CHEMICAL AND STRUCTURAL PROPERTIES
OF SOOT FROM DIVERSE SOURCES

C. Russo*, B. Apicella**, A. Tregrossi*, J. S. Lighty**, A. Ciajolo*
carmela.russo@irc.cnr.it
*Istituto di Ricerche sulla Combustione, CNR, Piazzale Tecchio, 80, 80125 Napoli, Italy.
**Department of Chemical Engineering, University of Utah, 50 S. Central Campus Drive, Salt Lake City, UT 84112-9203, United States.

Abstract
The characterization of soot generated in inverse diffusion flames (IDF) is meaningful for the study of soot formation, with particular regard to soot inception. Indeed, it has been found that IDF soot keeps on the features of incipient (young) soot particles as those formed in combustion systems as premixed and diffusion flames. This work regards a deeper characterization of carbon particulate collected from the exhaust of an ethylene IDF in comparison to young and mature soot sampled inside an ethylene premixed flame (PMXF). Elemental analysis, Raman and UV-Visible spectroscopy were carried out to evaluate soot aromaticity features. The comparison between soot from these two different flame configurations confirmed that IDF is a suitable source of young soot to be massively analyzed. The features of mature soot derived from laboratory scale flames resulted to be similar to those of soot emitted in practical combustion processes as diesel engines and coal pyrolysis.

Introduction
To avoid the complex fluido-dynamic fields featuring real combustion systems as engines, gas turbines, etc. [1], laboratory premixed and diffusion flames are the preferred experimental systems for studying soot formation in most of combustion research laboratories. To this regard, a premixed flame (PMXF) offers great advantages in the study of flame structures for theoretical and modelling purpose. Indeed, a PMXF, in which fuel and oxidizer are fully mixed prior to combustion, is a one-dimensional problem, where chemistry and transport are simplified allowing a relatively high experimental accessibility. From the point of view of mathematical models, computing laboratory premixed flames is a first step toward more complex configurations, so experimental results are also useful for the validation and development of detailed kinetic modelling of soot formation. Moreover, simple laminar premixed flames offer the possibility of easily changing the operative conditions to investigate the effects of parameters, such as temperature, air/fuel equivalence ratio (φ), fuel nature, residence time, etc., on the flame structure and on the formation, coagulation and growth of high molecular carbonaceous structures [2, 3]. For understanding soot inception process the main disadvantage of the premixed flame configuration is the too low amount of young soot produced limiting the massive sampling and the further detailed
characterization. The flame configuration known as an inverse diffusion flame (IDF) appears to be a good alternative for getting enough quantities of young soot which is massively formed on the fuel side of the flame and emitted without entering in the oxidation region, so avoiding further modification and destruction by oxidation [4]. A schematic representation of the PMXF and IDF is reported in Fig.1.

![PMXF and IDF Schemes](image)

**Figure 1.** Schemes of the premixed, PMXF, and inverse diffusion flames, IDF.

In this work soot samples derived from IDF and PMXF have been analyzed for better inferring the differences between young and mature soot. Moreover, the main bulk features, namely the H/C atomic ratio and UV-Visible absorption coefficients, of IDF and PMXF soot as representative of different typologies of soot coming from practical systems have been compared with those of soot formed in practical combustion processes as diesel engines and coal pyrolysis. The comparison has been extended also to reference carbon materials to assess the use of laboratory flames as sources of carbonaceous solids for practical applications.

**Experimental**

Carbonaceous particulate was sampled along the axis of a fuel-rich ethylene premixed flame (C/O=0.8, cold gas velocity= 4cm/s) produced on a water-cooled sintered-bronze McKenna burner (Holthuis & Associates). A stainless-steel, water-cooled, isokinetic probe (i.d. 2mm) was inserted vertically into the flame with a conical tip diameter of 3mm. Soot sampled at low height above the burner (HAB) was named nascent soot, whereas soot sampled before the maximum soot formation rate (intermediate HAB), and at the end of soot formation region (highest HAB) were named young and mature soot, respectively.
The IDF burner was designed after the system of Blevins et al. [4]. The flow rates of air, fuel, and nitrogen were 5 SLPM, 15 SLPM, and 60 SLPM, respectively. The visible flame height in a dark room was 60 mm. Carbon particulate matter sample was taken at 10 cm above the tip of the flame using a 10-cm-length stainless steel probe with a 1mm-i.d. capillary tip.

The organic compounds condensed and/or adsorbed on soot were separated from it by solubilization in dichloromethane (DCM).

Raman spectra were measured by means of a Horiba XploRA Raman microscope system with an excitation wavelength of λ = 532 nm (frequency doubled Nd:YAG-solid state laser, 25 mW). Hydrogen and carbon content 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 HP8453 spectrophotometer.

Data obtained on soot collected from diesel engine [5] and from coal pyrolysis [6] were also used for comparison. Briefly, diesel soot (DS) were collected from high pressure exhaust gas recirculation cooler, two of them came from a diesel engine bench (DS6 and DS9) and the other two (DS17 and DS19) were obtained from a vehicle after covering a given number of kilometers [5]. A particulate matter named Standard Reference Material 1650b (SRM) acquired in the National Institute of Standards and Technology, USA, was also analysed as reference diesel soot. Coal soot samples came from pyrolysis of a high volatile bituminous coal in a laminar drop tube reactor in N₂ and CO₂ atmospheres [6]. Beside combustion-formed soot, carbons derived from different sources, namely: coal tar pitch (CP) (H/C = 0.58), naphthalene pitch (NP) (Mitsubishi) (H/C = 0.54), N110 (CB110) and N330 (CB330) carbon black (Phillips Petroleum) (H/C=0.05), turbostratic (TMC) and graphitized (GMC) carbon black named mesoporous carbon (Aldrich) and fullerenic carbon (FC) (Aldrich) (H/C < 0.02), have been used as reference carbon materials for the UV-Visible spectroscopy and elemental analysis.

Results
Raman spectra have been preliminarily measured for IDF and young PMXF samples. A detailed deconvolution procedure has been recently used for evaluating as Raman spectra features change during soot formation in premixed flames of diverse fuels [7]. By implementing the same procedure on the Raman spectra reported in Fig. 2, aromatic layer lengths of about 1nm can be evaluated from the I(D)/I(G) ratio that resulted to be equal to ~ 0.7 for both IDF and young PMXF soot. Moreover, also the other Raman parameter sensitive to the disorder and size of aromatic rings, i.e. the G peak width, exhibits similar value. The Raman spectrum of a mature PMXF soot sampled at a higher height is also reported in Fig. 2 to put in evidence the differences between young and mature soot. Specifically, in comparison to mature soot lower I(D)/I(G) ratio and peak width can be observed for young soot.
The hydrogen content, in terms of atomic H/C ratio, and the specific mass absorption coefficient (@500nm) of soot and carbon samples are altogether gathered, respectively, in Fig. 3 and Fig. 4. Specifically, such properties are reported for soot samples derived from the IDF and PMXF, from coal pyrolysis, and diesel engines in comparison to carbon materials spanning over a large range of hydrogen content and different chemical structure.

The hydrogen content includes aliphatic and aromatic hydrogen contribution, so that it should be not a reliable proxy for the number of aromatic sp² bonds. To verify the reliability of a relationship between the H/C and aromaticity, the mass absorption coefficient has been considered as sensitive to the sp² aromatic content [8]. The mass absorption coefficients span for all soot samples and carbonaceous standards from 1 to 6 m²/g, while H/C ratio values vary from about 0 to 0.6.

Overall, it has been observed that for standard carbons, high absorption coefficients correspond to low hydrogen contents, whereas such inverse relationship appears verified just for some of diesel soot samples. This could depend on the oxygen content significantly present (10-20 wt.%) particularly in diesel soot samples [5]. The comparison among soot from all the different combustion sources indicates that a premixed flame is able to produce soot with a wide range of chemical properties showing the great flexibility of this flame reactor to synthesize carbonaceous materials with tailored features by selecting the appropriate combustion conditions.

As regards IDF and young PMXF soot the low mass absorption coefficient (around 2 m²/g) and the relatively high H/C atomic ratio (around 0.2) show to be rather
similar. It derives that the exhaust of an IDF is a suitable source of young soot particles allowing the collection in few time of significant amounts of precursor and young soot material.

On the other hand, a premixed flame offers the possibility of studying soot evolution and furnish at high residence times significant amounts of mature soot with a low hydrogen content and a high visible mass absorption coefficient similar to standard hard carbons.

![Figure 3. H/C atomic ratio of standard carbons and of soot collected from flame, coal pyrolysis and diesel engine.](image)

**Figure 3.** H/C atomic ratio of standard carbons and of soot collected from flame, coal pyrolysis and diesel engine.

![Figure 4. Mass absorption coefficient measured at 500nm of standard carbons and of soot collected from flame, coal pyrolysis and diesel engine.](image)

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**Conclusions**

Soot generated in an IDF was analyzed by using Raman and UV-Visible spectroscopy to evaluate its aromaticity and elemental analysis for hydrogen-to-carbon atomic ratio determination. The comparison with soot sampled along a different flame configuration as the PMXF demonstrated that IDF is a suitable source of young soot to be massively analyzed. The features of soot derived from
laboratory scale flames were also compared to soot formed in practical combustion processes as diesel motor engine and coal pyrolysis. Flame-generated particle properties, namely the H/C and the UV-Vis absorption coefficient, vary in the same range of values shown by soot derived from practical combustion processes. However, the relationship between hydrogen content and absorption coefficients, in turn related to soot aromaticity can fail in the case of soot coming from practical combustion systems.

References


