

# SOOT FORMATION PROPERTIES IN A PREMIXED TOLUENE-DOPED METHANE FLAME

C. Russo\*, L. Giarracca\*\*, F. Stanzione\*, A. Tregrossi\*, A. Ciajolo\*

carmela.russo@irc.cnr.it

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

\*\*Dipartimento di Ingegneria Chimica, dei Materiali e della Produzione Industriale,  
Università degli Studi di Napoli Federico II, P.le Tecchio 80, 80125 Napoli, Italy

## Abstract

The sooting structures of premixed methane and toluene-doped (0.8 vol.%) methane flames were analyzed by sampling and analysis of condensed phases. It was shown that the addition of very small amounts of toluene drastically changes soot yield and the properties of soot formed as inferred by detailed chemical and spectroscopic analysis.

## Introduction

The effect of operative parameters such as temperature and feed ratio on the amount and properties of combustion-formed carbonaceous species has been well assessed [1]. The formation of these pollutants, however, is also influenced by the fuel molecule in terms of aromatic and aliphatic character. Many practical petroleum-derived fuels comprise hundreds of aromatic compounds and aliphatic components, such as straight chain paraffins, branched chain paraffins, cycloparaffins and alkenes. Depending on the source of the parent crude oil and the refinery process, their composition may vary significantly. The future fuel supply will become more and more diversified. This trend will necessitate fundamental studies in well-defined and well-controlled environments to establish, among other aspects, synergistic effects on the chemical kinetic behavior of these fuel blends as compared to the cases with respective single fuel. Aromatic hydrocarbons are major components of petroleum-based fuels used for transportation and energy production, as gasoline, diesel, oil kerosene and heavy fuel oils. Aromatics are also key precursors of soot, which is an important combustion-derived air pollutant known to be harmful to both the environment and the human health. Most investigations have been reported on aliphatic hydrocarbon flames whereas few studies are available for aromatic compounds. Moreover, these studies have been mainly focused on the oxidation of pure aromatic compounds rather than on their mixtures with aliphatic hydrocarbons even though aliphatic/aromatic mixtures are more representative of practical liquid fuels as gasoline and diesel oils. As the simplest alkylated aromatic hydrocarbon, toluene is one of the most abundant aromatic component in gasoline and a typical component in gasoline surrogate

fuels. Furthermore, its major initial decomposition product, benzyl radical, is recognized as a key intermediate involved in the formation of polycyclic aromatic hydrocarbons and soot.

In this work the formation and the chemical and structural characteristics of soot produced in a laminar premixed flat flame of methane doped with a small percentage of toluene have been analysed and compared with the same data obtained in the methane flame burning in similar feed and temperature conditions.

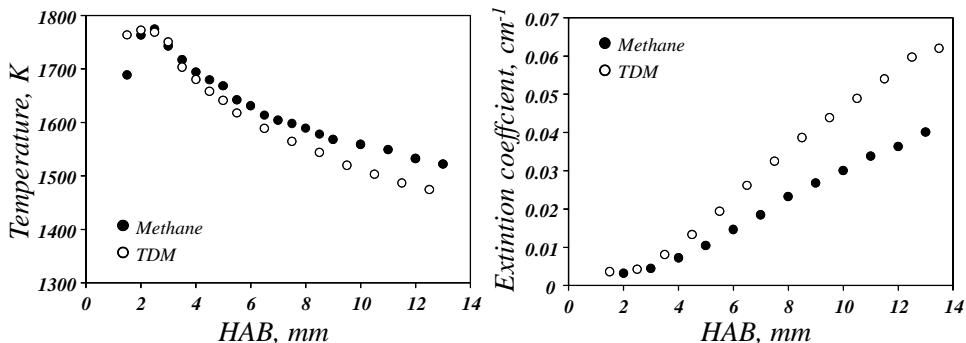
## Experimental

Methane [2] and toluene-doped (0.8 vol%) methane premixed flames burning at atmospheric pressure were produced on a water-cooled sintered-bronze McKenna burner (Holthuis & Associates). The addition of toluene slightly changes the C/O ratio, that moves from 0.6 to 0.66. To produce the toluene-doped flame, the liquid fuel was pre-vaporized and the cooling temperature of the burner was kept above the dew point of the feed mixture (70°C). Flame temperature, measured using a fast-response Pt/Pt-13% Rh thermocouple, was corrected for radiative losses and the uncertainty of the measured value was estimated to be as high as 100 K. In-situ extinction measurements have been carried out along the flame axis by means of a 5 mW He/Ne laser ( $\lambda=632.8$  nm). Condensed phases, sampled by a stainless steel, water-cooled, isokinetic probe, were collected in an ice-cooled trap and on a teflon filter placed along the sampling line and thereafter extracted with dichloromethane to separate the condensed species from soot. UV Visible absorption spectra of soot suspended in N-methyl-2-pyrrolidinone (soot concentration = 10 mg/l) were measured in a 1-cm quartz cell by using an UV-Visible spectrophotometer (HP8453). Soot 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

An overall description of the structures of the fuel-rich methane and toluene-doped methane (here named TDM) flames, is given in Fig. 1, showing temperature and extinction coefficient profiles as a function of the height above the burner (HAB). In both flames the temperatures profiles follow a similar rise-decay trend early in the first oxidation region (around 2 mm HAB) reaching a similar maximum value (approximately 1780 K). It can be noticed that after the maximum value the temperature goes down more rapidly in the TDM flame. The extinction coefficient, reported in the right part of Fig. 1, is measured with a 632 nm laser wavelength and can be mainly attributed to the absorption of soot particles. The higher extinction signal of the TDM flame in comparison to the methane flame is the first proof of the enhancing effect of toluene on the sooting tendency. Just the higher soot concentration can be responsible for the higher radiative losses leading to the faster

temperature decrease observed in the TDM flame (left part of Fig.1).

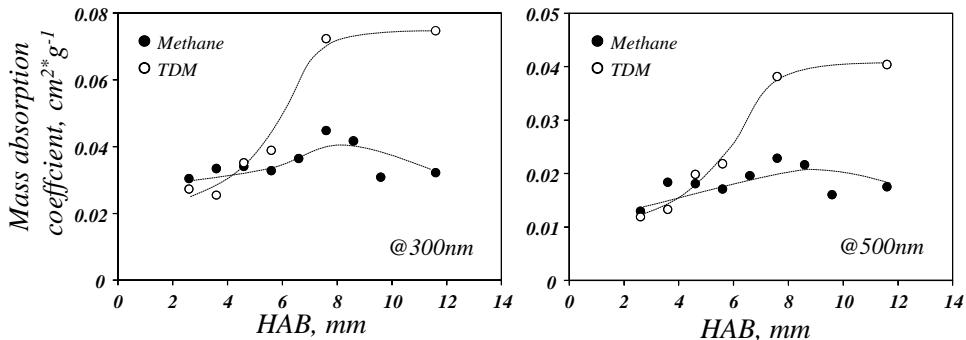


**Figure 1.** Temperature (left part) and extinction coefficient (right part) profiles measured along methane and TDM flames.

Given the different sooting tendency, soot properties have been investigated by means of spectroscopic tools to put in evidence also possible structural differences. An indication on the different aromaticity of soot formed in the methane and TDM flames has been given by determining the mass absorption coefficient measured in the UV (300 nm) and in the Visible (500 nm) and reported in Fig. 2 as a function of the HAB for both flames. It can be noticed that toluene doping causes a steep increase of soot absorption coefficient as opposed to the low and quite constant values measured for soot sampled along the methane flame. In particular at the end of the flame, the absorption coefficient of TDM soot is larger by a factor of 2 in comparison to that of methane soot. This behaviour indicates that the toluene doping not only enhances soot production, but also changes its structural properties in terms of aromaticity. These differences in terms of absorption coefficients among soot produced from aliphatic and aromatic fuels have been already put in evidence in previous works [1, 3], however the effect of toluene on soot optical properties is particularly striking if one considers the very low amount of toluene added to the feed flow (0.8 vol.%). Actually, only processes that affect the number and the size of  $sp^2$  clusters can change the absorption properties of carbonaceous materials [4]. Rather than to a significant increase of aromatic size not commonly found by comparative Raman and microscopic analysis, the enhancement of the  $\pi-\pi^*$  optical absorption, and thus of the absorption coefficient values, might be due to a better alignment of the  $\pi$  orbitals and/or to a partial delocalization of the  $\pi$  states over neighboring aromatic clusters. Just to verify if the different aromaticity is due to differences in the size of the aromatic layers featuring soot nanostructure, Raman spectroscopy has been performed.

The first order Raman region ( $1000-1800 \text{ cm}^{-1}$ ) of soot spectra is characterized by the two typical peaks of carbon materials around  $1600 \text{ cm}^{-1}$  (G or “graphite” peak) and  $1350 \text{ cm}^{-1}$  (D or “defect” peak). Beside the D and G bands, other minor modulations, induced by defects outside and inside the crystal lattice, occur next to

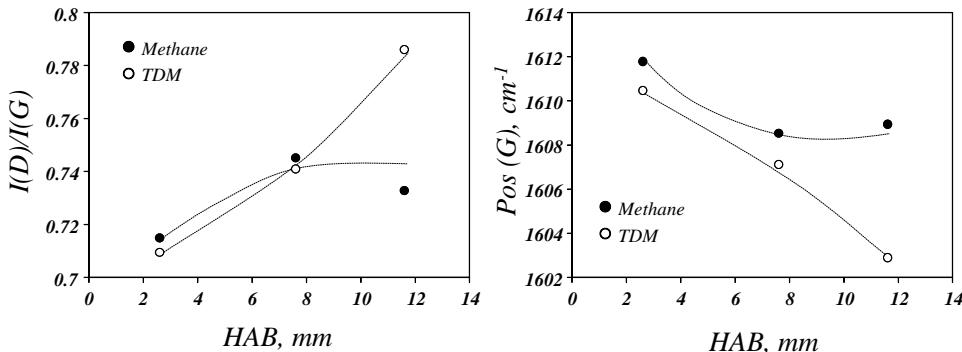
the G peak and in the 1100–1300 cm<sup>-1</sup> region.



**Figure 2.** Axial profiles of mass absorption coefficients measured at 300 nm (left part) and 500 nm (right part) of soot for the methane and TDM flames.

By means of an accurate spectral analysis and deconvolution procedure it is possible to make allowance of the contributions and features of the main and minor peaks to shed some light on differences not easily detectable on the raw spectra. A Lorentzian and a Breit–Wigner–Fano (BWF) curves were used to fit the D and the G peak, respectively. Two additional Lorentzian lines (D5 and D4) were used to fit the features at 1100–1300 cm<sup>-1</sup>, while a Gaussian line-shape has been chosen for the D3 band around 1500 cm<sup>-1</sup>[5]. Structural information can be derived from the examination of the G peak position (Pos(G)) reported in the right part of Fig. 3 for soot sampled along methane and TDM flames. The first observation regards the high Pos(G) which keeps well above the 1600 cm<sup>-1</sup> value for all soot samples. The G band has been assigned to the C=C stretching of all pairs of sp<sup>2</sup> atoms. It has to be reminded that, regardless the excitation wavelength, the G peak position takes a fixed value of 1580 cm<sup>-1</sup> in perfect and infinite graphite crystals [6], upshifted to 1600 cm<sup>-1</sup> for microcrystalline graphite, because of the effect of finite crystal size. It can be noticed that at low HAB soot from both flames presents similar Pos(G) (at about 1610 cm<sup>-1</sup>). However, methane soot keeps these high values of Pos(G) also at longer HAB, whereas TDM soot exhibits a decreasing trend, approaching values closer to that of micrographite (1600 cm<sup>-1</sup>). The Pos(G) of carbon materials is upshifted from the 1600 cm<sup>-1</sup> band limit of purely graphitic carbon by the presence of shorter sp<sup>2</sup> C-C bonds, featuring olefinic bonds and/or small aromatic layers. Hence the lower Pos(G) of TDM soot in comparison to methane soot can be attributed to a lower abundance of olefinic bonds (i.e. a higher abundance of sp<sup>2</sup> aromatic carbon) or to larger aromatic layer sizes. Another important Raman parameter for soot structural characterization, namely the I(D)/I(G), has been evaluated and is reported in the left part of Fig.3. Toluene doping causes a steeply increasing trend of the I(D)/I(G) ratio as opposed to the low and quite constant values measured for soot sampled along the methane flame. The I(D)/I(G) ratio is the main Raman parameter used for quantifying order/disorder giving a

quantitative measure of the size of the  $sp^2$  phase organized in ring clusters. The analysis of the relationship between  $I(D)/I(G)$  and  $L_a$ , i.e. the aromatic cluster size, for amorphous carbons given by Ferrari and Robertson has shown two different behaviours: one for  $L_a < 2\text{nm}$  with  $I(D)/I(G)$  varying as  $L_a^2$  and the other one with the inverse proportionality of  $I(D)/I(G)$  from  $L_a$ , according to the Tuinstra and Koenig law.



**Figure 3.**  $I(D)/I(G)$  ratio (left part) and G peak position (right part) of soot for the methane and TDM flames.

On the basis of microscopic examination, soot in-plane layer lengths have been found to be  $<2\text{nm}$  [7], so that the  $L_a$  has been estimated from the equation proposed by Ferrari and Robertson [6]. In the methane flame the  $L_a$  values oscillate around  $11\text{\AA}$ , whereas it definitely increases as soot ages moving from  $10.5$  to  $11.2\text{\AA}$  in the TDM flame. Actually, soot graphitization, intended as in-plane crystallite size growth, seems to be rather insignificant along both flames. However, the  $I(D)/I(G)$  ratio and  $\text{Pos}(G)$  values indicate that some soot aromatization occurs and it is more definite and effective in the TDM flame where soot formation is enhanced.

## Conclusions

The structures of atmospheric sooting premixed flames of methane and methane doped with small amounts of toluene have been analyzed by sampling and spectroscopic analysis. The addition of toluene in such small amounts (0.8 vol.%) to the feed flow did not alter significantly the C/O ratio and the temperature environment. Nevertheless, a striking effect of toluene addition was observed on soot yield as well as on soot properties. Some insights on the different soot structure have been obtained by means of spectroscopic tools, i.e. Raman and UV-Visible spectroscopy. The higher aromaticity of toluene-doped soot was testified by the much higher mass absorption coefficient and  $I(D)/I(G)$  ratio. This behaviour indicates that toluene doping not only enhances soot production, but also changes its structural properties in terms of aromaticity. These features, besides proving the more effective growth of soot from aromatic fuels are of concern about the possible higher environmental and health impact of aromatic-derived soot in respect to

aliphatic-derived soot because of its higher aromaticity.

### 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.

### References

- [1] Russo, C., Alfè, M., Rouzaud, J.-N., Stanzione, F., Tregrossi, A., Ciajolo, A., “Probing structures of soot formed in premixed flames of methane, ethylene and benzene”, *Proc. Comb. Inst.* 35:1885–1892 (2013).
- [2] Alfè, M., Apicella, B., Rouzaud J.N., Tregrossi A., Ciajolo A., “The effect of temperature on soot properties in premixed methane flames” *Combust. Flame*, 157: 1959–1965 (2010).
- [3] Tregrossi, A., Barbella, R., Ciajolo, A., Alfè, M., “Spectral properties of soot in the UV-Visible range”, *Comb. Sci. and Tech.* 179: 371-385 (2007).
- [4] Bond, T. C., Bergstrom, R. W., “Light Absorption by Carbonaceous Particles: An Investigative Review”, *Aerosol Sci. Technol.* 40: 27–67 (2006).
- [5] Russo C., Ciajolo A., “Effect of the flame environment on soot nanostructure inferred by Raman spectroscopy at different excitation wavelengths”, *Combustion and Flame* 162: 2431–2441 (2015).
- [6] Ferrari A. C., Robertson J., “Interpretation of Raman spectra of disordered and amorphous carbon”, *Phys. Rev. B* 61: 14095-14107 (2000).
- [7] Apicella, B., Pré P., Alfè, M., Ciajolo, A., Gargiulo, V., Russo, C., Tregrossi, A., Deldique, D., Rouzaud, J.N., “Probing structures of soot formed in premixed flames of methane, ethylene and benzene”, *Proc. Comb. Inst.* 35:1895–1902 (2015).