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Combustion and Flame 144 (2006) 730–743
Combustion and Flame
www.elsevier.com/locate/combustflame

A comparison of soot size and charge distributions from ethane, ethylene, acetylene, and benzene/ethylene premixed flames

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Received 15 November 2004; received in revised form 1 August 2005; accepted 3 September 2005

Available online 17 November 2005

Abstract

The size and electrical charge distributions of soot particles generated in rich premixed flames are examined using a nano-differential mobility analyzer (nDMA). The aim is to investigate how these distributions vary with the choice of fuel, diluent, and flame gas velocity. The measured soot size distributions are typically bimodal. The dynamics of the upper size mode is qualitatively independent of the fuel. At increasing heights above the burner this mode increases in diameter and volume fraction, but decreases in number concentration, as expected from surface growth and coagulation. At about 6 mm above the burner a small fraction of the particles, $<10\%$, acquire a bipolar charge. The charge is associated with the upper mode, where the fractions of positive and negative particles evolve to a Boltzmann distribution, whereas the lower mode remains electrically neutral. The existence of the lower mode depends sensitively on the choice of fuel, the flame gas velocity, and the diluent. Comparison to model calculations of flame structure reveals that as each of these are varied, the lower mode exhibits an inverse correlation with temperature, hydrogen atom, and pyrene concentrations.

Keywords: Soot; Nanoparticles; Charge; Combustion particles; Size distribution

1. Introduction

Recent studies have begun to apply electrical mobility measurements of particle size to investigate soot formation in flames [1–3]. This approach differs in a number of ways from the traditional methods of light scattering [4–9] and transmission electron microscopy (TEM) [8,10,11]. Light scattering and extinction provide noninvasive probes of soot number density and volume fraction. These optical methods respond to the sixth and third moments of the size distribution; consequently, large particles in the tail of the distribution heavily weight the derived information on number and volume and can obscure the small size end of the distribution. Soot is typically collected for TEM analysis using thermophoretic sampling. The TEMs provide a very useful visualization of the primary soot particles and their aggregates; however, construction of size distributions is hampered by the overlap of primary particles that occurs in two-dimensional images of soot aggregates [12,13].

Electrical mobility analysis of soot size relies on sampling particles from the flame and transporting them to the differential mobility analyzer (DMA).

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0010-2180/$ – see front matter
doi:10.1016/j.combustflame.2005.09.007

Recent advances in sampling techniques [2,14] have succeeded in quenching flame chemistry and avoiding soot aggregation during transport. Particles analyzed by the DMA are counted; thus, in contrast to light scattering, the mobility measurements are inherently number based. The soot volume fractions calculated from these mobility size distributions are in good agreement with simultaneous extinction measurements [1], which appear to validate the DMA approach. However, the same is not true for particle number concentrations.

The electrical mobility measurements [1,2,14] provide direct support for the growing evidence that soot size distributions are in general bimodal. They reveal in all flames an upper mode of relatively larger particles that grow with increasing height above the burner, as expected from optical and TEM soot data, and from the prevailing model of hydrogen abstraction–carbon addition (HACA) [15]. But under many conditions, correlating with relatively cooler flames, the DMA data show a lower size mode of particles in the 2–5 nm range that persist high above the burner, but appear not to grow as a function of height. This lower mode is ordinarily not evident in optical studies, but D'Alessio and co-workers [16,17] found an excess UV extinction to remain after accounting for the absorption by gas-phase components and attributed this to combustion formed organic nanoparticles. Sgro et al. [18] and Barone et al. [19] subsequently provided additional evidence for these particles using electrospray differential mobility analysis and atomic force microscopy of soot collected from flames. Very recent photoionization mass spectrometry data from low-pressure flames by Grotheer et al. [20] and small-angle X-ray scattering measurements by Hessler et al. [21] further corroborate the notion that two types of soot particles can coexist in flames.

Because the DMA measures the electrical mobility of particles, it is inherently well suited for examining the electrical charge of combustion-generated soot. Our earlier work [14,22] shows that, whereas the upper mode contains numerous charged particles, up to 30% positive and 30% negative, the lower mode remains electrically neutral. Although the number of particles decreases with height, the fraction of charged particles and the number of charges per particle increase. The particle evolution is such that it preserves a Boltzmann charge distribution. This behavior is shown to be consistent with a coagulation model that includes Coulomb interactions between the particles [22].

The behavior of the lower mode is different. Besides remaining neutral, previous work shows that, with increasing height above the burner, this mode retains a geometric mean diameter below 5 nm and remains at relatively constant intensity [2,14]. D'Anna et al. [23] and Zhao et al. [24] have begun to investigate how combustion models can explain the bimodal nature of the soot size distribution. Such efforts to improve soot models would benefit from experimental measurements exploring a wider range of combustion conditions than the premixed ethylene flames that have been examined to date. Thus, the purpose of the present paper is to broaden our database of soot size distribution measurements to a variety of different fuels that represent aliphatic, olefinic, acetylenic, and aromatic chemical classes. The experiments described herein explore how fuel choice affects the presence of the lower mode, as well as the extent to which the soot particles in the upper mode become charged. Measurements are reported that investigate the influence of flame gas velocity on the bimodal shape of the size distribution, and that examine the effect of changing the diluent in the feed gas from Ar to N_2 and CO_2.

2. Experimental methods

2.1. Flame generation and soot sampling

The premixed flames studied in the present work were generated using a 6-cm-diameter, water-cooled, sintered bronze plate McKenna burner. Gaseous fuel and O_2 flows were controlled by Tylan flow controllers adjusted to maintain a C/O ratio of approximately 0.67 for all of the flames studied. Ethane (>99.99%) and ethylene (>99.5%) were used as delivered from Michigan AirGas. For acetylene (industrial grade), the removal of acetone stabilizer from the fuel, using an ethanol–dry ice bath at $-70\,^{\circ}C$, was not found to have a noticeable effect on the soot measurements. Benzene (HPLC grade) was delivered via a syringe pump onto glass wool maintained at about $70\,^{\circ}C$ in a short section of tubing between the ethylene/air supply and the burner. For the flames studied here, the fuel flows varied from 1.2 to 1.9 L/min and the total cold feed-gas flows varied from 4.5 to 14 L/min.

The coaxial probe used to sample soot from the flames is described in detail in our earlier work [14,22]. It consists of a 1/8-inch-diameter stainless-steel inner tube through which a sample/diluent mixture is drawn, and a 3/16-inch outer tube that provides an annular space through which the diluent is delivered to the probe tip. The end of the outer tube is sealed except for a 0.3-mm pinhole that allows entry of the soot sample. This geometry provides an approximately 30:1 dilution to quench the flame chemistry immediately at the point of sampling. The diluted sample is drawn through the 40-mm-long inner tube by an ejector pump. The sample mixes with the