Nucleation and Growth and Carbonaceous Nano-Sized Particles

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Introduction

The details of the chemical mechanism responsible for the formation of nano-sized carbonaceous particles during the combustion of hydrocarbon fuels has illuded researchers for a long time. Briefly, fuels dissociate to form smaller molecules and radicals such as methyl. These react with oxygen to form water and carbon dioxide. However, when the carbon-to-oxygen ratio is sufficiently high there is not enough oxygen to oxidize all of the carbon. Under these conditions the hydrocarbon molecules form the aromatic molecule benzene and polycyclic aromatic hydrocarons (PAH) such as pyrene. Particle nuclei are thought to form when two pyrene molecules or similar PAH species coalesce to form stable particles. Up until now, is has not been possible to monitor the process of particle nucleation and the subsequent growth of these nuclei. Small-angle x-ray scattering is an ideal technique for in situ monitoring of particle nucleation and growth in combustion devices. It is most sensitive to particles in the size range from 1 to 100 nm [1]. Below we present some of our preliminary SAXS results aimed at providing more information about the detailed chemiical mechanism of soot formation.

Methods and Materials

A McKenna burner with a inner sintered disk of ¾" diameter and a ¼" wide outer disk was used to support a premixed laminar flame. This flame is shown in Fig. 1. The flame front, which is not visible in this figure, is stabilized at about 1 mm above the base of the burner by adjusting the speed of the flow of the premixed gases. The flow rates are ethylene 0.23 SLPM, oxygen 0.28 SLPM, and argon 0.93 SLPM. The speed of the premixed gas at the base of the burner is 84 mm-s^{-1} and the carbon-to-oxygen ratio is 0.82. The time-dependent behavior of the chemistry that produces carbonaceous particles may be determined by SAXS measurements at different heights above the base of the burner. This flame is similar to the flame studied bu Xu, Sunderland, and Faeth [2] and Zhao, Yang, Johnston, Wang, Wexler, Balthasar, and Kraft [3].

The experiments were performed at the 12 ID beam line [4]. A nine element CCD mosaic detector [5] was located 1.96 m from the flame and captured scattering profiles in about 1 sec. The incident x-ray beam was 246 by 70 μm and had an average flux of 1.6 x 10^{14} x-ray-s^{-1}-mm^{-2}. The SAXS apparatus [6] was calibrated by replacing the fuel-oxidizer mixture with octafluorocyclobutane [7]. Over 300 profiles were obtained at each of ten different heights that ranged from 4 to 16 mm from the base of the burner. After subtraction of the parasitic component of the scattered intensity, the Abel inversion [8] was performed to extract the local scattering densities at the center of the flame, which are shown in Fig. 2.

Fig. 1. Premixed flame of ethylene, oxygen, and argon. The x-ray beam is transported in vacuum by the two aluminum tubes.
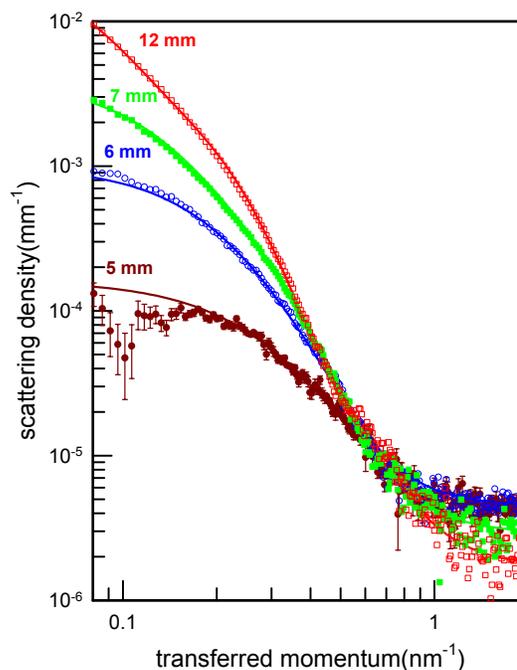
Fig. 2. SAXS scattering profiles at different heights above the base of the burner. The solid lines represent the least squares fit.

Results

The profiles in Fig. 2 were then analyzed in two steps. First, we assumed all of the particles are spheres with a constant electron density and applied the maximum-entropy technique [9] to determine the differential size distribution of the particles [10]. These calculations showed that there were two unique distributions plus a contribution from agglomerates. Second, we choose analytic functions for the two size distributions that mimic the previous results; the Schultz distribution [11] for the smaller incipient particles and the log-normal distribution for the larger primary particles. Again, we assumed the particles are spherical. In addition, Beaucage's unified expression [12] was used to model scattering from the aggregates and Guinier's expression, with a radius of gyration of 0.2 nm, was used to model the smaller species. Each profile was then reduced with a non linear least squares fit [13] to determine the contribution from the incipient, primary, and agglomerated particles and their properties. Dobbins has identified two distinct types of carbonaceous particles in hydrocarbon combustion [14]. One type, which is referred to as "tar" or "transparent" by some authors, has a liquid like character, an assumed density of 1.2 gm/mL, a C-to-H ratio of about two, and does not absorb or emit visible light. The other, which is referred to as carbonaceous or mature soot, has a density of about 1.8 gm/mL, a C-to-H ratio of six to eight, and absorbs strongly in the visible spectral region. From these results we calculate that the electron density of the smaller incipient particles is 348 nm^{-3} while for the larger primary particles it is 546 nm^{-3}. This distinction is consistent with the TEM observations performed on the same flame [15].

These results illustrate the power of absolute, *in situ*, SAXS measurements for the study of particle nucleation and growth and represent the first truly *in situ* measurements of particles between 1 and 15 nm. Particles were not detected at a height of 4 mm. From 5 to 12 mm both incipient and primary particles are detected. Aggregates were not detected at 5 mm, however, they were at all other heights. The scattering parameters for the aggregates are given in Table 1.

Table 1. Parameters of the soot aggregates as determined by Beaucage's unified equation, ref. 12.

height mm	I_A mm^{-1}	R_g nm	B_A
6	7.50E-4	10.0	8.20
7	2.50E-3	15.0	6.41
12	2.20E-2	25.0	4.51

At 14 and 16 mm only primary particles and their aggregates were detected. These results are consistent with the recent SMPS measurements of Zhao et al. [3], which were performed on a nearly identical premixed laminar flame of ethylene. However, whereas their Scanning Mobility Particle Sizer (SMPS) has a lower detection limit of 4 nm, SAXS can detect much smaller particles. It is the ability of SAXS to determine absolute particle size distribution functions, either by assuming a function for the distribution, or extracting the distribution with the maximum-entropy technique that allows us to use SAXS to study the fundamental properties of the chemical reaction

mechanism responsible for soot formation and the interplay between chemistry and fluid dynamics.
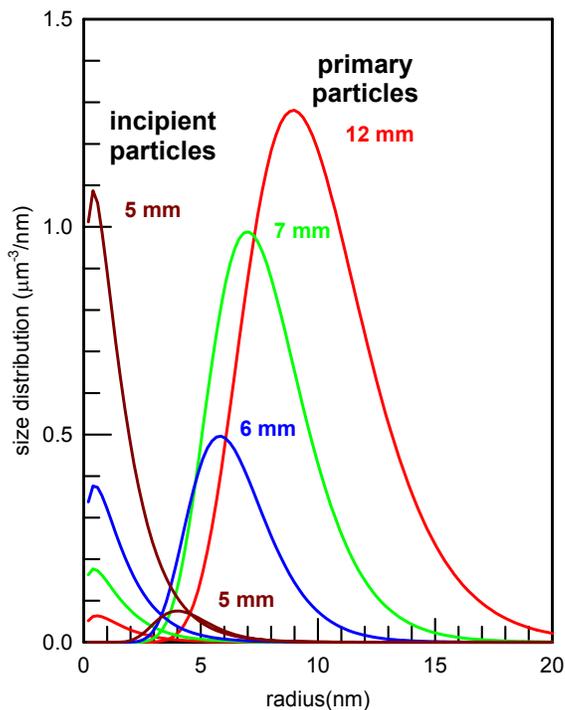
Fig. 3. Differential size distribution of carbonaceous particles determined from the SAXS profiles shown in Fig. 2. For clarity, the distribution for the primary particles has been divided by ten.

Discussion

In addition to the particle size distributions we may extract the mean diameter of the primary particles and the soot volume fractions of both the incipient and primary particles. The results for the mean diameter are shown in Fig. 4. In addition to results from SAXS we have included the TEM results on this flame [15], Zhao, et al's SPMS results [3], and Xu, Sunderland, and Faeth's TEM results [2]. Note, at 12 mm and beyond all of the results agree reasonably well. The soot volume fractions are shown in Fig. 5. Again, for comparison we include the SMPS results [3] and results from optical absorption measurements [2]. Here, we simply note that the apparently large discrepancy between the SMPS and SAXS results may be explained by the fact that the SMPS apparatus has a lower detection limit of 4 nm. The SAXS measurements indicate that at 5, 6, & 7 mm a significant fraction of the particles are smaller than 4 nm. Therefore, it is not surprising that the SMPS results underestimate the soot volume fraction.
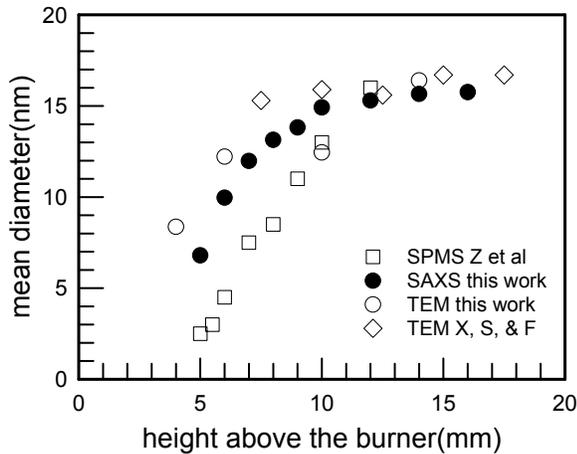
Fig. 4. Mean diameter of primary particles. SMPS results are from ref. 3 and TEM, X, S, & F are from ref. 2.
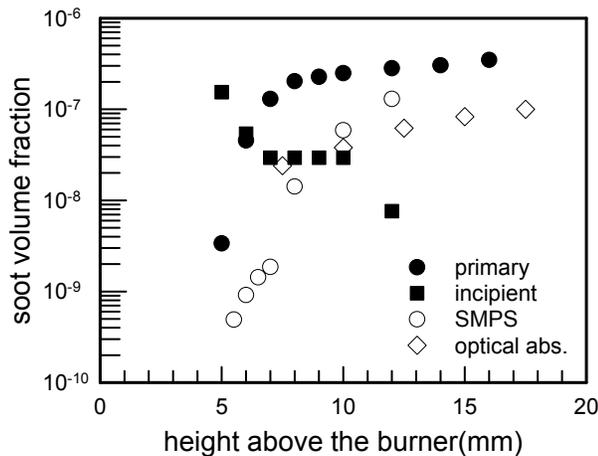
Fig. 5. Soot volume fractions. SMPS results are from ref. 3 and optical absorption results are from ref. 2.

The good agreement between SAXS, SMPS, and TEM measurements of the mean diameter of the primary particles at heights greater than 12 mm above the burner is not only encouraging, but also informative. We also note that our SAXS results for the primary particles are consistent with the primary particles measured by SAXS on *ex situ* pellet soot generated in a small diesel engine test facility. [16] They are also consistent with the smaller subunits measured by TEM [17]. The decrease in the number of incipient particles as the measurement location moves above the burner, along with the increase in the primary particle size, suggest that the smaller incipient particles observed with *in situ* SAXS are the "tar" like particles discussed by Dobbins and/or the "transparent" particles observed by D'Alessio and his colleagues [18] and [19]. This observation suggests that observations near the critical equivalence ratio will be very informative.

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