

Measurements of hydrogen content and visible specific absorption of soot to follow the structural transformation of carbon network

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Abstract

The relation between the optical properties, namely the mass absorption coefficient, and the H/C ratio of soot was studied as tool for following the structural transformation of solid carbon (soot) formed in premixed sooting ethylene flames. The aliphatic and aromatic hydrogen and the mass absorption coefficient of soot were quantified by FT-IR and UV-Visible spectroscopic analysis, respectively. The steep increase of the absorption coefficient and maximum soot formation rate was observed in correspondence of the aliphatic hydrogen loss. The higher reactivity of aliphatic hydrogen in forming radical active sites on soot particle surface was suggested to be responsible for the increase of soot concentration. The loss of aliphatic hydrogen and the corresponding steep increase of absorption coefficient testified the occurrence of thermal annealing and internal structural transformations in turn causing the termination of soot formation and growth.

Introduction

Atmospheric trace species as organic and inorganic particulate matter emitted from combustion processes may have different effects on the climate by absorbing and/or scattering the light in dependence on the chemico-physical properties as the size and the composition of the particles. The optical properties, and in particular the light absorption from combustion-derived carbon-based particles (soot), are parameters critical in calculating the effects of aerosols on radiative transfer and modeling how anthropogenic activities affect climate.

It has been argued that the H/C atomic ratio is a reasonable, but defective predictor of light absorption from carbon particles due to the complex effect of their composition and structural features on the absorption [1]. Moreover, carbon particles may have H/C ratios strongly varying in dependence on their source. In our previous work the relation between the H/C ratio and the absorption coefficient of flame-formed carbon particles was studied. It was shown that the mass absorption coefficient is relatively low and sensitive to H/C variations in the 0.3 down to 0.1 range whereas it steeply increases to very high values when the H/C value falls below 0.1, even for very small changes of the H/C ratio [2].

The effect of the type of C-H bonding (aliphatic or aromatic) on the mass absorption coefficient has been investigated in this work by quantitative FT-IR analysis of hydrogen linked to soot particles sampled in premixed ethylene flames. The contribution of both aliphatic and aromatic hydrogen was found to determine the production of hydrogen-rich low light-absorbing soot in the first phase of soot formation. As soot massively formed the early depletion of aliphatic hydrogen caused the production of hydrogen-poor carbons having a high absorption coefficient. The increase of the absorption coefficient for H/C below 0.1 demonstrates that there is no relationship between optical properties and hydrogen content for hydrogen-poor carbon materials. Thus, structural parameters as the size and the density of aromatic layers are suggested to be the main parameters affecting in a complex manner the absorption coefficient.

Experimental

In this work soot produced by premixed ethylene flames at a constant mixture composition and different cold-gas flow velocities, namely, different flame temperatures have been analyzed. Sooting ethylene/O₂ laminar flames burning at atmospheric pressure were produced on a water-cooled sintered bronze McKenna burner (d=60mm) (Holthuis & Associates) at constant C/O feed ratio (C/O =0.8) and different cold gas velocity, $v=3$ cm/s (LT-E) and 4 cm/s (HT-E).

Combustion-generated carbonaceous species were sampled along the flames and extracted with dichloromethane (DCM) to separate soot from the soluble condensed species. More details on the combustion system and in particular on the procedure used for the premixed benzene flame production are given elsewhere [3]. UV-Visible absorption spectra of samples suspended in N-methyl-2-pyrrolidinone (NMP) were measured on an HP8452A spectrophotometer.

H/C atomic ratio was measured on a Perkin-Elmer 2400 CHNSO elemental analyzer. UV-Visible absorption spectra of carbon samples suspended in N-methyl-2-pyrrolidinone (NMP) were measured on an HP8452A spectrophotometer.

FT-IR measurements were performed on a Perkin-Elmer 1600 FT-IR spectrophotometer. FT-IR analysis of carbon materials, soot and solid PAH standard have been performed in the 3400-600cm⁻¹ on dispersions prepared by mixing and grinding the samples in KBr pellets (0.25wt %) [4]. Details on the quantitative analysis of hydrogen are given in the following.

Results

The characterization of ethylene soot along with benzene and methane soot, in terms of composition and structure measured by using different techniques (UV-Vis, FT-IR, HRTEM and elemental analysis), is reported in previous work [2]. Overall, the specific mass absorption and the H/C atomic ratio of soot showed a sharp increase of the specific mass absorption for H/C ratio next to 0.1 [2]. Crossing the critical H/C threshold value of about 0.1 the specific mass absorption exhibited a wide variation along with the optical band gap decrease, demonstrating

the occurrence of soot structural transformations independently on the H/C [2].

By quantifying the amount of aromatic and aliphatic hydrogen contributing to the total tethered hydrogen some insight on the structural transformations leading to the increase of absorption can be obtained.

The qualification and quantification of hydrogen tethered to carbon materials has been obtained by FT-IR analysis of the C-H vibrational modes related to the different type of hydrogen that arise in the MID-IR range (from 4000 to 400 cm^{-1}). FT-IR spectra of soot sampled from LT-E and HT-E flames at short (SRT) and long (LRT) residence times are reported in Fig. 1.

It can be observed that the C-H stretching in the 3200-2800 cm^{-1} range is weak, in particular for aged soot (LRT). However, the C-H bending Out of PLANE (OPLA) of isolated (solo) and adjacent hydrogens of aromatic systems are still visible in the 900 and 700 cm^{-1} range and can be used to evaluate the aromatic hydrogen when the stretching C-H signal is too low to be detected. The OPLA region has been deeply investigated in terms of position and strength of these vibrational modes. The spectral analysis of PAH and alkyl-substituted PAH standard as well as of PAH spectral library (<http://webbook.nist.gov/chemistry/>) allows to assess that isolated hydrogens (solo) are located in the 890-870 cm^{-1} range, whereas two-adjacent hydrogens (duo) are located between 850 and 810 cm^{-1} . Three-adjacent hydrogens (trio) are detected in the 790-750 cm^{-1} region. Four-adjacent hydrogens (quatro) are detected in the 750-720 cm^{-1} region [5].

Due to the overlapping of bending modes, the OPLA region has been deconvoluted into its component vibrational modes and each peak multiplied by the appropriate absorption strength.

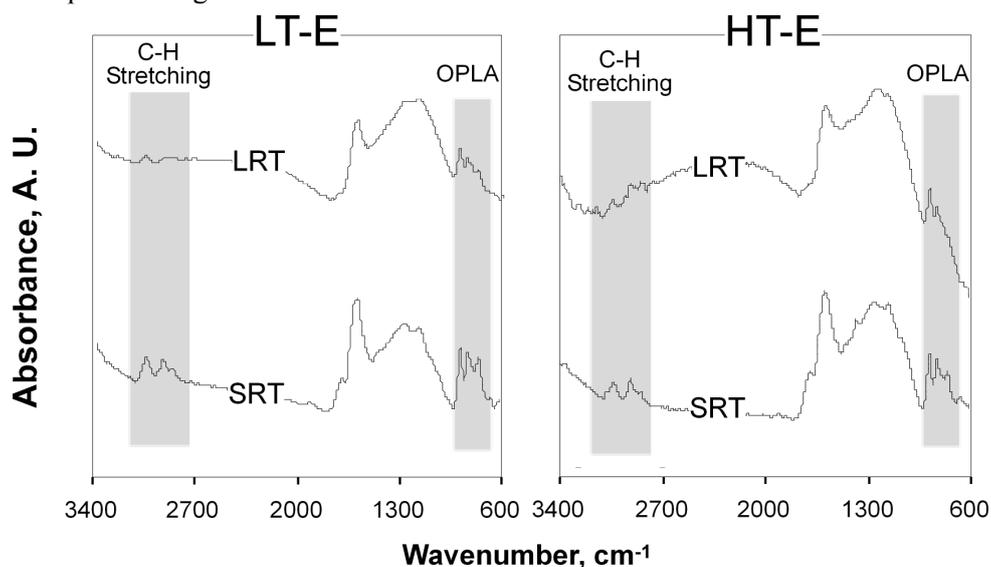


Figure.1 FT-IR spectra of soot sampled in LT-E and HT-E at SRT and LRT

The height of each bending C-H peaks coming out from deconvolution of the soot spectra has been multiplied by the corresponding absorption strength, derived from standard molecules, in order to quantify the aromatic hydrogen molar fraction X_H^{aro} whereas the aliphatic hydrogen molar fraction X_H^{ali} has been evaluated as difference between the total X_H , measured by means elemental analysis, and X_H^{aro} .

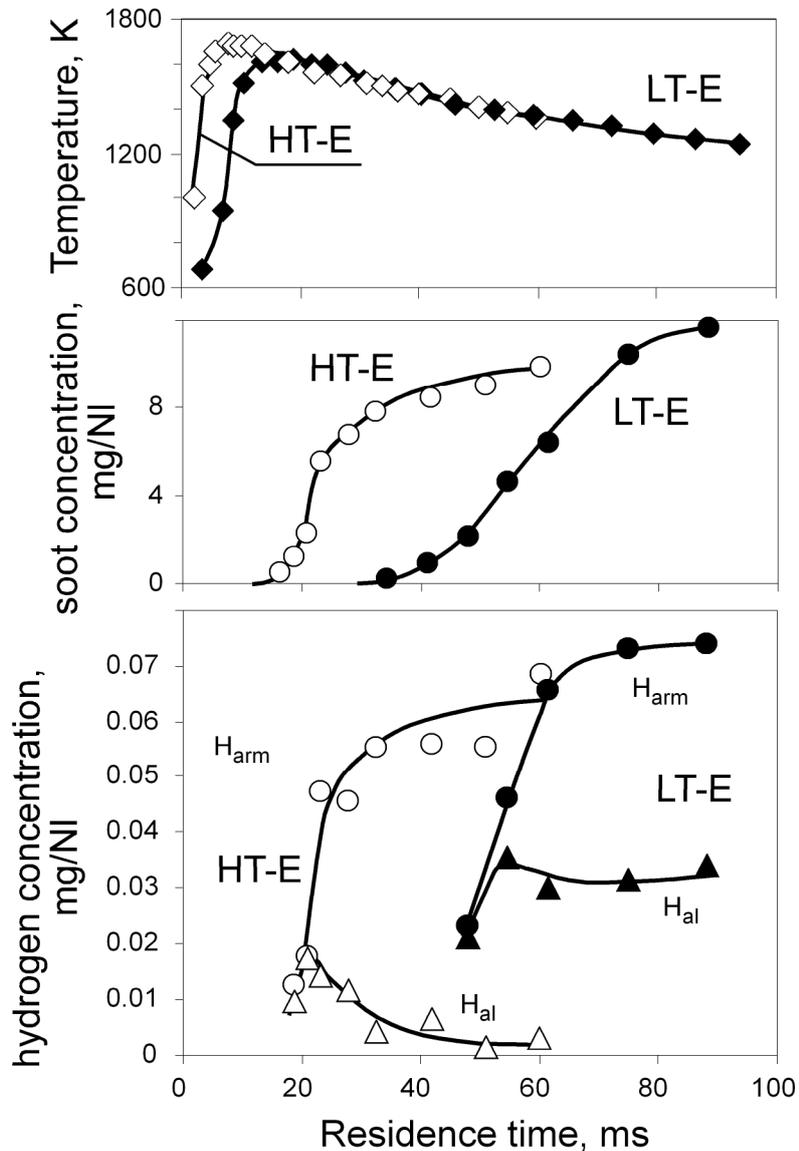


Figure 2. Temperature profile, soot and its aliphatic and aromatic hydrogen concentrations as a function of residence time in HT-E and LT-E flames

An overall description of the sooting flame structures in terms of axial profiles of temperature and concentrations of soot and its aliphatic and aromatic hydrogen is given in Fig. 2.

Soot formation is faster in the HT-E flame (middle part of Fig. 2), but in both flames similar final values of soot concentration can be observed. FT-IR analysis of soot has shown that aliphatic hydrogen is present mainly in form of methylene groups bridging aromatic rings, i. e. in form of cyclopentadiene rings. The energy required for the abstraction of the first hydrogen of such methylene groups is lower in respect to methyl and aromatic hydrogen [6]. Thus, in the first region of soot formation the large concentration of hydrogen radicals, as main abstracting agents, can cause the easier removal of methylene-group hydrogen accompanied by sp^3 - sp^2 rehybridization and formation of active radical sites.

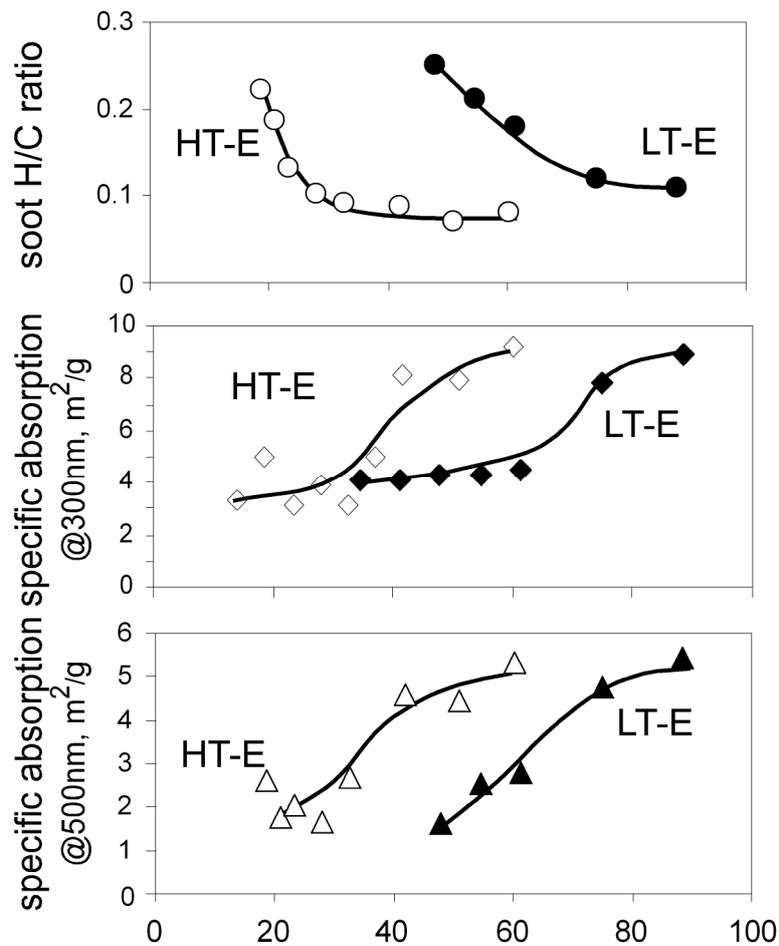


Figure 3. Soot H/C ratio and specific mass absorption measured at 300nm and 500nm as function of the residence time in LT-E and HT-E flames

The consequent increase of active sites available for surface growth justifies the steep increase of soot concentration in correspondence of the maximum consumption of aliphatic hydrogen (Fig. 2). At the end of soot formation process the main contributor to the total hydrogen content is the aromatic hydrogen. This behaviour is more marked in the HT-E flame where aliphatic hydrogen is completely absent and only aromatic hydrogen survives to a total dehydrogenation. Soot H/C ratio and specific mass absorption measured at 300nm and 500nm are reported in Fig.3 as function of the residence time. Consistently with the higher temperature, the variation of soot properties in terms of H/C ratio and absorption coefficient is faster in the HT-E flame in comparison to the LT-E flame.

A negligible hydrogen loss is noticed when soot formation and mass growth slow. In this last phase of soot formation the rise of the absorption coefficient is a signature of thermal annealing accompanied by an internal structural rearrangement.

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