Characterization of carbon particulate matter relevant in combustion

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The complexity of carbon particulate matter produced from combustion of hydrocarbon fuels requires for its complete characterization a wide array of diagnostic tools specific for the determination of structure, size and chemical composition. All these characteristics are important in relation to the source and evolution in combustion and atmospheric aerosols and to the environmental impact of the carbon particulate matter emitted from combustion processes. The contribution of combustion-derived particulate matter to the atmospheric aerosol is particularly relevant in the range of fine (<2.5μm) and ultrafine (<100nm) size range that is indicated as the most dangerous for human health. In this paper the main characteristics of fine and ultrafine carbon particulate matter produced in controlled combustion conditions and sampled by using batch sampling techniques are reported and the analytical approach used by our group has been briefly reviewed. Advantages and limitation of the techniques more recently developed have been analyzed, for building and resolving the analytical puzzle represented by carbon particulate matter characterization.

1. Methods

1.1 Sampling procedure
The experimental combustion system has been described in detail elsewhere (Ciajolo et al., 1994). Briefly, combustion products, including gaseous, tarry and solid material, were collected from premixed fuel-rich laminar flames produced on a commercial McKenna sintered bronze burner at atmospheric pressure. A water-cooled probe was used to sample combustion products. Light gases were on-line analyzed by gas chromatography (GC). Condensed phases were collected along the sampling line and extracted by dichloromethane (DCM) to separate the DCM-soluble species, containing polycyclic aromatic hydrocarbons (PAH), from the DCM insoluble species (soot). The DCM-insoluble fraction was re-extracted with N-methylpyrrolidinone (NMP) in order to detach species strongly adsorbed on soot (NMP-extract). By using NMP solvent and ultrasonic bath, stable soot suspensions were obtained to be analyzed by of spectroscopic, chromatographic and optical techniques.

1.2 Gaseous phase

Gaseous products were measured by on-line GC: C_1-C_6 HC were analyzed by a GC equipped with a flame ionization detector (FID); CO_2, CO, H_2, N_2 were analyzed by a GC with thermoconducibility detector (TCD) (Apicella et al.2002).

1.3 Condensed phases

The H/C and resistance toward oxidation of DCM-soluble fraction and soot as separated by the procedure before described, were obtained by elemental analysis and thermogravimetry (DTG), respectively (Alfè et al., 2009).

Soot aggregate and soot elementary particle sizes (macrostructure and microstructure) have been detected by Transmission Electron Microscopy (TEM). Nanostructural insights (~ 10 nm) were obtained by High Resolution-TEM (HRTEM, Galvez et al., 2002).

PAH up to 300 u were identified and quantified in the DCM-soluble fraction by GC coupled with mass spectrometry (GC-MS) (Tregrossi et al., 1999).

1.3.1. Size Exclusion Chromatography (SEC)

The SEC analysis of DCM-, NMP-extract and of soot suspended in NMP was carried out for the molecular weight (MW) evaluation on two different SEC columns able to furnish a reliable MW distribution in a wide range of MW (100-10^{10}). PL-gel styrenedivinylbenzene individual pore column was used to investigate the MW region (10-10^4u) (Alfè et al., 2007) and a Jordi Gel divinylbenzene (DVB) Solid Bead (non-porous) column was used in the particle-size region (10^5-10^{10}u) (D'Anna et al., 2009). The relation between molecular mass of polystyrene standards and retention time has been used for the MW evaluation (Apicella et al., 2003). The solvent used as eluent was NMP.

1.3.2. Atmospheric Pressure Laser Desorption Mass Spectrometry (AP-LDI-MS)

The size-segregated samples separated by SEC were further analyzed by AP-LDI-MS (Alfe et al., 2008).The AP-LDI source interface flange, housing the laser focusing elements and imaging system, was attached directly to the Agilent 1100 series LC/MSD ion trap SL (Agilent Technologies, Palo Alto, CA, USA) ion source flange. A nitrogen laser (337 nm) produced a 10-Hz pulsed beam of UV light.

1.3.3. Uv-visible absorption spectroscopy

UV-visible spectra of the samples suspended in NMP were measured on an HP 84523 Diode Array spectrophotometer (Apicella et al., 2004a).

1.3.4. Fluorescence spectroscopy

Fluorescence emission spectra of the samples were measured on a Perkin-Elmer LS-50 spectrofluorimeter (Apicella et al., 2004b).

1.3.5. Fourier Transform Infrared Absorption spectroscopy (FT-IR).

FT-IR analysis in the 3400-2700 cm^{-1} wavelength region of the DCM-extract dissolved in carbon tetrachloride was performed on a Perkin-Elmer 1600 FT-IR spectrophotometer (Ciajolo et al., 1997).

TEM, HR-TEM (nanostructure analysis), Dynamic Light Scattering (DLS), Time Resolved Fluorescence Polarization Anisotropy (TRFPA) and Fluorescence Correlation Spectroscopy (FCS) techniques (size evaluation) have been also applied in collaboration with CNRS and research groups from the University of Naples.

2. Results and discussion

The great variability of the physical and chemical properties of the combustion-generated carbon particles is related in a complex way to the different both sequential and concurring routes leading to soot formation.

In the first step of a typical fuel-rich combustion in premixed conditions, the fuel undergoes oxidation leading to small hydrocarbon radicals which progressively grow by successive addition (mainly by HACA mechanism, Frenklach et al., 1987) forming the first aromatic ring and larger polyaromatic structures. The growth by acetylene addition (HACA) and coalescent coagulation of aromatic precursors lead to primary particles and chain-like aggregates (Figure 1). To this regard it is still matter of debate if the transition from gas-phase to solid-phase species pass through an intermediate liquid/viscous state.

The progressive evolution of the combustion products increases the structural complexity of the "primeval soup" from a molecular scale length to a particle scale length (>10 nm). Moreover, the characterization problem is further complicated by the differences at a nanoscale length (i.e. dimension and orientation of the graphitic layers) arising in dependence on fuel (aliphaticity/aromaticity degree) and synthesis/combustion conditions (i.e. temperature, residence time, feed ratio).
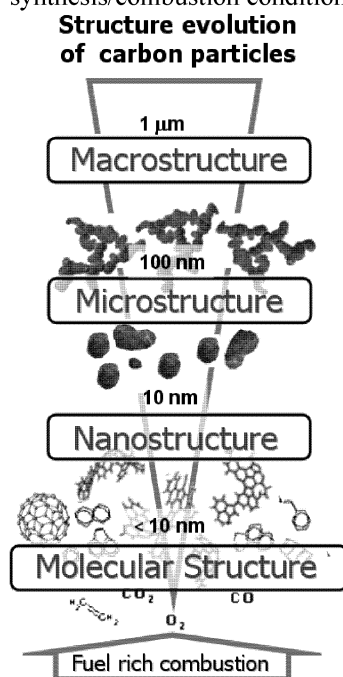

Figure 1. Structural changes in particulate formation process from precursors (<10nm) to fine particles (~1μm) in fuel rich premixed combustion.

In this framework a large array of analytical techniques is necessary to properly handle the characterization problem. Figure 2 reports the applicability range of specific diagnostics to the fuel-rich combustion products classified in dependence of their

physical state, MW and size. The advantages and limitation of each technique are briefly reported in the following scheme.

Diagnostics of combustion products	Molecular weight, u	size, nm	physical state	species
	10		gas-phase	$C_1H_X-C_2H_X-C_3H_X-C_4H_X$ benzene
	100	1		PAH (planar/curved structures) fullerenes
	1E3		liquid viscous tarry material	
	1E4			soot precursors
	1E5			
	1E6	10		soot elementary particles
	1E7			
	1E8		solid-phase	soot aggregates
	1E9	100		

(Diagnostic techniques labelled vertically: DLS, elemental analysis, Thermogravimetry, Transmission Electronic Microscopy (TEM), Size Exclusion Chromatography, absorption spectroscopy, fluorescence spectroscopy, LDI-MS, HPLC, GC-MS)

Figure 2. Classification of the condensed phases in soot formation with an indication of the diagnostics suitable for their separation, identification and size evaluation.

The conventional GC-MS techniques allow to obtain qualitative and quantitative determination of PAH and their isomers up to 300 u; the sample vaporization is indeed necessary hindering the analysis of low-volatile heavy aromatic species. A particle beam interface (Tregrossi et al., 1999) allows the direct injection of the sample in the MS ionization chamber without passing through the GC column. The disadvantage is the hard ionization (by electron impact) that can lead to the analyte fragmentation. Only PAH with low MW (<500) are detected.

The LDI-MS at atmospheric pressure (AP-LDI-MS) is a softer ionization technique compared with conventional vacuum LDI-MS systems leading to less fragmentation with the possibility of analyzing also solid materials. The m/z range is limited to about 3000 u and in order to obtain better results a polydispersed sample should be separated into fractions of narrow MW range.

SEC carried out by using different SEC columns allows to achieve a quite complete MW distribution of both soot and soot extract from 10^2u–10^{10}u, i.e. in the molecular to particle scale with the recovery of sample fractionated into well-defined MW ranges to be further analyzed. However, a calibration with standard molecules is necessary for converting the elution time in MW and the standard molecules should be as similar as possible to analyte molecules in order to avoid the structural and shape effects on the retention times.

DLS is an useful tool to obtain the hydrodynamic size of species down to nanometer size. However, this technique applied to polydispersed samples as carbon particulates has shown to be much more sensitive to the larger size components (>20 nm), thus hindering the correct evaluation of the lower MW fraction. Moreover, DLS cannot be

used for fluorescing species as the lower nanometric size carbon species usually are. TRFPA and FCS are complementary to DLS because they allow the hydrodynamic size evaluation of the carbon particulate fluorescing fractions. These techniques, however, should be effectively applied only on monodisperse fluorescing samples.

UV-Vis absorption spectroscopy is suitable at a molecular level in particular to have information on aromatic moieties of both soot and DCM-extract. The shortcoming is that the interpretation of absorption spectra of complex mixtures is generally complicated due to the overlapping of bands from different components. The interference of the solvent (NMP) on the UV absorption limits the visualization of the soot spectra down to 260 nm.

UV-Vis fluorescence spectroscopy is more specific and more selective than absorption spectroscopy, but the spectra deconvolution of complex mixture is difficult to be achieved and occurrence of self-quenching, self absorption and energy transfer processes when concentration increases, can depress and strongly modify the fluorescence signal.

FT-IR spectroscopy furnish a qualitative and semi-quantitative evaluation of the aromatic and aliphatic hydrogen content of the DCM-extract on the basis of the assignment of each peak to specific C-H groups. The major limitation of FT-IR is the choice of a suitable solvent that should be transparent in the IR region and able to dissolve the samples. Carbon tetrachloride (CCl_4) is a good compromise because of its transparency in IR region but it is less effective with respect to DCM in dissolving combustion samples.

In Figure 3 a general scheme of the size-segregated fractions measured with the above mentioned techniques in the carbon particulate is reported.

The carbon particulate microstructure and nanostructure has been analyzed by TEM, HRTEM analysis revealing large chain-like aggregates (~100-140nm) of primary particles (~20-40nm) embedded in amorphous-like material. Differences in the primary particles nanostructure constituting the aggregates have been observed in the particulates originating from the combustion of aliphatic and aromatic fuels (Alfè et al, 2009). The MW distribution of carbon particulate matter in a wide MW range (100-10^{10}u) is obtained by SEC and mass spectrometry of liquid (GC-MS) and solid (LDI-MS) phases. DCM-extract consists of a MW distribution in 100-400 u range (identified as PAH by GC-MS and LDI-MS) and of a smaller one in the 400-1200 u range (i, probably polymeric carbonaceous structures as inferred by AP-LDI-MS, Alfè et al., 2008). A higher MW distribution (~10^5u) is object of current studies. A multimodal MW distribution of soot can be obtained by SEC over a very wide MW range consisting of four main peaks: the MW distributions peaked at ~400u and at ~800 u are identified as large PAH (PAH with C>24) and polymeric carbonaceous structures, respectively, by LDI-MS (Alfè et al., 2008). The diameter of the higher soot MW distribution (~10^9u) is obtained by DLS while the ~10^6u distribution need further investigation.

All fractions of the combustion carbon particulates absorb in the UV-Visible, but only the lower size species exhibit fluorescence. The spectral features are related to some specific features of aromatic moieties giving insights on the internal electronic structure (hybridization sp^2/sp^3 states with their related hydrogen content, Tregrossi et al, 2007).
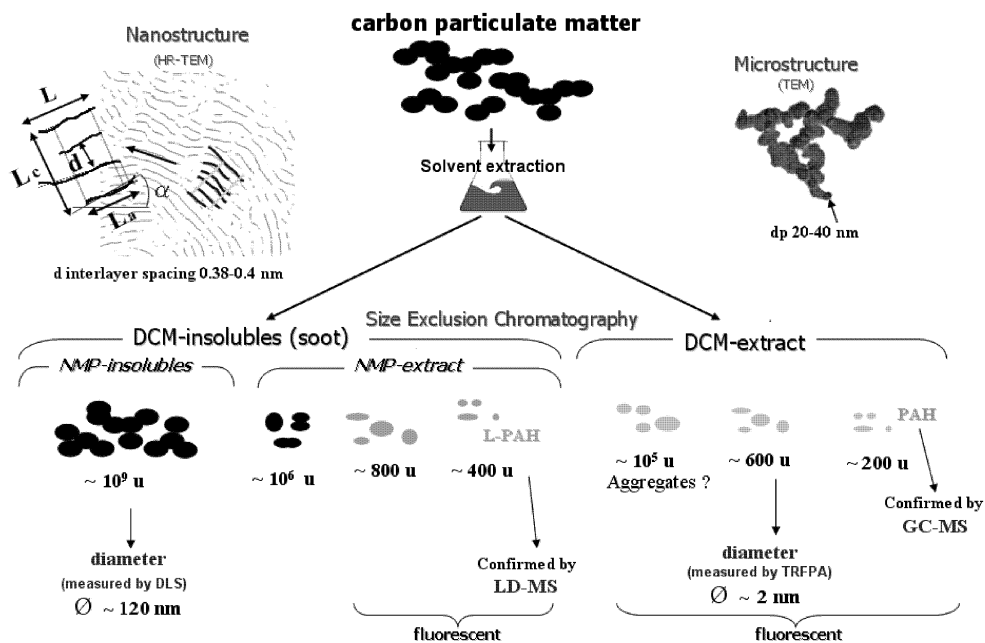
Figure 3. General scheme of carbon particulate characterization in fuel rich conditions.

References

Alfè M., Apicella B., Barbella R., Rouzaud J-N, Tregrossi A., Ciajolo A., 2009, Proceedings of the Combustion Institute 32, 697–704.

Alfè M., Apicella B., Tregrossi A., Ciajolo A., 2008, Carbon 46, 2059-2066.

Alfè, M., Apicella, B., Barbella, R., Tregrossi, A., Ciajolo, A., 2007, Energy Fuels 21 (1), 136-140.

Apicella, B., Barbella, R., Ciajolo, A., Tregrossi, A, 2002, Combust. Sci. Tech. 174 (11-12), 309-324.

Apicella B, Barbella R, Ciajolo A, Tregrossi A., 2003, Chemosphere 51, 1063–1069.

Apicella, B., Alfè M., Barbella R., Tregrossi, A., Ciajolo, A., 2004a, Carbon 42, 1583–1589.

Apicella, B., Ciajolo, A., Tregrossi, A., 2004b, Analitycal Chemistry 76 (7), 2138-2143.

Ciajolo A., Barbella R., D'Anna A., 1994, Combust. Sci. Technol. 100, 271–278.

Ciajolo, A., Apicella, B., Barbella, R. and Tregrossi, A., 2000, Combust. Sci. Technol. 153 (1), 19-32.

D'Anna A., Ciajolo A., Alfè M., Apicella B., Tregrossi A., 2009, Proceedings of the Combustion Institute 32, 803–810.

Frenklach M, Warnatz J., 1987, Combust Sci Technol. 51, 265–283.

Galvez A., Herlin-Boime M., Reynaud C., Clinard C., Rouzaud J.-N., 2002, Carbon 40, 2775–2789.

Tregrossi A., Ciajolo A., Barbella R., 1999, Combust. Flame 117, 553–561.

Tregrossi, A.; Barbella, R.; Ciajolo, A.; Alfè, M., 2007, Combust. Sci. Technol. 179 (1-2), 371-385.