Local Equivalence Ratio Measurement in Opposed Jet Flames of Premixed and Non-Premixed Methane-Air Using Laser-Induced Breakdown Spectroscopy

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ABSTRACT

Laser-induced breakdown spectroscopy (LIBS) has been applied to reacting flows to measure local air-fuel ratio. However, the LIBS signal is much weaker in flames rather than in non-reacting gases and more work is required to investigate the potential of this technique for measurements in reacting flows. The present study reports local equivalence ratio measurements of methane and air in an opposed-jet burner, which allowed independent control of flow rate and air-fuel ratio. The effects of delay time of the ICCD camera, laser pulse energy, premixed and diffusion flames on LIBS measurements of equivalence ratio were investigated. The dependence of intensity ratios of H/O and CN/O on equivalence ratio was quantified and it was found that H/O is less dependent on laser pulse energy and more sensitive for measurements of equivalence ratio. However, the presence of a flame within the laser beam led to significant measurement deterioration relative to non-reacting flows. This was corrected by increasing the laser pulse energy, which allowed a reduction of the variability of the induced plasma to improve and maintain the accuracy of the equivalence ratio measurements as in non-reacting flows, which is within 20%. The resulting measurement fluctuations of air-fuel ratio at different locations in the flat flames were evaluated for different flow and laser operating conditions. The established correlation between the intensity ratio of H/O and local air-fuel ratio allowed measurement of the spatial gradient of air-fuel ratio across opposed jet diffusion flames and showed good agreement with corresponding CHEMKIN calculations. The results demonstrate that instantaneous LIBS measurements of local air-fuel ratio with high spatial resolution may be feasible in premixed and diffusion flames.

1. Introduction

Laser-induced breakdown spectroscopy (LIBS) has been used widely to quantify species that are present in gases, liquids and solids for many different applications [1–3]. This technique possesses some advantages, including high spatial and temporal resolution and non-intrusive measurement. The LIBS technique employs a sufficiently high energy pulsed laser beam, which, when focused at a small volume into a gas, creates a local plasma. The high peak energy laser pulse breaks down the chemical bonds of substances and initiates the fragmentation of molecules into elemental components at the focal point. High temperature plasma is then generated, while atoms dissociated from target molecules are excited. The emitted light from these excited atoms during their relaxation process can be recorded and analysed to determine
the elemental compositions of the sampled substances qualitatively and quantitatively. If the plasma is optically thin and in local thermodynamic equilibrium, a relatively linear relationship exists between the intensity of the spectral line and the population of the excited state:

\[ I_{ij} = h \nu_{ij} A_{ij} n^* \frac{g_i e^{-E_i/kT}}{U^*(T)} \]  

(1)

In a plasma with temperature \( T \), a spectral line corresponding to a transition from energy level \( i \) to energy level \( j \) has intensity \( I_{ij} \) as shown in Eq. (1). \( A_{ij} \) is the transition probability, \( g_i \) is the degeneracy of the upper level, \( U \) is the internal partition function for the emitting species, \( h \nu_{ij} \) is the energy of a single photon of the excited species; \( n^* \) is the density of the emitting species; \( k \) is the Boltzmann constant and \( E_i \) is the energy of the upper level. In Eq. (1), \( A, g, U, h \nu, E, k, \text{ and } T \) are all stable for the specific spectral emission lines and given experimental conditions. Under certain conditions, the intensity of spectral line is proportional to the population of the atomic excited state.

LIBS has been used extensively for combustion diagnostics in recent years. Phuoc and White [5] used the line radiation of the H and the O (I) triplet to correlate with the equivalence ratio in methane-air mixtures. Stavropoulos et al. [2, 6] used LIBS to measure equivalence ratio in laminar methane–air premixed flames. Ferioli and Buckley [7] then used LIBS for direct measurement of atomic species over a wide range of mixture fractions of \( \text{C}_3\text{H}_8, \text{CH}_4 \) and \( \text{CO}_2 \) in air. Michalakou et al. [8] measured the local equivalence ratio in different methane-, ethylene- and propane-air mixtures. Mansour et al. [9] used LIBS to study local equivalence ratio measurements in turbulent partially premixed flames. Kiefer et al. [10] reported the investigation of LIBS and ignition behaviour of methane/air and dimethyl ether (DME)/air mixtures. Most of these studies successfully realized local equivalence ratio measurements of hydrocarbon fuels and air flames using the intensity of C, H, N and O on a Bunsen burner geometry [2, 6, 8, 10–15]. The intensity ratios of H/O and C/N in LIBS were usually used to determine the equivalence ratio of hydrocarbon fuels within the probe volume. The feasibility of LIBS measurements was studied in laminar [2, 6, 8, 10, 14] and turbulent [9, 12] flows in premixed [2, 6, 8–14, 16, 17] and non-premixed [5, 9, 10, 18] flames. Plasma in a stainless steel chamber [19–21], a reaction vial [16] and an engine [22] have also been investigated. These researchers investigated different factors influencing the LIBS measurements, including laser pulse energy, delay time with respect to the triggering signal (delay time), aperture time of the camera’s shutter (gate time), pressure of the gas and gas flow rate. In addition, LIBS has been used to measure the temperature [23] and gas density [24] in flames. Under these various conditions, LIBS has been demonstrated as a robust method to measure time-averaged mixture fraction in combustion.
Although the accuracy of LIBS in non-reacting flows is very high \[2, 25\], its precision in reacting flows is not clear and more research is required to assess the performance of the technique in such environment. Due to the complex flame effects on the laser beam and plasma, a proper indicator in the measured spectrum needs to be identified to determine the equivalence ratio in flames. In this study, the LIBS investigation was carried out in an opposed jet burner, which provided a simple one-dimensional (1D) flow and flat flame field. The aim of this work is to study the precision and application of LIBS measurements of local equivalence ratio in premixed and diffusion opposed jet flames. The behaviour of the emissions from CN, O, H and N species are analysed in premixed flames and the corresponding change of the measurement uncertainty at different locations of reacting flows is quantified for instantaneous measurement. An approach to improve the measurement accuracy in reacting flows is presented. Quantitative measurements of the equivalence ratio are presented and discussed under various laser pulse energies and flame types and successful comparison between measurements and CHEMKIN simulations in laminar diffusion flames is demonstrated.

2. Experimental apparatus

As shown in Fig. 1, the flow configuration consists of two identical, vertically opposed contracting nozzles ending with 30 mm diameter exit, creating opposed jet flows. The distance between the two jets was kept fixed at 30 mm. A co-axial flow of nitrogen was supplied by an annular nozzle of 50 mm exit diameter. The counterflow burner allowed the stabilisation of one or two flames, characterised by a constant strain rate across their area, depending on the choice of premixed fuel/air mixture injected from either one or both nozzles and the speed of the flow.
The laser beam of the LIBS system was generated by a Surelite III Q-switched Nd: YAG laser, producing pulses of 532 nm light with 5 ns pulse width and 10 Hz frequency. The pulse energy was varied between 80 and 406 mJ ± 5 mJ. The beam was redirected and adjusted by a periscope and then focused using a 300 mm focal length plano-convex spherical lens. The laser-induced breakdown took place at variable locations between the opposed jets. The spatial resolution of the measurement was approximately 1 mm estimated from the size of the plasma. A 35mm focal length UV Fused Silica Plano-Convex Lens collected the emissions at right angles and coupled the plasma light to an optical fibre (Model: Edmund 1000 µm diameter, 180-1150 nm). The fibre transmitted the light to a spectrograph (Model: Mechelle 5000 with a 50x25 µm input slit) and an ICCD camera (Model: Andor DH534-18F-03). Together, the combination of the ICCD and the spectrograph could measure the wavelength of light from 200 to 850 nm with spectral continuity (Spectral resolution: 0.125 nm at 500 nm). The time-resolved measurements were mainly characterized by two parameters: the delay time to the trigger signal and the aperture time of the ICCD shutter. Experimental synchronization was achieved through a multi-channel digital delay pulse generator (Model: NI PCI-6602). A Newport 6035 Mercury spectral calibration lamp and a Hamamatsu L7810 Xenon lamp were used to calibrate the wavelengths and the relative intensity respectively. In the experiment, the temperature of gas supply was at room temperature (20°C). The mixture of methane (BOC 99.0% purity) and air were controlled using digital mass flow controllers from Bronkhorst (accuracy: ±0.5% reading±0.1% full scale) and ensured well premixed conditions by flowing through perforated plates in a pipe.

3. Results and discussion

Figure 2(a) illustrates a typical raw LIBS spectrum in one of the tested flames, while Fig. 2(b) shows a plasma above the lower burner exit in premixed lean counterflow flames. For this
spectrum, the delay was set at 1000 ns with a 5 µs exposed gate of ICCD. The equivalence ratio of premixed methane/air was 0.6 and the strain rate was 120 /s. The influence of plasma background continuum emissions was very weak and could be neglected using this setting. The peak areas of neutral atomic nitrogen (N I) at 742.4, 744.2 and 746.8 nm, the oxygen triplet centred at 777.4 nm, hydrogen (H I) at 656.3 nm, CN (violet system, B2Σ+-X2Σ+) at 386.1, 387.1 and 388.3 nm were observed and integrated (H 650.0~661.1 nm, O 776.5~778.3 nm, N 742.0~747.7 nm, CN 387.8~388.6 nm) respectively for the spectral analysis of the equivalence ratio. The LIBS signals were averaged over 50 laser single shots, which provided a good signal-to-noise ratio and accuracy.

3.1 Effects of delay time and laser energy

A spectral line has an optimal temporal detection window determined by its ionization energy and excitation energy of a specific transition. This optimum window varies depending on the characteristics of the plasma. Before experiments in flames, delay time and laser pulse energy optimum parameters should therefore be determined. The equivalence ratio was kept at 0.6 and the strain rate at 120 /s. The laser beams were focused at x=0 mm, z=3 mm above the lower burner, which could be regarded as a non-reacting zone. Both the laser beam and plasma were not influenced by the flames at this measurement location.

![Fig. 3 Relative intensity of atomic emissions lines as a function of (a) delay time and (b) laser pulse energy](image)

Since the lifetime of a plasma is about 3~4 µs in this experiment and the background noise is fairly weak in such a short time, 5 µs gate time of the ICCD is appropriate and used for the collection of emissions and can avoid the background noise. In Fig. 3(a), the gate time and laser pulse energy were 5 µs and 125 mJ. The delay time was varied from 0.2 µs to 2 µs. It can be seen that, in the first 200 ns after the laser pulse, the atomic emission lines, such as H (656 nm) and O
(777 nm), appeared out of the continuum emission that weakens rapidly in this period. After 800 ~ 1000 ns, the spectrum decreased slowly and the continuum emission vanished. Then, the atomic lines such as H, O and N dominated the spectrum. In Fig. 3(b), the energy of excited laser was varied from 80 to 406 mJ, with 1000 ns delay time and 5 µs gate time. For this energy range, compared with H/O, CN/O and CN/N intensity ratios, the relative intensity H/O could be regarded as an independent index, which was not influenced by the laser energy. The H/O intensity ratio could work as a good indicator to determine the equivalence ratio in flames. Although high laser energy can help increase the intensity of plasma, it reduces the spatial resolution. There is a need for an appropriate compromise, which also depends on the specific flow, in order to choose the laser pulse energy. Higher laser pulse energy is required for measurements in flames and this is discussed further below. All the measurements reported in the rest of the paper were obtained with 1000 ns delay time and 5 µs gate time.

### 3.2 Measurements in premixed flames

When both jet flows had the same flow rates of premixed methane-air, two flat and symmetric flames were observed, as shown in Fig. 2(b). The strain rate and global equivalence ratio were 120 /s and 0.6 respectively. Plasmas were created along the centreline (x=0 mm) of the opposed jet burner at different heights above the lower burner exit. In this condition, the lower flame was at z=15 mm height due to buoyancy.

![Fig. 4 The plasma spectra as a function of height above the lower burner exit. The flame is at height 15 mm.](image)
Fig. 5 H/O intensity ratio as a function of height above the lower burner exit for different laser pulse energies (Error bars represent a 95% confidence interval). The flame is at height 15 mm.

Figures 4 and 5 show that, when the plasma was close to the flame, the absolute intensity of whole spectrum decreased greatly which increases the measurement uncertainty, but the H/O ratio remained roughly constant for several values of laser pulse energy and various locations and laser pulse energies. Therefore, even under the disturbance of flames, the H/O intensity ratio remained stable for different intensities of plasmas. As opposed to non-reacting flow measurements, the spectral amplitude of in-flame measurements would be decreased greatly when the plasma was close to flames. This attenuation mainly stems from the following reasons.

(1) The breakdown threshold is a strong function of density. According to the ideal gas law, the flames increase the temperature and greatly decrease the gas density. Kiefer’s research [23] reported that the breakdown threshold energy in flames (2000 K) was 2-3 times larger than that at 300 K. The decrease in laser energy absorption greatly reduces the plasma intensity and increases the measurement uncertainty.

(2) According to Eq. (1), the emission intensity is determined by the density of the emitting species. The low density gas in flames leads to lower emission intensity due to reduced number density of emitting species in the probe volume.

(3) When the laser beam encounters the flames, the beam is refracted through the gas due to the corresponding temperature and density spatial gradients. As the laser beam refraction is not uniform, the strong density gradients act as local lenses to change the laser propagation. Each portion of the laser beam is thus different and its focal point may be defocused or shifted in space. In the reacting zone, the intensity of the plasma is greatly reduced.
Therefore, all these factors lead to on average nearly 60% of the laser energy being transmitted, instead of being absorbed by the plasma, for 406 mJ laser pulse energy in flames, compared with 25% energy loss on average in the non-reacting flows.

Figure 6 shows the shot-to-shot variations of H/O intensity ratio obtained from 200 single shots in the reacting (x=0 mm, z=15 mm) and non-reacting zone (x=0 mm, z=3 mm) with 125 mJ and 406 mJ laser pulse energy, 120 /s strain rate and 0.6 equivalence ratio. Since the methane/air mixture was perfectly premixed, such variability of the H/O intensity ratio is mainly caused by the variation of the plasma, which reduces the emitted signal amplitude, and therefore, increases the noise level at the recorded spectra at the ICCD. In Fig. 6, compared with result in the non-reacting zone, the relative standard deviation in the reacting zone (x=0 mm, z= 15 mm) with laser pulse energy of 125 mJ rose from 20% to 80%. To improve the accuracy of the instantaneous measurement in flames, one method is to increase the laser energy, which induces stronger plasma. In this case, when the laser pulse energy was increased to 406 mJ in the reacting zone, the relative standard deviation of the probability function of H/O intensity ratio reduced to 20%, which leads to a narrow distribution again similar to that of the non-reacting case and similar (around 20%) uncertainty in the local instantaneous equivalence ratio measurement. Another method is to obtain more measurements, but it reduces the temporal resolution of LIBS. For the average of measurements from 50 laser shots, the estimated standard deviation of the fluctuations is about 1% in the non-reacting zone and 3% in the reacting zone for 406 mJ laser pulse energy. However, the latter method provides accurate measurement of the time-averaged value of equivalence ratio, while the former has the potential to deliver instantaneous local measurements of equivalence ratio.
3.3 LIBS Measurement errors in flames

To evaluate how the flames influenced the LIBS measurement uncertainty, 120 /s strain rate and lean premixed (Φ=0.6) flames were taken as the reference case (as shown in Fig. 2(b)) to quantify the in-flame measurement errors, using data from 200 single laser shot. In Fig. 7 and Fig. 8, due to the flat flames of the opposed jet burner, it is possible to maintain the gas density and temperature constant, and then change the laser beam propagation distance in flames. The laser beam started from the left side and propagates horizontally through a certain distance of the flat flames to create plasmas at certain locations. Maintaining the plasma at z=15 mm, its x value was varied from -30 mm to 30 mm in the flat flames.

For this case of LIBS measurements, which implies horizontal path propagation through the large refractive index gradients, stronger effects are to be expected. Propagation of the laser beam through multiple turbulent eddies causes a fluctuation in the irradiance, known as scintillation. The standard deviation of the irradiance is estimated as follows [26]:

\[
\sigma_I = (1.24C_r^2 k^{7/6} L^{11/6})^{0.5} \quad (2)
\]

\[
C_r = 79.0 \times 10^{-6} \left( \frac{P}{F^2} \right) C_T \quad (3)
\]

\[
C_T = \sqrt{\left( \frac{T_1 - T_2}{P} \right)^2} r^{-1/3} \quad (4)
\]

![Graph showing LIBS measurement errors in flames](image)

**Fig. 7** Accumulated averages of 200 plasma spectra obtained at different horizontal locations in the flames at 15 mm height from the lower burner exit.
Fig. 8. Relative standard deviation of H/O intensity ratio for 200 single shot spectra obtained at different horizontal locations in the flames at 15 mm height from the lower burner exit.

In Eq. (2), $C_n$ is the refractive index structure coefficient; $k$ is the wavenumber and $L$ is the propagation path length. In Eq. (3) and (4), $p$ is the atmospheric pressure in millibars and $\langle \rangle$ represents the ensemble average. $C_t$ is a measurable quantity defined by temperature differences $T_1$ and $T_2$ between two reference points separated by a distance $r$. According to the Equations, the errors vary with distance along the flame according to a nearly linear relationship. When the laser beam propagates through the flame zone, both the plasma intensity in Fig. 7 and the relative standard deviation of the H/O intensity ratio in Fig. 8 grow with the propagation path length along the flames, instead of the path length in the air. It can be seen that the relative standard deviation of signal intensity increases with the propagation distance in flames, an observation consistent with Eq. (2). Eq. (4) shows that the temperature gradient in the laser beam path determines the refractive index fluctuations and the intensity fluctuations. Since large temperature gradients are present in combustion, the refractive index structure coefficient $C_n$ is much greater than the value at atmospheric conditions.

Therefore, the overall uncertainty of the measurement of equivalence ratio is around 20% in the reacting zone. If the laser pulse energy is increased for the non-reacting case to 406 mJ, the standard deviation of the probability function of the H/O intensity ratio is reduced to 5%.

3.4 Correlation of equivalence ratio with relative intensity of different species
Fig. 9 Correlation of the equivalence ratio with the intensity ratio CN/O for different laser pulse energies in non-reacting zone (x= 0 mm, z=3 mm)

The intensity ratio CN/O has been shown to have a linear relationship with the equivalence ratio [27]. Figure 9 shows that, although CN/O intensity ratio varies linearly with equivalence ratio, it highly depends on the laser energy. Since molecule CN emission was less sensitive to the laser energy compared to atom lines for H, O and N, when the laser energy increased, CN intensity increased slower than O intensity, leading to the decrease of CN/O for higher laser energy (Fig. 3 (b)). Therefore, H/O ratio is a more accurate and robust indicator to determine the local equivalence ratio, compared to CN/O intensity ratio.

Fig. 10 Correlation of the equivalence ratio with the intensity ratio H/O of LIBS spectra

In order to extract quantitative mixture composition data from the spectra, a calibration was performed for a wide range of equivalence ratios. The laser pulse energy was 406 mJ. The laser beam was once again focused to the non-reacting zone. In Fig. 10, the intensity ratio of H/O
shows a nearly linear behavior with equivalence ratio. The uncertainty of the above calibration, determined from the standard deviation of the spread of the resulting probability function, was 5%. The experimental data is fitted with a polynomial function which could be used as a calibration curve. This equation has an initial value of 0.9557. The reason is that the noise of the recorded spectra by the ICCD and the presence of water vapour in the air contribute to an increased hydrogen intensity. It is noted that H/O intensity ratio has a higher slope as compared to CN/O ratio of Fig. 9 and therefore offers higher sensitivity for equivalence ratio measurements in addition to the reduced sensitivity to laser pulse energy.

### 3.5 Diffusion flames measurements

![Figure 11](image.png)

**Fig. 11** Spatial distribution of methane and Oxygen mole fractions in a methane-air counterflow diffusion flame obtained from LIBS measurements and CHEMKIN simulation. Methane and air streams both exit at speed of 50 cm/s

In order to evaluate the local equivalence ratio measurement across a diffusion flame, pure methane and air streams were ejected from the lower and upper jets with an average velocity of 50 cm/s respectively, producing a global strain rate of 33.3 /s. Co-flow of nitrogen was used to quench the secondary flames. The same operating condition was set up and simulated using GRIMech 3.0. The measurements started from the lower burner exit and progressed along the centreline (x= 0 mm, z= 0-30 mm) to the upper burner exit, using 406 mJ laser pulse energy. Figure 11 shows methane and oxygen mole fraction distribution along the centre line converted from the H/O intensity ratio using the calibration equation of Fig. 10, superimposed to the methane and oxygen fraction distribution in non-reacting flows obtained from GRIMech 3.0 simulation results. Although the experimental results are shifted by 2 mm, which is probably due to buoyancy effects acting on the flame, the agreement between the spatial gradient of the
methane and oxygen fractions obtained from simulations and experiments is excellent, which provides confidence in the ability of LIBS technique, based on the H/O intensity ratio, to measure the local equivalence ratio with high spatial resolution in flames.

4. Conclusions

In this paper, we studied the ability of the LIBS technique to quantify local variations of the mixture fraction of methane/air mixtures in premixed and diffusion opposed jet flames. The settings for the laser and ICCD were optimised for measurements in non-reacting and reacting flows. The behaviour of H, O and N atomic emission and CN molecular emissions for different air-fuel mixtures and laser energy were investigated. The presence of a flame increased the standard deviation of the measured local equivalence ratio greatly due to lower signal-to-noise ratio caused by the low gas density and laser beam steering caused by flames, which increase the variability of the resulting plasma. The measurement uncertainty presents a linear relationship with the path length in the flames, which is consistent with the theoretical equation. The results showed that the increased measurement uncertainty in reacting flows, relative to non-reacting flows, could be counteracted by increasing the laser pulse energy by a factor of 3, which led to around 20% uncertainty for the instantaneous measurement of the local equivalence ratio. Further increase of the laser pulse energy will reduce further the uncertainty. The measurements of the time-averaged value of the local equivalence ratio have a very small error, which only depends on the number of instantaneous shots that are averaged. The results showed that the intensity ratio H/O is more appropriate than the CN/O ratio for measurements in flames due to the low dependence on the laser pulse energy and the increased sensitivity of the H/O ratio for measurement of equivalence ratio. After appropriate calibration between the H/O intensity ratio and local equivalence ratio, the LIBS technique was successfully used to measure the local equivalence ratio across diffusion flames and the experimentally measured spatial gradient of the equivalence ratio within the reaction zone matched the corresponding CHEMKIN simulations, demonstrating the high spatial resolution of the LIBS technique and its applicability in reacting flows.

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