

# THERMAL TREATMENT OF CARBON-BASED MATERIALS RELEVANT IN THE COMBUSTION FIELD

C. Russo, B. Apicella, F. Stanzione, A. Tregrossi, A. Ciajolo

carmela.russo@irc.cnr.it

Istituto di Ricerche sulla Combustione, CNR, Piazzale Tecchio, 80, 80125 Napoli, Italy

## Abstract

In the context of searching for alternative sources of carbon materials this work concerns the study of the structure of carbon materials obtained by carbonization at low temperatures (<700 °C) of soot and tar-like material sampled in fuel-rich premixed flames. The structural evolution of flame-formed tar under thermal treatment was investigated by spectroscopic tools and compared to that of naphthalene pitch, a commercial analogue catalytically-produced from organic precursors.

## Introduction

Although seemingly unrelated to well defined carbon allotropes, such as graphene, fullerene, etc., ill structurally defined carbon materials, as flame-formed particulate and pitch produced by organic precursors, are characterized by small subunits PAH more or less randomly grouped/layered together. These carbon materials are relevant as potential easily-accessible source of novel carbon nanomaterials. Flame synthesis has recently emerged as a viable alternative method for the synthesis of carbon nanostructures. Without outside energy expenditure, fuel-rich combustion can readily provide high temperature and radical-rich conditions appropriate for the growth of different carbon forms. Ranging from large aromatic molecules up to more complex tarry and solid carbon species, flame-formed carbon species could constitute technologically relevant sources of nanomaterials as formed or after suitable treatments. The graphitizing character common to both combustion-formed carbon materials and commercial carbon pitch renders them liable to be graphitized by controlled heating in batch and flow reactors. In this work a mild thermal treatment of carbon-based materials relevant in the combustion field, as flame-formed tar and soot, has been carried. The structural evolution of flame-formed tar under thermal treatment was compared to that of naphthalene pitch, a commercial analogue catalytically-produced from organic precursors. The carbonization process of these carbon materials has been investigated by means of spectroscopic tools.

## Experimental

Soot and tar-like species were produced from a fuel-rich ethylene/oxygen premixed

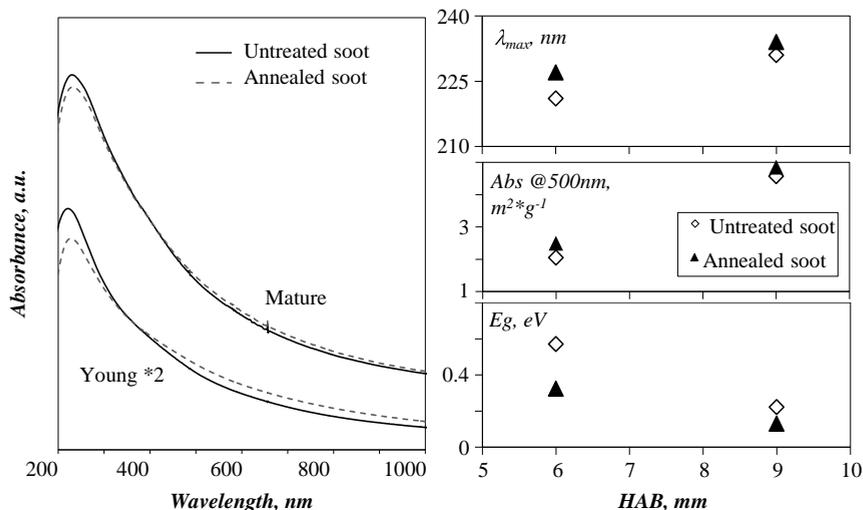
flame ( $C/O=0.8$ , cold gas velocity = 4 cm/s) stabilized on a water cooled sintered bronze McKenna (Holthuis & Associates) burner. Sampling was carried out by fast insertion of 75x12x1 mm quartz plates at two selected flame height, specifically 6 and 9 mm above the burner. The plate was inserted horizontally into the flame for the minimum time (400 ms) required both to collect sufficient material and to limit the thermal degradation of the deposited sample at flame temperature. The collected samples have been washed out with dichloromethane to avoid the inference of adsorbed organic compounds. Condensed species (CS) have been sampled at 9 mm above the burner with a isokinetic probe in order to obtain massive amount of material. CS generally exhibit an H/C atomic ratio varying in a small range (from 0.5 to 0.7) and are representative of tar-like carbon mainly constituted of small unsubstituted PAH (200-400 u). NP (Mitsubishi Gas-Chemical Company) is a complex mixture of PAH species having high molecular weight (200-1000 u) prepared by pyrolysis of naphthalene at 600°C, using HF/BF<sub>3</sub> as catalyst [1]. CS and NP, deposited between two 10x10x1 mm quartz plates, were thermally treated inside a quartz tube within a furnace under a flow of N<sub>2</sub> gas for 30 min at 300, 500 and 700°C. Within the same apparatus soot has been treated at 500°C for 1 h. The absorption spectra of soot before and after the thermal treatment were measured on an UV Visible spectrophotometer (HP8453) in the 190-1000 nm wavelength range. FT IR spectra of CS and NP were acquired in the 2500-3400 cm<sup>-1</sup> range on a Nicolet iS10 spectrophotometer. For all the samples, Raman spectra in the range of 900–3400 cm<sup>-1</sup> range were measured by means of a Horiba XploRA Raman microscope system with an excitation wavelength of 532 nm To minimize the probability of structural damages due to the thermal decomposition induced by the laser, the power of the excitation laser beam was reduced to about 0.1 mW.

## Results

### Soot

The carbonization was studied for soot sampled at 6 mm (here named young soot) and 9 mm (here named mature soot) above the burner. More information on the structural evolution of soot along the flame can be found in previous work [2]. The deposition on a transparent substrate of appropriate size allowed to measure the UV-Visible spectra before and after the thermal treatment, reported in the left of Fig. 1. Analyzing specific optical parameters, as the UV-Visible maximum position ( $\lambda_{\max}$ ), optical bang gap ( $E_g$ ) and mass absorption coefficient, reported in the right part of Fig. 1, it is possible to follow in detail the spectral variation associated to the carbonization process. The  $E_g$  has been calculated on the tail of UV-Visible spectra using the Tauc relationship [3]. The decrease of  $E_g$  [4] as well as the downshift of  $\lambda_{\max}$  [5] are good signature of the increase of the sp<sup>2</sup> carbon content. Comparing the spectra before and after heat treatment, it can be seen that young soot undergoes stronger modifications presenting a significant increase of the visible absorbance along with an appreciable downward shift of  $\lambda_{\max}$  and a

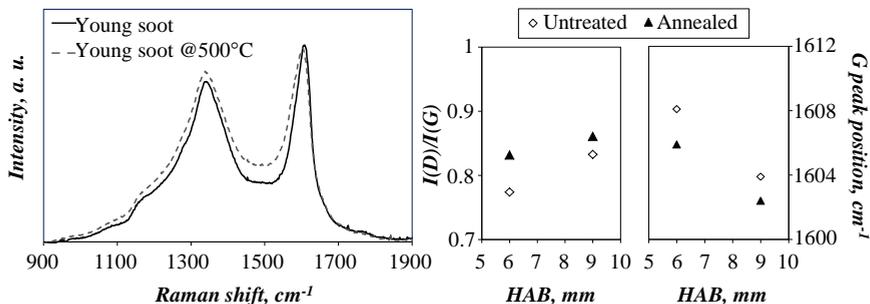
considerable decrease of the band gap energy.



**Figure 1.** UV-Visible spectra (left part) and absorption coefficient (measured at 500 nm), maximum absorption position and band gap (right part) of young and mature soot before and after the thermal treatment at 500°C.

As regards the mass absorption coefficient it can be considered a good proxy of soot aromatization occurring during thermal treatment since only processes that affect  $sp^2$  cluster size and shape can change carbon absorptive properties. To measure the mass absorption coefficient before thermal annealing, UV-Visible absorption spectra of soot suspended in N-methyl-2-pyrrolidinone (NMP) (soot concentration = 10 mg/l) were measured in a 1-cm quartz cell. The mass loss was calculated with a thermogravimetric analysis of the same young and mature soot powder setting up the same temperature rate and value of the furnace. A mass loss of 8 and 4.8% was measured for young and mature soot respectively. The same reduction was imposed to the optical path. With these assumptions, an increase of 22 and 6 % of the mass absorption coefficient was found for young and mature soot, respectively. Raman spectroscopy has been performed before and after the thermal treatment of young and mature soot. As example, the spectra of untreated and annealed young soot are reported in the left part of Fig. 2. The spectra were continuum subtracted with a linear correction between 900 and 1900  $cm^{-1}$ . The two typical peaks of carbon materials, near 1600  $cm^{-1}$  (G or “graphite” peak) and 1350  $cm^{-1}$  (D or “defect” peak), can be observed in the first order spectral Raman region, between 1000-1900  $cm^{-1}$ . The peaks broadness underlies the highly disordered structures of soot. Beside the D and G bands, other minor modulations, induced by defects outside and inside the crystal lattice, occur. A Lorentzian and a Breit Wigner Fano (BWF) curves were used to fit the D and the G peaks, respectively [6]. Two additional Lorentzian lines (D5 and D4) were used to fit the features at 1100-1300  $cm^{-1}$ , while a Gaussian function has been chosen for the D3 band

around  $1500\text{ cm}^{-1}$ . For highly disordered carbons, characterized by an aromatic cluster size smaller than 2 nm, the  $I(D)/I(G)$  ratio increases linearly with the crystal size following the equation proposed by Ferrari and Robertson [7].



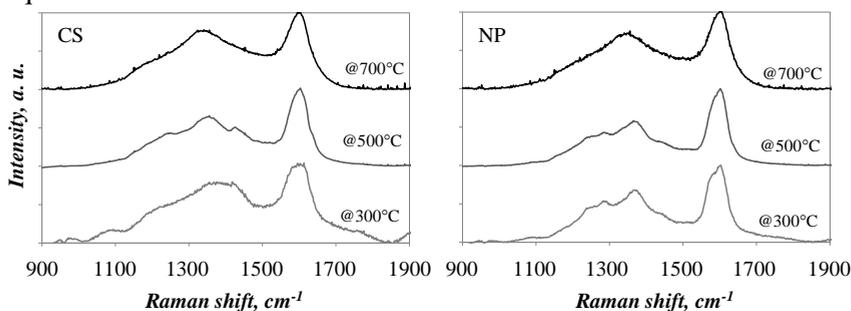
**Figure 2.** Raman spectra (upper part) and  $I(D)/I(G)$  ratio and G peak position (lower part) of young and mature soot before and after the thermal treatment at  $500^\circ\text{C}$ .

The G band has been assigned to the  $\text{C}=\text{C}$  stretching of all pairs of  $\text{sp}^2$  atoms. Some interesting information can be derived just from the examination of the G peak position for all soot samples reported in the right part of Fig. 2. The first observation regards the high G peak position which keeps well above the  $1600\text{ cm}^{-1}$  value for all soot samples. To this regard it has to be reminded that, regardless the excitation wavelength, the G peak position takes a fixed value of  $1580\text{ cm}^{-1}$  in perfect and infinite graphite crystals, upshifted to  $1600\text{ cm}^{-1}$  [7] for nanocrystalline graphite because of the effect of finite crystal size. The high G peak position of soot has been attributed to the presence of  $\text{sp}^2$  C-C bonds shorter than aromatic bonds presenting higher vibration frequencies and featuring olefinic chains and small aromatic layers [6]. The aromatization, as soot is thermally treated, is testified by the increase of the  $I(D)/I(G)$  ratio and the decrease of the G peak position, approaching values closer to the  $1600\text{ cm}^{-1}$  band limit of purely graphitic carbon.

### Tar-like carbon

The study of the transformations in moderately heated batch processes of both combustion synthesized and commercial tar-like materials has been performed applying Raman and FT-IR spectroscopy. The Raman spectra of CS and NP after their thermal treatment at  $300$ ,  $500$  and  $700^\circ\text{C}$  are reported in Fig. 3. They were continuum subtracted with a linear correction performed between  $900$  and  $1900\text{ cm}^{-1}$ , however up to  $500^\circ\text{C}$  the raw spectra exhibit an intense fluorescence background due to the presence of hydrogen-rich aromatic species [6]. The spectra reported in Fig. 3 exhibit features in common with those obtained for soot particles reported in Fig. 2, i.e. a G peak around  $1600\text{ cm}^{-1}$  and a broad complex band lying between  $1100$ - $1500\text{ cm}^{-1}$ . However, a careful examination of the spectra reveals noticeable differences in the D band region. Indeed up to  $500^\circ\text{C}$  substructures

characterize the sides of the D peak for all the tar-like materials. While in graphitic materials only one D line is observed, PAH molecules show few modes around  $1300\text{ cm}^{-1}$  [6]. It can be supposed that some merging of different PAH moieties, featuring CS and NP composition, can be responsible for the substructures of the D peak. Moreover, for hydrogenated aromatic compounds the coupling with C-H waggings has also to be considered, since the typical frequencies of these vibrations lie in the  $1250\text{-}1300\text{ cm}^{-1}$  spectral region [6]. However in the case of NP, the complex  $1100\text{-}1500\text{ cm}^{-1}$  band shows several well defined components at approximately  $1250$ ,  $1290$  and  $1375\text{ cm}^{-1}$ . To this regards it has to be reminded that NP is characterized by the presence of differently sized aromatic compounds but also naphthenic rings and alkyl groups at the edge of the molecules. Thus many C-C bonds having a different nature from those featuring purely aromatic polynuclear compounds are present in NP and could be responsible for these well defined vibrational modes. As shown in Fig. 3, only with the thermal treatment at  $700^\circ\text{C}$  Raman spectra acquire the characteristic shape of disordered carbons, with a broad and unique D band around  $1350\text{ cm}^{-1}$ .



**Figure 3.** Raman spectra of annealed (at 300, 500 and  $700^\circ\text{C}$ ) CS and NP.

With the thermal treatment there is also a gradual decrease of the fluorescence background due to the elimination of hydrogen resulting from the aromatization and condensation of the molecules. This is confirmed by the analysis of the infrared spectra of the annealed materials. The aliphatic hydrogen is preferentially removed and at  $500^\circ\text{C}$  reaches negligible values due both to the volatilization of the lighter compounds and to the dehydrogenation and coagulation processes.

## Conclusions

A mild thermal treatment of some carbon-based materials produced from organic precursors and relevant in the combustion field, as soot and condensed species, has been investigated by spectroscopic tools. Soot sampled on a quartz plate at different heights above the burner along an ethylene premixed flame has been treated at  $500^\circ\text{C}$ . The deposition on a transparent substrate allowed to perform UV-Visible spectroscopy on the samples to follow the change of specific optical features, such as the absorption maximum position, band gap and mass specific absorption. Younger soot undergoes stronger modifications presenting a significant

increase of the absorption coefficient and of the maximum absorption position and a considerable decrease of the band gap energy. This result is confirmed by the evolution of the Raman spectra, showing a significant increase of the I(D)/I(G) ratio and decrease of the G peak position for young soot after the thermal treatment. This finding suggests that a moderately heated batch process is more effective in the aromatization of less organized soot particles providing the mobility necessary to slight rearrangement in a not well stiff structure.

Similarities and dissimilarities between the thermal behavior of flame-produced tar-like materials and catalytically derived aromatic polynuclear mixtures have been also studied to compare combustion formed condensed species with a commercial analogue pitch. Until the complete loss of aliphatic functionalities, CS and NP do not lose their molecular nature, assuming the Raman spectrum characteristic typical of disordered carbonaceous materials only at 700°C. Ongoing works are devoted to increase the temperature of the thermal treatment up to 1000°C and to use a different reactor configuration. Indeed preliminary tests on a sealed batch crucible allow to heat also the volatile matter, a significant fraction of the tar-like materials, that in the flow reactor used in this work was lost.

### Acknowledgments

This work was financially supported by Accordo MSE-CNR- Ricerca di sistema elettrico nazionale- Project “Miglioramento dell’efficienza energetica dei sistemi di conversione locale di energia” PAR 2013-2014.

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