Small-Angle X-ray Scattering Studies of Soot Inception and Growth

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Introduction

The incomplete combustion of hydrocarbon fuels leads to the production of soot. A comprehensive theory or model that is capable of predicting the inception and growth of soot over a wide range of chemical and physical conditions is just beginning to emerge. Such a model is needed to help reduce the health hazards associated with soot production, improve the radiative transfer of energy in industrial applications, and devise efficient production process that use soot in various applications. The high spectral intensity of x-rays produced by the undulator at the Basic Energy Sciences Synchrotron Radiation Center of Argonne's Advanced Photon Source has allowed us to perform small-angle x-ray scattering (SAXS) studies of the initial distribution of soot particles formed by various fuels. SAXS provides an *in situ* probe of the morphology of soot in the region between 1 and 100 nm, complements the *ex situ* technique of electron microscopy, and bridges the gap between measurements of specific chemical species and wide-angle light scattering studies of larger soot particles.

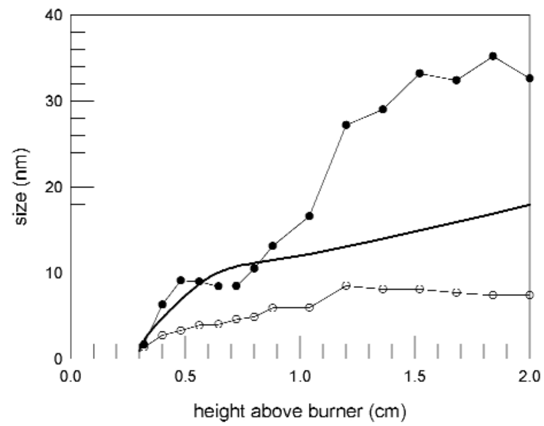

FIG 1. Results of a reduction of the scattering intensities from a toluene flame. The solid circles represent the mean diameter of a Shultz distribution and the open circles the square root of the second moment or dispersion of the distribution. The thick solid line represents a greatly simplified simulation of the formation of soot by toluene.

Methods and Materials

Complex fuels such as toluene, methylcyclohexane, hexane, and biphenyl in hexane have been studied in a flat-flame burner that supports a CH_4/H_2/air or CO/H_2/air diffusion flame stabilized by N_2 coflow.[1] This burner produces a nearly constant temperature region above the flame where the pyrolysis and combustion of the fuel occurs. Simple fuels such as acetylene, ethylene, and propylene have been studied in laminar flames in air. Kinetic information is obtained by performing SAXS measurements of the scattered intensity profile as a function of the height above the burner.[2] A mosaic detector of nine CCDs is used to measure the intensity of the scattered x-rays.[3]

Results

Toluene is known as a fuel that efficiently produces soot and is one of the first fuels we studied. The general behavior of the complex fuels is quite similar and indicates a polydispersed system for scattering lengths below 0.6 nm^{-1}. Scattering profiles for $0.075 \leq q(nm^{-1}) \leq 0.4$ were reduced with the expression for a Schultz distribution of polydispersed spheres.[4] The results of this reduction are summarized in Fig. 1. The solid circles represent the mean diameter and the open circles the square root of the dispersion. The solid line represents our simulation of soot formation that uses the mechanism and model developed by M. Frenklach and his colleagues.[5] The early part of toluene dissociation was modeled by the reaction mechanism for the pyrolysis and oxidation of toluene given by Alexiou and Williams.[6] The only points we would like to make with this comparison are that SAXS provides information in the early regions where the model is the most sensitive to slight changes of parameters and that the smallest of these is a factor of 10 smaller than previously detected with Lorentz-Mie scattering.

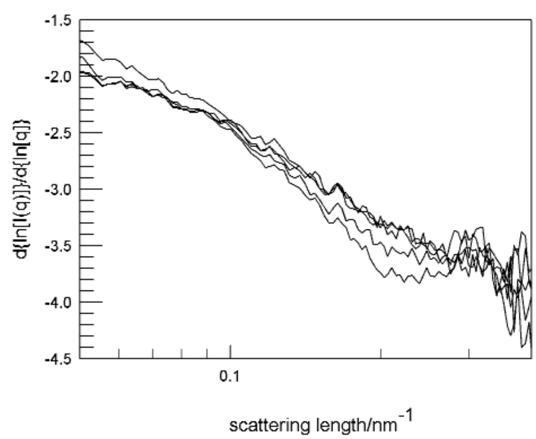

FIG 2. Test for a power law region d{ln[I(q)]}/d{ln[q]} as a function of scattering length from an acetylene flame as a function of distance above the tip of the acetylene inlet tube. The profiles were taken 3.5, 5.5, 9.5, and 15.5 mm above the tip of the tube used to introduce the acetylene. These positions correspond to reaction times of 35, 55, 95, 155, and 195 ms, respectively.

Under fuel-rich conditions, acetylene is known to produce copious amounts of soot and has been studied by many authors. The profiles at the lower scattering lengths, $q \leq 0.7$ nm^{-1}, behave similarly, while at higher scattering lengths they differ significantly. The similarities become even more apparent when we plot d{ln[I(q)]}/d{ln[q]} as a function of the scattering length for the region $q \leq 0.4$ nm^{-1} (Fig. 2). Here, we see that the slopes change monotonically and smoothly as we move to lower scattering lengths, and they are independent of the height above the burner. Furthermore, all of the curves are approaching a value of -1.8, which is expected for fractal aggregrates.[7]

Discussion

These results demonstrate that our *in situ* measurements agree with previous *ex situ* measurements and provide new information that may be associated with elementary particles. We conclude by noting that the forward Abel transform must be used to obtain the radial dependence of the observed scattering profiles. Once this has been accomplished, a detailed description of the morphology of the soot inception and formation may be developed.

Acknowledgments

The work presented here would not have been possible without the cooperation of the staff of the Basic Energy Sciences Synchrotron Radiation Center. Mark A. Beno, Guy Jennings, and Jennifer A. Linton were particularly helpful. This work and use of the Advanced Photon Source was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. W-31-109-ENG-38.

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