td>
</tr>
<tr>
<td>( d_g ) (nm)</td>
<td>148</td>
</tr>
<tr>
<td>( N ) (p/cm(^3))</td>
<td>2278688</td>
</tr>
<tr>
<td>( M_a ) (g)</td>
<td>6.80E-15</td>
</tr>
<tr>
<td>( d_p ) (nm)</td>
<td>24</td>
</tr>
<tr>
<td>( n_e )</td>
<td>1117</td>
</tr>
<tr>
<td>( M ) (mg/m(^3))</td>
<td>13</td>
</tr>
<tr>
<td>( D_f )</td>
<td>1.74</td>
</tr>
<tr>
<td>( \sigma_{\text{ext}} ) (m(^2)/g) (532 nm)</td>
<td>5.4</td>
</tr>
<tr>
<td>( \sigma_{\text{abs}} ) (m(^2)/g) (532 nm)</td>
<td>11.5</td>
</tr>
<tr>
<td>Albedo</td>
<td>0.33</td>
</tr>
</tbody>
</table>

Table 1. Average fractal aggregate properties for aggregates from both flaming and non-flaming combustion.
While there are clearly differences between the results obtained for aggregates from flaming combustion compared to those obtained for aggregates from non-flaming combustion, this aspect of the research is explained in greater detail elsewhere (7). What is of interest here is the potential of the DDA and RDG calculations, using the measured aerosol parameters, to reliably predict the measured angular intensity distributions and the measured mass scattering and mass extinction coefficients.

Figure 3. Variation in the prefactor, \( k_f \), for two values of the overlap parameter (\( \beta = 1 \) and \( \beta = 2.5 \)) and different values of the index of refraction.

Figure 4. Variation of the prefactor, \( k_f \), with the approximate fractal dimension for different values of the index of refraction.

In order to look at this question in more detail, calculations were performed using the DDA to determine the scattering efficiencies and then using the corresponding RDG approximation (either Eq. (6) or (7)) the values of the either the moment ratio, \( n_2/n_1 \), or prefactor, \( k_f \), necessary to yield agreement with the DDA calculations were determined. While there were found to be
some significant variations in the moment ratios and prefactors, depending upon the size of the aggregate, its morphology, and its index of refraction, the average values obtained were similar to those quoted in the literature. A sample of the type of variation obtained in these computations is shown below in Figures 3 and 4. In Figure 3 the prefactor is plotted vs the volume equivalent size parameter, $X_{eq}$, where $X_{eq} = 2\pi a_{eq}/\lambda$.

In principle, these calculations tend to indicate that the prefactor, since other parameters are either known or measured, is influenced by both the shape of the particle (via the overlap parameter or the corresponding approximate fractal dimension) and the absorbing or non-absorbing nature of the particle through its refractive index. For very small particles where the moment ratio, $n_2/n_1$, is valid rather than the approximate prefactor, $k_f$, the dependence on this properties is not so great as can be seen in Figure 5.

![Figure 5. Variation of the moment ratio, $n_2/n_1$, with the approximate fractal dimension for different values of the index of refraction.](image)

Clearly, ascribing certain subjective properties to the fractals of interest and then using prefactors or moment ratios indicative of these properties can significantly improve the ability of the RDG approximation to provide a more realistic and accurate prediction of the scattering and absorption properties of combustion-generated aerosols. Even in the absence of these subjective criteria and the use of a constant prefactor, the approximation is still of value and can provide reasonable estimates of the index of refraction for the primary particles comprising an aggregate.
If the approximate average fractal properties listed in Table 1 are used for both the DDA and the RDG calculations, then it is possible to define an approximate index of refraction that, in tandem with these measured parameters, produces an angular scattering signature and mass scattering, mass absorption and mass extinction coefficients that are in good to excellent agreement with the measurements. This is done in Figures 6 and 7 where the DDA calculations for the angular intensities are compared to the measured values for aggregates from both non-flaming and flaming combustion, respectively.

Figure 6. Comparison of DDSCAT calculations with angular scattering data obtained for aggregates from non-flaming combustion.

Figure 7. Comparison of DDSCAT calculations with angular scattering data obtained for aggregates from flaming combustion.
Figure 6 shows the results of these computations for non-flaming FAs with a refractive index of $m = 1.692 + 0.0375i$ while Figure 7 shows the results for flaming FAs with a refractive index of $m = 1.692 + 1.25i$, where the corresponding numerically calculated albedos are 0.884 and 0.334, respectively, in very good agreement with the measured values. For these numerical results, a volume equivalent radius of 212 nm was used for the non-flaming FAs and 190 nm for the flaming FAs. Although these values are somewhat higher than the values calculated using the data from Table 1, the qualitative agreement is quite good. For the numerically calculated curves of Figures 6 and 7, the approximate fractal dimensions (calculated from the overlap parameter) yielding the best agreement with the data are 1.79 for the flaming FAs and 2.16 for the non-flaming FAs, in excellent agreement with the experimental values cited above.

Computations were also made using the RDG approximation discussed above. For these simpler computations, the parameters used were the average values found in Table 2 and included $d_p$, $R_g$, $n_p$, $D_f$, and the volume equivalent diameter was defined by $d_{eq} = d_p(n_p)^{1/3}$ for aerosols from both the flaming and non-flaming fires. The results of the calculated angular distributions are shown below in Figure 8 for the non-flaming case where the assumed index of refraction is $m = 1.692 + 0.125i$ and in Figure 9 for the flaming case where the assumed index of refraction is $m = 1.692 + 1.25i$. The meaning of the results is self-evident in that the agreement of these calculations with the data is excellent and the agreement comparable to the more detailed DDSCAT computations.

Figure 8. Comparison of the RDG calculations with measured angular intensity data for aggregates from non-flaming combustion.
Figure 9. Comparison of the RDG calculations with measured angular intensity data for aggregates from flaming combustion.

In addition, the results of the comparison of mass scattering, mass extinction, mass absorption and albedos is shown in Table 2 below.

<table>
<thead>
<tr>
<th>Average coefficient, m²/g</th>
<th>Flaming data</th>
<th>Calculated from RDG</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \sigma_{\text{ext}} )</td>
<td>16.89 (14.17)</td>
<td>14.03</td>
</tr>
<tr>
<td>( \sigma_{\text{sca}} )</td>
<td>5.40 (5.07)</td>
<td>4.19</td>
</tr>
<tr>
<td>( \sigma_{\text{abs}} )</td>
<td>11.49 (9.09)</td>
<td>9.84</td>
</tr>
<tr>
<td>Albedo, ( \sigma_{\text{sca}}/\sigma_{\text{ext}} )</td>
<td>0.33 (0.36)</td>
<td>0.30</td>
</tr>
<tr>
<td>( \sigma_{\text{vis}} )</td>
<td>12.72 (9.95)</td>
<td>Non-flaming data</td>
</tr>
<tr>
<td>( \sigma_{\text{ext}} )</td>
<td>9.94 (8.87)</td>
<td>8.67</td>
</tr>
<tr>
<td>( \sigma_{\text{sca}} )</td>
<td>8.03 (6.99)</td>
<td>7.66</td>
</tr>
<tr>
<td>( \sigma_{\text{abs}} )</td>
<td>1.91 (1.88)</td>
<td>1.01</td>
</tr>
<tr>
<td>Albedo, ( \sigma_{\text{sca}}/\sigma_{\text{ext}} )</td>
<td>0.81</td>
<td>0.88</td>
</tr>
<tr>
<td>( \sigma_{\text{vis}} )</td>
<td>6.71 (5.58)</td>
<td></td>
</tr>
</tbody>
</table>

Table 2. Measured coefficients versus those calculated using the RDG approximation

In this table, the average values in parentheses exclude the larger coefficients measured for the combustion sources of polypropylene and No. 2 diesel fuel, since the aerosol data from these two combustibles have a significant impact on the average. While there is not perfect agreement between the measured and calculated coefficients, it is believed that this agreement could be improved through minor changes in some of the parameters, including the index of refraction. But the fact that the calculated values are so close to those measured when using the parameter
values obtained experimentally in Table 1 is remarkable, serving to reinforce the general applicability of the RDG approximation as an excellent tool for assessing the optical properties of fractal aggregates.

4. Conclusions

Both the detailed DDA calculations and the experimental data can be reasonably predicted using the simpler RDG approximation for fractal aggregates typical of those produced from combustion processes. While comparison of the detailed numerical calculations tend to indicate that the fractal power law and the resultant RDG approximation for scattering efficiency are dynamic functions of particle size, morphology and chemistry, the use of average prefactors coupled with the selection of appropriate values of the refractive index can yield valid predictions of the radiative transfer properties of these aggregates. Suggestions for the future would include expanding the DDA calculations to include fractal aggregates with larger numbers of primary particles and using SEM/TEM data to better define the primary particle diameters and degrees of overlap. The research to further develop these models using experimental data is continuing.

References


