LIBS and Chemiluminescence Measurements for Fuel/Oxidizer Mixing Monitoring

L. Merotto, R. Dondè, F. Migliorini, and S. De Iuliis
merotto.laura@gmail.com
IENI-CNR Milano, via Cozzi 53, Milano, Italy

Abstract
Real-time monitoring of local equivalence ratio is of primary importance for chemical combustion efficiency improvement. In this context chemiluminescence and LIBS measurements have been presented and performed in premixed and diffusion flames. The ratio of radicals chemiluminescence emission is proved to be related to equivalence ratio in premixed flames. H/O LIBS measurements giving the ratio of two characteristic spectral lines of fuel and oxidizer is also related to the equivalence ratio. In this work, the calibration curves of radicals chemiluminescence as well as LIBS measurements versus equivalence ratio have been derived for premixed flames. Moreover, the application to diffusion flames is here considered and for both sets of measurements the calibration curves derived from premixed measurements have been applied. Results concerning the equivalence ratio evaluation in the diffusion flame by using LIBS measurements have been compared with those obtained from chemiluminescence at the external cone. These results are discussed in the text.

Introduction

The energy efficiency monitoring and the related environmental impact are of primary importance in conventional as well as in innovative (e.g. waste / biomass) combustion systems. In this context the real-time monitoring is mandatory to gain local and time-resolved information of energy efficiency indicators. The development and implementation of innovative optical diagnostic techniques is an important tool for the optimization of energy efficiency. The local equivalence ratio, giving the ratio of the fuel and oxidizer, is a significant parameter able to give information on local mixing and consequently on energy conversion efficiency. This investigation is particularly appealing both in steady and especially transient regime combustion systems and, moreover, is mandatory to identify reactor configurations which promote the mixing and the complete energy conversion.

Flame chemiluminescence measurements is a promising tool for equivalence ratio monitoring, due to its simplicity when compared to other laser diagnostic techniques. The chemiluminescence emission of radicals such as OH*, CH* and C_2*, chemically formed within the flame front, occurs when the excited radicals return from an excited energy state to a lower energy state, emitting light at a

characteristic wavelength. Since these species are mainly produced in the reaction zone, chemiluminescence can be indicative of the reacting conditions in the flame. Experiments in premixed flames suggest that the intensity of the chemiluminescence from radicals could be a good marker of heat release. In addition, the ratio of emissions from excited species, such as CH*/OH* or C_2*/CH*, could be used for sensing the equivalence ratio at the conditions under study [1].

A novel and interesting approach to evaluate the local equivalence ratio is by employing Laser-Induced Breakdown spectroscopy (LIBS) measurements. This analytical technique is essentially based on focusing a pulsed laser beam into a spot and producing a plasma. The local electric field intensity is high enough to atomize and ionize molecules and atoms in the probe volume, which recombine and further relax, emitting a characteristic emission intensity at given wavelengths. From the emission spectral analysis, information about the elemental composition of the sample can be derived. Considering the application on a combustion system, H, O, C spectral lines can be easily detected. As widely reported in the literature, the ratio of two characteristic spectral lines of fuel and oxidizer (H/O and C/O) is related to the equivalence ratio [2].

In this work chemiluminescence and LIBS measurements have been carried out in methane/air premixed flame and calibration curves of the data as a function of equivalence ratio are derived. These results have been then applied to a diffusion flame. The mixing process is then investigated and discussed.

Materials and Methods

The experimental apparatus implemented in this work for both chemiluminescence and LIBS measurements is shown in Figure 1. The investigation has been carried out on a methane/air premixed flame produced by a cylindrical Bunsen burner (9 mm I.D.), varying the equivalence ratio (Φ) and keeping constant the total mass flow rate (5.3×10^{-5} kg/s), as well as on a methane diffusion flame with a 1.4×10^{-6} kg/s methane mass flow rate. As for chemiluminescence measurements, OH*, CH* and C_2* radicals emission intensities have been collected on the flame front. With this aim, a section of the flame front has been imaged with a magnification of 3 by using an achromatic lens (f = 100 mm) on a 0.5 mm pinhole, which ensures to select only the flame front (in the order of 400 μm) against the background flame luminosity.

The image of the pinhole is then collected by an intensified CCD camera (Dicam Pro, 12 bit) equipped with a UV-Nikon objective. The chemiluminescence of OH*, CH* and C_2* radicals is separately detected using interference filters centred at the emission wavelength of the radicals, and positioned just in front of the objective. The radical species and the corresponding interference filters are the following: OH* at 309 nm ± 5 nm, CH* at 430 nm ± 5 nm, and C_2* at 516.5 nm ± 5 nm. Images are collected with a 40 pixels/mm resolution and result from an average of 16 acquisitions. The f number value for the DICAM camera has been set to 11.

For LIBS measurements, a pulsed Nd:YAG laser (Continuum, 7 ns FWHM) at the fundamental wavelength (1064 nm), with 1 Hz repetition rate and 220 mJ pulse energy was used to produce the plasma by means of a 80-mm focal length lens. As for the spectral analysis, the flame has been imaged onto an optical fibre by using an achromatic lens (f = 100 mm) with 1:1 magnification. The fibre is connected to the entrance slit of a spectrograph (ANDOR Technology Shamrock 303i) coupled with an ICCD camera (iStar 334T). The spectra have been collected by using a 150 grooves/mm grating (0.28 nm resolution). Each spectrum results from the average over 100 acquisitions in order to increase the signal to noise ratio.

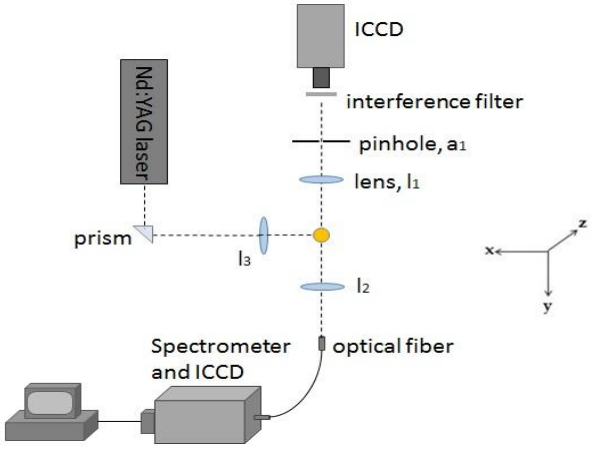

Figure 1. Chemiluminescence and LIBS measurements setup.

Results Discussion

Premixed flame

Chemiluminescence measurements were performed around the stoichiometric conditions, with the equivalence ratio (Φ) ranging from 0.9 to 1.5.

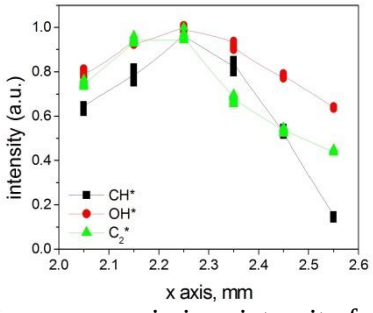

Figure 2. Chemiluminescence emissions intensity from OH*, CH* and C_2*.

In Figure 2 the chemiluminescence emission from OH*, CH* and C_2* radicals vs. radial position in the flame (x axis in Figure 1) is reported for Φ=1. As it can be

seen in the figure, the maximum value of the chemiluminescence intensity of all radicals is at about 2.3 mm from the center, that is the flame front position.
The C_2*/CH* and CH*/OH* ratios are plotted in Figures 3 and 4, respectively, versus equivalence ratio. Comparing the data obtained in this work and those reported in Migliorini et al.[3] and in Kojima et al. [4], a good agreement is obtained even considering the different experimental condition investigated.

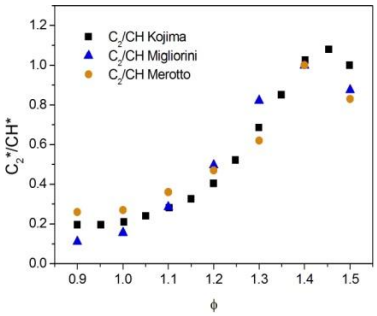

Figure 3. C2*/CH* intensities ratio versus equivalence ratio.

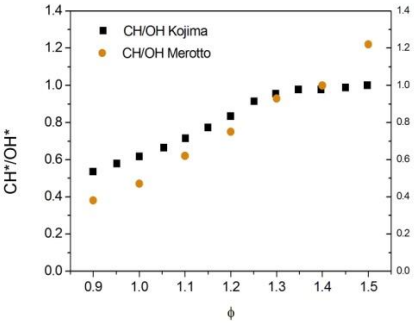

Figure 4. CH*/OH* intensities ratio versus equivalence ratio.

As for the CH*/OH* ratio, Kojima's trend displays a plateau above Φ=1.3, while a linear increase at least up to Φ=1.5 has been obtained in this work.
As for LIBS measurements, H and O lines have been considered as representative of fuel and oxidizer, respectively. Then, H/O lines ratio has been evaluated by varying the equivalence ratio and the results are reported in Figure 5. A linear trend is obtained with R^2=0.9977, as shown in the figure.
The aforementioned calibration is used to estimate Φ for the diffusion flame, as reported in the following Section.

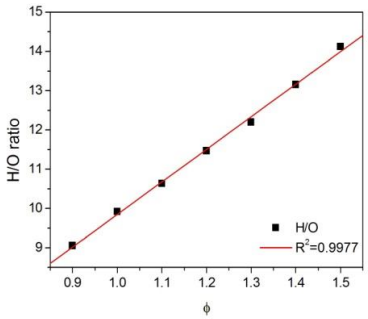

Figure 5. H/O LIBS intensities ratio versus equivalence ratio.

Diffusion Flame
In Fig. 6 (black square) the H/O ratio from LIBS measurements is reported versus the radial position of the diffusion flame (5 mm height). In the same figure (right

axis) the corresponding equivalence ratio is shown as obtained by inverting the relationship reported in Figure 5. High Φ values are obtained in the center of the flame, while the equivalence ratio decreases moving toward the external part of the flame. Since the calibration has been derived for a limited range value of the equivalence ratio, such values are extrapolated.

The chemiluminescence emission from OH*, CH* and C_2* radicals vs. radial position in the flame have been obtained for the diffusion flame. The results obtained by both chemiluminescence and LIBS measurements are plotted together in Figure 7. As it can be seen in the figure, the peaks of the chemiluminescence measurements from the three radicals under analysis are located at about 4 mm from the burner axis as it is underlined with the red line in the figure. It is worth noting that the value of the estimated Φ from LIBS measurements is about 1 in the position corresponding to the flame front underlined by chemiluminescence measurements. These results confirm the fact that LIBS measurements and in particular H/O LIBS signals ratio can account for local equivalence ratio distribution also in a diffusion flame. However, as for chemiluminescence, if one takes into account the radicals emission ratios in the diffusion flame and the related calibration behaviour obtained from premixed flame, the values of Φ near the peak of chemiluminescence measurements are scattered. These results have not been reported here, and are essentially due to the fact that no correction of CO_2* emission have been performed. More work is needed to address such issue.

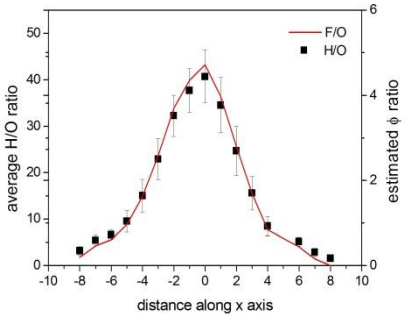

Figure 6. Estimated equivalence ratio vs. radial position.

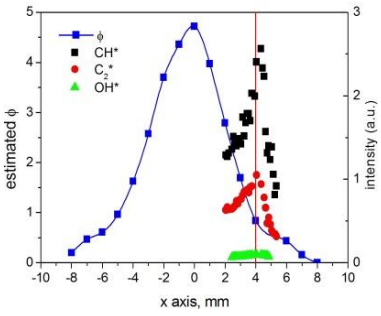

Figure 7. Chemiluminescence and LIBS results for diffusion flame.

Concluding Remarks

In this work chemiluminescence and LIBS measurements have been carried out in methane/air premixed and diffusion flames. C2*/CH* and CH*/OH* radiation emission ratios have been evaluated at the flame front by changing the equivalence ratio in the premixed flame. H/O LIBS measurements are also evaluated varying the equivalence ratio just above the burner mouth in the dark cone of the premixed flame. While in the case of LIBS measurements the investigation can be performed all over the flame, chemiluminescence analysis can be carried out in the external

cone of the flame. The comparison has been performed around the "diffused" flame front. The following conclusions can be derived.

- For the premixed flame, the monotonic trend of C2*/CH* and CH*/OH* chemiluminescence ratio versus the equivalence ratio proved that these parameters can be used for sensing the equivalence ratio.
- In the same flame, the linear dependence of H/O LIBS ratio versus the equivalence ratio is also appealing for equivalence ratio monitoring. Moreover, the radial profile of the equivalence ratio with a peak in the center is consistent with the radially air diffusion inside the flame.
- By using the two calibration curves corresponding to the two sets of analysis, the value of fuel to air ratio (F/O) obtained from LIBS measurements is close to stoichiometric conditions at the radial location where OH*, CH* and C2* intensity peaks also are located.
- It seems reasonable to infer that the ratio of the radical chemiluminescene intensity can also be applied to the non-premixed case at least where the radical species are present. Moreover, in this context LIBS analysis can also be applied whatever the fuel/air condition (temperature and composition). This is very promising for the local equivalence ratio evaluation and generally for the investigation of the mixing processes.

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