RAMAN SPECTROSCOPY AND ATOMIC FORCE MICROSCOPY OF SOOT SAMPLED IN HIGH-PRESSURE DIFFUSION FLAMES

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Abstract

The objective of the present work is to assess the effect of pressure on nanostructure, morphology and dimension of soot particles from a set of co-flow methane/air laminar diffusion flames stabilized in a high-pressure combustion chamber. To this aim, particles produced in a pressure range between 5 and 20 bar have been collected by thermophoresis and characterized by means of Raman spectroscopy and Atomic Force Microscopy (AFM). First-order Raman spectra have been acquired at different heights above the burner for each pressure. No significant changes in the nanostructure and composition of soot particles were detected as a function of pressure, while nanostructure and composition have been observed to change with particle residence time within flame. From AFM measurements, Particle Size Distribution Functions (PSDs) have been obtained through a dimensional statistical analysis. PSDs have been found to be mostly bimodal, with a first particle mode below 10 nm slightly decreasing with pressure and a second particle mode between 10 and 20 nm rather constant with pressure. Moreover, a comparison between PSDs from AFM and PSDs from Transmission Electron Microscopy reported previously showed a good complementarity between those two techniques. This study represents a first attempt to characterize and correlate the structural and morphological properties of soot particles produced at high-pressures, which are the typical operating conditions of most practical combustion devices.

Introduction

Soot is defined as a class of flame-formed carbon nanoparticles, whose main properties can be sensibly different as a function of combustion parameters [1]. Particularly, some characteristics with important practical implications, such as oxidative reactivity [2] and optical properties [3], can be significantly different. One of the most important parameters influencing soot formation is pressure, since many practical combustion devices operate under high-pressure conditions, such as

high performance aviation propulsion systems and terrestrial engines. The increase in the pressure of combustion has already been demonstrated to increase the rate of soot formation, due to increased collision rate between PAHs, leading to soot particle nuclei [4]. However, there is a lack of information regarding the influence of pressure on morphology, composition and structure of soot in the literature. In this work, nanostructure, size and morphology of soot particles produced in a set of laminar diffusion flames stabilized at elevated pressure (from 10 up to 20 bar) have been investigated by means of Raman spectroscopy and Atomic Force Microscopy.

Experimental

The high-pressure flames studied in our work were stabilized on a circular co-flow laminar diffusion type burner (fuel tube ID=3 mm; co-flow air nozzle ID=25mm). The burner was inserted into a high pressure combustion chamber (ID=25 cm, height=60 cm), designed to operate at pressures up to 110 bar. The methane mass flow rate and the co-flow air mass flow rate were kept constant to 0.55 mg/s and 0.41 g/s, respectively. Investigated pressures were P=10, 15 and 20 bar.

The sampling system used to collect particles from flame by thermophoresis was composed by a circular sampling disk, equipped with ten probe arms, and connected to a motor drive. The disk is kept in rotation and controlled through a programmable control system, which allows to insert the probe arm through the flame cross-section at a given height above the burner rim. The flame is allowed to recover from the disturbance induced by the insertion of probe arm by stopping the disk rotation once the probe arm has completed a sweep. through the flame. A more detailed description of the system can be found in previous works [5, 6]. Soot particles were collected at different residence times, i.e. at different heights above the burner rim (HAB), HAB=3, 5 and 8 mm. It is well-established that the flame heights and hence the residence times do not change with pressure when the fuel mass flow rate is kept constant in buoyancy-dominated laminar coflow diffusion flames [7].

Raman analysis was performed on particles collected by multiple sweeps of TEM grids (single insertion time=28.3 ms; total insertion time~340 ms). A Raman microscope (Horiba XploRA) equipped with a 100X objective (NA0.9, Olympus) and a frequency doubled Nd:YAG laser source (λ=532 nm, 12 mW maximum laser power at the sample) was used. AFM measurements were performed on particles collected on mica substrates with a single insertion of 4.24 ms, using a Scanning Probe Microscope NTEGRA Prima from NT-MDT at room temperature and 30% relative humidity. The instrument was operated in semi-contact mode in air, using NANOSENSORS™ SSS-NCHR super-sharp silicon probes with nominal tip radius of 2 nm. The AFM images were obtained over selected areas ranging from 20X20 μm^2 to 2X2 μm^2.

Results and discussion

The composition and nanostructure of particles produced in flames at the different

pressures have been explored by measuring Raman spectra. All the spectra are characterized by the presence of the typical carbon materials peaks, the so-called G and D peaks [8], together with a fluorescence background, characteristic of the organic component of the carbon particle. The ratio between the intensity of the two prominent peaks, I(D)/I(G), has been directly correlated to the size of the aromatic domains L_a composing the particles [8]. For highly amorphous carbon materials, when L_a is smaller than 2 nm, I(D)/I(G) is proportional to the amount of aromatic sp^2 hybridized carbon respect to the total sp^2 hybridized carbon [9].
The ratio I(D)/I(G) vs HAB for the three investigated pressure is reported in Figure 1. At P=10 bar, data are reported only for HAB=5 mm and HAB=8 mm, since at HAB=3 mm there was not enough materials collected on the substrate in order to perform Raman measurements. Data reported in Figure 2 clearly show that carbon nanostructure of soot particles mainly changes due to different residence times. Increasing HAB, and so increasing particle residence time in flame, the ratio I(D)/I(G) move from about 0.85 ($L_a \approx 1.15$ nm) to about 1 ($L_a \approx 1.3$ nm), due to an increase in the graphitic order of soot particles. On the other hand, within the experimental uncertainties, measured I(D)/I(G) values follow the same trend as function of the three pressure investigated.

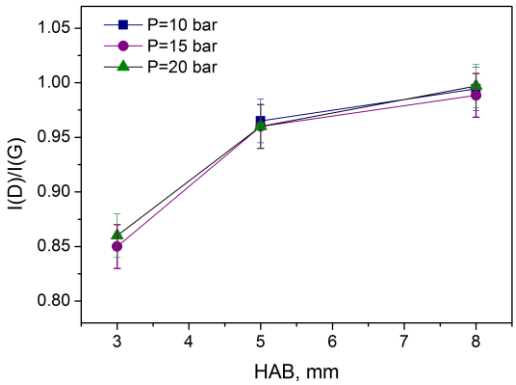

Figure 1. I(D)/I(G) ratio from the Raman spectra of soot particles as a function of flame heights at different pressures.

Moreover, in addition to I(D)/I(G), the ratio between the slope of the fluorescence signal in the Raman bands and the absolute intensity of the G peak, m/I(G), can be evaluated from Raman spectra too [10]. This quantity is proportional to the amount of fluorescence component in the carbonaceous sample, with respect the total sp^2 carbon, and so it furnishes indication on the relative content of the organic carbon, OC, with respect to the total sp^2 carbon in the collected soot particles. Calculated values of m/I(G) ratio vs HAB for the three pressures are reported in Figure 2 (left side), together with atomic hydrogen percentage values determined from m/I(G) (Figure 2, right side) using the following relationship [10]:

$$H[\text{at\%}]=21.7+16.6*\log\{m/I(G)[\mu\text{m}]\} \quad (1)$$

Again, m/I(G) ratio shows significant differences as a function of residence times in the flame. Particularly, the hydrogen content in soot particles decreases as the residence times increase. No notable differences can be detected changing the pressure between 10 and 20 bar.

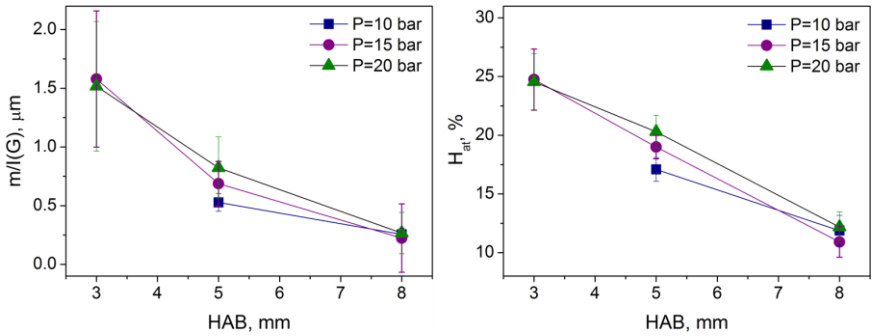

Figure 2. m/I(G) ratio (left) and atomic hydrogen content as a function of flame heights at different pressures (right).

Morphology and dimension of soot samples have been analyzed by acquiring AFM images and measuring the maximum height H_{max} and the base diameter D_{base} of the particles. Then, particle volume was calculated assuming a cone shape for the impacted particle with a base diameter corresponding to D_{base} and a height corresponding to H_{max}. The particle equivalent diameter was then calculated from the measured particle volume, under the hypothesis of a spherical shape. In this way particle size distributions (PSDs) are generated by counting the number of particles over the relative range of equivalent diameters [11].

From AFM measurements PSDs appear to be mostly bimodal, with a first mode of particles having diameter lower than 10 nm, and a second mode of particles within the size range of 10-20 nm. Therefore, each PSD was fitted using a weighted sum of two normal distribution functions [12]. The results of the fitting analysis are summarized in Figure 3, where the mean diameters of the two particle modes are reported for the different sampling conditions. The particle mode below 10 nm, D_{eq} I Mode, shows a slight decrease as the pressure increases, while it remains rather constant increasing sampling height. For the second mode, D_{eq} II Mode, a correlation between particle mean diameter and pressure is not apparent. However within the experimental uncertainty the particle mean diameter can be considered rather constant with pressure.

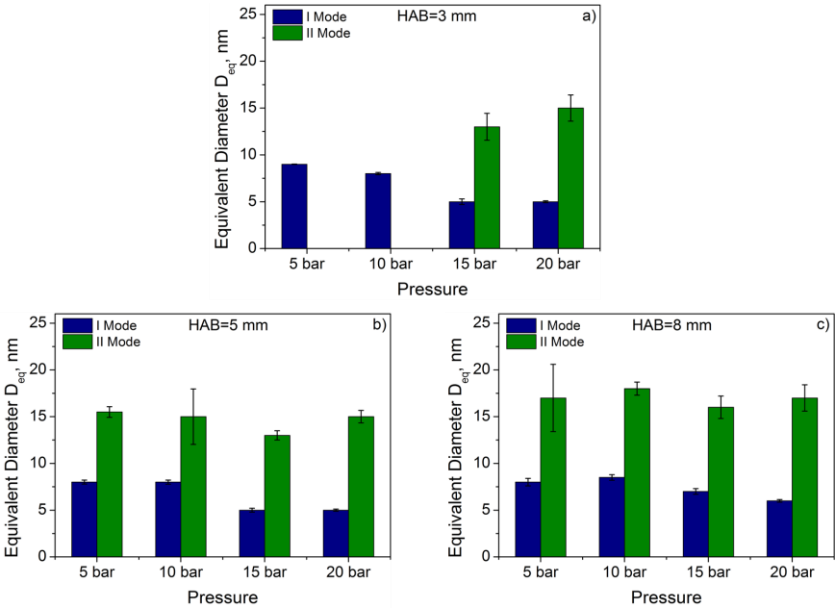

Figure 3. AFM equivalent diameter of soot particles as a function of pressure at HAB=3 mm (a), HAB=5 mm (b) and HAB=8 mm (c).

A comparison between PSDs from AFM and PSDs from TEM (reported in Reference 6) is shown in Figure 4 for H=3 mm, P=5 bar and H=3 mm, P=10 bar. It is possible to note that AFM data can be considered as complementary to the TEM data. Indeed, the AFM data cover particle size range between 5 nm and 20 nm, while TEM data cover the particle size range between 10 nm and 40 nm.

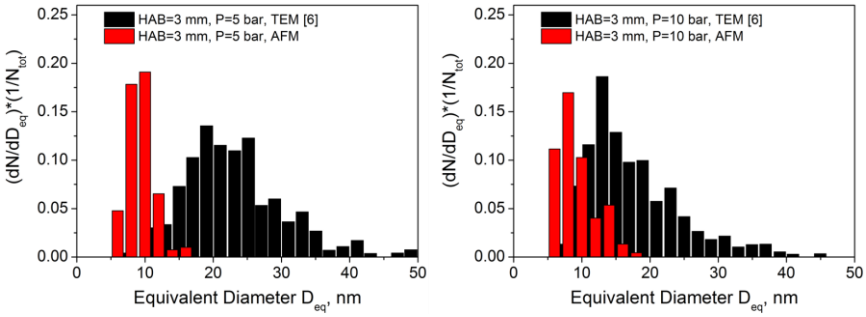

Figure 4. AFM PSDs (red bars) and TEM PSDs from Ref. 6 (black bars) at HAB=3 mm, P=5 bar (left side) and HAB=3 mm, P=10 bar (right side).

Conclusions

Soot particles produced from methane diffusion flames stabilized at elevated pressures and collected by thermophoresis have been characterized by Raman spectroscopy and Atomic Force Microscopy. The analysis of I(D)/(I(G) and m/I(G)

ratios from Raman spectra showed no significant changes as a function of pressure, while nanostructure and composition have been observed to change with particle residence time within flame. PSDs were obtained from AFM, revealing a slight decrease with pressure of particle diameters below 10 nm and a good complementarity with PSDs from TEM measurements [6].

References

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