Laser-induced breakdown spectroscopy for lambda quantification in a direct-injection engine

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A B S T R A C T
We apply laser-induced breakdown spectroscopy (LIBS) to determine local lambda values (i.e. the normalized air-fuel mass ratio) at the ignition location $\lambda_{ip}$ in a direct-injection single-cylinder optical research engine. The technique enables us to determine variations of $\lambda_{ip}$ for different fuel injection strategies, as well as correlations between variations in $\lambda_{ip}$ and the combustion dynamics. In particular, we observe that fluctuations in $\lambda_{ip}$ are not the major cause of cycle-to-cycle variations in the combustion process. Moreover, our experiments identify insufficient lean $\lambda_{ip}$ values as a source of misfires in lean combustions. In a combination of LIBS with laser-induced fluorescence (LIF), we obtain additional information about the two-dimensional $\lambda$ distribution. These results demonstrate the potential of LIBS to monitor $\lambda$ values during mixture formation in gasoline engines.

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1. Introduction

The local value of the parameter $\lambda_{ip}$ (i.e. the air-fuel mass ratio normalized to the stoichiometric value) at the ignition position in a gasoline engine is of significant importance to understand the combustion dynamics. Among others, $\lambda_{ip}$ critically affects relevant combustion properties such as mass burn duration and indicated mean effective pressure (IMEP). Thus, cycle-to-cycle fluctuations of the combustion process are possibly also caused by $\lambda_{ip}$ variations. This may, e.g. lead to misfires – due to insufficient $\lambda_{ip}$ values at critical engine operating points, e.g. in the regime of a lean combustion. Thus, we require techniques to determine absolute values of $\lambda_{ip}$ – also aiming at the multi-dimensional imaging of $\lambda_{ip}$ distributions in the ignition region. Laser-induced breakdown spectroscopy (LIBS) exhibits a rather simple, but powerful method to achieve this goal – also in combination with laser-induced fluorescence (LIF) for two-dimensional imaging.

The basic idea of LIBS is to focus a sufficiently intense laser beam onto a sample, generate a laser-induced plasma, atomize all particles in the plasma and excite them to higher energy levels. As the plasma cools down, the atoms and ions relax to lower energy states, emitting light with characteristic spectral lines – which serve to determine specific elements. Due to this rather simple principle and experimental implementation, LIBS is already a well-established tool in many fields of science and engineering [1]. LIBS was also applied in experiments, dealing with combustion diagnostics [2–7]. Ferioli et al. [6] applied LIBS to the exhaust gas system of a spark ignition engine to determine spatially-averaged cycle-resolved $\lambda$ values of the combustion process. Phouc et al. [2] used LIBS in methane-air premixed conditions to simultaneously ignite and monitor $\lambda_{ip}$ values. Further work applied LIBS to non-premixed conditions, e.g. in a turbulent burner or a lean combustor [3]. The first implementations of LIBS for in-cylinder $\lambda_{ip}$ measurements were performed by Joshi et al. [5] in a single-cylinder natural gas engine. Gross [8] applied LIBS to a direct-injection gasoline engine with optical access. However, due to weak signal to noise ratios the latter work permitted only cycle-averaged determination of $\lambda_{ip}$ for stratified operation.

We also note related experiments on spark-induced breakdown spectroscopy (SIBS), which applies the spectral emission of plasmas from conventional spark plugs for fuel concentration measurements [9,10]. Fansler et al. [9] applied SIBS to in-cylinder measurements on a transparent engine and achieved individual-cycle measurements of the local fuel concentration. Implementations of LIBS in combustion diagnostics may apply different strategies to determine $\lambda_{ip}$ from plasma emission lines. Typically, we may use a characteristic emission line to determine the fuel concentration and another characteristic emission line to determine the air (oxidizer) concentration. The ratio of the emission lines permits us to draw conclusions on $\lambda_{ip}$. As an example, we note spectral lines corresponding to atomic carbon (C) or molecular carbon nitride (CN) – which is generated by recombination at later times in the slowly cooling plasma [6]. Both lines may be related to the fuel concentration. However, due to large signal (rp. large signal-to-noise ratio) in most cases the characteristic emission of atomic hydrogen (H) at 656 nm is used to determine the fuel concentration [2]. We note that we have to consider possible background emissions by water vapor in this case. The air concentration is typically determined

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by the emission of atomic oxygen (O) at 777 nm or nitrogen (N) at 744 nm [5].

While LIBS reveals information only on the particular focal spot of the plasma, combustion diagnostics also requires image information, e.g. two-dimensional distributions of λ. Planar LIF is a technique to enable two-dimensional imaging of fuel mixtures [11]. The fluorescence is hereby emitted from electronically excited states of specific species (tracers). The two most frequently used classes of tracers are aliphatic ketones and aromatics. The properties of ketones have been studied in [12,13]. Aromatic hydrocarbons are typical components of commercial fuels. They exhibit a strong absorption in the UV region and can therefore be excited by e.g. frequently quadruple Nd:YAG lasers at 266 nm. The relaxation of the excited aromatic molecules can occur in three different ways. First, by non-radiative decay via vibrational and rotational energy transfer. Second, by spontaneous emission of a photon, i.e. fluorescence. Hereby, the molecule is transferred to an excited vibrational/rotational state of the electronic ground state. Therefore, the emitted light is red-shifted compared to the excitation wavelength. Third, by electronic excitation of colliding molecules (oxygen) – oxygen quenching. By using aromatics, the quenching is the major drawback – reducing the fluorescence signal significantly.

In commercial fuels, a variety of fluorescing aromatics is present. A full quantification of the fluorescing molecules is difficult, since several components with different photophysical properties fluoresce at the same time [11]. Anyhow, the use of commercial fuels allows simple qualitative visualization of mixture formation. For quantitative measurements, we require a way to absolutely calibrate the qualitative visualization of mixture formation. Richter et al. [14] used simultaneous LIF and Raman scattering to calibrate the LIF images by the Raman signal. However, the spectrum clearly reveals the required atomic lines are most dominant in the emission spectrum.

2. Experimental setup for LIBS

Fig. 1 depicts the experimental setup for LIBS in the direct-injection gasoline engine with optical access. The single-cylinder engine includes 4 valves, a 82 mm bore and a 86 mm stroke which result in a displacement volume of 454 cm$^3$. The compression ratio is 9.6. During all measurements, the engine was fired continuously. The engine speed was set to 1200 rpm. In order to perform measurements close to real engine conditions, we used ambient air and a reference fuel (CEC-RF 08-A-85) as cylinder charge. The fuel can be injected in two different ways. The first injector is centrally mounted at the cylinder head. This exhibits the typical setup of a direct-injection system. The second injector is located at the inlet manifold 80 cm upstream the intake valves. Due to the rather long way towards the combustion chamber, this setup yields an almost perfect homogeneous mixture – which we use for calibration of the LIBS measurements. The spark plug (placed between the exhaust valves) is replaced by a Nd:YAG laser ignition system operating at 1064 nm, providing laser pulses in the nanosecond regime. The laser is focused by a lens with a focal length of 15 mm and propagates through an entrance window into the combustion chamber. The laser spot diameter is approximately 10 μm and located 6 mm behind the entrance window. The exhaust is equipped with a broad-band oxygen sensor (Bosch, LS7151), which measures the time-averaged global λ value in the combustion process. In parallel, we measure the pressure variation in the engine during individual combustion cycles on a pressure detector (Kistler, 6043Asp).

The engine offers four optical accesses to the combustion chamber, i.e. a cylindrical quartz glass ring below the cylinder head, two pent roof windows located at the frontside and backside of the engine, as well as a quartz glass disk inserted into the piston. We collect the radiative plasma emission through the pent roof window on the backside of the engine, couple it into an optical fiber, spectrally separate the relevant emission lines of hydrogen at 656.2 nm and oxygen at 777 nm by a cold mirror and optical bandpass filters, and detect the signals on photomultiplier tubes (Hamamatsu, H7732–10). The signals are displayed and stored on an oscilloscope (Tektronix, TDS5034). During post-processing the signals are time-averaged between 500 – 1000 ns after optical breakdown, as in this time interval the atomic lines are most dominant in the emission spectrum.

3. Combustion diagnostics by LIBS

In a first experiment, we replaced the detection setup for the hydrogen and oxygen line (as discussed above) by a Czerny–Turner spectrograph (Acton Spectra Pro 2500i) and an ICCD camera (Roper Scientific PI-MAX) to monitor a full spectrum of the laser-induced plasma emission. Fig. 2 shows the spectrum, recorded 500 ns after optical breakdown. The spectrum clearly reveals the required atomic lines of hydrogen and oxygen with a signal-to-noise ratio of 10:1 and 7:1 respectively. The background noise has its origin in the continuum emission of the plasma formed by recombination of electrons. Therefore, the calibration curve (Fig. 3) does not intersect the point

![Fig. 1. Experimental setup for LIBS.](image-url)
3.1. Calibration

Quantitative determination of \( \lambda_{ip} \) values requires calibration of the LIBS signal. Therefore, we inject fuel through the inlet manifold to permit formation of a very homogeneous mixture in the combustion chamber. The injection location is about 80 cm upstream the combustion chamber, giving a sufficiently long mixing path for homogenization. We measure the global (temporally averaged) \( \lambda \) value by the oxygen sensor in the exhaust. Since the mixture is homogeneous, the local \( \lambda_{ip} \) is equal to the global \( \lambda \). The global \( \lambda \) can be varied by adapting the injected fuel mass. Fig. 3 shows the LIBS intensity ratio of the spectral lines for oxygen and hydrogen vs. the global \( \lambda \) value, determined by the oxygen sensor in the exhaust. The data points are averaged over 100 combustion cycles. The error bars are defined by standard deviation. We note that the LIBS signal is quite stable - as indicated by the small standard deviation (~1%). The plot shows also a linear fit to the data points. As the fit clearly indicates, the LIBS intensity ratio shows a very good linearity with \( \lambda \) (\( R^2 = 0.99 \)). This enables quantitative determination of \( \lambda_{ip} \) values from our LIBS spectra - which we will discuss in the following sections. We note that pressure changes affect the inclination of the linear fit. Thus, the calibration factor between the LIBS intensity ratio and \( \lambda \) will be different in alternative engine geometries, at different engine load or for different ignition timing.

\[
\lambda_{ip} = \frac{m_{air}}{m_{fuel}} \propto \frac{I_O}{I_H}
\]

3.2. Cycle-to-cycle \( \lambda_{ip} \) fluctuations determined by LIBS

We investigate now fluctuations in \( \lambda_{ip} \), determined by LIBS for three different injection strategies. In the following all timings are expressed in degrees of the crank angle (°CA) before top dead center (BTDC). In a first approach, we inject the fuel into the inlet manifold, i.e. similar to the setup for calibration. In a second approach, we directly inject the fuel during the intake stroke at an early timing of 330 °CA BTDC. The latter is a typical injection timing for direct-injection homogenous engine operation. In a third approach, we directly inject the fuel during the compression stroke at a timing of 90 °CA BTDC. In all measurements, the global mixture is stoichiometric (i.e. \( \lambda_{global} = 1 \)), the injection pressure is set to 5 MPa for direct injection, and the ignition timing is set to 17 °CA BTDC.

Fig. 4 shows the \( \lambda_{ip} \) values, determined by LIBS in the three injection strategies for 50 consecutive combustion cycles. Each data point corresponds to one individual combustion cycle. In addition, we give the mean value \( \lambda_{ip} \) and the standard deviation \( \sigma_{\lambda_{ip}} \) in the figure. In the case of injection into the inlet manifold (Fig. 4(a)), the cycle-to-cycle fluctuations of \( \lambda_{ip} \) around the stoichiometric value (\( \lambda_{ip} = 1.01 \)) are very small, i.e. yielding a standard deviation of \( \sigma_{\lambda_{ip}} = 0.016 \). This supports our assumption of a homogeneous mixture (as it was also relevant for the calibration procedure, as discussed above). In the case of direct injection at 330 °CA BTDC (Fig. 4(b)), the fluctuations in \( \lambda_{ip} \) are considerably larger (\( \sigma_{\lambda_{ip}} = 0.099 \)). The averaged value is still very close to stoichiometric conditions (\( \lambda_{ip} = 1.02 \)), but the \( \lambda_{ip} \) values spread from \( \lambda_{ip}^{\min} = 0.85 \) to \( \lambda_{ip}^{\max} = 1.3 \). Therefore, even the fuel is injected in the intake stroke - permitting a relatively large time slot for mixture preparation, the mixture is not perfectly homogenized at ignition timing.

Finally, in Fig. 4(c) the case of injection at the compression stroke (90 °CA BTDC) is shown. We get very strong cyclic variations (\( \sigma_{\lambda_{ip}} = 0.204 \)) in a range of \( \lambda_{ip}^{\min} = 1.0 \) to \( \lambda_{ip}^{\max} = 1.8 \). Moreover, the average \( \lambda_{ip} \) shifts to the regime of a lean mixture (\( \lambda_{ip} = 1.36 \)). This behavior is not surprising, as such late injection does not permit a sufficiently long preparation time of the mixture. Therefore, this injection timing is not relevant for homogeneous engine operation.

3.3. Dependence of mass burn duration upon \( \lambda_{ip} \)

In the following, we discuss correlations of the \( \lambda_{ip} \) values, determined by LIBS and thermodynamic combustion properties, calculated from pressure data. It is of particular interest how variations in \( \lambda_{ip} \) induce cycle-to-cycle fluctuations in the combustion process. Moreover, we want to figure out, if misfires at lean combustion are caused by insufficient \( \lambda_{ip} \).

In the experiment, we choose an operation point beyond the lean combustion limit (\( \lambda_{global} = 1.4 \)). The direct injection timing is set to 330 °CA BTDC and the ignition timing is shifted to 29 °CA BTDC. Fig. 5 shows mass burn durations (as determined from pressure data), plotted vs. \( \lambda_{ip} \) for 200 consecutive combustion cycles. The mass burn duration indicates the time (measured in °CA), which the combustion process takes to burn a certain fraction of
engine load. For example, the 5 – 50% mass burn duration is the time difference between the points when 5% and 50% of the fuel is burned. The fluctuations of the mass burn duration characterize the cycle-to-cycle stability of the combustion process. Fig. 5(a) shows the duration to burn 0 – 5% of the injected fuel. The middle graph (Fig. 5(b)) shows the 5 – 50% mass burn duration and Fig. 5(c) the 50 – 90% mass burn duration, respectively. Each data point represents one individual combustion cycle. The upper figure depicts also a linear fit and the corresponding coefficients of determination $R^2$ (square of sample correlation coefficient). The coefficient of determination is a statistical measure of how well the regression line approximates the real data points. Moreover, $R^2$ indicates the proportion of variance in one variable (mass burn duration) accounted for by differences in the other ($\lambda_{ip}$) [15]. For better visibility, we do not show error bars in the graph.

The data for the 0 – 5% burn duration indicate a trend to longer combustion duration for leaner mixture, i.e. larger $\lambda_{ip}$ values. We note that the scatter of data points around the regression line is quite large. Thus the coefficient of determination is small ($R^2 = 0.25$). Therefore, the effect of $\lambda_{ip}$ on the early phase of combustion is low and only a minor part of variations in early burn duration are caused by $\lambda_{ip}$ fluctuations. However, due to the weak correlation we must consider a high uncertainty of the fit. In Fig. 5(b,c) (which shows the 5 – 50% and 50 – 90% mass burn duration), we observe no trend of the data. There is no significant correlation ($R^2 = 0.14$, $R^2 = 0.10$). Therefore, the variations in later burn durations can not be explained by $\lambda_{ip}$ fluctuations. The lower correlations compared to Fig. 5(a) are expected, since the LIBS measurement records only the ignition location, i.e. the region of the initial combustion stage. In the later phases of combustion also other parameters (e.g. spatial fuel distribution, in-cylinder flow field) affect the combustion dynamics. Therefore, the effect of $\lambda_{ip}$ on the later combustion dynamics decreases.

In summary, the weak correlation in Fig. 5 indicates, that fluctuations in $\lambda_{ip}$ are not the dominant source for cycle-to-cycle variations of the combustion process. We suspect, that fluctuations in the in-cylinder flow field cause the cycle-to-cycle variations in the mass burn duration for all phases of combustion [16].

3.4. Dependence of mean effective pressure upon $\lambda_{ip}$

In a similar way discussed above for the mass burn duration, we also investigate the dependence of the indicated mean effective pressure (IMEP, [17]) vs. $\lambda_{ip}$ (see Fig. 6). The data show 200 consecutive combustion cycles with the same engine operation parameters as introduced above. From the data we see, that no misfires occur for cycles with $\lambda_{ip} < 1.35$. In the range $1.35 < \lambda_{ip} < 1.45$, the misfire rate increases rapidly. For mixtures with $\lambda_{ip} > 1.45$, almost all cycles show misfire. Thus, large $\lambda_{ip}$ values (i.e. lean mixtures) are obviously an important source of misfires – as expected. We note that even in the regime with $\lambda_{ip} < 1.35$ the variance of IMEP is still quite large, i.e. ($\text{cov}_{\text{IMEP}} = 21\%$). This leads to a labile engine condition. We suspect that also these variations are caused by fluctuations in the flow field in the cylinder.

4. Experimental setup for combined LIF–LIBS

We extend the experimental setup for LIBS to permit two-dimensional imaging of $\lambda$ by LIF. To calibrate the LIF images, we simultaneously record LIBS signals at the ignition point. Fig. 7 shows a schematic of the combined LIF–LIBS setup. The setup consists of the major parts, already described in Section 2, as well as an optical excitation and detection system for LIF. As previously we use the reference fuel CEC-RF 08-A-85, whereas no additional tracers are added. As mentioned in Section 1, the fuel contains aromatics which can be used for LIF measurements. They have a strong broad-band absorption in the UV region (\(<320\text{ nm})$. Therefore, we use the fourth harmonic of a pulsed Nd:YAG laser (Quantel, Brilliant B) at 266 nm for
excitation. The pulse duration is 5 ns and pulse energy is about 40 mJ. The laser beam is focused by a cylindrical concave and spherical convex lens to generate a light sheet (approximately 1 mm thin and 40 mm wide). We guide the light sheet through the window in the piston crown into the combustion chamber and overlap it spatially with the ignition plasma. The LIF signal is red-shifted with respect to the excitation wavelength and is in the interval 270 – 350 nm. In order to suppress scattered laser radiation and self absorption effects, we filter the signal spectraly (transmitting 320 – 370 nm). An ICCD camera (LaVision, Nanostar) detects the LIF signal perpendicular to the direction of the laser beam. To protect the ICCD camera from the very bright emission of the laser-induced plasma, we delay the LIBS measurement by 100 μs with respect to the LIF laser trigger.

5. LIBS-assisted LIF-imaging of mixture formation

Simultaneous recording of LIF and calibrated LIBS signals enables us to compare the LIF signal at the ignition point to λ_ip values, as determined by LIBS for 45 consecutive operation cycles. The figure also depicts the regression line to the whole dataset. We note, that the scatter around the regression line is quite large and therefore the coefficient of determination is low (R² = 0.36).

Different sources for the scatter of the LIF signal can be identified. Fluctuations in the residual gas distribution change the amount of oxygen quenching and therefore affect the LIF signal. Additionally, the LIF signal is sensitive to variations in the temperature distribution. Moreover, mixture formation is a dynamic process. Therefore, λ_ip may vary between the LIF and temporally delayed LIBS measurements – causing a further source of error. In contrast the LIBS data does not suffer from these effects and is therefore very stable relative to the LIF data (compare Fig. 3). Using the regression line as calibration curve for the LIF images, we obtain two-dimensional λ distributions. We note, that the error in the quantitative λ distribution is large due to the uncertainty of the calibration curve. In order to minimize the effect of this error, we calibrate only measurements coincident with the calibration curve (set in black). Data points in larger distance to the calibration curve are not calibrated (set in gray). In addition to λ_ip, the combination of LIBS and LIF gives valuable information on the two-dimensional fuel distribution.

Fig. 9 shows typical calibrated LIF images of λ for single operation cycles and different injection strategies. Color coding indicates λ values. Due to the calibration the uncertainty in λ is larger for very lean or very rich mixture. To indicate this uncertainty, we plot regions with λ > 2 or λ < 0.5 with gray-shaded or black-shaded lines, respectively. The position of the plasma (LIBS) is also indicated by a black circle and the corresponding λ_ip is given in the figure. All images are recorded at an ignition timing of 17 °CA BTDC and global stoichiometric mixture (λ_global = 1). Fig. 9(a) shows the λ distribution for injection via the inlet manifold. The image shows a very homogeneous mixture close to λ = 1, i.e. as expected for injection via the inlet manifold. We note that minor variations in the image are due to inhomogeneities in the laser light sheet and noise of the LIF signal. Fig. 9(b) shows the LIF image taken for direct injection at 330 °CA BTDC. Compared to injection via the inlet manifold, the fuel distribution becomes more inhomogeneous. Downstream from the ignition point, we observe a rich cloud with up to λ ≈ 0.8 – whereas between the injector and the intake valves the mixture is lean (λ > 2). If we proceed to later injection, i.e. at 180 °CA BTDC and 90 °CA BTDC (see Fig. 9(c,d)) the mixture becomes even more inhomogeneous. The images in Fig. 9(c,d) exhibit rich regions with λ < 0.8 and regions where almost no fuel is present with λ ≫ 2. Between these regions, we observe steep λ gradients. We note that at the ignition point the mixtures depicted in Fig. 9(c,d) differ strongly from the stoichiometric case — as we expect it for late direct injection. Thus, the images in Fig. 9 clearly indicate the potential of combined LIF–LIBS measurements to obtain conclusive data of mixture distribution.

6. Conclusions

In our work we demonstrate the feasibility of laser-induced breakdown spectroscopy (LIBS) for simultaneous ignition and λ_ip quantification.
in a direct-injection engine with optical access. We discuss the calibration of LIBS signals to monitor λ_ip values at the ignition point in combustion engines. Our data confirm that fuel injection into the inlet manifold yields very low cycle-to-cycle variations of λ_ip. For direct injection into the intake stroke, we observe considerably larger fluctuations of λ_ip. Moreover, we investigate correlations of variations in λ_ip (as determined by LIBS) and pressure traces in the combustion process. The results show that fluctuations in λ_ip are not the major cause of cycle-to-cycle variations of the combustion process. Our data also show that lean λ_ip values are a source of misfires in the combustion. In an extension of the LIBS experiments, we combined the technique with laser-induced fluorescence (LIF) to monitor two-dimensional λ distributions. We record LIF images for different injection strategies. We find that injection into the inlet manifold yields an almost perfect uniform mixture – whereas direct injection into the intake stroke yields considerable λ gradients, which increase with later injection timing.

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