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Local air-fuel ratio and gas velocity measurements in flames using LIBS

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Abstract

Turbulent combustion is an important but complex technical process that takes place in many industrial devices, such as internal combustion engines and gas turbines. Laser-based techniques are widely applied to the combustion research, since they are able to provide important information without severe interferences with the process and with high temporal and spatial resolution. Among these techniques, Laser-induced Breakdown Spectroscopy (LIBS) is an experimental technique that can deliver a manifold of information through the laser-induced plasma. In the current work, laser-induced plasma is used to develop novel diagnostic methods for the measurement of the gas composition and velocity in flames.

This research firstly evaluated and improved the instantaneous LIBS measurement of local equivalence ratio in methane-air opposed-jet flames. It was found that the increased measurement uncertainty in reacting flows, relative to non-reacting flows, could be counteracted by increasing the laser pulse energy and using a proposed filter method, which resulted in a 10% uncertainty for single-shot measurements in flames.

LIBS measurements in binary hydrocarbon mixtures, including CH_4 , C_3H_8 , CO_2 and air, were also investigated. The effects of blends on LIBS spectra were analysed. While limitations exist, it was shown that LIBS results can be used to infer the binary fuel blends and the Wobbe index of the mixture.

Further, a novel seeding-free velocimetry technique, Laser-Induced Plasma Image Velocimetry (LIPIV) was proposed and developed, which is based on recording the displacement of plasma as it gets convected by the gas flow field. It was found that the uncertainty of the novel technique is about 1 m/s along the axis perpendicular to the direction of the laser beam and 3.6 m/s along the laser beam axis and its spatial resolution is about 5 mm. This technique was then successfully applied to measure the gas flow in a non-reacting turbulent jet.

Finally, local equivalence ratio and velocity measurements were performed in a swirl-stabilised non-premixed burner at an air-fuel ratio of 0.72 (overall equivalence ratio) and Reynolds number of 29,000. It was shown that, although the quenching effects and plasma deformation effects increased the measurement uncertainty, the velocity results still verified the feasibility of applying the LIPIV in reacting flows after applying the proposed methods. In conclusion, combined measurements of composition and velocity using the laser-induced plasma are demonstrated in realistic combustion geometries.

Declaration of originality

The present PhD thesis is an own original work of Zhengjie Shi and all else is appropriately referenced.

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Nomenclature

A	transition probability (1/s)
C	coefficient
C_m	the spreading coefficient
C_n	the refractive index structure coefficient
C_p	heat capacity at constant pressure [J/(kg·K)]
C_q	the turbulent intensity normalized by the bulk flow velocity
C_T	measurable quantity defined by temperature differences T_1 and T_2
D	diameter [mm]
D_b	diameter of entrance laser beam[mm]
D_h	distance between the two burners [mm]
d_0	laser beam focal spot size [μm]
D_f	fuel nozzle diameter [mm]
E	energies state [eV]
E_1, E_2	energy levels [eV]
$E_{\text{electronic}}, E_{\text{vibrational}}, E_{\text{rotational}}$	electronic, vibrational and rotational components of energy [eV]
F	experimental parameter for LIBS optical system
f	focal length of the focus lens, or coefficient factor [mm], [-]
f_{int}	initial interaction between the sample and the laser
f_{exc}	excitation/ionization mechanism leading to atomic emission
f_{det}	characterization of the radiation environment, (optically thick or thin).
G_s	specific gravity
G_Φ	axial flux of angular momentum
G_χ	axial flux of axial momentum
g	statistical weights of the transition upper level
H	Hamiltonian, sum of the potential energy or the total enthalpy or hydrogen atom [-], [kJ/mol], [-]
h	Planck's constant [m ² kg/s]
h_α	specific enthalpy of species α . [kJ/kg]
I	emission intensity
I_a, I_b	transition lines
I_t	turbulent intensity
I_w	Wobbe index
i	i-th energy level
$J_{\alpha j}$	total diffusive mass flux for the species α in the j-direction [kg/(m ² s)]

j	j -th energy level
L	the propagation path length. [m]
l	spatial location [m]
$l_{t+\Delta t}$	the plasma location at time $t+\Delta t$ [m]
$\bar{l}_{0,t+\Delta t}$	the mean value of the plasma location at $t+\Delta t$ in the quiescent field. [m]
L_x	dimension along the x axis [mm]
L_z	dimension along the z axis [mm]
L_t	Taylor microscale [m]
$L_{h, \text{turbulent}}$	the length of the hydrodynamic entry region along the pipe [m]
k	Boltzmann's constant [$\text{m}^2 / (\text{kg s}^2 \text{K})$]
K	the wavenumber
M_α	mass production rate of species α [kg/s]
n	the number of emitting species or energy levels
n_e	electron number density [cm^{-3}]
Pe	laser pulse energy [mJ/pulse]
p	pressure [Pa]
R	intensity ration between two transition lines, or burner radius [-] or [mm]
r	distance between point 1 and point 2, or correlation coefficient [m] or [-]
r_o	the outer radius of the swirler [m]
S	the LIBS signal [Intensity, a. u.]
S_Φ	the source term
s	quantum number
S_w	swirl number
T	temperature [K]
t	time [s]
U	partition function or axial velocity [-] or [m/s]
U_b, U_0	bulk velocity [m/s]
U_χ	axial component of velocity [m/s]
U_θ	tangential component of velocity [m/s]
u	velocity [m/s]
u^*	velocity uncertainty component [m/s]
V_0	area-averaged velocity [m/s]
V	radial component of velocity [m/s]
V_c	higher heating value [kJ/mol]
ν	frequency of the light or the kinematic viscosity of the gas [Hz] or [m^2/s]

W swirl component of velocity [m/s]
 w electron impact width [nm]
 w_α molar production rate of species α [mol/s]
 X Cartesian position [m]
 x,y,z spatial coordinates [m]
 Y_α mass fraction production rate of species α [1/s]
 Z mixture fraction (mole fraction)

Greek symbols:

Δt time interval [s]
 Δl displacement [m]
 τ_{ij} the viscous stress tensor [m²/s²]
 κ the thermal conductivity [W/(mK)]
 ε the effective diffusivity [m²/s]
 σ standard deviation
 λ the wavelength of transition [nm]
 Ψ wavefunction
 Ψ_{total} wavefunction in total
 Ψ_e, Ψ_v and Ψ_r the electronic, vibrational and rotational components
 ρ mass density [kg/m³]
 ΔE the energy difference between the upper and lower levels of the transition. [eV]
 $\Delta\lambda_{\text{Stark}}$ Stark effect broadening [nm]
 μ reduced mass of the electron and proton
 η the collection system efficiency
 Δv vibration energy level difference [eV]
 Φ stoichiometric mixture equivalence ratio or generalized scalar flow variable

Abbreviations

a.u. arbitrary unit
 CARS coherent anti-stokes raman spectroscopy
 DGV Doppler global velocimetry
 HHV Higher heating value
 ICCD Intensified Charge-Coupled Device
 MCP micro-channel plate
 MFC mass flow controller

MTV	molecular tagging velocimetry
NIR	near-infrared
Re	Reynolds number
rms	root mean square
RSD	relative standard deviation
SNR	signal to noise ratio
LDV	laser Doppler Velocimetry
LIBS	laser induced breakdown spectroscopy
LIF	laser-induced fluoresce
LPIV	laser induced plasma image velocimetry
LPG	liquefied petroleum gas
LTE	local thermodynamic equilibrium
p.d.f.	probability distribution function
PIV	particle image velocimetry
FWHM	full width at half maximum
UV	ultra-violet

Chapter 1 Introduction

In this chapter, an introduction to the laser-aided techniques in combustion and a brief literature review are provided to explain the motivation and objectives of this work. The recent developments of the Laser-induced breakdown spectroscopy (LIBS) are introduced in detail, since it provides a foundation to develop a novel velocimetry technique.

1.1 Background

A flame is the visible, gaseous part of the reaction process during combustion applications. During the combustion process, many reactions that occur in the flames create a region of high local heat release. Flames constitute a particularly complex phenomenon, since chemical reactions occur in the presence of heat and mass transport processes. Various burner designs are available that produce flow fields and mixing of hydrocarbon fuels with an oxidizer, such as the ambient air or oxygen, that allow controlled ignition and combustion of fuel mixtures for different applications. In most burners, the flow field at the flame region is turbulent, which is therefore characterised by a wide range of temporal and spatial scales. Furthermore, the turbulence of the flow comprises instantaneous vortical structures, commonly called ‘eddies’, which can enhance mixing, heat and mass transfer processes. Measurements in combustion process are essential in order to understand the local characteristics that influence the reacting zone, determine combustion stability and control CO, NO_x and soot emissions.

It is common in the study of flames to use multiple quantities, such as temperature, velocity, chemical composition and concentration. As these quantities provide basic and important information on the physics of the underlying phenomena, the development of measurement methods, which can quantify them and, if possible, simultaneously at an instant in time and with high spatial resolution become a key issue for scientists. In addition, methods that can be applied to real combustor geometries are desirable.

For example, flame chemiluminescence [1] is a simple technique, which is based on the chemical excitation of species in flames. A camera records the light emitted from chemically excited OH species, denoted OH*. The local equivalence ratio and reacting processes can be monitored using this technique and the technique represents a convenient and straightforward way to diagnose combustion conditions [1–3]. However, the flame chemiluminescent intensity

signal is usually weak and noise may interfere with the measurements. This technique is limited by the signal-to-noise ratio (SNR) of the measurement.

Unlike the flame chemiluminescence, in the last few decades, a large amount of progress has been made with laser-based diagnostic techniques [4,5]. Laser diagnostics typically use a laser in combination with several external optics (*e.g.* mirrors, lens *etc.*) and a camera to carry out non-intrusive measurements with a high degree of accuracy, sensitivity and spatio-temporal resolution [6], which cannot be achieved by using probe-based methods, such as the Pitot tube anemometer or thermocouple methods. There are now many laser diagnostic techniques [7–9] that can be used to measure the parameters that describe flames. For instance, Particle image velocimetry (PIV) [10–13], Laser induced fluorescence (LIF) [8,14–17] and Laser-induced breakdown spectroscopy (LIBS) [4,5,18] have been widely used in combustion diagnostics to perform velocity, certain species and atomic concentration measurements respectively. The theories and features of the laser diagnostics used in combustion are briefly discussed below.

1.2 Literature review of laser diagnostics in combustion

This section reviews specifically the existing approaches widely used in combustion diagnostics for composition, temperature and velocity measurements. These techniques are usually not restricted to single quantity measurement and researchers develop them for simultaneous measurements of multiple quantities, as discussed in the following sections.

1.2.1 Composition measurement techniques

During combustion, fuels must be mixed with oxidants at an appropriate ratio in order to react and release the maximum possible heat. The normalised mixture ratio of fuel and oxidants (*i.e.* the equivalence ratio) influences the efficiency of combustion and the generation of pollutants, which also affect ignition, transition and stability of combustion. The measurement of the local equivalence ratio is therefore an important part of flame diagnostics. LIBS, Raman spectroscopy [19] and LIF have been used to measure equivalence ratio of fuel-air mixtures and are detailed below.

LIBS (Laser-Induced Breakdown Spectroscopy) for mixture composition

LIBS is a laser-aided method of atomic and molecular emission spectroscopy that uses a laser-generated plasma as excitation source for mixture composition measurements and, sometimes, as hot vaporization and even atomization of liquid fuels source. This technique has the ability to interrogate gas samples *in situ* and remotely without any preparation. By monitoring the spectral emission line wavelengths and corresponding intensities, qualitative and quantitative analysis of the mixture composition can be carried out.

A typical LIBS system consists of Nd: YAG solid-state laser, spectrometer with a wide spectral range and high sensitivity, fast response rate and time-gated detector. The laser pulse duration is of the order of 10 ns, generating a power density, which can exceed $1 \text{ GW} \cdot \text{cm}^{-2}$ at the focal point. If the beam energy density is sufficiently high, a plasma is created when focused at a 'point' in a gas. The high peak energy laser pulse first breaks the chemical bonds of substances in the local gas and initializes the fragmentation of molecules into elemental components in the focal volume. Then, a high temperature ionized plasma is generated, while the dissociated atoms from target molecules can be excited. The emitted light from the excited atoms during their radiative relaxation process can be recorded and analysed to determine the elemental composition of the sampled substances. In LIBS, if the plasma is optically thin and in local thermodynamic equilibrium (LTE) (which will be discussed in Chapter 2), the intensity of different spectral emission lines has a linear correlation with the population of the corresponding atomic excited state.

The spectrometer then records the electromagnetic radiation emitted from the plasma over the widest wavelength range possible, maximising the number of emission lines detected for each particular element. The majority of elements have emission lines within the commonly used wavelength range of spectrometers from UV (ultraviolet) to NIR (near-infrared). The spectral resolution of the spectrometer can also affect the quality of the LIBS measurement, since high resolution systems can better separate spectral emission lines in close proximity, which reduces the interference (crosstalk) and increases the selectivity. A delay generator accompanies the spectrometer and detector, which accurately gates the detector's response time, allowing a high temporal resolution of the spectrum.

The technique has been used widely to quantify the concentration of species that are present in gases or solids for many different applications, such as detecting metals and toxic substances [20–22]. More recently, it has also been used to measure fuel-air ratio of gaseous mixtures in reacting flows [23–26]. LIBS possesses many advantages compared to other optical techniques, including high spatial resolution, low cost equipment, fast response time and potential for application to realistic combustors. In addition, LIBS does not require the addition of other substances in a flow for the measurement and is not very sensitive to emitted light from other sources. Therefore, in principle, it has the potential to deliver measurements in practical combustors. A detailed review of the LIBS technique is presented in Chapter 1.3.

Raman spectroscopy & CARS (Coherent Anti-Stokes Raman Spectroscopy)

Raman spectroscopy [27–29] is a spectroscopic technique that can observe vibrational, rotational and other low-frequency modes in a system. This technique involves exciting a gas sample with a laser beam and detecting the scattered light from the illuminated spot. The majority of the scattered light is of the same wavelength as the incident light and is described by Rayleigh scattering theory. Only a very small amount of the scattered light has a different wavelength due to the interactions between the source light and molecular vibrations, phonons or other excitations in the system. The shift in energy delivers information about the vibrational modes in the system, which vary depending on the composition of the gas. This technique has been applied to composition measurement of mixtures in the field of chemistry for a long time [7,30]. However, when applied as a combustion diagnostic, the SNR (signal-to-noise ratio) in a reacting flow is relatively low, which increases the measurement uncertainty [31,32].

Unlike Raman spectroscopy, coherent anti-Stokes Raman spectroscopy (CARS) employs multiple photons to address the molecular vibrations and produces a coherent signal [33–35]. As a result, CARS is orders of magnitude stronger than spontaneous Raman emission. The strong signal makes CARS suitable for species detection in combustion applications. Besides the composition measurement using CARS, extended usage [36–38] of CARS for temperature measurements is based on the theory that the population of states follows the temperature dependent Boltzmann Distribution.

The laser pulse energy for LIBS technique is in the order of 100 mJ/ pulse. However, Raman setup requires a much higher excitation energy (higher than 1 J/pulse) [39]. The cost of the

associated equipment for Raman and CARS methods is high, the sources of errors are extensive and their applicability to realistic combustors is limited due to low signal intensity and interference with other sources of emitted light (*e.g.* flame chemiluminescence). Compared with LIBS, Raman and CARS methods has a smaller probe volume (less than 1 mm) and less intrusive to the flow field. [39]

LIF (Laser Induced Fluorescence)

LIF is another spectroscopic method in which atoms or molecules are excited by the absorption of laser light, followed by spontaneous emission of light over a short duration (below 100 ns). The collected emitted intensity signal is a function of molecular number density, which is mainly influenced by the gas temperature, pressure and bath gas composition. LIF is widely used for studying molecular structure, species detection and flow visualization.

For low number density species, LIF has advantages over Raman scattering, yielding higher precision and accuracy, especially in flames with strong fluorescence interference. LIF remains mainly restricted to limited species measurement [40,41]. In combustion, radicals of OH, CH, CO and NO have been measured by LIF techniques [42,43], in order to identify the flame front location and pollutant formation processes. Nevertheless, in order to conduct practical CO-LIF [44,45], both the requirement of high-energy excitation laser light at ultraviolet regions (around 230 nm) and interference from other species like CO₂* are still a challenge.

For quantitative analysis, systems are preferred where the fluorescence signal can be attributed to single species. Therefore, it is popular to add well-characterized fluorescing tracers to non-fluorescing fuels. Tracer-based LIF techniques have been used for experimental studies in fluid mechanics and combustion for several years [46–49]. By adding appropriate tracers into the flow, the tracers can act as representatives for the local fuel concentration or equivalence ratio in experiments. Reboux *et al.* [49] took advantage of the strong quenching of toluene LIF by O₂ to directly measure the fuel air ratio. This technique is often referred to as fuel/air ratio laser-induced fluorescence (FARLIF). Schulz *et al.* [46–48] used FARLIF technique for the measurement of temperature, fuel concentration and equivalence ratio. Ideally, the tracer should yield LIF signal intensities that are directly proportional to the desired quantity and should not be influenced by the ambient conditions. Unfortunately, signals from all fluorescent tracers show at least some dependence on local temperature, pressure, and bath gas variation.

Mismatch in fuel and tracer properties can lead to substantial systematic measurement errors. For example, adding tracers will change the overall mixture composition; the breakdown of the molecular structure of typical tracers like ketones, aldehydes or amines during combustion can be different from that of parent fuel. Therefore, the cost of equipment for equivalence ratio measurement using LIF is high, with difficulty in finding appropriate tracers for harsh conditions. In realistic combustor measurement, the SNR of LIF is still relatively low. Compared with LIBS, LIF measurements rely on the presence of tracers and the laser wavelength has to be chosen appropriately. To realize quantitative measurement, the laser beam profile of LIF should be uniform and stable from pulse to pulse. In comparison, LIBS only needs the enough laser pulse energy to breakdown the gas.

Besides, LIF is also extended to the measurement of the temperature, which typically requires two laser sources [50] and the measurement of velocity in flow, which is practical only for sonic or supersonic flows [51], due to the short lifetime of tracers.

1.2.2 Temperature measurement techniques

In combustion, reliable temperature measurement is a challenge because it is difficult to measure without interfering with the combustion process. It remains difficult to obtain high spatial and temporal resolution temperature measurements. At fixed pressure, the temperature of a gas is inversely proportional to the gas density. Rayleigh Scattering thermometry and approaches with LIBS both measure gas density directly and obtain the temperature using this principle [52,53]. Thermographic LDV (Laser Doppler Velocimetry) is a more recent approach utilizing concepts from LDV and phosphor thermometry to measure temperature. These techniques are discussed below.

Rayleigh scattering thermometry

Rayleigh scattering thermometry [54–57] is based on the elastic scattering of light by gas molecules. It uses Rayleigh scattering theory, developed by Lord Rayleigh (John William Strutt, 3rd Baron Rayleigh), which is valid for particles, atoms or molecules, which are smaller than the wavelength of the incident light. It is assumed that the wavelength of the scattered light is the same as the incident light. The intensity of the scattered light is inversely proportional to the fourth power of the wavelength. The scattered light intensity from a molecule or a particle is also proportional to the Rayleigh scattering cross section, which is an intrinsic property of a

molecule. The scattered light intensity measured by the detector depends on the number density of molecules in the gas. All molecular species in a probe volume contribute to the scattering process, and thus the gas density can be measured. For the ideal gas, at fixed pressure, the gas density is inversely proportional to the temperature, and then the temperature can be obtained [56].

The Rayleigh scattering signal is orders of magnitude weaker than Mie scattering and generally requires a clean gas environment, free from soot, dust particles and similar contaminants, to minimize interference with the measurement. Due to the Doppler effect originating from the thermal motion of the molecules, the Rayleigh scattering light from molecules has a broadening of spectral lines. The filtered Rayleigh scattering technique employs a narrow absorption line optical filter at the central frequency of a single-mode laser, which can block the spectrally unbroadened scattered light from non-moving or only slowly moving particles. Only the spectrally broadened part of the molecular gas Rayleigh line can pass the optical filter and be used for measurement. The broadened part carries the information of the Rayleigh scattering with a high SNR, without interference with the contribution of the unbroadened light. Therefore, this thermometry technique can be combined with Particle Image Velocimetry (PIV) [57–59], since it can suppress scattered light from seeding particles, as well as emission from soot generated in flames and background flame light emission. However, the technique has to be performed with a narrow band laser that matches the atomic filter exactly. In addition, temperature data processing requires the exact information of the species-specific Rayleigh cross-section in each volume and the spectral shape of the emission [56].

This makes this technique costly (narrow band laser is quite expensive) and difficult to apply in practical combustors. In addition, if the pressure varies in the considered process, the assumed conversion of the gas density into temperature is not possible anymore. Finally, the ability to eliminate completely the light scattered from other sources is not perfect and the signal-to-noise ratio (SNR) can be low. In comparison, the LIBS-based temperature measurement used less costly equipment. By focusing a laser beam into one point, the temperature can be obtained from the LIBS spectra, which is described in details below.

LIBS-based technique for temperature measurement

Besides the gas composition measurement, LIBS has also been used for the measurement of gas temperature. There are different ways that this can be achieved. One method tracks the

concentration of a major species, such as nitrogen. The gas temperature can be retrieved since the nitrogen signal, a measure of the density of the nitrogen, is inversely proportional to the local temperature [52]. Another method, proposed by Kiefer [60], uses the relationship between the gas temperature before breakdown and the “breakdown energy” threshold, *i.e.* the minimum energy necessary to breakdown the gas molecules. The broadening of a line in the plasma spectrum is proportional to the plasma electron density. The width of atomic lines is used to measure the gas density at atmospheric pressure, and then, in turn, estimate the gas temperature [53].

Unfortunately, the LIBS-based thermometry technique relies on difficult calibration procedures of premixed mixtures [53,60]. However, LIBS does not require the addition of other substances in a flow for measurements and is not very sensitive to emitted light from other sources. The spatial and temporal resolution of the temperature measurement is consistent with LIBS velocimetry and equivalence ratio measurements, which is discussed in Chapter 6. Therefore, in principle, it has the potential to deliver measurements in practical combustors.

Thermographic LDV (laser Doppler Velocimetry)

Thermographic LDV uses a combination of LDV and phosphor thermometry to measure, simultaneously, the velocity and temperature of ‘seeding’ particles added in a gas flow. The thermographic phosphors are inert and insensitive to pressure and local gas composition and have, in general, a melting point higher than 2000 K [61–63]. The luminescent properties of these phosphors depend on temperature - when excited by incident laser light, the emission of the phosphors is a function of phosphor temperature. The light scattered by the particles is used for simultaneous measurement of velocity. The technique requires careful selection of phosphor particles and, currently, there are no appropriate phosphor particles for combustion applications. The temperature range measured by this technique is still therefore limited and not appropriate for combustion application.

In addition, even if the phosphor ‘seeding’ particles for combustion applications become available, the technique requires quite expensive lasers and, depending on the approach used to extract the temperature information, high speed detectors may be needed. Finally, the required addition of ‘seeding’ particles to the flow generates complications related to safety and makes it difficult to apply the technique in practical combustors.

1.2.3 Velocity measurement techniques

The Pitot tube anemometry [64,65] and hot-wire anemometry [66,67] are classical methods for flow velocity measurement, which have been used widely in both industry and research for decades. The harsh conditions of the combustion process, such as the high flame temperature and the complex species present in the reacting zone, make the use of these probe-based techniques difficult to, use in flames, since the probe may get damaged. Advances in laser diagnostic techniques have led to laser-aided velocimetry methods increasingly being used in favour of probe techniques, in combustion research.

Laser Doppler Velocimetry (LDV)

LDV [68–73] is a point measurement technique that can be used to obtain local gas velocity with a high temporal and spatial resolution in reacting and non-reacting flows. An incident continuous laser beam is split into two beams. A fringe pattern can be created at the intersection of the two incident laser beams. As a micron-sized particle, seeded in the flow, moves through the fringes, the photodetector records a signal burst, whose amplitude is modulated by the fringe pattern. The signal frequency is proportional to the flow velocity component perpendicular to the fringes. LDV is already a standard velocity measurement technique for turbulent flows, capable of measuring the entire turbulent spectrum [69,71,72]. A typical commercial LDV technique [74] has a spatial resolution of typically a few millimetres long. The temporal resolution is of the order of 1 ms, depending of the seeding density of the tracers. This technique requires the addition of ‘seeding’ micron-sized particles in the flow, which makes it difficult to apply in practical combustors.

One extension of the LDV technique is the Doppler Global Velocimetry (DGV), which measures the Doppler shift of the frequency of the scattered light from ‘seeding’ particles [75,76]. By using a molecular iodine filter to measure the Doppler shift (similar in principle to the filter used in Rayleigh scattering thermometry), the two dimensional gas flow velocity field can be obtained. However, again this technique requires the addition of ‘seeding’ particles to the flow, which limits its application to practical combustors. In addition, since it measures the Doppler shift superimposed to the frequency of the light, it is commonly applicable to high speed external aerodynamic flows rather than in reacting environments.

PIV (Particle Image Velocimetry)

Similar to the LDV technique above, micron-sized particles or droplets are added to the flow and two images of scattered light from particles after laser sheet illumination are recorded by a CCD camera. If the two successive images are obtained with a short time delay relative to each other, the short displacement of the ‘seeding’ particles that occurs during the time between the two images can be estimated with a correlation-based method. The measured displacement can be converted into an instantaneous velocity field after using the known time delay between the image pair. It is important however that the ‘seeding’ particles have the appropriate characteristics so that they can respond perfectly to the surrounding gas flow velocity fluctuations and, consequently, their measured velocity also represents the velocity of the gas.

In common PIV configurations, the time delay between two images is between 1 and 1000 μs . The time delay must be long enough to be able to determine the displacement of the tracer particles with sufficient resolution and short enough to avoid particles with an out-of-plane velocity component leaving the laser light sheet between subsequent illuminations. The two images are divided into a grid made up of cells or “interrogation windows”, which also determines the spatial resolution of this technique. A cross-correlation algorithm is typically used then to calculate the average displacement of the particles in the corresponding window of each image. This is used with the known time delay to estimate the 2D velocity field. After decades of development [9,77–81], PIV has become an established technique for instantaneous planar flow velocity measurement. Extensions of the PIV technique include stereo-PIV [82–84] using two cameras with different viewing angles to calculate 3 components of the velocity field, time-resolved PIV [85,86], using both a high-speed laser and PIV camera to monitor the transient process, and tomographic PIV [87,88] using multiple cameras to record simultaneous views of the illuminated volume.

As for the LDV technique, PIV has a major disadvantage that the flow must be ‘seeded’ with particles or droplets. The measurement accuracy relies on the ability of particles to accurately follow the fluid flow. In addition, deposition of particles on optical window, added on the wall of confined flows, can cause severe practical measurement problems.

Up to now, there are some alternatives to the use of tracer particles for optical velocimetry. Such alternative techniques include molecular tagging velocimetry (MTV) [89–91], laser-

induced thermal acoustics [92,93] or magnetic resonance velocimetry [94,95], but their use remains restricted due to the high experimental complexity. For example, in MTV, the specific molecular marker is written into the gas and the velocity is measured by computing the marker's displacement over a known delay. MTV generally needs to be performed with appropriate long lifetime tracer molecules in flows and a UV wavelength laser. The fluorescence from the molecules are also subject to quenching caused by pressure or other species; laser-induced thermal acoustics is difficult to be applied to flames due to lack of local gas composition information that is necessary for the interpretation of the behaviour of the acoustic signal.

In the literature mentioned above, the commonly used laser based measurement techniques summarized in Table 1.1 are limited to a measurement of a single quantity and some (CARS, Rayleigh scattering thermometry, *etc.*) are difficult to set up and use in a practical combustor environment. They usually require a repeatable, high-quality laser beam profile, homogeneous particle, a dye substance, or molecular species 'seeding' in the flow, complex calibration process and are quite expensive.

Compared with other techniques, LIBS is a lower cost measurement technique that can deliver a manifold of information based on the emitted light from the laser-induced plasma. Using the information of the plasma spectra and the breakdown threshold, the elemental composition [22,96,97] and gas temperature [53,60] measurements have been studied. However, the accuracy of LIBS measurements in reacting flows and the ability to deliver instantaneous local measurements of mixture composition has not been properly assessed. The current research aims to evaluate the ability of the LIBS technique to measure local mixture composition in reacting flows. Then, it intends to extend the application of the LIBS technique to hydrocarbon mixtures and assess its ability to monitor the variability of the hydrocarbon mixture composition. Finally, the research develops a novel *seeding-free* technique, based on laser-induced plasma, that can measure multiple quantities, including instantaneous, local gas flow velocity, elemental mixture composition and possibly temperature.

Table 1.1 A brief summary of the combustion diagnostics techniques

Technique	Quantity	Extension measurement	Features
LIBS	Atom concentration	Temperature	Measure atomic or molecular species concentration with a high SNR
Raman spectroscopy	Species concentration	Temperature	Measure multispecies concentration
CARS	Species concentration	Temperature	Point measurement using three laser sources with a high SNR
LIF	Species concentration	Temperature	Measure limited molecular species
Rayleigh scattering thermometry	Temperature	Velocity/pressure	Require a clean environment free from soot, dust particles
LDV	Velocity	Temperature	Point measurement with seeding particles
PIV	Velocity	Temperature	Field measurement with seeding particles
MTV	Velocity	Temperature [90]	Nonintrusive optical measurement without seeding particles

1.3 Literature review of Laser Induced Breakdown Spectroscopy (LIBS)

During the last two decades, LIBS (laser-induced plasma spectroscopy) has been applied to combustion processes and it has been shown that important properties, influencing the local flame characteristics, such as the fuel-air ratio, can be obtained from atomic species measurement, as shown in Table 1.2. Hanafi [98] carried out experiments on helium, argon, nitrogen and air using ruby laser radiation to evaluate the spectral emission characteristics of these gases. Electron temperature and electron density were analysed as well as the temporal behaviour of the plasma. Phuoc and White [4] used the line radiation at the wavelength of the H-lines and the O (I) triplet in plasma to correlate with the equivalence ratio in methane-air

mixtures. Stavropoulos *et al.* [22] investigated the influence of laser pulse duration on LIBS calibration curves. Two Nd: YAG lasers, delivering pulses of 35 ps and 5 ns respectively, were used to create plasmas on aluminium, manganese, iron and silicon targets and on prepared stoichiometric samples of these metals in a matrix. Optimum experimental conditions were identified for LIBS to be used reliably. Stavropoulos *et al.* [5] used LIBS as an analytical tool for equivalence ratio measurement in laminar methane–air premixed flames. Molina *et al.* [99] studied the effect of temperature and CO₂ concentration on LIBS measurements of alkali fumes. D’Ulivo [100] used LIBS to study the deuterium/hydrogen ratio in gas reaction products. Ferioli and Buckley [101] used LIBS for direct measurement of atomic species over a wide range of mixture fractions (mole fraction) of C₃H₈, CH₄ and CO₂ in air. The strength of the C, O, and N lines in the spectral window 700–800 nm was investigated for binary mixtures of C₃H₈, CH₄ and CO₂ in air. Kawahara *et al.* [102] implemented a multi-fibre Cassegrain optical system coupled to an intensified CCD spectrometer to study the physics of laser-induced plasma in air spatially, temporally and spectrally. Zimmer and Tachibana [103] conducted phase-locked LIBS measurements of equivalence ratio in a lean premixed combustor, which operated with strong thermo-acoustics oscillations and found that stoichiometry changes within one oscillating cycle by about 3%. Michalakou *et al.* [104] measured the local equivalence ratio in different methane-, ethylene- and propane-air mixtures.

Eseller *et al.* [105] developed an ungated, miniature LIBS-based sensor for studying CH₄-air and biodiesel flames. Joshi *et al.* [106] presented the first demonstration of simultaneous use of laser sparks for engine ignition and LIBS measurements of in-cylinder equivalence ratios of natural gas and air. Mansour *et al.* [107] used LIBS to measure local equivalence ratio in turbulent partially premixed flames. Kiefer *et al.* [97] reported the investigation of the laser-induced breakdown and ignition behaviour of methane / air and dimethyl ether (DME) /air mixtures. Moreover, the optical emission from the laser-induced plasma was utilized for determining the mixture composition by means of LIBS. In Zimmer and Yoshida’s study [108], experimental results obtained with LIBS to retrieve local compositions were presented for an ambient pressure up to 5.0 MPa in a test cell. Majd *et al.* [18] used a spatially-resolved LIBS system to analyse methane–air diffusion flames. This LIBS configuration included an entrance slit and a non-gated detector and delivered reduced background continuum emission, increased SNR by up to eight times and enhanced spatial resolution.

Böker and Brüggemann [109] discussed two measurement techniques for temperature determination of laser-induced plasmas in a gas at pressures relevant to combustion engines. Plasmas induced by laser breakdown in air at initial pressures ranging from 0.3 MPa to 2.5 MPa were investigated using optical spectroscopy. Zhang *et al.* [110] studied the quantitative local equivalence ratio measurements of premixed kerosene/air gas at elevated pressure by LIBS technique. Experiments were performed in a high temperature test cell, which was designed and manufactured for simulated supersonic combustion conditions. Do and Carter [111] measured hydrocarbon fuel concentration in reacting flows using short-gated LIBS with 25-ns gate delay. Nitrogen (568 nm) and hydrogen (656 nm) atomic emission lines were selected to establish a correlation between the spectral line intensities and fuel concentration. These correlations were effective in a wide range of fuel mole fraction (7–90% methane/air and 5–93% ethylene/air mixtures) and independent of flow velocity. Kotzagianni *et al.* [26,112] proposed a novel calibration scheme for LIBS in the methane-air mixtures. The intensity ratios H (656 nm) over O (777 nm) and C₂/CN were found to depend on the mole fraction of methane in the ranges of 0~0.3 and 0.3~1.0. LIBS was applied to turbulent non-reacting and reacting jets. Both the mean mixture fraction (mole fraction) and the rms measurement showed the expected trends.

Researchers also conducted experimental research in combustion using LIBS and PIV to measure the instantaneous, local concentration of different elements and gas flow velocities in flames [5,21,111,113–116]. Such information is necessary for improved understanding of the interaction between local flow strain rate and local mixture fraction during the reaction process.

In these papers mentioned above, researchers employed LIBS to study the equivalence ratio through the intensity of C, H, N and O [4,5,18,97,101,103–108,110,111,114–117] in a Bunsen burner [5,18,97,103–105,114,115,117] or Opposed jet flow [4]. For other atoms, Hanafi *et al.* [98] studied the emission intensity of He, Ar, N and air; Molina *et al.* [99] studied the Na and D radiation; D'Ulivo *et al.* [100] studied the D to H ratio. Atoms such as H, C, O and N in emission spectrum were frequently used to quantitatively analyse the concentration of atoms in plasma. The ratio between emission intensities of H/O and C/N in LIBS were usually used to determine the equivalence ratio of hydrocarbon fuels within the probe volume.

In terms of different flow and flame patterns, laminar [5,97,104,115,117] and turbulent [103,107] flows and premixed [5,97,117,100,103–105,107,111,114,115] and nonpremixed [97]

flames were studied. Papers [4,18] studied the diffusion flame patterns. The plasma behaviour in pressurised stainless steel chambers [98,109,110], alkali exhaust gases [99], reaction gases products in a reaction vial [100] and natural gas engines [106] was also observed and investigated. Different factors in the measurements of LIBS, laser pulse energy, time delay, gate time of camera, pressure of the gas and ungated-camera were frequently evaluated. Researchers studied temporally, spatially and spectrally the development of plasmas. Important parameters for combustion processes, such as strain rate, temperature and temporal evolution of plasma were detected and evaluated.

1.4 Motivation and objectives

Based on the literature review related to LIBS, it is evident that much effort has been undertaken to conduct LIBS in elemental concentration/air-fuel ratios in various experimental apparatus (In this research, the air-fuel ratio is converted into mixture mole fraction or equivalence ratio). However, LIBS is still subject to variations in the laser spark and resulting plasma, which often limits measurement reproducibility. Most of the LIBS studies focus on non-reacting conditions using temporally averaged measurements and do not evaluate the uncertainty of measurements in reacting flows. To realise instantaneous measurements of local air-fuel ratio in non-premixed flames, it is necessary to evaluate and improve the precision of LIBS in the reaction zone.

Further, the majority of the previous LIBS investigations in combustion for quantitative measurements are limited to pure or simple mixed gases [26,96,114]. The experimental data obtained from these investigations [18,106,107,117] do not suit a complex mixture of fuel blends, which may be composed of CH_4 , CO_2 and H_2 or other gases. The study also applies the LIBS technique into mixtures of different hydrocarbons and air. The effects of gas blends on LIBS spectra are further investigated. In industry, the Wobbe index is an indicator of the interchangeability of fuel gas mixtures, such as natural gas, liquefied petroleum gas (LPG) and is frequently defined in the specifications of the gas supply and the transport utilities. The Wobbe index is used to compare the combustion energy output of different fuel gas compositions supplied to an appliance. The definition of Wobbe index can be seen in equation (1.1). If V_c is the higher heating value (HHV), or higher calorific value, and G_s is the specific gravity (the ratio between the density of an actual gas and the density of air), the Wobbe index, I_w , is defined as:

$$I_w = \frac{V_c}{\sqrt{G_s}} \quad (1.1)$$

The usefulness of the Wobbe index is that for any given orifice, all gas mixtures that have the same Wobbe index will deliver the same amount of heat. The Wobbe index is determined by the hydrocarbon fuel composition that may be composed of CH₄, C₂H₆, C₃H₈, H₂, CO₂, *etc.* Therefore, it is important to investigate the effects of different hydrocarbon blends on LIBS spectra. As a consequence, LIBS ability to monitor the fuel Wobbe index can also be evaluated.

In addition, although PIV has been used widely in combustion to measure the velocity field, PIV technique requires the introduction of ‘seeding’ particles in the flow in order to be able to measure the flow velocity. Such addition of particles is not always possible or feasible and, for certain conditions, ‘seeding’ particles may not perfectly follow the fluid motion, which affects the accuracy of velocity measurements. In particular, close to a reaction zone, high temperature gradients exist, which may influence the ability of particles to follow the local gas flow, increasing the uncertainty of PIV based gas velocity measurements. Finally, the addition of ‘seeding’ particles in real combustors, *e.g.* gas turbine combustors, to measure flow velocity is not usually a viable option. This is because the high temperature and high pressure of the real combustor make it difficult to add particles, and the deposition of particles on the optical window also causes severe issues for continuous measurements. The nonintrusive techniques, such as MTV, have to depend on certain species like biacetyl [89], supramolecule [90], acetone [91] and so on to perform measurements. The availability of an alternative method to measure gas flow velocity without the need of ‘seeding’ particles or any tracer molecules is, therefore, a very useful development. The motivation of the current research is to explore the possibility to develop such a novel technique. In addition, it would be an advantage to be able to use such velocimetry technique simultaneously with LIBS for mixture composition measurements.

The current research first explores the application of LIBS technique for local and instantaneous measurements of equivalence ratio in premixed and non-premixed methane-air flames. An opposed-jet burner is used as the testing rig. Then, the research develops and evaluates the LIBS technique for measurement of local mixture fraction of different fuel blends under controlled flow conditions, including blends of CH₄, C₃H₈, H₂ and CO₂. The development of correlations between LIBS spectral intensity ratios and Wobbe index in non-

reacting flows will also be attempted. This study assesses LIBS measurement accuracy and limitations in determining the local mixture fraction of fuel blends.

The second part of the research is to develop Laser-Induced Plasma Image Velocimetry (LIPIV), a novel technique for measurement of flow velocity through tracking the motion of plasma induced by a laser beam, as it is convected by the local flow. The applicability and accuracy of this velocimetry technique will be evaluated. LIPIV will be combined with LIBS in order to deliver local measurements of mixture fraction and velocity. These techniques will be applied to non-reacting and reacting flows, which include a turbulent jet flow and a swirl-stabilised flame.

1.5 Outline of the thesis

This thesis is split into eight chapters and, following the introductory Chapter 1, it is structured as follows.

Chapter 2 introduces the basic information on the use of LIBS for quantitative analysis. The theoretical assumptions on the state of the plasma are discussed. The assumptions are necessary in order to ensure reliability of the LIBS analysis. Some methods to extract quantitative information from LIBS spectra are also presented.

Chapter 3 provides a detailed description of the optical setup of the LIBS system, the considered flow arrangements and the experimental conditions. Description and characteristics of the optical setups for LIBS and LIPIV are given.

Chapter 4 presents LIBS results in methane-air opposed jet flames. After the calibration of LIBS in methane-air mixtures, the accuracy and precision of LIBS results in non-reacting and reacting flows are investigated and analysed. This chapter provides procedures to improve the SNR (signal to noise ratio) of LIBS measurement to realise instantaneous measurement of mixture composition. The LIBS measurements of air-fuel ratio in non-premixed flames are finally compared with CHEMKIN simulation results (a software tool for solving complex chemical kinetics problems).

Chapter 5 describes mixture composition measurement in different gas blends using LIBS. The LIBS technique is used to measure different hydrocarbon blends, including CH_4 , H_2 , C_3H_8 , CO_2 and air. Both atomic and molecular emissions from the plasma are observed and analysed. The intensity ratios of species lines present in the spectra are used to infer compositions.

Chapter 6 focuses on the development of the gas velocity measurement technique of Laser Induced Plasma Image Velocimetry (LIPIV). The fluid-dynamic characteristics of laser-induced plasma are analysed spatially and temporally. The LIPIV technique is calibrated in a quiescent field. The measurement uncertainties of the velocity component along the laser beam axis and the component perpendicular to the laser axis are quantified, using different image processing methods. The calibrated velocimetry technique is then used to measure the velocity field of a turbulent non-reacting jet with a circular cross-section.

Chapter 7 presents local fuel-air ratio and velocity measurements in a non-premixed turbulent swirling stabilised flame. This burner is operated at a Reynolds number of 29,000 and a swirl number of 0.58. The reason behind the selection of such burner is to conceptually imitate the mixing and combustion process in swirl-stabilized gas turbine engine-like burners. A single camera approach for LIPIV is also proposed and evaluated through comparison with results from a double camera LIPIV system.

Chapter 8 summarizes the main findings of the thesis. Recommendations for the continuation of this work are also presented.

Chapter 1 Introduction

Table 1.2 Use of LIBS for gas composition measurements

Author	Burner	Laser source	Pulse energy	Mixture	Results	Year
Hanafi <i>et al.</i> [98]	a stainless-steel chamber	Ruby laser at 694.3 nm	1500 mJ	helium, argon, nitrogen, and air	spectral emission characteristics namely electron temperature and electron density	2000
Phuoc and White [4]	jet diffusion flame	Nd: YAG laser at 1064 nm	10 to 50 mJ	methane-air mixtures	fuel to air ratio by the intensity ratio of H/O	2002
Stavropoulos <i>et al.</i> [117]	Bunsen burner	Nd: YAG laser at 1064 nm	40~120 mJ,	methane-air	equivalence ratio with ratio of H/O	2005
Stavropoulos <i>et al.</i> [5]	Bunsen burner	Same as previous paper		methane-air	H/O intensity ratio with the flame equivalence ratio was established	2005
Molina <i>et al.</i> [99]	an oxygen/natural-gas glass furnace	Nd: YAG laser at 1064 nm,	360 mJ	Oxygen/ natural gas	Effects of CO ₂ concentration and gas temperature on LIBS spectra	2005
D'Ulivo <i>et al.</i> [100]	an reaction vial	Nd: YAG laser pulses at 1064 nm	300 mJ	headspace gases, essentially HD+H ₂	deuterium/hydrogen numeric ratio (β)	2006
Feroli and Buckley [101]	Tube exit	Nd: YAG laser at 1064 nm	48 and 366 mJ	propane and methane in air.	equivalence ratio measurement with C/(N+O)	2006
Zimmer <i>et al.</i> [114]	a partially-premixed hydrogen-air burner	Nd: YAG laser at 532 nm	15-110 mJ	hydrogen-air	direct ignition and local composition of a mixture measurement with H/O and H/N	2007
Zimmer and Tachibana [103]	a small turbulent premixed burner	Nd: YAG laser at 532 nm	50-240 mJ	methane-air	hydrogen excitation was crucial for equivalence ratio measurement	2007
Kawahara <i>et al.</i> [102]	in air	Nd: YAG laser at 532 nm	50, 110 and 170 mJ	air	spatially, temporally, and spectrally evolution of laser-induced plasma	2007
Michalakou <i>et al.</i> [104]	Bunsen burner	Nd: YAG laser at 1064 nm	75 mJ	methane, ethane, propane and air	local equivalence ratio with the H/O and C/O ratios	2008
Eseller <i>et al.</i> [105]	Bunsen burner	Nd: YAG laser at 532 nm	189, 200 mJ	methane, biodiesel and air	equivalence ratio with LIBS signals of N, O and H	2008
Sschin Joshi <i>et al.</i> [106]	natural gas engine	Nd: YAG laser at 1064 nm	21, 26 mJ,	natural gas and air	equivalence ratio with ratios of H/O and H/N	2009

Chapter 1 Introduction

Author	Burner	Laser source	Pulse energy	Mixture	Results	Year
Mansour <i>et al.</i> [107]	the concentric flow conical nozzle burner	Nd: YAG lasers at 1064 nm	100 mJ	natural gas and air	equivalence ratio with LIBS signal of C, H, O and N	2009
Letty <i>et al.</i> [116]	tube exit	Nd: YAG laser at 1064 nm	370mJ	methane-air	electrical and laser spark emission comparison	2010
Kiefer <i>et al.</i> [19]	Bunsen burner	Nd: YAG laser at 532 nm	20 mJ	methane, dimethyl ether and air	equivalence ratio with intensity ratios of H/O	2011
Majd <i>et al.</i> [18]	Bunsen burner	Nd: YAG laser at 1064 nm	100 mJ	methane-air	equivalence ratio with intensity ratios of H/O using an ungated detector and a slit	2011
Böker and Brüggemann [109]	a high pressure combustion chamber	Nd: YAG laser at 532 nm	23.9~30.8 mJ	air	laser induced spark ignition process	2011
Zhang <i>et al.</i> [110]	a high temperature test cell	Nd:YAG laser at 532 nm	50-200 mJ	kerosene-air	equivalence ratio with intensity ratios of H/O and H/N	2012
Zimmer and Yoshida [108]	high-pressure test cell	Nd:YAG laser at 1064 nm	60-195 mJ	N ₂ , O ₂ , CH ₄ and CO ₂	equivalence ratio under high-pressure conditions with a ratio of C/N and C/O	2012
Do and Carter [111]	Hencken burner in premixed mode	Nd:YAG laser at 532 nm	20-160 mJ	methane, ethylene and air	fuel concentration with the line intensity of N and H	2013
Yuan <i>et al.</i> [118]	an enclosed bluff-body swirling n-heptane spray flame	Nd:YAG laser at 1064 nm	140 mJ	n-heptane-air	H/O and C ₂ /CN ratios as a function of methane mole fraction	2014
Lee <i>et al.</i> [25]	a two-phase jet	Nd: YAG laser at 532 nm	100 mJ	gasoline-air	simultaneous measurement of the equivalence ratio and droplet concentration	2016
Kotzagianni <i>et al.</i> [112]	a swirl flame a turbulent jet	Nd:YAG laser at 1064 nm	40 mJ	methane-air	H/O and C ₂ /CN ratios as a function of methane mole fraction, instantaneous measurements in flames	2016

Chapter 2 Quantitative analysis theory for LIBS

2.1 Introduction

Laser-induced plasma evolution in a gas is coupled with various processes, including complex electromagnetic and fluid dynamics. Studies [119–124] have been conducted in the area of determination of plasma properties, such as temperature, composition, enthalpy, viscosity, thermal and electrical conductivity. It is important to understand the electromagnetic theory of laser-induced plasma, to ensure the reliability of the LIBS quantitative analysis. Therefore although the theory is already described elsewhere [6,125], it is briefly summarised below. The dynamics of the plasma within the fluid is discussed later in Chapter 6.

2.2 Quantum mechanics of plasma

In quantum physics, a quantum mechanical system or particle that is bound (a bound state is a special quantum state of a particle subject to a potential such that the particle has a tendency to remain localised in one or more regions of space) can only take on certain discrete values of energy. This contrasts with classical particles, which can acquire any level of energy. These discrete values are called energy levels. The term is commonly used for the energy levels of electrons in atoms, ions or molecules, which are bound by the electric field of the nucleus, but can also refer to energy levels of nuclei or vibrational or rotational energy levels in molecules. Electrons in atoms and molecules can change energy levels by emitting or absorbing a photon. Since every particle has its own discrete orbits, the characteristics of photon emitted due to an energy level decrease can work as a unique tag of particles. Plasma is an electrically neutral medium of unbound positive and negative particles. The excited ions and electrons in plasma continue to transit between energy levels and emit or absorb photons.

Laser-induced plasma emission consists of atomic and ionic spectral lines characteristic of the constituent species. The emission process can be understood using a simple two-level system, as shown in Figure 2.1. Figure 2.1 shows a pair of energy levels E_1 and E_2 , where $E_2 > E_1$. The energy difference ΔE is given by:

$$\Delta E = E_2 - E_1 = h\nu \quad (2.1)$$

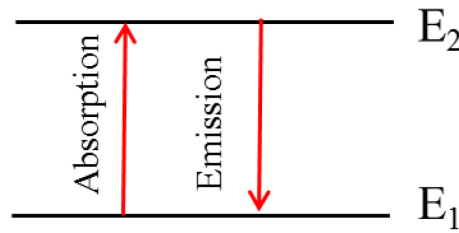


Figure 2.1 Absorption and emission processes between two discrete energy levels

where h is the Planck constant and ν is the radiation frequency of a single photon. The transition between two energy levels refers to a photon emitted or absorbed.

2.2.1 Atomic spectroscopy

In the atoms, similar to the Earth's orbit of the Sun held by gravity, the atomic electrons and protons are held together by the electromagnetic force. Due to the discretization of angular momentum postulated in early quantum mechanics by Bohr model, the electron in hydrogen atom can only have certain allowed distances and energies from the proton. The hydrogen atom is the earliest example of an experimental observation, which shows that an atom only has discrete amounts energy. Unlike the spectra of all other atoms, the hydrogen spectra show a remarkable series of lines converging smoothly to shorter wavelengths. The series are widely known as Balmer series. The mathematical relationship, prompted by Balmer, between the wavelengths and a running number is shown in Figure 2.2.

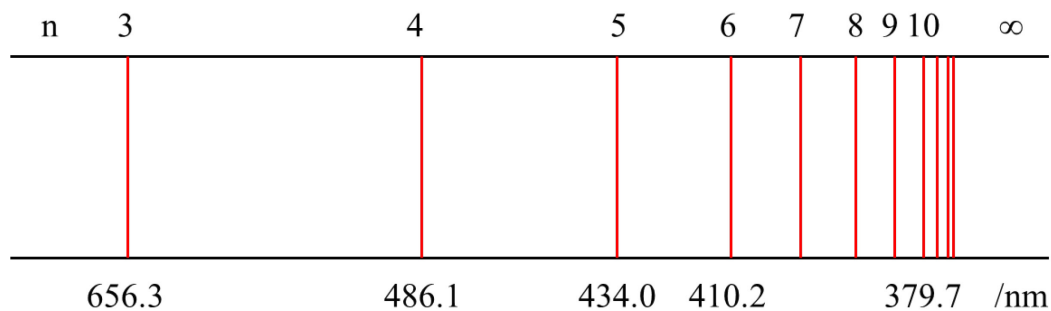


Figure 2.2 The Balmer series of lines in the emission spectrum of the hydrogen atom

The description the behaviour of an electron as a wave rather than as a particle requires a quite different theoretical approach, known as quantum mechanics [125]. As the basis of quantum

mechanics, the time independent Schrödinger equation (Eq. 2.2) for a particle moving in one dimension with energy E is:

$$H\Psi = E\Psi \quad (2.2)$$

where H is the molecular Hamiltonian, which is an operator describing all the internal interactions occurring in an atom or a molecule, as well as any interactions that the system has with external fields, and Ψ is a wavefunction, which is the mathematical representation of the wave that in quantum mechanics replaces the classical concept of trajectories.

The Hamiltonian, H , is the sum of the potential energy, $-e^2/4\pi\epsilon_0 r$, due to the Coulombic attraction between the electron and the nucleus placed at a distance r apart and the quantum mechanical equivalent of the kinetic energy:

$$H = -\left(\frac{e^2}{4\pi\epsilon_0 r}\right) - (h^2/2\mu)\nabla^2 \quad (2.3)$$

where μ is the reduced mass of the electron and proton [125]. According to the Pauli exclusion principle, each orbital can be occupied by only 2 electrons, which must have opposite intrinsic angular momentum, or spin, described by the quantum number s ($s = +1/2; -1/2$). The wave functions resulting from solution of the Schrödinger equation show that the atomic orbitals, so-called 1s, 2px, 2py ..., which illustrates the more accurate atom structure. From Figure 2.2, the convergence limit of the energy levels at $n=\infty$ corresponds to the ionization of the hydrogen atom (H) in the process:

$$H + h\nu = H^+ + e^- \quad (2.4)$$

in which the quantum radiation $h\nu$ has sufficient energy to remove the electron. As the free electron can have any amount of kinetic energy, which is not bound to the atom. The acceleration or deceleration of the negatively charged free electron can form a continuum beyond the ionization limit.

For polyelectronic atoms in their lowest energy state (the ground state), according to the Aufbau principle, subshells are filled one after the other. The order of occupation is usually as follows in Figure 2.3.



Figure 2.3 Polyelectronic energy levels

The comparative simplicity of the spectrum of the hydrogen atom and one-electron ions and of the theoretical interpretation is lost when a second electron is present. When there is only one electron in the atom, only one Coulombic force is present between the charged nucleus and the electron. Even the introduction of a second electron adds a second type of Coulombic force, which is the repulsion between the two electrons. Therefore, the Schrödinger equation (Eq. (2.2)) is no longer exactly soluble. Approximations must be made to calculate the electronic energy levels. The polyelectronic atom has far more complex spectral emission lines than the hydrogen. In the polyelectronic atoms and molecules, the probability of the electronic transitions between different orbitals is determined by selection rules. The Spin Rule says that allowed transitions must involve the promotion of electrons without a change in their spin. The Orbital Rule says that if the molecule has a centre of symmetry, transitions within a given set of p or d orbitals (*i.e.* those which only involve a redistribution of electrons within a given subshell) are forbidden.

2.2.2 Molecular spectroscopy

Besides the relatively simplicity of the hydrogen spectrum and polyelectronic atoms, in molecules a further electrostatic interaction is introduced, that of repulsion between the positively charged nuclei. There are two more sources of energy present in molecules. One is

the vibrational motion of the nuclei. Since the molecules are held together by electrons in bonding molecular orbitals, these bonds between atoms tend to behave like springs, whose strength varies from one molecule to another. A further source of energy is the overall rotation of the molecule. Generally, the quanta of rotational energy are small compared with those of vibrational energy, which are in turn small compared to those of electronic energy.

Due to the fact that the nuclei in a molecule are much heavier than the electrons and therefore move much more slowly, the Born-Oppenheimer approximation assumes that the motion of atomic nuclei and electrons in a molecule can be separated, which allows the wave function of a molecule to be broken into the electronic and nuclear (vibrational and rotational) components as follows.

$$\Psi_{total} = \Psi_e \times \Psi_v \times \Psi_r \quad (2.5)$$

where Ψ_e , Ψ_v and Ψ_r represent the electronic, vibrational and rotational components respectively. This factorization results in the total energy of a molecule being broken into three components.

$$E = E_{\text{electronic}} + E_{\text{vibrational}} + E_{\text{rotational}} \quad (2.6)$$

In order to illustrate the molecular energy levels, a configurational coordinate diagram is shown in Figure 2.4.

The x-axis represents the distance between the atoms and the y-axis the energy of the system. Figure 2.4 shows a schematic of a typical energy level diagram with closely spaced rotational and vibrational energy levels, with energy differences of 0.01 to 0.1 eV. Larger energy level spacings, with energy differences of about 1 eV, are due to various electronic states (related to the valence electron's mean distance from the nucleus), and the even larger binding energies of the inner electrons.

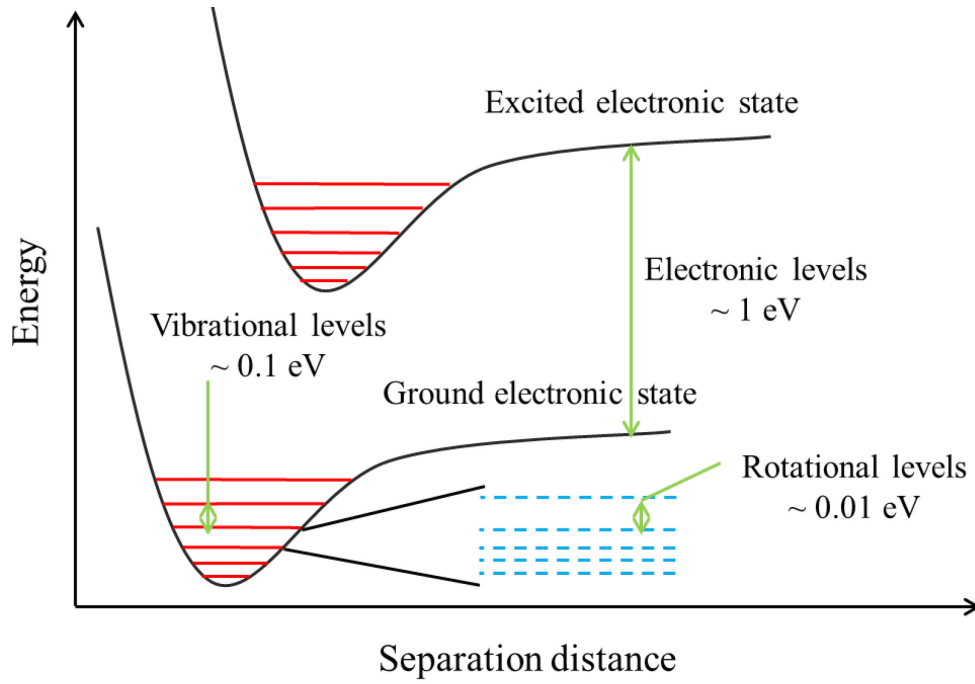


Figure 2.4 Typical energy level diagram of an atom or molecule showing the electronic states and associated vibrational and rotational energy levels

2.3 The spectroscopic and electromagnetic characteristics of laser induced plasma

For nanosecond pulse laser, when the laser beam is focused at a point in a gas and the energy density is high enough, the local gas molecules are broken down into atoms and ions. The laser-induced plasma emission consists of atomic and ionic spectral lines of the constituent species generated by the transitions between energy levels, superimposed on a broad-band continuum that is the result of electron-ion recombination and free-free interactions. Identifications of the spectral lines and measurements of their intensities provide qualitative and quantitative information. However, the spectral emission from the plasma is not only determined by the concentration of element in the sample, but also by the properties itself. Many factors, such as the excitation source (energy, power density, wavelength), the sample and surrounding gas, influence the spectral emissions of plasma. The complexity of the phenomena involved can be appreciated by using a simple derivation of the dependence of the LIBS signal on these processes. The obtained intensity signal S can be mainly influenced by three interrelated functions [6]:

$$S = A f_{int} f_{exc} f_{det} \quad (2.7)$$

where A is the spontaneous transition probability of the chosen transition; the initial interaction between the sample and the laser, f_{int} ; the excitation/ionization mechanism leading to atomic emission, f_{exc} ; the characterization of the radiation environment, f_{det} (optically thick or thin). The problems of stoichiometric material for f_{int} are an important factor for LIBS in solids, which are not severe in gas. Factors, f_{exc} and f_{det} , influenced the accuracy and precision of LIBS results, since the properties of excited species and the detection efficiency determine the SNR (signal-to-noise ratio) of the measurement. The factor f_{det} including the quenching effects in plasma is important in LIBS as well.

In order to simplify LIBS measurements, experiments are generally based on these assumptions [124]:

- The plasma state is in LTE (local thermodynamic equilibrium);
- The plasma is optically thin for the measured spectral lines.

In laser-induced plasmas, the duration of the plume emission is long compared with both the radiative lifetimes of the emitting species and the laser pulse length. Plasma emission is not a direct consequence of the photo-excitation mechanism. It is widely recognized [6] that only neutral atoms and singly charged ions are present to a significant degree. Therefore, in the calculation, only neutral and singly ionized particles are considered. The equilibrium distribution of energy among the different states of the assembly of particles is determined by the temperature, T , defined for each particular form of energy. It may happen that an equilibrium distribution exists for one of these forms of energy, but not for another. Complete thermodynamic equilibrium would exist when all forms of energy distribution are described by the same temperature. In practice, this situation cannot be fully realized. In LIBS, a key atmospheric concept is Local Thermodynamic Equilibrium (LTE). If the atmosphere was not in LTE, the temperature would be hard to define. LTE means that over time scales of interest all independent degrees of freedom in the system are in equilibrium with each other. In this state, the collision processes must be much more important than the radiative ones, so that the non-equilibrium of radiative energy can be neglected. The plasma electronic excitation temperature T and the electron density n_e , which can be derived from the plasma emission data, can be used to describe the plasma characteristics. Therefore, the basic formulas for the calculations of plasma characteristics are listed below.

2.3.1 LTE (Local Thermodynamic Equilibrium) criterion

The corresponding lower limit of electron density n_e is given by the McWhirter criterion [6]:

$$n_e \geq 1.6 \times 10^{12} T^{0.5} (\Delta E)^3 \quad (2.8)$$

where ΔE (eV) is the highest energy transition for which the condition holds and T (K) is the plasma temperature. This criterion is a necessary condition for LTE.

Under LTE conditions, the population of the excited levels for each species follows a Boltzmann distribution:

$$n_i^s = \frac{g_i}{U^s(T)} n^s e^{-E_i/kT} \quad (2.9)$$

$$I_{ij} = n_i^s A_{ij} = \frac{A_{ij} g_i}{U^s(T)} n^s e^{-E_i/kT} \quad (2.10)$$

where A_{ij} is the transition probability, n_i^s indicates the population density of the excited level i of species s , g_i and E_i are the statistical weight and the excitation energy of the level respectively, n^s is the total number density of the species s in the plasma, k is the Boltzmann constant, I_{ij} is the measured line intensity corresponding to the transition between the upper level i and the lower level j and $U^s(T)$ is the internal partition function of the species at temperature T :

$$U^s(T) = \sum_i g_i e^{-E_i/kT} \quad (2.11)$$

Here, the internal partition function describes the statistical distribution of each species corresponding to different ionization stages of the same element of plasma, in thermodynamic equilibrium.

2.3.2 Plasma temperature

After linearization of the expression Eq. (2.10), the familiar form of Boltzmann equation is obtained. For the same species, the slope of line can be obtained to calculate the plasma's temperature.

$$\ln \frac{I_{ij}}{g_i A_{ij}} = \ln \left(\frac{n^s}{U^s(T)} \right) - \frac{E_i}{kT} \quad (2.12)$$

The equation above has a slope of $-1/kT$. Therefore, the plasma temperature can be obtained via linear regression without knowing n^s or $U^s(T)$.

2.3.3 Plasma electron density

The profile of a line is the result of many effects, but, under typical LIBS conditions, the main contribution to the line width comes from the Stark effect. The electric field generated by electrons in the plasma perturbs the energy levels of the individual ions, thereby broadening the emission lines. The Stark broadening of a well-isolated line is thus a useful tool for estimating the electron density. For typical LIBS conditions, the contribution from ion broadening is negligible and equations become:

$$\Delta\lambda_{Stark} = 2w\left(\frac{n_e}{10^{16}}\right) \quad (2.13)$$

where, assuming that other sources of broadening are negligible, the value of n_e can be derived. w is the electron impact parameter (or half-width). $\Delta\lambda$ is the FWHM (full width at half maximum) in nanometres. Another spectroscopic method to measure electron density is Saha-Boltzmann method [6]. The method requires measuring the population ratio of two successive ionization states of the same element, which is used for accurate measurements.

2.3.4 Quantitative determination of the element concentration

As a result, the quantitative measurement of LIBS can be obtained through the equation below:

$$I_{ij} = FC^s A_{ij} \frac{g_i e^{-E_i/kT}}{U^s(T)} \quad (2.14)$$

where C^s is the concentration of the emitting species in the plasma. The experimental parameter F takes into account the optical efficiency of the collection system.

2.4 Summary

In summary, these methods for quantitative LIBS analysis are based on simplified hypotheses. These typically include uniform mixture, LTE and optical thinness. In practice, the choice of quantitative analysis method should be made after careful consideration of the specific aims of an experiment. Through this formula and spectrum of LIBS measurements, the plasma temperature, the electron density and the number of emitting species can be derived.

Chapter 3 Experimental setup

3.1 Introduction

This chapter presents the experimental apparatus and facilities used in the context of this research. The research consisted of LIBS measurements in methane-air opposed-jet flames and in different hydrocarbon blends, the development of laser-induced plasma image velocimetry (LPIV) and its application in a turbulent jet and in swirl-stabilized flames. This chapter firstly describes the flow configurations of the counterflow burner, the hydrocarbon mixture calibration jet, the turbulent air jet and the swirl stabilised burner. Then, the two different detection systems for mixture compositions and velocity measurements are introduced and applied to obtain measurement in these four flow conditions.

3.2 Flow configuration

3.2.1 Counterflow burner (opposed-jet burner)

Compared with the other experimental systems in the literature for LIBS study, the counterflow burner can suit best the purpose of this investigation, which allows an independent control of strain rate in a 1D flow field. The relatively simple configuration fulfils the purpose of this research by offering controllable flat flames, which makes LIBS measurements conveniently conducted in non-reacting and reacting regions of flows of identical mixtures of air and fuel.

The counterflow burner used in this work is identical to the one used by Katsikadakis [126], which follows the original design used by Mastorakos [127], Orain [128] and Pacitti [129]. In Figure 3.1, this burner consists of two identical, vertically opposed contracting nozzles. Each nozzle had a 90 mm contraction length and a contraction area ratio of 9. After the contraction, each nozzle had a straight section of length 52 mm. In order to shield the inner reactant jets from ambient air and quench the diffusion flames formed around the edges of the counterflow flames, a co-axial flow of nitrogen was supplied by an annular nozzle of 50 mm diameter outlet. The distance between the two nozzles was adjustable through a linear system ranging from 0 to 350 mm. The majority of the burner material was stainless steel grade 316. The cooling water pipe material was copper. The opposed jet burner allowed the stabilisation of one or two flames. The burner was also characterised by a constant strain rate across the area, depending on the choice of premixed fuel/air mixture injected from either one or both nozzles and the speed of the flow, as shown in Figure 3.1.

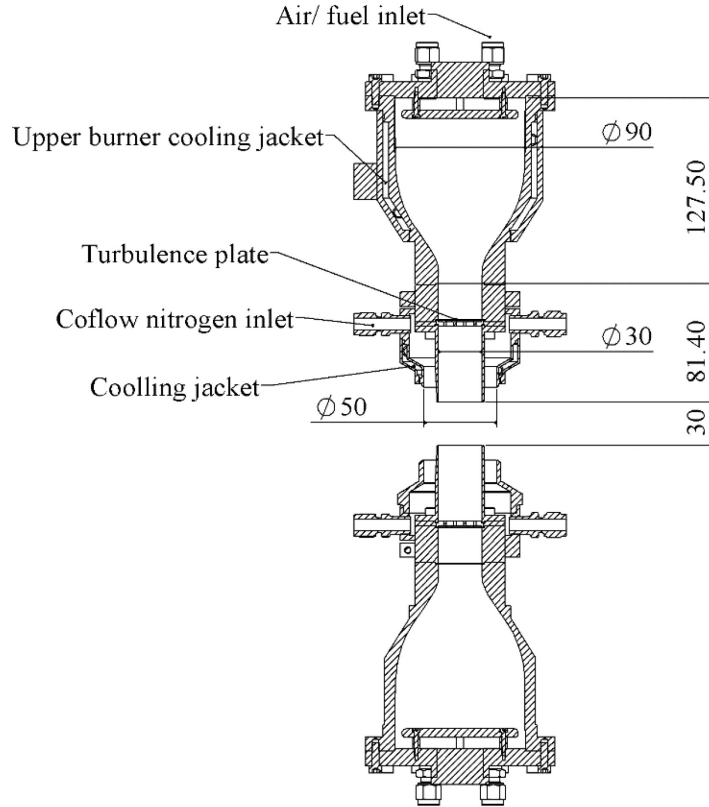


Figure 3.1 Schematic of the burner nozzles geometry [126] of the opposed jet burner; dimensions in mm

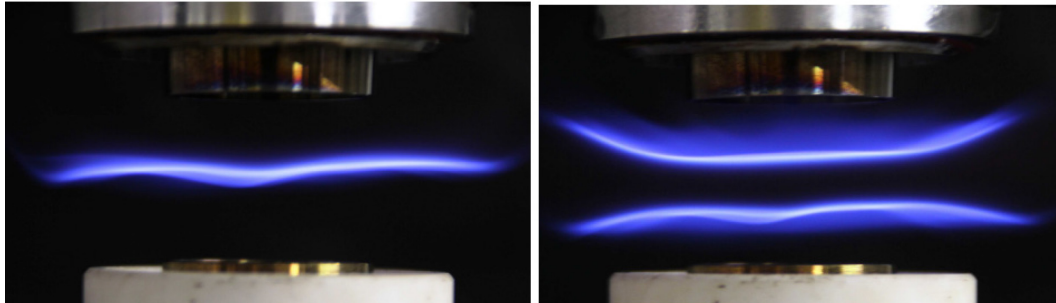


Figure 3.2 Examples of single (left) and twin (right) flames stabilised in the opposed jet burner [126]

Since heating of the upper nozzle caused by the heat released from the flames resulted in momentum changes of the two streams, a water cooling jacket was added into the burner. In addition, the cooling plate with water circuit inside was used as well, for the purpose of protecting the gas supply pipe from heating, as shown in Figure 3.1.

The dry and filtered air was supplied at 6 bar (g) by a laboratory compressor, which passed through an oil removal filter before connecting to the experimental apparatus. The airflow to

the top and bottom nozzles of the burner were controlled using mass flow controllers from Bronkhorst (accuracy: $\pm 0.5\%$ reading $\pm 0.1\%$ full scale) with $40\ \mu\text{m}$ inline filters attached before the inlet of each mass flow controller. The methane (99.5% purity) was delivered from pressurized bottles and its flowrate was controlled using digital mass flow controllers from Bronkhorst (accuracy: $\pm 0.5\%$ reading $\pm 0.1\%$ full scale) and ensured well premixed conditions by flowing through perforated plates in pipes. The co-flow of nitrogen was supplied by pressurized bottles and its flowrate was controlled with a calibrated rotameter (Platon), ranging from 0-100 l/min. The schematic of the gas delivery system is shown in Figure 3.3. These flow rates were controlled by using custom written Labview interface.

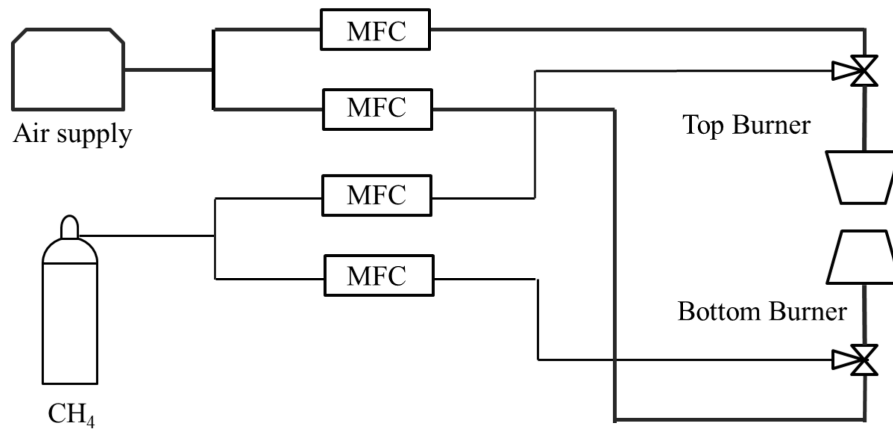


Figure 3.3 Schematic of gas delivery system. The MFC indicates the digital mass flow controller.

In the counterflow (opposed-jet) burner, the bulk flow strain rate is defined as:

$$\text{Strain rate} = \frac{2U_b}{D_h} \quad (3.1)$$

where U_b is the area-averaged velocity at the nozzle jet exit and D_h is the distance between the two jets. For the turbulent flows, a second term should be added to the equation above, which involves the turbulent strain rate [127]:

$$\text{Strain rate} = Re_t^{1/2} \frac{C_q U_b}{L_t} \quad (3.2)$$

where the turbulent Reynolds number is:

$$Re_t = \frac{C_q U_b L_t}{\nu} \quad (3.3)$$

In these equations, C_q is the turbulent intensity normalized by the bulk flow velocity (u'/U_b , where u' is the rms of the axial flow velocity), L_t is the Taylor microscale and ν is the kinematic viscosity of the gas. Then, the strain rate of the turbulent flow is given:

$$\text{Strain rate} = \frac{2U_b}{D_h} + \frac{C_q^{3/2} U_b^{3/2}}{\sqrt{\nu L_t}} \quad (3.4)$$

As the burner is operated at laminar conditions in this experiment, the Eq. (3.1) is used to estimate the strain rate for the current study.

3.2.2 Hydrocarbon fuel calibration rig

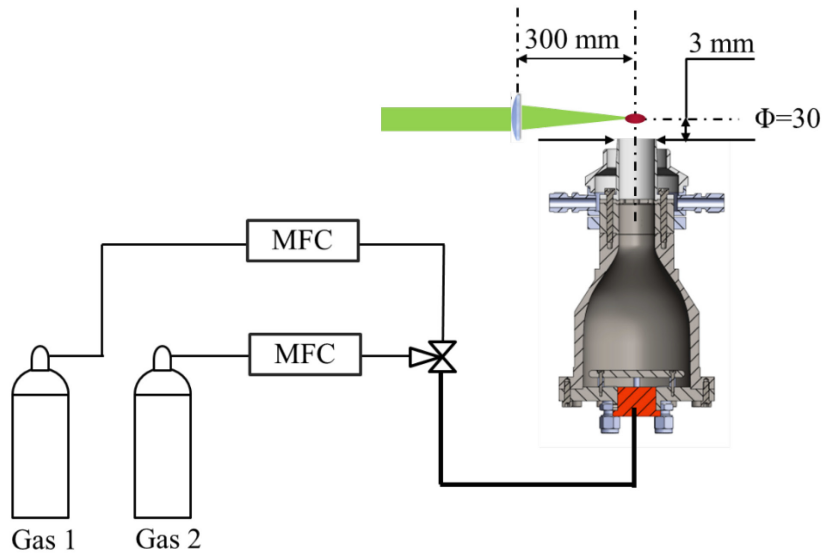


Figure 3.4 Schematic of the experimental arrangement used for LIBS calibration with various binary hydrocarbon mixtures

In order to calibrate the binary fuel mixture, two different gas fuels from the pressurized bottles were used, as shown in Figure 3.4. The flow rates of the gases were controlled by mass flow controllers (Bronkhorst) and then mixed in the pipe. The laser beam was focused 3 mm above and at the centre of the 30 mm diameter lower burner, where the mixture was uniform, so as to develop the LIBS calibration curves for hydrocarbon mixtures. To investigate the effect of laser pulse energy, the laser energy was set at 125 mJ and 406 mJ. The LIBS system remained the same as that used in the counterflow flames experiments.

Various mixtures of air, CH₄, C₃H₈, H₂ and CO₂ were used in the experiments in order to investigate the relationship between the LIBS spectrum and the mixture composition.

3.2.3 Free round turbulent jet

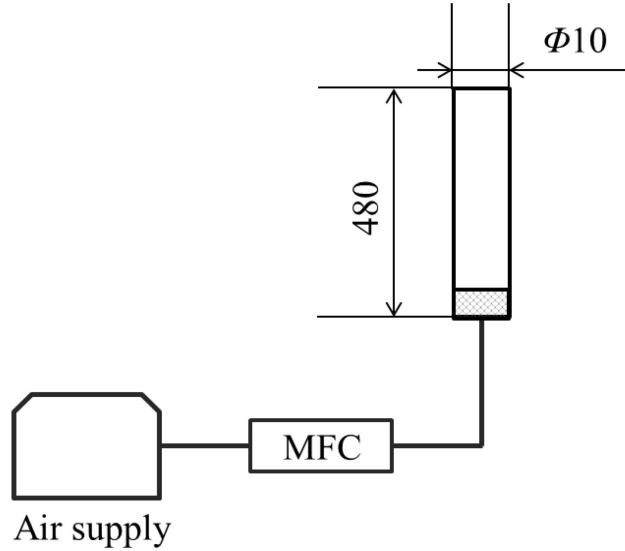


Figure 3.5 Schematic of the experimental arrangement for the round turbulent air jet formed by a straight pipe

In Figure 3.5, for the velocity measurements in a turbulent non-reacting air jet, the air flowed through the mass flow controller (Bronkhorst) to a mesh configuration to straighten the supplied flow and ensure symmetrical flow at the jet exit. After the mesh, the jet air flow developed through a round straight pipe with a length of 480 mm and 10 mm inner diameter before being injected into the atmosphere.

In order to remove the effects of pipe entrance, a certain length of the pipe is necessary to allow a fully developed pipe flow, whose flow characteristics no longer change with pipe length. The length of the hydrodynamic entry region along the pipe is a function of Reynolds number. In the case of a turbulent flow:

$$L_{h,turbulent} = 1.359D(Re)^{1/4} \quad (3.5)$$

where Re is the flow Reynolds number, based on the pipe hydraulic diameter D . The length is 0.185 m, which is far shorter than 0.48 m for the pipe in this experiment. The pipe is long

enough for a fully developed pipe flow at the jet exit. The turbulent intensity I of the air flow at the core can be estimated as:

$$I = 0.16Re^{-1/8} \quad (3.6)$$

Turbulent jets play an important role in burners and chemical reactions, by providing a means of mixing different fluids. Generally, three types of nozzles are commonly used, namely smoothly contracting nozzles, long pipes and orifice plates. Compared to smoothly contracting nozzles, the exit velocity profile of a long straight pipe jet is not uniform. Due to the fully developed boundary layer in the pipe, the exit velocity profile fits an empirical power law. Among the three types of axisymmetric nozzles, the pipe jet has the lowest rate of mixing with ambient fluids [130], which will be discussed in Chapter 6.

3.2.4 Swirl-stabilized burner

In the gas turbine combustion chambers, flames are stabilized by a flow recirculation zone, which works as an ignition source to the incoming reactants. The recirculation zone is usually initialized by the introduction of a swirling motion to the inlet gas flow, which can be realized using a swirler. The swirl motion is coupled with strong mixing of momentum, temperature and species. The understanding of the mixing process is important for flame stabilisation, emission control and efficiency improvement. For this part of the study, an unconfined swirl-stabilised burner is introduced.

The flow configurations, described in the previous sections, were mainly simple flow arrangements. The swirl burner provides results close to the realistic application, which can prove the feasibility of the local mixture composition and velocity measurement techniques in real combustors. The swirl burner rig consists of an atmospheric burner, operated with a mixture of methane and air. The burner had a built-in swirl generator, which was used to obtain swirling flow with different mixing degrees (swirl numbers). This swirl burner was based on the design of Dixon *et al.* [131] and replicated in the work of Milosavljevic [132]. Stetsyuk [133] previously conducted PIV, PLIF and Rayleigh scattering measurements in the flow of this burner. As shown in Figure 3.6, the burner consists of two cylindrical parts for the swirl and axial air flow with a central pipe for the fuel supply. The axial nozzle was located at the centre, which was a 15 mm internal diameter and 0.75 m long pipe. This pipe was fixed by

three locking screws, placed at 25 mm upstream of the end of the burner tube. The air passed through the outer 50.8 mm internal diameter pipe and developed in the annulus for 264 mm. The swirl number in this burner was adjusted by changing the air supply into the two streams, namely axial and swirl (Figure 3.6). The axial air was introduced from four symmetrical entries at the lower part of the drum. The swirl air was introduced tangentially from symmetrical entries around the upper drum. The tangential velocity was generated by using a swirl generator, consisting of six tangential slots milled into the wall of the pipe.

Similar to Stetsyuk's experiment [133], for the experiments on the swirl burner rig, the air referred as swirling component was measured by a KDG Rotameter Series 2000, which has 1.2 % of indicated flow and plus 10.4% full scale reading. The axial flow component was measured by a Fisher Control Limited flowmeter at a maximum flow of 1000 (l/min) with an accuracy of Class 1.6. The flow rate of the mixture of the air supplied to the central fuel pipe during operation at isothermal conditions was measured by a Platon flowmeter with an accuracy of 1.25%.

The swirl number is defined as the ratio of the axial flux of angular momentum to the axial flux of axial momentum, which is used to characterize the intensity of swirl in enclosed and fully separated flows [134].

$$Sw = \frac{G_\phi}{G_\chi r_o} \quad (3.7)$$

where G_ϕ is the axial flux of angular momentum

$$G_\phi = 2\pi \int_0^\infty \rho U_x U_\theta r^2 dr \quad (3.8)$$

and G_χ is the axial flux of axial momentum:

$$G_\chi = 2\pi \int_0^\infty \rho U_x^2 r dr + 2\pi \int_0^\infty p r dr \quad (3.9)$$

where p is the static pressure, r_o is the outer radius of the swirler and U_x and U_θ are the axial and tangential components of velocity at radius r respectively. The swirl number of the

secondary air has been calculated in the work of Milosavljevic [132,135] using velocity data measured by LDV.

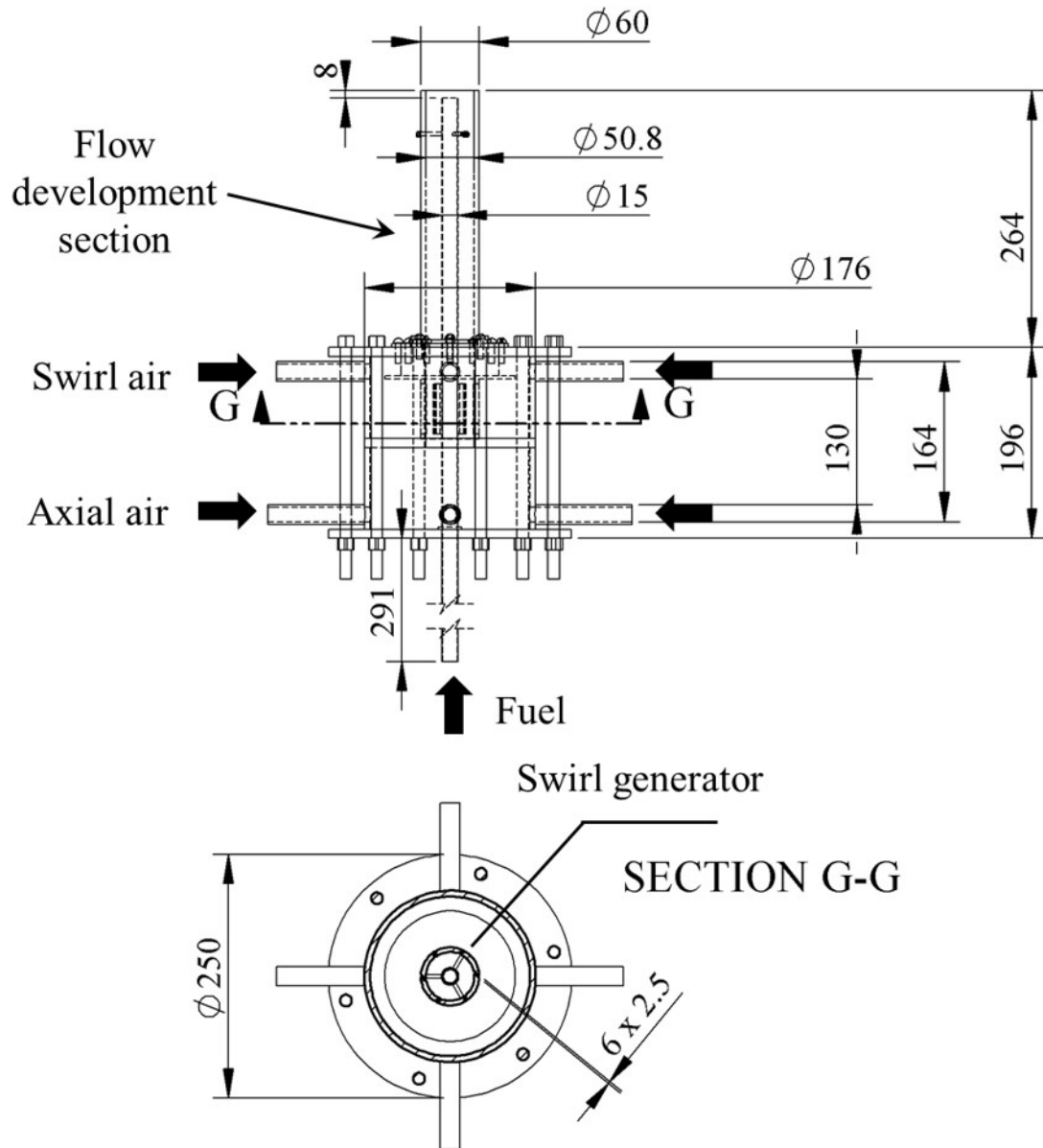


Figure 3.6 Cut view of atmospheric swirl burner. The burner consists of two cylindrical bodies for the swirl and axial air flow with a central fuel pipe. The fuel flow is injected through an axial nozzle, consisted of a pipe of 15(mm) internal diameter D_f , 0.75(m) long and centred within the surrounding circular duct by three screws at 25(mm) upstream end of the burner tube. The combustion air passes through the outer 50.8(mm) internal diameter pipe D . The swirl number varied by dividing the air supply into two streams namely axial and swirl.

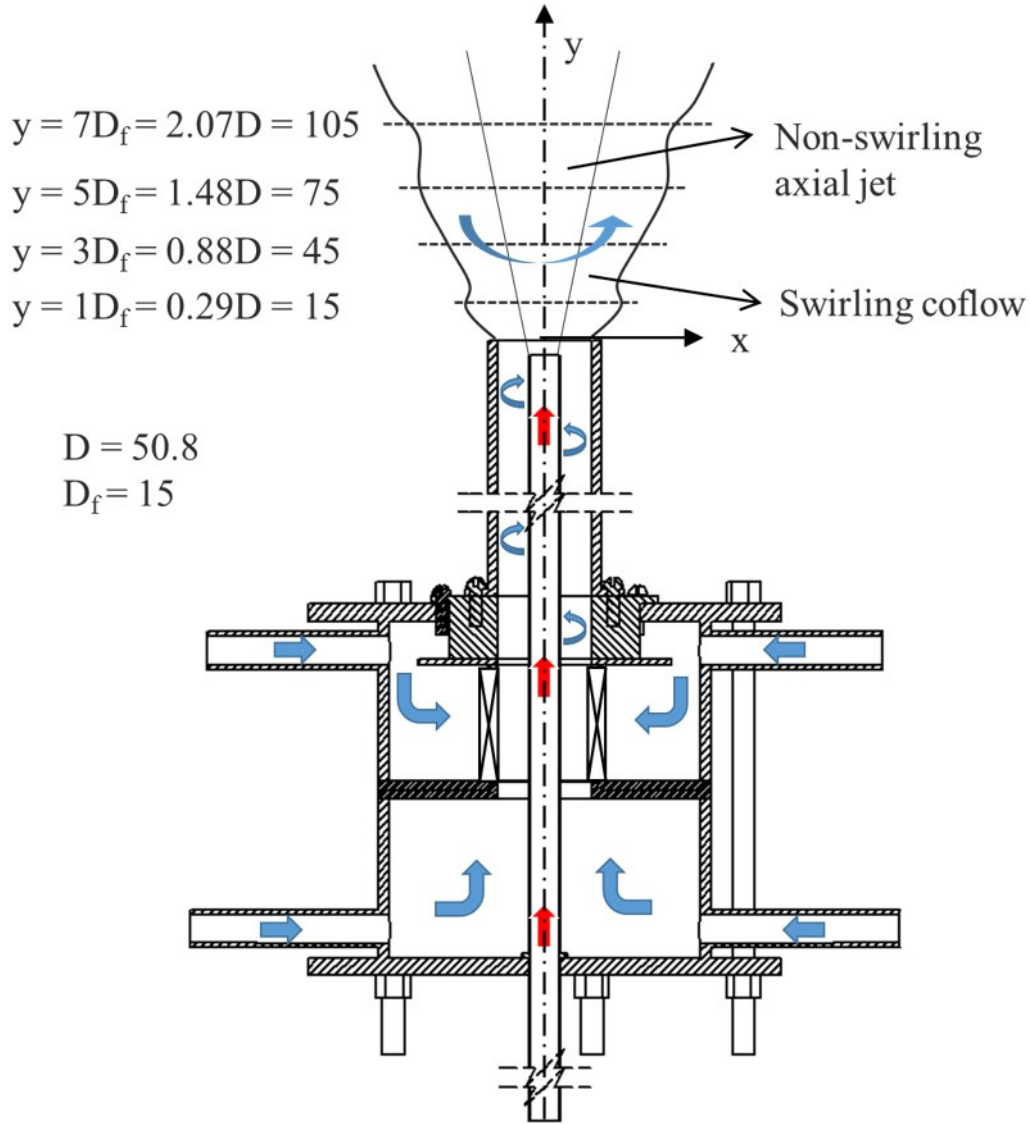


Figure 3.7 A schematic view of laser induced plasma positions for local mixture composition and velocity measurements and flow arrangement. Laser sheet positions are shown in absolute values (mm), normalized by the fuel pipe internal diameter D_f and by the burner internal diameter D .

In the study of the swirl burner flow, the velocimetry experiments were firstly conducted in isothermal conditions with a swirl number of 0.58. Then, by keeping the momentum of the central pipe gas the same as for the air flow in the isothermal flow experiment, the central pipe gas was replaced by methane fuel. In the reacting experiments, a controller, which is seen in Figure 3.8, was used as a safety device. If the flame extinguished during the experiment, the drop of the temperature detected by the thermocouple triggered the controller to shut off the solenoid valve for the supply flow to the fuel jet. Measurements were obtained at the near burner region and at the locations presented in Figure 3.7.

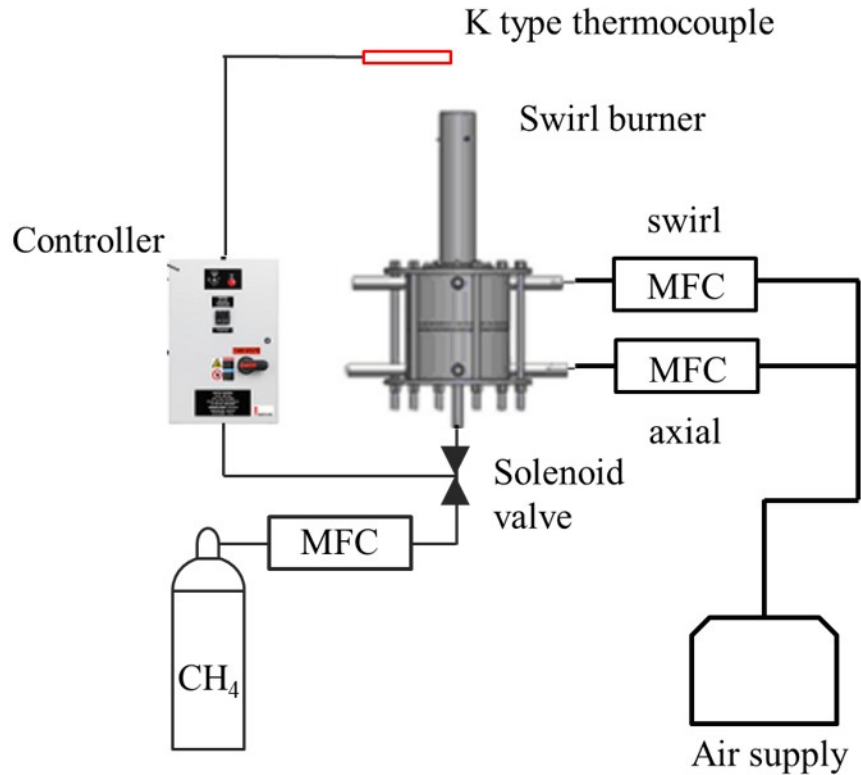


Figure 3.8 Schematic of the flow arrangement for the swirl stabilised flame experiment

3.3 Optical arrangement

The optical setup for the laser-induced plasma based measurements consists of a laser setup, focusing optics, an ICCD camera / spectrometer and associated control devices. This section provides a summary of each component used for the present research during both spectroscopic and velocimetry studies.

A class IV high power Q-switched Nd: YAG frequency-doubled 532 nm laser from Continuum Inc. was used to induce the plasma. The laser beam was produced at the fundamental wavelength of 1064 nm rated at 900 mJ and passed through frequency doubler to produce green light at wavelength of 532 nm rated at 406 mJ at the exit port of the laser. The laser pulse width was in the range of 3-5 ns at FWHM. The laser beam has 0.5 mrad divergence and 9.5 mm beam diameter, operated with frequency of 10 Hz. The pulse energy was varied between 80 and 406 mJ $\pm$ 5 mJ. The beam was redirected and adjusted by a periscope and then focused using a 300 mm focal length plano-convex spherical lens.

3.3.1 Focusing lens

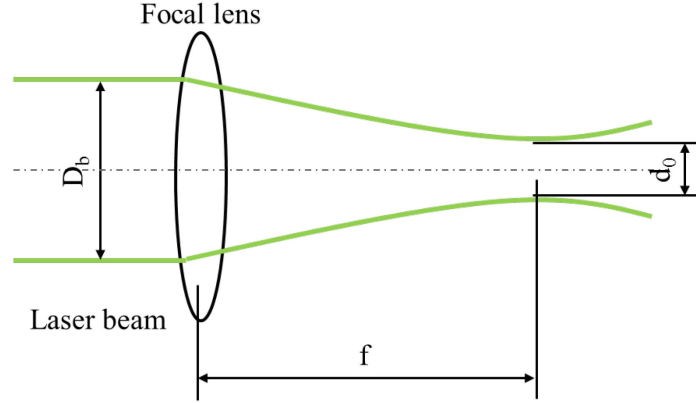


Figure 3.9 Focusing of a Gaussian beam

The laser beam, which follows a Gaussian distribution, is focused by a lens to obtain a smaller beam spot. As shown in Figure 3.9, the diameter of the focused spot, d_0 , is defined as the diameter, which contains 86% of the focused energy. The focus spot is determined by [136]:

$$d_0 = \frac{2f\lambda}{D_b} \quad (3.10)$$

where f is the focal length of the focus lens, D_b is the entrance beam diameter, λ is the wavelength. The spot size in this experiment can be computed as $d_0=33.6 \mu\text{m}$ diameter. In practice, due to the laser and doublers deterioration, the real focused spot is larger than it would be for pure Gaussian beam (TEM 00⁸). In addition, different optical components and alignment errors can influence the quality of the beam, leading to the increase of real spot size. The spot size can only give an approximation of the probe location. The laser-induced breakdown occurs before the focused spot, as long as the energy density is higher than the breakdown threshold. Therefore, for the high laser energy pulse, the plasma location is close to the laser upstream direction.

In this work, the intensity ratios between two spectral lines were used to remove the laser beam intensity fluctuations. Averaging of spectra (50 shots) was performed in order to remove the image noise as well. The laser-induced breakdown was conducted at variable locations between the opposed jets. The spatial resolution of the measurement depends on the size of the plasma, which is discussed in Chapter 4.

3.3.2 Spectral and imaging detectors

Table 3.1 Main characteristics of ICCD and spectrograph

Description	Value
Resolution (pixels)	1024 x 1024
Frame rate at maximum resolution (Hz)	0.5
Pixel size (μm)	13 x 13
Wavelength range (nm)	200-975
Spectral resolution ($\lambda/\Delta\lambda$)	4000

A 35 mm focal length UV Fused Silica Plano-Convex Lens collected the light emission 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). A second ICCD camera (Model: Andor DH534-18F-03, field of view 11.5 x 11.5 mm^2 , resolution=11.2 $\mu\text{m}/\text{pixel}$) was used to record images of the laser-induced plasma.

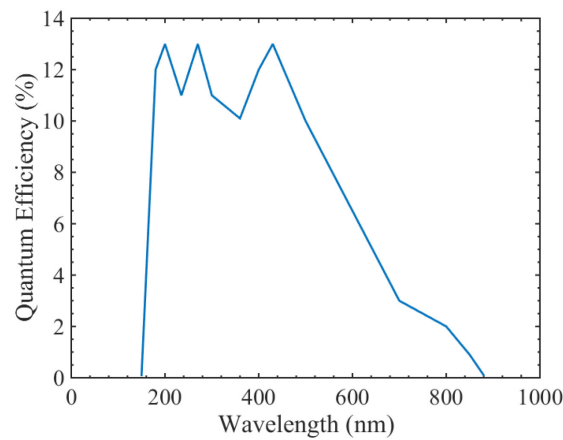


Figure 3.10 Quantum efficiency of the Photocathode of Andor DH534-18F ICCD

An ICCD consists of an image intensifier and CCD module. The image intensifier includes three functional elements: a photocathode, a micro-channel plate (MCP) and a phosphor screen. These three elements are mounted one behind the other. When photons fall onto the photocathode, the photoelectrons generated are accelerated towards the MCP by an electrical voltage. When these multiplied electrons hit the phosphor screen, the electrons are converted by the phosphor screen to photons that are guided to the CCD. The intensifier is typically 1 to 2 inches in diameter by about 1 inch thick. Besides amplifying, the image intensifier can be

switched on or off at nanosecond time scales, making it the fastest shutter, which suit best the purpose of high temporal resolution spectroscopy of plasma.

The amplification process of the intensifier has a cost that unwanted thermally generated electrons are generated and amplified as well. The uncertainty in electron trajectories causes a loss in spectral resolution. Therefore, the ICCD has very high sensitivity but its quantum efficiency is relatively lower compared to a normal CCD, as shown in Figure 3.10.

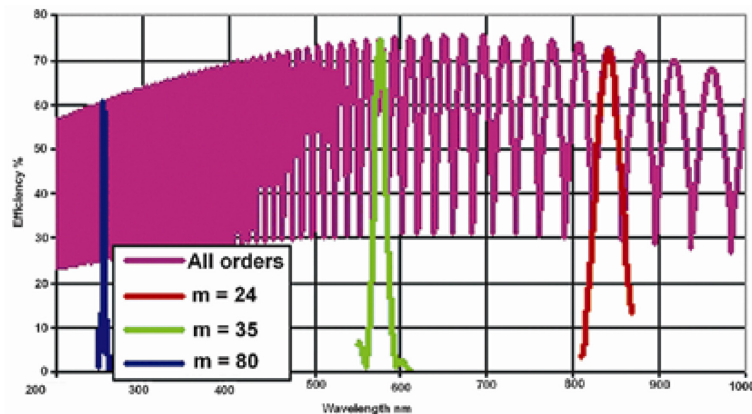


Figure 3.11 Echelle grating efficiencies data from Andor [137]

Echelle gratings produce a series of different orders over the entire spectral range of interest (*e.g.* the ME5000 model produces 80 orders), as shown in Figure 3.11. When the grating is used in the Littrow angle, the grating efficiency is at its maximum in the middle of each order. However, the efficiency drops to about half of this value at the extremities of each order. Echelle gratings are blazed for all wavelengths in a spectral range for a given diffraction order. These two efficiencies existing in the spectrometer mainly contribute to the deformation of the obtained spectrum, compared to the original spectrum.

It is clear that there are very large noise levels at the lower wavelengths (200 - 350 nm) in Figure 3.12. This is caused by a lack of signal from the light source. In this work, a Newport 6035 Mercury spectral calibration lamp and a Hamamatsu L7810 Xenon (Xe) lamp were used to calibrate the wavelengths and the relative intensity respectively. The relative efficiency correction was applied through these procedures. The spectral irradiance of the Xe calibration lamp is shown in Figure 3.12, provided by the manufacturer Andor. The measured spectrum from the Xenon lamp is plotted as well. Then, the relative efficiency correction factor curve could be calculated through the method of dividing obtained spectrum by original spectrum at

each wavelength. The above correction factor curve was derived and could be used to convert the measured spectrum into accurate spectrum, which represented the absolute intensity of each spectral line.

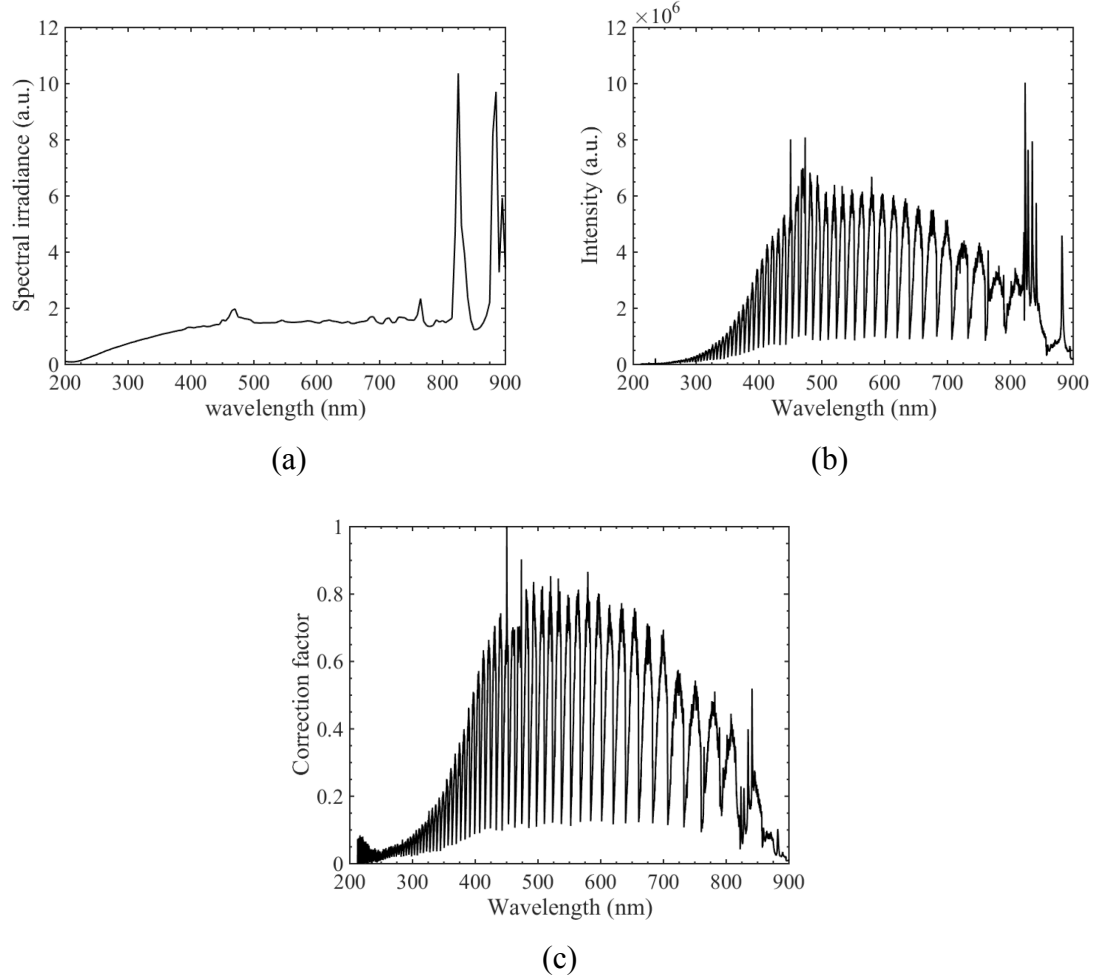


Figure 3.12 (a) Spectral irradiance profile of the Xenon calibration lamp, (b) raw spectrum obtained by ICCD before correction (c) correction factor calculated from original spectrum and obtained spectrum

3.3.3 Synchronization system

As the laser-induced plasma is a pulsed source, the resulting spectrum evolves rapidly in time. At the earliest time, the plasma light is dominated by a continuum that has little intensity as a function of wavelength. This continuum light can seriously interfere with the detection of weaker emissions from elements present in the plasma. For this reason, a delay between the laser pulse and the gate time of the ICCD should be set to remove the interference of the continuum light. Therefore, it is important to accurately synchronize the laser and ICCD in the order of nanoseconds.

Chapter 3 Experimental setup

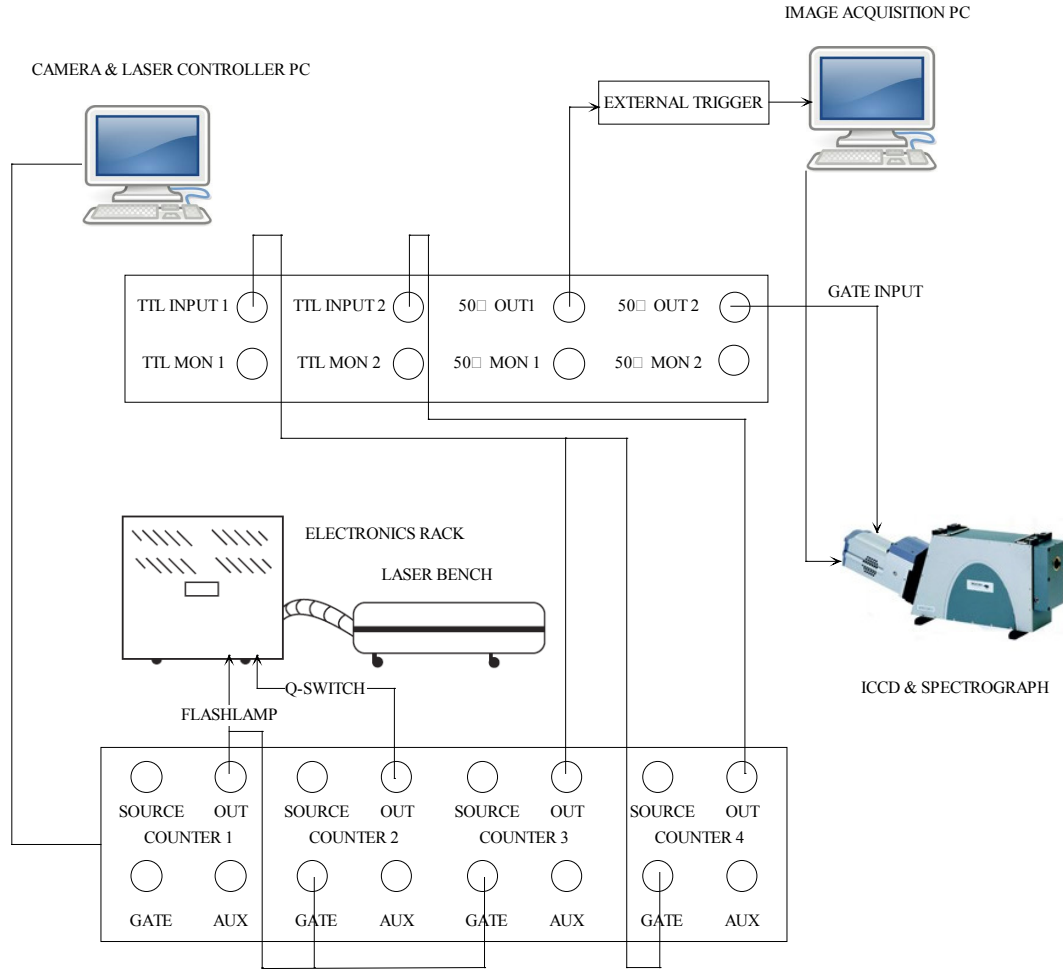


Figure 3.13 Synchronization system

In this experiment, an oscilloscope was used to check the delay between signals and a photodiode was employed to check the delay between Q-switch signal and laser pulse, which was found to be about 150 ns. In Figure 3.13, a multi-channel digital delay pulse generator (Model: NI PCI-6602) and a signal voltage converter were implemented for accurate synchronization of the signals. In both Figure 3.13 and Figure 3.14, a signal from counter 1 triggered the flashlamp of the laser and from counter 2 controlled the Q-switch of the laser to send laser pulse. At the same time, counter 3 for the shutter triggering was also activated by the signal from counter 1. The shutter signal then triggered the ICCD gate after a tiny delay of 1 μ s to avoid the interference of white light. In a cycle time shown in Figure 3.14, a tiny delay (typically 150 ns) was set after the Q-switch triggers the laser pulse. This system can ensure that shutter and gate keep opening during the same period of time to capture the light emission from the plasma. The laser flashlamp is fired continuously at 10 Hz. The laser Q-switch is

triggered at 10 Hz after the flashlamp. The ICCD is triggered every 2 seconds to record the image. These signals are controlled electronically through the Labview software.

This synchronization system was used in the LIBS experiment and similar settings for the system were used for the plasma image velocimetry experiment as well. The only difference was the timing setting strategy at different operating conditions of the experimental facility.

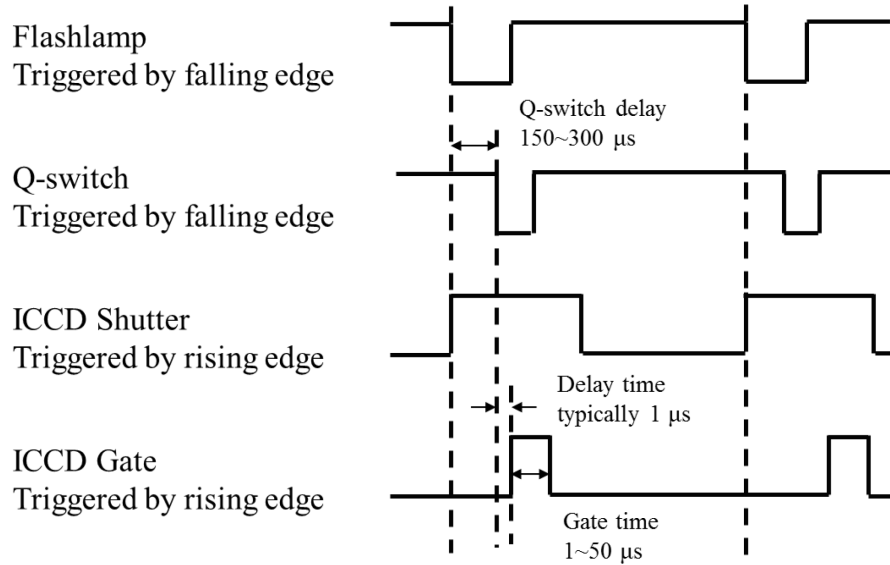
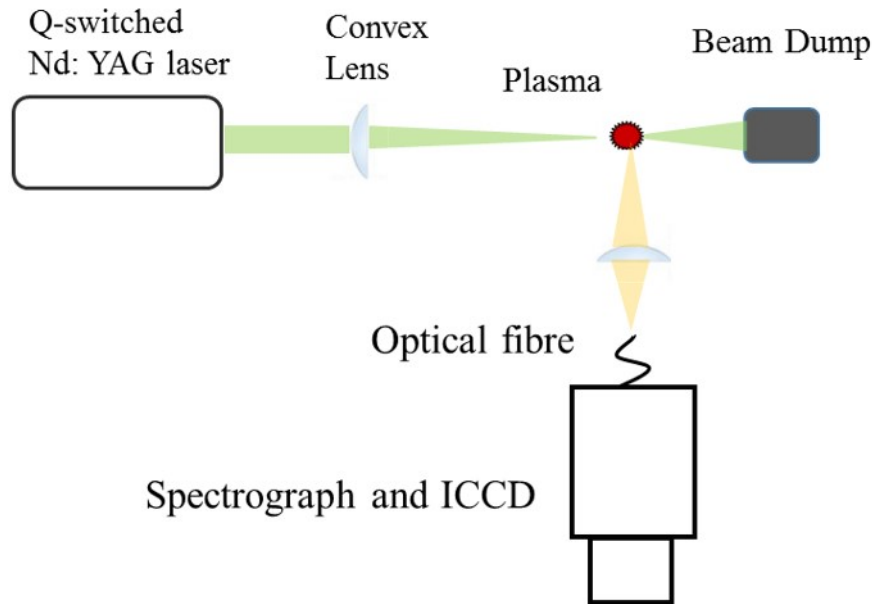


Figure 3.14 Time sequence of signals

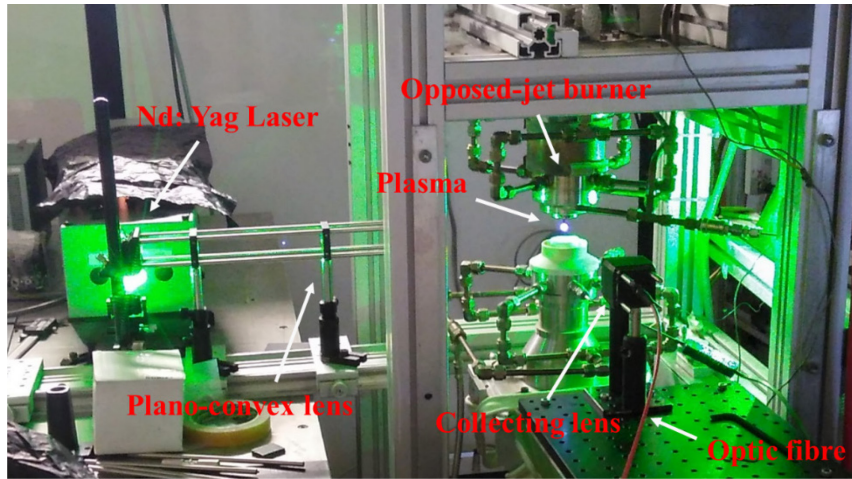
3.3.4 Optical setup of LIBS

The laser-induced breakdown took place at variable locations between the opposed jets. The spatial resolution of the measurement depends on the size of the plasma, which is around 1 mm diameter and will be discussed in Chapter 4. Both the image of the plasma and emitted light spectrum from the plasma were obtained for the measurements in the opposed jet flames. The time-resolved measurements of plasma were mainly characterized by two parameters: the delay time to the trigger signal and the aperture time of the two ICCD shutters. Experimental synchronization was achieved through the multi-channel digital delay pulse generator to control the laser generator and the ICCDs. After the laser fires, after a delay about 1 μ s, the ICCDs were triggered to take the spectrum and image of the laser-induced plasma, as shown in Figure 3.15.

In the LIBS measurement and acetone LIF measurement below, the fuel mole fraction or mixture fraction mentioned in the thesis represent the mole fraction of measured gas in the probe volume. Since all the measurements were performed in gas, the measured fuel mole fraction or mixture fraction also equal the volume fraction.



(a)



(b)

Figure 3.15 Schematic diagram (a) and experiment setup (b) of the LIBS system

3.3.5 Optical setup of Laser-Induced Plasma Image Velocimetry (LIPIV)

A novel measurement technique for velocimetry in fluid flows is proposed and developed in the current work, which is based on LIBS, since it shares most of the hardware, and does not require the introduction of either ‘seeding’ particles or other substances in the flow. Instead of

tracking the velocity of ‘seeding’ particles, the convected laser-induced plasma by the flow is tracked as a function of time. The method estimates the flow velocity vector from the displacement of the plasma within a time Δt , as shown in Figure 3.16. The Laser-Induced Plasma Image Velocimetry (LIPIV) technique is proposed and evaluated in this work, which will be discussed in Chapter 6 and Chapter 7.

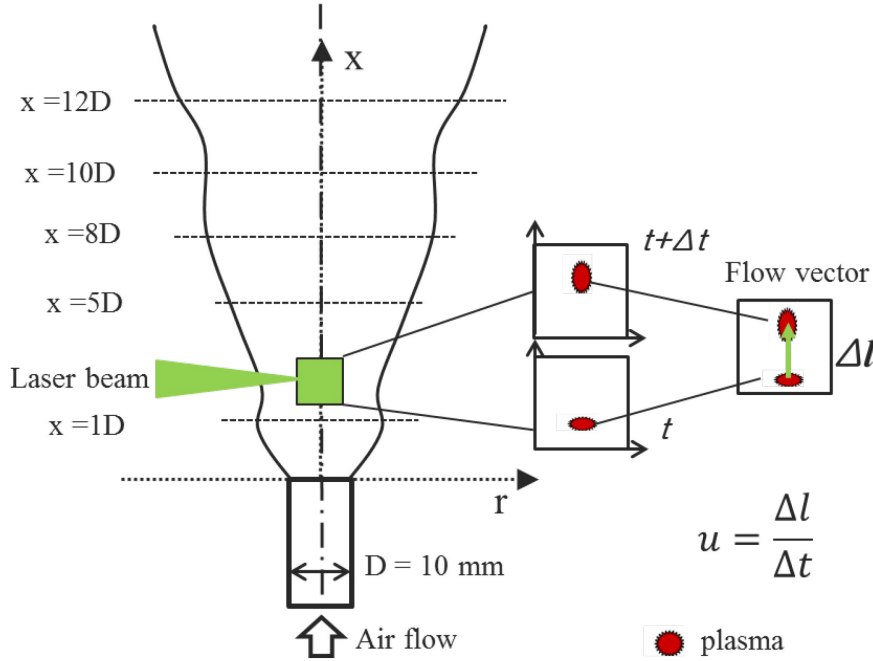


Figure 3.16 Concept of Laser-Induced Plasma Image Velocimetry (LIPIV) applied to a turbulent jet flow. The LIPIV technique measures the flow velocity vector by using the temporal displacement of the laser-induced plasma in a flowing fluid. For this reason, two sequential images of the plasma with time delay Δt are used.

The plasma intensity spans several orders of magnitude in its lifetime. For the velocity measurement, the emitted intensity from the plasma of the first image is nearly 10,000 times stronger than that of the second image. The time delay between the two images is of the order of $100 \mu\text{s}$ as well. Normal single PIV camera cannot satisfy this demand. A good option is to place two ICCD cameras in a stereo arrangement. Using a Scheimpflug adaptor can help eliminate the off-axis defocusing effects. However, this type of arrangement needs more calibration and image post-processing work, as shown in Figure 3.17 (a), resulting from that each image is recorded at different angles. Placing the two ICCDs on opposite sides of the plasma can eliminate the perspective distortion, as shown in Figure 3.17 (b). However, for arrangement of ICCDs, the reflection of plasma light from opposite camera lens interferes with

the plasma image. The issues of two types of arrangement arise from the different detection paths for the two ICCDs. The result is very sensitive to the inhomogeneities of the optical paths.

The arrangement of ICCDs in Figure 3.18 can minimise the effects using a beam splitter. With the careful alignment, the optical paths for the ICCDs are identical, which ensures the accuracy of the LIPIV velocity measurement.

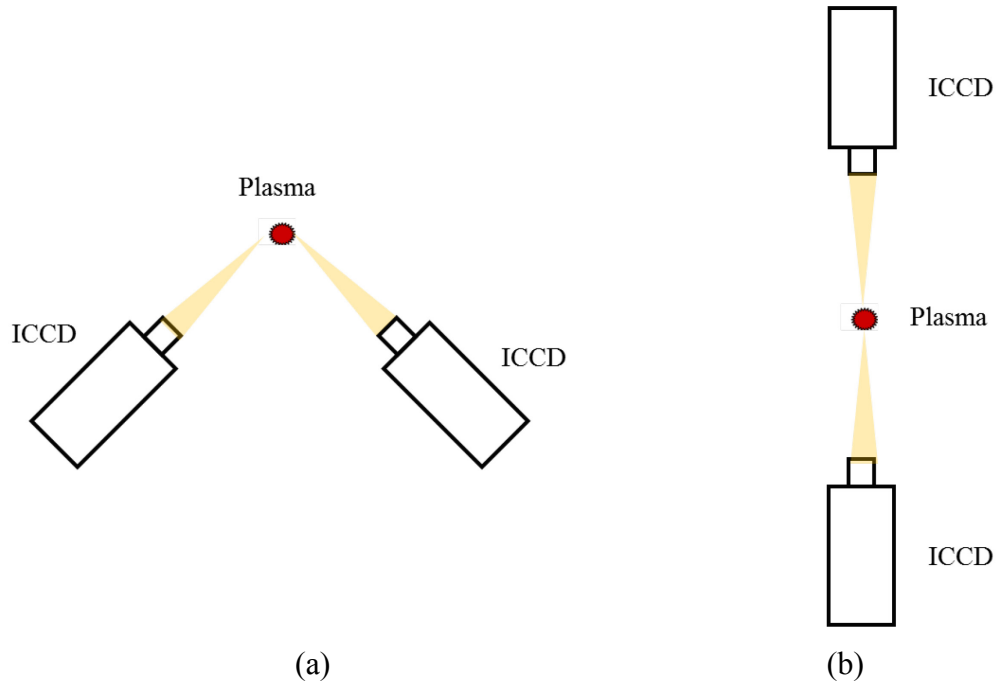


Figure 3.17 Stereo arrangement of ICCDs (a) opposite arrangement of ICCDs (b)

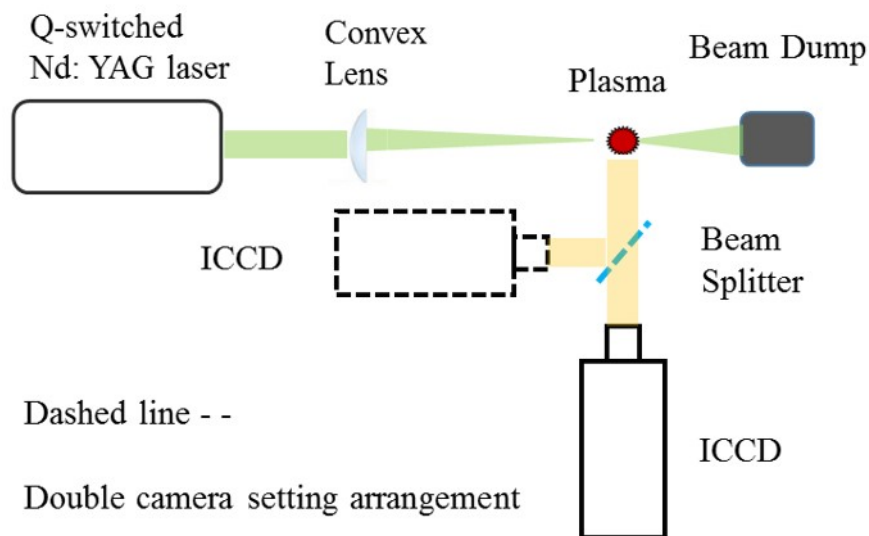


Figure 3.18 Schematic diagram of the laser induced plasma image velocimetry (LIPIV) setup

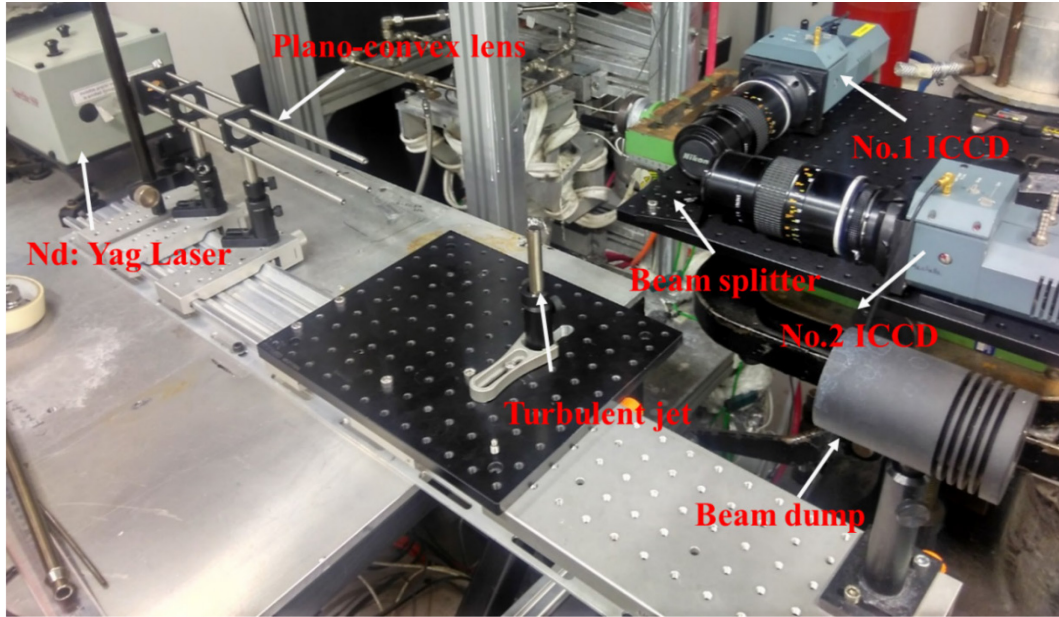
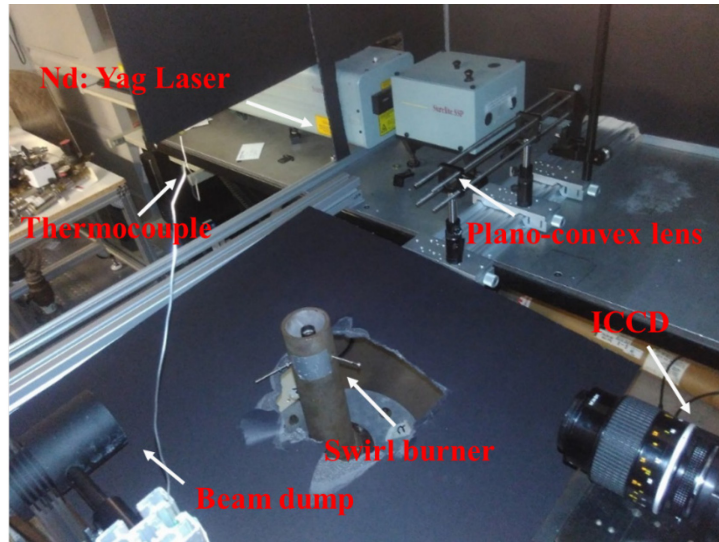


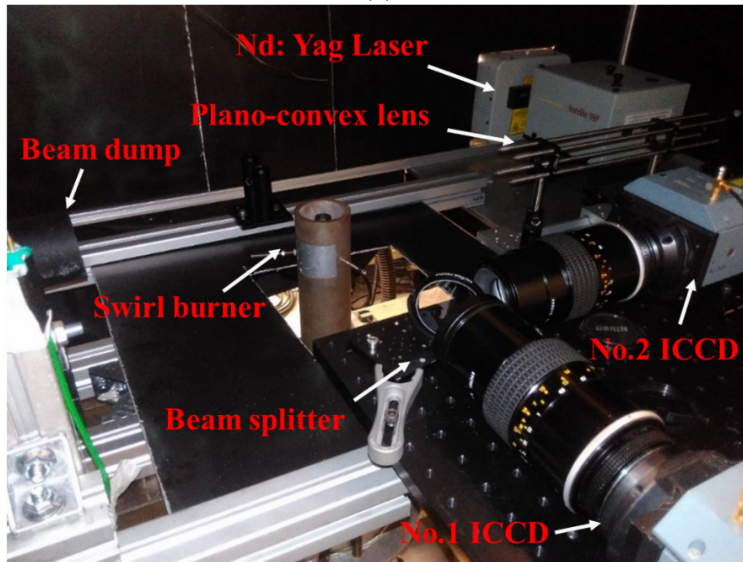
Figure 3.19 The laser-induced plasma image velocimetry (LIPIV) setup for the turbulent jet experiment

In Figure 3.18, the laser beam of the LIBS system was generated by the Surelite III Q-switched Nd: YAG laser, producing pulses of 532 nm light with a nominal 3-5 ns pulse width and 10 Hz frequency. The laser pulse energy in this experiment was kept at 125 mJ. Sharing most of the same hardware of LIBS, both two ICCD cameras (Andor DH534-18F-03) with Nikon Micro-NIKKOR AI 105mm f/4 lenses were used to record the plasma with a field of view $26 \times 26 \text{ mm}^2$ with resolution of $25.3 \text{ }\mu\text{m}/\text{pixel}$. An uncoated pellicle beamsplitter with a reflection-to-transmission ratio of 8:92 for wavelengths between 400 nm and 2400 nm was used as the beam splitter. Due to the high intensity of the plasma emissions at early times after the laser pulse, reflective light was used to record the first image of the plasma and transmitted light for the second low-intensity image of the plasma.

In addition, sharing most of the same hardware with double camera LIPIV, this study also evaluated the LIPIV with single camera in Chapter 7. As shown in Figure 3.18, only one ICCD without beam splitter was used to capture the plasma image after a certain delay. The single camera system velocity was calculated through the spatial displacement between the location in the flow field and the location in the quiescent field. The image time window was $100 \text{ }\mu\text{s} \sim 110 \text{ }\mu\text{s}$ after the laser pulse. For the double camera LIPIV, in the low fuel-rich zones, the first image was taken at $1 \text{ }\mu\text{s}$ and the second was taken at $100 \text{ }\mu\text{s}$ after the laser pulse.



(a)



(b)

Figure 3.20 Single camera (a) and double camera (b) systems of the LIPIV

3.4 Summary

This chapter presented the experimental apparatus used in this research. The optical setup was based on a typical LIBS system. In both LIBS and LIPIV experiments, the same high power laser and synchronization system were used. The Andor DH534 ICCDs coupled with spectrograph for spectrum or with lens for image were employed in the research. All of the equipment was controlled by using a custom written Labview program.

Chapter 4 Measurements of equivalence ratio in methane-air opposed-jet flames using LIBS

4.1 Introduction

Equivalence ratio measurement in flames is necessary in order to control mixing processes and to avoid problems, such as the generation of pollutants and instabilities in the combustion process. In order to apply the LIBS into realistic non-premixed systems, this work also extended the methane mole fraction range from 0 up to 100% [112]. Because it was found that the LIBS measurement encountered increased dispersion of the values of equivalence ratio in fuel-rich mixtures and high temperature regions [101]. To realize the instantaneous measurement in turbulent non-premixed flames, this chapter focused on the improvement of LIBS accuracy and precision in flames.

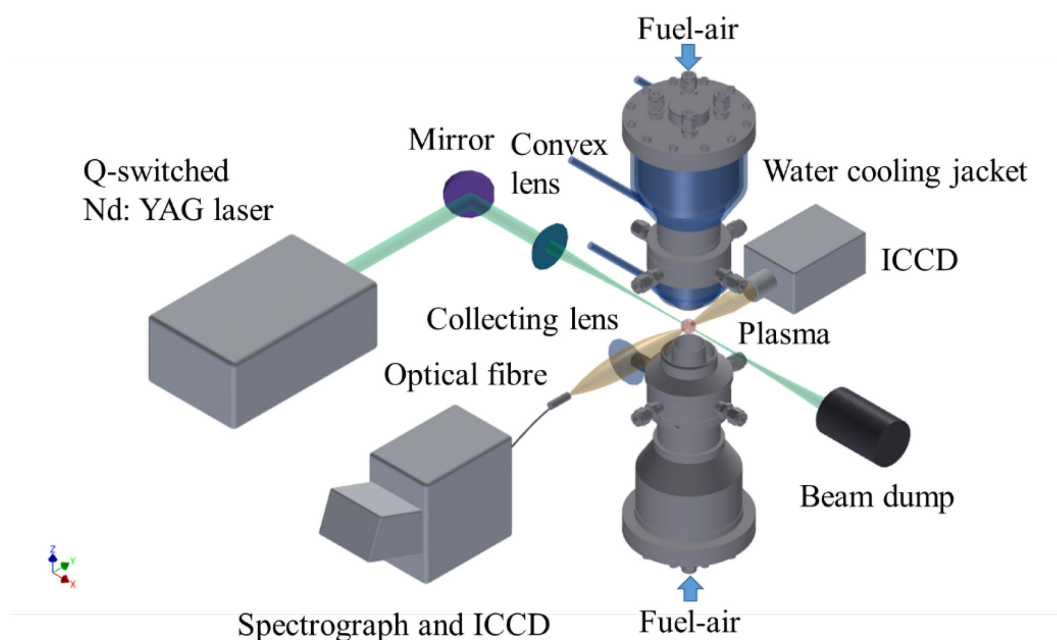


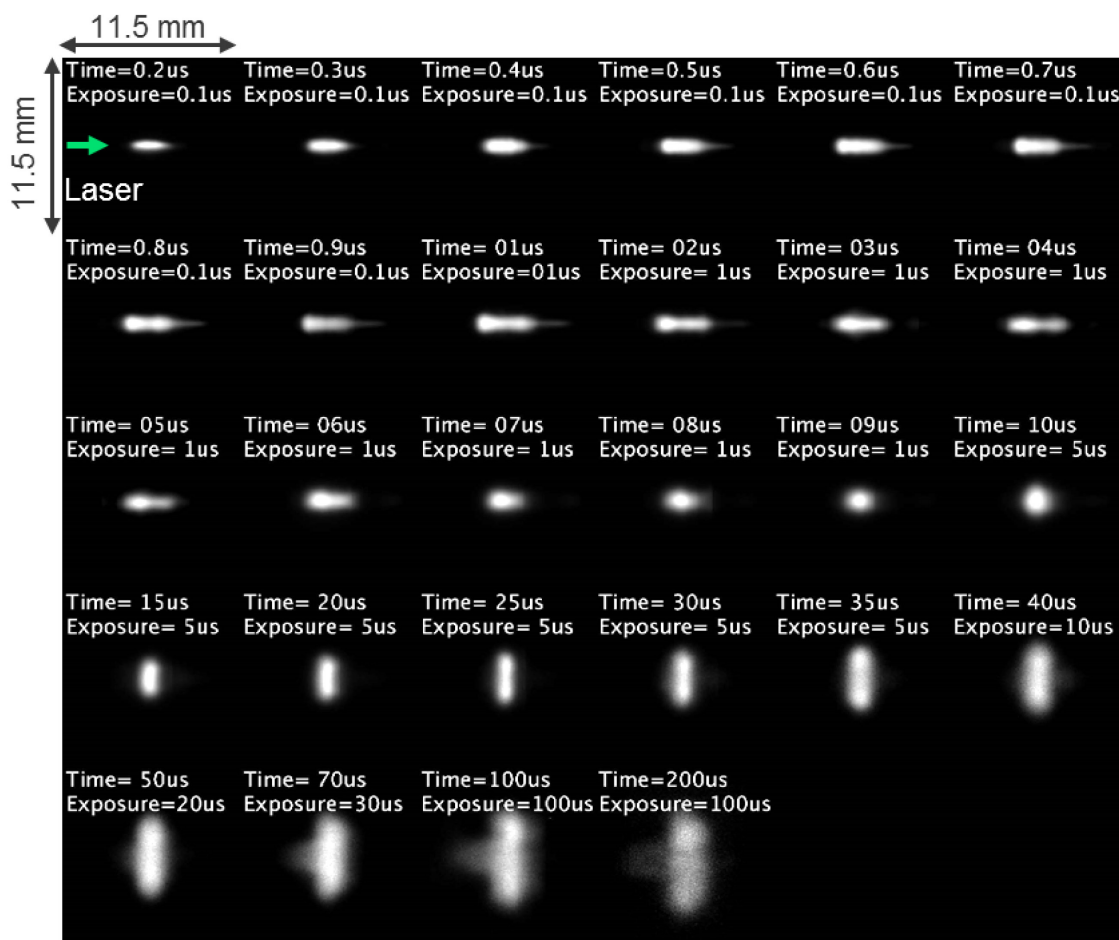
Figure 4.1 Schematic of LIBS experiment in the counterflow burner

In this chapter, the LIBS technique is used to measure the local equivalence ratio in the opposed-jet burner rig, as shown in Figure 4.1. The temporal development of the images and spectra of the laser induced plasma in flows of pure air and methane-air mixtures are presented firstly and compared. After considering the behaviour of the spectral lines from different species, the correlations between the mixture fraction of methane-air mixtures and the LIBS spectra were established. The uncertainty analysis of this technique was then conducted, which shows that the SNR (signal-to-noise ratio) determines the measurement accuracy. Then, the effect of the presence of the flame on the instantaneous LIBS measurements was quantified

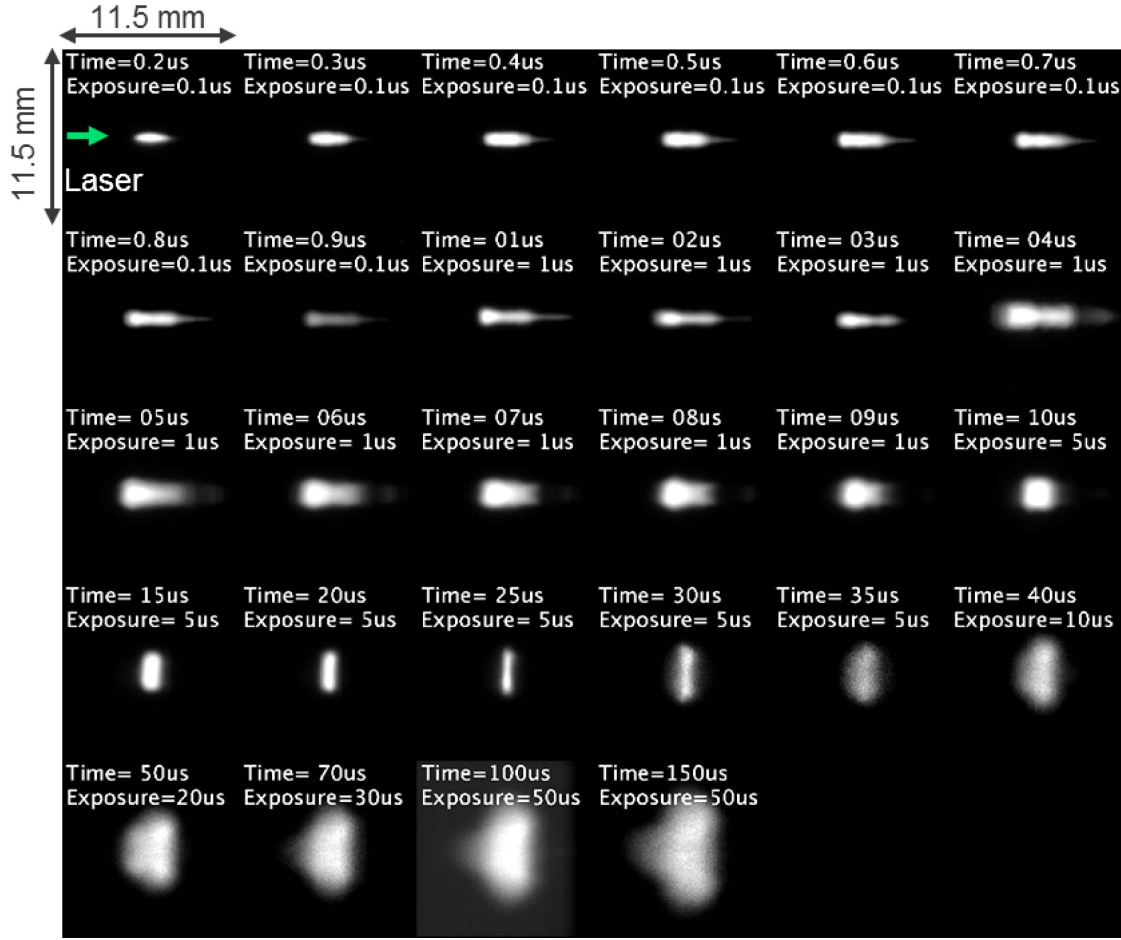
and offset by increasing the laser energy and using a newly developed data processing method. The technique was finally applied to the measurement of local air-fuel ratio in a laminar diffusion flame stabilised in the opposed jet burner and the measured spatial distribution of local air-fuel ratio was compared to numerical results from the detailed chemistry CHEMKIN GRI 3.0 model.

4.2 Results and discussion

4.2.1 Spatial and spectral temporal evolution of a laser-induced plasma



(a)



(b)

Figure 4.2 Measured sequences of the temporal development of a laser induced plasma, generated by an incident laser pulse with 125 mJ energy, in air (a) and in the non-reacting zone of premixed methane-air mixture with equivalence ratio of 0.6 (b)

Firstly, the laser-induced plasma was generated in both pure air and the non-reacting zone of premixed methane-air mixture with equivalence ratio of 0.6. Figure 4.2 shows typical sequences of the temporal evolution of the plasma with an incident laser pulse with energy 125 mJ in the air and the methane-air mixture between times of 0.2 μ s and 100 μ s after the laser pulse. The laser beam propagated from the left-hand side of the image and the dimensions of all images were 11.5 mm horizontally and 11.5 mm vertically. In this experiment, the emitted spectra and plasma images could be recorded simultaneously by simply changing the delay time of the ICCD gate. Since the intensity of the emitted light spans several orders of magnitude during the lifetime of the plasma, the image-intensifier gate of the ICCD had to be adjusted to an appropriate level for each condition, especially when the plasma intensity became very weak after 30 μ s. Each image displays the time after the laser pulse and the exposure time and was normalized by its own maximum intensity. Figure 4.2 shows that the size and shape of the

generated plasma in the pure air and the non-reacting methane-air mixture are different, with stronger intensity and larger size for the methane-air mixture compared to that of the air, due to the existing of more visible spectra lines, such as H at 656 nm and CN at 388.3 nm. Since the laser beam inducing the plasma is focused by a 300 mm focal length lens, it results in a formation of an axially symmetric but cylindrically asymmetric spark geometry, which generates toroidal-shaped vortices at late times after the plasma formation. The flow patterns developed during the decay of the laser-induced plasma are formed by the asymmetric laser energy deposition caused by the optical breakdown method of focusing laser beam. This observation is in agreement with references [138–142].

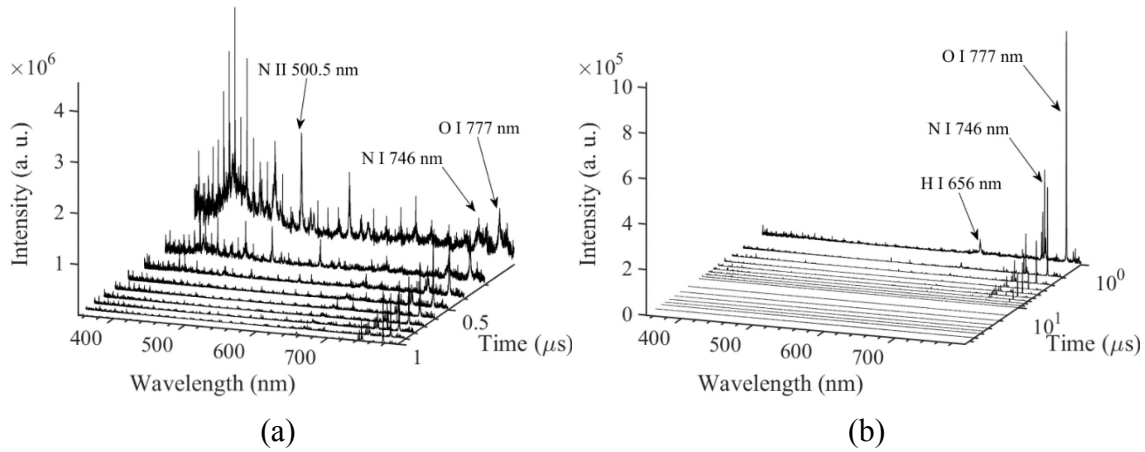
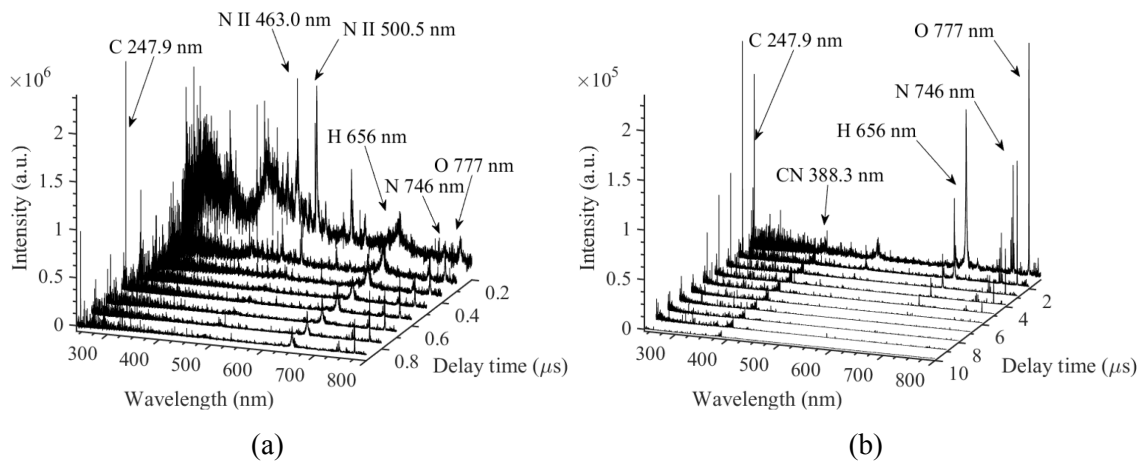
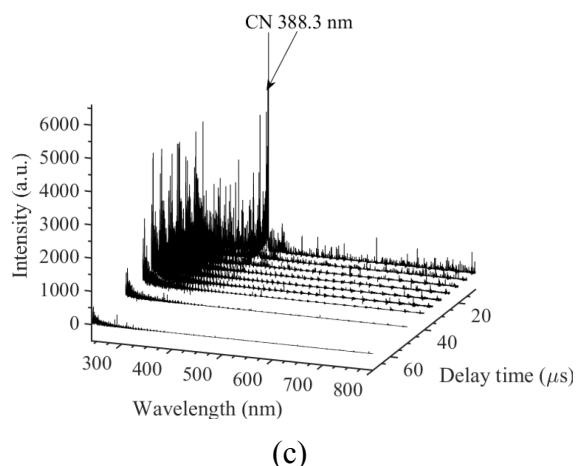


Figure 4.3 Temporal evolution of the LIBS spectra after the incident laser pulse with 125 mJ energy in air. The spectra are ensemble averages at specific times after the laser pulse over 50 realisations. (a) 0.1~1 μ s (b) 1~100 μ s in air





(c)

Figure 4.4 Temporal evolution of the LIBS spectra after the incident laser pulse with 125 mJ energy in the non-reacting zone of premixed methane-air mixture with equivalence ratio of 0.6. The spectra are ensemble averages at specific times after the laser pulse over 50 realisations. (a) 0.1~1 μ s (b) 1~10 μ s and (c) 10~100 μ s in methane-air mixtures.

Immediately after the Q-switched Nd:YAG laser with nanosecond pulse width was fired, the plasma spectra were dominated by continuous light caused by the bremsstrahlung effect and recombination radiation. Figure 4.3 (a) and Figure 4.4 (a) shows that during time delays of 0~1 μ s after the laser pulse, the plasma was created with strong continuous emission background lights and it expanded quickly both horizontally and vertically (Figure 4.2 (a) and (b)). These spectrally continuous emissions contained little information about the plasma composition and are usually regarded as noise in LIBS measurements. During this process, the high energy level ionic emissions, such as N II at 463.0 nm and N II at 500.5 nm, co-existed with the continuous emissions. The intensity of these emissions was very strong and decayed rapidly within a time of 1 μ s. The low energy level neutral atomic emission lines, such as H I (656 nm), N I (746 nm) and O I (777 nm), appeared out of the continuous emission that weakened gradually in this period. Figure 4.3 (b) and Figure 4.4 (b) show that, at time delay of 1 μ s after the laser pulse, the spectral intensity decreased and the continuous background emission vanished in the time window of 1~10 μ s. The neutral atomic emissions dominated the spectra until 10 μ s. Typically, the time window from 1 μ s to 10 μ s, which is dominated by the neutral atomic emissions, is the main time window for LIBS measurements, since it avoids the continuous emissions and collects most of the atomic emissions. The plasma images in Figure 4.2 show that the shape of the plasma remained similar and, towards times around 10 μ s, it started expanding radially away from the laser beam direction. At later times, the plasma continued to cool down and the atoms recombined to form new molecules. The molecular emission CN (388.3 nm $\Delta v=0$ of the CN band system $B^2\Sigma^+-X^2\Sigma^+$) and C_2 (516.5 nm $\Delta v=0$ of C_2 swan system $d^3\Pi_g-a^3\Pi_u$), observed

when methane mole fraction is higher than 0.3, continued to emit light until around 50 μs , as shown in Figure 4.4 (c). During this time window, the plasma images of Figure 4.2 show that the plasma expanded strongly away from the direction of the laser beam and gradually decayed. After time of 50 μs , the spectrometer was not sensitive enough to record the spectra and only the ICCD with high gain at the intensifier was able to record the plasma images (Figure 4.2). Theoretically, at this time, the plasma was already very cool and only molecules existed with weak emissions. As a consequence, the plasma evolved from a hot spot into widely dispersed parts in the field as it decayed.

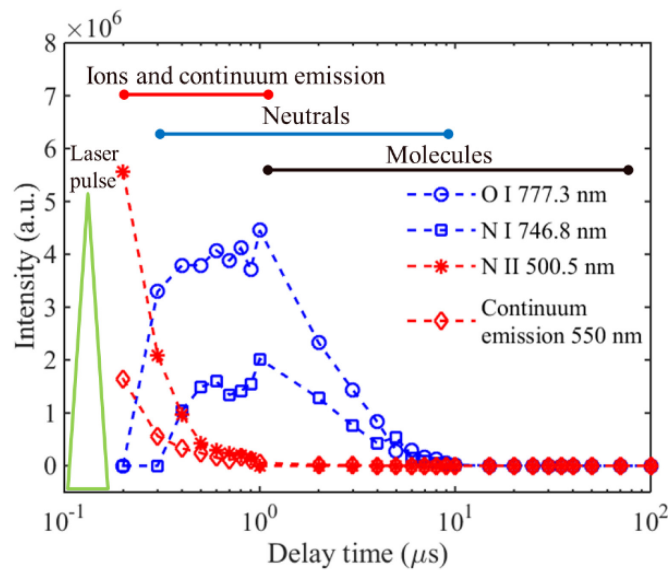
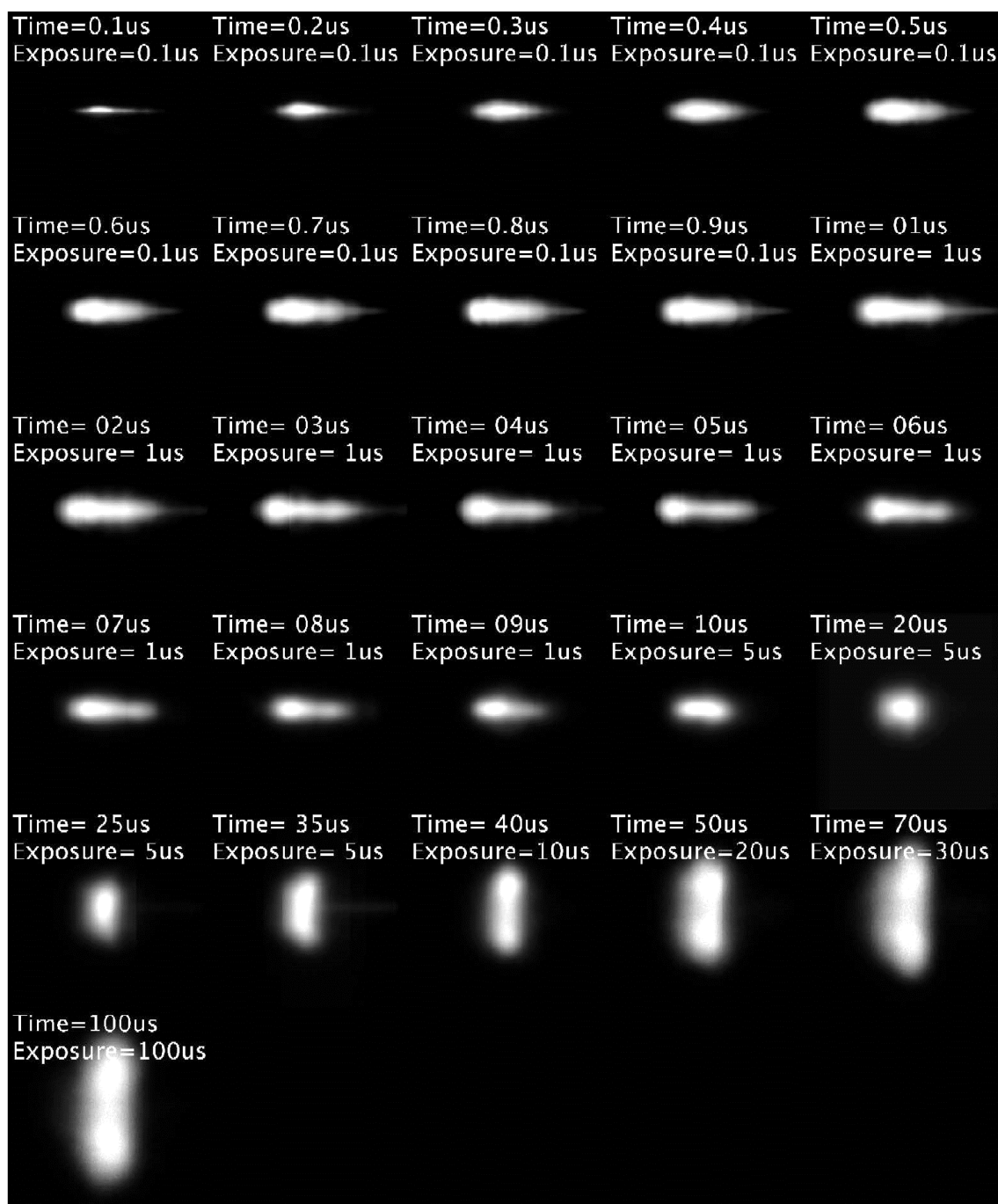


Figure 4.5 Temporal evolution of intensity of plasma emissions, generated by an incident laser pulse with 125 mJ energy in the non-reacting zone of premixed methane-air mixture with equivalence ratio of 0.6

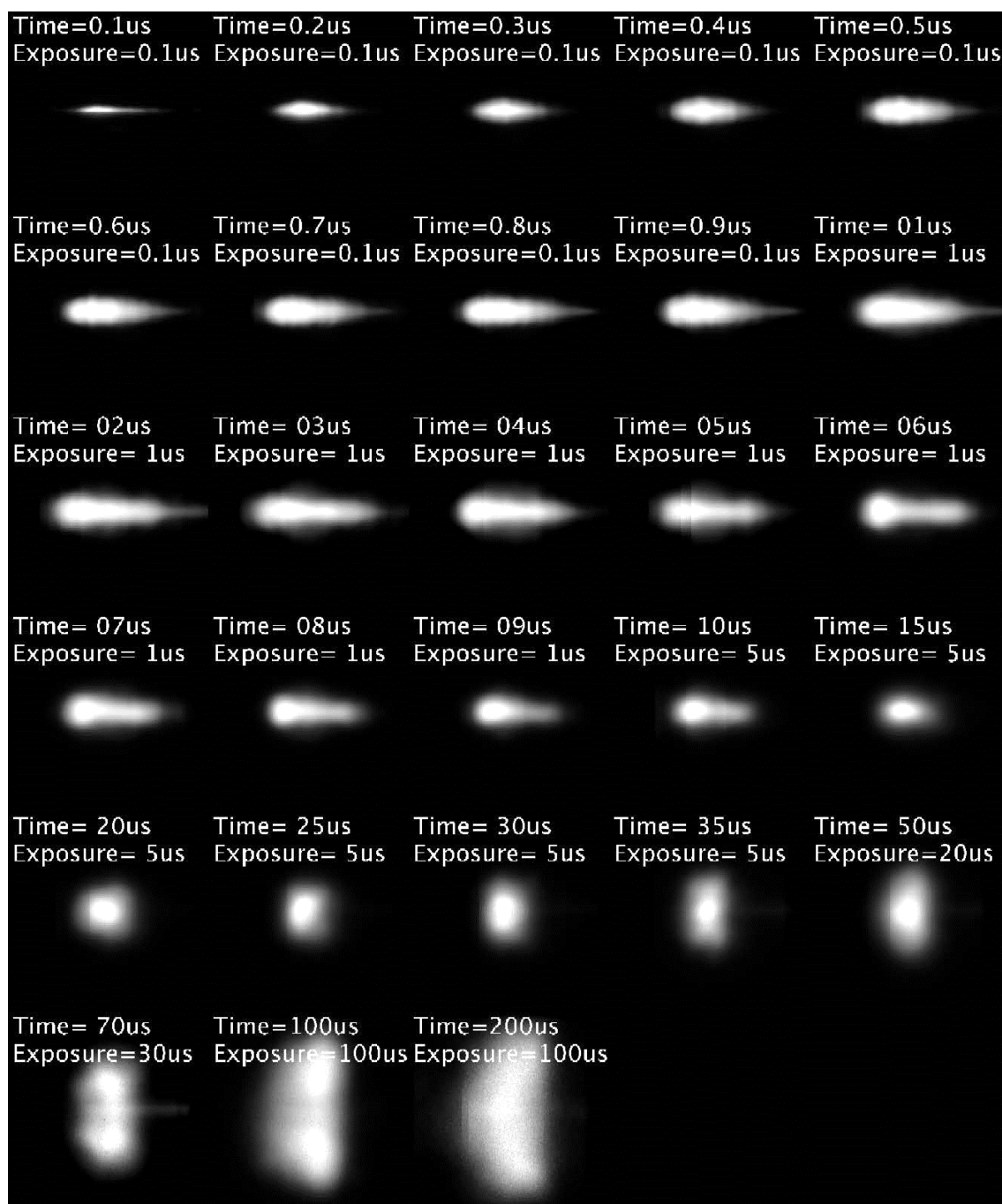
Figure 4.5 presents the three stages of the temporal evolution of the laser-induced plasma in the non-reacting zone of premixed methane-air mixtures, including ionization stage from 0 to 1 μs , neutral atomic emission from 1 μs to 10 μs and molecular emission from 5 μs to 100 μs . The emission line at 550 nm was chosen as the indicator of the continuous background emissions. Variations of the laser pulse energy and the sensitivity of the spectrometer can lead to small changes in the duration of the three stages described above. Nevertheless, the time scales and the sequences of the three stages remain the same. A similar temporal evolution of spectral lines is also observed in some references [25,102]. For general purpose of LIBS measurements, the time window 1 μs ~ 10 μs [5,104] is commonly used to collect the intensity from different atomic lines. In this study, in order to evaluate the LIBS measurement over a large range of methane-air mixtures, different time windows 1 μs ~ 6 μs (mainly collecting the

atomic emissions) and 1~50 μs (collecting both atomic and molecular emissions) were used for comparison.

4.2.2 Plasma spatial evolution in different gases

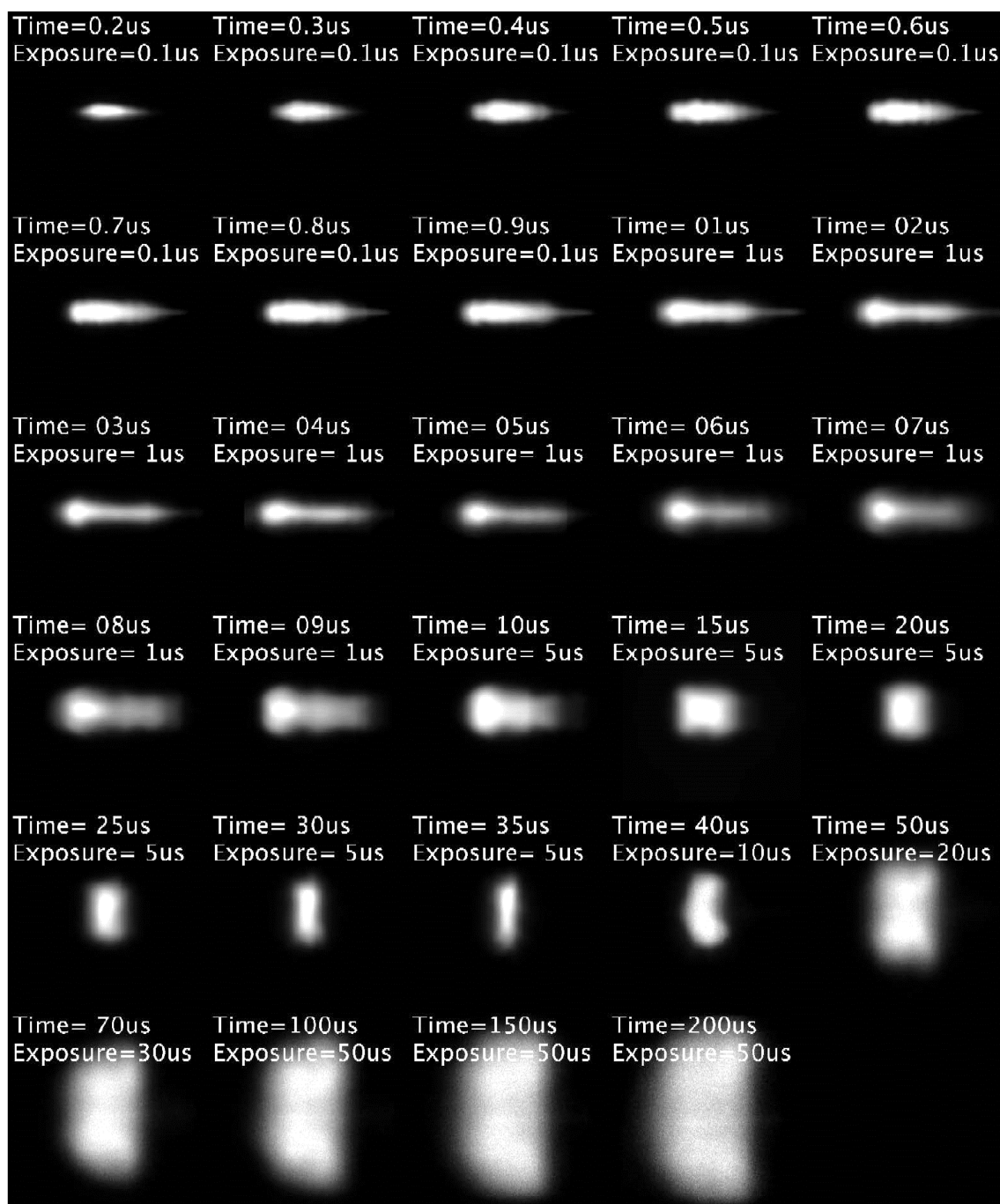


260 mJ in air (a)

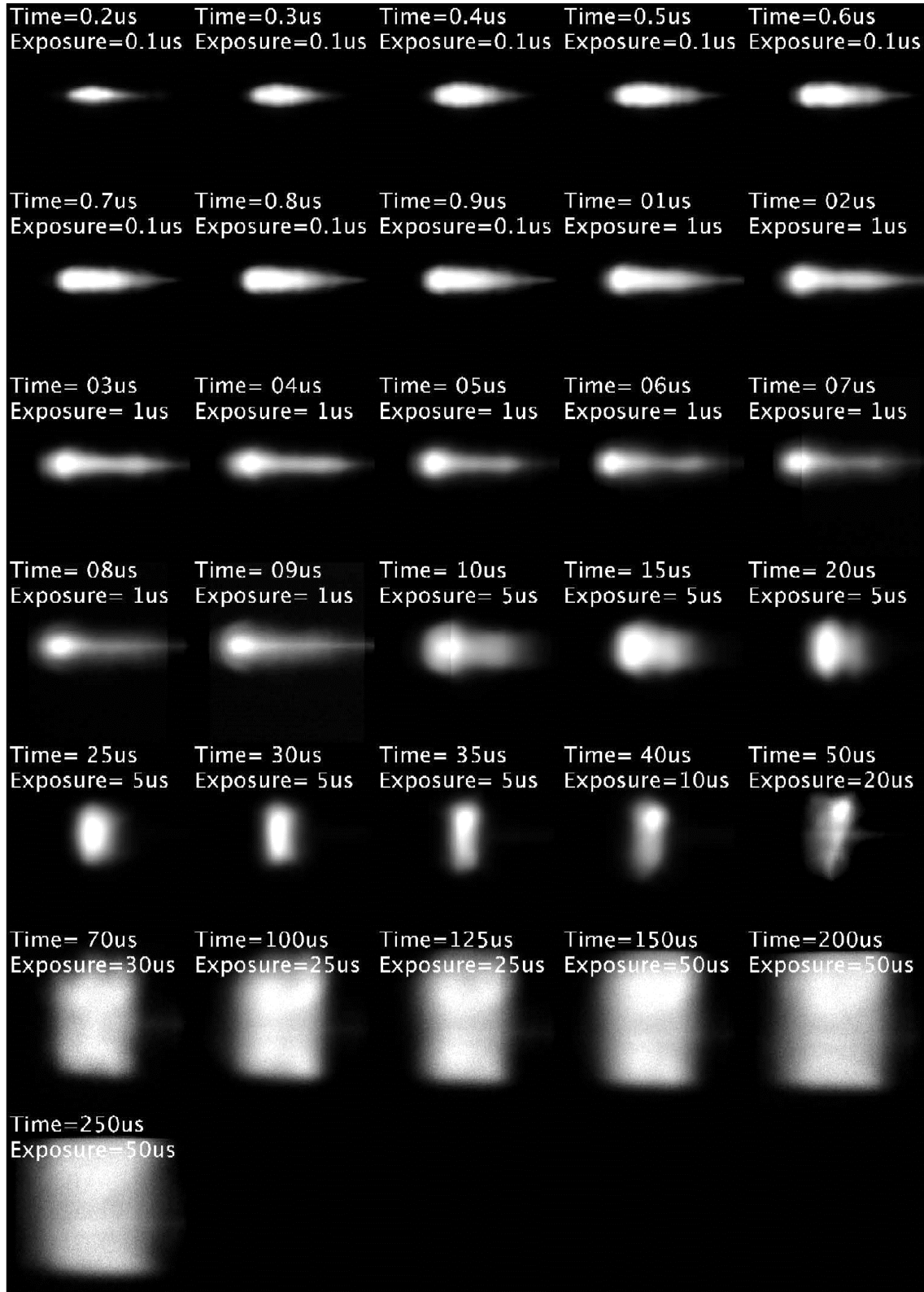


406 mJ in air (b)

Figure 4.6 Sequences of the temporal development of laser induced plasma, generated by incident laser pulse with 260 mJ energy (a) and 406 mJ energy (b) in air



260 mJ in methane-air mixture with equivalence ratio of 0.6 (a)



406 mJ methane-air mixture with equivalence ratio of 0.6 (b)

Figure 4.7 Sequences of the temporal development of laser induced plasma, generated by incident laser pulse with 260 mJ (a) and 406 mJ (b) in the non-reacting zone of premixed methane-air mixture with equivalence ratio of 0.6

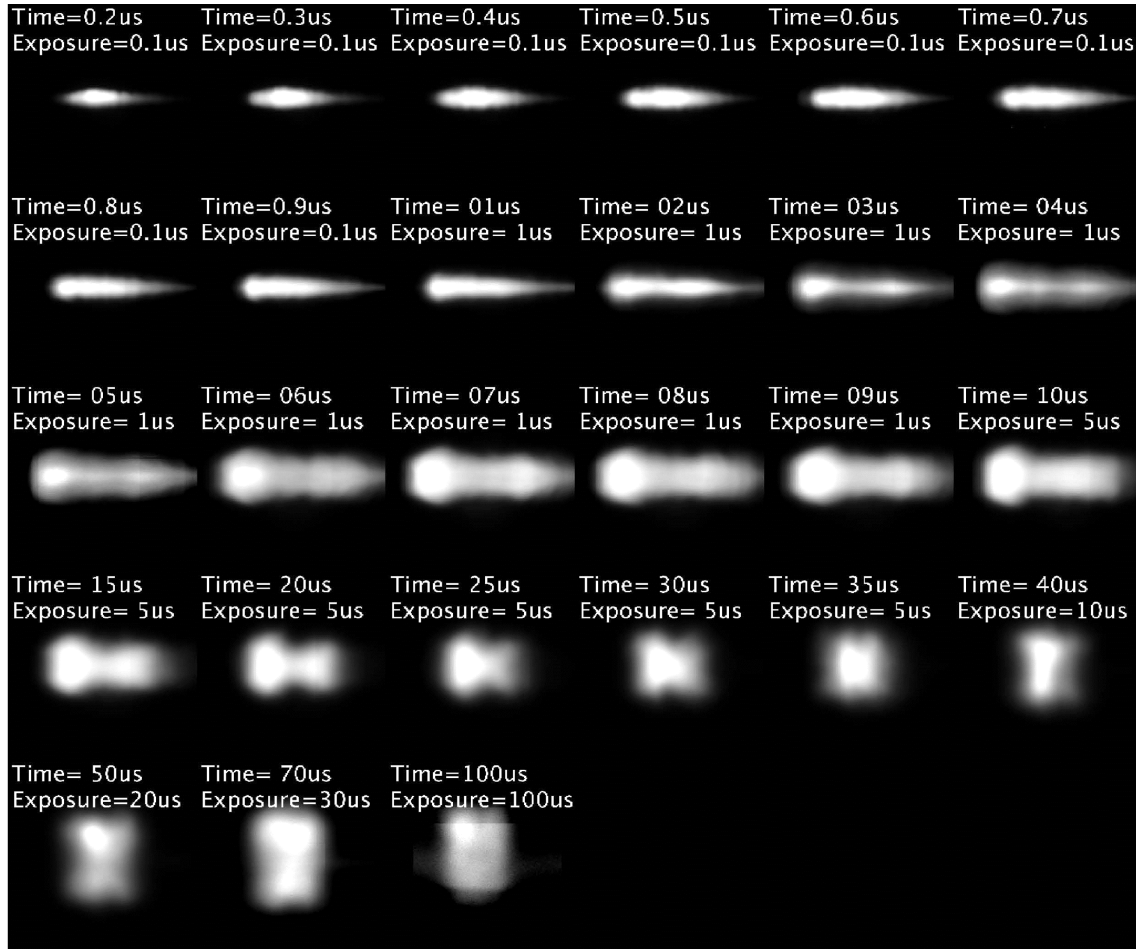


Figure 4.8 Sequences of the temporal development of laser induced plasma, generated by incident laser pulse with 406 mJ energy, in premixed propane-air mixture of 15% propane and 85% air

Figure 4.6, Figure 4.7 and Figure 4.8 show the effects of the laser pulse energies in air and different fuel lean mixtures. It can be found that the increase of laser pulse energy leads to larger plasma size and stronger intensity in both air and methane air mixtures. The laser-induced plasma in methane-air mixtures is stronger, compared to the plasma in air. A possible reason is the high atom concentrations in the methane-air mixtures compared to air, since the spectral lines intensity is proportional to species concentration in Eq. (2.14). This increase of plasma intensity is observed in the propane-air mixture, as expected. All these plasma have similar expansion and collapse processes within their lifetime. Due to the instability of laser pulse output, the plasma shape has slight differences at various conditions.

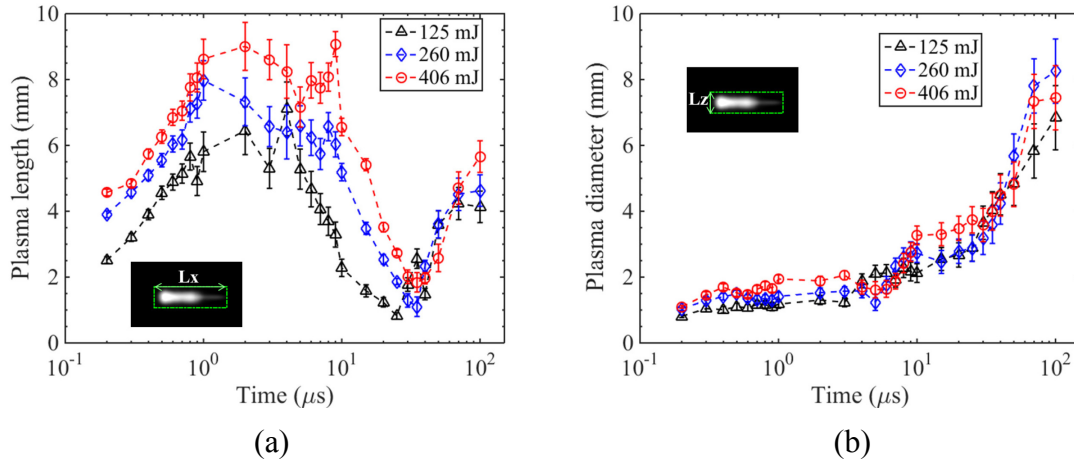


Figure 4.9 Plasma length L_x (a) and diameter L_z (b) as a function of time after the laser pulse for different laser pulse energies. Plasma is induced in the non-reacting zone of premixed methane-air mixture with equivalence ratio of 0.6. X and Z coordinates are along and normal to the direction of the laser beam respectively.

Figure 4.9 shows the temporal evolution of the plasma dimensions in the non-reacting zone of premixed methane-air mixtures. In this figure, both the plasma length L_x and diameter L_z increased with time after the laser pulse and began to decrease at around 1~2 μs . However, after around 20 μs , both L_x and L_z began to increase continuously again until the plasma decayed. From Figure 4.2 and Figure 4.4, it can be seen that the plasma and the molecular spectra were already very weak and difficult to be recorded by the spectrometer after 30 μs . The peak dimensions of L_x and L_z during the time window of 0.2~10 μs determined the probe volume of the LIBS measurement, during which most of the spectral emissions were captured. Therefore, for LIBS measurements in the non-reacting zone of premixed methane-air mixtures with a laser pulse beam with energy of 125 mJ, the main emissions of plasma radiated within 30 μs . The probe volume dimensions were around 5 mm x 1.5 mm x 5 mm. Increase of the laser energy by a factor of 3 increased the plasma length L_x by around 50%, while the diameter L_z remained the same. In this study, the laser beam direction was oriented perpendicular to the main flow of the opposed jets, so that only the smallest dimension of the probe volume L_z was affected by the flow. Although large size plasma could deliver higher SNR, the decrease in the spatial resolution should also be considered. Therefore, there was a compromise between the SNR and spatial resolution, which determined the selection of the laser energy for LIBS measurements. There is a possibility that the majority of the observed emitted species originate from the initial breakdown process within 0.1 μs . Although the plasma gradually expands afterwards, the spectral emissions originating from the initial breakdown spot mainly convey the information of the original kernel. As a consequence, the spatial resolution of the LIBS

measurements may be better than the dimensions of the plasma suggest. This possibility still needs to be verified.

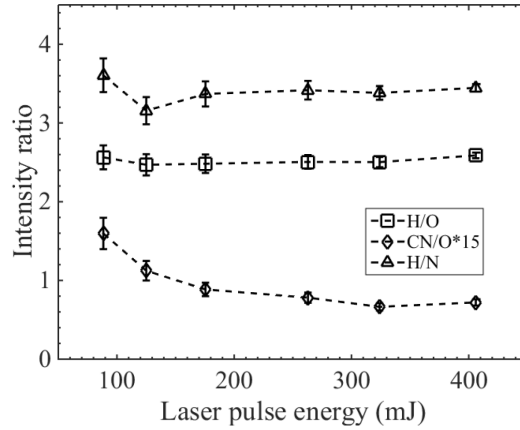


Figure 4.10 Relative intensity of atomic emissions lines of 50 averaged spectra as a function of laser pulse energy in the non-reacting region of methane-air mixtures with equivalence ratio of 0.6

In Figure 4.10, the energy of the excitation laser was varied from 80 to 406 mJ, with 1 μ s delay time and 5 μ s exposure time. In this energy range, compared to H/N and CN/O intensity ratios, the relative intensity H/O could be regarded as an independent index, which was not influenced by the laser energy due to their stronger SNR in the spectrum.

4.2.3 Correlation of equivalence ratio of premixed methane-air mixture with LIBS spectral intensity ratios

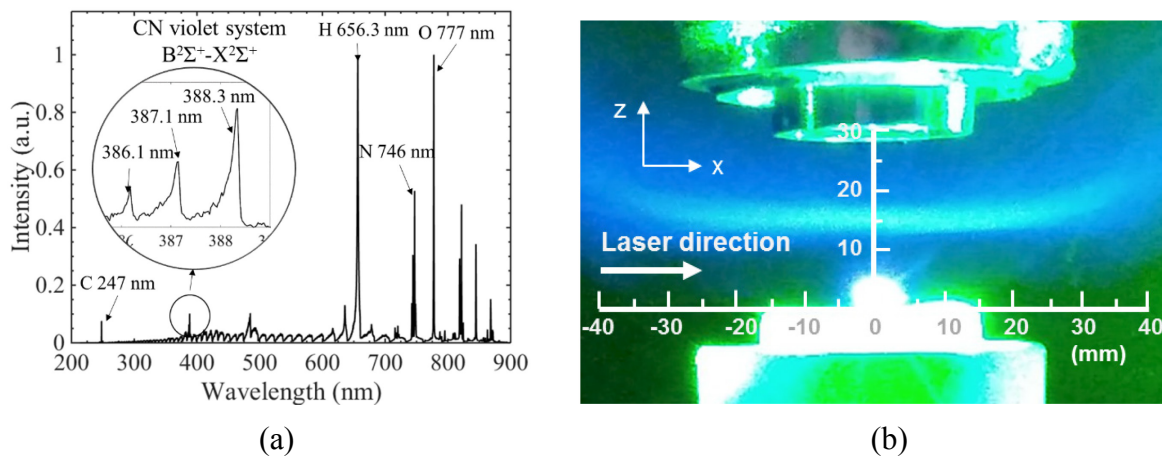


Figure 4.11 (a) Typical LIBS full spectrum (raw data) measured at time 1 μ s ~ 6 μ s after the laser pulse in the non-reacting premixed methane-air mixture and (b) Image of lean ($\phi=0.6$) premixed methane-air flames with strain rate 120 s^{-1} and laser induced plasma at $z=3$ mm from the lower jet exit

Table 4.1 Premixed flames operating conditions

Parameters	Values
Bottom nozzle flow rate	71.8 l/min air + 4.53 l/min CH ₄
Top nozzle flow rate	71.8 l/min air + 4.53 l/min CH ₄
Nozzle area-averaged velocity	1.8 m/s
Reynolds number	3564.4
Strain rate	120 s ⁻¹
Flow rate uncertainty	3%
Equivalence ratio	0.6 (5.93% CH ₄)

Figure 4.11 (a) illustrates a typical raw LIBS spectrum (averaged spectra of 50 shots) at 3 mm above the lower nozzle jet exit, while Figure 4.11 (b) shows the plasma image at 3 mm above the lower nozzle exit in lean ($\phi=0.6$) premixed opposed jet methane-air flames. The spectrum was recorded with time delay 1 μ s after the laser pulse and with 5 μ s exposure time of the spectrometer. The laser beam was focused on the centreline ($x=0$ mm) and at $z=3$ mm above the lower jet exit, which was in the non-reacting zone. Therefore, both the laser beam and the plasma were not influenced by the flames at this measurement location. The influence of plasma background continuous emissions was very weak and could be neglected at the selected time window. The peak intensities of neutral atomic nitrogen (N I) at 742.4, 744.2 and 746.8 nm, oxygen (O I) centred at 777.4 nm, hydrogen (H I) at 656.3 nm, CN (violet system, B² Σ^+ -X² Σ^+) at 388.3 nm were observed. The corresponding intensities were quantified by integrating over a range of wavelengths, namely H 650.0~661.1 nm, O 776.5~778.3 nm, N 742.0~747.7 nm, CN 387.8~388.6 nm and C₂ 516~517 nm respectively for the spectral analysis that can quantify the local equivalence ratio. The LIBS spectra were averaged over 50 laser single shots. Due to the reduction of measurement accuracy and precision in flames [101], researchers used the time-averaged results to detect the air-fuel ratios in turbulent flames [107,112]. Although instantaneous LIBS measurement has been conducted into the flames [106,112,143], the accuracy and precision of the technique still need to be improved. The present study aims to evaluate and improve the ability to obtain instantaneous local equivalence ratio measurements in flames with the LIBS technique.

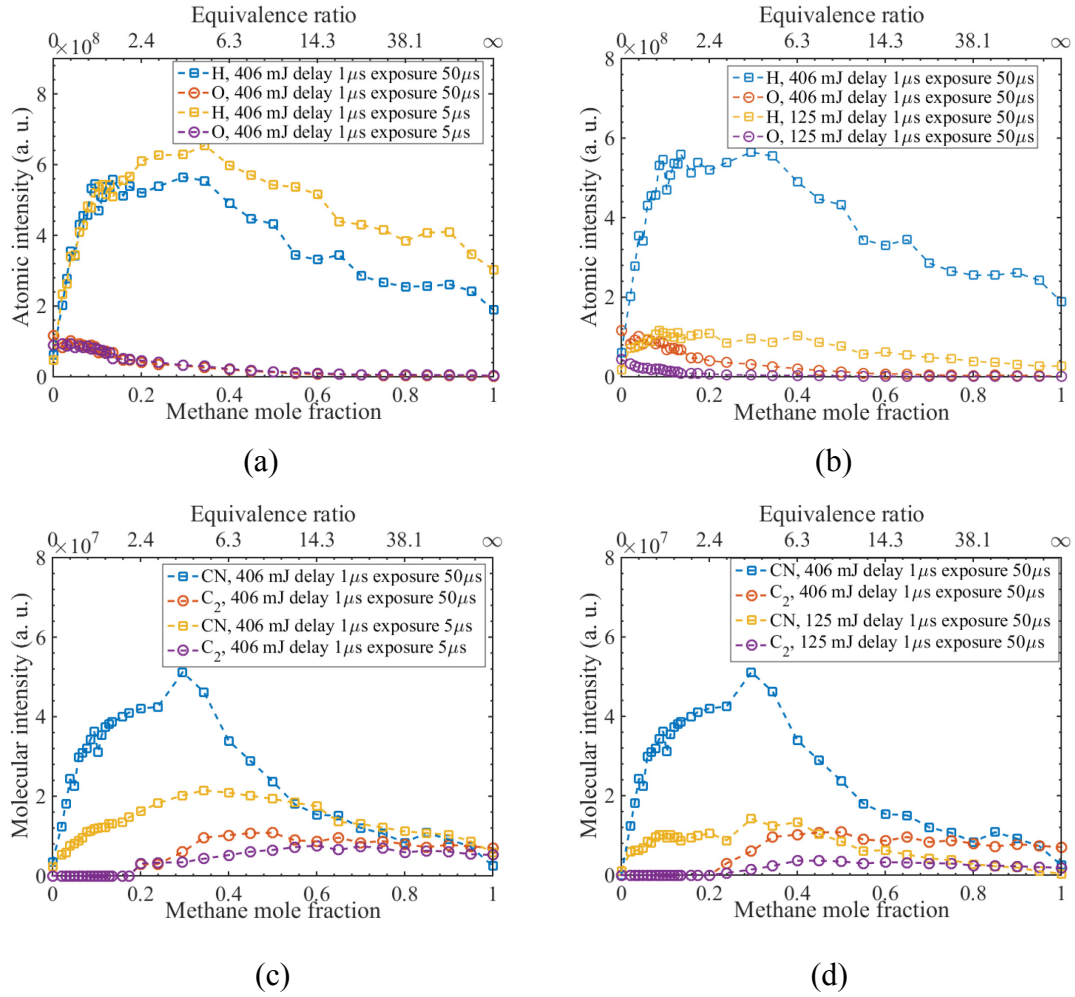


Figure 4.12 Total intensity of spectral lines of H (a) (656 nm) and O (b) (777 nm) atomic lines and CN (c) (388 nm) and C₂ (d) (516 nm) molecular bands as a function of methane mole fraction in non-reacting premixed methane-air mixtures.

Figure 4.12 shows the total intensities of the atomic lines H 656 nm and O 777 nm and of the molecular lines CN 388.3 nm and C₂ 516.5 nm, as a function of methane mole fraction in premixed methane-air mixtures. Laser pulse energies 125 mJ/pulse and 406 mJ/pulse were used in the calibration measurement with 1 μ s delay and 5 μ s/ 50 μ s gate time. From Figure 4.12 (a) and Figure 4.12 (b), the main atomic emissions H and O show different trends with the increase of methane mole fraction. The oxygen line decreased monotonically with the mole fraction, due to the reduction of oxygen concentration and the quenching effects of high fuel concentration, as reported in Ferioli and Buckley [101]. In contrast, after a linear increase, the hydrogen line reached a plateau and then began to decay at around 0.4 mole fraction. Different from the suggestion of Eq. (2.14), the intensity of hydrogen was not proportional to species concentration in the whole range, which was probably caused by the self-absorption quenching effects. Figure 4.12 (c) and Figure 4.12 (d) show that CN emissions increased to the maximum at 0.3 mole fraction and eventually decreased to zero due to the lack of nitrogen atoms. The intensity of C₂

began to appear in the spectra after 0.2 mole fraction and kept increasing until 0.5 mole fraction. Eventually, C_2 intensity decreased to a small value at 1.0 mole fraction. In these figures, under different laser pulse energies and time windows, the curves demonstrated similar trends. Compared to the intensity of the atomic emissions of H and O, the intensity of the molecular emissions CN and C_2 were sensitive to length of the time window, since their radiations last over a long time.

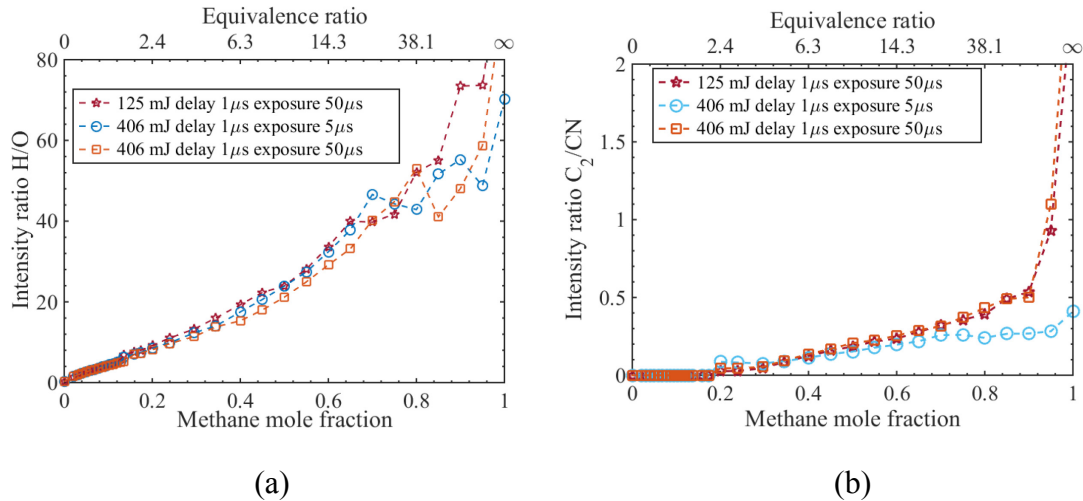


Figure 4.13 Correlation of premixed methane-air equivalence ratio with the intensity ratio H/O (a) and C_2/CN (b) of the LIBS spectral lines

Although the complex mechanism in plasma emissions is still not fully understood, a correlation of the intensity ratio H/O and C_2/CN with the methane mole fraction has been used in combustion [112]. Together, H/O and C_2/CN intensity ratios can act as accurate and robust indicators to determine the local equivalence ratio for different mole fraction ranges. In order to extract quantitative mixture composition data from the spectra, a calibration was performed for a wide range of equivalence ratios. The laser beam was focused to the non-reacting zone. In Figure 4.13 (a), the intensity ratio of H/O shows a nearly linear behavior with equivalence ratio in methane mole fraction range of 0.0~0.8. Because in the high concentration methane mixtures, the oxygen emissions became very weak, which has a low SNR. Compared to that, Figure 4.13 (b) shows that the molecular emissions C_2/CN is a better indicator for high mole fraction of methane mixtures from 0.3~1.0. Both these two intensity ratios were not sensitive to the laser pulse energy. However, due to the longer duration of the molecular emissions, the intensity ratio C_2/CN time window was more sensitive to the time window width chosen compared to that of the H/O. In this study, to ensure high SNR, 1 μs delay and 50 μs gate time were used in the measurements, when it was necessary to collect the molecular emissions. The uncertainty of the above calibration, determined from the standard deviation of the spread of

the resulting probability function, was within 5%. The experimental data could be fitted with a polynomial function, which could be used as a calibration curve.

4.2.4 LTE (Local Thermodynamic Equilibrium) of laser-induced plasma

In order to realise instantaneous local mixture composition measurements, the shot-to-shot variation of LIBS spectra needs to be precisely evaluated. Gas-fuelled industrial gas turbine combustors usually operated at fuel lean conditions. Therefore, we choose to evaluate the LIBS measurements by using as reference premixed methane-air counterflow flames with equivalence ratio of 0.6 and flow strain rate of 120 s^{-1} , as shown in Table 4.1. First, the validity of the LTE should be discussed, since only in such a situation the emitting species concentration can be deduced from the intensity of the spectral lines.

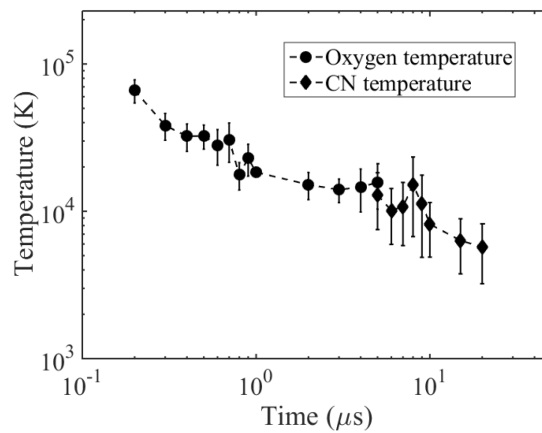


Figure 4.14 Temporal evolution of the plasma temperature (from Eq. (2.10)) during the breakdown process with incident laser pulse energy of 125 mJ in a non-reacting zone premixed methane-air mixture with equivalence ratio of 0.6

Based on the spectra shown in Figure 4.4, the plasma temperature was calculated using the Boltzmann equation, Eq. (2.10), in which the ratio of emission intensities of transitions associated with the same emitting species could be used [144]. This simple method gives an approximation of the overall plasma temperature. In Figure 4.14, for times between 0.3 μs and 5.0 μs , the atomic emissions O I at 715.7 nm, 777.2 nm, 822.2 nm and 844.6 nm are used to calculate the plasma temperature due to their higher SNR in the spectrum. For times between 5.0 and 20 μs , since the atomic emissions are already very weak, the intensity ratio between molecules emissions CN at 358.5 nm and 388.3 nm ($\Delta v=1, 0$ of the CN band system $\text{B}^2\Sigma^+-\text{X}^2\Sigma^+$ respectively) can be used to calculate the temperature. Figure 4.14 presents the temporal evolution of the plasma temperature. This temperature temporal evolution was also observed

by Kawahara *et al.* [102]. From Yacin *et al.* [145], the relationship between the laser energy and plasma temperature is as follows:

$$T \propto Pe^{0.18} \quad (4.1)$$

where T is the plasma temperature and Pe is the laser pulse energy. Due to the small value of the exponent of Eq. (4.1), the plasma temperature was very weakly dependent on the laser pulse energy. The impact of laser pulse energy mainly influences the size of the plasma and the persistence of a given temperature in the process. Therefore, the temperature evolution can be used to calculate the LTE for plasma emissions for different pulse energies and plasma intensities.

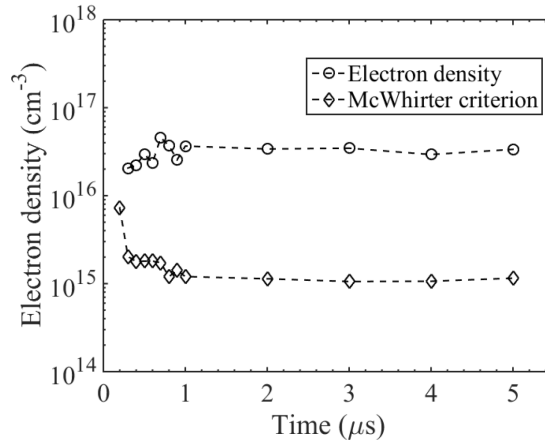


Figure 4.15 Temporal development of calculated electron density and its lower limit for plasma generated by incident laser pulse with energy of 125 mJ in a non-reacting premixed methane-air mixture with equivalence ratio of 0.6

Since, for LTE condition, atomic and ionic states should be populated and depopulated predominantly by electron collisions, relatively high electron density can ensure a high collision rate. This criterion is a necessary, though insufficient, condition for LTE. The corresponding lower limit of electron density N_e is given (cm^{-3}) by the McWhirter criterion [146] in Eq. (2.8). In this calculation, $\Delta E = 1.7$ eV was taken for the N I 742.4 nm transition [147]. The Stark broadening of a well-isolated line is a useful tool for estimating the electron density in Eq. (2.13). In this work, the electron density was deduced from the Stark broadening [146] of the N I 742.4 nm transition line in the measured spectra. In this equation, the electron impact width interpolated for a given temperature from the values in ref. [148]. The Stark broadening of a line $\Delta\lambda_{\text{Stark}}$ is expressed as the FWHM of the intensity distribution around the spectral line in nanometres.

Figure 4.15 presents the electron density N_e , calculated from the N I 742.4 nm transition line and its lower limit as a function of time. The value of N_e was at least one order of magnitude higher than the lower limit for atomic emissions at different times. In addition, as the McWhirter criterion deriving from the plasma temperature did not depend on plasma intensity, the validity of LTE was safely assumed in the experiments and the LTE was very robust even for each instantaneous LIBS measurement.

4.2.5 Measurements and uncertainty analysis in premixed flames

According to Eq. (2.14), the intensity I_a of an arbitrary transition line, a, of the spectrum emitted by a stable laser induced plasma in a gas mixture, which is mainly influenced by the collection efficiency of the optical system, can be determined as follows.

$$I_a = \eta_a I_{ij} = \eta_a h \nu_{ij} A_{ij} n^s \frac{g_i e^{-E_i/kT}}{U^s(T)} \quad (4.2)$$

where η_a is the efficiency of the collection optics to measure the intensity of spectral line a. This factor includes all uncertainties contributed by the collection system. It is found in this study that the fluctuation of η_a is inversely proportional to the plasma intensity, which is determined by the SNR. For LIBS measurements of local equivalence ratio, an intensity ratio between two transition lines is usually used to eliminate the intensity fluctuations between different laser pulses. The ratio R of intensities at spectral lines a and b is:

$$R = \frac{I_a}{I_b} = C(T) \frac{\eta_a n_a}{\eta_b n_b} \quad (4.3)$$

$$C(T) = \frac{(v_{ij} A_{ij} g_i)_a U_b(T)}{(v_{ij} A_{ij} g_i)_b U_a(T)} e^{-(E_{ai} - E_{bi})/kT} \quad (4.4)$$

In Eq. (4.3), n_a and n_b are the numbers of excited atoms. Thus, under LTE conditions, $C(T)$ is treated as a constant because the plasma temperature is very weakly dependent on the plasma energy. The relative uncertainties of the intensity ratio R can be calculated through the following equations:

$$\frac{dR}{R} = \frac{\partial R}{\partial \eta_a} \frac{d\eta_a}{R} + \frac{\partial R}{\partial \eta_b} \frac{d\eta_b}{R} + \frac{\partial R}{\partial n_a} \frac{dn_a}{R} + \frac{\partial R}{\partial n_b} \frac{dn_b}{R} \quad (4.5)$$

$$\sigma_R = \sqrt{(\sigma_{\eta_a})^2 + (\sigma_{\eta_b})^2 + (\sigma_{n_a})^2 + (\sigma_{n_b})^2} \quad (4.6)$$

where η_a and η_b are the collection efficiencies of spectral lines a and b respectively; σ_R is the relative uncertainty of the measured value; σ_{η_a} , σ_{η_b} , σ_{n_a} and σ_{n_b} are the relative uncertainty associated with efficiencies of η_a and η_b and atom numbers of n_a and n_b , respectively. The uncertainty for both n_a and n_b , resulting from the mass flow controllers that meter the supplied gases, are less than 2%. Therefore, the measurement accuracy in premixed flames mainly depends on the recorded spectrum.

From Eq. (4.5) and Eq. (4.6), in principle, the measurement uncertainty mainly depends on the mixture variation and camera efficiency. During a single shot measurement, the factors, including intensity ratio, intensity of spectral emission lines, plasma size, plasma image intensity, spectrum intensity and plasma location, are selected to be explored, in order to find the source resulting in shot-to-shot measurement variation.

In statistics, the Pearson correlation coefficient is a measure of the linear correlation between two variables. When Pearson's correlation coefficient is applied to a sample (x_i, y_i) , the formula is as follows:

$$r = r_{xy} = \frac{\sum_{i=1}^n (x_i - \bar{x})(y_i - \bar{y})}{\sqrt{\sum_{i=1}^n (x_i - \bar{x})^2} \sqrt{\sum_{i=1}^n (y_i - \bar{y})^2}} \quad (4.7)$$

where n , x_i and y_i are one dataset $\{x_1, x_2, \dots, x_n\}$ containing n values and another dataset $\{y_1, y_2, \dots, y_n\}$ containing n values as well. If $r_{xy}=1$, then X and Y are perfectly, positively, linearly correlated. If $r_{xy}=-1$, then X and Y are perfectly, negatively, linearly correlated. If $r_{xy}=0$, then X and Y are completely, non-linearly correlated. That is, X and Y may be perfectly correlated in some other manner, in a parabolic manner, perhaps, but not in a linear manner.

Table 4.2 Correlation coefficients between images and spectra

	H/O	H	O	Size	<i>I_{image}</i>	<i>I_{spec}</i>	<i>X_{centre}</i>
H/O ratio	1.00	0.00	-0.32	0.05	0.04	-0.07	0.09
H intensity	0.00	1.00	0.94	0.65	0.70	0.98	-0.27
O intensity	-0.32	0.94	1.00	0.61	0.66	0.94	-0.27
Plasma size	0.05	0.65	0.61	1.00	0.97	0.62	0.41
<i>I_{image}</i>	0.04	0.70	0.66	0.97	1.00	0.66	0.36
<i>I_{spec}</i>	-0.07	0.98	0.94	0.62	0.66	1.00	-0.32
<i>X_{centre}</i>	0.09	-0.27	-0.27	0.41	0.36	-0.32	1.00

The plasma was created at the flame centre ($z=15$ mm) in the opposed jet burner. The condition was operated at 10 Hz, in reacting methane-air mixture with equivalence ratio of 0.6 and flow strain rate of 120 /s. The image and spectra of plasma were obtained simultaneously with 1 μ s delay and 50 μ s gate time. Among the 300 images and their corresponding spectra, the indices, including H and O intensities and their intensity ratios, were extracted from the spectra. H and O represent the absolute intensity in spectra at 656 nm and 777 nm. Plasma size is in mm². *I_{image}*, *I_{spec}* and *X_{centre}* represent the intensity of the spectra, the plasma image intensity and the horizontal location of the plasma centre respectively. As shown in Table 4.2, the correlation coefficients between H/O intensity ratio and other parameters are all below 0.1 except with the O intensity. H/O intensity ratio appears to be independent of the plasma size, location and intensity, which is mainly influenced by the H and O intensity, as expected from Eq. (4.6).

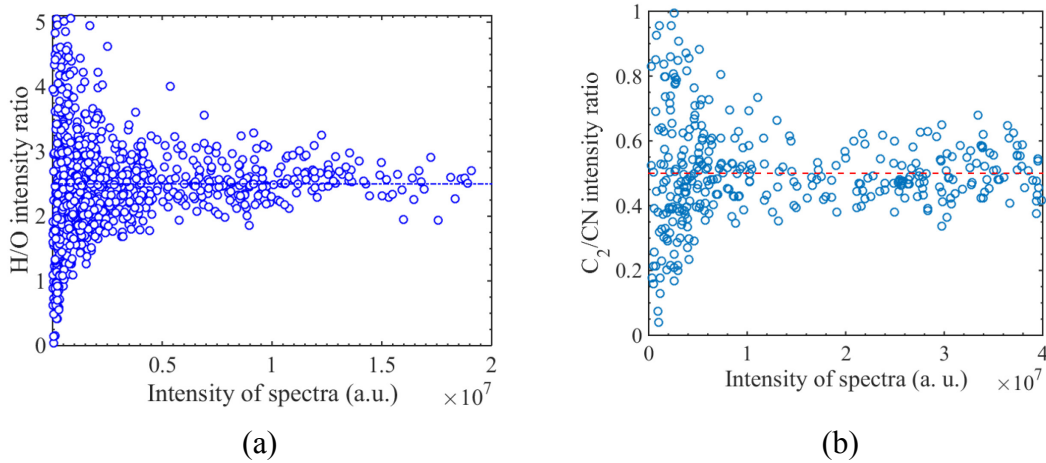


Figure 4.16 Instantaneous measurements of H/O (a) and C_2/CN (b) intensity ratios as a function of the intensity of the whole spectrum measured in premixed methane-air flames with equivalence ratio of 0.6 and 50% methane in methane-air mixture, respectively.

After using the ICCD and spectrometer to measure the image and spectra of plasma simultaneously in the methane-air premixed mixtures, it was found that the emitted spectra from the plasma were almost independent of the laser pulse energy, plasma shape, plasma size and plasma locations, which was consistent with the expectation of Eq. (4.5) and Eq. (4.6). The intensity of whole spectra is integrated as a SNR index to quantify the instantaneous LIBS measurement uncertainty. Figure 4.16 (a) shows that the accuracy and precision of instantaneous measurements increase with the plasma intensity. Each circle on the graph represents one instantaneous measurement of H/O intensity ratio inside the premixed fields, including the reactants, flames and products. In the high methane mole fraction results, Figure 4.16 (b) shows that C_2/CN intensity ratio has similar distribution as H/O ratios. Compared with H/O ratio uncertainty (10% for $SNR > 0.4 \times 10^7$), C_2/CN has a relatively large uncertainty (15% for $SNR > 1 \times 10^7$) due to quenching effects. In this study, both the low quantum efficiency of the ICCD compared to a non-intensified CCD and the small slit-like aperture of the spectrometer, which is used to ensure high spectral resolution, make the accuracy of the instantaneous measurements very sensitive to SNR. Therefore, increasing the SNR is the most important method to decrease the uncertainty of LIBS measurements of local equivalence ratio.

4.2.6 Flame effects on LIBS measurements

To evaluate how the flames influenced the LIBS measurement uncertainty for flow strain rate of 120 /s and lean premixed flames of methane-air mixture with $\Phi=0.6$ were still used as the

reference case (as shown in Figure 4.11 (b) and Table 4.1) to quantify the in-flame measurement errors.

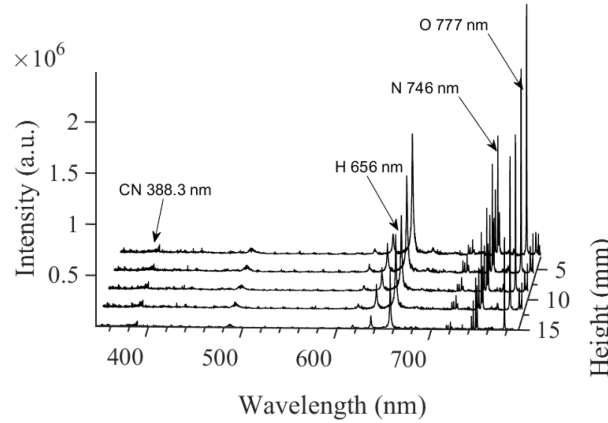


Figure 4.17 The emitted spectra (50 averaged) from the laser-induced plasma as a function of height above the lower burner exit. The laser beam pulse energy was 125 mJ and the selected time delay after the laser pulse for the spectral measurements was 1 μ s delay and 5 μ s gate time. The flame is at height 15 mm ($z=15$ mm) from the low nozzle jet exit.

When both jet flows had the same flow rates of premixed methane-air, two flat and symmetric flames were observed, as shown in Figure 4.11 (b). Plasmas were created along the centreline ($x=0$ mm) of the opposed jet burner at different heights above the lower nozzle jet exit. In this condition, the lower flat flame was at $z=15$ mm height due to buoyancy. Figure 4.17 and Figure 4.18 show that, when the plasma was close to the flame, the intensity of the whole spectrum and plasma decreased greatly which increased the measurement uncertainty. Compared with plasma evolution in non-reacting conditions of Figure 4.2 and Figure 4.4, the plasma in the flames had similar temporal behaviour in shape and spectra. But their sizes and intensities were relatively weak with large variations. In Figure 4.18, instantaneous measurement of plasma image and its spectra in the non-reacting zone and reacting zone are presented respectively. Figure 4.18 (a) shows a strong plasma and its spectra with a high SNR of 5.6×10^7 intensity in the non-reacting zone. In Figure 4.18 (b), the plasma in the flames has a smaller size and noisy spectra with a low SNR of 0.2×10^7 intensity. Due to flame effects, the plasma became horizontally asymmetric as well. The comparison between them shows how the flames deform and attenuate the plasma, resulting in low SNR and measurement precision. Figure 4.19 illustrates that the averaged H/O intensity ratio remains stable for various locations and laser pulse energies. Figure 4.20 shows that the atomic spectral lines in flames decrease slightly in width. According to Eq. (2.8), the low gas density in flames had a lower electron density n_e , which attenuated the Stark broadening effects on spectral lines in width. This change in

emissions was so small that it was neglected in this study, since both H and O line widths were attenuated slightly. Therefore, even under the disturbance of flames, the averaged H/O intensity ratio still remained stable for different intensities of plasmas. As opposed to the non-reacting flow measurements, the spectral amplitude of in-flame measurements would be decreased greatly when the plasma was close to flames, which increased the measurement uncertainty. This attenuation mainly stems from the following reasons.

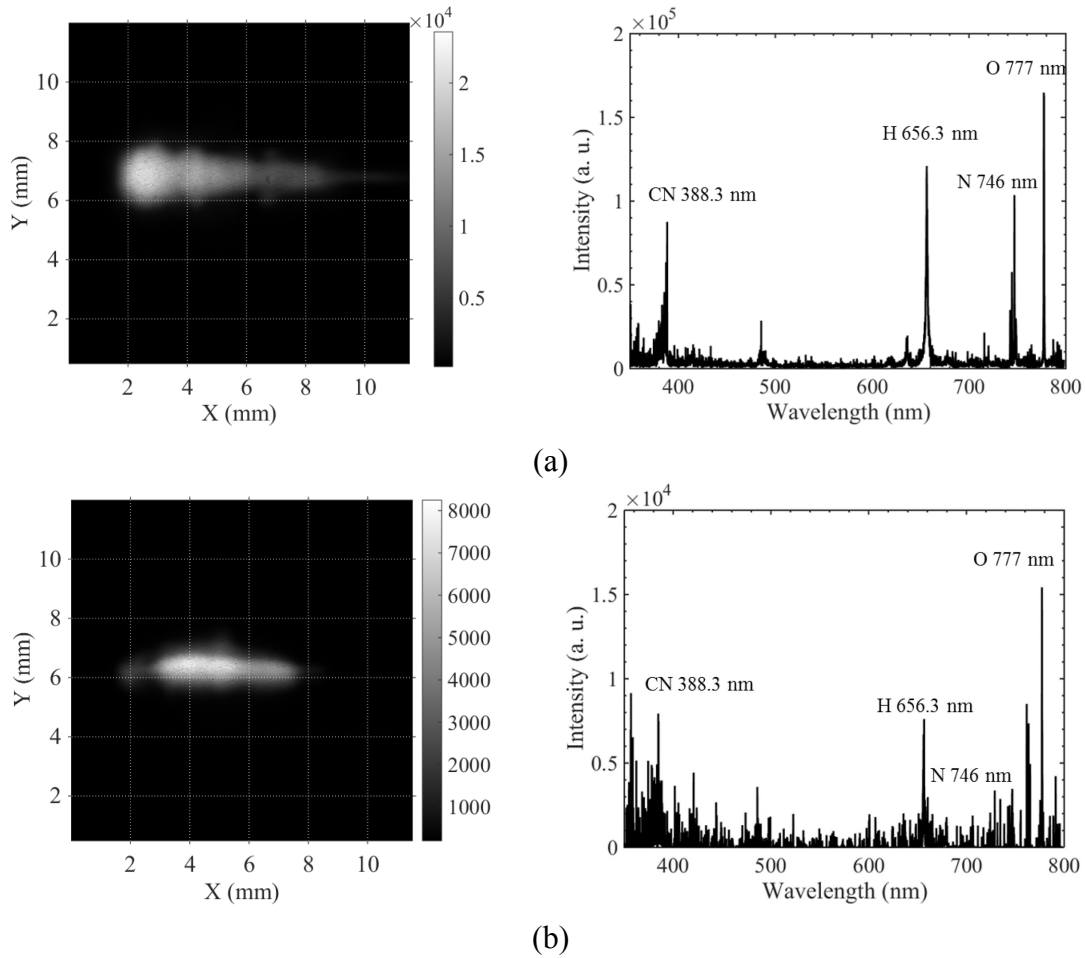


Figure 4.18 Instantaneously measured image and the spectra of the laser induced plasma at time $1 \mu\text{s}$ delay and $50 \mu\text{s}$ gate time after the laser pulse in the non-reacting zone (a) at $x=0$ mm, $z=3$ mm and in the reacting zone (b) at $x=0$ mm, $z=15$ mm of a premixed methane-air mixture with equivalence ratio of 0.6. The pulsed laser beam energy was 406 mJ.

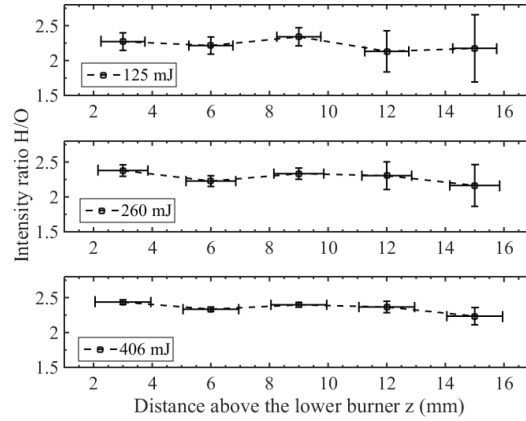


Figure 4.19 H/O intensity ratio as a function of height above the lower nozzle jet exit for different laser pulse energies (Error bars represent a 95% confidence interval). The flame is at height 15 mm.

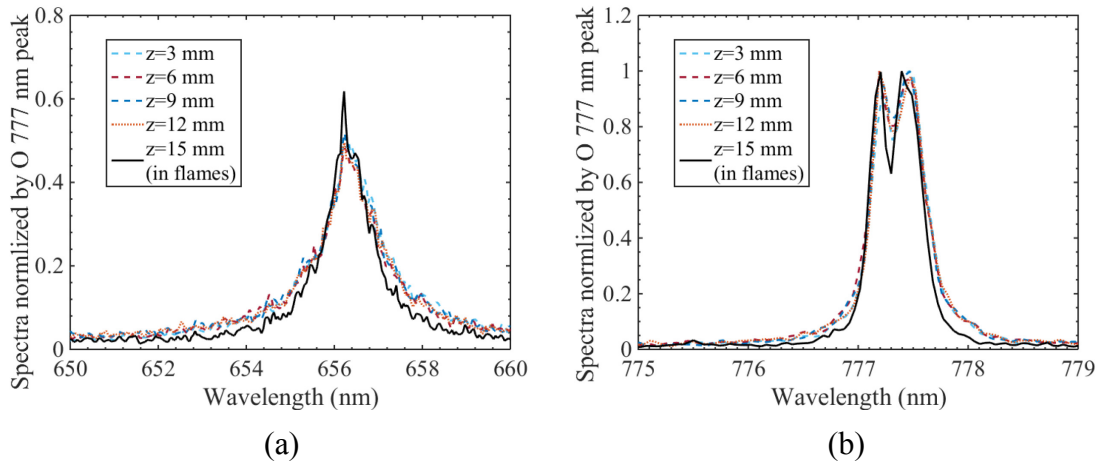


Figure 4.20 Normalized intensity at H I 656 nm (a) and O I 777 nm (b) spectral emission lines at different locations showing the effects of the flames (gas density) on the emission line widths

(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 [60] 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. (2.14), 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, as shown in Figure 4.21.

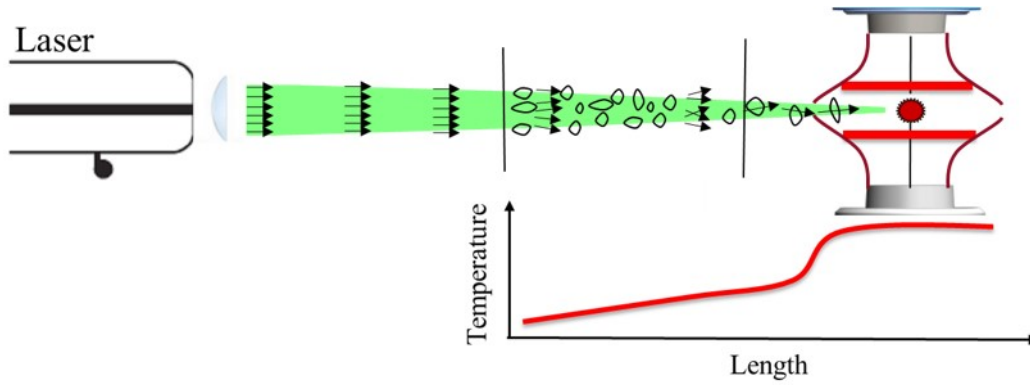


Figure 4.21 Schematic of temperature gradient and turbulent eddies effects on the LIBS measurements in the reacting flow experiment

Therefore, all these factors lead to nearly an average transmission of 60% of the laser energy, 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.

In Figure 4.22, Figure 4.23 and Figure 4.24, due to the flat flames of the opposed jet burner, it is possible to maintain the gas density and temperature almost constant, and then change the laser beam propagation distance in flames. The laser beam started from the left side and propagated horizontally through a certain distance of the flat flames to create plasma at target locations. Maintaining the plasma at $z=15$ mm, its x value was varied from -30 mm to 30 mm in the flat flames, using spectra from 200 single laser shot at each location.

For these LIBS measurements, it is expected to increase the horizontal path of laser beam propagation through large refractive index gradients of the flames with an increase of the value of x leading to stronger effects on the measured spectra. Propagation of the laser beam through multiple turbulent eddies with variable density causes fluctuations in the irradiance, known as scintillation. The standard deviation of the irradiance is estimated as follows [149]:

$$\sigma_I = (1.24 C_n^2 K^{7/6} L^{11/6})^{0.5} \quad (4.8)$$

$$C_n = 79.0 \times 10^{-6} \left(\frac{p}{T^2} \right) C_T \quad (4.9)$$

$$C_T = \sqrt{\langle (T_1 - T_2)^2 \rangle} r^{-1/3} \quad (4.10)$$

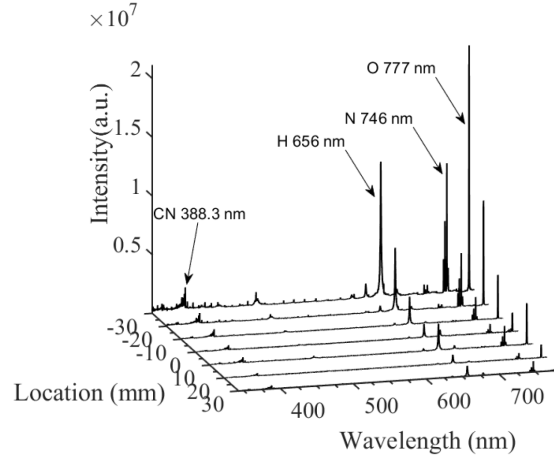


Figure 4.22 Accumulated averages of 200 plasma spectra obtained at different horizontal locations in the flames at 15 mm height from the lower nozzle jet exit.

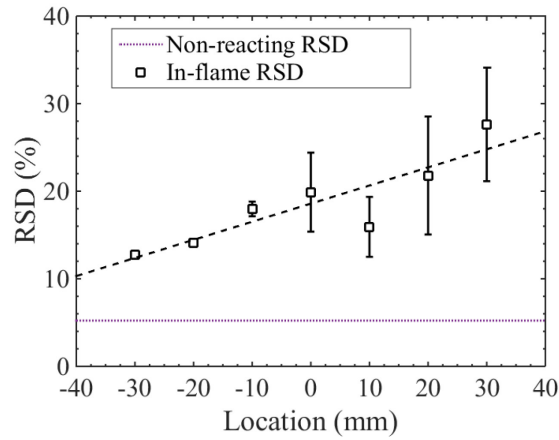


Figure 4.23 The RSD (relative standard deviation) of H/O intensity ratio measurement of single shot obtained at different horizontal locations in the flames at 15 mm height from the lower nozzle jet exit.

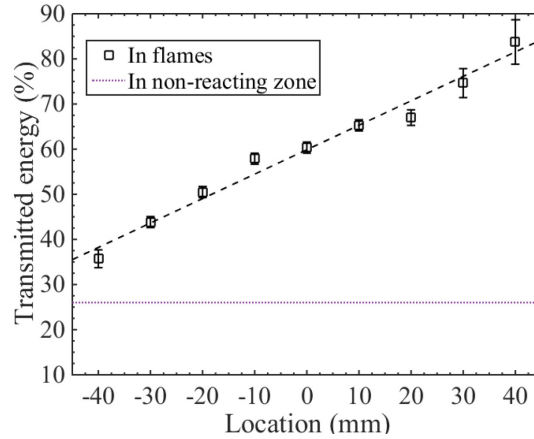


Figure 4.24 The averaged transmitted laser pulse energy for 406 mJ pulse as a function of the laser beam path length through the flames.

In Eq. (4.8), C_n is the refractive index structure coefficient; K is the wavenumber and L is the propagation path length. In Eq. (4.9) and (4.10), 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 propagated through the flame zone, both the plasma intensity in Figure 4.22 and the accuracy of the instantaneous measurement in Figure 4.23 decreased with the propagation path length along the flames, instead of the path length in the air, consistent with Eq. (4.8). Eq. (4.10) shows that the temperature gradient in the laser beam path determines the refractive index fluctuations and the intensity fluctuations. Since large temperature gradients were present in combustion, the refractive index structure coefficient C_n was much greater than the value at atmospheric conditions. Figure 4.24 illustrates that the averaged transmitted energy, measured by a power meter behind the plasma, increased with the propagation path length along the flames, which was consistent with the theory and the spectra as well.

Therefore, the overall uncertainty of the instantaneous measurement of equivalence ratio may exceed 30% in flames if the ‘bad’ measurements with low SNR are not removed. Such a large variation limits the accuracy of instantaneous measurements. A data processing method was proposed to remove the points with low SNR. Considering the SNR distributions of H/O and C₂/CN, thresholds 0.4×10^7 and 1×10^7 intensities were applied respectively for H/O and C₂/CN intensity ratios. These points, whose intensities are lower than the threshold, were removed. Through this method, the data left still had a small measurement uncertainty even in flames.

4.2.7 Data processing method

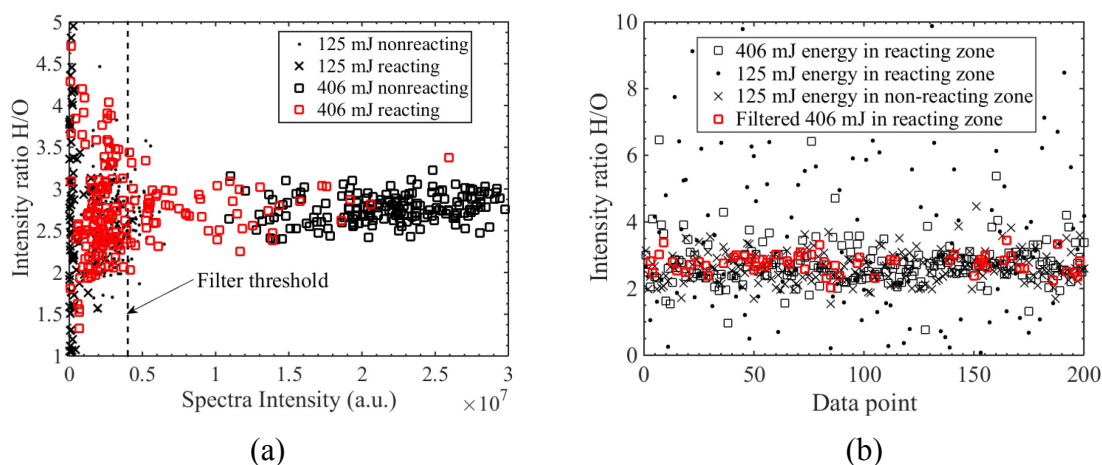


Figure 4.25 Intensity ratio H/O obtained in mixture of CH₄-air for 200 single shot spectra using 125 mJ and 406 mJ laser pulse energy in reacting and non-reacting zones with equivalence ratio of 0.6

Figure 4.25 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. Since the methane-air mixture was perfectly premixed, such variability of the H/O intensity ratio was mainly caused by the variation of plasma SNR. In Figure 4.25 (a), the increase of laser pulse energy can lead to better SNR and reduce the variation in both non-reacting and reacting zones. Compared to results in the non-reacting zone, the reacting zone measurement intensity for both 125 mJ and 406 mJ data moved towards the left side in Figure 4.25 (a). Their relative standard deviations (RSD) in the reacting zone ($x=0$ mm, $z=15$ mm) rose from 20% to 80% and from 10% to 20% for 125 mJ and 406 mJ results respectively. In Figure 4.25 (b), after applying the threshold of 0.4×10^7 intensity to filter the ‘bad’ data, measurements with laser pulse energy of 406 mJ in the reacting zone maintained a very narrow distribution, which is below 10%. Therefore, by using higher laser pulse energy and the threshold level for the raw data, the RSD for laser pulse energy of 406 mJ in the reacting zone is still below 10% for instantaneous measurements. Similarly, for high fuel concentration, threshold (1×10^7 intensity) was applied for C₂/CN intensity ratio. The relative standard deviation was below 15%.

4.2.8 LIBS measurements in diffusion flames

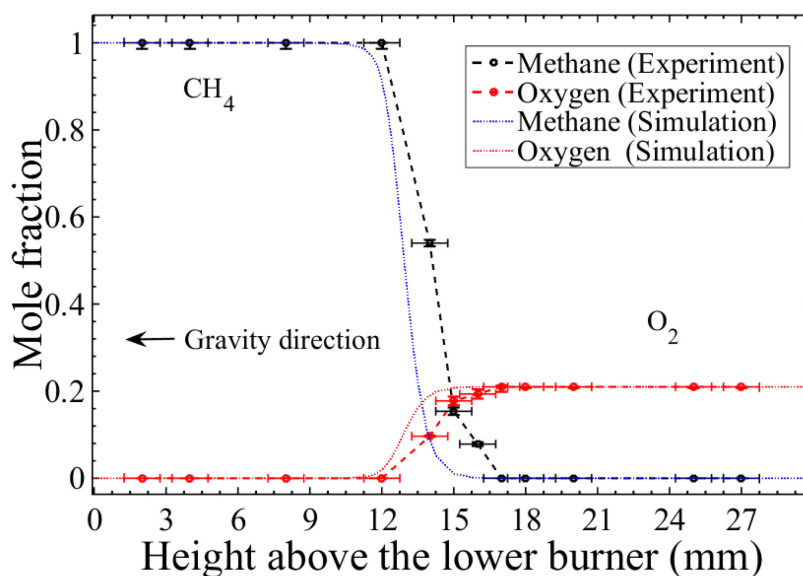


Figure 4.26 Spatial distribution of methane and oxygen mole fractions in a methane-air counterflow diffusion flame obtained from LIBS measurements and CHEMKIN simulation. Methane and air streams both exit the jets at area-averaged velocity of 50 cm/s

Table 4.3 Operating conditions for diffusion opposed jet flame

Parameters	Values
Bottom nozzle flow rate	21.2 l/min CH ₄
Top nozzle flow rate	21.2 l/min air
Nozzle area-averaged velocity	0.5 m/s
Reynolds number of air	993.1
Reynolds number of CH ₄	910
Strain rate	33.3 s ⁻¹
Flow rate uncertainty	3%

In order to evaluate the local equivalence ratio measurement across a laminar diffusion flame, pure methane and air streams were injected from the lower and upper jets with an area-averaged velocity of 50 cm/s respectively, producing a global flow strain rate of 33.3 /s, as shown in Table 4.3. Co-flow of nitrogen was used to quench the secondary flames at large radial locations. The same operating condition was set up and simulated using CHEMKIN GRIMech 3.0. The measurements started from the lower nozzle jet exit and progressed along the centreline ($x=0$ mm, $z=0\sim30$ mm) to the upper nozzle jet exit, using 406 mJ laser pulse energy. Figure 4.26 shows the methane and oxygen mole fraction distributions along the centre line using the calibration results from Figure 4.13, 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 1.5 mm, which is probably due to buoyancy effects acting on the flame, there is a good agreement between the simulation and experimental results.

4.3 Summary

In this chapter, the ability of LIBS technique to quantify local variations of the mixture fraction of methane/air mixtures was studied in both premixed and diffusion flames. The behaviour of plasma was analysed spatially, spectrally and temporally. The factors, including laser pulse energy, delay time and exposure time of the ICCDs, were investigated. Appropriate calibration between the H/O and C₂/CN intensity ratios and local equivalence ratio has been performed. The relationship between plasma image and spectra also shows that the LIBS result is independent of the plasma shape and the uncertainty of intensity ratios H/O and C₂/CN depends on the SNR of each laser shot. The presence of a flame at the location of the LIBS measurements increased the standard deviation of the measured local equivalence ratio greatly due to lower SNR caused by the low gas density and laser beam steering caused by the high refractive index gradients in the flames. The measurement uncertainty followed a linear relationship with the path length of the laser beam in the flames, which is consistent with the theory. Therefore, increasing the SNR of the measured spectra is the main method to ensure accuracy of the instantaneous LIBS measurement in flames.

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 and using a proposed processing method based on the calculation of the SNR of the spectra, which resulted in uncertainty below 10% for the instantaneous measurement of local mixture composition even in flames. When methane mole fraction is higher than 50%, the instantaneous measurement uncertainty increases to 15% due to quenching effects.

Finally, the LIBS technique was 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.

Chapter 5 LIBS measurements in hydrocarbon blends

5.1 Introduction

In Chapter 4, the LIBS technique was applied to a methane-air mixture. The potential of the technique to be used with different gases is investigated here. This investigation also involves assessing the capability of the technique to measure fuel composition in fuel blends independently, as well as the equivalence ratio as previously shown. The effects of different hydrocarbon gas blends on the LIBS spectra are evaluated.

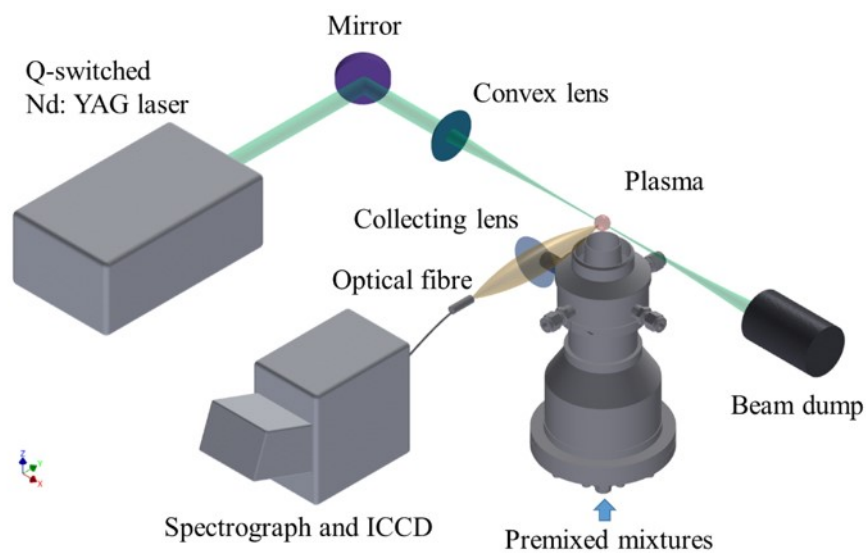


Figure 5.1 Schematic of LIBS and flow arrangement for hydrocarbon blends measurement

In this chapter, LIBS measurement of mixture composition was investigated over a wide range of mixture fractions of C_3H_8 , CO_2 , H_2 , CH_4 and air. As shown in Figure 5.1, the LIBS experiment is conducted in premixed hydrocarbon mixtures, supplied from the lower nozzle of the counterflow burner after the upper nozzle is removed. Both atomic and molecular emissions were used to detect compositions in binary mixtures of hydrocarbons. The dependence of the atomic and molecular emissions on the concentration of hydrocarbon fuels was explored, as well as the influence of laser power. The quenching effects on LIBS spectral intensity emissions were also discussed due to the nonlinear behaviour of spectra for various hydrocarbon mixtures.

5.2 Results and discussion

5.2.1 LIBS in CH₄ and C₃H₈ mixtures

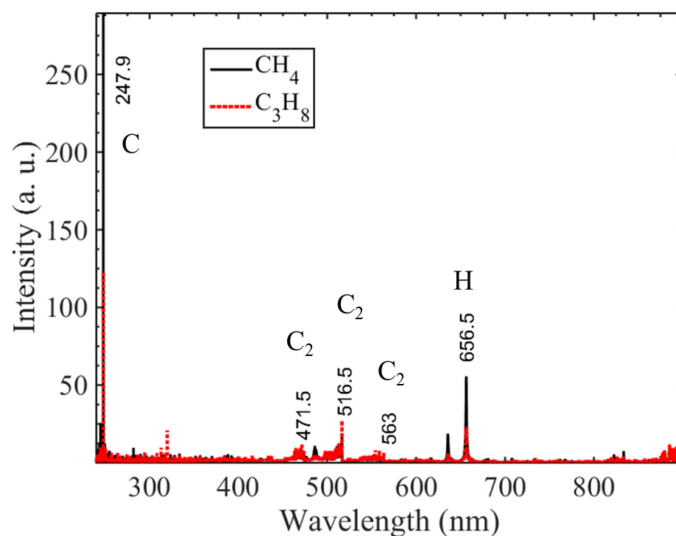


Figure 5.2 Comparison of LIBS spectra in pure CH₄ and C₃H₈ gases with 1 μ s delay, 50 μ s gate time and laser pulse energy of 406 mJ

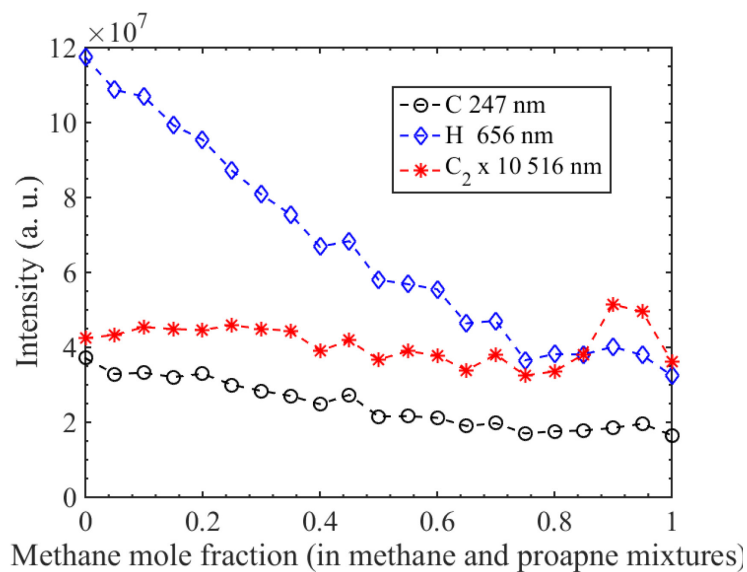


Figure 5.3 Total intensity of C, H and C₂ spectral lines of the LIBS spectra. Measurements are in methane and propane mixtures with 406 mJ laser pulse energy and the spectra are recorded with delay time 1 μ s and gate time 50 μ s.

The measured spectra were the averages over 50 laser shots, collected with a 1 μ s delay and 50 μ s gate width. Since both pure methane and propane consist of H and C atoms, they should have similar peaks of atomic and molecular spectral lines. The element concentration difference between methane and propane in the plasma volume led to the intensity variations in the spectra. In the spectra of Figure 5.2, atomic lines, H at 656.6 nm and C at 247 nm, and molecular lines, C₂ swan band at 471.5 nm, 516 nm and 563.5 nm, were all observed in the spectra. The molecular intensity of C₂ was stronger for pure propane, resulting from its higher

concentration of C atoms. However, the atomic lines of C and H were relatively weak for pure propane, compared to pure methane spectra.

This trend can also be observed in Figure 5.3, which shows the intensity for the spectral lines of C, H and C_2 as a function of the methane mole fraction in mixtures of methane and propane. Similar observations have been reported by other researchers [101,112]. This decay in atomic emissions cannot be explained by Maxwell Boltzmann equation (Eq. (2.10)), since the optically thin assumption is not fully satisfied. This decay is similar to quenching of atomic emissions observed during LIF measurements, due to radiationless decay [101] (Decay of an atom or molecule from an excited state to a lower energy state without the emission of electromagnetic radiation). In the plasma evolution, a variety of processes can result in quenching, such as excited state reactions, energy transfer, complex-formation and collisional quenching. The complex mechanisms within the plasma volume render the quenching of excited states in plasma impossible to model theoretically.

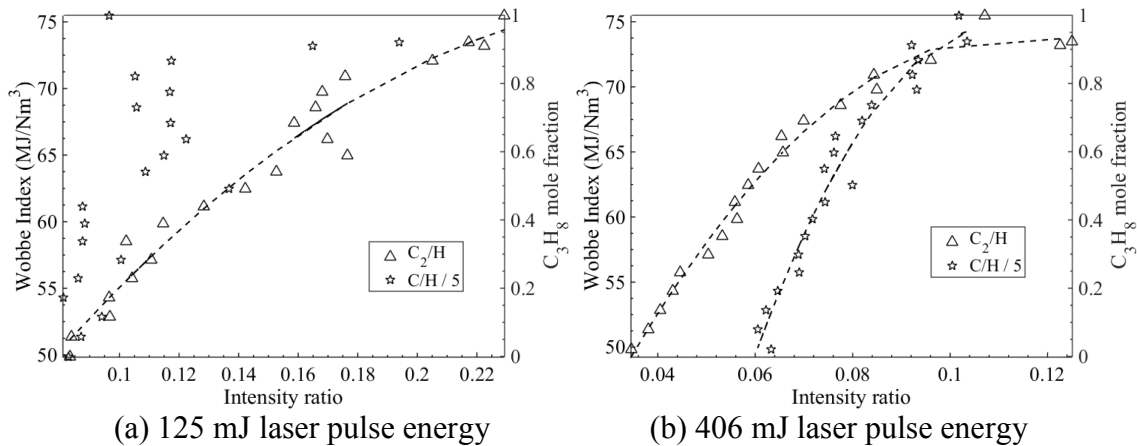


Figure 5.4 Averaged intensity ratios of C_2/H and C/H , appearing in the LIBS spectra, as a function of the mole fraction of propane. Measurements are in premixed propane-methane mixtures with laser pulse energy of 125 mJ (a) and 406 mJ (b), and the spectra are recorded with delay time 1 μ s and gate time 50 μ s.

Although the hydrocarbons contain the same elements, the abundance of C and H atoms plays a major role in LIBS spectral emissions from propane-methane mixtures. Figure 5.4 (a) shows that the C/H curve has a large variation and does not work properly for the determination of mixture fraction or Wobbe index for the low laser pulse energy of 125 mJ. This phenomenon was mainly caused by the quenching of high concentration of C and H atoms, which reduced the SNR of the measurement. As observed in Figure 5.4 (b), for binary mixtures of methane and propane using high pulse energy of 406 mJ, C/H and C_2/H intensity ratios were found to

depend monotonically and almost linearly on the mole fraction of propane. Both these intensity ratios were measured in the non-reacting zone of premixed propane-methane mixture and the spectra were recorded with delay time 1 μ s and gate time 50 μ s. In order to ensure the SNR, higher pulse energy was more suitable for the high atom concentration fuels. The curves can be used to infer propane/methane fuel mixture compositions. Based on the measured composition of a fuel mixture, the Wobbe index of the fuel blend can also be obtained using the information of Figure 5.4.

5.2.2 LIBS measurements in C_3H_8 and air mixtures

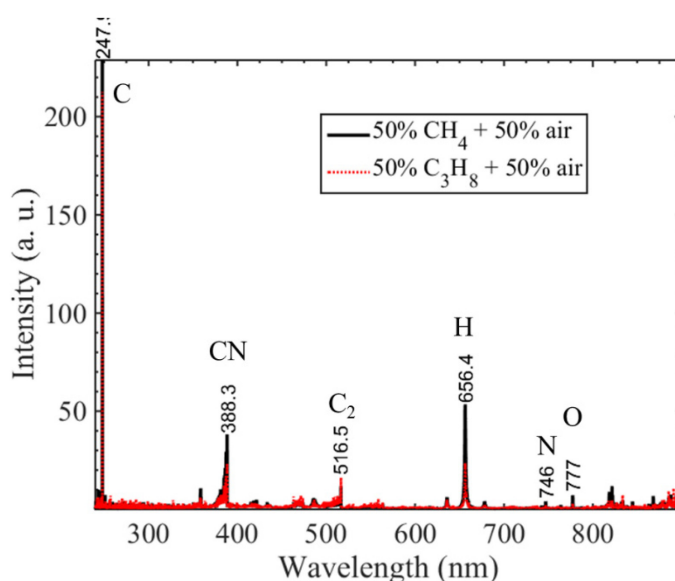


Figure 5.5 Comparison of the LIBS spectra of non-reacting methane-air mixture and propane-air mixture with spectra recorded with 1 μ s delay, 50 μ s gate and 406 mJ laser pulse energy

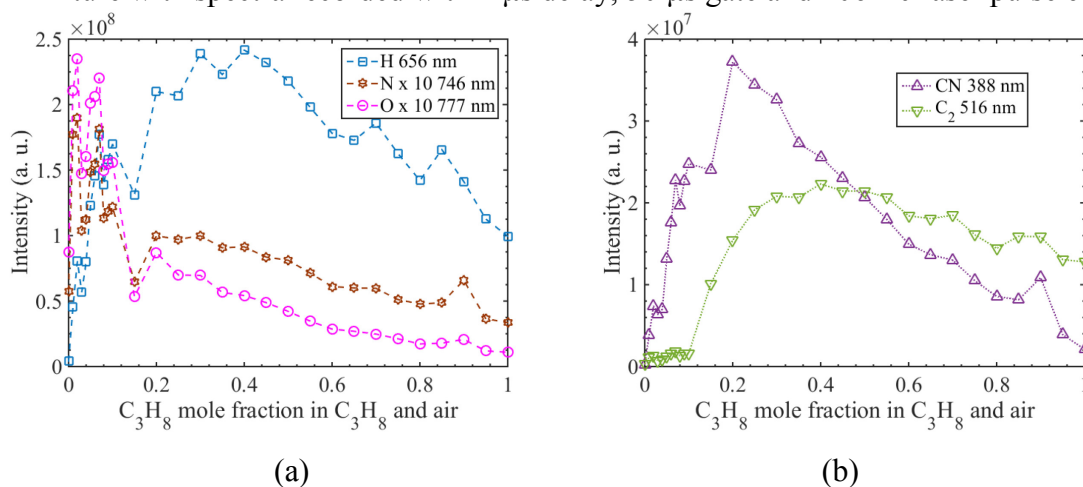


Figure 5.6 Total intensity of H (656 nm), N (746 nm) and O (777 nm) atomic lines (a) and CN (388 nm) and C_2 (516 nm) (b) molecular bands of the LIBS spectra in non-reacting premixed propane-air mixtures as a function of propane mole fraction. Spectra were recorded with 1 μ s delay, 50 μ s gate and 406 mJ laser pulse energy.

Similar to the methane-air mixture spectra, which were investigated in the previous chapter, the propane-air mixture spectra consist of atomic and molecular emission lines, as shown in Figure 5.5. Compared with the methane-air spectra, the atomic lines are relatively weak and the molecular lines are strong in the propane-air spectra. This decay in atomic emissions is same as the trend in pure methane and propane mixtures, as shown in Figure 5.6.

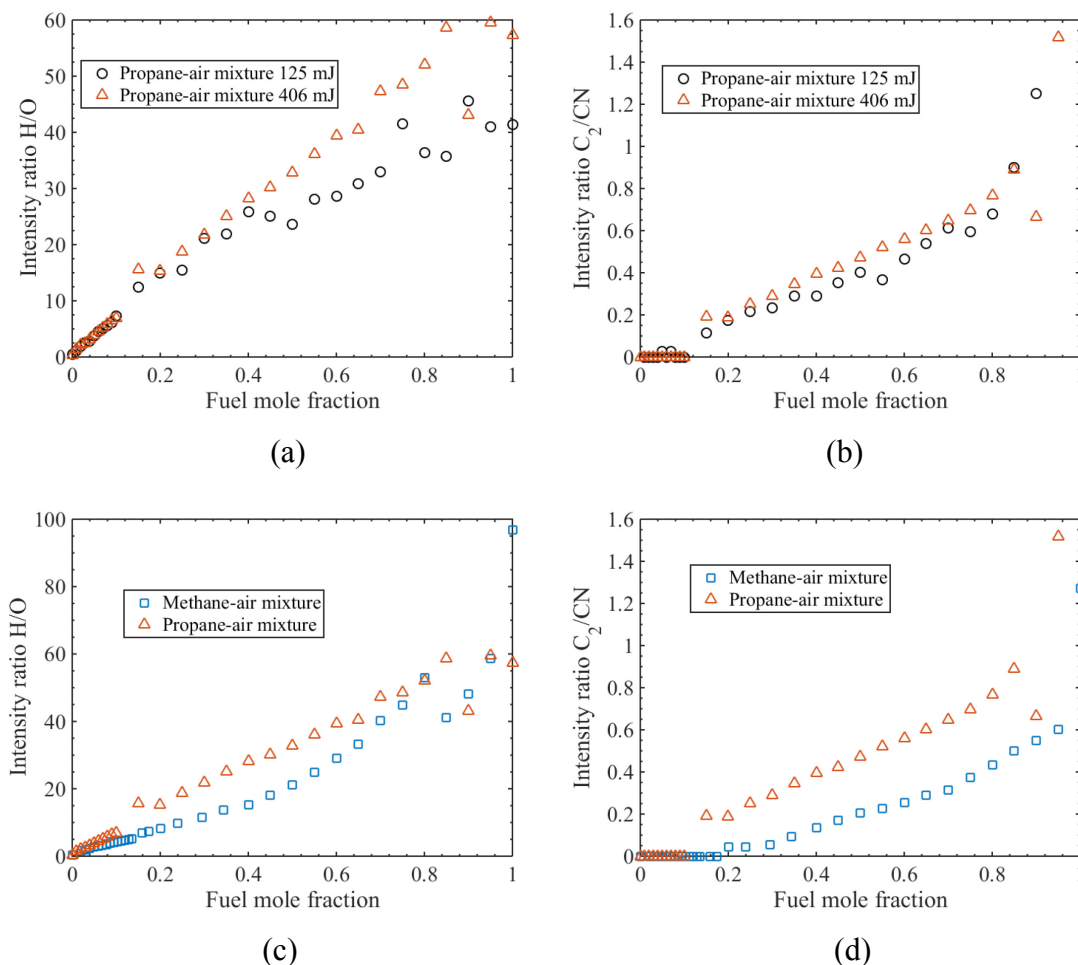


Figure 5.7 Correlation between propane mole fraction and intensity ratio of H/O (a) and C_2/CN (b) of the LIBS spectra measured in non-reacting premixed propane-air mixtures. H/O (c) and C_2/CN (d) intensity ratios of the LIBS spectra measured in non-reacting premixed methane-air and propane-air mixtures. LIBS spectra were measured with 1 μs delay, 50 μs gate and 406 mJ laser pulse energy.

Figure 5.7 illustrates quantitative concentration measurements with LIBS based on an experimental calibration under different laser pulse energies and mixture compositions. Figure 5.7 (a) and Figure 5.7 (b) show that lean premixed propane – air mixtures have nearly the same curve for different laser energies. In Figure 5.7 (c) and Figure 5.7 (d), it can be seen that both the premixed methane-air and propane-air mixtures show a linear relationship between fuel

concentration and the different intensity ratios. Similar to the calibration curve of methane-air mixtures, the propane-air mixture compositions also can be inferred from the H/O and C₂/CN intensity ratios, but the calibrations, as expected, are not identical to those for premixed methane-air mixtures.

5.2.3 LIBS measurements in CO₂ and CH₄ mixtures

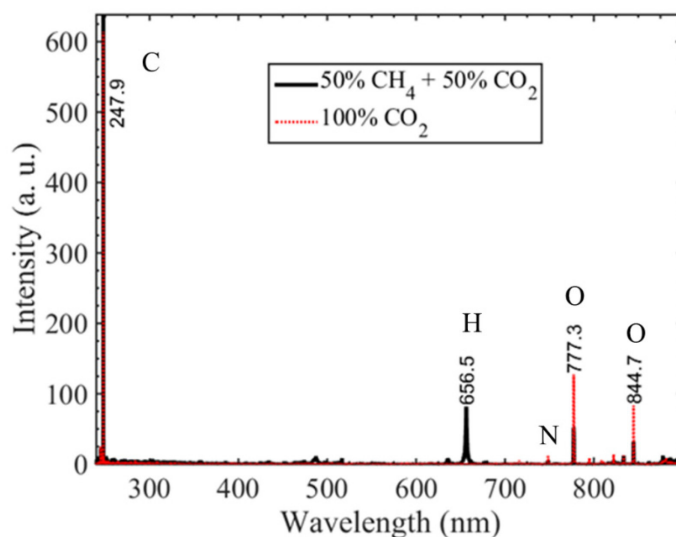


Figure 5.8 LIBS spectra from Pure CO₂ and a premixed CH₄+CO₂ mixture recorded with 1 μ s delay, 50 μ s gate and 125 mJ laser pulse energy

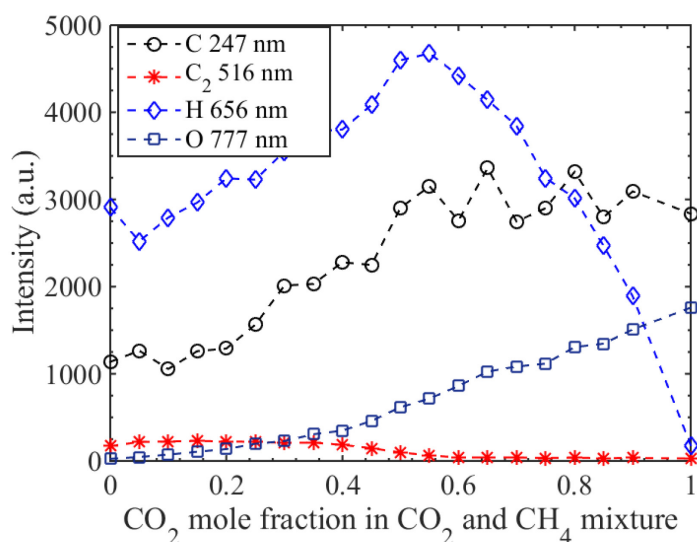


Figure 5.9 Intensity of different emission spectral lines as a function of CO₂ mole fraction measured in premixed CO₂ and CH₄ mixtures with 1 μ s delay, 50 μ s gate and 125 mJ laser pulse energy

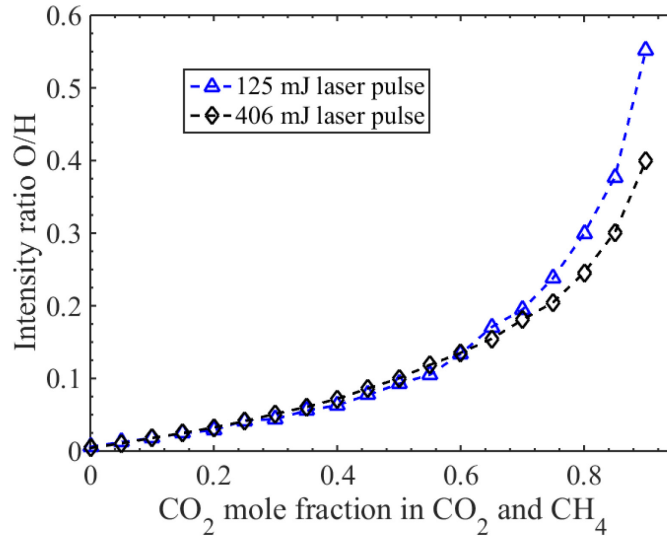


Figure 5.10 Effect of laser pulse energy on O/H intensity ratio as a function of CO₂ mole fraction. LIBS spectra measured in premixed CO₂ and CH₄ mixtures with 1 μ s delay and 50 μ s gate.

In industrial applications, the supplied natural gas fuel blend generally contains a certain amount of CO₂. The variation of CO₂ concentration in a fuel blend may be responsible for the initiation of combustion instabilities. Based on the above industrial background, the LIBS spectra were investigated in a wide range of CO₂ and CH₄ mixtures, from pure CO₂ to pure CH₄, as shown in Figure 5.8. The purpose was again to assess the ability of LIBS to act as a monitoring sensor of fuel blend variability. For a typical spectrum of a CO₂ and CH₄ mixture (50% CH₄+50% CO₂), the atomic lines C, H and O and molecular lines C₂ appeared in the spectra of Figure 5.8, as expected.

In Figure 5.9, the nonlinear behaviour of H and C₂ spectral line intensities with the mole fraction of CO₂ in the CH₄ and CO₂ mixture was observed, as previously, due to quenching effects at high C concentration. Other spectral line intensities, including O and C, increase with the concentration of CO₂ in the mixture. However, the C spectral line intensity remains constant for CO₂ mole fractions above 50% due to quenching.

In the mixture of the CO₂ and CH₄, the O line from the CO₂ and H line from the CH₄ can be used to infer the CO₂ mole fraction for different laser pulse energies, as shown in Figure 5.10. Therefore, the intensity ratio O/H is directly related to the CO₂ mole fraction in the mixture. This monotonic relationship between the intensity ratio and CO₂ concentration provides a good method to measure CO₂ concentration from LIBS spectra in CO₂ and CH₄ mixtures. This

demonstrates again the ability of LIBS to act as a sensor to monitor variability of supplied fuel blend and quantify the resulting Wobbe index.

5.2.4 LIBS measurements in CO₂ and air mixtures

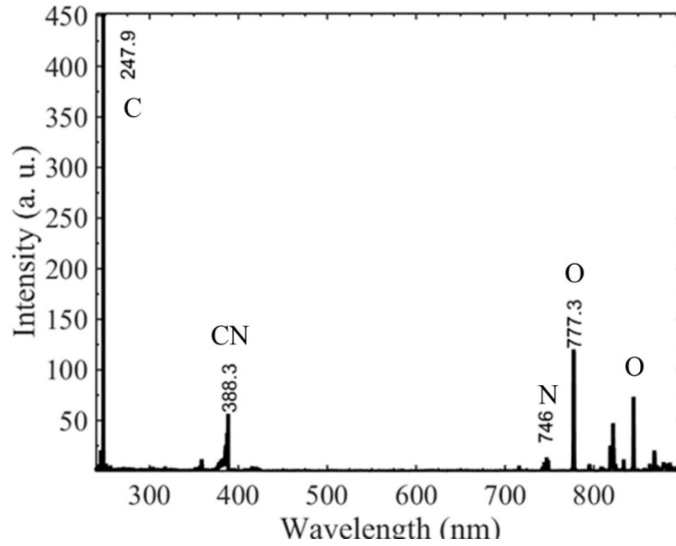


Figure 5.11 LIBS spectra measured in premixed mixture of 50% CO₂ and 50% air with 1 μ s delay, 50 μ s gate and 125 mJ laser pulse energy

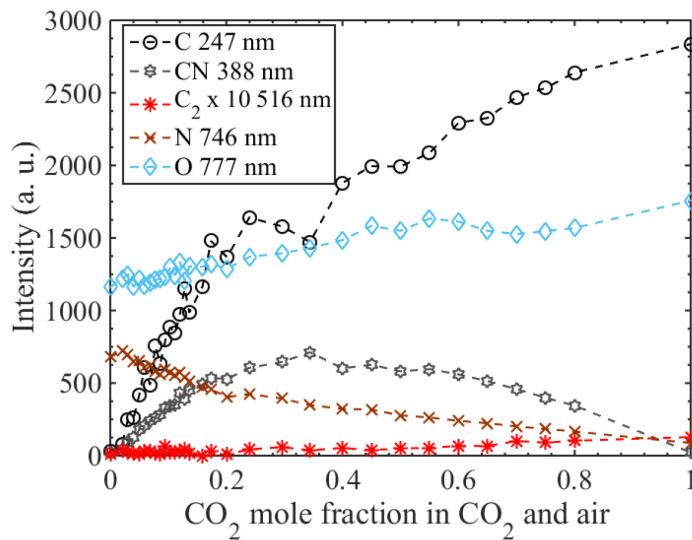


Figure 5.12 Different spectral line emission intensities as a function of CO₂ mole fraction in premixed CO₂ and air mixtures. LIBS spectra measured with 1 μ s delay, 50 μ s gate and 125 mJ laser pulse energy.

LIBS spectra from premixed CO₂ and air mixtures are shown in Figure 5.11 and provide important references to the study of mixtures of reactants and products, which are commonly present in combustors. In the CO₂ and air mixture LIBS spectra, all the spectral lines except the H line were observed, as expected. In Figure 5.12, as the CO₂ mole fraction exceeds 0.7,

the atomic and molecular lines become saturated and begin to decay with the increase of CO_2 mole fraction. Comparison to results for mixtures of CH_4 and CO_2 diluents in air are very useful. Since both molecules have the same number of carbon atoms, the substitution of CO_2 by CH_4 represents significant hydrogen addition. In Figure 4.12 and Figure 5.12, it can be found that methane-air spectra intensity saturates at 0.3 mole fraction, which is faster than the CO_2 -air mixture. It indicates that the hydrogen can increase the emission saturation speed. Further comparisons between CO_2 -air mixture and CH_4 -air mixture spectra will be analysed in section 5.2.8.

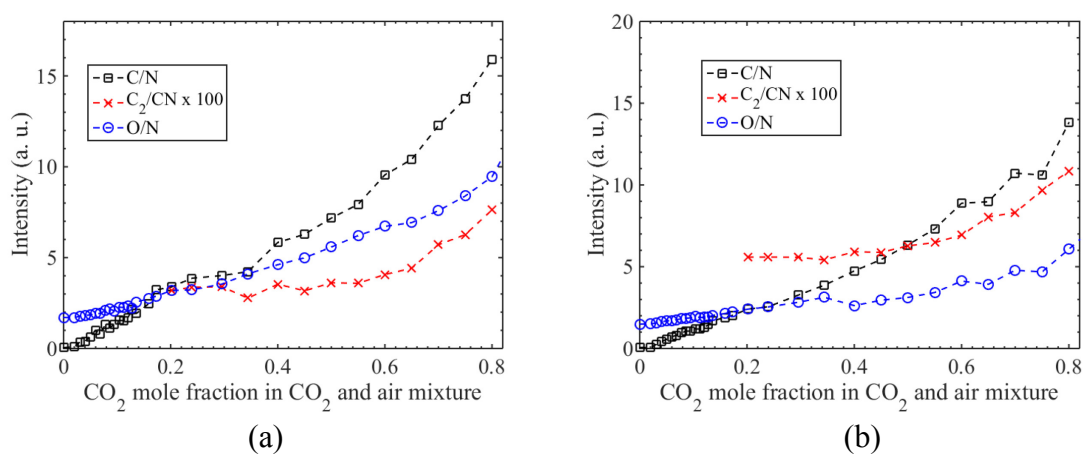


Figure 5.13 Intensity ratio of C/N as a function of CO_2 mole fraction in premixed CO_2 and air mixtures. LIBS spectra measured with 1 μs delay, 50 μs gate and laser pulse energy of 125 mJ (a) and 406 mJ (b)

Figure 5.13 shows that, although the nonlinear behaviour still exists without hydrogen elements, the atomic intensity ratios C/N and O/N and molecular intensity ratio C_2/CN , can still perform well as indicators for the CO_2 mole fraction in the mixtures. Each point corresponds to the average of 50 shots. Therefore, for binary CO_2 mixtures (CH_4 - CO_2 mixture and CH_4 - air mixture), the CO_2 concentration can be measured directly using LIBS. In methane-air flames, the difference between the spectra of reactants (CH_4 and air) and the spectra of products (CO_2 , H_2O and N_2) is very small, as discussed in Chapter 4. It is still difficult to use LIBS to measure CO_2 concentration in methane-air flames.

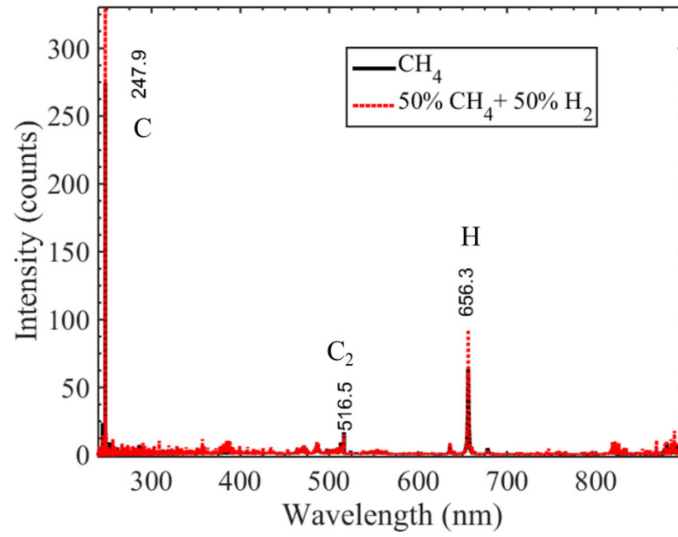
5.2.5 LIBS measurements in H₂ and CH₄ mixtures

Figure 5.14 Comparison of LIBS spectra of pure methane and a premixed methane-hydrogen mixture, measured with 1 μ s delay, 50 μ s gate time and 406 mJ laser pulse energy

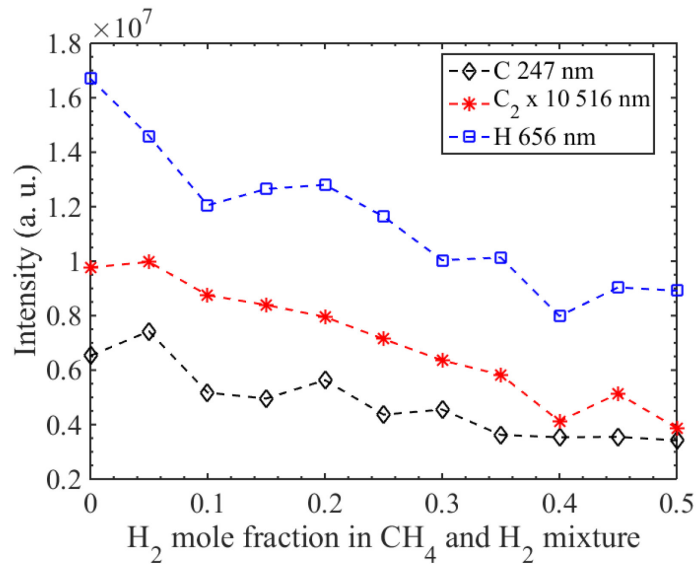


Figure 5.15 Effect of H₂ concentration on the intensity of different spectral lines in premixed methane and hydrogen mixtures. LIBS spectra measured with 1 μ s delay, 50 μ s gate and 125 mJ laser pulse energy.

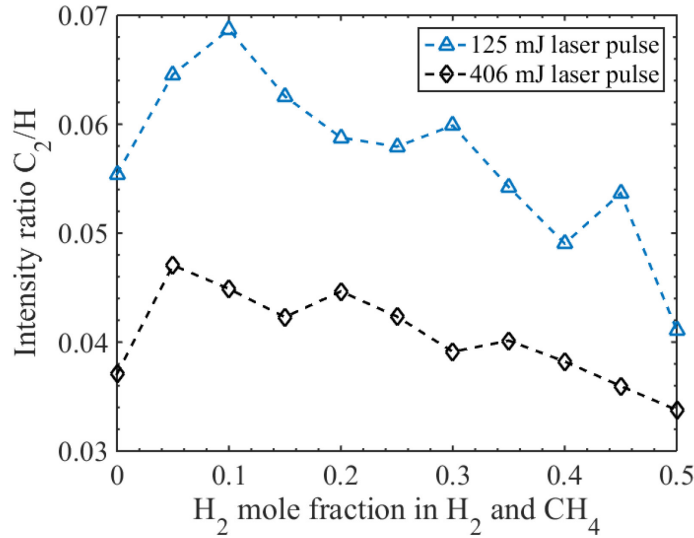


Figure 5.16 Effect of laser pulse energy on intensity ratio C_2/H as a function of H_2 mole fraction in premixed methane-hydrogen mixtures, measured with 1 μs delay and 50 μs gate

The addition of hydrogen gas into methane can increase the flame speed and decrease soot formation in flames. Generation of hydrogen by using available energy from renewable sources has been proposed for future sustainable energy. Therefore, monitoring of variability of hydrogen concentration in fuel blends may be important for control of combustion processes in industrial power plants and LIBS may be a candidate for online monitoring of fuel blends.

The LIBS spectra, presented in Figure 5.14, show that hydrogen concentration increases the intensity of the H spectral lines at 656 nm remarkably, as expected. However, the observed changes on the intensity of the C and C_2 spectral lines are small. A possible explanation is that the H atoms in CH_4 are already at high concentration and the displacement of CH_4 by H_2 in the mixture is not large enough to reduce the C atoms in the LIBS spectra.

Figure 5.15 illustrates the variation of the intensity of spectral lines of C 247 nm, C_2 516 nm and H 656 nm as a function of H_2 mole fraction in the H_2 and methane mixtures. LIBS spectra were measured with a delay of 1 μs and a gate of 50 μs and laser pulse energy of 125 mJ. The spectra for each condition are based on an average of 50 shots. It could be seen in Figure 5.15 that all these spectral lines decreased with H_2 concentration. A main reason is that the displacement of methane by H_2 in the mixture dilutes the elemental concentration of H in the resulting mixture inside the LIBS sampling volume.

Figure 5.16 shows the intensity ratios of C_2/H as a function of the mole fraction of H_2 in the mixtures. Due to the dilution effect of the increased H_2 addition to the methane - H_2 mixture, the intensity ratio does not show a linear relationship with the H_2 mole fraction. It is necessary, when inferring the local H_2 composition in methane, to consider not only the intensity ratio but also the intensity of each spectral lines. Therefore, when LIBS is used to monitor the H_2 concentration in fuel blends, the full LIBS spectra should be analysed firstly to infer all the elements existing in the mixture. Secondly, the intensity of spectral lines and the intensity ratios between elements need to be considered using the information in Figure 5.15 and Figure 5.16. Then, the H_2 concentration in mixture and the Wobbe index can be obtained. If the mixture contains more than two constituents, more information about the mixture besides the LIBS spectra is needed.

5.2.6 LIBS measurements in H_2 and air mixtures

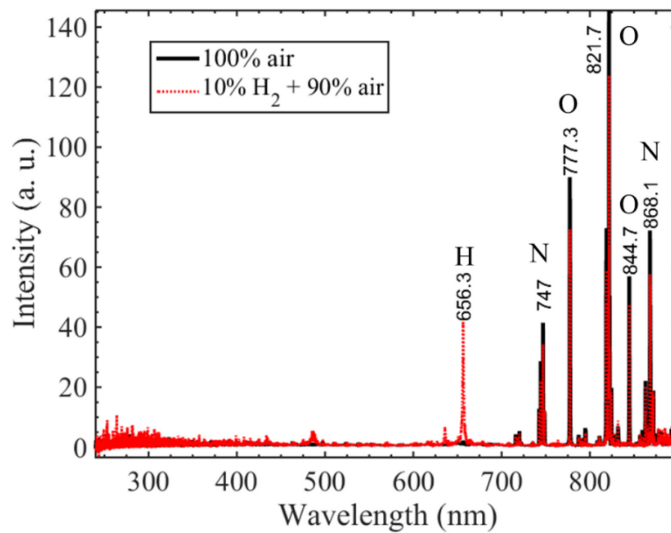


Figure 5.17 LIBS spectra for a mixture of 10% H_2 and 90% air and for pure air, measured with 1 μs delay, 50 μs gate and 125 mJ laser pulse energy

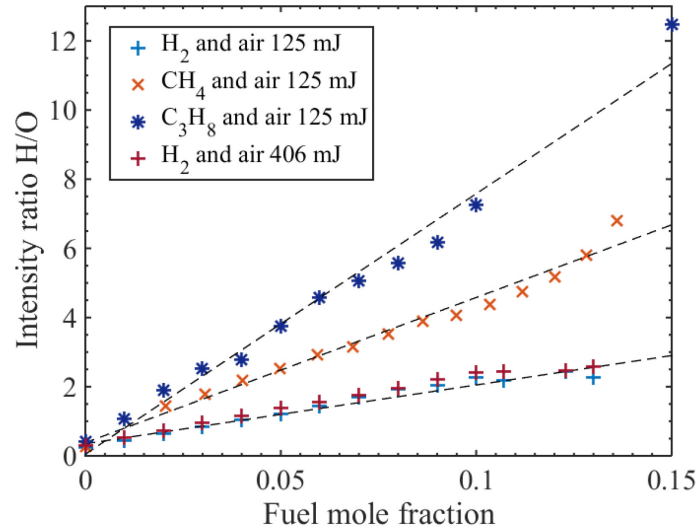


Figure 5.18 Correlation between fuel mole fraction in air and intensity ratio of H/O spectral lines of the LIBS spectra, measured with 1 μ s delay, 50 μ s gate and 125 mJ laser pulse energy

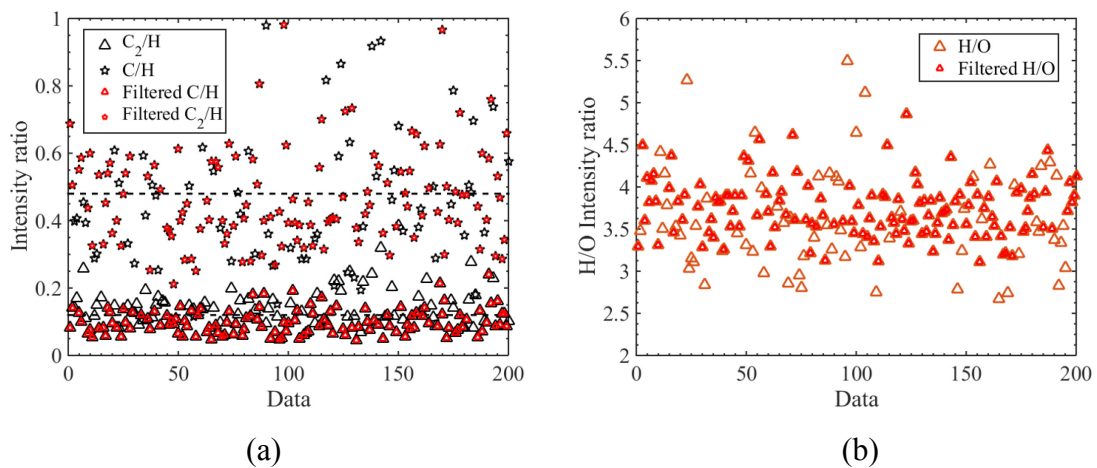
The LIBS spectra from hydrogen and air mixtures can provide important information to assist with the understanding of the observed atom H effects. Figure 5.17 shows that the addition of hydrogen reduces the N and O spectral line intensities, as expected. Due to the strong emission from atom H, the spectra are very sensitive to the addition of hydrogen. 10% hydrogen addition results in the strong H atomic line at 656 nm in the spectra. Figure 5.18 illustrates the intensity ratio of H to O spectral lines as a function of corresponding fuel mole fraction in the mixtures of hydrogen, methane or propane with air. Each data point is an average of 50 laser shots, obtained with 1 μ s delay relative to the laser pulse and 50 μ s gate time. These relationships remain linear over the range of corresponding fuel mole fractions from 0 to 0.15, which includes pure Hydrogen as well as methane and propane.

The H has complex effects on the LIBS spectra of fuel-air mixture. In the lean conditions, the ratio H/O increases by a factor of 2 from H₂ to CH₄ and a factor of 2 from CH₄ to C₃H₈. This result agrees approximately with the number of H atoms and O atoms in each fuel. However, in the fuel-rich mixtures, the H atoms already have a high concentration and the quenching effects of H become obvious. Under the conditions, the increase of fuel concentration does not lead to the increase of H emission in the spectra and the linear relationship between the spectral intensity and H atom concentration does not exist, as shown in Figure 4.12 and Figure 5.6 (a). Therefore, for Wobbe index measurements, the intensity of H lines does not represent the H atom concentration directly. Other elemental intensity should be considered as well.

5.2.7 Shot-to-shot variations of LIBS measurements in different hydrocarbon mixtures

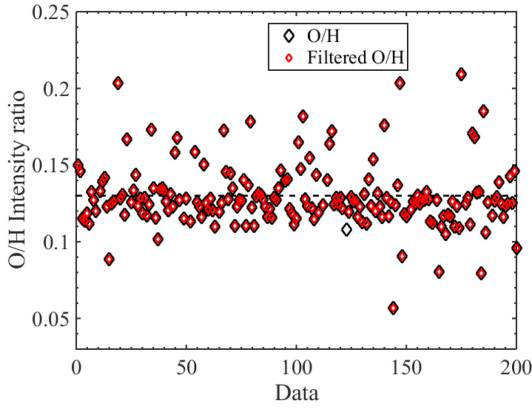
Hydrocarbon fuel blends may be subject to temporal fluctuations of fuel composition, which must be detected correctly from any sensor that is trying to monitor the process and quantify the Wobbe index. Therefore, in order to use LIBS with appropriate precision for online-monitoring of the Wobbe index of the fuel blends, there is a need to assess the uncertainty of instantaneous LIBS measurements in various hydrocarbon mixtures. As a consequence, LIBS measurements were carried out in premixed hydrocarbon mixtures and the results are based on the analysis of 200 shots for each condition.

Chapter 4 evaluated the shot-to-shot variations of LIBS measurements of mixture composition in methane-air mixtures and quantified the variation of the relative intensity ratios used to infer the composition. It also identified the origin of the variation and developed an approach that reduces the measurement uncertainty in reacting flows. In this section, the shot-to-shot variation of the measured mixture composition by LIBS in hydrocarbon fuel blends or mixtures of other hydrocarbon with air (apart of methane-air mixtures) is quantified. Figure 5.19 shows the typical shot-to-shot variations of the relative intensity ratios of the LIBS spectral lines and the RSD (relative standard deviation) for a variety of non-reacting mixtures. In Chapter 4, it has been found that the main difference between the non-reacting and reacting LIBS spectra is that, the reacting flames decrease the SNR of the spectra. Using the filter method to remove low SNR results, the shot-to-shot variation is not influenced by non-reacting or reacting conditions.

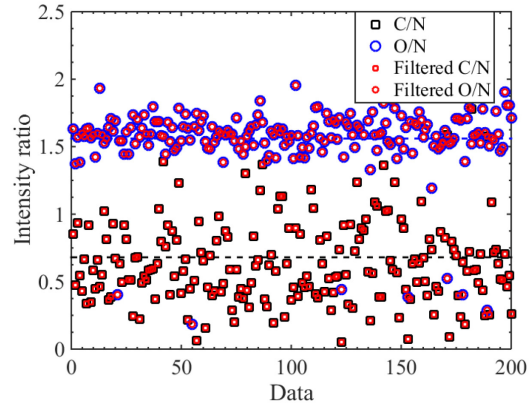


(a) 50% CH₄ and 50% C₃H₈ mixtures (44% RSD for C₂/H and 38% RSD for C/H, 36% RSD for filtered C₂/H and 21% RSD for filtered C/H with SNR threshold of 2×10^7 intensity)

(b) C₃H₈ and air mixtures with equivalence ratio=1.0 (12% RSD and 8.8% RSD for filtered H/O with SNR threshold of 1×10^7 intensity)



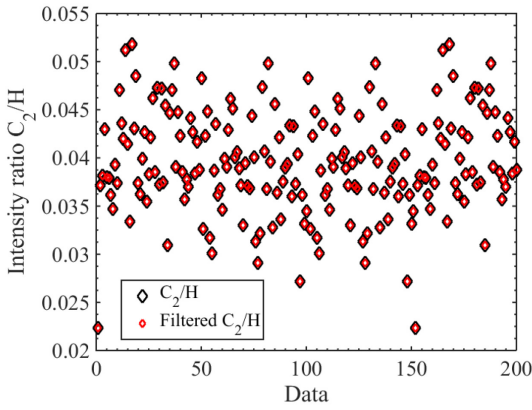
(c)



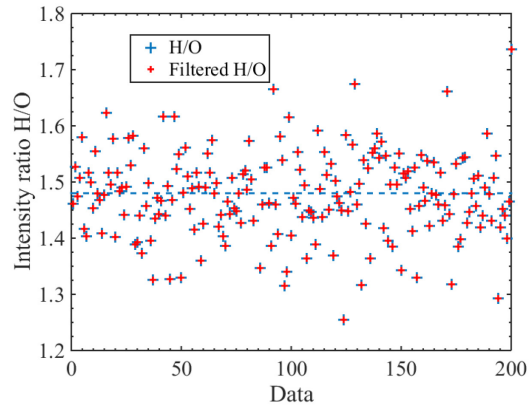
(d)

(c) 50% CH₄ and 50% CO₂ mixtures (17% RSD for O/H and 17% RSD for filtered with SNR threshold of 1×10^7 intensity)

(d) 6% CO₂ and 94% air mixtures (45% RSD for C/N and 16% RSD for O/N, 45% RSD for filtered C/N and 16% RSD for filtered O/N with SNR threshold of 1×10^7 intensity)



(e)



(f)

(e) 15% H₂ and 85% CH₄ mixtures (14% RSD for C₂/H, 14% RSD for filtered C₂/H with SNR threshold 1×10^7 intensity)

(f) 5% H₂ and 95% air mixtures (6% RSD for H/O, 6% RSD for filtered H/O with SNR threshold of 1×10^7 intensity)

Figure 5.19 Variation of different intensity ratios of spectral lines of shot-to-shot LIBS spectra measurements obtained in non-reacting different premixed hydrocarbon mixtures using laser pulse energy of 406 mJ pulse, 1 μ s delay and 50 μ s gate time. The corresponding mixture composition and the resulting shot-to-shot fluctuations are indicated in each label.

The fluctuations of the intensity ratios vary significantly for different hydrocarbon mixtures, as shown in Figure 5.19. In Figure 5.19 (a)~(e), each data point corresponds to a single shot measurement with the LIBS system in perfectly premixed mixtures having the indicated composition. Therefore, the observed variation is due to measurement error associated to the LIBS technique. Similar to the results and theories of the methane-air mixture fluctuations of Chapter 4, the LIBS precision became worse in mixtures when the measurements were

conducted in the combustion region and with high concentration of hydrocarbon fuels, which increases the quenching effects and reduces the Signal-to-Noise Ratio (SNR). By increasing the laser pulse energy and filter out the low SNR data, using the method proposed in Chapter 4, the uncertainty can be reduced to some extent. In Figure 5.19 (a) and (b), the uncertainty in $\text{CH}_4/\text{C}_3\text{H}_8$ and $\text{C}_3\text{H}_8/\text{air}$ mixtures is reduced after applying the filter method. However, for mixtures in Figure 5.19 (c)~(f), the data with high SNR still have a large variation. Filtering out the ‘bad’ data cannot increase the accuracy. The mixtures containing high concentration of fuel have large RSD in LIBS results. This could potentially suggest that a greater stochasticity of the plasma processes might be associated with the reduction of the intensities of the emission lines and their following detection, leading to a larger variation in the fuel-rich mixtures [112]. In addition, the spectrometer has relatively low quantum sensitivity to the C emission at 247 nm, as shown in Figure 3.12.

Therefore, in lean hydrocarbon-air mixtures, the uncertainty of LIBS measurements of mixture composition is around 10%. In fuel-rich mixtures, the uncertainty of LIBS measurements rises to 30%. When measuring the Wobbe index, the gas is already the fuel-rich mixture. The uncertainty of Wobbe index measurement has a 30% uncertainty, generally. After filtering out the ‘bad’ data with low SNR, the non-reacting or reacting conditions do not affect the results.

5.2.8 Quenching effects in LIBS measurements

The Maxwell Boltzmann equation (Eq. (2.10)) describes the relationship between the excited species population and the spectral intensity. The intensity of spectral emission is proportional to the excited concentration for a limited concentration range. However, at high concentrations of the excited species, the linear dependence is not satisfied anymore. The main reason is the significant collisional quenching between certain species. Collisional quenching occurs when the excited species contact with an atom or molecule that can facilitate non-radiative transitions to the ground state.

From most of hydrocarbon mixtures discussed above, it can be found that the atomic lines appear weaker for fuel-rich mixtures. These experiments show that the chemical composition, especially the abundance of C and H atoms, plays a major role in LIBS spectra of mixtures of air and hydrocarbons. The abundance of C and H atoms can result in saturation and even decay

of atomic spectral line intensities, perhaps caused by quenching effects between the species themselves.

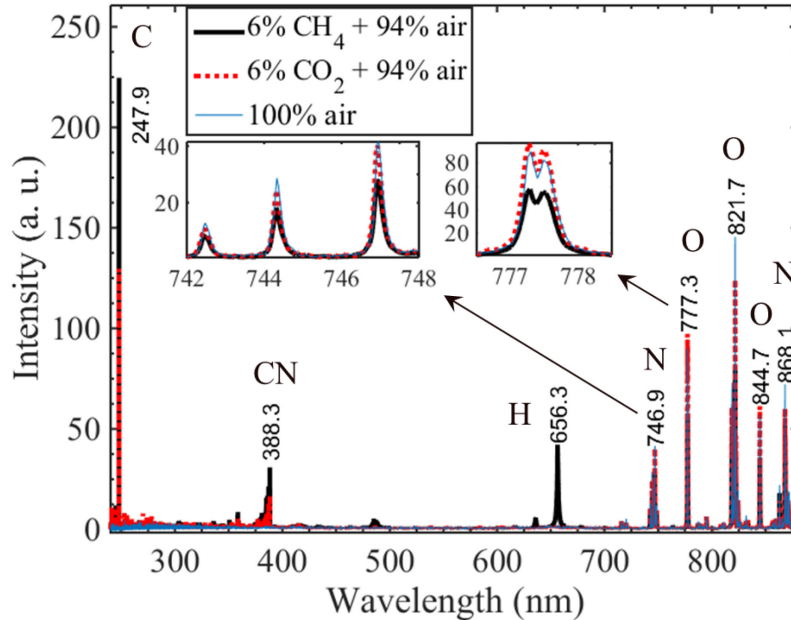


Figure 5.20 Comparison of LIBS emission spectra of CO_2 and CH_4 - air premixed mixtures and pure air, measured with 1 μs delay, 50 μs gate time and 125 mJ laser pulse energy.

Figure 5.20 compares LIBS spectra, measured with 1 μs delay, 50 μs gate time and 125 mJ laser pulse energy, in premixed mixtures of 6% CH_4 in air, 6% CO_2 in air and pure air. Through the comparison of CO_2 and CH_4 in air, the CN emission is increased by the presence of hydrogen. Compared with the pure air spectra, the addition of CH_4 also decreases the O and N lines. Similar results are observed in the addition of C_3H_8 in air as shown in Figure 5.21. To a large extent, the presence of hydrogen changes the relative concentrations of molecules that recombine in the cooling plasma. The emitting and quenching species in the plasma are also changed, which influences the N and O emissions. Therefore, the experiments showed that the addition of even small quantity of hydrogen increases the CN emissions perceptibly and decreases the atomic emissions, such as O and N, as shown in Figure 5.17 and Figure 5.20.

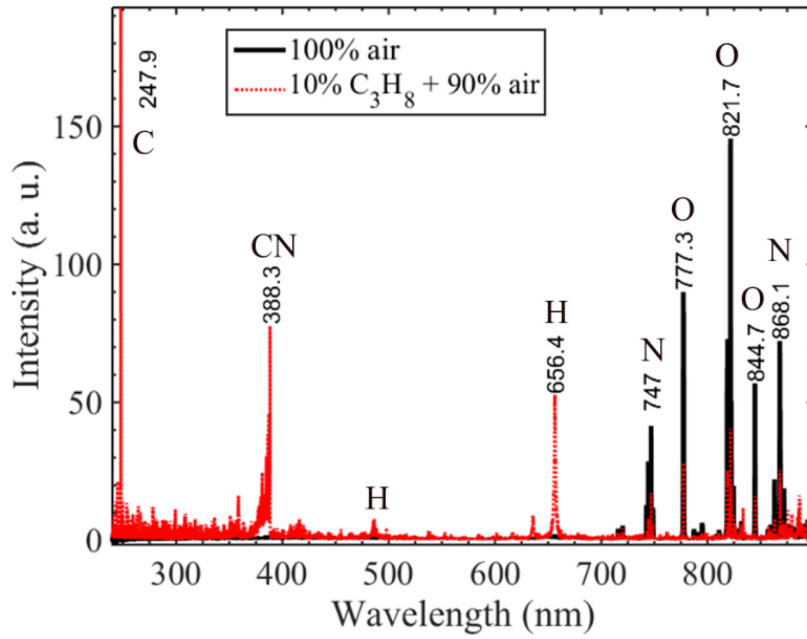


Figure 5.21 Comparison of LIBS emission spectra of pure air and propane-air mixtures, measured with 1 μ s delay, 50 μ s gate time and 125 mJ laser pulse energy

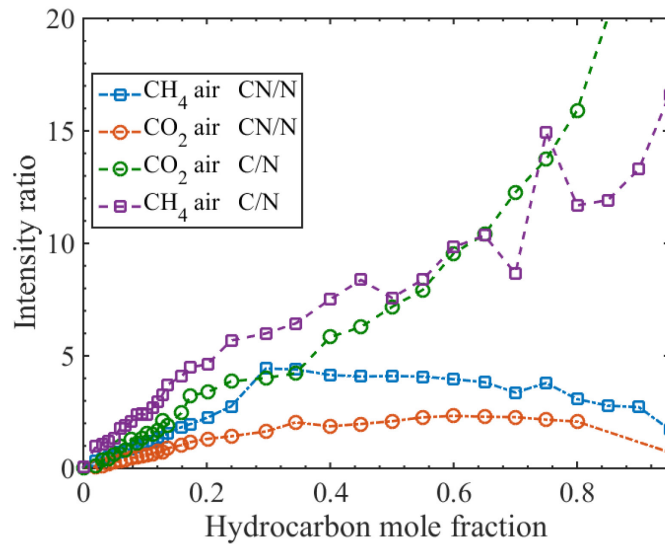


Figure 5.22 Intensity ratios of the LIBS spectral lines CN/N and C/N as a function of the mole fraction of methane or carbon dioxide, measured in non-reacting premixed mixtures with 1 μ s delay, 50 μ s gate time and 125 mJ laser pulse energy.

Figure 5.22 shows that the intensity ratios of CN/N and C/N as a function of mole fraction of CO₂ or CH₄ in air. Over a wide range of mole fraction, CN/N intensity ratio illustrates the effects of the presence of hydrogen, which increases the CN emissions for all mole fractions. The C/N intensity ratio also includes the quenching effects of hydrogen on the N line, thereby resulting in the lower C/N intensity ratio in CO₂ and air.

Therefore, H emission is an important indicator in LIBS measurement, due to its strong intensity and existence in hydrocarbon fuels. However, as mentioned above, H has complex effects on the LIBS spectra. On the one hand, hydrogen increases the CN emissions perceptibly and decreases the atomic emissions, such as O and N. On the other hand, in the lean fuel - air mixtures, the intensity of H has a linear relationship with number of H atoms in each fuel. In the fuel-rich mixtures, the linear relationship between the spectral intensity and H atom concentration does not exist, due to the quenching effects. This conclusion is valid for both addition of hydrocarbons fuels into air (in Figure 4.12 and Figure 5.6) and replacement of CO₂ with CH₄ in CO₂ in and air mixtures (in Figure 5.20 and Figure 5.22).

5.3 Summary

The results presented in this chapter illustrated the use of LIBS as a sensor for evaluation of the mixture composition of hydrocarbon mixture blends. The LIBS spectra were obtained in premixed binary hydrocarbon fuel blends and demonstrated the ability to infer the fuel blend composition using different intensity ratios for different mixtures. This demonstrates that real time monitoring of variation of the resulting Wobbe index due to fluctuation of the mixture composition is possible with the LIBS technique. While limitations exist, the spectral line intensity and the intensity ratios of different spectral lines can be used to infer the composition of fuel blends and the resulting Wobbe index, especially for binary hydrocarbon mixtures. If the blended fuels have more than two constituents, additional information is required for the determination of Wobbe index using LIBS. Therefore, each fuel blend must be specified and calibrated in advance in order to assess the accuracy of LIBS measurements and their ability for real time monitoring of fuel composition.

After applying the filter method, in lean hydrocarbon-air mixtures, the uncertainty of LIBS measurements of mixture composition is around 10%. In the fuel-rich mixtures, the uncertainty of LIBS measurements of mixture composition increases to 30%, which is mainly caused by the quenching effects (the reduction or limitation of an excited-state population). The contribution of quenching effects on the spectral intensities of the LIBS spectra was investigated. It was found that the addition of hydrogen, either as pure hydrogen or as a component in hydrocarbons, increased CN spectral line intensity and decreased atomic emissions for spectral lines of O and N. Rich mixtures of hydrocarbon in air also lead to the decay in the intensity of the spectral atomic lines due to the increased concentration of C and H. The complex mechanisms increase the difficulty of LIBS measurements in blends.

Chapter 6 Laser-induced plasma image velocimetry (LIPIV)

6.1 Introduction

Chapter 4 and Chapter 5 use the LIBS plasma spectra to obtain mixture composition measurements. This chapter develops a novel laser-induced plasma image velocimetry (LIPIV) technique that is based on tracking the laser-induced plasma as a function of time in space. Therefore, the laser-induced plasma behaviour is analysed spatially, temporally and spectrally. The dependence of the accuracy of velocity measurements with the technique on the delay time between subsequent plasma images and the image processing methods are evaluated in quiescent air. The velocimetry technique is then used to measure the velocity field of a straight round turbulent air jet and compared to typical behaviour of turbulent jets.

6.2 Fluid dynamic characteristics of laser-induced plasma

Besides the electromagnetic and spectral properties discussed in Chapter 2, the laser-induced plasma generates complex fluid mechanics phenomena locally in a gas as well. The understanding of the flow induced by the plasma is important for the development of the velocimetry technique. Due to the complexity of the plasma, the magnetic field induced by the electrical current passing through the plasma is neglected and the whole plasma is in the LTE state. At the start of the breakdown, a plasma kernel forms along the axis of the laser beam. Then, the majority of the laser energy is absorbed by the kernel front facing towards the laser beam, resulting in the ionic region expanding from the focal point towards the lens (Figure 6.1). To model the plasma temporal evolution in a gas, researchers [150] resort to numerical methods to solve the mass, momentum and energy transport equations.

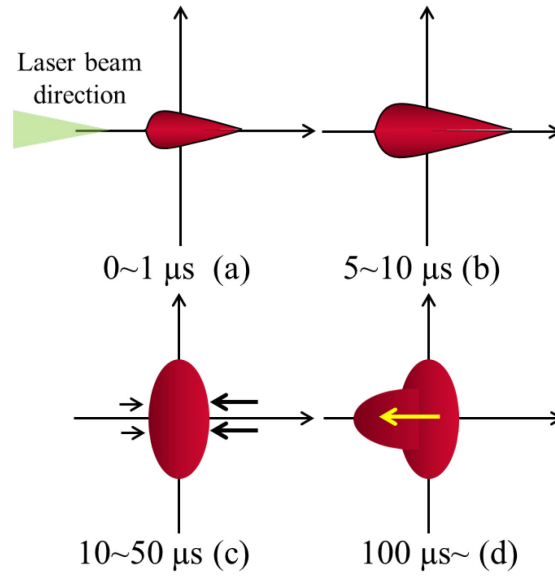


Figure 6.1 Typical temporal evolution process of nanosecond laser induced plasma. [142,151]

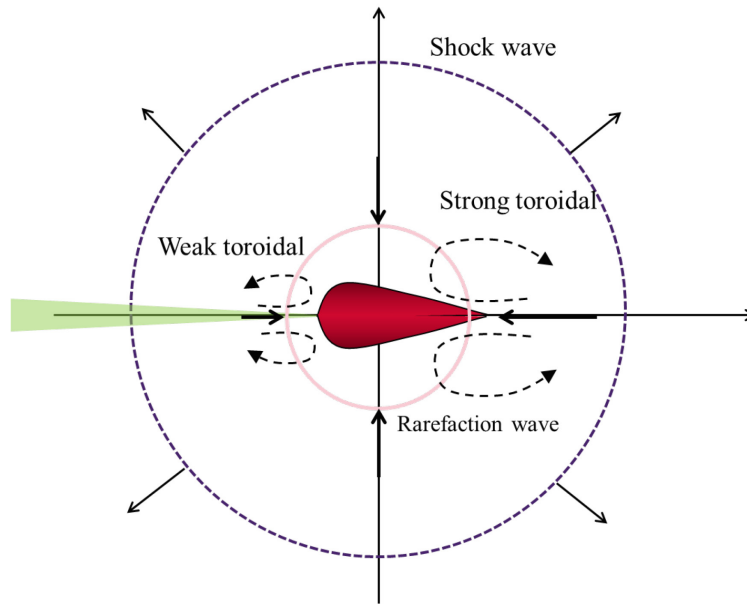


Figure 6.2 Relative position of shock and rarefaction waves and initiating plasma kernel at a time of around 5 μs after the laser pulse. [142]

The laser-induced plasma decay process in a gas has been studied both experimentally and numerically by several researchers [138–142]. When the plasma is created in a gas, a shock wave moves outwards. The temperature and pressure of the inner gas region begin to decrease with time. The plasma size increases in the first 5 μs after its creation. As shown in Figure 6.2, the rarefaction wave produces a pressure gradient towards the plasma centre. The gas with lower density is accelerated more by the pressure gradient than the gas of high density in a Taylor instability [152]. As a consequence, the right hand side hot gas in Figure 6.2 moves

more persistently inwards than the left hand side gas, which is less dense, and subsequently it is accelerated to a higher velocity, which decays rapidly. This velocity difference between the laser-induced plasma gases results in vortex generation, which is more persistent at the front of the laser beam rather than at the region behind the focal point. The subsequent collapse of the two opposed jet-like fronts generates vortices that form a toroidal shape around the optical axis of the laser beam from around 5 μs after the laser pulse [138]. This toroidal flow structure deforms the ellipsoidal shape of the plasma, so that its principal axis is changed orthogonally with time (see Figure 6.1(b) and Figure 6.1(c)). Since the toroidal structure is not symmetric, the laser-induced flow velocity along the laser beam axis at a later time is towards the laser source and generates a third lobe in that direction, as shown in Figure 6.1(d). The measured temporal evolution of the plasma images of Figure 4.2 confirm the schematic description of Figure 6.1. Therefore, due to the asymmetric energy distribution in the gas and subsequent asymmetric expansion, the asymmetric collapse of the plasma leads to the collapsing front moving towards the laser beam direction. Some researchers attribute the generation of the third lobe to the gas movement ‘upstream’ from the focal point due to the ionized front of the plasma propagating towards the laser at the early stages of the laser-induced plasma [153]. However, this movement is not expected to last for a long time when the laser pulse ends. Therefore, most of the studies attribute this process to the over-expanded region explained above. Since these plasma kernel structures are developed due to the vertical motions generated by the interaction of the pressure field and the flow, caused by the asymmetric deposition of laser energy along the laser beam direction, the behaviour of the plasma is sensitive to the initial pressure field. These processes have been analysed by different researchers using various techniques, including LIF, shadowgraphy and imaging [142,151,154]. This process is similar to the observed flow for plasma-induced by electrical sparks [155].

Therefore, the asymmetric laser energy deposition and the ionization effects determine the fluid properties in the post-breakdown period and the flow pattern is characteristic of the laser induced plasma decay. This induced flow will be considered in the subsequent development of the Laser Induced Plasma Image Velocimetry (LIPIV) technique.

6.3 Plasma behaviour in quiescent air

The spatial, temporal and spectral behaviour of the laser-induced plasma was presented in Chapter 4 and some characteristics, relevant to the velocimetry technique are considered here again. As shown in Figure 4.2 of Chapter 4, the laser-induced plasma image was recorded with an Andor ICCD camera for 125 mJ laser pulse energy and at a time of $100\ \mu\text{s} \sim 110\ \mu\text{s}$ after the laser pulse. We examine here the details of the plasma at the beginning of the breakdown. Figure 6.3 shows that the laser-induced plasma expands outwards in all directions from the focal volume. Since the optical energy enters the plasma from the focusing lens side, this side has the largest expansion rate. The overexpansion of the inner gas causes the pressure void in the centre, eventually, reversing the direction of flow and filling the pressure void. At time of $10\ \mu\text{s}$, the plasma is sheared into two parts. One part remains on the optical axis, indicated as the lobe shape, and the other part forms a toroidal ring surrounding the laser beam axis, which is then pulled into a vortex pair between 20 to $200\ \mu\text{s}$, as seen in Figure 6.3.

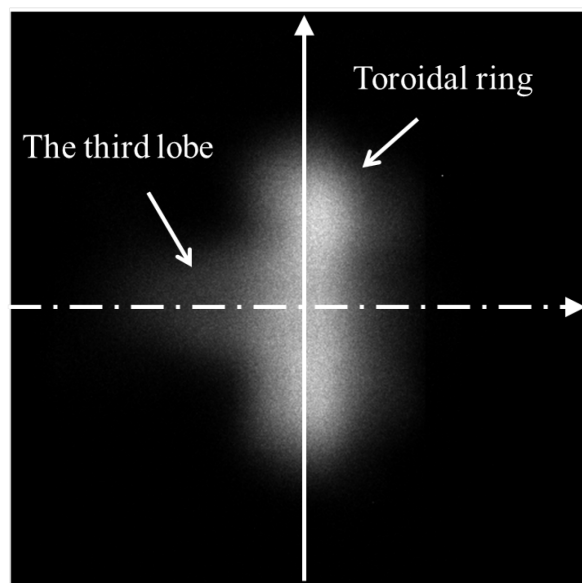


Figure 6.3 Plasma image obtained with 125 mJ laser pulse energy during the $100\ \mu\text{s} \sim 110\ \mu\text{s}$ time window in air

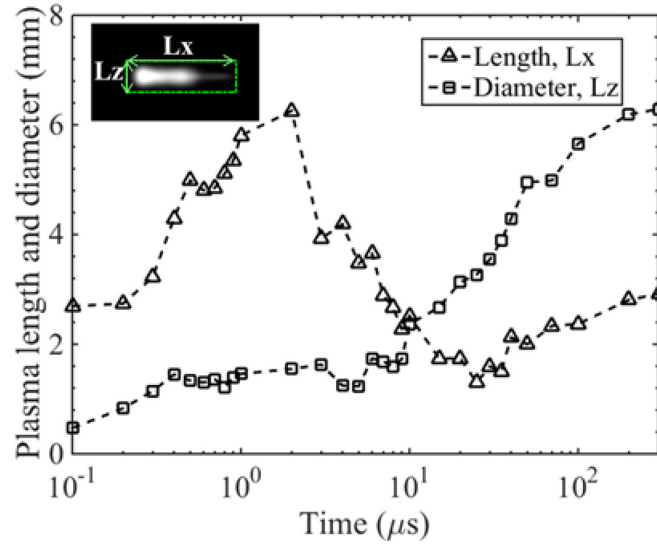


Figure 6.4 Plasma length L_x and diameter L_z as a function of time after a laser pulse with 125 mJ pulse energy in air. X and Z coordinates are along and normal to the direction of the laser beam respectively

In Chapter 4, Figure 4.9 shows the temporal evolution of the plasma in methane-air mixtures. Similar to Figure 4.9, Figure 6.4 shows the plasma size temporal evolution in air. It can be found that both the horizontal length L_x and the vertical diameter L_z increased with time after the laser pulse and began to decrease after around 1~2 μs . After 20 μs , both the L_x and L_z began to grow continuously again until the plasma disappeared due to the void collapse in plasma. The lengths of L_x and L_z jointly determine the probe volume at different times. Therefore, for a laser pulse with energy of 125 mJ in air, the probe volume grows up to around 2.5 mm x 5 mm x 5 mm region at time 100 μs after the laser pulse initiation, which is important for the spatial resolution of the laser induced plasma velocimetry technique. As was also shown in Chapter 4, larger size plasma leads to larger Signal-to-Noise Ratio (SNR) of the detected spectral intensities, which means that temporal tracking of the plasma for velocimetry measurements is easier. At the same time, larger size plasma reduces the spatial resolution of the velocity measurement in a flow. Therefore, there is a need to compromise between SNR of LIBS spectral intensity and spatial resolution of the LIPIV technique.

Typically, the temporal and spatial resolution of LIPIV is around 100 μs and 5 mm, respectively. It is useful to compare this to the other velocimetry techniques mentioned in section 1.2.3. The temporal resolution of PIV [156] is generally as small as 100 μs . Its spatial resolution is determined by processing algorithms that average the velocity of tracers over a spatial region called the interrogation window. Reducing the size of the interrogation window can lead to

higher spatial resolution; however, the SNR ratio of the data is also reduced, leading to greater uncertainty. Hot-wire anemometers use a very fine wire, of the order of several micrometres, which corresponds to its spatial resolution. Its temporal resolution can be as small as $1\ \mu\text{s}$ with a continuous analogue output. A typical commercial LDV technique [74] has a spatial resolution of typically a few millimetres long, which corresponds to the size of the probe volume of the intersecting beams. The temporal resolution of LDV can be high, of the order of $1\ \text{ms}$, depending of the seeding density of the tracers. In comparison with these other techniques, the temporal resolution of LIPIV shows potential for measuring high frequency velocity fluctuations, however, it may be limited by its low spatial resolution. The spatial resolution could be improved by reducing the laser pulse energy and focus spot size. However, the laser pulse energy cannot be reduced below the energy required for gas breakdown, which ensures the gas can still be ionised. With these considerations in mind, the spatial resolution could be improved up to $1\ \text{mm}$.

6.4 LIPIV methodology

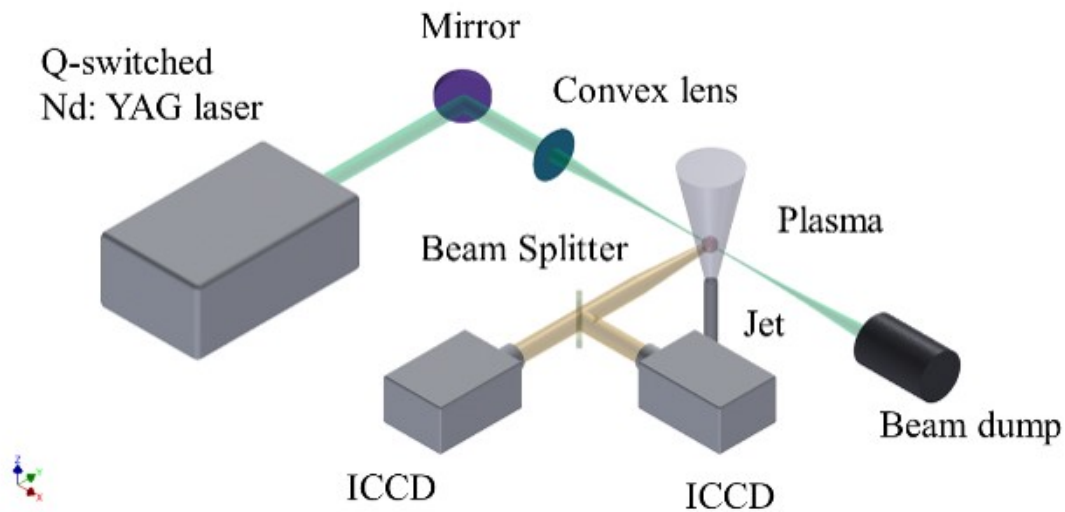


Figure 6.5 Schematic diagram of the LIPIV experiment setup

For the LIPIV experimental arrangement of Figure 6.5, a focused pulsed laser beam generates plasma at a point of a fluid flow. The local fluid velocity vector convects the induced plasma in a fluid flow during its lifetime. As a consequence, if the plasma is recorded at two instances in time with delay Δt , its displacement due to the flow field can be quantified and, as a consequence, the flow velocity is estimated using the known time delay.

For the LIPIV method, the measured velocity $u_m(x, t)$ can be decomposed as:

$$u_m(x, t) = u(x, t) + u^*(x, t) \quad (6.1)$$

In Eq. (6.1), u is the velocity component of the flow field and u^* is a velocity component originated by the laser induced plasma, which represents an uncertainty. The contributions to u^* of Eq. (6.1) include:

- (a) The asymmetric pressure wave in the flow with respect to axes perpendicular to the laser beam axis, generated by the laser-induced plasma, may disturb the local flow field.
- (b) The fluctuations of the laser beam shape, camera sensitivity and buoyancy effects on the plasma displacement.

Therefore, the original mean flow velocity and the time-averaged root mean square of the velocity fluctuations u_{rms} can be calculated by Eq. (6.2) and Eq. (6.3), after removing the corresponding uncertainty components from the measured velocity.

$$\bar{u} = \bar{u}_m - \bar{u}^* \quad (6.2)$$

$$u_{rms} = \sqrt{u_{m,rms}^2 - u_{rms}^{*2}} \quad (6.3)$$

These measurements are estimated by averaging over a certain number of measured instantaneous velocities, obtained from different laser-induced plasma realisations.

6.5 Results and discussion

6.5.1 LIPIV calibration in quiescent gas field

In quiescent air, the original flow velocity is zero and the resulting velocity uncertainty u^* of Eq. (6.1) can be evaluated independently. In addition, the effects of the image processing methods and timing settings for the plasma recordings can be evaluated and optimized.

Processing I: bounding box centre

The first image processing method for tracking the laser-induced plasma is based on a bounding box centre approach.

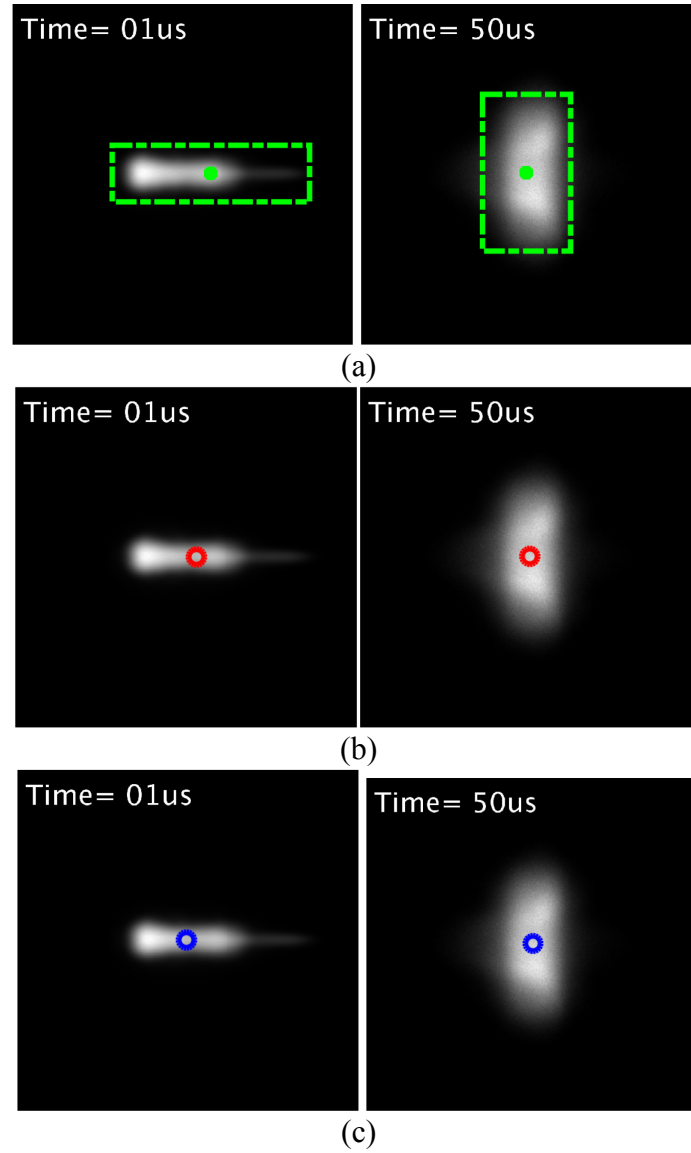


Figure 6.6 Plasma image processing methods based on bounding box centre (a), geometric centre (b) and weighted centroid (c) of the plasma. The laser beam was incident from the left hand side and all the images spanned 11.5 mm horizontally and 11.5 mm vertically. The identified plasma centre is green for the bounding box centre method, red for the geometric centroid method and blue for the weighted centroid.

To process the pair of recorded plasma images, they are firstly converted into binary format. The smallest rectangle containing the plasma was identified on the image, using a developed MATLAB code, as shown in Figure 6.6. The main concept of the underlying processing is that the smallest rectangle containing the plasma is less sensitive to plasma shape and noise presented on the image. When using this method, the first image was obtained at time $1\ \mu\text{s}$ after the laser pulse initiation, which helped locate the plasma kernel. Then, after a delay time ranging from $25\sim 300\ \mu\text{s}$, the second image was recorded. A moderate delay time between the two plasma images allowed a plasma displacement of the order of 1 mm, which was large

enough to reduce the uncertainty and ensure proper temporal and spatial resolution. The centre of the bounding rectangle can be identified directly from the intersection of the two diagonals of the rectangle (green spot on images). The centroid was then tracked for the time delay between the two images and the displacement was quantified. Since the camera position is fixed during the experiment, the plasma displacement can be calculated simply from the plasma centre difference between the two sequential images in Figure 6.6. The two-dimensional velocity vector was then calculated from the displacement and the time delay and two velocity components were estimated, namely the horizontal component, which was along the laser beam axis, and the vertical component, which was normal to the axis of the laser beam. The velocity in quiescent air must be zero. Therefore, the deviation of the measured velocities from zero represented the contribution of the flow induced by the laser-induced plasma and uncertainties related to the image processing method.

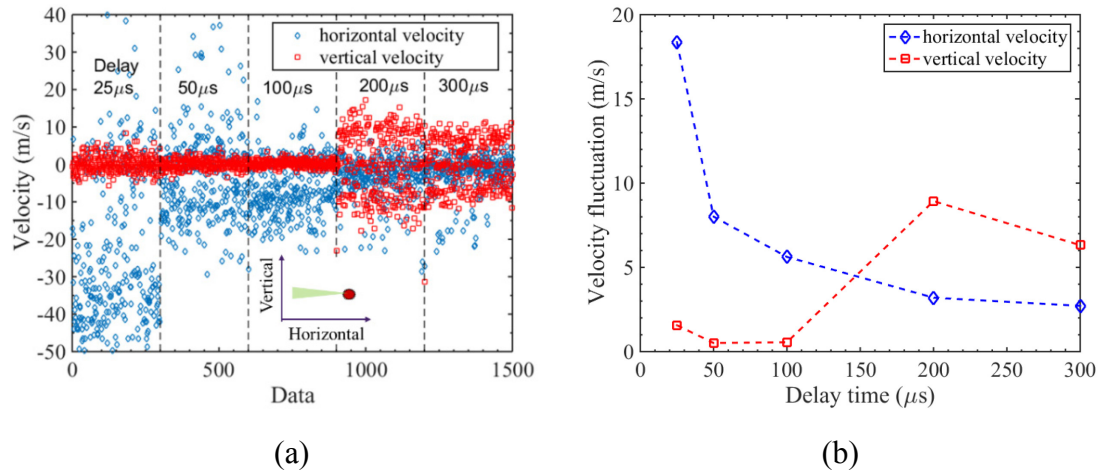


Figure 6.7 Bounding box centre of plasma tracking method in quiescent air using different time delays between the two images of the laser induced plasma. Note that the first plasma image is recorded always at time 1–2 μs after the initiation of the laser pulse. (a) Scatterplot of instantaneously measured two components of flow velocity. Results for each time delay setting were based on 300 laser shots. (b) Standard deviation of velocity fluctuations as a function of time delay between the two plasma images.

The size of the bounding boxes on the images of Figure 6.6 (green dash line) are 2.0 mm x 0.7 mm and 2.3 mm x 2.1 mm for time delay after the laser pulse initiation of 1–2 μs and time delay 50–60 μs respectively. This size determines the spatial resolution of the velocity measurement technique. The width and height of the bounding box equalled L_x and L_z respectively in Figure 6.4. It can be seen that, during the time windows 25 ~ 300 μs for LIPIV, both the width and height of the plasma continued to grow with the time delay. A compromise

between proper plasma displacement (affecting the accuracy of the velocity measurement) and spatial resolution of the LIPIV technique should be considered.

Figure 6.7 (a) shows the shot-to-shot velocity variation and the resulting standard deviation of the velocity fluctuations of the laser induced plasma as a function of the delay time between the recorded plasma images in quiescent air. The influence of the timing settings for LIPIV was evaluated as well. The optimum time delay should lead to minimum standard deviation of velocity fluctuations for both velocity components. Figure 6.7 (b) shows that delay times 50 μs and 100 μs between the two plasma images (note that the first plasma image is recorded always at time 1-2 μs after the initiation of the laser pulse) are more suitable for laser-induced plasma velocity measurement, since the velocity variation is relatively small. In addition, Figure 6.4 shows that the spatial resolution of 50 μs and 100 μs time delays is relatively high. For the geometric centre and weighted centroid processing methods, the spatial resolution of LIPIV remains the same as for the bounding box method. Therefore, for this time delays in the range of 50 to 100 μs , the spatial resolution of the measurement is reasonable both horizontal and vertical velocity components.

Processing II: geometric centre

The second image processing method for tracking the laser-induced plasma is based on evaluating the geometric centre of the plasma.

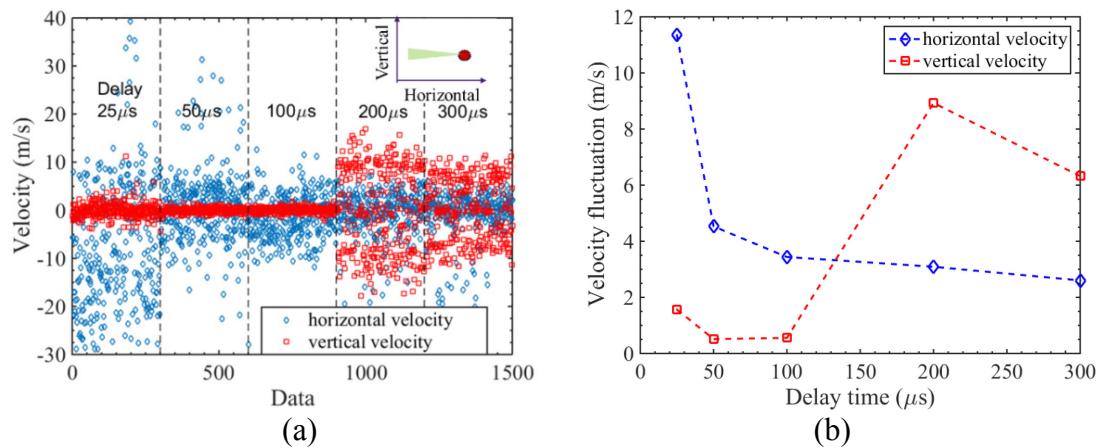


Figure 6.8 Geometric centre of plasma tracking method in quiescent air using different time delays between the two images of the laser induced plasma. Note that the first plasma image is recorded always at time 1-2 μs after the initiation of the laser pulse. (a) Scatterplot of instantaneously measured two components of flow velocity. Results for each time delay setting were based on 300 laser shots. (b) Standard deviation of velocity fluctuations as a function of time delay between the two plasma images.

Figure 6.6 shows the geometric centre of the plasma (red spot on images). This is determined following similar processing procedures as for the bounding box centre method. The only difference was that the last step extracted the location of the mass centre of the binary plasma on the image, which was then tracked over the time delay between the two images and the displacement was quantified. The two-dimensional velocity vector was then calculated from the displacement and the time delay and two velocity components were estimated, namely the horizontal component, which was along the laser beam axis, and the vertical component, which was normal to the axis of the laser beam. This was obtained using the same approach as for the bounding box centre.

Figure 6.8 (a) shows the shot-to-shot velocity variation and the resulting standard deviation of the velocity fluctuations of the laser induced plasma as a function of the delay time between the recorded plasma images in quiescent air. The influence of the timing settings for LIPIV was evaluated as well. The optimum time delay should lead to minimum standard deviation of velocity fluctuations for both velocity components. Figure 6.8 (b) shows that delay times 50 μs and 100 μs are more suitable for laser-induced plasma velocity measurement, since the velocity variation is relatively small. The spatial resolution of this method follows the same behaviour of the bounding box method in Figure 6.4.

Processing III: weighted centroid

The third image processing method for tracking the laser-induced plasma is based on a weighted plasma centroid approach.

This approach is different from the two previous processing methods. It calculates the weighted centroid of the plasma directly from the greyscale images of the plasma intensity rather than binarised images. Figure 6.6 shows the weighted centroid of the plasma (blue spot on images).

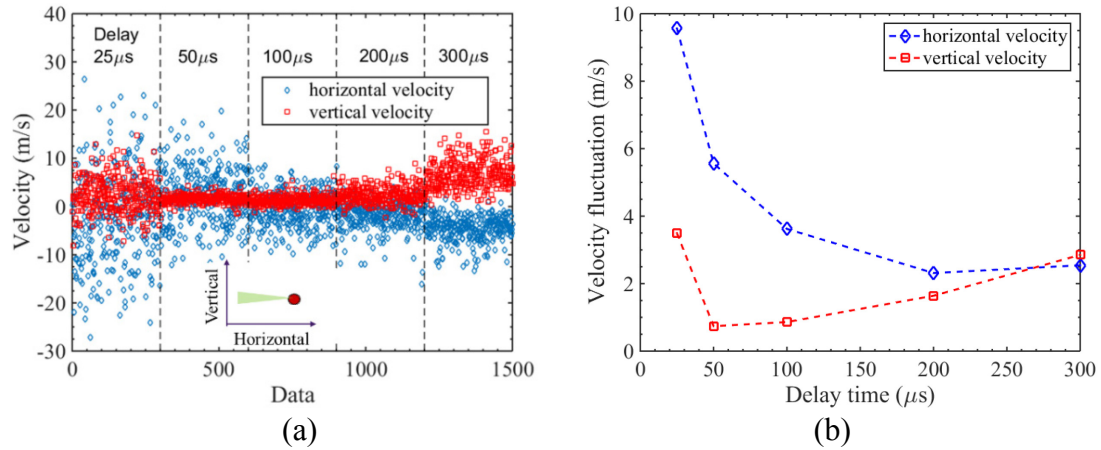


Figure 6.9 Weighted centroid of plasma tracking method in quiescent air using different time delays between the two images of the laser induced plasma. Note that the first plasma image is recorded always at time 1-2 μ s after the initiation of the laser pulse. (a) Scatterplot of instantaneously measured two components of flow velocity. Results for each time delay setting was based on 300 laser shots. (b) Standard deviation of velocity fluctuations as a function of time delay between the two plasma images.

Figure 6.9 (a) shows the shot-to-shot velocity variation and the resulting standard deviation of the velocity fluctuations of the laser induced plasma as a function of the delay time between the recorded plasma images in quiescent air. The weighted centroid method is used to identify the plasma centre. The influence of the timing settings for LIPIV was evaluated. The optimum time delay should lead to minimum standard deviation of velocity fluctuations for both velocity components. Figure 6.9 (b) shows that delay times from 50 μ s and up to 200 μ s are more suitable for laser-induced plasma velocity measurement, since the velocity variation is relatively small. The spatial resolution of this method also follows the same behaviour as the bounding box method in Figure 6.4. For time delays 50 μ s and 100 μ s, the spatial resolution of measurement is relatively small. The velocity fluctuations of Figure 6.9 are smaller than for the two other processing methods, which indicates that the weighted average centre method leads to the lowest uncertainty.

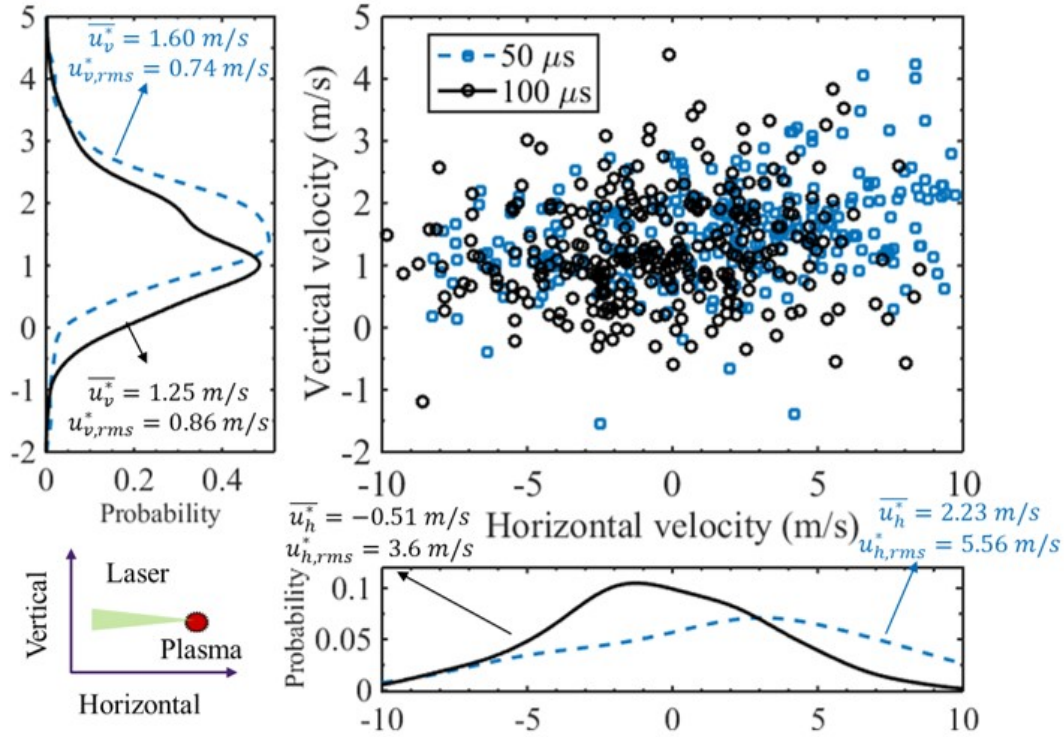


Figure 6.10 Scatterplot of 300 instantaneous LIPIV measurements in quiescent air for 50 μs and 100 μs delay times between the recorded plasma images using the weighted centroid method (squares for 50 μs and circles for 100 μs time delays). The left graph is a histogram of the vertical velocity component and the bottom graph is a histogram of the horizontal velocity. The vertical velocity is normal to the axis of the pulsed laser beam and the horizontal component is along the laser beam axis. $\bar{u}_h^*$ and $\bar{u}_v^*$ represent the horizontal and vertical mean velocity in quiescent air, respectively. $u_{h,rms}^*$ and $u_{v,rms}^*$ represent the horizontal and vertical rms (standard deviation) of the velocity, respectively.

Through the comparisons of the different types of plasma processing results, it was found that the effect of the processing methods on the results was small. The plasma displacement was not sensitive to the processing methods. All of these results show that the velocity fluctuations are smaller using time delay between 50 and 100 μs between the two plasma images with the first image being recorded at time delay of 1-2 μs after the laser pulse initiation. Since the weighted centroid method has smaller velocity uncertainty than other methods in the quiescent field, it was selected to for the flow velocity measurements. The testing indicated that delay time settings of 50 μs and 100 μs are suitable to track the plasma centroids, as shown in Figure 6.9 (b).

The histogram in Figure 6.10 presents the distributions of the instantaneous velocity measurements for horizontal and vertical components with time delays of 50 μs and 100 μs using the weighted centroid method. In quiescent air, the real flow velocity was zero and the

only existing component was u^* of Eq. (6.1). From the results, using 100 μs delay between the two plasma images, the horizontal direction measurement had ± 3.6 m/s uncertainty and the vertical direction had 1.0 m/s uncertainty. The 100 μs systematic uncertainty $\overline{u}^*$ was -0.51 m/s horizontally and 0.86 m/s vertically. Fellouah [157] estimated that the Kolmogorov length scale of the flow in a turbulent jet with Reynolds number 6000-10000 was of the order of 0.1 mm. The plasma size is at least one order of magnitude higher than the Kolmogorov scale. This indicates that LIPIV has limited spatial and temporal measurement resolution in the jet flow presented below. The velocity variation u^*_{rms} , which indicates the measurement uncertainty, is different for the directions along and perpendicular to the laser beam axis, namely 1 m/s and 3.6 m/s.

6.5.2 Turbulent jet velocity measurements

In the turbulent jet flow experiment, the velocity component of the jet flow is negligible in the direction normal to the jet axis, compared to the velocity along the jet axis. Therefore, the results above show that the axial velocity component has a velocity uncertainty of 1 m/s.

The streamwise mean velocity distribution along the jet axis is measured for an area-averaged velocity of 50 m/s at the jet exit, resulting in Reynolds number of 34,000. Figure 6.11 shows the mean flow velocity for 50 μs and 100 μs time delays between plasma images along the centreline axial direction with good accuracy. The theoretical curve was plotted using the

simple expression [158]: $\frac{\bar{u}(x)}{\bar{u}(0)} = \sqrt{1 - e^{-\left(\frac{D}{2C_m x}\right)^2}}$, where C_m is the spreading coefficient which is 0.075 in this study, $\bar{u}(x)$ is the mean axial velocity along the centreline at distance x from the jet exit and D is the jet exit diameter. According to Eq. (6.2), the uncertainty component from u^* was removed from the measured mean value. A potential core like region was observed up to $x/D < 3$. The centreline velocity decay started at $x/D = 4$, then the velocity decreased monotonically in the downstream region after $x/D = 8$. This centreline velocity was proportional to minus one-half power of distance x from nozzle exit. Compared to jet flows generated by a contraction and sharp-edge orifice pipes, the jet flow from long pipes, as used here, has the lowest velocity decay rate along the centreline [130]. The measured mean velocity is in good agreement with the expected jet behaviour along the centreline.

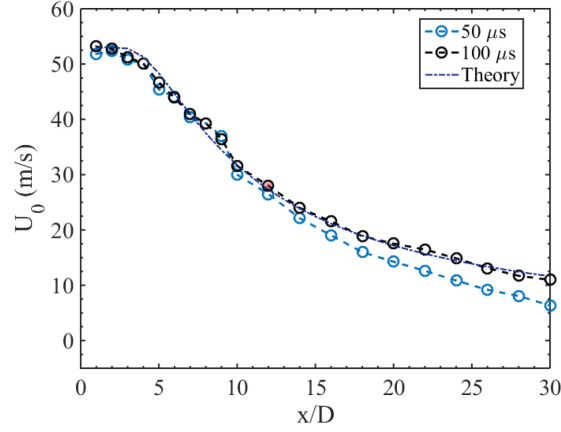


Figure 6.11 Mean axial velocity for different time delays between the recorded plasma images along the jet centreline averaged over 300 instantaneous velocity measurements at each point.

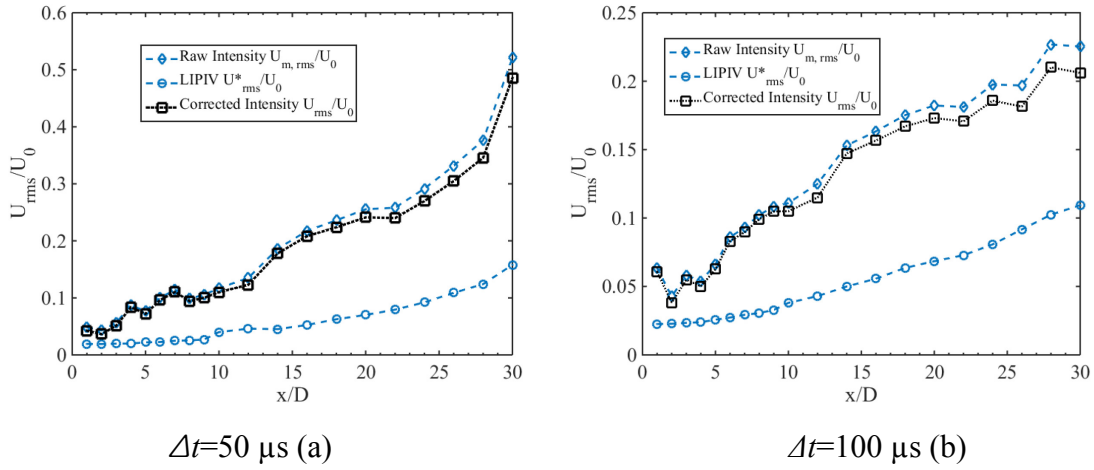


Figure 6.12 Normalized rms of axial velocity fluctuations along the centreline of the jet using time delay of 50 μs (a) and 100 μs (b) between plasma images. The first plasma image was always at time delay of 1 μs after the laser pulse initiation.

The distribution of the rms velocity along the jet centreline normalized by the centreline mean velocity is presented in Figure 6.12 for 50 μs and 100 μs delay time between the two recorded plasma images. The ‘raw’ turbulent intensity $U_{m,rms}/U_0$ also consists of the original flow field intensity $U_{m,rms}/U_0$ and the uncertainty U_{rms}^*/U_0 induced by the technique. Similar to Eq. (6.3):

$$\frac{U_{rms}}{U_0} = \sqrt{\left(\frac{U_{m,rms}}{U_0}\right)^2 - \left(\frac{U_{rms}^*}{U_0}\right)^2} \quad (6.4)$$

After the subtraction of the U_{rms}^*/U_0 component from the ‘raw’ intensity $U_{m,rms}/U_0$ in Eq. (6.4), the corrected turbulent intensity U_{rms}/U_0 can be obtained in Figure 6.12. For the corrected turbulent intensity curve with 50 μs time delay in Figure 6.12 (a), the corrected intensity

becomes inconsistent with the theoretical values as the mean velocity decays, since the effect of the relatively large U^* component with $50 \mu\text{s}$ on low flow velocity was difficult to be removed completely. The corrected turbulent intensity with time delay $100 \mu\text{s}$ between the plasma images in Figure 6.12 (b) provides a final corrected jet flow turbulent intensity that is according to expectations. Compared to turbulent intensity results of jet flows initiated from contraction and sharp-edged orifice results [159,160], a jet flow initiated from a long pipe nozzle has relatively lower turbulent intensity, which reaches to around 0.2 at $x/D = 30$. This can be explained by the differences in the exit velocity profiles of the nozzles. The ‘top-hat’ shape for contraction nozzle and ‘M’ shape for sharp-edged orifice exit velocity profiles are different from the fully developed pipe flow velocity profile [130] delivered by a long pipe nozzle leading to a relatively weak entrainment of surrounding air into the jet flow, resulting in relatively lower turbulent intensity.

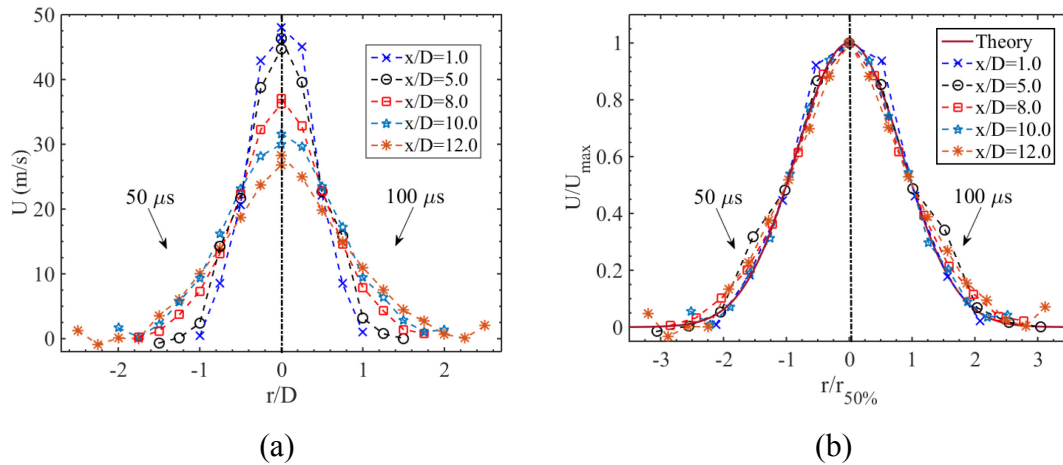


Figure 6.13 Radial profiles of the mean (a) and normalized mean (b) axial velocity obtained at different axial locations from the jet exit. The results are averaged over 300 instantaneous velocity measurements at each point. The left and right hand sides of each graph show the results for $50 \mu\text{s}$ and $100 \mu\text{s}$ delay times between the recorded plasma images respectively.

The theoretical curve was plotted using a Gaussian profile normalized by the centreline velocity and the half jet width.

Figure 6.13 presents radial profiles of the mean and normalized mean axial velocity at different axial distances from the jet exit. The left side of each graph of Figure 6.13 shows the results for $50 \mu\text{s}$ delay time between the plasma images and the corresponding right hand side for $100 \mu\text{s}$ delay time. The measured mean axial velocity is similar for both delay times. The normalisation of the radial profiles of the mean axial velocity is calculated with the centreline velocity at each axial location for the velocity and with the dimension of the half width of the jet at each axial distance. (The half width of the jet is defined as the radial distance from the

centreline of the jet, where the local mean velocity is equal to half of the local centreline mean velocity). According to previous studies [16,161,162], this normalisation leads to self-similar axial velocity profiles. This is confirmed from the findings of Figure 6.13 (b), which provides confidence on the ability of the proposed LIPIV method to measure the flow velocity.

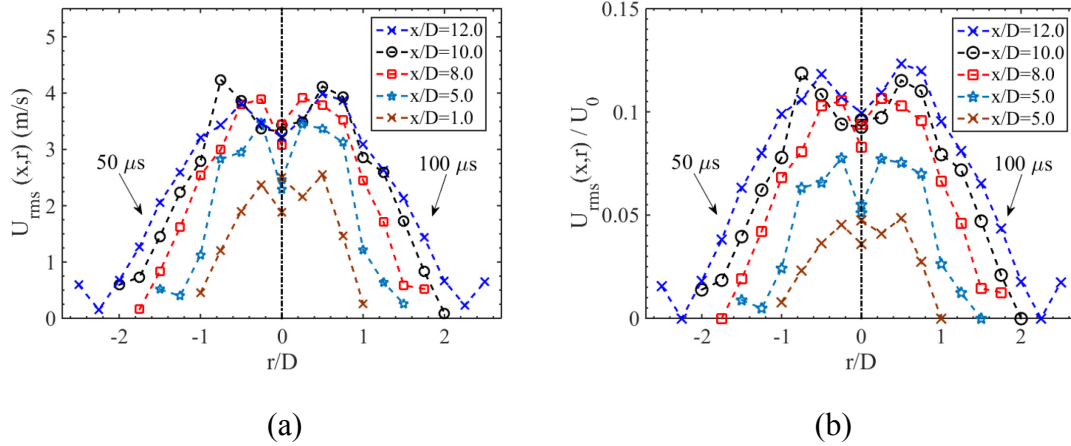


Figure 6.14 Radial profiles of the rms and normalized rms of the axial velocity fluctuations obtained at different axial locations from the jet exit averaged over 300 instantaneous velocity measurements at each point. The left and right hand sides of the graph show the results for $50 \mu s$ and $100 \mu s$ delay times between the recorded plasma images respectively. Normalisation is by the axial mean velocity U_0 .

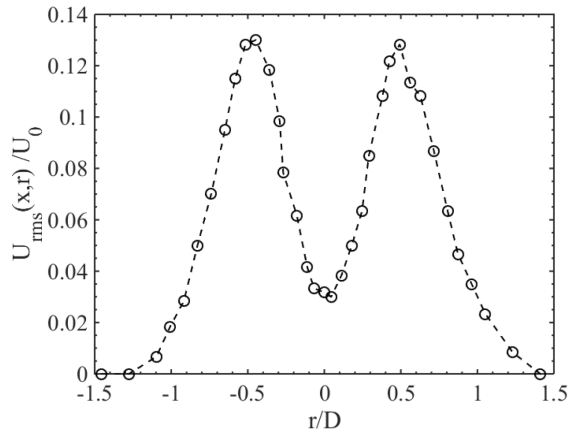


Figure 6.15 Radial profiles of Reynolds normal stress in the round free pipe jet at $x/D=3$ [163]

Figure 6.14 shows the rms of the axial velocity fluctuations as a function of the radial distance normalised by the jet exit diameter. The shape of the radial profiles for the rms of the axial velocity fluctuations is in agreement with the hot-wire anemometry results in Figure 6.15 [163], which confirms again the ability of the LIPIV to obtain accurate flow velocity measurements. Normalisation is by the axial mean velocity U_0 .

6.6 Summary

In this chapter, a novel approach was presented for point flow velocity measurements using the displacement of laser-induced plasma, which does not require the introduction of either ‘seeding’ particles or any other substances in the fluid. The details of the image processing and the associated data processing for the measurement of the flow velocity using images of the temporal evolution of the plasma were presented. An evaluation of the accuracy of the velocity measurements and its dependence on the image processing method and the selected delay time between the subsequent plasma images were performed. The accuracy of this technique was evaluated in quiescent air surroundings. Eventually, the LIPIV was shown to be effective in quantifying the turbulent properties of a jet flow.

The results demonstrate consistent LIPIV measured flow velocity with the reported information in the literature for mean velocity and turbulent intensity of axial velocity fluctuations in a jet flow. The advantages and limitations of this technique can be summarized as follows:

Advantages

- Simple equipment: only a pulsed laser and two cameras are required, compared with MTV techniques.
- Method is suitable for harsh environments, such as combustion chambers, where ‘seeding’ particles cannot be introduced. It doesn’t rely on any special molecule or atom species existed in gas flows before measurements.
- Image processing is fairly simple to develop, compared with the spatial correlation algorithms in PIV or MTV.
- Good accuracy can be achieved in a turbulent flow, especially in high-speed flows. LIPIV has a constant uncertainty of ± 3.6 m/s along the direction of the laser beam axis and ± 1.0 m/s along the direction perpendicular to the laser beam axis.
- The spectrum of the emitted light as shown in Fig. 3 from the plasma can be used to measure local mixture compositions simultaneously with flow velocity.

Limitations

- The velocimetry approach can currently only be applied to gas flows.

- Since the laser-induced plasma generates a gas flow, which may generate reactive species and pressure waves, the technique causes some disturbances to the flow that is to be measured.
- In contrast to Particle Image Velocimetry, which is a planar technique, Laser-Induced Plasma Image Velocimetry (LIPIV) is typically applied to obtain point measurement. However, it is possible to organise an optical arrangement for simultaneous, multiple point measurements.
- The spatial resolution of the velocity measurements is limited by the size of the laser-induced plasma about 5 mm. The resolution can be improved up to 1 mm, with lower laser pulse energy.
- In the low speed flow (less than 10 m/s), the uncertainty of LIPIV is relatively large compared with the local flow speed. This technique is more suitable for high speed flow measurements, such as the real gas turbine combustors exhaust gas flow. This is because the displacement of the plasma caused by the local flow is much larger than the development of the plasma itself.
- In the complex combustors, the non-uniform temperature or pressure can deform the plasma, which increases the uncertainty of LIPIV.

Chapter 7 Local mixture fraction and velocity measurements in swirl stabilised flames using laser induced plasma

7.1 Introduction

This chapter evaluates the mixture fraction (fuel mole fraction) and velocity measurements using laser induced plasma in a swirl-stabilised burner. Both fuel mole fraction and velocity radial profiles were measured at different locations in the near burner region of the coaxial jet arrangement with swirling annular air flow surrounding the central axial injection of gas jet (methane fuel). The purpose of the chapter is to demonstrate the capability of the developed laser induced plasma measuring techniques in a realistic nominally non-premixed burner configuration.

It is emphasised that the laser induced plasma measuring methods do not require the addition of either ‘seeding’ particles for flow velocity measurements, as required by, for example, Particle Image Velocimetry (PIV), of any fluorescing substances for fuel concentration measurements, as required by, for example, laser induced fluorescence methods for fuel. The ability of the laser induced plasma methods to measure fuel mole fraction and velocity in a swirl-stabilised burner opens the possibility to obtain measurements in a real gas turbine combustor operating, as normal, with real fuels without any addition of substances for measurements. In addition, limited optical access is needed for the application of the laser induced plasma measurement methods.

The swirl burner configuration was introduced in Chapter 3. The burner had an outer air flow stream diameter of $D = 50.8$ mm and inner fuel nozzle diameter of $D_f = 15$ mm. The measurements were obtained up to $y/D_f = 7$ inner fuel nozzle diameters downstream of the burner exit at operating conditions of air stream Reynolds number of 29000 and 0.58 swirl number, as shown in Figure 3.7. Here y is the axial downstream coordinate with origin on the centreline at the exit plane of the burner.

In order to compare the mixture fraction and velocity results with the results of Stetsyuk [133], the operating conditions for both reacting and isothermal measurements of the study are summarized in Table 7.1 and Table 7.2. The LIBS measurements in the reacting conditions are firstly presented. The velocity measurements in isothermal conditions are then conducted. Since it was found that the plasma images deteriorated faster in the swirling flames than in the

counterflow flames of Chapter 4 (Figure 4.2), a new image processing method was developed. Finally, the velocity profiles using LIPIV in reacting conditions were shown. In this chapter, 100 instantaneous measurements of both mixture fraction and velocity were performed at each location. The LIPIV velocity measurements using single camera and double camera systems were also evaluated, as shown in Figure 7.1. The measurement uncertainties related to the flow rates are also summarized in Table 7.1 and Table 7.2.

Table 7.1 Operating conditions (reacting, methane-air flames)

Parameters	Value	Computed uncertainty
Swirl number	0.58	± 0.0288 ($\pm 5.0\%$)
V_{axial} l/min	350	± 8.2 ($\pm 2.34\%$)
V_{swirl} l/min	550	± 14.4 ($\pm 2.62\%$)
V_{CH_4} l/min	68	± 0.85 ($\pm 1.25\%$)
U_{CH_4} m/s	6.42	± 0.08 ($\pm 1.25\%$)
u_{air} m/s	8.46	± 0.420 ($\pm 5.0\%$)
Re_{air}	28662	± 1422 ($\pm 5.0\%$)
$Re_{\text{fuel (CH}_4)}$	5743	± 71.8 (1.25%)
Equivalence ratio	0.72	± 0.037 ($\pm 5.15\%$)

Table 7.2 Operating conditions (non-reacting, isothermal flow)

Parameters	Value	Computed uncertainty
Swirl number	0.58	± 0.0288 ($\pm 5.0\%$)
V_{axial} l/min	350	± 8.2 ($\pm 2.34\%$)
V_{swirl} l/min	550	± 14.4 ($\pm 2.62\%$)
$V_{\text{f (air)}}$ l/min	40	± 0.5 ($\pm 1.25\%$)
$U_{\text{fuel(air)}}$ m/s	3.77	± 0.047 ($\pm 1.25\%$)
u_{air} m/s	8.46	± 0.420 ($\pm 5.0\%$)
Re_{air}	28662	± 1422 ($\pm 5.0\%$)
$Re_{\text{fuel (air)}}$	3770	± 47.1 ($\pm 1.25\%$)

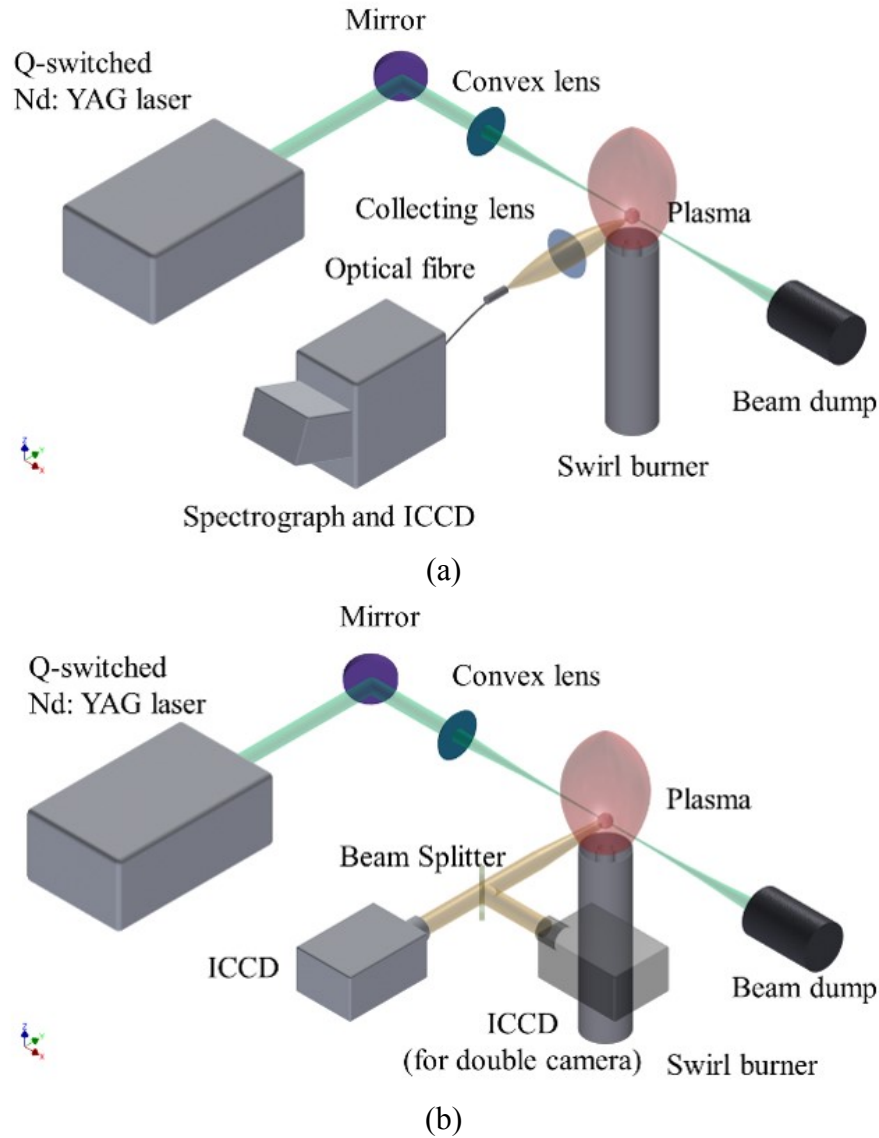


Figure 7.1 Schematic diagram of the LIBS (a) and LIPIV (b) experiment setup with the swirl stabilised burner

7.2 Results and discussion

7.2.1 Local mixture fraction (fuel mole fraction) measurements

7.2.1.1 LIBS data processing method

Using the developed signal processing method of LIBS spectral intensities of Chapter 4, if the SNR (signal-to-noise ratio) of the measured value is lower than a threshold, the value is removed from the results to ensure the accuracy of the measurements. In addition, similar to the LIPIV method in section 6.4, the Eq. (6.2) and Eq. (6.4) show that, when measuring the turbulent flows, the fluctuations of results can originate from the technique and the turbulent flow. For the LIBS measurements in perfect premixed mixtures in Chapter 4, the measured

mixture fraction variation mainly results from the LIBS technique, including the effects of the laser beam quality and the detection system. In the turbulent non-premixed conditions, it is assumed that the LIBS uncertainty in non-premixed conditions is similar to that in the perfect premixed conditions. The measured mixture fraction contains the variations from the LIBS technique and the mixture itself.

Therefore, when calculating the rms of the fluctuations of mixture fraction measurements, the variation due to LIBS is subtracted to obtain the original mixture fraction variations of the flow, as illustrated in the propagation of uncertainty formula in Eq.(6.4).

7.2.1.2 LIBS mixture fraction measurements

Figure 7.2 shows a typical methane flame, stabilised at the burner exit during operation with global air-fuel ratio (global equivalence ratio) of 0.72 and swirl number of 0.58 for the operating conditions of Table 7.1. LIBS measurements of mixture fraction are presented below, which were obtained using the procedure that was described above.

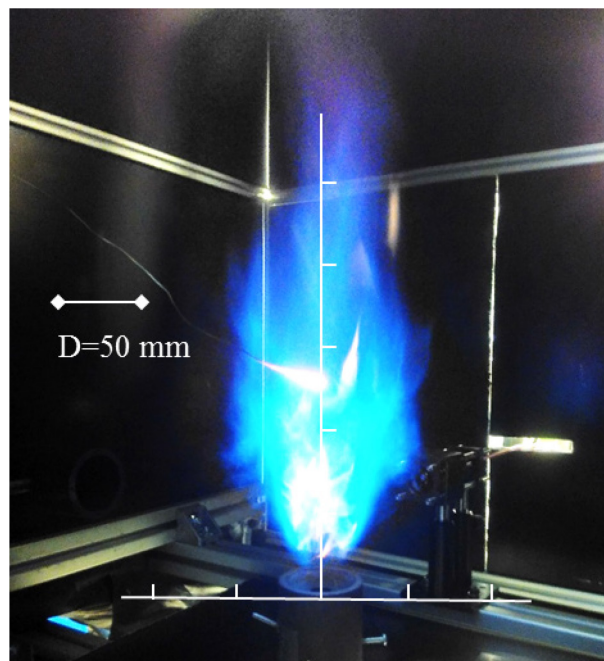


Figure 7.2 Photograph of a lifted swirl stabilized flame with a global air-fuel ratio (equivalence ratio) of 0.72 and swirl number of 0.58 under the operating conditions of Table 7.1. A thermocouple that is seen on the image was used to detect the flame temperature in order to provide a safety protection from incidental blow-off.

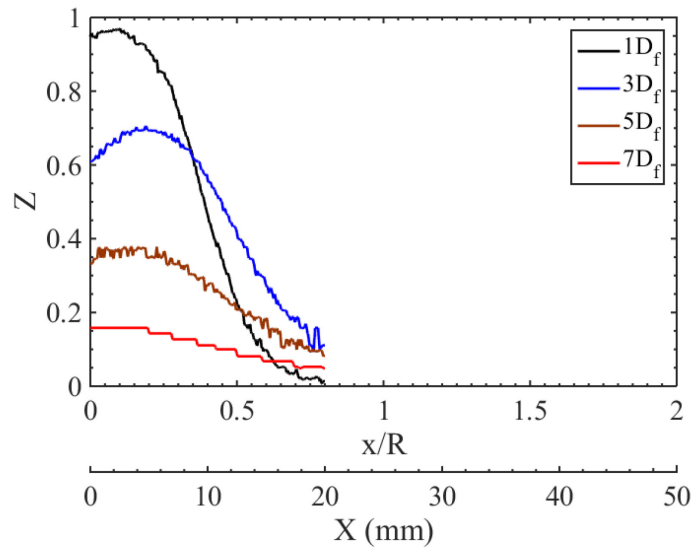


Figure 7.3 Radial profiles of mean mixture fraction (fuel mole fraction), measured using LIF with acetone as a tracer, in the non-reacting flow at different normalized axial distances y/D_f on a plane going through the centre of the burner flow as a function of radial distance x , normalised by the radius R of the burner, for *swirl number* of 0.58. The values are averaged over 1500 instantaneous images [133]

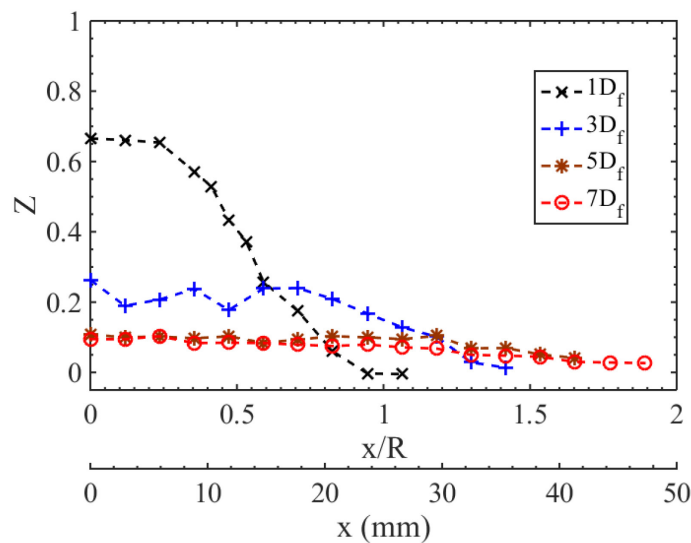


Figure 7.4 Radial profiles of mean mixture fraction, measured using LIBS, in the reacting flow at the same normalized axial distances y/D_f as those of Fig. 7.3 as a function of radial distance x , normalised by the radius R of the burner, for *swirl number* of 0.58. The values are averaged over 100 instantaneous measurements at each location.

According to earlier processing method in section 4.2.7 of Chapter 4, if the SNR (the intensity of the whole spectra) was lower the threshold of 0.4×10^7 intensity (a. u.), ‘bad’ data were removed from the results. Using the calibration scheme presented in [164] and the scheme presented in Figure 4.13, the H/O spectral intensity ratio of the LIBS spectra was used as the indicator for the local mixture fraction determination for conditions with mixture fraction

below 50%, and the C₂/CN spectral intensity ratio was used for mixture fractions higher than 50%. Therefore, for an instantaneous LIBS spectrum, the processing process is as follows:

- 1) The SNR of the spectra is compared with the threshold (0.4×10^7). If the SNR is lower than the threshold, the point is removed from the results. If the SNR is higher than the threshold, continue to Step 2.
- 2) The H (656 nm) /O (777 nm) intensity ratio of the spectra is calculated. If the H/O ratio is lower than 31 (mixture fraction < 50%), Eq. (7.1) is used to convert H/O intensity ratio into the mixture fraction. If the H/O ratio is higher than 31 (mixture fraction > 50%) and the SNR is higher than 1×10^7 intensity, Eq. (7.2) is used to convert C₂/CN intensity ratio into the mixture fraction.

$$z = -3.3 \times 10^{-5} \left(\frac{H}{O} \right)^2 + 0.018 \left(\frac{H}{O} \right) - 0.018 \quad (7.1)$$

$$z = 1.5 \times 10^{-4} \left(\frac{C_2}{CN} \right)^2 - 0.0099 \left(\frac{C_2}{CN} \right) + 0.69 \quad (7.2)$$

where z represents the mixture fraction of the LIBS measurement. H/O and C₂/CN are the intensity ratios in the LIBS spectra.

As shown earlier, successful breakdown at each point in reacting flows requires laser pulse energy of 406 mJ combined with 1 μ s delay and 50 μ s gate time for accurate instantaneous LIBS measurements. 100 instantaneous measurements were performed at each point in the flow and the reported results are averages. Figure 7.3 shows the mean mixture fraction (mole fraction) distribution, measured by Stetsyuk [133] using acetone LIF in the same burner for the non-reacting conditions of Table 7.2. Figure 7.4 shows the mixture fraction distribution (mole fraction), measured with LIBS, under reacting conditions, plotted at the same scale as the results of Figure 7.3. Unfortunately, the comparison between the two measurements can only be performed between non-reacting and reacting conditions, since it was not possible to obtain non-reacting mixture fraction measurements with the LIBS technique due to safety restrictions. Therefore, the evaluation of the LIBS measurements can only be qualitative.

Compared to the acetone LIF results under non-reacting conditions of Figure 7.3, the mixture fraction results measured by LIBS of Figure 7.4 demonstrate that the fuel jet is wider. The mixing rate of methane was higher than the acetone in both radial and axial directions. This result is expected due to the effect of reaction. The hot products expanded and modified the velocity field, resulting in faster mixing of the central methane jet with the annular swirling air flow. For example, acetone LIF results [133] shows that the flow recirculation zone that is present at the burner exit is larger under reacting conditions.

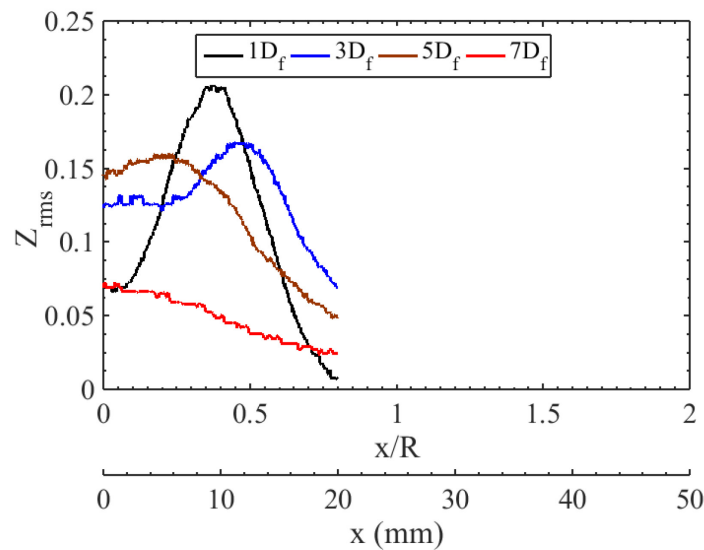


Figure 7.5 Radial profiles of standard deviation of mixture fraction fluctuations, measured using LIF with acetone as a tracer, in the non-reacting flow at different normalized axial distances y/D_f on a plane going through the centre of the burner flow as a function of radial distance x , normalised by the radius R of the burner, for *swirl number* of 0.58. The values are averaged over 1500 instantaneous images [133]

The rms of the mixture fraction fluctuations, measured by LIBS in the reacting flow, is presented in Figure 7.6 and demonstrates qualitatively similar behaviour as Figure 7.5. At the largest axial location from the burner exit, $y/D_f=7$, both measurements show very similar magnitude. Towards the edges of the swirling flow, the mixture fraction fluctuations are reduced as expected. This trend was also consistent with Kotzagianni *et al.*'s LIBS measurements in a jet diffusion flame [112], although there was no swirl air flow in the outer coaxial tube for that jet. In the jet diffusion flame measurement [112], LIBS technique also reproduces good self-similar results of mixture fractions in the axisymmetric jets. For very rich locations, the rms values can be higher than the true rms since C_2/CN ratio tends to have a large uncertainty.

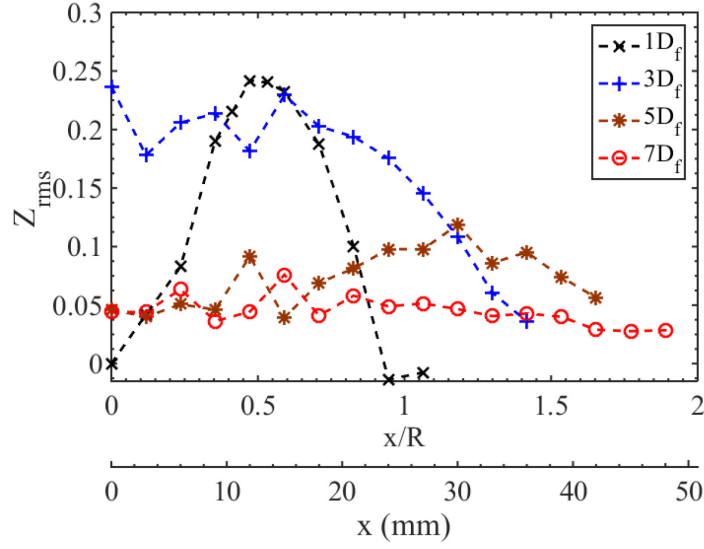


Figure 7.6 Radial profiles of standard deviation of mixture fraction fluctuations, measured using LIBS, in the reacting flow at the same normalized axial distances y/D_f as those of Fig. 7.5 as a function of radial distance x , normalised by the radius R of the burner, for *swirl number* of 0.58. The values are averaged over 100 instantaneous measurements at each location.

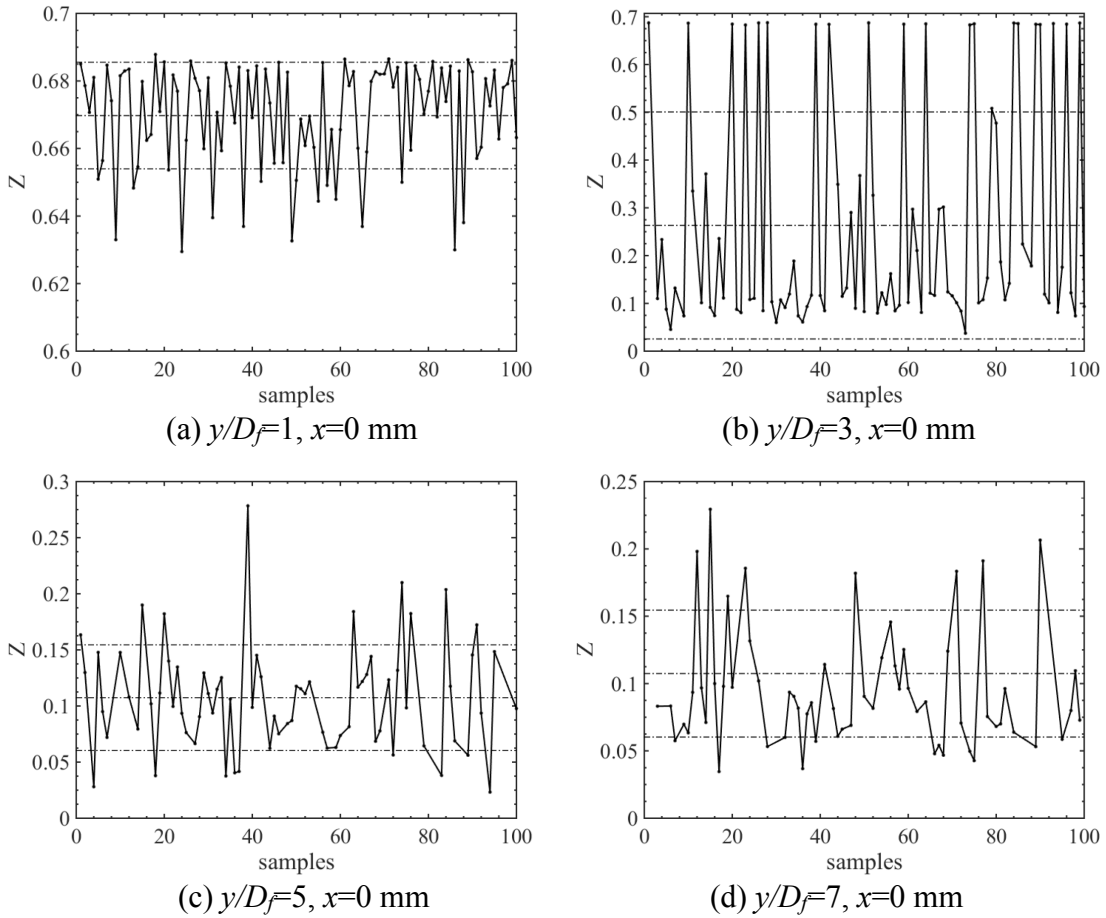


Figure 7.7 Plots of the 100 samples of local, instantaneous mixture fraction measured by LIBS at the locations (a) $y/D_f = 1$, (b) $y/D_f = 3$, (c) $y/D_f = 5$ and (d) $y/D_f = 7$ on the centreline $x = 0$ mm of the reacting flow

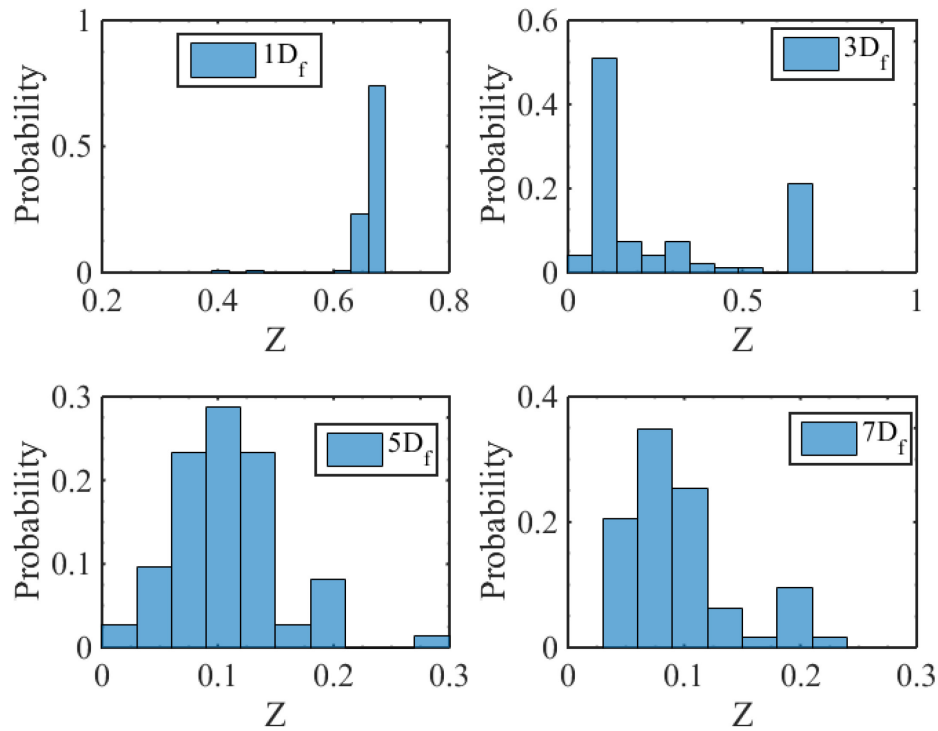


Figure 7.8 Corresponding p.d.f. of the 100 samples of local, instantaneous mixture fraction measured by LIBS at the locations (a) $y/D_f = 1$, (b) $y/D_f = 3$, (c) $y/D_f = 5$ and (d) $y/D_f = 7$ on the centreline $x = 0$ mm of the reacting flow

Figure 7.7 shows the variations of the 100 LIBS instantaneous measurements of mixture fraction at different downstream locations along the centreline of the reacting flow. Figure 7.8 shows the p.d.f. of the mixture fractions at different heights along the centreline. In this figure, at $y/D_f = 1$, the mixture fraction distribution is concentrated. At $y/D_f = 3$, the distribution appears to be bimodal. This may arise because the centreline of the methane jet oscillates in the surrounding swirling gas/flame region. The measured mixture fraction at $y/D_f = 3$ could then either be high, if the probe volume was aligned to the jet centreline, or low if the probe volume was displaced from the jet centreline. The large fluctuation of the mixture fraction also represents that the strong mixing process occurred at this height. With the continuation of mixing processes along the centreline, at $y/D_f = 5$ and 7, the mixture fraction distribution has a small skewness, which indicated the mixtures has been mixed quite well.

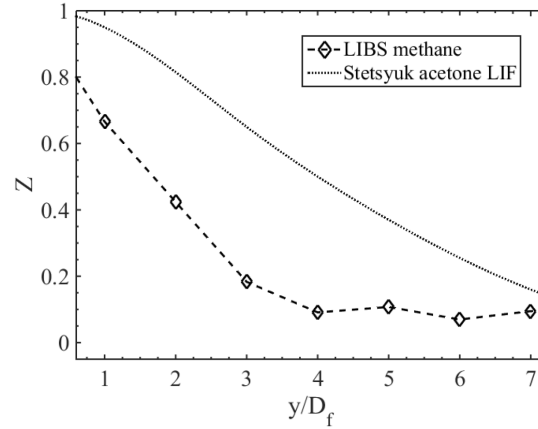


Figure 7.9 Comparison between the mean mixture fraction, measured by LIBS in the reacting flow and by acetone LIF in the non-reacting flow [133], along the centreline of the burner.

Figure 7.9 shows the comparison of the mean mixture fraction, measured by LIBS in the reacting flow and by acetone LIF in the non-reacting flow. The difference between the acetone-LIF and LIBS results in Figure 7.9 is calculated from the mean distance of the two mixture fraction curves at same x-axis values. On average, the LIBS curve is 0.23 lower than the acetone LIF curve. In the later part of PIV and LIPIV comparison, the difference of velocity profiles is also calculated using the same average difference method. Therefore, the reacting flow LIBS measurements decay faster than the LIF results, which is also consistent with increased mixing that is present in the reacting flow.

7.2.2 Velocity measurements in non-reacting flow of the swirl stabilised burner

This section presents velocimetry measurements obtained with laser-induced plasma (LIPIV) in the non-reacting flow conditions of Table 7.2. Different optical configurations of the LIPIV method are considered first and compared to evaluate the accuracy of the measurements.

7.2.2.1 Single camera LIPIV method

In order to reduce the complexity of the LIPIV measurement technique, a single camera LIPIV system is proposed and tested in this section. The double camera LIPIV records images of the same plasma at two instances in time t and $t+\Delta t$ to calculate its displacement. For the single camera LIPIV system, two images of the plasma are recorded, the first in the quiescent flow field and the second in the flow field under investigation at time $t+\Delta t$ when the laser induced plasma is generated at time t . The plasma displacement is then calculated by obtaining the difference between the plasma locations on the images in the flow field of interest and the

quiescent flow field. The main factor influencing the plasma location in the two flow fields is the velocity of the flow field that is to be measured, so that the displacement can be obtained in Eq. (7.3).

$$\Delta l = l_{t+\Delta t} - \bar{l}_{0,t+\Delta t} \quad (7.3)$$

where $l_{t+\Delta t}$ is the plasma location at time $t+\Delta t$ after the initiation of the laser pulse and $\bar{l}_{0,t+\Delta t}$ is the mean value of the plasma location at $t+\Delta t$ after the laser pulse in the quiescent flow field. Compared to the double camera LIPIV, which records two images of the plasma in the flow field of interest at different times, the single camera system obtains the velocity by subtracting the change of the plasma kernel location relative to its mean location at the same time after the laser pulse in the quiescent field. In this way, the single camera system is simpler to obtain the flow velocity, although the uncertainty of the plasma location in the quiescent field contributes to the flow velocity uncertainty.

7.2.2.2 LIPIV velocity results

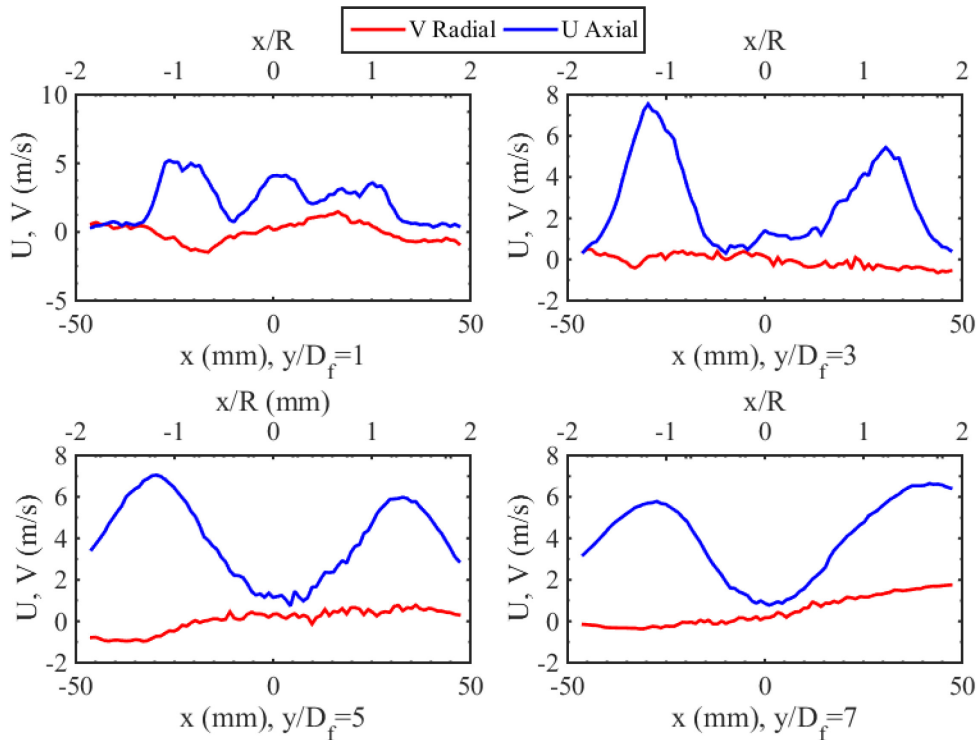


Figure 7.10 Axial and radial mean velocity profiles of the non-reacting flow, measured with PIV in the near burner region without swirl for *swirl number* of 0.58 at different normalized axial distances of $y/D_f = 1, 3, 5$ and 7 . Mean velocity computed from 1000 instantaneous PIV images. [133]

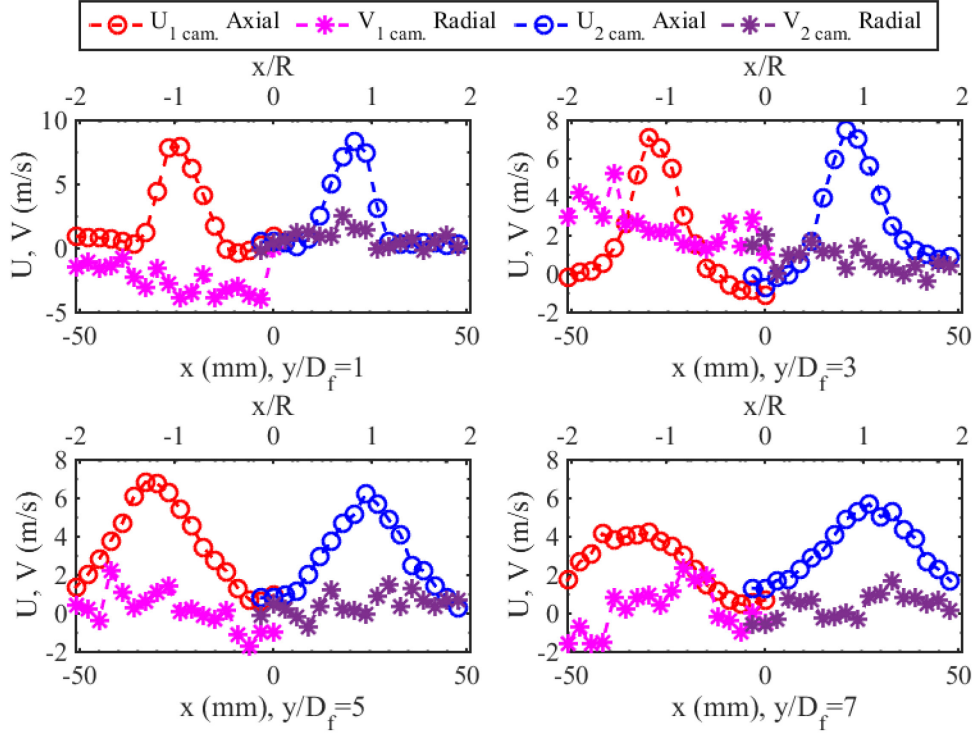


Figure 7.11 LIPIV mean velocity measured in isothermal flow with *swirl number* of 0.58 and averaged over 100 instantaneous velocity measurements at each point. Radial profiles of axial and radial mean velocity components at $y/D_f=1, 3, 5$ and 7 . The left side results are from the single camera approach and right side results are from the double camera approach respectively.

In order to assess the LIPIV measurements, measurements from PIV results [133] under the same conditions in Table 7.2 are used. Figure 7.10 shows PIV radial and axial velocity profiles from [126] at four different distances, namely $y/D_f = 1, 3, 5$ and 7 , from the burner exit in the non-reacting flow.

Figure 7.11 presents the velocity profiles measured by LIPIV at four different heights of $y/D_f = 1, 3, 5$ and 7 using 125 mJ laser pulse energy, which was shown to be appropriate for measurements in air. In Figure 7.11, the left side and right side velocity measurements were performed using single camera and double camera LIPIV systems respectively. By calculating the measured velocity profile difference at four axial heights, it was found that the average differences between the single and double camera LIPIV results were 0.75 m/s and 1.85 m/s for the axial velocity and radial velocity, respectively. The differences were small by considering the variations from the asymmetry of burner configuration and the LIPIV uncertainty. The radial velocity component had a relatively large deviation from the measurements of the other techniques, which was caused by the low magnitude of this velocity component and the laser pulse energy drift and radially asymmetrical development of the

induced plasma. Comparison between double camera and single camera LIPIV velocity measurements show that the axial velocity component measurements are in good agreement.

The velocity measurements in Figure 7.10 and Figure 7.11 obtained with PIV and LIPIV were slightly asymmetrical, caused by the burner configuration itself. The comparison between PIV and double camera LIPIV shows that the mean velocity profiles have differences of 1.6 m/s for axial velocity and 0.7 m/s for radial velocity. The differences were not only caused by the LIPIV technique. The PIV measurement uncertainty also contributed to the differences. Since the particle of PIV in swirl flow had a relatively high swirl component of velocity perpendicular to the laser sheet, it was easy for the particles to flow outside of the laser sheet. Failure to capture the particles in the sequential images of PIV also resulted in the increase of PIV uncertainty. The comparison between the PIV and LIPIV velocity measurements obtained under the same flow conditions still show good agreement. This provides confidence on the ability of the LIPIV technique to obtain measurements in a complex swirling flow.

The PIV measurements of the rms of the velocity fluctuations are shown in Figure 7.12, which the corresponding LIPIV rms of velocity fluctuations is presented in Figure 7.13. In Figure 7.13, the rms differences between double and single camera LIPIV profiles were 0.22 m/s for axial velocity and 1.1 m/s for radial velocity, respectively. The rms results of double camera LIPIV and PIV had differences of 1.9 m/s for axial velocity and 1.8 m/s for radial velocity. As with the mean velocity results, the measurements of the rms of the velocity fluctuations of the axial component with the two different techniques are in good agreement qualitatively. The shape of the rms of the axial velocity profile using different techniques was similar. The PIV measurements of the rms velocity were relatively higher than the results from the other techniques, probably caused by some remaining noise on the images. The LIPIV rms of the radial velocity fluctuations had large uncertainty and variations remain across the profiles, which are due to measurement error. Therefore, the LIPIV results were consistent with the other techniques for the measurement of the axial velocity component. The radial velocity still had a relatively large variation due to limitations of the technique. The LIPIV measurements with two cameras helped to reduce the uncertainty of the radial component and improved the agreement with the other techniques.

Therefore, since both PIV and LIPIV measurements were conducted at the same isothermal flow conditions, these results showed a good agreement among them. The differences between

PIV and double camera LIPIV were only 1.6 m/s for axial velocity and 0.7 m/s for radial velocity. The remaining differences between the results could be explained by the asymmetrical velocity profiles occurring at different radius and the measurement uncertainty from the two techniques. The LIPIV technique with two cameras performed better than the single camera only for the radial velocity component measurements. However, the single camera LIPIV system demonstrated high potential for successful velocity measurements in complex flows.

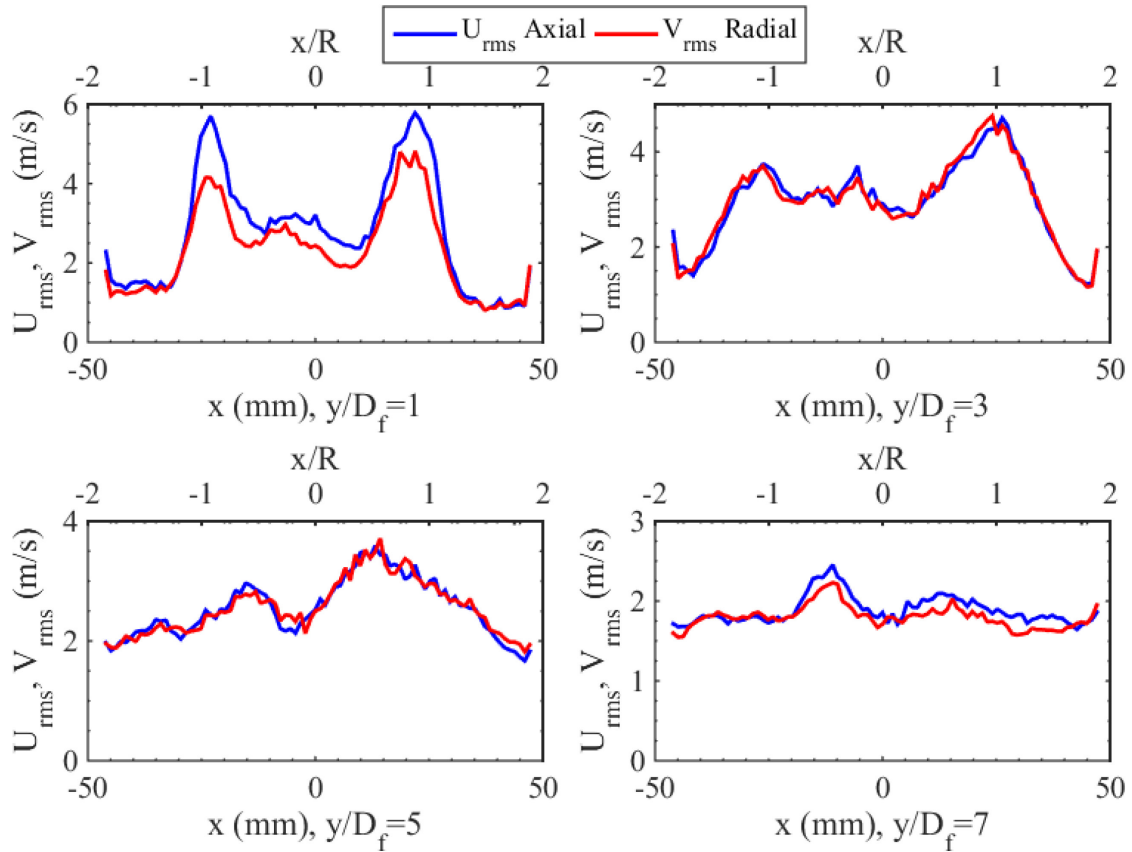


Figure 7.12 Measured PIV rms of the velocity fluctuations profiles for isothermal conditions with *swirl number* of 0.58 at different normalized axial distances, $y/D_f = 1, 3, 5$ and 7. Mean velocity computed from 1000 instantaneous images. [133]

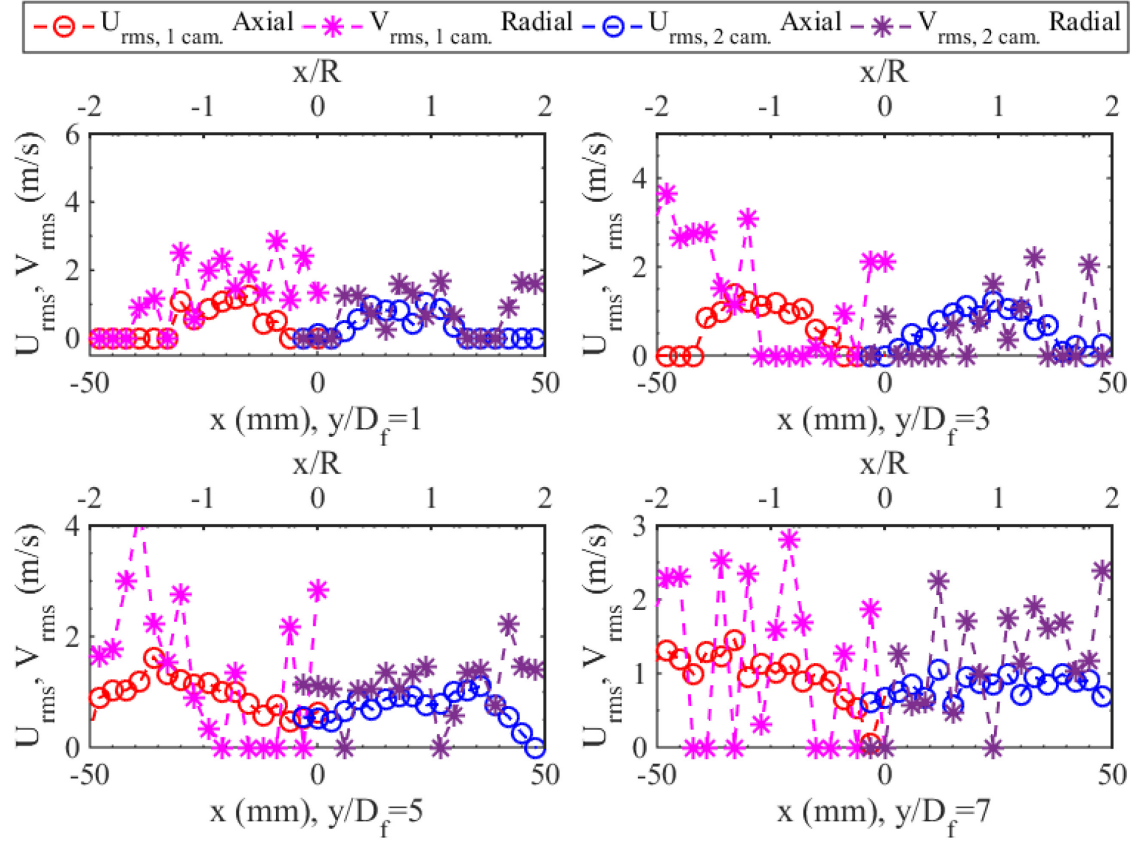
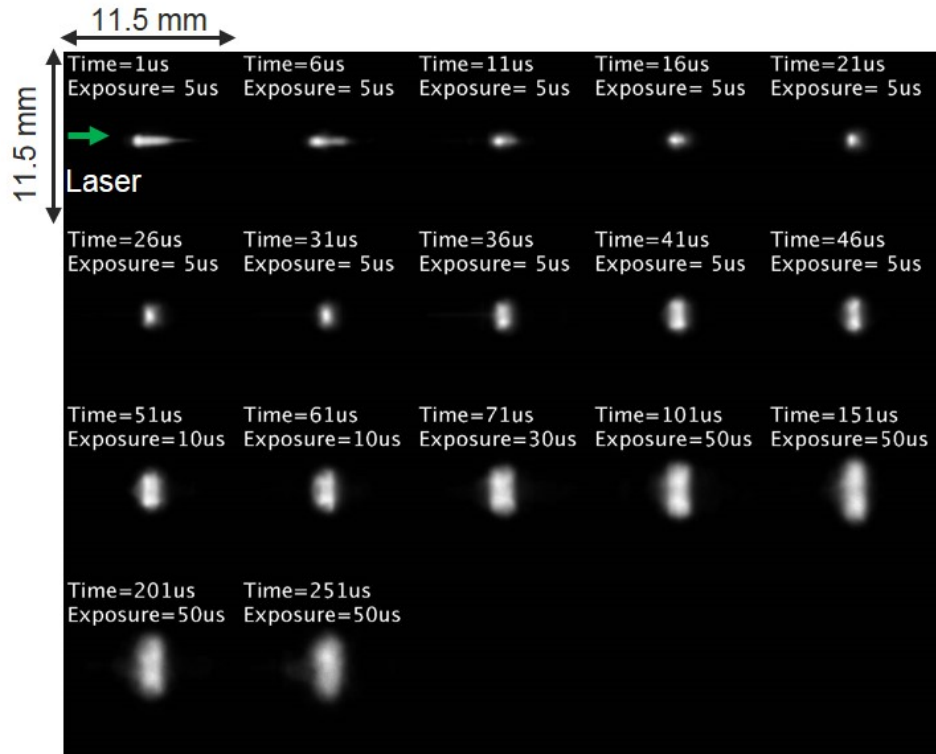


Figure 7.13 LIPIV measurements of rms of the velocity fluctuations for the isothermal flow with *swirl number* of 0.58, obtained from 100 instantaneous measurements at each point. Radial profiles of rms of the axial and radial component of velocity fluctuations at $y/D_f=1, 3, 5$ and 7 . The left side results are based on the single camera system and the right side results are based on the double camera system respectively.

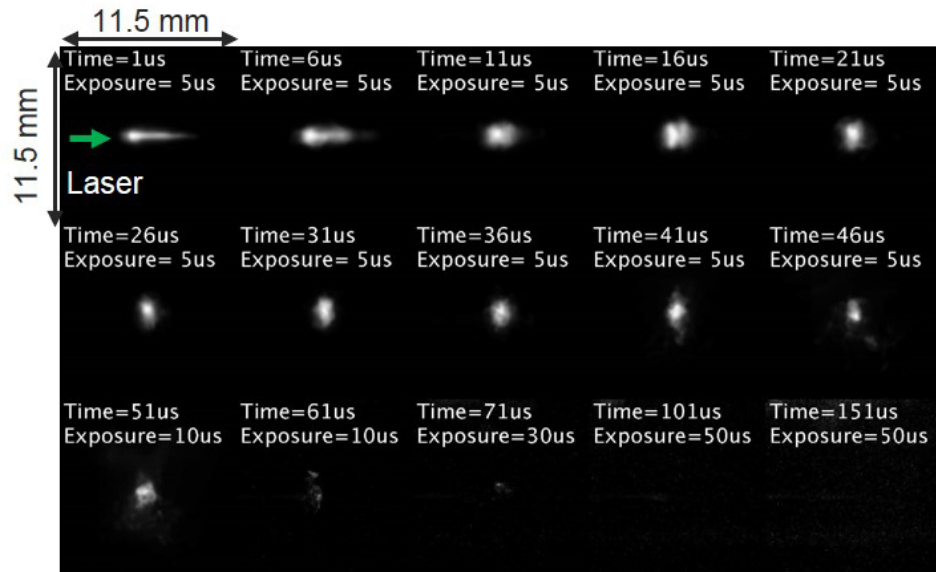
7.2.3 LIPIV sources of uncertainties and image processing in reacting flow conditions

Different from the measurements in the isothermal flow conditions, the LIPIV technique is subject to additional sources of uncertainty in reacting flows, which affect the velocity measurement. These issues in the reacting flows are discussed below.

(1) Quenching effects under fuel-rich mixture conditions



(a)



(b)

Figure 7.14 Temporal evolution of laser-induced plasma in air (a) and pure methane (b) using laser pulse energy of 406 mJ. Each image is an average of 50 instantaneous images of plasma and normalized by the maximum intensity in each image.

As discussed in Chapter 4 and Chapter 5, the high concentration of hydrocarbon fuels quenches the emitted light from the plasma. This quenching effect becomes an important issue for plasma image velocimetry in reacting flows. Figure 7.14 (a) shows that the laser-induced plasma in air is stable and lasts for a long time, even more than 300 μ s after the initiation of the laser pulse.

However, the laser-induced plasma in pure methane has blurred edges and its shape is slightly asymmetrical, as shown in Figure 7.14 (b). Compared to the air plasma, the methane plasma cannot be detected by the ICCD after times of around 50 μs after the initiation of the laser pulse. Therefore, it was necessary to use shorter time gap between images in order to measure the flow velocity in the high fuel concentration region of the flow. Therefore, both the shorter time delay between images and the quenched plasma on the recorded images led to an increase in the uncertainty of the velocity measurements in the fuel-rich zones.

(2) High temperature decreases plasma intensity

As analysed in detail in Chapter 4, the gas temperature rise in the reacting flow leads to lower local density, which reduces the emitted intensity from the plasma. Although the emitted plasma intensity is decreased in flames, the increase of the laser pulse energy demonstrated in Chapter 4 that can offset the intensity reduction in flames. Therefore, compared to 125 mJ laser pulse energy employed in isothermal conditions, a laser pulse energy of 406 mJ was used to counteract the high temperature attenuation in flames.

(3) Contribution of emitted light from the flame to the emitted intensity from the plasma

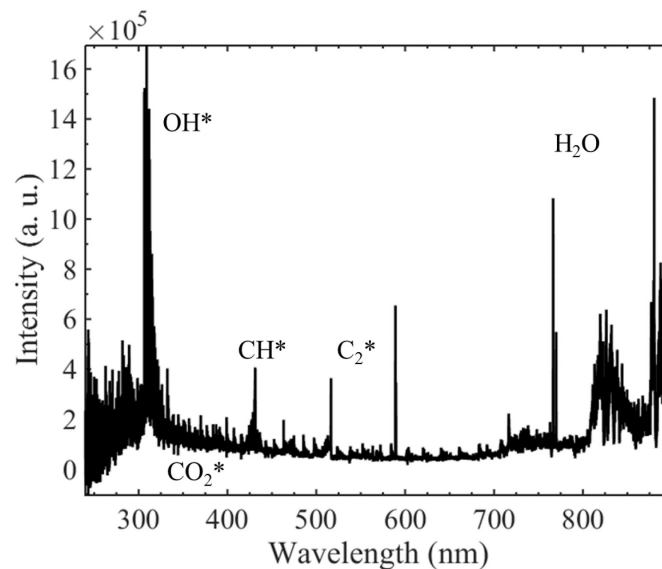


Figure 7.15 Spectra of the emitted chemiluminescent intensity from diffusion-like flames present in the swirl stabilised burner

As shown in Chapter 4, the emitted intensity from the laser-induced plasma is much stronger at early times after the initiation of the laser pulse, so that the first image of the laser induced plasma of double camera LIPIV system is not influenced by the flame light emissions. At times 50 μs ~ 100 μs after the initiation of the laser pulse the plasma emitted intensity is already quite

weak. As a consequence, the second image of the plasma of the LIPIV double camera system is affected by contributions from light emitted from the flame. Figure 7.15 presents the chemiluminescence spectra emitted from the flame in the swirl-stabilised burner for the conditions of this experiment. It was found that chemiluminescent emissions from OH^* radicals at 310 nm and CH^* radicals at the 425 nm band were quite strong in the spectra. In addition, broadband emissions from CO_2^* chemiluminescence were uniformly distributed in the spectra and it was difficult to be filtered. In this study, an Edmund optical high pass filter with spectral cutoff at 450 nm was mounted on the camera to reduce the contribution of flame chemiluminescence on the recorded plasma images. By using this optical filter, emissions at wavelengths below 450 nm were removed from the plasma images, which eliminated a large part of the spectral emissions from flame chemiluminescence.

However, the optical filter could not remove all the broadband flame chemiluminescent emissions. The weighted centroid method of Chapter 6 was used for the identification of the centre of the plasma during isothermal conditions, which is required for plasma tracking in time for LIPIV velocity measurements. Since in reacting flows the contribution from the emitted intensity from the flame on the plasma image must be removed from the image, a novel post-processing method is proposed to process the plasma images in flames.

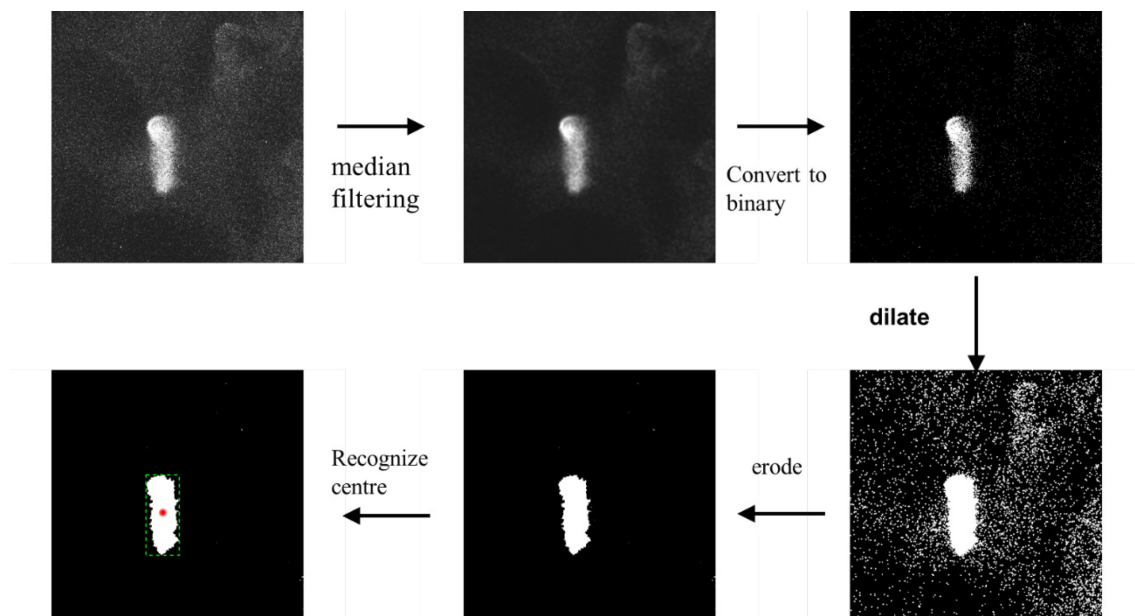


Figure 7.16 Post-processing of the recorded laser-induced plasma images in flames during the LIPIV velocity measurements in reacting flows

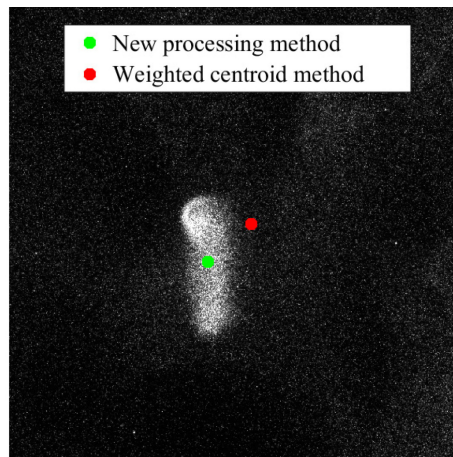


Figure 7.17 Comparison between the weighted centroid method and the new processing method

Figure 7.16 shows the steps that were followed for the plasma image processing. A 2-D median filtering was firstly applied to the plasma image to reduce noise. The resulting greyscale image was then converted to a binary format image. Dilate and erode methods were then applied to the binary format image to remove isolated spot noise. Finally, the centroid of plasma was identified. Figure 7.17 shows that the weighted centroid method was greatly affected by the flames noise on the image, leading to the deviation of the plasma centre in red colour. In contrast, the new processing method successfully tracked the plasma centre in green colour.

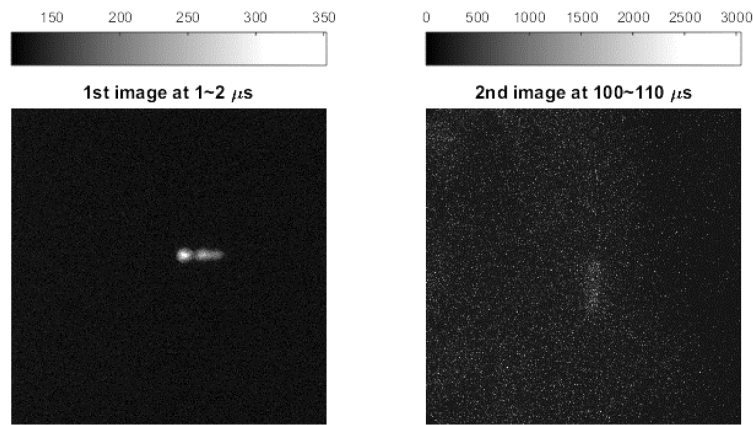
(4) Non-uniform gas temperature field deforms the plasma

An additional source for the LIPIV technique is related to the large temperature gradients of the flame. Chapter 4 demonstrated that the laser beam quality changed during its propagation through high refractive index gradients, which may result in deformed plasma kernels. Since the plasma temporal evolution is very sensitive to the initial conditions of the plasma, the plasma centroid displacement may be more influenced by the initially deformed plasma kernel than by the flow field. In such circumstances, the plasma displacement may not represent the effect of the local flow velocity. Since the local temperature gradients vary from pulse to pulse, currently there is no obvious method to counteract the uncertainty increase of the LIPIV velocity measurement. Therefore, during the LIPIV measurements in the reacting flow, several criteria were proposed in order to eliminate measurements associated to deformed plasma and ensure the accuracy of the velocity measurement. These criteria included:

- i. The plasma intensity in the plasma images (maximum plasma intensity in the first image should be between 500 and 1800 intensity (a. u.)). If the first plasma image

intensity is too weak (350 maximum intensity) as shown in Figure 7.18 (a), the second plasma image is greatly influenced by the flame chemiluminescence. If the first plasma image intensity is too strong, it indicates that the plasma may be induced on the soot in the flames. The soot plasma spatial evolution process does not follow the process in the gas.

- ii. The plasma size (The plasma size should be between 5000 and 5000 pixels, $25.3 \times 25.3 \mu\text{m}^2/\text{pixel}$). Similar to the criterion i, the small plasma has a very weak SNR with high uncertainty. If the plasma size is too large, it can be caused by the strong flame signal or the induced plasma on the soot, as shown in Figure 7.18 (b).
- iii. Plasma orientation, which was based on the angle between the x-axis and the major axis of the plasma. The orientation angle should be larger than 50° . Because the plasma is symmetrical about the x-axis. The angle is about $80^\circ\sim 90^\circ$. If the angle is less than the threshold, it means that the plasma is not symmetrical about the x-axis, due to the deformation of plasma kernel in Figure 7.18 (b) and (c). The displacement of the development of plasma itself can overwhelm the effects of flow field.



(a)

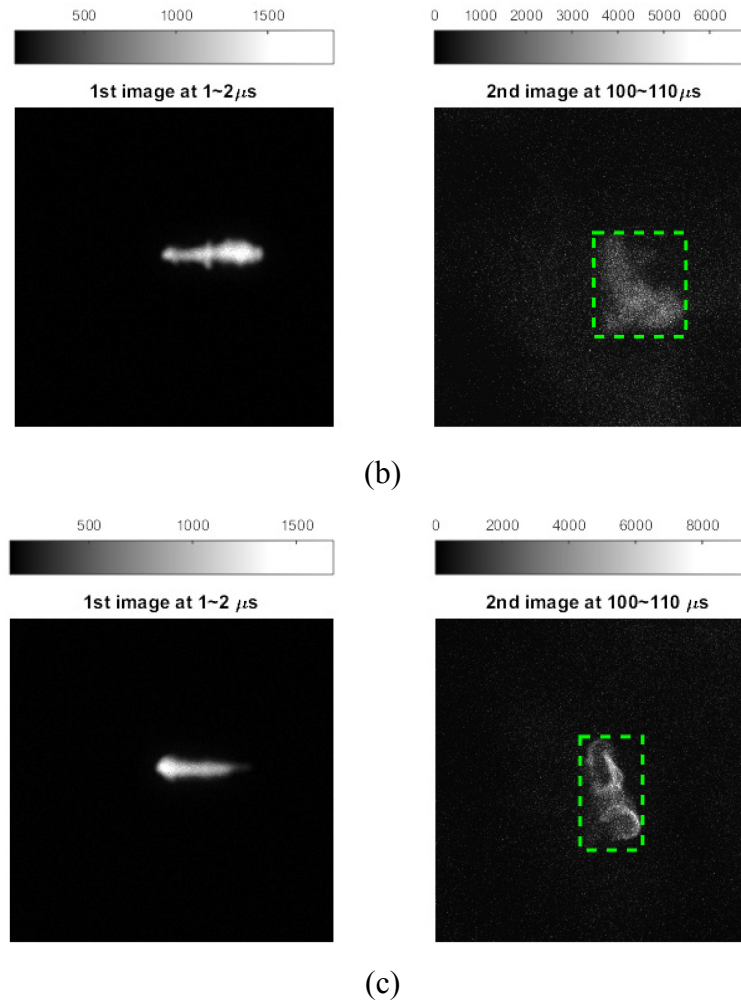


Figure 7.18 Examples of bad images influenced by the flames. Examples of low plasma intensity in the plasma images (a), improper plasma size (b) and improper plasma orientation (c).

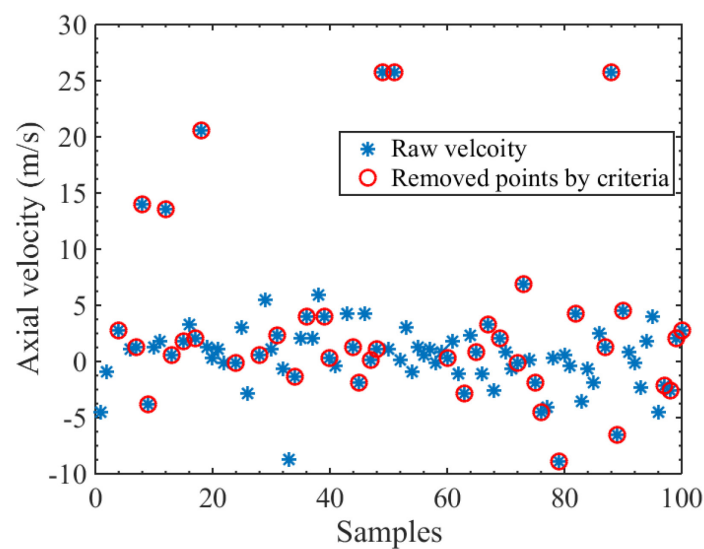


Figure 7.19 The raw LIPIV axial velocity measurements in the reacting flow with operating conditions of Table 7.1. 100 data points are shown and the rejected measurements are indicated which were removed after applying the processing criteria.

Figure 7.19 presents the effect of the proposed criteria of the data processing approach for reacting flows LIPIV measurements after being applied on the raw axial velocity measurements. The red circle data were removed from the raw data after applying the processing criteria, so that the remaining data are, of good accuracy. However, there were still some data that were highly deviated from the mean. The potential remaining erroneous data could be filtered by eliminating data that are outside a certain number of standard deviations away from the mean value.

In conclusion, the sources of errors (2) and (3) for the LIPIV velocity measurements could be offset by using the described measures. For sources of errors (1) and (4), the uncertainty was reduced to a certain degree, but not eliminated fully. Therefore, compared to the LIPIV measurements in the isothermal flow, the in-flame measurements had a relatively large uncertainty in the measurements, which mainly influenced the rms of the velocity fluctuations.

7.2.4 Velocity measurements in reacting flow of the swirl stabilised burner

Figure 7.20 presents the mean velocity profiles measured by PIV technique in the reacting flow [133] using the DLR fuel blend (14.5 l/min CH₄ + 21.79 H₂ l/min + 29.34 N₂ l/min) [165]. Figure 7.21 presents the mean velocity using LIPIV for methane fuel results, where the left side and right sides measurements are performed using a single camera system and a double camera system respectively. The momentum of the methane remained the same as the DLR fuel blend in PIV measurements. Compared with the measurements in the isothermal conditions, there were more challenges in the reacting conditions. Due to the quenching effects in the high fuel concentration region, the points at $y/D_f=1$, $x = 0 \sim 18$ mm were measured using 24 μ s time delay between the two images. The first image was obtained at 1 μ s and the second was obtained at 25 μ s times after the initiation of the laser pulse with 406 mJ laser pulse energy. For the measurements at other locations, the delay time between two images was still about 100 μ s and the laser pulse energy remained 406 mJ. Every measurement represents an average over 100 single shots.

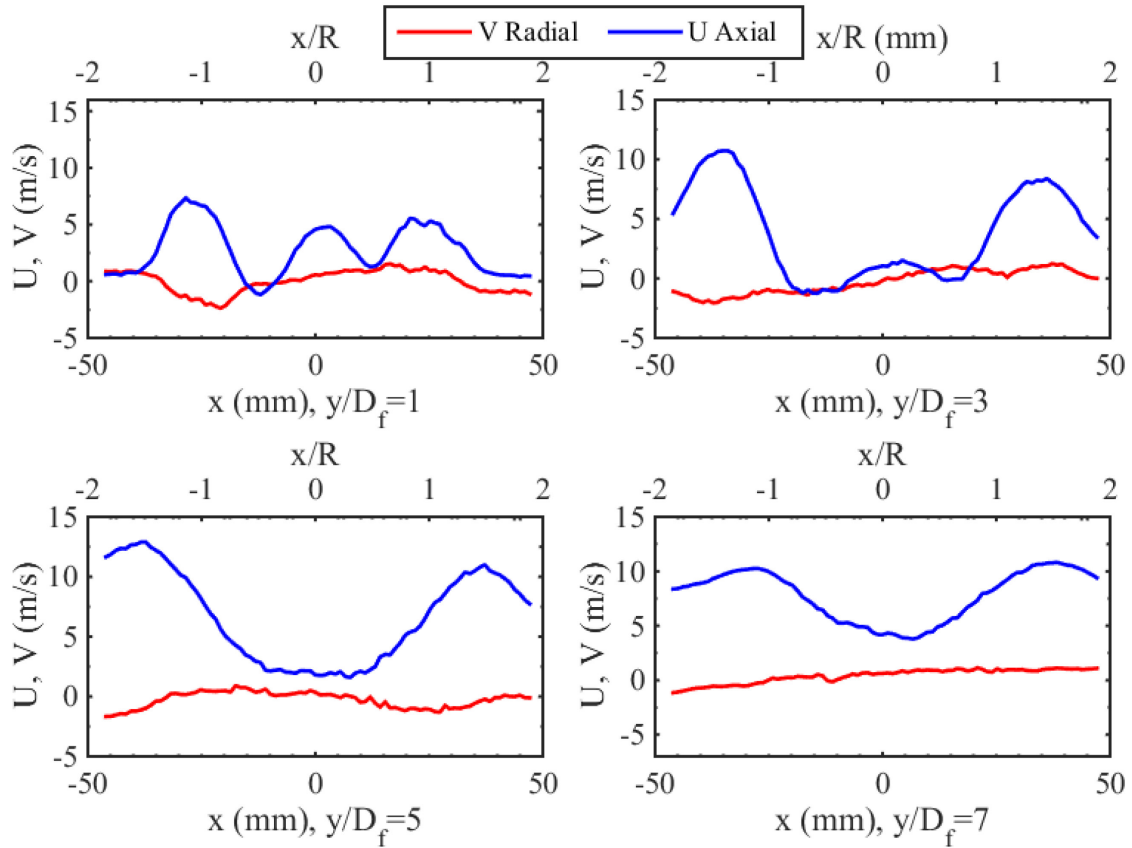


Figure 7.20 Axial and radial mean velocity profiles of the reacting flow operating with DLR fuel blend (14.5 l/min CH_4 + 21.79 H_2 l/min + 29.34 N_2 l/min), measured with PIV in the near burner region without quarl for *swirl number* of 0.58 at different normalized axial distances of $y/D_f = 1, 3, 5$ and 7. Mean velocity computed from 1000 instantaneous PIV images. [133]

Differences between the PIV in Figure 7.20 and the double camera LIPIV in Figure 7.21 velocity profiles were about 3 m/s for axial velocity and 2.2 m/s for radial velocity. However, LIPIV had higher uncertainty due to the sources of errors that were presented in the reacting flows, as explained in section 7.2.3. The comparison between the PIV and LIPIV mean velocity measurements obtained under similar flow conditions in the reacting flow show good agreement qualitatively.

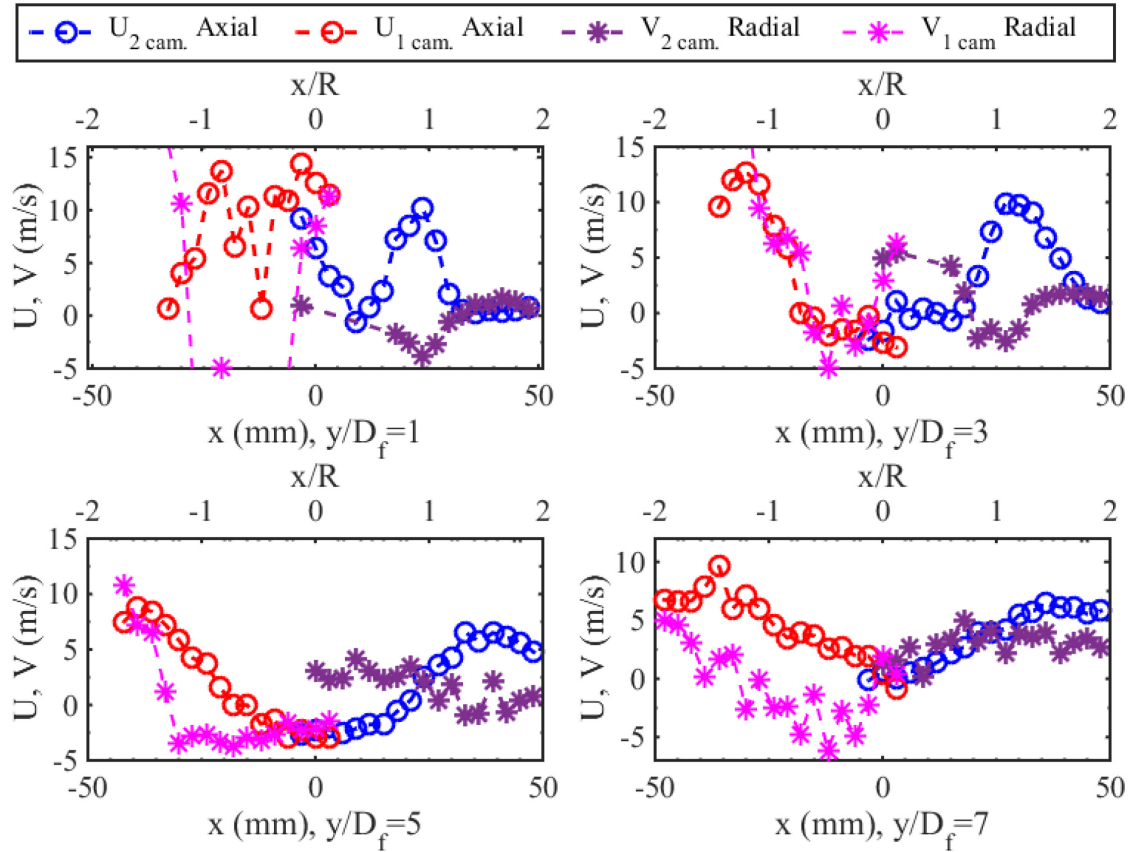


Figure 7.21 LIPIV mean velocity measured in the reacting flow with *swirl number* of 0.58 and averaged over 100 instantaneous velocity measurements at each point. Radial profiles of axial and radial mean velocity components at $y/D_f=1, 3, 5$ and 7 . The left side results are from the single camera approach and right side results are from the double camera approach respectively. The measurements at $y/D_f=1, x = 0 \sim 18$ mm were measured using time delay of $24 \mu s$ between the two images. The rest points were using $100 \mu s$ time delay between images.

In Figure 7.21, the differences between single and double camera LIPIV profiles were 1.3 m/s for axial velocity and 5.2 m/s for radial velocity, except the results at $y/D_f=1$. The LIPIV single camera system axial velocity measurements were consistent with the LIPIV double camera system results. However, the single camera radial velocity component deviated largely from the measured values of the other techniques. The LIPIV single camera system did not work well in the reacting flows, especially for the measurements of the profile at $y/D_f=1$. Compared to the LIPIV single camera measurements in the non-reacting flows, in reacting flows, the laser-induced plasma displacement between the flow field and the quiescent field was not only determined by the velocity of the flow field. As mentioned above, other factors, such as the local temperature gradients in the flame and quenching effects at fuel rich regions, deform the plasma and change its shape, resulting in changes of the displacement measurement.

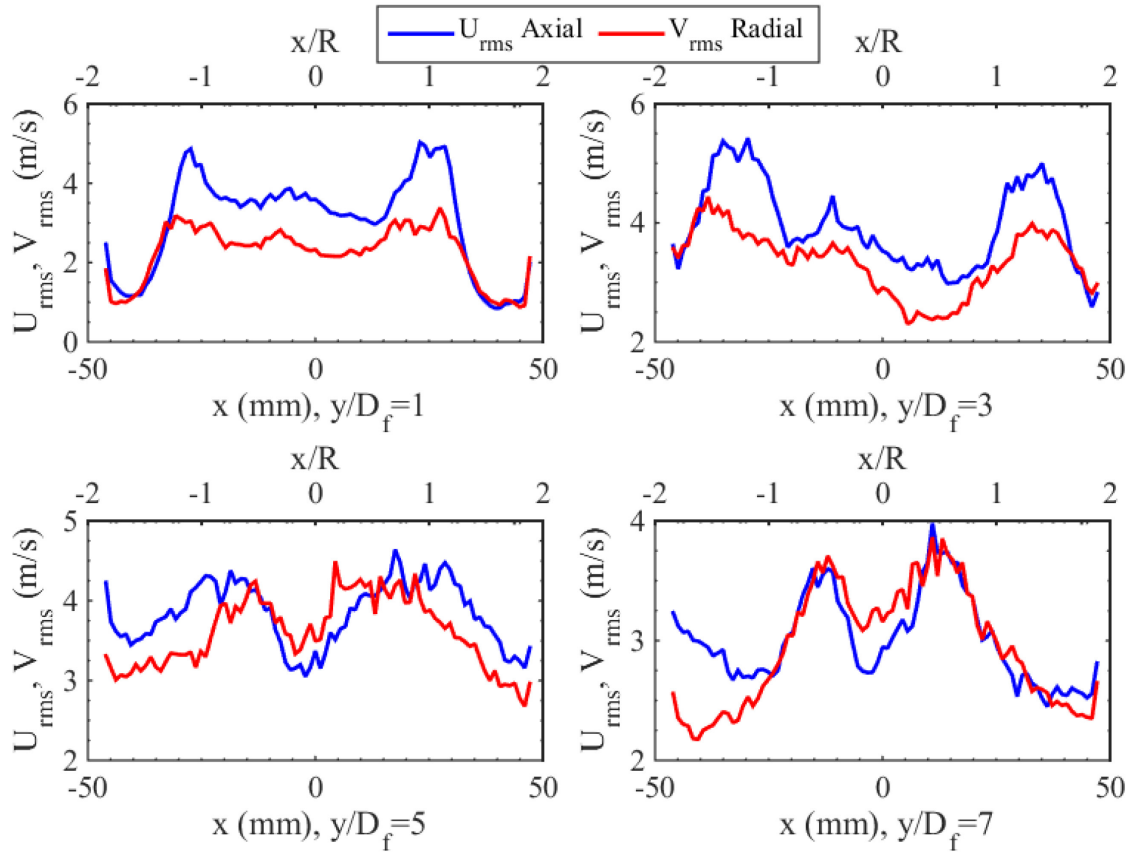


Figure 7.22 Measured PIV rms of velocity fluctuations profiles for reacting conditions with DLR fuel blend with swirl number of 0.58 at different normalized axial distances, $y/D_f = 1, 3, 5$ and 7 . Mean velocity computed from 1000 instantaneous images. [133]

Figure 7.22 and Figure 7.23 present the rms of the velocity fluctuations measured by PIV and LIPIV double camera system respectively. The difference between the rms results of the techniques was 1.35 m/s for axial velocity. Such difference can be caused by various reasons, including the difference in the fuel types, optical ‘noise’ on the images and the geometry of the experimental rig. Due to the flame and quenching effects, the rms of the radial velocity fluctuations were not accurate and varied significantly along each radial profile. For the rms of the axial velocity fluctuations, there is still possibly 1~2 m/s velocity fluctuations caused by the technique in the flames, overwhelming the original rms velocity. Therefore, the profiles of the rms of the velocity fluctuations were different from the PIV results.

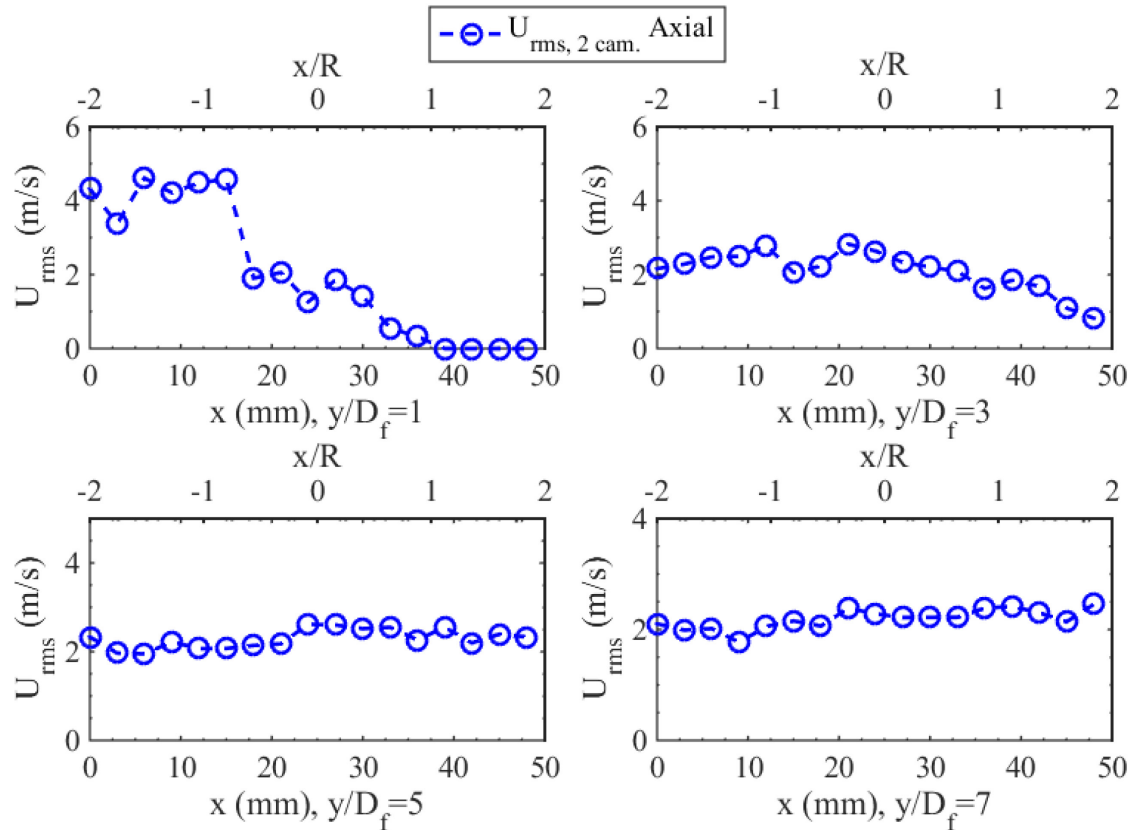


Figure 7.23 LIPIV measurements of the rms of the axial velocity fluctuations for the reacting flow with *swirl number* of 0.58, obtained from 100 instantaneous measurements at each point. Radial profiles of rms of the axial component of velocity fluctuations at $y/D_f=1, 3, 5$ and 7. The points at $y/D_f=1$, $x = 0 \sim 18$ mm were measured using time delay $24 \mu s$ between the two images. The rest points were using $99 \mu s$ time delay between images. The measurements were obtained with a double camera system.

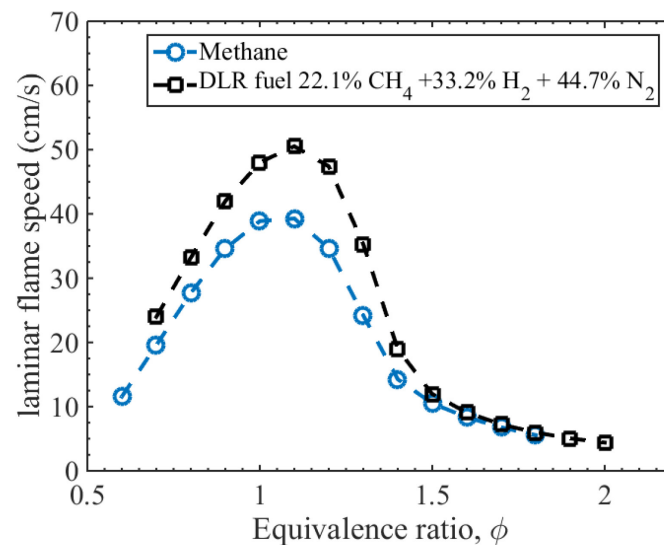


Figure 7.24 Laminar flame speeds of Methane or DLR fuel blend-air mixture as a function of equivalence ratio. The results were obtained with CHEMKIN using GRI Mech 3.0.

Figure 7.24 shows the laminar flame speed for mixtures of air with methane and DLR fuel blend, obtained from CHEMKIN using GRI Mech 3.0. The difference in the velocity profiles could partly occur due to the fuel types and the difference in the reaction speed. Generally, the DLR fuel laminar flame speed was nearly 30% higher than the methane. The higher heating values (HHV) of DLR and methane are 358.35 kJ/mol and 889 kJ/mol, respectively. In addition, the combustion products were also different.

Therefore, to maintain the measurement accuracy, LIPIV two camera system should be used for velocity measurements in reacting flows. After applying the spectral high pass optical filter and the proposed new post-processing method, the measurement uncertainty was reduced to a certain degree. The remaining uncertainty was mainly caused by quenching effects at fuel rich regions (*e.g.* burner central jet region close to the exit) and the deformation of the plasma, which greatly increased the uncertainty of the low mean value radial velocity component and contributed to around 1~2 m/s variation of the axial velocity component.

7.3 Summary

In this chapter, both LIBS and LIPIV were applied to the non-reacting and reacting flow of a swirl-stabilised burner. Mixture fraction and mean velocity measurements were presented and discussed.

LIPIV velocity measurements in isothermal flow conditions were consistent with corresponding PIV velocity measurements. In non-reacting flows, the velocity measurements with a proposed simplified LIPIV system operating with a single camera was in good agreement with results from a two camera LIPIV system. Due to its simplicity, the single camera LIPIV system has a wide range of applications.

In reacting flows, compared with PLIF technique using acetone, the LIBS technique directly measured the local mixture fraction in flames and the results demonstrated the faster mixing process in reacting flows than in non-reacting flows. For LIPIV velocity measurement in flames, several measures, including increasing the laser pulse energy, addition of a spectral high pass optical filter and using a proposed post-processing method, were obtained to increase measurement accuracy. It was found that the single camera LIPIV was not suitable for the reacting flow measurements, due to flame interference with the plasma temporal development. Although the quenching effects and plasma deformation effects increased the uncertainty of

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this technique, especially of the rms of the velocity fluctuations, the measured mean velocity with a double camera LIPIV system still verified the feasibility of the technique for velocity measurements in reacting flows with reasonable accuracy.

Chapter 8 Conclusions

This thesis developed diagnostic methods for the measurement of gas mixture composition and flow velocity using laser-induced plasma. The research firstly evaluated and improved the instantaneous LIBS measurement of local equivalence ratio in methane-air flames. LIBS measurements were performed in different binary hydrocarbon mixture blends, including CH₄, C₃H₈, CO₂ and air and analysed to assess the ability for measurements in non-reacting and reacting fuel-air mixtures, as well as the ability of LIBS to be used as a sensor to monitor temporal variations of fuel blends and the resulting Wobbe index of the fuel. A unique velocimetry technique was proposed and developed, namely Laser Induced Plasma Image Velocimetry (LIPIV), which tracks the temporal movement of laser induced plasma in flows and does not require the addition of ‘seeding’ particles into the flow. LIPIV was tested in quiescent air firstly and then its measurement ability was verified in a non-reacting turbulent air jet flow. Finally, both local air-fuel ratio and velocity measurements were performed in a swirl stabilised coaxial jet burner with central axial injection of gas fuel flow and annular swirling air flow. The main conclusions of the thesis are as follows.

8.1 LIBS (Laser induced breakdown spectroscopy) measurements of local gas composition

- In mixtures of methane and air, the influences of the camera delay time, exposure time and laser pulse energy on LIBS gas mixture composition measurements were investigated. The dependence of spectral intensity ratios of H/O and C₂/CN on methane-air mixtures was quantified over a wide range of conditions extending from pure air to pure fuel. It was found that H/O and C₂/CN intensity ratios depend monotonically on the mole fraction of methane in the ranges of 0.0-0.8 and 0.3-1.0 respectively.
- In reacting regions, due to the attenuation of the spectral emissions from the plasma by flames and density gradients, the stability of H/O intensity ratio was reduced. The resulting increase of measurement uncertainty was then compensated by increasing the laser pulse energy and applying a new processing method on the raw data. It was found that the developed method reduced the variability of the induced plasma to improve the accuracy of the local air-fuel ratio measurements in flames to the same level as for non-reacting flows, which was within 10%. For very rich fuel compositions (methane mole

fraction > 50%), this variation increased to 15% due to quenching effects of the spectral emissions by the fuel.

- The established correlations between the spectral intensity ratios of H/O and C₂/CN with local air-fuel ratio allowed measurement of the spatial gradient of air-fuel ratio across opposed jet diffusion flames. The results showed good agreement with corresponding CHEMKIN calculations and demonstrated the feasibility of instantaneous LIBS measurements of local air-fuel ratio in premixed and diffusion flames.
- It was found that, the results of binary mixtures of hydrocarbon fuels and air had similar relationships between the intensity ratios and the hydrocarbon fractions, compared with the methane-air mixtures. The intensity ratios such as H/O or C₂/CN could still be used as good indicators to infer the hydrocarbon and air mole fractions.
- For binary mixtures of hydrocarbon fuels, it was shown that the spectral intensity ratios of C₂/H for CH₄/C₃H₈ mixtures and H₂/CH₄ mixtures, and of O/H for CH₄/CO₂ mixtures could be used to infer the compositions of binary mixtures.
- The influence of quenching effects on LIBS spectra was assessed. It was found that the presence of hydrogen increased CN emissions and decreased atomic emissions, such as O and N. In addition, rich mixture of hydrocarbon in air led to the non-linear decay of the emitted intensity at different atomic lines. While limitations exist, the LIBS spectrum, the spectral intensity and intensity ratios between lines could be used to infer the binary mixture composition and the Wobbe index of fuels.

8.2 LIPIV (Laser-induced plasma image velocimetry) for local flow velocity measurements

- The LIPIV technique was proposed for the first time for flow velocity measurements based on tracking the laser induced plasma and was calibrated in quiescent air. The different time delays between two plasma images and the post processing methods to calculate the plasma displacement between two consecutive images were developed and evaluated. It was found that a 100 μs time delay between the plasma images and a

weighted centroid method for the identification of the centre of the plasma led to smallest variations of plasma displacements in a quiescent field, which led to velocity uncertainty of ± 3.6 m/s along the direction of the laser beam axis and ± 1.0 m/s along the direction perpendicular to the laser beam axis. In non-reacting conditions, the technique had a spatial resolution of 5 mm for laser pulse energy of 125 mJ. Compared with PIV and LDV techniques, the temporal resolution of LIPIV shows potential for measuring high frequency velocity fluctuations, however, it may be limited by its low spatial resolution. The spatial resolution could be improved by reducing the laser pulse energy and focus spot size.

- Velocity measurements using LIPIV in a turbulent air jet showed very good agreement with the expected development of the flow field in jets. It was shown that, both the velocity decay along the centreline of the jet and the radial profiles at different downstream positions from the jet exit were consistent with theoretical values.
- As part of the development of the new LIPIV technique, a simplified LIPIV system based on a single camera was proposed. Instead of using the plasma displacement between two consecutive images of the plasma, the single camera LIPIV used the displacement between the plasma location in the flow field at a specific time after the initiation of the laser pulse and in the quiescent field at the same time after the initiation of the laser pulse. In non-reacting swirl flows, it was found that the double camera LIPIV and single camera LIPIV flow velocity measurements were consistent, suggesting that the simplified LIPIV technique has the potential to be applied to a wide range of applications.
- The LIPIV was applied to the swirl burner with Reynolds number of 29000, 0.58 swirl number and 0.72 global air-fuel ratio of methane-air mixtures. In the isothermal conditions, both the single camera and double camera velocity measurements agreed well with related results using different optical techniques. However, in the reacting flow, the contribution resulting from flame chemiluminescent emissions on the plasma emitted intensity, quenching effects of the plasma at fuel rich regions and non-uniform temperature fields increased the uncertainty of LIPIV velocity measurements. By using a spectral high pass optical filter (cut-off wavelength at 450 nm) and a newly developed post-processing method, it was found that only the LIPIV double camera system

successfully measured the flow velocity in reacting flows with slightly increased uncertainty relative to the non-reacting flow.

- Both the mixture fraction and velocity profiles in swirl-stabilized flames showed that the methane flame of this study had a larger fuel jet spreading angle than the DLR fuel using for acetone PLIF mole fraction measurements and PIV velocity measurements reported by Stetsyuk [133].
- The developed LIPIV technique and the single camera system have the potential to be applied to real combustors to quantify the local velocity measurements in the exhaust gases without the introduction of ‘seeding’ particles. This can be achieved with minimum optical access through an endoscope on the wall that can deliver the laser pulse and detect the emitted spectral intensity.

8.3 Recommendation for future work

There are several recommendations related to the evaluation of the laser induced plasma methods that this thesis examined. These recommendations are related to the better understanding of the source of uncertainties that may influence the accuracy of the mixture composition and the velocity measurements using laser induced plasma.

- The probe volume of the LIBS technique still needs to be investigated. The species, which contribute to the emissions on the LIBS spectra, may have originated from the initial plasma spot or from the surrounding ambient gas as the plasma expands. It is necessary to study how the plasma interacts with the surrounding gas, so that the probe volume of LIBS can be accurately defined.
- Although measurements with the LIBS technique are performed under the assumptions of optically thin and LTE plasma, quenching effects exist, influencing the spectral emissions from the plasma, leading to non-linear behaviour of the emitted spectral intensity from different species present in the plasma. The physics of the plasma quenching effects need to be studied to understand the behaviour of plasma emissions.

- Since the laser-induced plasma spectra are also related to the local gas density, it is possible to use the measurement of gas density to quantify the local temperature at constant ambient pressure. Therefore, using the laser-induced plasma, it is possible to extend the developed LIBS and LIPIV techniques to measure local mixture composition, temperature and velocity simultaneously. The main difficulty for the extension for temperature measurement is the spectrometer accuracy. Since the temperature is very sensitive to spectral changes, it is difficult to measure the instantaneous temperature accurately using the recorded LIBS spectra so far [53,60].
- Another temperature measurement method using LIBS has the potential to be developed by measuring the shock wave speed initiated by the breakdown. At the beginning of laser-induced breakdown, a shock wave is formed. The wave decays with time and eventually becomes a sound wave. The sound speed in ideal gas is related to the temperature and the gas properties. Since the LIBS result can provide the local gas composition information, the temperature can be calculated from the sound speed. This technique requires using Schlieren imaging [151] to visualise the shock wave, while the mixture composition is available from the LIBS measurement.
- By measuring the mixture fraction, flow velocity and temperature in combustors simultaneously using the same laser-induced plasma, the turbulent heat fluxes and the mass fluxes can be obtained through the correlations between the quantities. The net effects of the turbulence in the turbulent flames can be quantified.
- The current research found that the LIPIV velocity uncertainty mainly results from the asymmetrical development of the plasma shape. Under different ambient conditions, the initial energy distribution of the plasma varies from pulse to pulse. If it is possible to know the physics of the plasma development processes, the uncertainty of the plasma image velocimetry technique, caused by variation of plasma between shots, can be greatly reduced.
- Extending the laser induced plasma techniques to measure at different locations simultaneously will allow simultaneous measurements in space. A laser beam splitter can be used to generate multiple laser beams and focus them at different locations in space to induce multiple plasmas simultaneously in a flow field. In this way, mixture

composition and velocity measurements can be obtained at the same time at different locations in a flow, which increases the measurement speed and provides instantaneous spatial information in a flow.

- LIBS has been operated by using a Nd:YAG laser, whose pulse has a nanosecond duration. However, the plasma induced by short laser pulses (femtosecond or picosecond duration) has different behaviour, which can lead to improved measurements of mixture fraction, temperature and velocity. This technique requires development in the long term, especially as femtosecond and picosecond lasers become widely available [166,167].
- Finally, the developed laser induced plasma based measurement techniques have the advantage of not requiring the addition of any substances added in the flow, either tracers to measure the concentration of substances or ‘seeding’ particles to measure the flow velocity. In addition, ideas are available on methods to measure the gas temperature without any addition of substances as well. Therefore, the laser induced plasma techniques offer the potential to obtain measurements in real combustors, *e.g.* gas turbine combustors for aeroengines or power generation, spark ignition or compression ignition internal combustion engines, with minimum optical access to the combustion chamber. Such approach has the unique potential to measure simultaneously mixture fraction, flow velocity and temperature in combustors under realistic operating conditions and requires further development in the future.

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