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Probing gas-to-particle transition in a moderately sooting atmospheric pressure ethylene/air laminar premixed flame. Part II: Molecular clusters and nascent soot particle size distributions

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ABSTRACT

A comprehensive investigation was conducted on a sooting ethylene laminar premixed flame. The present contribution focuses on measurements of soot nuclei by: a) thermophoretic sampling on fine wires followed by microscopy analysis and b) high-dilution probing followed by High-Resolution Differential Mobility Analysis (HR-DMA). The results complement Part I that was focused on the characterization of the gas composition and of soot properties by optical measurements, and highlighted significant artifacts induced by the heat loss associated with the presence of a stagnation plate. Significant novelties in the diagnostics include: the ability to perform spatially resolved thermophoretic measurements on fine wires straddling a critical temperature range that rules out artifacts brought about by either condensation of nonvolatiles or surface kinetics, as demonstrated by the invariance of particle size with the wire residence time in the flame; and the *high-resolution* capability of the DMA revealing the presence of small ($D < 3$ nm) nanoparticles both at lower heights in the flame, where younger soot is present, and further downstream at the same location where more mature soot is present. At the location at which both thermophoretically collected particles and HR-DMA data are available, the size distribution functions are in good agreement, except for the smallest particles that are quantifiable only by HR-DMA. Comparison of soot volume fraction and particle sizes from multiple techniques reveals good self-consistency, especially in the region where somewhat more mature soot particles are present (HAB $\geq$ 12.5 mm). A simplified three-dimensional model of the HR-DMA sampling procedure using a finite element solver package reveals the perturbation introduced by the "cold" probe to the temperature–time history experienced by the sampled aerosol and provides the input parameters for a one-dimensional streamtube model of the perturbed flame that included detailed chemistry. Even though additional work is needed to make the HR-DMA determination of the small particle peak fully quantitative, the developed database provides a useful benchmark for experimental validation of soot nucleation models, casting a shadow on established measurements that rely on commercial instrumentation with lower resolution.

1. Introduction

The critical and still missing link to a fundamental understanding of soot formation in flames is its nucleation (also termed inception), that is, the formation of the first soot nanoparticles or carbonaceous molecular clusters [1–3]. Although the nucleation step contributes little per se to the total soot loading and eventual emissions from combustion processes, it plays a key role by providing the active sites for surface growth by acetylene addition [4], which is thought to be responsible for the bulk of the overall soot production [4–6]. Probing soot inception is a challenge in many respects, even when one operates under conditions of incipient or very modest soot loading to minimize interference resulting from the presence of copious soot amounts in a flame. In view of uncertainties and shortcomings of various techniques, it is desirable to apply multiple diagnostics to characterize concurrently the gaseous phase and the particle-phase in the small dimensional range where gas-to-particle transition occurs in a single flame. Such diagnostics can be applied with relative ease in laboratory laminar flames under modest soot loadings, which explains why such flames have been the object of many fundamental studies [1–8].

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In the preceding Part I of this study [9] we reported on measurements in an ethylene–air atmospheric–pressure premixed flame for the characterization of gaseous species including soot precursors up to 3-ring aromatics and of the soot phase using optical techniques. We also highlighted the effects on the soot ensemble properties of localized cooling of burnt gases because of the presence of a commonly used stabilizing plate downstream of the burner outlet. We now turn our attention to the soot inception in the same flame, using two other probing techniques: thermophoretic sampling on fine substrates to retain spatial resolution and on-line High-Resolution Differential Mobility Analysis (HR-DMA) of sampled and quickly diluted flame products, to measure the size distribution function (SDF) of carbonaceous material. We introduce some novelties in both techniques warranting further comments. We will touch also on aspects of modeling the insertion of probes in the flame environment.

After the pioneering work of Dobbins and Megaridis [10] in the '80s, thermophoretic sampling has been extensively used to size up soot particles deposited on microscope grids and analyzed off-line by a variety of techniques [2,3,10–14], including Scanning and Transmission Electron Microscopy (SEM and TEM) [10], Laser Desorption Mass Spectrometry (LDMS) [11], Atomic Force Microscopy (AFM) [12,13] and, more recently, the "gentler" Helium Ion Microscopy (HIM) [14]. Driven by thermophoretic drift of soot particles down a temperature gradient established between the flame environment and the cooler substrate, sampling is particle-size independent in the high Knudsen number regime, that is, for particle diameters much smaller than the mean free path at the prevailing conditions. The technique nearly invariably relies on bulky contraptions to support the grid on which particles are deposited, which precludes its use to examine details of soot evolution in flame with adequate spatial resolution and may cause sampling artifacts (i.e. localized cooling as discussed in Part I [9]) that can modify the quality and quantity of collected soot even when spatial resolution is not a key factor. Soot number concentration and volume fraction can be inferred by estimating the particle thermophoretic velocity and monitoring the growth rate of a thermocouple bead as a result of soot deposition [15]. Koylu et al. [16] extended the technique to the case in which an electron microscope grid was used as substrate. These authors achieved accurate spatial positioning in the flame but did not show either evidence of good spatial resolution, as they reported their data in 10 mm spatial intervals, or avoidance of potential sampling artifacts. Thrusting a bulky object in a flame is bound to cause significant and unquantifiable perturbations, which rules out its use for detailed soot profiles. In the present contribution, we consider the case of much smaller substrates kept at relatively high temperature as compared to what has been used in the past, which may help on both counts of minimizing flame perturbation and sampling artifacts and potentially allowing for spatially-resolved soot measurements in flame environments with sharp gradients.

As regards to the second sampling technique, in an effort to clarify the mechanisms of the transition from the gas to the particle phase leading to soot formation in flames, many studies have reported measurements of ultrafine ($D < 100$ nm) SDFs of particles formed under incipiently sooting conditions by performing on-line Differential Mobility Analysis (DMA) of sampled and quickly diluted flame products [2,3,17–35]. These studies were performed with commercially available DMA systems with a maximum nominal resolution of 10 and, in most cases, with a lower detection limit of 2.5–3 nm. The group in Naples extended the lower dimensional range of DMA measurements below 3 nm by relying on a Vienna type DMA with improved performances in the small dimensional range [24,30–32,34]. Nevertheless, the quantitative measurement of the soot nuclei even in this study was affected by limitations in both instrument performance [36] and dilution sampling, as well as particle charging artifacts [37]. In this study, we used a High-Resolution-DMA (HR-DMA) that is capable of measuring the electric mobility of carbonaceous material, as either particles, molecular clusters or isolated molecules, potentially with diameters below 1 nm [36–38]. In practice, the inability to completely freeze coagulation during sampling and the need to charge the particles leaves the quantification of particles with diameters below 5 nm still uncertain [37], despite the fact that the data reported in this article were obtained by minimizing and quantifying such artifacts to an unprecedented extent. A detailed assessment of the instrument performances and of possible experimental artifacts was presented in a separate article [37] and is only briefly discussed here.

The objective of this article is to help fill the knowledge gap of critical aspects of the transition from the gas phase to the first soot nanoparticles or carbonaceous molecular clusters through the simultaneous application of these complementary diagnostics [2,3]. In addition, we wish to bring to the fore limitations of each of these techniques via computational modeling of the probing technique.

2. Experimental and computational methods

2.1. Burner and flame conditions

As per Part I [9], the flame investigated in this study is the same atmospheric-pressure laminar premixed flame of ethylene/air with C/O ratio of 0.69 and cold-gas velocity of 58.7 mm/s. The flame was stabilized on a (400 CPSI, cell per square inch) stainless steel honeycomb burner with an outlet diameter of 48 mm. Pure nitrogen with a velocity of 21 cm/s was flown through an outer annular region (OD = 76 mm) of the same honeycomb to shield the flame from external disturbance. A 1.6 mm thick brass plate, 150 mm in diameter, was placed at a 40 mm Height Above the Burner (HAB) to further suppress flame flickering and hot gas buoyant acceleration. In Part I we already commented on the equivalence of this burner with the more common water-cooled sintered plate McKenna burner that is routinely used in soot studies [9,20,39–41].

2.2. Thermophoretic Sampling (TS) and microscopy image analysis

The particle collecting substrate has to have several attributes. It should be

i. suitable for high-temperature environments, chemically inert and, possibly, electrically conductive;
ii. sufficiently cold and small to maximize thermophoretic velocity and consequently allow for short sampling times, to minimize the surface rearrangement of soot particles and the residence time of the sampled particles in the thermal boundary layer surrounding the substrate;
iii. compatible with multiple microscopy techniques for subsequent post-mortem analysis, to provide information not only on size but, possibly, morphology and structure; and
iv. as small as possible to minimize intrusiveness and local flame perturbation and eventually enable measurements with adequate spatial resolution, the feasibility of which is one of the goals of the present investigation.

As to potential artifacts of the technique, in addition to the unavoidable perturbation associated with the intrusiveness of thrusting the substrate quickly into the flame, we should consider the following ones: if the surface temperature is too high, there may be chemical kinetics affecting the adsorption and rearrangements of deposited atoms/molecules on the surface. There is an upper temperature beyond which these effects will be non-negligible. Vice-versa, if the temperature is too low, there may be physical condensation of heavier species such as the