Instantaneous Measurement of Local Concentration and Vapor Fraction in Liquid-Gas Mixtures by Laser-Induced Breakdown Spectroscopy

Akihiro KIDO**, Kenji HOSHI***, Hiroto KUSAKA***, Hideyuki OGAWA**** and Noboru MIYAMOTO****

Laser-induced breakdown spectroscopy (LIBS) with atomic emission excited with a focused high-energy ND: YAG laser was applied to quantify the concentration and the vapor fraction of liquid-gas mixtures. With LIBS it is possible to quantify local concentrations accurately even in liquid-gas mixtures as the ratio of the number of fuel-borne hydrogen atoms to nitrogen or oxygen atoms in the ambient gas. The ratio has a strong linear relation with the ratio of the peak emission intensities regardless of phase of the fuel. As the full width at half maximum (FWHM) of the emission peak from the fuel-borne hydrogen increases linearly with the liquid fraction due to the Doppler shift with micro-explosions, the FWHM yields the fuel vapor fraction. Simultaneous, high-resolution measurements of equivalence ratios and vapor fractions in an intermittent fuel spray in a pressurized atmosphere were obtained with this method. The results showed that the tip of the intermittent spray has a richer mixture with a lower vapor fraction.


1. Introduction

Understanding the mixture formation process in fuel sprays, including the evaporation and entrainment mechanism is essential to improve combustion efficiency and exhaust gas emissions, and here quantitative measurements of local and instantaneous fuel concentrations are necessary to describe the phenomena and characteristics. However, it is not easy to measure the fuel concentration distributions quantitatively as the fuel spray contains both gas and liquid phases in a spatially complicated and un-steady structure. Several methods of measurement have been developed to determine the fuel concentration distribution in a fuel spray, but there are no methods with sufficiently high spatial and time resolutions as well as accuracy to cover a wide range of fuel concentrations.

A field where gas and liquid coexist can be analyzed with optical measurements of the absorbance and scatter at two wavelengths[1] and with an exciplex method[2]. These methods have limitations, however, imposed by the experimental conditions as a special tracer or a fuel with tracer is necessary. Laser-induced breakdown spectroscopy (LIBS) which has been applied to gas analysis has the advantage that it requires no special tracer, it has no limitations on the wavelength of laser light, and has a high accuracy over a wide range of mixture strengths, from lean to rich.

In the research reported here LIBS was applied to quantitative measurements of fields, where the gas and liquid components coexist, and the simultaneous measurement of fuel concentration and evaporation rate was achieved. The experiments were expanded to an analysis.
of the evaporation and mixture formation processes in an intermittent fuel spray in a heated compressed vessel.

2. Theory of Atomic Emission

2.1 Emission intensity

The number of excited atoms per the unit time and unit section, \( R \), is given as follows:\(^3\):

\[
R = N_1 \Delta \tau B_{12} u(\nu) \left[ \text{m}^{-2} \text{s}^{-1} \right]
\]  

(1)

Here, \( N_1 \): Number density of lower level, \( \Delta \tau \): Thickness of absorbance; \( B_{12} \): Einstein’s absorbance coefficient \( \left[ \text{m}^3 \text{J}^{-1} \text{s}^{-2} \right] \); \( u(\nu) \): Energy density of excitation laser \( \left[ \text{Jm}^2 \text{Hz}^{-1} \right] \).

Defining the cross section of the incident laser, \( \Delta S \), and the volume, \( \Delta V = \Delta z \Delta S \), the absorbed energy, \( W \), is given as:

\[
W = R \Delta S \ h \nu = N_1 \Delta V B_{12} u(\nu) h \nu \left[ \text{Js}^{-1} \right]
\]  

(2)

Here, \( h \): Planck’s constant \( \left[ \text{Js}^{-1} \right] \), and \( \nu \): Vibration number of excitation wavelength \( \left[ \text{s}^{-1} \right] \).

The atomic emission energy, \( E \), is obtained from the quantum yield, \( \eta \), and Eq. (2) as follows:

\[
\eta = A_{21} / (A_{21} + K_{21})
\]  

(3)

\[
E = \eta W = N_1 \Delta V B_{12} u(\nu) h \nu \left[ \text{Js}^{-1} \right]
\]  

(4)

Here, \( A_{21} \): The Einstein spontaneous transition coefficient; and \( K_{21} \): The non-irradiative transition constant.

For pulsed laser excitation, the measured intensity of the atomic emission, \( I \), is obtained by introducing the excitation period of the laser, \( \Delta t \left[ \text{s} \right] \), the measurement solid angle, \( \Omega \left[ \text{sr} \right] \), and a constant that originates in the characteristics of the device, \( \alpha \), into Eq. (4) as follows:

\[
I = \alpha (\Delta \Omega / 4 \pi) \ h \nu \Delta \tau
\]  

(5)

When high power laser light is irradiated at the molecules, they dissociate to atoms. Therefore, Eq. (5) is rearranged to Eq. (6) using the dissociation rate, \( \xi \), as follows:

\[
\xi = N_1 / N_0
\]  

(6)

\[
I = \alpha (\Delta \Omega / 4 \pi) \ h \nu \xi N_0 \Delta V B_{12} u(\nu) h \nu \Delta \tau \left[ \text{J} \right]
\]  

(7)

Here, \( N_0 \) is the number density of the molecule.

Equation (7) is the basic equation for the measurements of the atomic emission and clearly shows that the intensity, \( I \), strongly depends on \( N_0 \), \( \xi \), and \( \Delta V \).

2.2 Spectrum profile

It is reported that the Doppler broadening is enhanced by micro explosions of droplets when a high energy laser beam is introduced into the fuel spray\(^4\). The quantity of the vibration number increase, \( \Delta \nu \), due to the Doppler effect is as follows:

\[
\Delta \nu = \nu_0 V_z / c
\]  

(8)

Here, \( \nu_0 \): the vibration number without the Doppler broadening, \( V_z \): the velocity of the atom to the measurement direction, and \( c \): velocity of light.

When it is approximately estimated that a liquid droplet of normal hexane of 50 \( \mu \text{m} \) diameter becomes gas phase plasma at \( 5 \times 10^4 \text{ K} \) with \( 3.2 \times 10^4 \text{ times} \) the volume of the liquid phase droplet due to micro explosions, \( V_z \) is estimated to be \( 10^5 \text{ m/s} \). Here, it is assumed that the plasma behaves like an ideal gas and that the micro explosion completes during the excitation laser pulse duration, 8 ns. The Doppler shift of the excitation wavelength of hydrogen atoms with the \( V_z \) is calculated to be about 0.5 nm, where the central wavelength of atomic emissions of H is 656 nm. Consequently, the liquid fraction of the fuel can be determined from the full width at half maximum (FWHM) of the H atom spectra which increases with increases in the liquid fraction.

3. Experimental Procedure

3.1 Experimental apparatus

In this investigation a laser beam was focused with a convex lens to obtain high energy densities, and the focused region in a fuel spray was evaporated, broken down, excited, and emitted atomic emissions. Figure 1 shows the experimental apparatus for the measurements of atomic emissions in the field where gas and liquid components from vaporizing fuel coexist. The test vessel has inlet and outlet pipes for the charge gas, a T type 25 \( \mu \text{m} \) diameter thermocouple, a fan to agitate the inside of the vessel, quarts windows, and a common rail fuel injector. The temperature in the vessel is controlled with a heater. Normal hexane was mainly used as the test fuel.

The measuring field including the gas and liquid components from the fuel was irradiated by a focused beam of an Nd: YAG laser with an 80 mJ/pulse at 1064 nm and a beam diameter of 8 mm. The laser beam was condensed by a convex lens with a focal length of 70 mm. The scattered light signal from the focal point was gathered into the optical tube and led to the spectrometer, with an optical resolution of 0.1 nm, and a multi channel CCD detector.

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**Fig. 1** Experimental apparatus
To establish the calibration curve for the FWHM of hydrogen atom emission spectra and the liquid fraction, a gas and liquid coexistence field with a preset liquid fraction is formed in a vessel as shown in Fig. 1. The gas and liquid coexistence field was formed with rapid decompression in the vessel containing a gaseous fuel and nitrogen mixture at high pressure. The liquid fraction was calculated with the fuel vapor pressure given by the Antoine’s equation. This experimental system was also used for the measurements of the fuel spray.

3.2 Quantification procedure

Figure 2 shows typical atomic emission spectra with a plasma emission which appears at the bottom of the atomic emission. In this measurement, the atomic concentration is quantified only by the atomic emission, and the plasma emission has to be subtracted from the measured intensity(5). Here, two kinds of parameter, the height of peak intensity, I, and the area of the band spectra, S, were used for the quantification. To quantify the liquid fuel fraction, the S parameter, was used as the spectrum broadens with micro explosions.

The fuel concentration was quantified with the emission intensity ratio of hydrogen and nitrogen and the liquid fraction was derived with the FWHM at the atomic emission of hydrogen. Here, emissions at 656 nm and 871 nm were used for hydrogen and nitrogen respectively(6). The emissions at 656 nm can be regarded as almost exclusively from hydrogen because the emission from carbon is quite weak(7). Therefore, the equivalence ratio in the fuel spray can be quantified from the intensity ratio with hydrogen and nitrogen or oxygen. The quantification from dichloromethane can also be performed from the intensity of chlorine.

4.2 Calibration curve for equivalence ratios in hydrocarbon mixtures

Figure 4 shows the relation between the equivalence ratios of propane – nitrogen mixtures and the emission ratios of hydrogen and nitrogen. The open circles show the data from the height of peak intensity, $I_H/I_N$, and the solid circles are from the area of the band spectra, $S_H/S_N$. Both intensity ratios correlate well with the equivalence ratio for the wide range of equivalence ratios, from below 0.1 to above 10, and an equivalence ratio can be quantified from Fig. 4. For measurements of the lean mixture, $I_H/I_N$ is more appropriate than $S_H/S_N$ due to the better linearity of $I_H/I_N$.

Figure 5 shows the relation between the atomic number ratio of hydrogen and nitrogen, $N_H/N_N$, and the intensity ratio, $I_H/I_N$, for various kinds of fuels under atmospheric pressure. In the experiments, the fuels were introduced from the evaporator to the flow cell with nitrogen as the carrier gas, and the fuel concentration is calculated from the saturated pressure. The intensity ratio,
The intensity ratio, $I_H/I_N$, correlates well with $N_H/N_N$ regardless of the kind of fuel. This suggests that all molecules in the measured region dissociate completely and emit atomic emissions. The relation between the atomic emission ratio, $S_H/S_N$, and the equivalence ratio for normal hexane is shown in Fig. 6. Here, the open and solid circles show the data for ambient pressures of 0.1 MPa and 1.0 MPa respectively. While $S_H/S_N$ for 0.1 MPa increases linearly with increases in the equivalence ratio for a wide range of equivalence ratios, the increase in $S_H/S_N$ for 1.0 MPa almost saturates at an equivalence ratio of 5. This saturation can be explained as quenching of hydrogen emissions is stronger under richer and higher pressure conditions. However, for an equivalence ratio range below 5, $S_H/S_N$ correlates well with the equivalence ratio regardless of the ambient pressure. Thus, the intensity ratio, $S_H/S_N$, can be used to quantify the mixture strength independent of fuel property and ambient pressure except at pressurized and rich conditions.

### 4.3 Calibration curve for the liquid fuel fraction

Doppler broadening of atomic emissions, which is caused by micro explosions, is the signal that enables calculating the liquid fraction. Gas and liquid fuel mixtures form with a preset liquid fuel fraction in the experimental vessel as explained in section 3.1, and the mixtures were excited with the focused laser beam, and the FWHM of the hydrogen emissions was measured. Figure 7 shows the relation between the FWHM and the number of hydrogen atoms in the liquid fuel. The FWHM increases linearly with increases in the number of atomic hydrogen in the liquid fuel regardless of the overall equivalence ratio in the vessel, $\phi$.

Figure 8 shows the influence of the equivalence ratio on the FWHM for mixtures without a liquid phase. The equivalence ratios affect FWHM little while the FWHM increases with increases in the ambient pressure, maybe caused by the pressure broadening of the atomic emission spectra. Like the equivalence ratio is measured from the atomic emissions, the liquid fraction can be simultaneously quantified with Fig. 7 used as the calibration curve in the following experiments.

### 4.4 Accuracy of the quantification

Figure 9 shows the relative error in the emission ratio quantified with the emission intensity. Here, the relative error was defined as the ratio of the average value of ten measurements and the maximum deviation from the average value. The relative errors in the emission ratios, $I_H/I_N$ and $S_H/S_N$, are less than 2.5% near the equilibrium ratio, but increase on both the lean and rich sides.

Figure 10 shows the relative errors in the liquid frac-
Fig. 9 Relative error in the equivalence ratio quantified with emission intensity

Fig. 10 Relative error in liquid fraction quantified with FWHM

Fig. 11 Schlieren images of hexane sprays

Fig. 12 Equivalence ratio and vapor fraction at a point in a hexane spray

4.5 Application to fuel sprays

Figure 11 shows schlieren images of hexane sprays at various elapsed times after the start of injection, $\Delta t$, injected by a common rail injector with the injection pressure 40 MPa and the injection duration 2.06 ms. Here, the ambient pressure was 1.0 MPa and the temperatures were 60°C and 190°C. Evaporation of hexane is remarkable with the 190°C ambient temperature, as the temperature exceeds the boiling point at 1.0 MPa.

Figure 12 shows the results of simultaneous measurements of equivalence ratio and vapor fraction in a hexane spray under the same conditions as in Fig. 11. The measurement position is 60 mm from the nozzle tip on the central spray axis, also shown in Fig. 11 with a solid circle. The equivalence ratio and the vapor fraction were quantified with the calibration curves shown in Figs. 6 and 7, and all data in Fig. 12 are averages of ten measurements.

Just after the tip of the fuel spray reaches the measuring point, the equivalence ratios increase, reach the maximum value at $\Delta t = 1.8$ ms, and then decrease. The vapor fractions decrease before $\Delta t = 1.5$ ms, then increase slightly, before slowly decreasing again. This phenomenon can be explained by the characteristics of an intermittent fuel spray that shows a fuel rich region just upstream of the spray tip. With increases in the ambient temperature, $\phi$ increases with the vapor fraction, maybe due to the decrease in ambient gas density with increases in ambient temperature. The higher vapor fraction with higher ambient temperature shows the increase in vaporization.

5. Conclusions

Laser-induced breakdown spectroscopy, LIBS, was used to simultaneously quantify the concentration and the vapor fraction of liquid-gas mixtures with atomic emission
sector profiles without seeding of additives. The results may be summarized as follows:

1. Local equivalence ratio of even the liquid-gas mixtures was instantaneously quantified with the ratio of the number of fuel-borne hydrogen atoms to the number of nitrogen or oxygen atoms.

2. The liquid fraction of a fuel spray was quantified with the full width at half maximum, FWHM, of the hydrogen emission as the FWHM linearly increases with increases in the liquid fraction due to a Doppler shift brought about by micro-explosions.

3. The method made it possible to obtain simultaneous, high-resolution measurements of the equivalence ratio and vapor fraction in an intermittent fuel spray in a pressurized atmosphere.

4. The tip of the intermittent spray has a richer mixture with lower vapor fraction than the rest of the spray.

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