Ultrafine Combustion Aerosol Generator*

T. G. Cleary, G. W. Mulholland, L. K. Ives, and R. A. Fletcher
National Institute of Standards and Technology, Gaithersburg, MD 20899

J. W. Gentry
Department of Chemical and Nuclear Engineering, University of Maryland, College Park, MD 20742

We are able to produce a narrowly distributed combustion aerosol with a mean particle size of about 10 nm by operating a laminar diffusion burner with acetylene fuel in the nominal "presooting" condition. Number concentrations of approximately 10^6 particles/cm^3 are obtained. The mean particle size obtained by transmission electron microscopy (TEM) and by diffusion battery (DB) is 7 nm and 10 nm, respectively. Both measurements indicate a narrow size distribution with a geometric standard deviation of less than 1.4. Laser microprobe mass spectroscopy (LAMMS) indicates that the particles are composed of phosphorous and sulfur compounds, arising from acetylene fuel impurities, in addition to carbonaceous material.

The sooting tendencies of laminar diffusion flames are often characterized by the height at which the diffusion flame starts to emit a stream of particles (Glassman, 1987). For acetylene we observe a "visible" (to the unaided eye) sooting point that occurs sharply as the fuel flow is increased from 0.57 cm^3/s (no visible soot) to 0.58 cm^3/s (flame visibly soot). The combustion aerosol described here is produced at fuel flow rates below this "visible" sooting point. To our knowledge this is the first time that steady-state generation of nearly monosize ultrafine aerosols has been observed in a diffusion flame.

The laminar diffusion burner (Figure 1) used in our study is based on the design of Santoro et al. (1983). The burner produces a constant particulate output for several hours. This burner has also been used to produce a constant output of smoke agglomerates by operating above the sooting point (Samson et al., 1987; Cleary, 1989). Commercially available acetylene with a minimum purity of 99.6% (Matheson[1] purified cylinder acetylene) is burned in filtered air (flow rate fixed at 40 L/min) with no particles detected prior to ignition. The acetylene flow rate for this study was fixed at 0.47 cm^3/s.

During the start-up of the generator, care is taken to minimize the possibility of a deflagration of a fuel-air mixture. First the chimney is removed, then the fuel and air flow rates are set. The fuel is ignited, then the chimney is replaced and bolted to the burner assembly.

[1] Certain commercial equipment, instruments, and materials are identified in this article to specify adequately the experimental procedure. In no case does such identification imply recommendation or endorsement by the National Institute of Standards and Technology or University of Maryland, nor does it imply that the material or equipment identified is necessarily the best available for the purpose.

0278-6826/92

Aerosol Science and Technology 16:166-170 (1992)
Published 1992 by Elsevier Science Publishing Co., Inc.

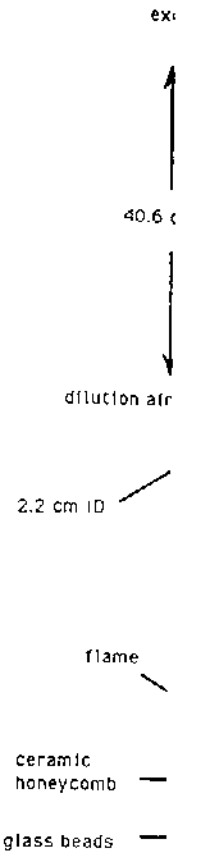

FIGURE 1. Sch
generator is cons

The burner
particle samp
croscopy. Pre
sample for the
stream from t
precipitator we
up to 1 hour
did not yield a
smoke was col
support grid by
stream 5 cm a

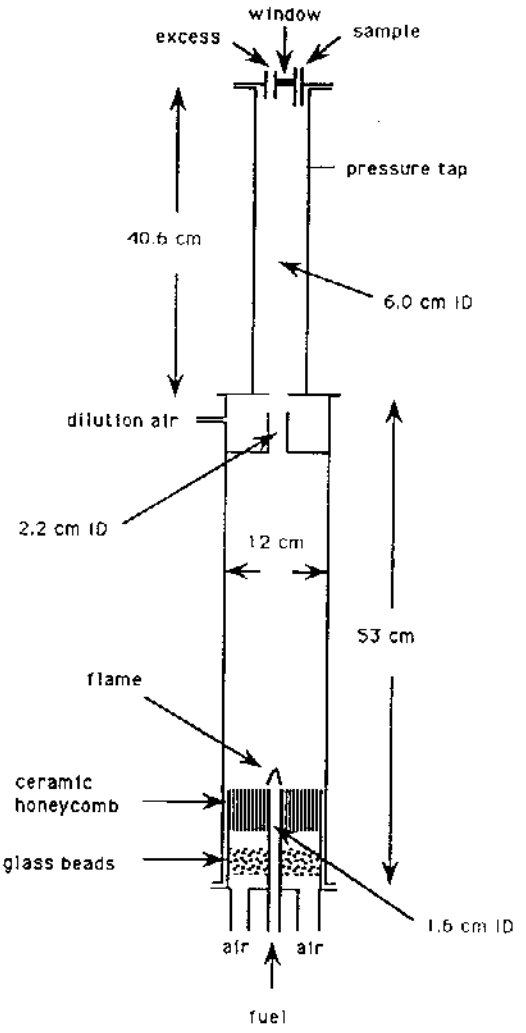

FIGURE 1. Schematic of smoke generator. The generator is constructed from brass.

The burner chimney was removed during particle sampling for the electron microscopy. Previous attempts to collect a sample for the electron microscopy downstream from the generator using a thermal precipitator were unsuccessful. Sampling for up to 1 hour with the thermal precipitator did not yield a sufficient particle load. The smoke was collected on a TEM carbon film support grid by placing the grid in the smoke stream 5 cm above the flame with the grid surface perpendicular to the fluid flow. The grid was held for 1 second above the flame and then removed for 5 seconds. This process was repeated several times to obtain an adequate loading on the grid. The sampling grid was a standard electroformed copper 200 mesh disk. A thin, electron-transparent carbon film supported by the grid provides a substrate for the particles. The particles are driven to the grid mainly by thermophoresis. Particles were observed to deposit very close to the copper grid bars. The thermal inertia of the copper keeps this region cooler while in the heated stream. In Figure 2 the transmission electron micrograph (taken with a Philips EM 430, operated at 300 kV) shows that the particles are mainly spherical with few agglomerates. A total of 172 particles were sized from the micrographs to obtain a log mean number diameter of 7 nm with an associated geometric standard deviation of 1.4.

A DB was used to measure diffusion coefficients, and thus the size, of the particles. The instrument used in this study consisted of glass capillary array stages whose channels have diameters of 25 or 50 μm and lengths from 5 to 15 mm (Brown et al., 1984). The penetrations (ratio of outlet to inlet number concentration) measured at a number of aerosol flow rates for several array stages were processed to determine "hypothetical diffusion coefficients" of monodisperse aerosols having theoretical penetrations equal to the experimental values. These data are plotted in Figure 3. The area under a curve through the data points is the log mean diffusion coefficient. Also, the variance can be determined from the intercept. For acetylene flow rates below the "visible" sooting point, the mean particle diameters were found to be essentially independent of acetylene flow rate with values between 9 to 12 nm. For an acetylene flow rate of 0.47 cm^3/s, the log mean number diameter was 10.1 nm and the log mean standard deviation was less than 1.4. The larger particle size obtained with the DB

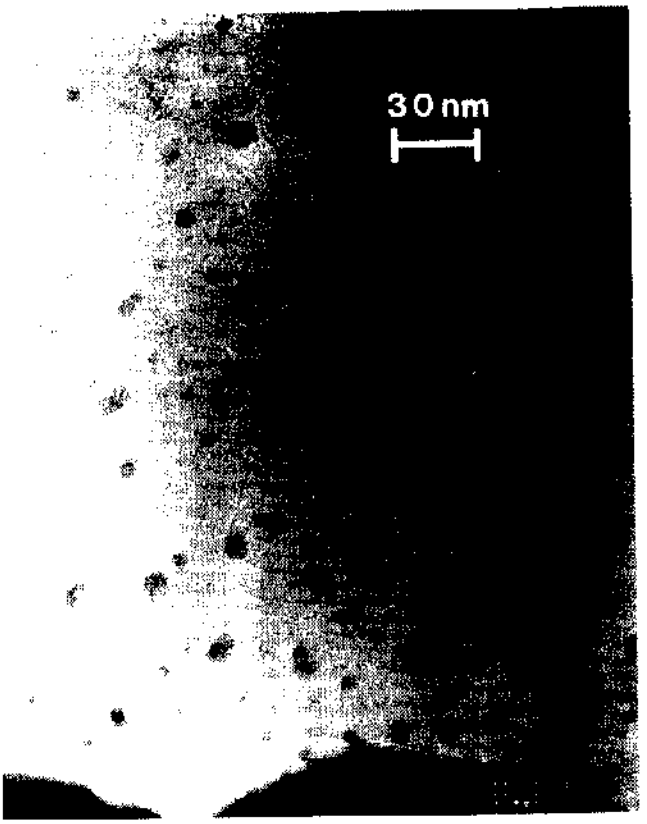

FIGURE 2. Transmission electron micrograph of the ultrafine smoke particles.

compared with the TEM size may be due to coagulation as the particles move through the burner chimney and to diffusion losses.

The particle composition was examined by sampling the particles a few centimeters above the flame on a prewashed quartz cover slip for 3 hours and analyzing the particles deposited on the cover slip with a laser microprobe mass analyzer. A similar method was used for analyzing soot particles on quartz fibers (Currie et al., 1987; Fletcher, 1989). The laser microprobe mass analyzer utilizes an Nd:YAG laser to ablate and ionize particles, and a time-of-flight mass spectrometer to analyze the mass of the ionized material (Hercules et al., 1982). Figure 4 is a LAMMS spectrum of the ultrafine smoke, with the carbon cluster peaks corresponding to C_3^- to C_9^-, an HSO_4^- peak at 97, and phosphorous oxide peaks at 63 (PO_2^-) and 79 (PO_3^-). The origin of the phosphorous and sulfur is most likely the acetylene fuel, which contains phosphine (about 10 ppm) and sulfur compounds (about 5 ppm) (Matheson Gas Data Book, 1966).

The aerosol generator described above is a simple design and has a constant output. The generator may be used as a particle source for researchers interested in studying ultrafine aerosols. It has been shown to produce nearly monosized combustion particles approximately 10 nm in diameter at concentrations of 10^6 particles/cm^3. The key design feature of the generator is operating the burner at acetylene flow rates corresponding to presooting conditions. The presence of certain trace contaminants in the acetylene fuel may be necessary for the production of the ultrafine particles. It may be possible to use a variety of fuels and introduce parts per

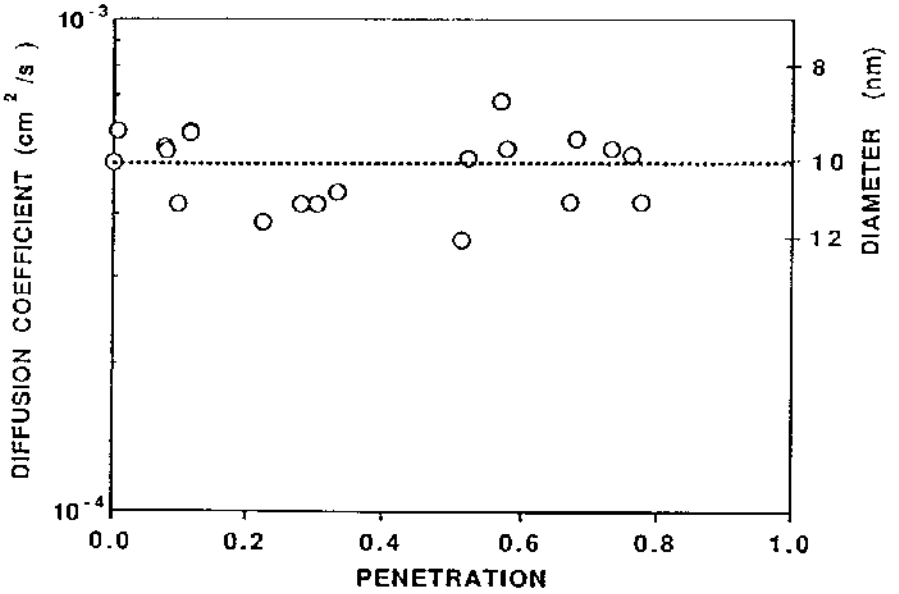

FIGURE 3. DB results for the ultrafine aerosol. The dashed line corresponds to monodisperse particles with diameters of 10.1 nm.

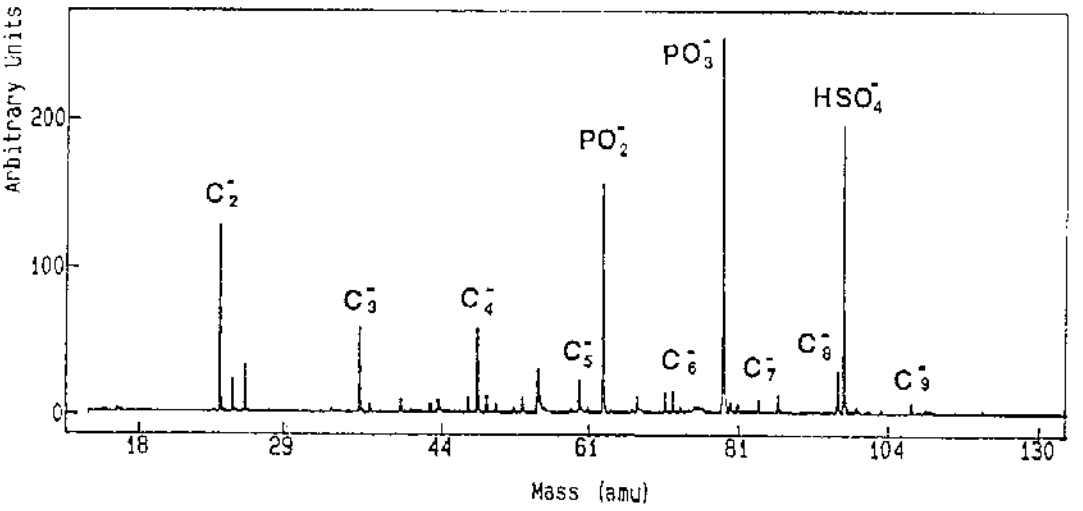

FIGURE 4. LAMMS negative ion spectrum of the ultrafine particles.

million amounts of gaseous inorganics to produce other ultrafine particles under pre-sooting conditions.

REFERENCES

Brown, K. E., Beyer, J., and Gentry, J. W. (1984). *J. Aerosol Sci.* 14:133–145.

Cleary, T. G. (1989). Measurements of the Size Distribution and Acrodynamic Properties of Soot. Masters thesis. University of Maryland.

Currie, L. A., Fletcher, R. A., and Klouda, G. A. (1987). *Nucl. Instrum. Methods Phys. Res.*, Sect. B 29:346.

Fletcher, R. A. (1989). *Anal. Chem.* 61:914.

Glassman, I. (1987). *Combustion*. Academic Orlando, Fla, p. 366.

Hercules, D. M., Day, R. J., Balasamugan, K., Dang, T. A., and Li, C. P. (1982). *Anal. Chem.* 54:280A.

Matheson Gas Data Book. (1966). The Matheson Company, Inc. East Rutherford, New Jersey,

Samson, R. J., Mulholland, G. W., and Gentry, J. W. (1987). *Langmuir*. 3:272–281.

Santoro, R. J., Semerjian, H. G., and Dobbins, R. A. (1983). *Comb. and Flame* 51:203–218.

Received February 20, 1991; accepted November 14, 1991.