Numerical Simulation and Experimental Measurements of Soot and Organic Nanoparticles in Opposed-Flow Diffusion Flames of Methane, Ethylene and Propane

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1. Introduction

In recent years attention of researchers has been focused on the combustion generated particles in order to have a deeper knowledge on their formation and develop combustion systems with higher efficiency and lower environmental impact [1,2]. Opposed-flow configuration allows to study behavior and sooting tendency of fuels, avoiding fluidodynamic problems fundable in diffusion flames laminar or turbulent. On the other hand, for co-flow flames, the study of particles inception and growth is much more complex than the opposed-flow system because the co-flows are intrinsically two dimensional compared to a quasi-one dimensional opposed-flow [3]. Moreover, soot formation in opposed-flow diffusion flames has been extensively investigated because of its relevance to turbulent flames in the laminar flamelet model.

In the present work, three different fuels: ethylene, methane and propane, in comparable conditions, have been investigated, experimentally and by numerical simulation. The experimental detection of combustion-byproducts is attempted by UV laser induced emission spectroscopy. The fourth harmonic of a pulsed Nd:YAG laser (266 nm) is used, in order to enhance fluorescence from molecular particles within the flame and also allows larger soot particles to heat up and emit incandescent radiation [4].

Modeling of particulate concentration is performed by using a detailed gas-phase chemical kinetics coupled with aerosol dynamical equations using a discrete size spectrum [6-8]. The Comparison of model results with laser induced emission signals, is proposed, in order to contribute to understanding of the process of particle inception and dynamic in diffusion controlled conditions.

2. Experimental conditions

The opposed-flow burner system was the same as that of Olten and Senkan [5]. Methane, ethylene and propane diffusion flames were stabilized between two opposed jet nozzles (ID 2.54 cm). The oxidizer stream, oxygen and argon, was introduced from the upper nozzle; the fuel streams, containing fuel and argon, were introduced from the lower nozzle. All gases used were of high purity.

Screens were used at the exit of each jet to establish uniform gas flow velocities and to generate stable, flat flames. Using a mild vacuum through the holes in the annular section of the bottom burner, combustion products and shield gas were vented out of the system.

Using a translation system (0.1 mm), sampling position within the flame was changed by moving the entire burner assembly up or down with respect to the fixed sampling volume. In all the flames investigated velocity of oxidizer and fuel stream were kept constant at 16.1 and 13.2 cm/s, respectively. Therefore, the global strain rate, defined as the sum of the fuel and the oxidizer nozzle exit velocities divided by the nozzle separation distance, was maintained constant at 37.7 s⁻¹ for the three flames. Percentage of hydrocarbon in fuel stream was fixed at
75% in Ar, whereas the oxidizer streams consisted of 20% by volume O\textsubscript{2} and the remaining Ar. The distance between the two burners was maintained at 1.5 cm for all flames. These conditions resulted in flames stabilized on the oxidizer side of the stagnation plane for all flames [3].

Spectrally resolved, laser induced emission measurements were performed using the fourth harmonic (\(\nu=266\)nm) of a pulsed Nd-YAG laser as exciting source. The energy of the laser pulse was kept constant at 1.5mJ with a pulse duration of 8ns. Detection was by a gated ICCD camera and the signal was focused onto the 280 nm entrance slit of a spectrometer. Emission spectra, averaged over 150 scans, were recorded by using an acquisition duration of 20 ns synchronized with the laser pulse. A correction was applied for the wavelength-dependent sensitivity of the camera. Calibration of laser induced emission signals (LIF and LII) was made by measuring the scattering signal for cold ethylene.

3. Model Development

Kinetic scheme used for modeling the flames provides two section: gas phase section, with all reactions of oxidation and pyrolysis of fuels and growth until large PAHs, and particle section. The latter is built dividing all the range of interest, i.e. particles from 1 nm to 200 nm, into 26 sections, making the scheme able to predict particle concentration and particle size distribution simultaneously with gas phase [6-8]. Both radical and stable specie are considered for each section so that reactions are written as for gas phase taking into account for gas-to-particle reactions, i.e. nucleation, surface growth, addition of PAHs from gas phase and coagulation of both PAHs and particles. Further details of scheme are reported elsewhere [6-8]. Cunningham’s theory is considered to calculate diffusivity of particles. Thermophoretic effect, strongly enhanced in opposed-flow configuration, is taken in account for all sections [9].

4. Results and discussion

Three flames of different fuels have been studied both experimentally and numerically. In the chosen experimental conditions the flame front and the soot formation zone are located on the oxidizer side. Particles are hence transported away from the flame toward the stagnation plane. In this way soot oxidation is absent and the flame is classified “soot forming” as reported in the literature [3]. Typical emission spectra for the ethylene flame are reported in Fig.1. It shows the different laser induced emission spectra taken at different flame location: starting from the fuel side the spectrum shows a broad fluorescence signal peaked at about 330 nm, across the stagnation plane the spectra shows a fluorescence with a maximum at 430 nm and a continuum which extends into the visible that is attributable to incandescence of soot particles; in the oxidizer side, close to the maximum flame temperature the emission spectrum shows a fluorescence peaked at 300 nm. Moreover in all location it is observable a strong scattering signal at 266 nm.

Usually fluorescence at 300 nm is correlated to benzene and derivatives whereas higher molecular mass compounds are linked to higher wavelength. LII is generally used to detect soot, because its spectroscopic behavior [4]. Modeling helps to localize both maximum of temperature and stagnation plane for all flames. Moreover predictions of particles concentration and size allows us to compare different wavelength signals to different particle classes.
In particular four fundamental types of particles by molecular mass can be distinguished: high-molecular mass PAHs with masses between 300 and 1000u, (particles with equivalent sizes of about 1nm), molecular particles with masses between 1000 and 10,000u (particles with equivalent sizes from 1 to 3nm), nanoparticles with masses between 10,000 and 100,000u (particles with equivalent sizes from 3 to 6nm) and primary soot particles with masses higher than 100,000u (particles with equivalent sizes larger than 6).

Comparison between the measured signals of fluorescence and incandescence at different wavelengths and different particle classes concentration, obtained by numerical simulation, are reported in Figs. 2 for methane, in Fig. 3 for ethylene and in Fig. 4 for propane.

Looking at relative position of particles respect to stagnation plane and maximum temperature allows to carry out some considerations. Thermophoresis and diffusivity joined with convection move particles from flame front zone to stagnation plane and even over this point. In the fuel side, close to the stagnation plane particles formed found very low temperature (lower than 900°K) that strongly enhances coagulation. Moreover, high concentration of PAHs, joined to low temperature, leads to a high nucleation rate, forming new particles in fuel side. Hence, two route of formation for particles can be individuated: the first one, depending from radical formation and growth by addition of C2H2 and PAHs from gas phase, is located close to flame front; the second one is prevalently due to coagulation of both PAHs and particles and is located across stagnation plane. These two different mechanisms lead to types of particles different in structure and spectroscopic behavior: particles formed through radical mechanism are prevalently structures biphenyl-like, whereas particles from coagulation are more similar to cluster of PAHs sheets. This behavior is found for all types of fuels.

Consideration on sooting tendency of different fuel can be carried out as well. Volume fractions comparison shows a higher tendency of propane to produce particles with dimensions higher than 3 nm. Methane on the opposite does not form soot particles, producing prevalently PAHs and small particles. For a complete analysis of fuel emissions is important taking into account not only soot production but also other pollutants; for this purpose experimental detection and modeling predictions for the whole range of particulate matter and large PAHs of gas phase formed in combustion.

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*Fig. 1 Emission spectra measured in the ethylene opposed-flow flame in different flame zone.*
**Fig. 2** Qualitative comparison between LIF and LII emissions at different wavelengths and particle classes for methane LIF@300 (□) LIF@330 (○) LIF@430 (◊) LII@550 (Δ) compared with HMM-PAH (___), particles from 1nm to 3nm (- -) particles from 3nm to 6nm (____ - - - -) particles larger than 6nm (____). Modeled stagnation plane SP (dashed vertical line) and flame front Tmax (solid vertical line) are also reported.

**Fig. 3** Qualitative comparison between LIF and LII emissions at different wavelengths and particle classes for ethylene LIF@300 (□) LIF@330 (○) LIF@430 (◊) LII@550 (Δ) compared with HMM-PAH (___), particles from 1nm to 3nm (- -) particles from 3nm to 6nm (____ - - - -) particles larger than 6nm (____). Modeled stagnation plane SP (dashed vertical line) and flame front Tmax (solid vertical line) are also reported.
5. Conclusions

Opposed-flow flames of methane, ethylene and propane have been numerically and experimentally investigated. A laser induced emission spectroscopy has been used in order to detect different combustion generated species. Comparison with model predictions has been done in order to better understand the evolution of particulate in flame. The complete kinetic scheme, here used, simultaneously provides both gas-phase and particle reactions, based on sectional method. Signals at different wavelengths and different particle classes can be individuated and compared for all the flames. Two different zone of formation of particulate can be distinguished for this flame configuration: close to flame front, in the oxidizer side, radical-molecule mechanism, involving C2H2 and PAHs, results predominant, whereas in the fuel side, due to low temperatures, coagulation of PAHs and particle are the main route to form and let grow new particles.

6. References