2-D LIBS of LPG and Electrolytic OxyHydrogen mixture flame

Seok Hwan Lee, H. Thomas Hahn, Jack J. Yoh
School of Mechanical and Aerospace Engineering Seoul National University
1 Gwanakro, Gwanakgu, Seoul, 151-744, South Korea

1 Introduction

The LIBS is based on the optical spectroscopy of laser-induced plasma generated by the breakdown of the target in its gas, liquid or solid state. There are several successful applications of LIBS to combustion analyses as such to include identification of industrial exhausts [1,2], determination of fuel equivalence ratio in off gas and flame [3-5], and composition measurements of hydrocarbons [6].

Previously, LIF (laser induced fluorescence) has been used to measure combustion radicals such as OH, CH and CN. Raman spectroscopy has been used to measure CH4, H2O and CO concentrations in flame [7]. The chemical species in the flame is also evaluated by LIBS. Eseller et al. used LIBS with an ungated detector for diagnosing methane and biodiesel flame [8]. They used N, O and H LIBS signals from a CH_4/air flame to determine the equivalence ratio in the flame. Mansour et al. evaluated the turbulent premixed flame using double pulse LIBS method [9]. And Kiefer et al. evaluated the methane and DME(dimethyl ether) flame using LIBS [10]. They provided the optimal laser energy to generate laser plasma and the fuel air equivalence ratio according to the flame radial position. Rai et al. measured the metallic particle in the hydrocarbon flame for rocket engine health monitoring using LIBS [11]. Previous studies of LIBS for combustion diagnostics are focused on the measurement of chemical species in the small local volume or 1-dimensional positions. But, the 2-D mapping of chemical species by LIBS has not been attempted previously.

EOH (electrolytic oxyhydrogen) gas is a stoichiometric mixture of hydrogen and oxygen produced from water through electrolysis [12]. As the water electrolysis is quite instantaneous, it can be produced on demand without the need for storage. Thus the EOH gas is safer and easier to use than its alternative, namely hydrogen gas. Nonetheless the combustion mechanism of the EOH-hydrocarbon mixture has not been studied in detail in the literature.

In this paper, we have developed a 2-dimensional LIBS mapping which can provide chemical species information about the flame. A 2-D LIBS mapping allows the spatial extension of the conventional point measurement to areal mapping concept similar to LIF and Raman spectroscopy in combustion. The information about the dissociated chemical species and particle (soot) are unique feature of the system not attainable via conventional LIF and Raman spectroscopy. We present both atomic and molecular chemical contours of LPG, LPG-EOH mixture and LPG-AIR mixture flames using LIBS.

2 Experiment

Correspondence to: jjyoh@snu.ac.kr (Jack J. Yoh)

Figure 1 shows the experimental set-up. A Brown Gas Generator (Best Korea, BB-2000) generates EOH (electrolytic oxyhydrogen) gas. The generated EOH gas is mixed with LPG(C3H8) gas through the mass flow controllers (MFCs) to control flow rates. The mixed fuel is fed into the burner which has a 0.68-mm diameter opening. The Reynolds number for our case is about 100, corresponding to a laminar flame condition. The burner traverses along the x, y axis to draw 2-D mapping images. The burner used in our experiment is a torch used for welding, and thus the resulting flame may not be symmetrical.

The LIBS system is used to map out the contour of flame chemical information. The plasma is generated by a laser beam (Continuum Inc., Powerlite) with a 532-nm wavelength through a convex lens having a 120-mm focal length. Since the flame has different density according to the fuel, the laser energy generating plasma is changed for different fuel mixture. So the selected laser energies for generating plasma are 200 mJ for LPG 50 ccm (cubic centimeter per min), LPG 50 ccm-EOH 10 ccm mixture, LPG 50 ccm-AIR 10 ccm mixture flame and 500 mJ for EOH 500 ccm, EOH 500 ccm-LPG 70 ccm mixture flames. These laser energies are minimum values for generating laser plasma which provides enough LIBS signal. The plasma light is collected by a quartz lens having a 100 mm focal length which is perpendicular to the laser shooting direction for LIBS analysis. The collected plasma light is sent to the echelle spectrometer (Andor Mechelle 5000) which has 0.1 nm resolution and an ICCD (Andor iStar 1024 x 1024) for recording the signal. The 2 μs delay time and 20 μs TTL width are used for LIBS measurement. The several atomic and molecular band peak are selected for mapping of chemical signal (C : 247.8 nm, CN band : 388.3 nm, C_2 : 516.2 nm, H : 656.2 nm, O 777.3 nm). Also, laser is irradiated from left side and plasma light is collected with 90 º configuration of laser direction. So, the LIBS signal at left side flame is higher than at right side flame.

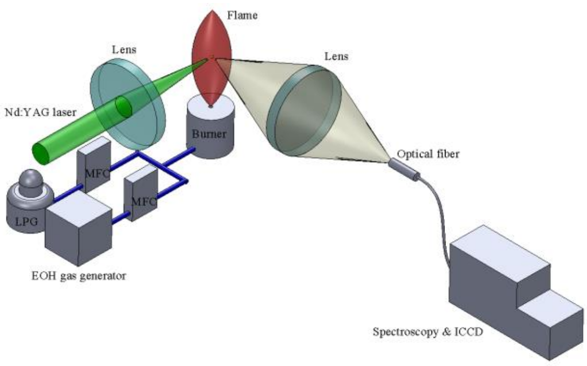


Figure 1. Experimental setup

Figure 2 (a) shows the image of flame for LPG 50 ccm. This hydro-carbonic flame has some zones which are called yellow, dark and blue zone [13]. The dark zone is basically an indication of fuel pyrolysis and soot inception. This zone is followed by a yellow-luminous zone where soot burning is dominant. The flame species contour is obtained by traversing the burner at 0.5-mm steps in 28-mm height and 16-mm width grid. Figure 2 (b) represents a LIBS spectrum at a single position (-1 mm, 0 mm) in the flame and thus multiple mapping of the entire grid can be performed to provide the chemical species information about the area. Every measurement presented here will correspond to the averaged quantity obtained by taking 10 shots at each position. The error of LIBS signal is about 10 % in all cases.

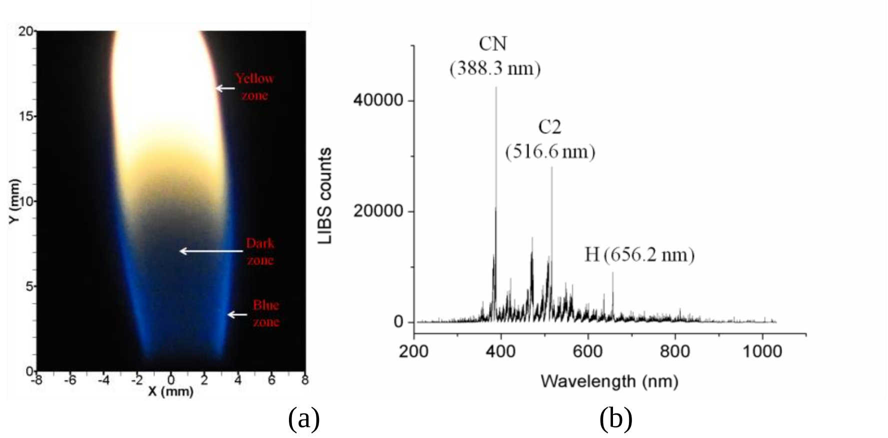
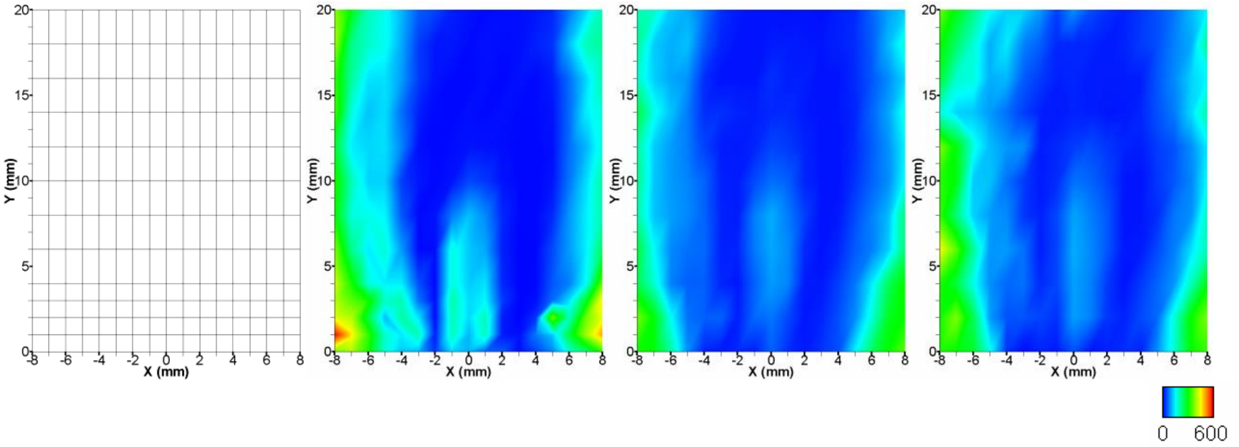


Figure 2. (a) Flame image of LPG 50 ccm, (b) LIBS spectrum of LPG flame at a single position (-1 mm, 0 mm) from 200 mJ laser energy at 2 µs delay time. Three peaks of CN (388.3 nm), C_2 (516.6 nm) and H (656.2 nm) are identified.

3 Results

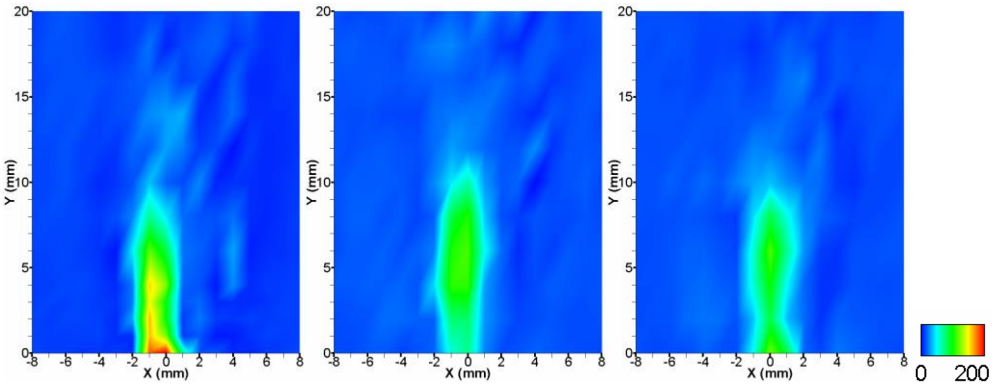
Figure 3 (a) shows the measurement grid for LPG 50 ccm flame. Each measurement corresponds to a spectrum similar to fig. 2(b). Figure 3 (b) shows the LIBS contour of the base signal at LPG 50 ccm alone flame. A base is an averaged intensity of the entire LIBS spectra from 320 to 350 nm. Figure 3 (c) and (d) show the LIBS base signal mappings at LPG 50 ccm–EOH 10 ccm and LPG 50 ccm-AIR 10 ccm mixtures flames, respectively. The base signal depends on the plasma intensity which is related to the density field of flame, thus providing the flame density information. LPG 50 ccm alone flame is shown to have high density at the fuel jetting region, and mixture flames (LPG 50 ccm-EOH 10 ccm, LPG 50 ccm-AIR 10 ccm) have relatively lower density at corresponding region due to the existence of oxygen in the mixture fuel. In the mixture cases, the primary oxygen and fuel burn from inside toward outside, so the density in the fuel jetting region becomes low. The burning region has low density field and the outside of flame has high density field due to a high air concentration for all cases. Thus when analyzing a flame with LIBS, one must use signal to base ratios or peak to peak ratios to avoid any unwanted signal change due to the difference in density.

Figure 4 (a), (b) and (c) show the C_2/base LIBS ratio mapping for LPG 50 ccm alone, LPG 50 ccm-EOH 10 ccm mixture and LPG 50 ccm-AIR 10 ccm mixture, respectively. When the laser induced plasma from organic substance is generated, there are known pathways leading to production of excited species in the previous LIBS study [14]. Three main routes can be cited as: (i) fragmentation of the original compound to directly release carbon dimmers, (ii) reaction in the plume of atomic and ionic constituents of the original compound with the air surrounding the plasma leading to production of CN, and (iii) recombination of C and N atoms from the compound in the plasma to produce both C_2 and CN. The molecular formula of LPG is C_3H_8. Since there is no nitrogen in the LPG fuel, CN signal comes from the recombination between carbon in LPG and nitrogen in air. C_2 LIBS signal is originated from the fragmentation of the carbonic fuel. So C_2/base signal represents the fuel concentration in fig. 4 (a). On the other hand, the LIBS signal ratio intensities for both LPG 50 ccm-EOH 10 ccm mixture and LPG 50 ccm-AIR 10 ccm mixture are lower than for LPG 50 ccm alone. This means that the concentration of unburned fuel in the flame decreases with the EOH gas and AIR addition.



(a) (b) (c) (d)

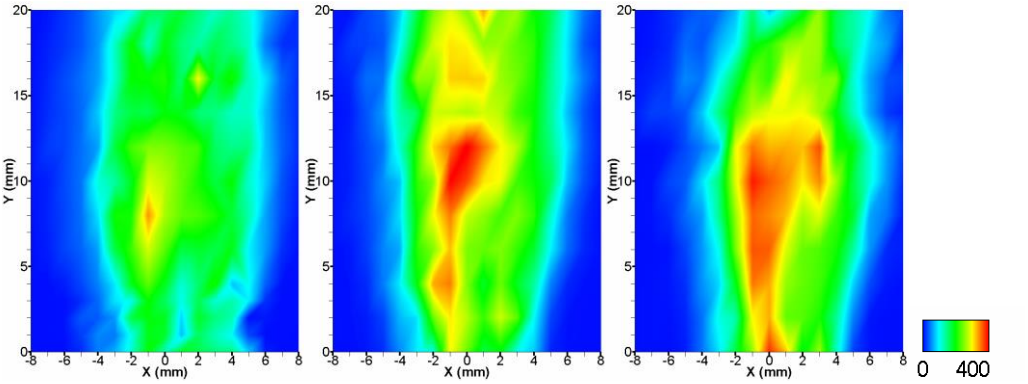
Figure 3. Density mapping of LPG flame using LIBS base signal (a) measurement positions, (b) LIBS base signal mapping of LPG 50 ccm flame, (c) LIBS base signal mapping of LPG 50 EOH 10 ccm, (d) LIBS base signal mapping of LPG 50 AIR 10 ccm with 200 mJ laser energy and 2 μs delay time. (base : average signal from 320 nm to 350 nm)



(a) (b) (c)

Figure 4. C_2/base LIBS signal ratio mapping for (a) LPG 50 ccm (b) LPG 50 ccm-EOH 10 ccm mixture (c) LPG 50 ccm-AIR 10 ccm mixture flame with 200 mJ laser energy and 2 μs delay time.

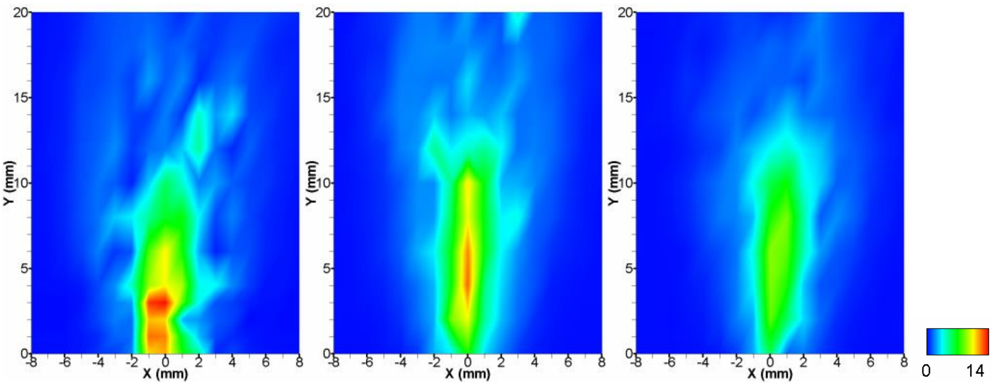
Figure 5 (a), (b) and (c) show CN/base LIBS ratios mapping for LPG alone, LPG 50 ccm-EOH 10 ccm mixture and LPG 50 ccm-AIR 10 ccm mixture flames, respectively. CN LIBS signal is originated from recombination between the carbon and the nitrogen from air component [14]. If the carbonic fuel is dissociated by the oxidation, the carbon atom can be recombined with the nitrogen from air easily. LPG 50 ccm alone flame has uniform CN LIBS signal distribution in fig. 5(a). But, for LPG 50 ccm-EOH 10 ccm mixture and LPG 50 ccm-AIR 10 ccm mixture cases, CN LIBS signal is high in the middle of the flame. Since we add the EOH and AIR or oxygen, the carbonic fuel is dissociated easily. Also, the signal distribution of CN/base LIBS signal at LPG 50 ccm-AIR 10 ccm mixture flame is broader than LPG 50 ccm-EOH 10 ccm mixture flame near the middle of the flame since the nitrogen in the mixture reacts with carbonic fuel directly.



(a) (b) (c)

Figure 5. CN/base LIBS signal ratio mapping for (a) LPG 50 ccm (b) LPG 50 ccm-EOH 10 ccm mixture (c) LPG 50 ccm-AIR 10 ccm mixture flame with 200 mJ laser energy and 2 µs delay time.

Figure 6 (a), (b) and (c) show H/O LIBS signal ratios for LPG 50 ccm, LPG 50 ccm-EOH 10 ccm mixture and LPG 50 ccm-AIR 10 ccm mixture flames, respectively. H/O LIBS ratio can be used for measuring fuel air equivalence ratio in the flame [10]. So H/O LIBS signal ratio has high intensity at the fuel jetting region in the figures. The H/O LIBS ratio for LPG 50 ccm-EOH 10 ccm mixture in fig. 6 (b) has lower intensity than for LPG 50 ccm alone flame due to increasing oxygen concentration in fig. 6 (a). When we add EOH to LPG flame, the distance of fuel jetting region is longer due to increase of fuel jetting speed shown in fig. 6 (b). Also, the high intensity H/O ratio region became sharp with adding EOH gas since the fuel is burned from inside of flame due to the presence of oxygen in the flame in fig. 6 (b). And the H/O LIBS ratio for LPG 50 ccm-AIR 10 ccm mixture in fig. 6 (c) is lower than LPG 50 ccm-EOH 10 ccm mixture. This is because there is no additional hydrogen, but oxygen from air is added to the flame at LPG 50-AIR 10 ccm flame.



(a) (b) (c)

Figure 6. H/O LIBS signal ratio mapping for (a) LPG 50 ccm (b) LPG 50 ccm-EOH 10 ccm mixture (c) LPG 50 ccm-AIR 10 ccm mixture flame with 200 mJ laser energy and 2 µs delay time.

4 Conclusions

We have conducted the two-dimensional spectroscopic mapping of flame via LIBS in the combustion gases of LPG, LPG-EOH mixture, LPG-AIR mixture for the first time. The LIBS base signal provides density information of a flame via the relation between density and LIBS signal ratio represents the rate of dissociation of carbonic fuel. H/O LIBS signal ratio provides fuel air equivalence ratio in the flame. Thus we conclude that the present LIBS 2-D mapping can provide crucial information related to the flame such as density, atomic and molecular chemical concentration, and fuel/air equivalence ratio.

5 Acknowledgment

The financial support of this work was provided by the National Research Foundation of Korea under the National Space Laboratory (NSL-2009) Project, contracted through the IAAT and WCU (World Class University) Program (R31-2008-000-10083-0) at Seoul National University.

References

[1] Zhang H, Yueh F-Y, Singh J P. (1999). Laser-induced breakdown spectrometry as a multimetal continuous-emission monitor. Appl. Optics 38: 1459.

[2] Buckley S G, Johnsen H A, Henchen K R, Hahn D W. (2000). Implementation of laser-induced breakdown spectroscopy as a continuous emissions monitor for toxic metals. Waste Manage. 20: 455.

[3] Ferioli F, Puzinauskas P V, Buckley S G. (2003). Laser-induced breakdown spectroscopy for on-line engine equivalence ratio measurements. Appl. Spectro. 57: 1183.

[4] Ferioli F, Buckley S G, Puzinauskas P V. (2006). Real-time measurement of equivalence ratio using laser-induced breakdown spectroscopy. Int. J. Engine Reserch 7: 447.

[5] Stavropoulos P, Micalakou A, Skevis G, Couris S. (2005). Quantitative local equivalence ratio determination in laminar premixed methane-air flames by laser induced breakdown spectroscopy (LIBS). Chemical Phy. Lett. 404: 309.

[6] Ferioli F, Buckley S G. (2006). Measurements of hydrocarbons using laser-induced breakdown spectroscopy. Combust. and Flame 144: 435.

[7] Egermann J, Seeger T, Leipertz A. (2004). Application of 266-nm and 355-nm Nd:YAG laser radiation for the investigation of fuel-rich sooting hydrocarbon flames by Raman scattering. Appl. Optics 43: 5564.

[8] Eseller K E, Yueh F Y, Singh J P. (2008). Laser-induced breakdown spectroscopy measurement in methane and biodiesel flames using an ungated detector. Appl. Optics 47: 144.

[9] Mansour M S, Imam H, Elsayed K A, Abbass W. (2009). Local equivalence ratio measurements in turbulent partially premixed flames using laser-induced breakdown spectroscopy. Spectrochim. Acta Part B 64: 1079.

[10] Kiefer J, Troger J W, Li Z S, Alden M. (2011). Laser-induced plasma in methane and dimethyl ether for flame ignition and combustion diagnostics. Appl. Phys. B 103: 229.

[11] Rai V N, Cook R L, Singh J P, Winstead C, Yueh F-Y. (2003). Laser-induced breakdown spectroscopy of hydrocarbon flame and rocket engine simulator plume. AIAA J. 41: 2192.

[12] Yadav M X, Sawant S M, Anavkar J A, Chavan H V. (2011). Investigations on generation methods for oxy-hydrogen gas, its blending with conventional fuels and effect on the performance of internal combustion engine. J. Mech. Engi. Reser. 3: 325.

[13] Ahsan R C, Subramanyam R G. Laser induced fluorescence measurements of radical concentrations in hydrogen-hydrocarbon hybrid gas fuel flames. Int. J. Hydrogen Energy. 25: 1119.

[14] Lucena P, Dona A, Tobaria L M, Laserna J J. (2011). New challenges and insights in the detection and spectral identification of organic explosives by laser induced breakdown spectroscopy. Spectrochem. Acta B 66: 12