



## Full Length Article

## Structure and size of soot nanoparticles in laminar premixed flames at different equivalence ratios

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## ABSTRACT

In this work, the physicochemical properties of flame-formed soot particles are investigated in a set of ethylene/air premixed flames as function of the equivalent ratio. The objective of this study is to highlight the peculiar characteristics of the particles produced under quasi-clean combustion conditions in comparison with soot formed in richer flames.

The size distribution of flame-formed soot nanoparticles was measured by differential mobility analysis; particle composition by Raman and UV–vis light absorption spectroscopy and morphology by atomic force microscopy.

Our results evidence that the particle size distribution is strongly affected by the flame equivalence ratio. Slightly rich flames produce mono-modal PSD with very small particles of only few nanometers. Bi-modal size distribution are found in richer flames when larger particles, i.e., 5–20 nm, are formed. Change from a mono-modal to a bi-modal particle size distribution can be related to changes in particle graphitization as evidenced by a slight increase of the in plane average size of the polyaromatic units within the particles,  $L_a$ , and a change in particle optical properties.

## 1. Introduction

Combustion processes under fuel-rich conditions lead to the formation and emission of a wide set of carbon-based by-products. The incomplete combustion of hydrocarbon fuels causes the formation of polycyclic aromatic hydrocarbons in the gas-phase, PAHs, high-molecular mass compounds in the condensed-phase and soot particles in the solid/aerosol phase.

Over the last decades, the formation and fate of combustion-formed soot particles have attracted a great deal of interest due to a series of motivations. These, for instance, include the numerous and ascertained adverse effect on the human health [1,2]. Soot particles can, in-fact, act as carriers for surface-adsorbed PAHs that are known to be highly toxic because of their mutagenic and carcinogenic properties [3]. Additionally, soot particles themselves are often associated with adverse health effects especially for the respiratory tract [2,4] and particularly when their size is at the nanoscale level. Moreover, combustion is well known to be a major source of the atmospheric ultrafine particles, i.e., particle whose size is lower than 100 nm, which are among the leading causes of concern for the air-quality in urban areas [5]. Indeed, ultrafine particles, due to the very small size, are the most critical for

penetration and lung deposition and translocation to other parts of the body [6].

The emission of combustion-formed soot nanoparticles also poses complex implications in affecting the environment and climate forcing due to the occurrence of multiple processes such as the direct radiative forcing due to solar absorption; indirect effects produced, for instance, by influencing the liquid, mixed phase, and ice in clouds; and changes in the snow and ice optical properties due to soot particles deposition [7].

Once emitted, combustion-formed particles typically undergo further chemical and physical transformations either within the exhaust manifolds or in the atmosphere as a result of reactions with other pollutants and/or photo-physical effects due to sunlight radiation. Nevertheless, it is important to clarify the correlation between the particle properties and the combustion conditions in order to determine a better source assignment of air pollutants.

Fuel rich combustion is a source of carbonaceous material composed by particles whose size, morphology, chemical and structural composition can display a considerable variation. As a result, the operating conditions of a combustion process and/or post combustion systems have significant effects on both particle loads and chemico-physical

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properties. For instance, the combustion temperature [8], the pressure [9], the nature and the chemical composition of the fuel mixture [10,11], the extent of fuel/air premixing [12], the oxygen index [13], are some of the main combustion parameters that significantly affect soot formation and properties. For instance, recent contributions revealed that combustion conditions are also effective in producing soot particles with different hygroscopic properties [14,15], thus with a different tendency to act as condensation nuclei for water and ice cloud formation [16].

The formation of soot particles in laminar premixed flame conditions begins with the formation of very small particles, whose size is of the order of only few nanometers, i.e., the nucleation particle mode [17]. Further particle growth process that occurs either by coagulation and/or by heterogeneous surface reactions leads to the formation of a second mode of particles, i.e., the accumulation mode, whose mean particle size is typically of the order of 5–20 nm. It is this second class of particles that contributes, as primary particles, to the formation of soot aggregates with the typical fractal-like morphology.

In this work we investigate the chemico-physical properties of carbon nanoparticles produced in laminar premixed flames at different C/O ratios, i.e., at different equivalence ratios,  $\Phi$ . Soot particle characterization has been performed by differential mobility analysis, DMA, for particle size distribution measurements and by Raman and UV–vis spectroscopy for chemical/structural characterization. In addition, soot morphology has been studied by atomic force microscopy, AFM.

The range of the selected equivalence ratios allows setting flames with different sooting conditions: from those producing only nucleation mode particles to those characterized by a bimodal shape of the soot particle size distribution. This allows us to produce and characterize soot particles from different combustion conditions.

## 2. Experimental

Several sets of laminar premixed ethylene-air flames were stabilized on a water cooled sintered bronze McKenna burner, widely used in combustion community for producing flat premixed flames [18].

The cold gas stream velocity, composed by ethylene and air, was kept constant at 10 cm/s for the whole set of flames while the equivalence ratio was varied from  $\Phi = 1.72$  (C/O = 0.57) to  $\Phi = 2.58$  (C/O = 0.85). As a result, the stabilized flames presented different color luminosity, spanning from an almost bluish-colored flame for the  $\Phi = 1.72$  condition to a strong yellow-colored flame at the equivalence ratio  $\Phi = 2.58$ .

Combustion products were extracted from the flames by means of a tubular dilution probe as described in several earlier studies [17,19–23] and briefly illustrated in Fig. 1a. Soot nanoparticle sampling was done at a fixed distance by positioning the probe at 15 mm from the burner surface.

Particle size distributions were measured on line using a differential mobility analyzer (DMA) system (Vienna-type DMA model TapCon 3/150) that allows particle classification within the size range 1–40 nm with a size resolution  $\Delta d/d = 0.2$ . In this experimental configuration, the flame products are sampled through a very small orifice, i.e., 200  $\mu\text{m}$ , located on the bottom side of the horizontal tubular probe. Sampled combustion products were rapidly mixed with a nitrogen flow to dilute the sampling flow by  $\sim 10^3$  [22,23]. Such sampling procedure prevents particle from coagulating, and allows quenching the chemical reactions throughout the sampling line as described in earlier works [19,20]. The sampled soot particles, suspended in the  $\text{N}_2$  flow, are first charged using a radioactive (Am-241) bipolar diffusion charger and subsequently selected through the DMA to be finally counted by a Faraday cup electrometer.

Off-line Raman spectroscopy analyses were performed on soot particles sampled with a tubular probe similar to that used for the on-line DMA measurements except for a larger size of the orifice that allows sampling at a lower dilution ratio and therefore collects a larger

amount of material in a shorter time. The flame-formed carbonaceous material was collected on Teflon filters (Merk Millipore Fluoropore PTFE, pore size 0.45  $\mu\text{m}$ ) and analyzed by Raman spectroscopy.

Raman spectra of sampled soot particles were measured by placing the Teflon filters under the Raman microscope (Horiba XploRA) equipped with a 100X objective (NA0.9, Olympus). The laser source was a frequency doubled Nd:YAG laser ( $\lambda = 532$  nm, 12 mW maximum laser power at the sample). Spectra were obtained with a laser beam power of 1%, and an accumulation-exposure time of 5 cycles of 30 s each. For each sample, several spots were randomly selected and averaged to obtain statistically relevant Raman spectra.

For morphological analysis, AFM measurements were conducted on soot particles collected by thermophoresis via rapid insertion of a cold substrate in the flame by means of a pneumatic actuator that assures a fast sampling time, as shown in Fig. 1b. Freshly cleaved mica disks were used as substrate to have an atomically flat background in AFM images. AFM measurements were performed with a Scanning Probe Microscope (NT-MDT NTEGRA), at room temperature and 30% relative humidity. For morphological imaging of samples, to reduce tip effects during the measurement, the instrument was operated in semi-contact mode in air and using super-sharp silicon probes (NANOSENSORSTM SSS-NCHR), which have nominal tip radius of 2 nm, a 125-mm long cantilever with a spring force constant of 42 N/m, and a range of resonance frequency 204–497 kHz. The AFM images were obtained with a scan rate of 0.3–0.5 kHz over selected areas ranging from 20  $\mu\text{m} \times 20 \mu\text{m}$  down to 2  $\mu\text{m} \times 2 \mu\text{m}$  (1024  $\times$  1024 pixel resolution). The calibration of the AFM scanner vertical movement was performed by means of the NT-MDT SiC/0.75 calibration sample, which has a uniform distribution of 0.75 nm height steps on its surface. The AFM images were not filtered.

Spectrally resolved, UV–visible line-of-sight absorption by the flame-formed particles collected via thermophoresis on quartz substrates were measured in the spectral range 200–650 nm by an Agilent UV–visible 8453 spectrophotometer (Agilent Technologies, USA) with an uncertainty of the order of  $10^{-3}$ .

## 3. Results and discussion

In Fig. 2 we report the contour plot of the soot particle size distributions, PSDs, obtained for various C/O ratios for a fixed height above the burner, i.e., 15 mm. Such a flame position corresponds to an average particle residence time of 20–25 ms for the flames examined and is well above the particle inception zone for all the conditions investigated. At relatively low C/O ratios, i.e. from 0.57 to 0.61, the PSD is unimodal and only nucleation particles are present.

Unimodal distributions are apparent in Fig. 2a and b where the contour plots of the number and volume PSD are respectively reported. The chemical/molecular structure of these particles remains a subject of ongoing research and the soot research community seems to have a consensus on the size of the just-nucleated particles. In laminar premixed flames, as well as in some other flame configurations, the particle size distribution is often bimodal with the first mode peaking about 1.5–3 nm and a second mode composed by larger particles whose average size changes as function of the flame residence time and equivalence ratio [20–23,28–31]. The occurrence of flame conditions in which only very small nanoparticles, i.e., 2–3 nm, are formed and these sizes are preserved at higher residence time, i.e., no mass growth, were previously observed by in-situ measurements such as light extinction and scattering measurements [24], by fluorescence measurements [26–28], and recently by laser induced incandescence measurements [25].

It is clear in Fig. 2 that the particle size distribution changes as the flames get richer. As the C/O ratio increases, a widening of the PSD to include particles with larger sizes occurs, and subsequently a clearly bimodal shaped PSD develops and a clear dip between the two particle modes is observed at C/O > 0.63. For such richer flame conditions, a particle accumulation mode is present and the mean particle size

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