Spatially Resolved SAXS Studies of Soot in a Diffusion Flame

J.P. Hessler, S. Seifert, R.E. Winans

Chemistry Division, Argonne National Laboratory, Argonne, IL, U.S.A.

Introduction

A comprehensive model that is capable of predicting the nucleation and growth of soot over a wide range of chemical and physical conditions is just beginning to emerge and has been documented in various workshops [1] and symposia [2]. This year we performed, for the first time, *in situ*, spatially resolved, small-angle x-ray scattering (SAXS) studies of soot formed in a diffusion flame. Both *ex situ* and *in situ* techniques have been used to characterize the soot formation process. Generally, the *in situ* measurements have been performed with light in the ultraviolet, visible, or infrared spectral regions and include absorption [3], induced [4] and natural [5] incandescence and wide-angle elastic scattering [6]. These scattering measurements provide information on the morphology of particles that are larger than 15 nm, while absorption and incandescence measurements have been used to detect particles with mean radii between 1.8 and 10 nm. We note that with light in the ultraviolet or visible spectral region, it is difficult to extract information on the morphology of particles in the 1- to 100-nm region. Transmission electron microscopy provides this information [7], but it is an *ex situ* technique. SAXS is ideally suited to provide *in situ* measurements in this important region [8]. In 1986, W.A. England presented the first *in situ* SAXS studies of soot morphology [9]. Unfortunately, he used a second-generation x-ray source, and his exposure times had to be quite long. Recently, we reported the first use of a third-generation x-ray source that utilizes an undulator to enhance the intensity of the x-rays and thereby allows us to obtain a scattering profile in a few seconds [10]. This year, we performed more detailed measurements that allow us to extract a spatially dependent background, which we attribute to a temperature/density gradient that is produced by the flame front, and to perform Abel inversions, which provide radial information from a series of line-of-sight observations. Our results may be described in terms of a bimodal distribution of soot particles. The larger particles correspond to primary particles, while the smaller particles are polycyclic aromatic hydrocarbons (PAHs), which are known to be the precursor molecules of soot.

Methods and Materials

Our SAXS apparatus has been described previously [11]. Briefly, it consists of a high-brilliance undulator, a double-crystal monochromator, and the components needed to transport, focus, define, and monitor the incident x-ray beam. Typically, 10^{12} x-rays per second are incident on the sample, which is located at BESSRC beamline station 12-ID-C at the APS. The fuel, propylene, is injected into the center of a flat-flame burner [12]. A stable cylindrical flame that showed incandescence up to a height of approximately 100 mm was used. A total of 136 SAXS profiles were obtained at 33 different heights above the tip of the burner by using two linear translation stages to move the flame with respect to the beam of x-rays.

The scattering measurements obtained with this system are line-of-sight measurements that we refer to as the "integrated scattering intensity," which may be written at follows:

$$I(q,X) = 2\int_X^\infty \frac{r \cdot i(q,r)}{(r^2 - X^2)^{1/2}} dr \qquad (1)$$

where $I(q,X)$ is the scattering intensity at the transferred momentum q in the laboratory coordinate system, $i(q,r)$ is the local scattering intensity at the same transferred momentum in the cylindrical coordinate system centered on the flame, X is the distance from the center of the flame in the laboratory system, and r is the distance in the cylindrical system. The local scattering intensity, $i(q,r)$ is given by the inverse Abel transformation:

$$i(q,r) = -\frac{1}{\pi}\int_r^\infty \frac{[dI(q,X)/dX]}{\left(X^2 - r^2\right)^{1/2}} dX \ . \qquad (2)$$

The Abel transform and its inverse have been discussed by many authors; we use the approach developed by Dasch [13].

Results

This year, our first significant observation was that diffusion flames have a spatially dependent background that must be properly treated when scattering results are being analyzed. Our second observation was that all of our scattering data may be described in terms of a bimodal distribution of particles. By performing SAXS experiments on an effusive beam of naphthalene, $C_{10}H_8$, and its dimmers, trimmers, and tetramers, we established that the smaller particles are PAHs [14].
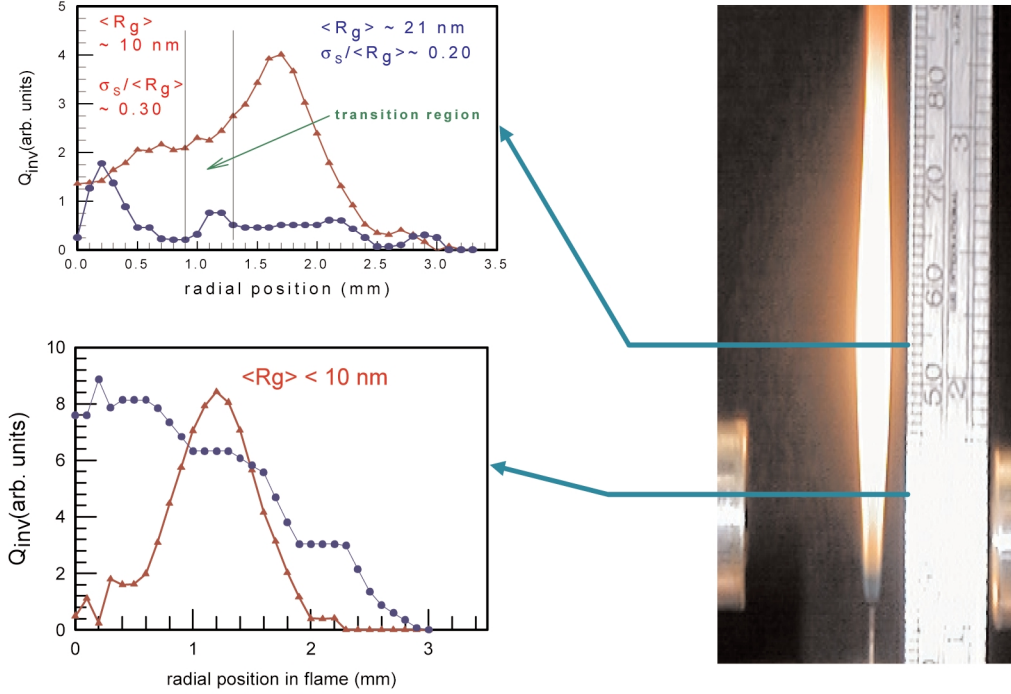
Information about the number density of the two

FIG. 1. Radial dependence of the relative concentrations of primary soot particles (red triangles) and PAHs (blue circles) at two different heights in a propylene diffusion flame.

species in the bimodal distribution may be obtained by calculating the Porod invariant,

$$Q_{inv} = \int q^2 i(q) dq \; . \tag{3}$$

By subtracting the integral associated with the PAH species from the total integral, we obtained a quantitative picture of the relative concentrations of each of the two species that make up the bimodal distribution of soot particles. Our results for two different locations in the diffusion flame are shown in Fig. 1. At the lower position, the relative concentration of PAH species dominates, and the primary particles are uniformly distributed about the flame front. At the widest part of the flame, the relative concentration of the primary particles dominates, and their properties depend upon their position within the flame. Near the center, they are relatively small and quite dispersed, with $\langle R_g \rangle$ of ~10 nm and $\sigma/\langle R_g \rangle$ of ~0.3. The mean value of the radius of gyration is $\langle R_g \rangle$ and the width of the distribution is σ. Between 0.9 and 1.3 mm from the center, a transition region is observed. At larger distances, the primary particles are larger and less dispersed, with $\langle R_g \rangle$ of ~21 nm and $\sigma/\langle R_g \rangle$ of ~0.2.

Discussion

These results clearly demonstrate that SAXS can provide detailed information on the spatial dependence of the distribution of soot particles formed during combustion. This information has allowed us to identify a bimodal distribution in the relative concentrations of the soot species and begin to map the spatial dependence of the two types of species. We are now in a position to design experiments that will overlap previous measurements with optical techniques and address some of the fundamental issues of soot inception and formation.

Acknowledgments

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