Measurement of Biofuel Vapor Concentration in Sprays using new Planar Laser-Induced Fluorescence

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Abstract

A novel laser-induced fluorescence strategy for fuel concentration measurements is developed to study the evaporation and mixing processes of first and second generation bio-fuels. The method is based on the use of appropriate molecular tracers mixed in non-fluorescent model fuels. Standards and bio- fuels were characterized, and model fuels and appropriate molecular tracers were selected. The fluorescence properties of the fuels and molecular tracers were studied under thermodynamic conditions representative of real combustion engine conditions. Finally, a specific methodology for absolute concentration measurements adapted to multi-component fuels has been developed to be applied under thermodynamic conditions representative of automotive and aviation combustion chambers.

1. Introduction

The automotive and aviation industries are presently confronted with the twin crises of fossil fuel depletion and environmental degradation. Indiscriminate extraction and lavish consumption of fossil fuels have led to reduction in underground-based carbon resources. The search for alternative fuels, which promise a harmonious correlation with sustainable development, energy conservation, efficiency and environmental preservation, has become highly pronounced in the present context. The fuels of bio-origin can provide a feasible solution to this worldwide petroleum crisis. Gasoline and diesel-driven automobiles are the major sources of greenhouse gases (GHG) emission [1–3]. Scientists around the world have explored several alternative energy resources, which have the potential to quench the ever-increasing energy thirst of today's population. Various biofuel energy resources known as the first-generation biofuels include biomass, biogas, primary alcohols, vegetable oils, biodiesel… [4]. Learning from the experience of other industries, the aviation industry is therefore looking at second-, or next-generation biofuels that are sustainable. This new generation of biofuels is derived from non-food crop sources. Second-generation biofuels must have the ability to directly substitute traditional jet fuel for aviation (known as Jet A and Jet A-1) and have the same qualities and characteristics. This is important to ensure that manufacturers do not have to redesign engines or aircraft and that airlines and airports do not have to develop new fuel delivery systems. At present, the industry is focused on producing biofuels from sustainable sources that will enable the fuel to be a "drop-in" replacement to traditional jet fuel. Drop-in fuels are combined with the petroleum-based fuel either as a blend or as a 100% replacement. All these alternative energy resources are largely environment-friendly but they need to be evaluated on case-to-case basis for their advantages, disadvantages and specific applications. Some of these fuels can be used directly while others need to be formulated to bring the relevant properties closer to conventional fuels. However, the benefits (e.g. pollution, consumption, engine operability), of using such alternative fuels are not clearly established. In particular, key physical processes such as evaporation of the liquid fuel and air/fuel mixing are vital for improved combustion processes and in turn cleaner and more efficient combustion devices. It is therefore important to determine the status of mixing, local concentrations, gradients, and their temporal evolution. As most technical combustion processes are turbulent in nature such studies have to be performed with high temporal and spatial resolution. For experimental studies a useful measurement approach is to use planar laser induced fluorescence diagnostic (PLIF) to obtain maps of scalar quantities. However, up to now, spectroscopic properties of biofuels which are multi-component fuels remain unknown and adequate fluorescent tracers for probing these biofuels have not been identified yet. As a result, no optical methodology has been developed to measure fuel vapour concentration in biofuel sprays. The objective of this study is then to propose and develop innovative PLIF strategies to measure fuel distribution and mixture formation when biofuels are used in aeronautical and automotive combustion chambers. In particular, the fluorescence of various biofuels like biodiesels (Esters, EMHV) and Biomass-To-Liquid (BtL) and potential fluorescent tracers (either present naturally in the fuel or chemically added) that could be used as probe molecules with these fuels are studied.

2. Methodology

The success of PLIF fuel imaging must not deter from the fact that there are a number of important aspects that have to be addressed in order to obtain reliable results from such measurements. Most important for the use of fluorescence tracers is a proper understanding of the photo-physical response, i.e. how the absorption and fluorescence quantum yield of the tracer molecules depends on temperature, pressure and gas composition. There are also concerns about co-evaporation and diffusion of tracer and traced molecules that may be important under some experimental conditions [5]. If the tracer and base fuel are not properly matched in terms of evaporation dynamics, the spatial distribution of tracer and base fuel may be different leading to unquantifiable errors in measuring the fuel distribution. This can be solved in some cases by considering the use of a blend of several tracers with overall evaporation characteristics that mimics that of the base fuel or by considering the evaporation dynamics that shows that the relevance of sequential evaporation critically depends on the ambient pressure and temperature conditions [5]. Furthermore, it is important to ensure that the addition of tracer molecules does not alter the combustion process [6, 7], i.e., flame speed…. For instance, it has been shown for that toluene or 3-pentanone addition to iso-octane fuel has a negligible effect on combustion performance with somewhat increasing impact towards leaner mixtures [7]. This suggests that care needs to be taken to match the equivalence ratio after adding the tracer and to ideally perform some baseline experiments to either rule out or at least quantify the impact of tracer addition on overall combustion performance. Lastly, the tracer chemistry must follow the chemical consumption rate of the traced molecules to guarantee a faithful measurement of the parent fuel concentration. From these considerations, the ability of the fluorescence tracer must match the evaporation of the fuel (i.e. distillation curve), so that tracer concentration in the spray will be representative of fuel concentration. Figure 1 shows the distillation curves for the standards fuels and biofuels presently studied. Depending of the species composition of fuel, the distillation curve presents large differences in behaviour with temperature. Biofuels like esters (EMHV) have a distillation curve revealing the presence of liquids components with high boiling points. In the opposite case, BtL as well as standard Jet A1 fuels show distillation curves ranging between 160 and 240 °C, i.e. liquid components with a high volatility. Between these two limits, fuels like diesel have a broad distillation curve extending on a large temperature range.

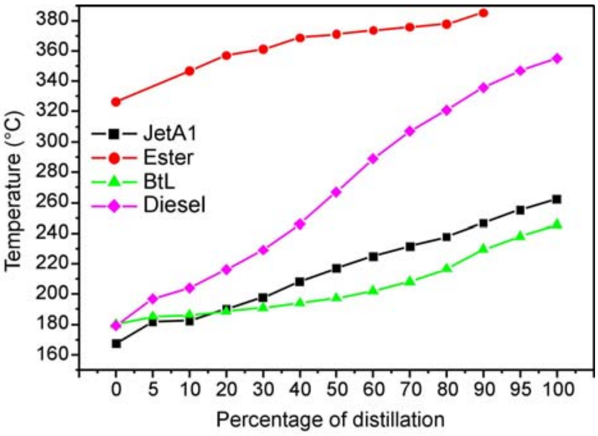


Figure 1: Distillation curve

Probing these fuels using PLIF requires then a selection of adequate fluorescent tracers fit to match the distillation curves. The experimental methodology adopted in the present work has been to initially choose and characterize fuels and appropriate fluorescence tracers with evaporation properties similar to the fuel's one. During the second phase, the fluorescence properties of fuels and tracers were studied under thermodynamic conditions representative of real engine conditions. Spectroscopic experiments were performed in a high temperature – high pressure test cell for various conditions of temperature, pressure and buffer gas. In addition, effect of fluorescence cross-talks between the fluorescent tracers were analyzed and accounted for to quantify the fluorescence measurements. In parallel to this work, the co-evaporative characteristics of the tracers and fuels were also studied using thermodynamic simulations to insure of the good selection of fluorescent tracers. Innovative measurement strategies for absolute fuel vapour concentration measurements of alternative fuels based on the use of Planar Laser-Induced Fluorescence (PLIF) technique can be developed in regard to the experimental results obtained in the preceding phases.

3. Laser-induced fluorescence

Laser-induced fluorescence (LIF) is an incoherent, linear and non-elastic optical process. One of the main advantages of LIF applied to organic molecules relies on its capability to produce a large fluorescence yield, which offers the possibility of instantaneous probing of flowfield with good temporal (~ 10 ns) and spatial (~ 100 x 100 μm^2) resolution. Analysis of the fluorescence signal allows to measure concentration of the probed species and gas temperature. However, this analysis requires the knowledge of the fluorescent properties of probe molecules. Indeed, once the molecule is excited by the laser beam via the absorption process, several processes of deactivation of the populations of the excited state (*via* radiative and non-radiative processes) take place simultaneously, complicating then the analysis of the fluorescence signals. In order to evaluate these effects, an experimental spectral database of the probed organic compounds needs to be elaborated from the analysis of the spectroscopic properties (fluorescence, absorption…) with temperature, pressure and chemical composition.

4. Experimental setup

Spectroscopy experiments are performed in an optical-accessible gas cell at temperatures ranging from 400 to 900 K. The experimental setup is shown in Figure 2. Liquid fuel was pressurised in a 1.0 litre reservoir and nitrogen and oxygen were supplied by pressurised bottles. The three tanks were connected to a Controlled Evaporator and Mixer (CEM) which heated and mixed fuel vapour with a mixture of N_2 and O_2 at controlled mass flowrates and temperature. The molar fraction of fuel in the mixture exiting the CEM is fixed to 0.3 %. The outlet of the CEM was connected to a stainless steel cell preheated at temperature between 400 and 900 K (controlled with a type K thermocouple), where the gas mixture was injected. Optical access was provided by three UV-silica windows, two of which were used for laser access and one for detecting fluorescence. In each experiment, the fuel/carrier gas mixture was excited by UV pulses from a frequency-quadrupled Nd:YAG laser at 266nm with a repetition rate of 10 Hz. Fluorescence from part of the illuminated fuel was collected at right angle by a spectrograph. The light dispersed by the grating was recorded using a 16-bit intensified CCD camera. The spectral resolution of the detection system was about 1 nm. Each fluorescence spectrum recorded for a given condition was averaged over 300 single-shot measurements, with correction for beam attenuation due to absorption and normalisation by laser energy. An equivalent set of measurements was also acquired immediately afterwards with the same laser energy in the cell evacuated from any fuel vapour to allow subtraction of background light from fluorescence. Spectra were corrected for the spectral response of the detection system using calibration from the emission spectrum of a deuterium lamp. Temperature (± 1 K accuracy) and fuel vapour molar fraction (± 2 % accuracy) were thoroughly controlled and particular attention was paid to perform measurements at steady state conditions. Accounting for all these sources, uncertainty on fluorescence signals could be estimated to be about 10 %.

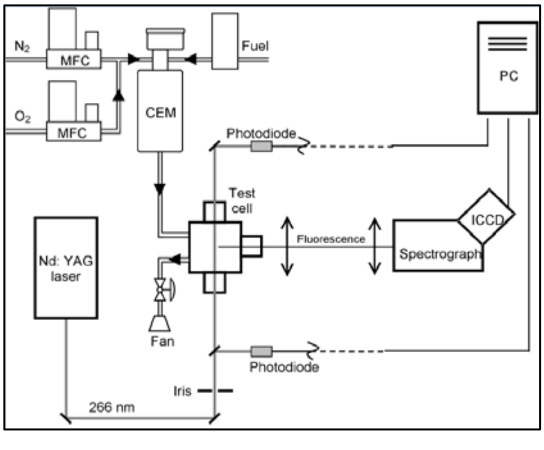


Figure 2: High-pressure and High Temperature Experimental setup

5. Results

5.1. Fluorescence of standard and biofuel fuels

Spectral measurements were performed to measure the fluorescence properties of standard and biofuels fuels. Results of the fluorescence measurements allow a classification of the optical fuel performances into three categories. The first family, which certainly is the simplest case for fluorescence strategy, groups together the BTL and the EMHV biofuels. These fuels produce very weak fluorescence signals due to impurities staying after their refining. Therefore, they can be assumed as non-fluorescence fuel. Probing the evaporation of these fuels would then require the adding of one or two fluorescent tracers with adequate thermodynamic properties matching the overall evaporation characteristics of the fuel. Properties of Jet A1 (kerosene) represent the second case. This standard fuel displays a fluorescence spectrum with two distinct bands (Figure 3). The fluorescence spectra of the jet fuel in the 270-310 nm spectral range can be reasonably attributed to a unique aromatic compound, 1,2,4-trimethylbenzene while the second fluorescence band located between 310 nm and 420 nm has to be reproduced from the fluorescence of several two-ring aromatics belonging to the naphthalene's family. As shown in Fig. 2, the intensity of the fluorescence emission decreases faster with temperature for the high-frequency band (260 to 310 nm) than for the low-frequency band (310 to 420 nm). Similar dependences of kerosene vapour fluorescence on other scalar parameters like pressure and O_2 concentration open possibilities for kerosene vapour PLIF for measuring equivalence ratio in kerosene/air flows via a dual channel filtered detection of kerosene fluorescence [5]. No seeding of the fuel with fluorescent tracers is then necessary.

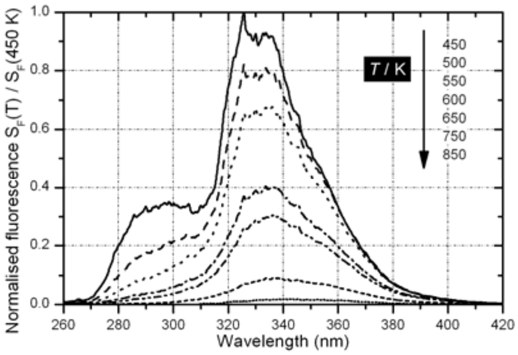
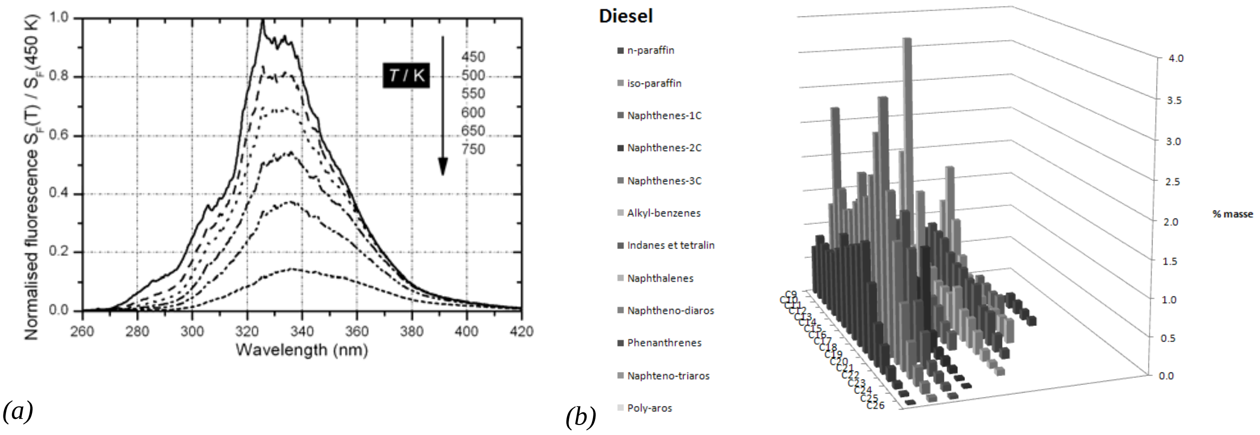


Figure 3: Temperature dependence of fluorescence spectra of Jet A1

The third category regrouping standards fuels like diesel differs from the other ones. Diesel fuel emits a fluorescence signal ranging from 270 to 400 nm with a fluorescence peak comparable to the kerosene fluorescence (Figure 4a). Contrary to kerosene, the fluorescence signal results from the excitation of a large number of molecules which prevents any direct quantitative measurement of fuel concentration. Indeed, as shown in figure 4b, the species composition of the diesel fuel (several hundreds of molecules) has the drawback to have many aromatics relevant to the mono- to fourth-ring aromatics families. Their excitation produces a lot of fluorescence bands which overlap each other, limiting then an identification of the fluorescent tracers responsible of this fluorescence. Thus, no quantitative measurements are possible from the direct analysis of this fluorescence. A strategy to overcome this limitation consists in the elaboration of a surrogate fuel composed with a chemical assembly of non-fluorescent molecules (3-4 molecules) and fluorescent tracers (2-3 molecules) specifically selected for fitting the thermodynamic evaporation properties of the diesel fuel and for getting fluorescence properties adapted for quantitative measurements of fuel concentration.



(a) *(b)*

Figure 4: (a) Temperature dependence of fluorescence spectra of diesel fuel, (b) species distribution of diesel fuel from 2D gas chromatography.

5.2. Choice of fluorescent tracers

The fluorescent tracers which be used with biofuels and standards fuels were deduced from their thermodynamic data found in literature and from spectroscopic data performed in the test cell. The objective of this work was to find potential fluorescent tracers with low and high boiling points which match the evaporation properties of the standards fuels and biofuels. The fluorescence spectra of these molecules were carried out in order to determine their spectroscopic properties such as fluorescence intensity, spectral range of emission, fluorescence behaviour with temperature… For instance, Figure 5 displays the evolution of fluorescence with temperature for a high volatility molecule, i.e. 1,2,4-trimethylbenzene. A large decrease of the fluorescence spectrum ranging from 270 to 360 nm is observed with temperature. Similarly, the 1,2,4-TMB yield equally exhibits a slightly steeper exponential fall-off with temperature, and corresponds roughly to three orders of magnitude over a range of 600 K. It is also interesting to notice that this behaviour doesn't depend on the base fuel in which the tracer is diluted. Performing similar measurements for the other fluorescent tracers allow then the definition of an experimental data base allowing the selection of the fluorescent tracers for probing the different fuels.

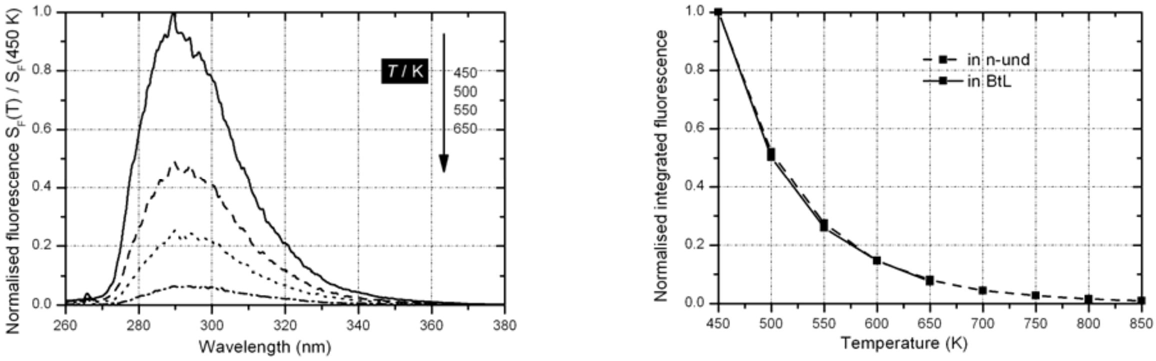
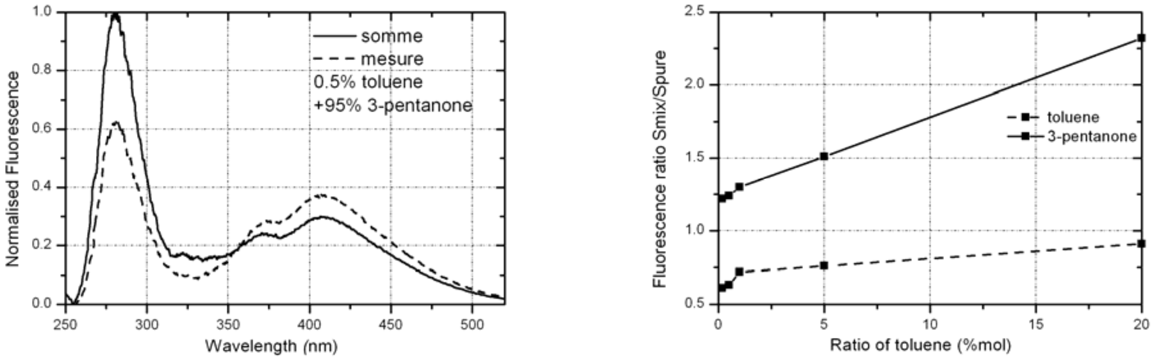


Figure 5: Temperature dependence of 1,2,4-trimethylbenzene fluorescence

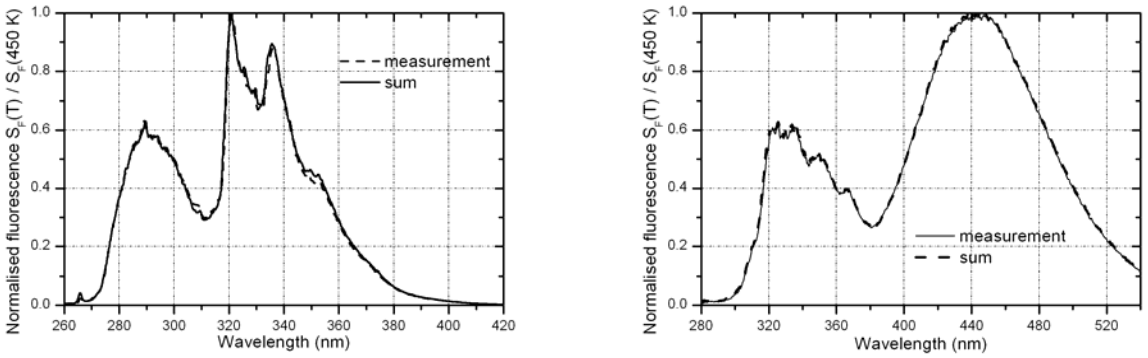
As mentioned previously, fuels like diesel require the excitation of several fluorescent tracers in order to obtain simultaneous optical data associated to the different fuel volatilities. A validation of this experimental approach assumes that any photophysical interaction between the fluorescent tracers must be involved. Indeed, energy transfer arising from collisional processes between both tracers could change their fluorescence efficiencies when present in the mixture. In order to assess such effect, several fluorescent tracer mixtures were initially considered. The first composition consists of a ketone/aromatic mixture which is the combination classically used in internal combustion engines [6]. Figure 6a displays the comparison between the fluorescence spectra of the 3-pentanone/toluene mixture and the one rebuild from the fluorescence of pure fluorescent tracers weighted by their concentration. Significant variation of toluene and 3-pentanone fluorescence peak intensities is then observed when both molecules are mixing. This effect probably comes from non-radiative energy transfer arising between the close first excited electronic states S_1 of toluene and 3-pentanone. A decrease of the toluene fluorescence while an increase of the 3-pentanone fluorescence is observed compared to the case where the fluorescent tracers are pure. Moreover, the efficiency of this energy transfer is depending on the concentration of tracers into the mixture (Figure 6b), which prevents any reliable measurements of fuel concentration as initially proposed [6].



(a) *(b)*

Figure 6: (a) Fluorescence of ketone/aromatic mixture, recorded at 450K, (b) fluorescence emission ratio

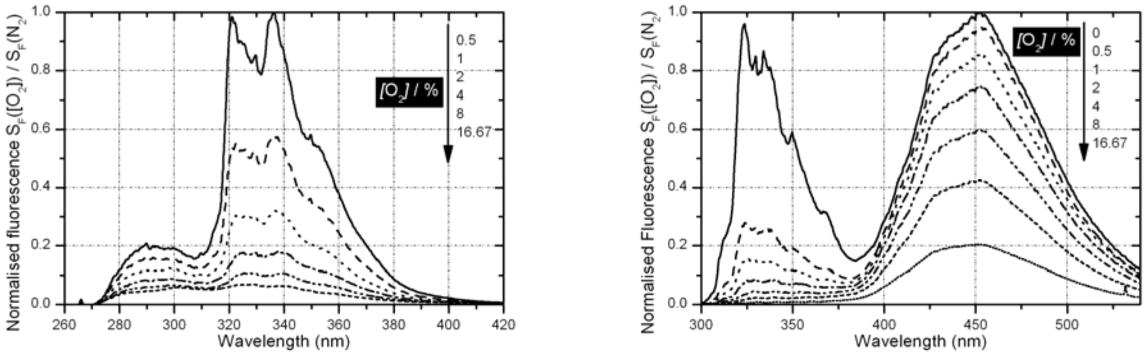
By contrast, no photophysical interaction is observed when two aromatics are mixed together. Figure 7 depicts the result for two aromatic mixtures, 1,2,4-trimethylbenzene/acenaphthene and naphthalene/fluoranthene. For each mixture, the comparison between the fluorescence spectrum of the fluorescent mixture and the one rebuild from the fluorescence spectrum of each component weighted by their concentration shows a very good concordance, demonstrating no energy transfer between the tracers. The fluorescence properties recorded on pure tracers remain unchanged and thus, a binary aromatic mixture represents a good solution for measuring the fuel concentration in case of fuels having a broad distillation curve. Like for pure tracers, the base fuel doesn't change the fluorescence signal of the tracer mixture and its behaviour with temperature.



(a) *(b)*

Figure 7: (a) Fluorescence of 1,2,4-trimethylbenzene/acenaphthene mixture, (b) fluorescence of naphthalene/fluoranthene mixture, both recorded at 450K.

In case where fuel evaporation experiment is performed in gas mixtures containing oxygen, the quenching of fluorescence by oxygen is also necessary to estimate. For instance, Figure 8a shows a small decrease of the fluorescence of 1,2,4-trimethylbenzene with oxygen concentration while the reduction of acenaphthene fluorescence on the same range is larger. For the naphthalene/fluoranthene mixture, the reduction of the naphthalene signal is larger than the fluoranthene's one.



(a) *(b)*

Figure 8: (a) Oxygen dependence of Fluorescence signal of 1,2,4-trimethylbenzene/acenaphthene mixture, (b) oxygen dependence of fluorescence signal of naphthalene/fluoranthene mixture, both recorded at 450K

These behaviours are well illustrated in Figure 9, where the Stern-Volmer coefficients, displaying the evolution of the inverse integrated fluorescence signal with oxygen concentration are plotted. The fluorescence of the different tracers present significant difference with temperature and oxygen concentration.

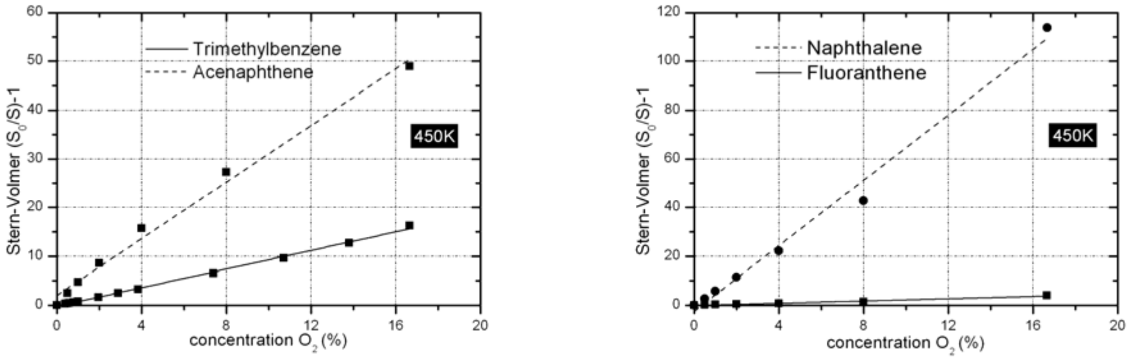


Figure 8: (a) Stern-Volmer coefficient of 1,2,4-trimethylbenzene and acenaphthene in mixture, (b) Stern-Volmer coefficient of naphthalene and fluoranthene in mixture, recorded at 450K

Finally, Results from these exhaustive spectroscopic study allow the selection of the best fluorescent tracers presenting good thermodynamical and spectral fluorescence properties. For diesel fuel, a combination of naphthalene and fluoranthene is the best solution while 1,2,4 trimethylbenzene and acenaphthene were selected for BtL (Table 1). In particular, their fluorescence occurs in different spectral ranges, which allows a simultaneous detection of the fluorescence signals, as observed in Figure 7.

Table 1: Physical properties of some fluorescent tracers

Molecule	**Formula**	**Molar Mass (g/mol)**	**Boiling temperature (°C)**
1,2,4-trimethylbenzene	C_9H_{12}	120.18	170
Naphthalene	$C_{10}H_8$	128.19	218
Acenaphthene	$C_{12}H_{10}$	154.21	279
Fluoranthene	$C_{16}H_{10}$	202.25	382

These fluorescence properties can now be used to derive strategies for imaging quantities such as equivalence ratio and temperature, which completely characterise spray evaporation, only in the mixing regions of non-burning and burning sprays, upstream from the flame front. In these specific regions, oxygen can be considered as the main quencher of fuel fluorescence. Visualisation of mixing process requires simultaneous 2D-imaging of fuel and oxygen concentrations in the flow with a temporal resolution faster than the timescales of mixing and chemical reaction. As shown previously, the tracers fluorescence are seen to be a specific function of temperature, oxygen concentration and fuel concentration for a 266 nm excitation wavelength. Detection of fluorescence from the couple of fluorescent tracers with this excitation wavelength over two specific spectral ranges can provide dual-parameter imaging, yielding for example equivalence ratio in addition to temperature. Collection of both fluorescence signals on two separate ICCD cameras with appropriate spectral filters may be one of the possibilities because of their different temperature and oxygen dependencies. Using the same experimentally-determined strategy for kerosene fluorescence [10], along with a calibration point in a reference flow where thermodynamic parameters are well known, an iterative processing routine of both instantaneous fluorescence signals, combined with the closure relation for species composition can be used to determine the desired quantities. Note that this data reduction implies that the ratio between both tracers remains constant during the experiments. This assumption remains valid for temperatures up to 1100–1300 K, where fuel pyrolysis may be observed.

3. Conclusion

Fluorescence measurements of standard fuels and biofuel tracers were performed in a high pressure high temperature test cell. Results led to the development of new laser induced fluorescence diagnostic strategies able to investigate the effects of biofuels on evaporation and mixing process occurring in combustion chambers. The strategies are based on the selection of fluorescent tracers matching the fuel properties in terms in terms of evaporation dynamics.

Furthermore, these tracers display attractive fluorescence properties allowing quantitative measurements of fuel concentration. This study will be then applied in specific aeronautical and automotive combustion chambers for fuel concentration measurements.

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