

On planar laser-induced fluorescence with multicomponent fuel and tracer design for quantitative determination of fuel concentration in IC engines

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Abstract: This paper first presents an exposition of the theory relevant to quantitative planar laser-induced fluorescence measurements in an engine, at a level commensurate with the expertise of a specialist engineer. It is intended to provide a grounding in the technique, its theoretical basis, and a source of references. Second, this paper presents the design of a multicomponent fuel and fuel tracer set that may be used for quantitative planar laser-induced fluorescence (PLIF) where time and crank-angle resolved knowledge of the vaporization of different fuel fractions is required. Such a fuel is presented and shown to exceed the specifications of accepted single-component fuel tracers. The fuel distillation characteristics, construction, and key features are discussed in the context of the theory.

Keywords:

1 INTRODUCTION

Planar laser-induced fluorescence (PLIF) is an experimentally straightforward laser diagnostic technique that has been extensively demonstrated for visualizing species of combustion and reacting flows [1, 2]. An image formed at right angles to a laser sheet, resonant with an absorption in a fluorescing species, is in part due to a quantity of emitted light from a given chemical species. The emitted light can be imaged on to a CCD or CMOS detector and thus measure properties of the emitting species in two dimensions. The quantity of light depends upon a number of aspects of the system, including the species concentration and the temperature. The simplicity of this principle has led to the extensive application of PLIF for imaging and qualitative assessment of these parameters.

Pointwise laser-induced fluorescence[†] (LIF) has been shown to be a practical quantitative method

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[†]Henceforth LIF and PLIF will be taken to refer implicitly to the distinct pointwise and planar (imaging) diagnostics respectively.

for determining both species concentrations and temperatures in combustion environments [3, 4]. The combination of the quantitative potential for LIF and the simplicity of PLIF imaging have prompted great interest in spatially resolved quantitative PLIF (Q-PLIF) measurements of species concentrations and temperatures. However, quantitative LIF measurements often use spectral and time domain information to calculate the dependence of the signal on the parameter of interest: this is not possible with PLIF with today's CCD and CMOS detectors. Spectral information is usually obtained by dispersion, which requires an orthogonal spatial dimension that is not available with PLIF. Current imaging detectors are not able to take multiple time-resolved measurements on the typical timescales of fluorescence. How then, if at all, is PLIF to be made quantitative without these degrees of freedom? What does the fluorescence depend on, and how may it be controlled? The first object of this paper is to review, in engineering terms but with reference to the relevant physics, the experimental practicalities of quantifying a measurement based on a PLIF image.

PLIF is a desirable technique for internal combustion (IC) engine research where the visualization of sprays and combusting flows (see Fig. 1(a) and

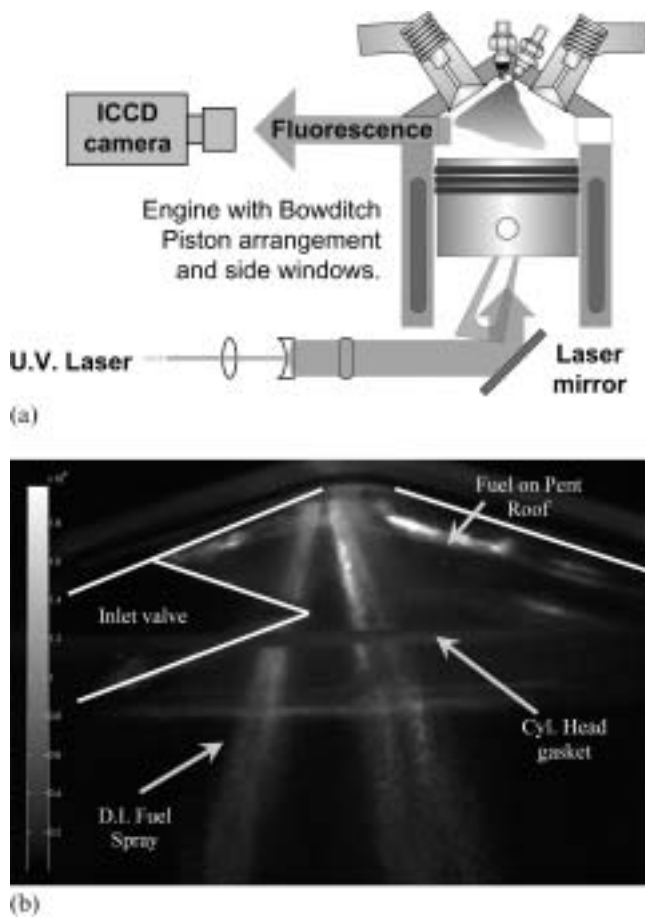


Fig. 1 (a) Typical PLIF set-up for fuel distribution measurements in an engine with optical access; (b) example of a PLIF image taken using an arrangement similar to that in (a) in a GDI engine, showing the fuel plumes, the inlet valve, and the pent-roof geometry

(b) for illustration) is critical to the understanding, modelling, development, and optimization of new IC engine operating modes. Arguably, one of the most important aspects for the coming generation of direct injection (DI) and homogeneous-charge compression ignition (HCCI) is fuel preparation. The direct application of PLIF to fuel is made difficult because it is not a single species. Gasoline comprises a large number of different species, some of which fluoresce. PLIF images may be taken using standard gasoline; however, the result is further biased by the properties and concentrations of those species which do fluoresce – generally, the heavier and less volatile fractions. Objective measurements can be made using non-fluorescing pure-component fuels (e.g. pure isooctane) and a fluorescent tracer. The immediate problem is that the properties of the fluorescent tracer are difficult to match with interesting pure-

component fuels, giving rise to different behaviour in an engine. In particular, the issue of co-evaporation of tracer and fuel is difficult to achieve and to model under the transient conditions of interest. The second purpose of this paper is to describe the design and modelling of a three-component fuel and tracer set that may be used to investigate fuel distributions of light, medium, and heavy fractions of fuel in a modern engine.

2 LINEAR PLIF

The generation of a PLIF signal is, in many ways, simpler than understanding its origins in terms of photons of light from a laser and the interaction with the molecular species. However, to quantify the LIF signal, it is necessary to understand the LIF process and how each aspect of the process can be affected by other factors: this is arguably clearest when each effect is related mathematically in an expression for the PLIF signal, and correspondingly in a diagram for the physical effect.

It is possible to relate the component parts of the LIF process to movement of stored energy between states inside the molecule, as shown in Fig. 2. Figure 2 shows a diagram in which each line represents a state, in any one of which an electron in a molecule may exist. The states can have different energies, and a given electron can move between the states, subject to certain rules and the conservation of energy. One way for the electron to change its energy is to absorb a photon of light energy. Crudely speaking, this is only possible if the energy of the photon is equal to the change in energy of the electron in changing states. Photons can be absorbed (an electron moves to a state of higher energy) and emitted (an electron moves to a state of lower energy) in this way. Were it not for the complication of additional rules, and other methods for electrons to change energy levels, then PLIF would be reduced to the simple process of absorption and emission (in a different direction) of a photon of light from a molecule. Detecting the number of these photons would directly imply the number of molecules present. Regrettably this is not the case, and it is necessary to examine the diagram for additional detail. Again, each concept will be examined in the context of its implications for PLIF.

At this point it is instructive to refer to the expression for a PLIF signal intensity, in the regime where the signal is proportional to the laser intensity,

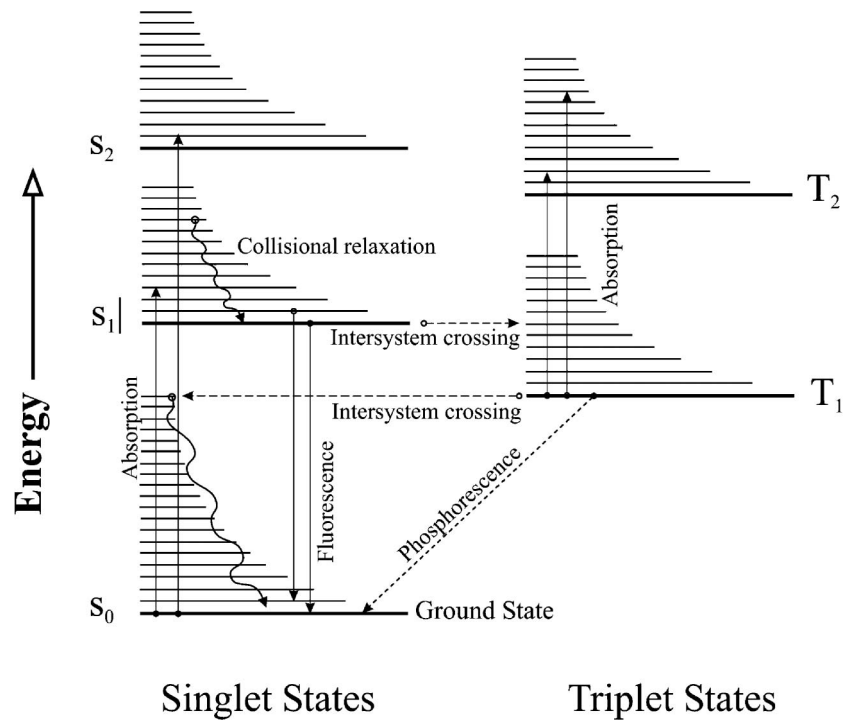


Fig. 2 The allowed internal energy states of an aromatic fluorescent molecule, adapted from reference [5]. Each line represents an energy state: the bold lines represent fundamental electronic states (S = singlet, T = triplet); the lighter lines represent energy stored in rotational and vibrational energy modes of the molecule. Arrows represent changes (transitions) in energy between energy states

given by equation (1)

$$I_{\text{PLIF}} = I(\lambda)N_0(T)IXB_{\text{abs}}^{0 \rightarrow 1} \frac{A_{\text{fl}}^{1 \rightarrow 0}}{A_{\text{fl}}^{1 \rightarrow 0} + Q^{1 \rightarrow 0}(P, T, N) + \dots} \times \frac{E_{\text{photon}}}{c} \quad (1)$$

The coefficients of equation (1) correspond directly to processes occurring in Fig. 2. These effects will be described and the meaning of the elements of equation (1) will be discussed in the following subsections. It should be noted that this expression is only valid for sufficiently ‘weak’ laser intensities – the measure of a weak intensity is discussed in the following section.

2.1 Absorption

PLIF begins with the absorption of laser light. In equation (1) $I(\lambda)$ is the laser intensity at a wavelength λ , which interacts with $N_0 l A$ molecules with a probability $B_{\text{abs}}^{0 \rightarrow 1}$ of causing absorption to occur in those molecules. N is used here to represent a number density of molecules, and $l A$ the volume of the imaged laser sheet. The product of these coefficients of the PLIF signal gives the number of molecules that have absorbed a photon, i.e. the

transfer of energy from a photon of light (in the laser beam) to an electron gaining energy inside a molecule. The electron here, by way of example, is taken to be in a state S_0 (see Fig. 2) and the absorption is causing the electron to move to a state S_1 with a higher energy. Clearly, if the electron is not in a state S_0 to begin with, that molecule cannot contribute to absorption from that level. Therefore, N_0 is considered, the number density of molecules with electrons in the energy state prior to the absorption event.

Absorption by the tracer used in PLIF is necessary for generating LIF. However, absorption also necessarily affects the number of photons present in the beam, and therefore the quantity of fluorescence the laser will go on to induce elsewhere. Furthermore, in addition to absorption by the tracer species, there may be absorption owing to other constituents, including those in the fuel and those introduced from elements that the fuel passes through, such as pumps, pipe work, and injectors. Q-PLIF relies on knowledge of the laser flux through a given point to infer the concentration from the quantity of fluorescence. It is therefore essential to understand and quantify the spatial effect of absorption on the light sheet. To minimize variations in the intensity of

the light beam in PLIF, absorption from all sources should be minimized; thereafter, assuming low levels of absorption, Beer's Law [given in equation (2)] may be used to account for absorption.

$$\begin{aligned}\delta I(x + \delta x) &= -I(x)\sigma(\lambda)N_0(x, T)\delta x \\ I(x) &= I_{x=0} e^{-\sigma(\lambda)\int_0^x N_0(x, T)dx}\end{aligned}\quad (2)$$

where $\sigma(\lambda)$ is the *absorption cross-section*, defined as the equivalent area that a molecule would have as a solid object to attenuate the light passing through its volume. The relationships between the absorption cross-sections and absorption probabilities is instructively described by Hilborn [6, 7]. In a homogeneous medium ($N_0(x) = \text{const}$) the result for the laser intensity, $I(x)$ is a simple exponential decay. In the general case, $I(x)$ is a complex function that requires knowledge of the species distribution, i.e. that which is being measured. In this case, it is necessary to seek a self-consistent value for N_0 that predicts the correct level of absorption and number distribution predicted by the PLIF image, with the assumption that there are no other effects on the magnitude of the fluorescence or absorption. Where absorption is not caused by a single species (fluorescing or non-fluorescing) this analysis will be flawed unless extra terms are added to the exponent to account for the population and absorption cross-section of all absorbing species; such data are not derivable from the PLIF signal in general. Finally, scattering can have a similar effect to absorption in attenuating the laser beam along a given line. Significant scattering or reflection at a single point (e.g. a droplet) can direct laser intensity into multiple directions and complicate the local intensity contributing to absorption. In conclusion, to account for the effect of the absorption and scattering on a laser beam, the total effect should ideally be small because it is difficult to be precise when making corrections.

The absorption process is fundamentally temperature dependent. The temperature dependence is introduced through the population of electrons in the absorbing level, $N_0 = N_0(T)$. The temperature affects the average energy stored by a molecule, both as kinetic and internal energy. One mechanism for storing internal energy is for electrons to move from lower to higher energy states inside the molecule. At a high temperature the distribution of electrons in states is spread over a larger number of levels than at a low temperature. Therefore, dependent on the energy of the absorbing state, N_0 may increase or decrease with temperature. In the unlikely event that a single lower state is responsible for absorption and

its energy is known, the change in population at equilibrium may be modelled. The temperature dependence of absorption and the inhomogeneous temperature fields found in engines makes this aspect difficult to quantify. It is therefore important to excite tracer species at wavelengths which cause absorption from levels with a weak temperature dependence [8, 9].

Finally, it is important to appreciate the effect that laser intensities that are too strong (saturating) have on the understanding of PLIF seen thus far in the current paper. The authors have already said that the absorption of a photon understandably causes the transfer of an electron from a lower state to an upper state. This molecule now does not have an electron in the lower state and N_0 has been reduced by one. This effect will reduce the ability of the medium to absorb until the electron returns to the original state (by fluorescence or otherwise) after a time τ . The characteristic intensity for which this effect is a problem is given by the *saturation intensity*

$$I_{\text{sat}} = \frac{hc}{\lambda\sigma(\lambda)\tau} \quad (3)$$

Where hc/λ is the energy of a photon (h is Planck's constant, c is the speed of light) and λ is the wavelength of the pump light. Therefore, intensities (measured in W/cm^2) close to, or higher than this will not result in fluorescence that is well described by the analysis given here. The saturation intensity is a limit on the signals that can be produced using PLIF in the unsaturated, or linear, regime. PLIF can be attempted in the saturated regime (see discussion on quenching) but the interpretation is very different and concerns processes not described here.

2.2 Fluorescence

Once absorption has taken place and an electron has been excited to a higher state in a molecule, fluorescence is one of several processes that may occur for the molecule to return to its original state and release its energy. Were fluorescence the only possible mechanism, then it would be straightforward to interpret the fluorescence as above. However, the various processes compete, resulting in only some probability of a quantum of energy absorbed being released as fluorescence: this leads to an idea of the *fluorescence quantum efficiency*, ξ_{Fl} . This is given in equation (4) by

$$\xi_{\text{Fl}} = \frac{A_{\text{fl}}^{1 \rightarrow 0}}{A_{\text{fl}}^{1 \rightarrow 0} + Q^{1 \rightarrow 0}(P, T, N) + \dots} \quad (4)$$

Where $A_{\text{h}}^{1 \rightarrow 0}$ is the rate at which photons would be emitted from the excited energy state (i.e. fluorescence), $Q^{1 \rightarrow 0}$ is the rate at which the upper state electrons are de-excited by quenching (with no photon emitted), and the ellipsis allows for other processes. $A_{\text{h}}^{1 \rightarrow 0}$ is a constant for a given state of a given molecule, and values of this are available in the published literature. However, quenching is not a constant and has a value that depends strongly on the total pressure, the partial pressure of other species in the medium and weakly on the temperature. Quenching is caused by collisions and near collisions between molecules. The collision rate increases with pressure (as $\sim P^2$) owing to the change in the density of the gas; and with temperature (as $\sim T^{1/2}$) owing to the change in the r.m.s. speed of the gas molecules. Furthermore, the quenching will change as a result of how 'hard' the collisions between molecules are and this is a function of the speed of collision and the temperature. The probability of a collision causing quenching is related to the species that are colliding, e.g. O_2 is generally more efficient at quenching states than, say, N_2 . Quenching is therefore also a function of the gas composition. In conclusion, the quenching rate is a difficult quantity to model and predict. Practical illustrations of the curious effect of quenching on fluorescence yield are given for toluene with respect to species concentration [10, 11] and temperature [12, 13].

For many tracer species at pressures found in an engine, the quenching rate is much faster than the fluorescence rate, causing the fluorescence quantum efficiency to be strongly pressure (and partly temperature) sensitive in a given medium. It is essential to have a value for the fluorescence quantum efficiency for quantitative PLIF. Several methods have been used to identify the total rate ($R = A_{\text{h}}^{1 \rightarrow 0} + Q^{1 \rightarrow 0}(P, T, N) + \dots$). In the case of LIF, it is possible in some cases to measure the time dependence of the LIF signal, which will decay with this rate, R , exponentially. However, for PLIF it is not practically possible, with modern CCDs, to record the time dependence of the signal in two dimensions. The commonly applied alternative is to apply a method to 'calibrate' for the overall quantum efficiency of a tracer species in a medium of known composition at a given temperature and pressure.

The calibration process generally involves recreating the range of conditions that will be seen experimentally in a comparable controlled environment with known temperature and pressure [14]. For each temperature, pressure, and tracer concentration to be measured, a controlled measurement must be

taken that determines the fluorescence quantum efficiency in that situation. These values may then be used to understand experimental data. For IC engines, the major unknown in this analysis is temperature. In many PLIF experiments the temperature dependence is simply ignored because so little can be done to measure it. Therefore, it is important to select a tracer species for which the temperature dependence of the fluorescence quantum efficiency is small. Quenching is currently a significant obstacle to achieving quantitative PLIF measurements.

2.3 Intersystem crossing and phosphorescence

The remaining aspects of Fig. 2 that must be considered are intersystem crossing and phosphorescence; these are relatively little-explored phenomena with respect to PLIF. Electron states inside fluorescent molecules can be grouped together by the total angular momentum the molecule has when the electron is in that state. The diagram in Fig. 2 shows two groups of levels that have been labelled 'singlets' and 'triplets'. To a first-order approximation, a photon (absorbed or emitted) does not act on the angular momentum of an electron. Therefore, it is impossible for an electron to move between a singlet and a triplet state using a photon alone.

Intersystem crossing is a process that occurs inside a molecule involving the movement of an electron between singlet and triplet states. This process is affected by molecular rotation and vibration, and by collisions. When intersystem crossing has taken place, an electron cannot (to a first-order approximation) emit a photon in order to return to a lower energy state. Triplet states are therefore relatively long-lived (microseconds up to seconds), and when they finally emit a photon (by a higher order process) this is generally at a longer wavelength, with lower intensity and long after the fluorescence intensity has decayed. This is phosphorescence and is seen in tracer molecules such as 2,3-butanedione (biacetyl).

Intersystem crossing (and subsequent quenching or phosphorescence) are a loss mechanism between absorption and fluorescence, in a similar way to direct quenching. It is difficult to distinguish the difference between the processes using LIF, but were it possible, the rate of intersystem crossing would be one of the additional terms after the ellipsis in equation (4) for the fluorescence quantum efficiency, ξ_{Fl} . This term is likely to have a dependence on the temperature and on the local composition of the medium. It has been speculated that this dependence may be very strong for tracers such as toluene [13].

In conclusion, there are many processes (which in turn are difficult to quantify) that can affect the quantity of fluorescence seen from a given concentration of a tracer. Only by careful measurement of these parameters, or the gross quantum efficiency, for given conditions is it possible to begin to measure *quantitative* concentrations (or other parameters) using PLIF.

2.4 Tracer PLIF

The selection of suitable tracers for LIF of fuel concentrations is already the subject of much discussion. However, greater use can be made of information about tracers in the context of the previous discussion on absorption and fluorescence. The most important parameters of a fuel tracer include

- (a) the absorption cross-section at convenient laser wavelengths, and temperature dependence;
- (b) absolute fluorescence quantum efficiency and its variation as a function of the conditions;
- (c) fluorescence lifetime;
- (d) fluorescence spectrum as a function of the conditions;
- (e) chemical stability and toxicity in hydrocarbon fuels.

The absorption characteristics are determined by the types of bonds present in the molecule. The most common bond is the C–H bond which absorbs very little down to wavelengths where air itself is absorbing (~ 180 nm). The same is true of many other single bonds. Double bonds (e.g. C = O, C = N, C = S etc.) containing two electrons tend to absorb at longer wavelengths because of the manner in which the electrons are held between the respective atoms when there is more than one electron present. In the current paper tracer molecules with double bonds are considered and the interested reader is referred to the literature [5, 15, 16] for further details.

The fluorescence lifetime and spectrum are determined by the excited state levels in the tracer molecule. The fluorescence quantum efficiency is directly related to the fluorescence lifetime and both depend on the quenching rate. However, the relative change in quantum efficiency is significantly affected if the quenching rate is much faster than the fluorescence rate, $A_{\text{fl}}^1 \rightarrow 0$. Tracers like 2-propanone (acetone) have very fast $A_{\text{fl}}^1 \rightarrow 0$ rates (\sim few ns) and are therefore affected little by quenching. Aromatic tracers tend to have much slower $A_{\text{fl}}^1 \rightarrow 0$ rates (~ 100 ns), and are therefore affected much more strongly by changes in the quenching rate. Conversely, tracer species with longer fluorescence lifetimes produce fluorescence

that is readily separated from scattered light (Rayleigh and Raman) which emerges instantaneously. Fast gated detectors can be used to image PLIF images immediately after the laser pulse has passed, minimizing cross-talk with other optical effects. Short gate times also ensure that the images are captured for the instants in time when the fluorescence is much more intense than the background light, chemiluminescence and incandescence in the combustion system being imaged.

The fluorescence spectrum of a tracer species is not the same as its absorption spectrum. In fact the fluorescence spectrum is invariably shifted toward the red from the absorption and resembles the reflection of the absorption spectrum (e.g. see Fig. 3). The separation of the absorption and emission spectra is known as the Stokes-shift and is principally caused by the spatial separation of energy states of electrons in a molecule. The Stokes-shift importantly means that the majority of fluorescence is not re-absorbed by the tracer species; however, this does not mean that the fluorescence is not absorbed by other species, particularly certain products of combustion. Additionally, the shift enables the spectral separation of scattered laser light (Rayleigh, Mie) from the fluorescence, which is important in the case of scattering media such as sprays. In these cases a spectral filter can be used which absorbs at the excitation wavelength, but transmits the fluorescence. In the case of toluene, normally excited at 248 or 266 nm, a Schott WG280 filter is normally placed between the camera and the sample to absorb some of the scattered laser light and transmit the majority of the fluorescence, e.g. see reference [17].

When applying tracer PLIF it is necessary to be able to tune the absorption and fluorescence signals with the concentration of tracer present, so as to achieve the combination of good fluorescence and low absorption (sometimes conflicting conditions) across the region of interest. Therefore, tracer PLIF is not applied to pure fluorescent species; rather tracers are added to a non-absorbing, non-fluorescing 'fuel', with similar physical attributes. When low-concentrations tracers are used, it is necessary to pay considerable attention to the purity of the 'fuel' and its absorbance/fluorescence. Very small concentrations of aromatic compounds at part-per-million concentrations can absorb significantly in the ultraviolet (UV), and fluoresce much more efficiently than the ketones. It is important to ensure sufficient purity of the base fuel and audit the introduction of impurities from fuel preparation systems such as pumps and injectors. Conventional

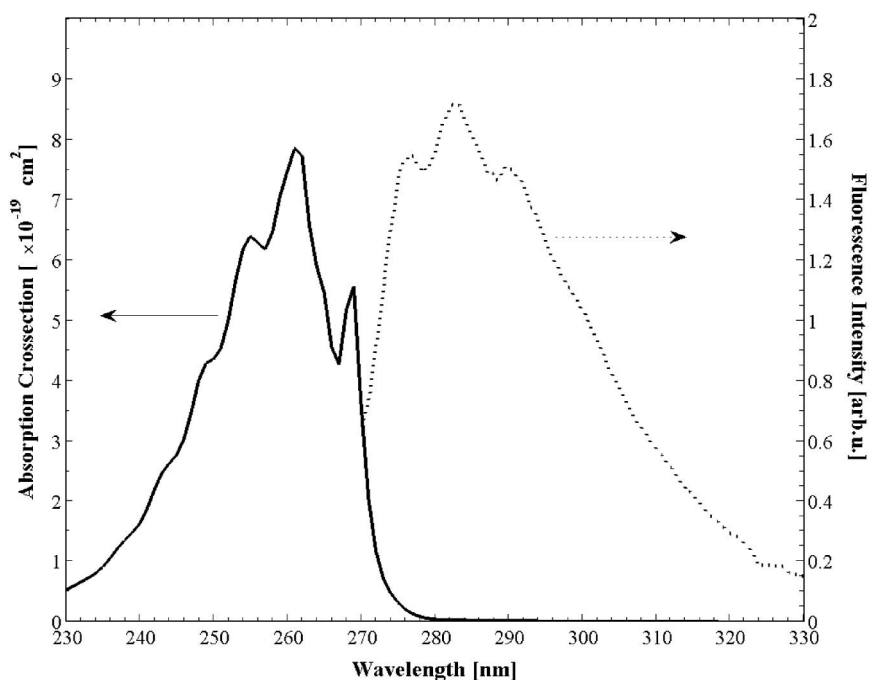


Fig. 3 Absorption and fluorescence spectra of toluene taken from (0.1 per cent) measurements in spectroscopically pure grade isooctane at standard temperature and pressure (STP).

gasoline and standard grades of component fuels are often strongly absorbing and fluorescing, therefore it is often necessary to consider high-pressure liquid chromatography (HPLC) grade or spectrophotometric grade fuels. Again, given the temporal and spectral differences in the emission of fluorescence by aromatics, aldehyde, and ketone groups, there is considerable scope for discrimination in the detection system using spectral filters and detector gating.

3 DESIGN OF A MULTI-COMPONENT FUEL FOR TRACER PLIF

3.1 Introduction

Tracer PLIF is based on the premise that the fluorescent tracer behaves 'in every way the same as the fuel' to which it is added. Two issues are immediately evident: first, fuels are not, in general, single compounds, rather a mixture of many substances with different properties. Second, fuels are generally introduced into engines in liquid form (often as droplets) from which they evaporate. The process of evaporation is not straightforward to model and it is not a trivial task to match the coevaporation properties of two substances (e.g. specific heat, latent heat of vaporization, diffusivity, h-bonding, etc.) in addition to the other properties (e.g. RON, MON, viscosity, aromatic concentration, energy density, etc.).

Single-component fuels with coevaporating tracer pairs have been in use for some time, even where little justification for the assumption exists. The closeness of coevaporation may be described by a 'coevaporation ratio', C_{vap} , defined as the vapour-phase tracer to fuel (or fuel fraction) ratio normalized by the tracer to fuel fraction molar ratio overall [see equation (5)]

$$C_{\text{vap}} = \frac{[\text{tracer}_{\text{vap}}]}{[\text{fuel} - \text{fraction}_{\text{vap}}]} \frac{[\text{fuel} - \text{fraction}]}{[\text{tracer}]} \quad (5)$$

For systematic effects in the evaporation to be smaller than the typical precision of an engine PLIF measurement, it is required that the coevaporation ratio should lie between 0.85 and 1.15 whenever more than 5 per cent of a fuel fraction is in the vapour phase. Figure 4 describes the evaporation of isooctane with either acetone or 3-pentanone, and shows considerable deviation from coevaporation. Non-ideal (non-Raoult's Law) mixing between the polar ketones and the non-polar paraffin result in the non-linear behaviour in the vaporization. This effect is reduced as the mixture approaches equal proportions; this is of little consequence for tracer PLIF as the mixture is optically thick at around 10 per cent tracer. Finally, the addition of the ketones to the mixture increases the overall volatility (vapour pressure) of the mixture by around 10 per cent at about 303 K.

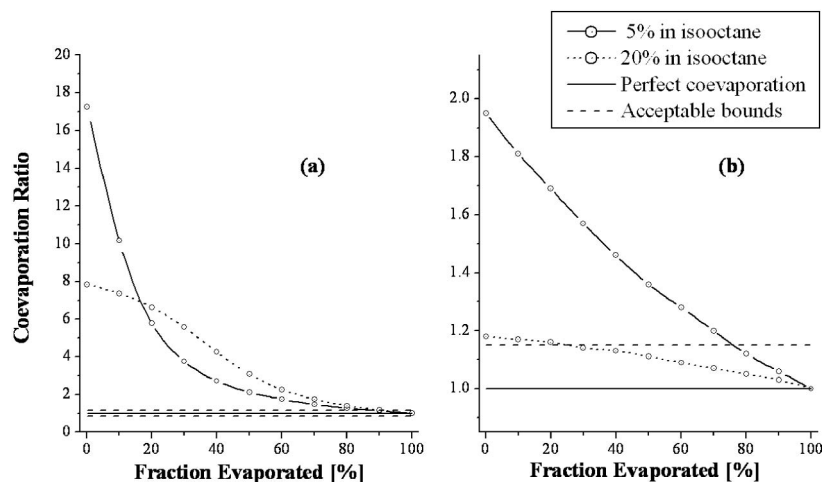


Fig. 4 Coevaporation of (a) acetone/isooctane, (b) 3-pentanone/isooctane mixtures at 303 K

Real fuels consist of many components and boil over a wide range of temperatures. To characterize a ‘real fuel’ it is therefore necessary to re-invent standard gasoline as a set of non-absorbing non-fluorescing (i.e. saturated hydrocarbon) components. The set of components should in every possible way behave exactly as standard gasoline and particularly vaporize in the same way: this will be referred to as a ‘multi-component fuel’. To the multi-component fuel may be added appropriate tracers, so as to coevaporate with different fractions of the fuel such that each tracer will identify the spatial distribution of that fraction in the engine. The separate identification of different fuel fractions is essential so as to understand the progressive vaporization of the fuel and the way in which the variation in local air–fuel ratio develops; in effect this is the ‘distillation’ of fuel in an engine during vaporization.

A number of studies have been undertaken to examine both the issue of coevaporation and the fractionation of fuels in an engine. Early work has done much to emphasize the practical importance of PLIF [21] and showed significant merit for qualitative diagnostics, but did not identify the coevaporation issue for quantitative interpretation. The issue of coevaporation has been identified more recently by a number of authors, in particular the coevaporation of pure isooctane reference fuel with a ketonic tracer [22, 23].

Early work to examine the effect of different fuel fraction led to the addition of tracers of different volatility to a single fuel, e.g. see reference [24]. In these cases, quantitative interpretation was not possible given that the coevaporation of the fuel fraction and tracer is not provable. Two-component exciplex tracer fuels have been modelled and used for

quantitative PLIF diagnostics [25]. A three-component ketone tracer fuel has also been developed [26]; however, this application did not include a calibration of the temperature and pressure effects on the fluorescence yield. A second 3-component fuel has been demonstrated with ketonic/aromatic tracers [23]. This fuel is most similar to the fuel described here, yet this fuel/tracer set has been shown not to meet the criteria for coevaporation as defined in this paper. Moreover, it will be shown in this paper that it is not straightforward to generate a complete coevaporating fuel/tracer set consisting of pairs of pure fuel and pure tracer components.

Ideally a multicomponent fuel would be represented by a large number of tracers, each closely matched to a distinct fraction of the fuel. Unfortunately, we are restricted to naturally occurring tracer species, which are few in number for much of the vaporization curve up to normal boiling points of 350 K. Above 350 K many aromatic species exist which are able to fluoresce and can be paired with a non-fluorescing component for coevaporation. The more volatile tracers are mostly oxygenates and the polar nature of their bonding means that they do not coevaporate well with the non-polar hydrocarbons.

The following sections report on the modelling of a multicomponent fuel consisting of three distinct *fuel fractions* that do not consist of one single component fuel. Each *fraction*, rather than each pure fuel *component*, will be shown to quasi-coevaporate with tracers suitable for PLIF in IC engines. The use of designed fuel fractions, as opposed to pure components, introduces an element of *tunability* in the fuel fraction volatility, which facilitates tighter specification of the fuel coevaporation with tracer.

3.2 Approach to multicomponent fuel tracer PLIF

In order to infer the evaporative behaviour of a multicomponent fuel from that of three tracers, each tracer should coevaporate, at least approximately, with a fixed, matching (light, medium or heavy) multicomponent fuel fraction. 'Coevaporate' in this sense means that the ratio of the tracer concentration to that of its fuel fraction should remain, as far as possible, the same in both liquid and vapour phases throughout the evaporation process, to within the accuracy of the PLIF measurement.

To find a fuel blend that gives satisfactory coevaporation, some preliminary vapour liquid equilibrium (VLE) calculations were performed with an in-house Shell program that uses a modified Redlich–Kwong equation of state [27] and liquid activity coefficients derived from the UNIFAC group contribution method [28]. The coevaporation ratios given by an equilibrium model are not strictly relevant to evaporation in a manifold or cylinder because, here, the equilibrium state of the mixture is generally 100 per cent vapour and evaporation is usually a non-equilibrium, diffusion-controlled process. Consequently, the present authors have also derived 'diffusion-controlled' coevaporation ratios with a Shell in-house model for diffusion-controlled evaporation. However, as the diffusion-controlled model has not yet been validated, only the results from the equilibrium model are presented in any detail.

3.3 Design procedure

The first step was to tabulate tracer properties (such as those in Table 1) and identify three that would fluoresce when excited with a convenient wave-

length, evaporate at appropriate temperatures, and not degrade once mixed with the multicomponent fuel. Acetone (2-propanone) was selected as the light fraction tracer, toluene (methylbenzene) was selected as the medium fraction tracer, and 1,2,4-trimethylbenzene was selected as the heavy fraction tracer. Initially, VLE calculations were used to identify a three-compound blend such that each compound coevaporated acceptably with one of the tracers. Unfortunately, the compounds identified to coevaporate with the selected tracers could not be sourced economically in practical quantities.

In the following iteration, a new principle for design of the fuel was devised: the fuel should consist of three fractions, but should not be restricted to three pure components, in order to achieve coevaporation with the tracers. The iteration therefore began with a six-compound multicomponent fuel blend, using three pairs of readily available compounds such that one compound from each of three pairs was more volatile, and the other less volatile, than the corresponding tracer species. By selecting suitable pairs and adjusting the proportions, a composition was found for which, according to the VLE calculations, each pair evaporated in the same proportion to the tracer to within the required tolerance. The trial mixtures were subjected to VLE calculation of the coevaporation ratio and the blend iterated until a suitable value could be achieved. The calculations were performed for a range of temperatures representative of conditions in an inlet manifold, although only the results for the worst case (lowest temperature; 303 K) are presented.

Figure 5 shows the coevaporation ratios for the new multicomponent fuel. The coevaporation ratios (with respect to each fuel component pair) of the

Table 1 Table of selected common tracers and their properties taken from the literature. Note: spectral properties vary considerably with the environment and phase – the values also vary considerably in the literature. Therefore, these values should be taken as a guide only. Further accurate fluorescence data and the environment may be found in references (5, 8, 13, 18–20)

Fluorescent tracer			Absorption @ 293 K		Fluorescence	
Name	Group	T_{boil} (°C)	Band (nm)	$\sim X_s$ ($\times 10^{-20}/\text{cm}^2$)	Band (nm)	Lifetime T_0 (ns)
Propanal (propionaldehyde)	Aldehyde	49	220–340	1	300–550	
2-propanone (acetone)	Ketone	56	220–340	4	350–550	4.0
Butanal (butyraldehyde)	Aldehyde	75	225–345	1	300–550	
2-butanone (ethylmethylketone/EMK)	Ketone	80	220–335	2	330–360	
Benzene	Aromatic	80	230–270	31	265–325	397
2,3-butanedione (biacetyl)	Ketone	88	220–480	8	440–510	50
N,N-diethylethanamine (triethylamine/TEA)	Aliphatic	89			260–500	
3-pentanone (diethylketone)	Ketone	102	220–330	6	330–600	
Toluene (methylbenzene)	Aromatic	111	225–275	42	270–330	177
1,2,4-trimethylbenzene	Aromatic	168	220–285	23	270–350	77

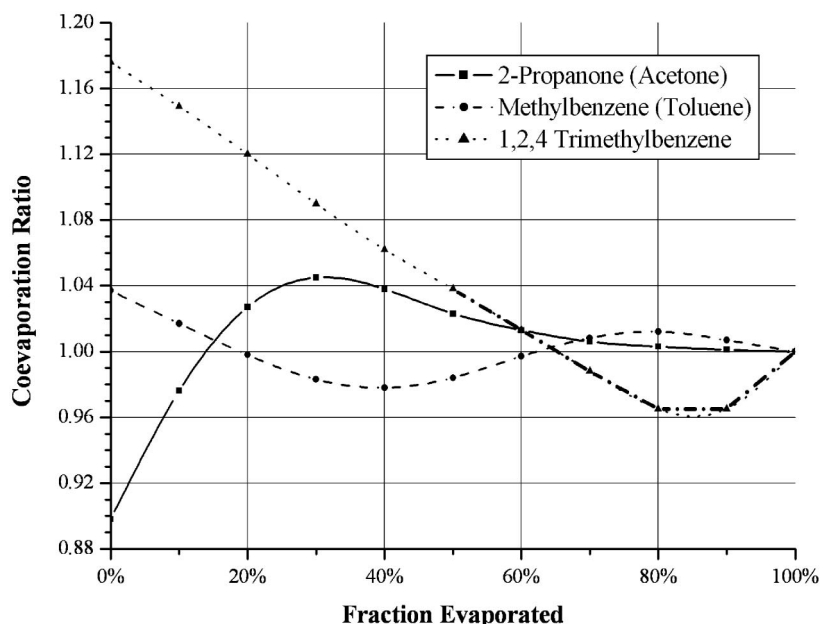


Fig. 5 Coevaporation ratios at 303 K according to equilibrium VLE calculations. The bold region of the trimethylbenzene curve shows the region where greater than 5 per cent of the heavy fuel fraction has evaporated

tracers across the range of fractions evaporated compares favourably with the chosen criteria and the accepted pure component fuel coevaporating pairs.

Figure 6 shows the calculated American Society for Testing and Materials (ASTM) curves for the component fuel with the addition of each tracer at 5 per cent (the *maximum* potential tracer concentration). This shows that there is little variation in the overall fuel volatility when the tracers are added.

On blending the six-component mixture, it was found that one of the intended components

(*n*-butane) was most readily available as a mixture with other C_3 and C_4 compounds. The extra compounds altered the phase equilibria slightly so a final small adjustment was made to the blend. The volume composition of this final blend is given in Table 2. The resulting 'coevaporation ratio' for each tracer is shown as a function of fraction evaporated in Fig. 5. The coevaporation ratio for the 1,2,4-trimethylbenzene tracer (used with the heavy fraction) is relatively high for small fractions evaporated (>1.15 at <10 per cent vapour). This could be corrected by using more isododecane in the blend but this would be of little benefit as less than 5 per cent of the heavy fraction is vaporized until the overall fraction evaporated exceeds about 50 per cent. The region where more than 5 per cent of the heavy material is evaporated is marked by the bold segment of the line in Fig. 5. The stated blend gives the best calibration in this region.

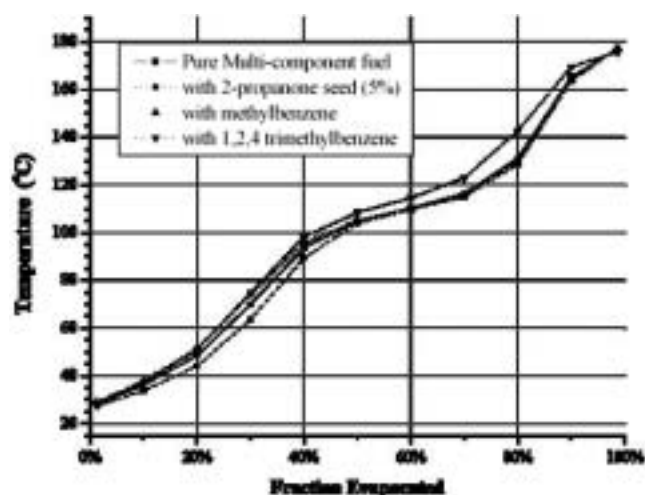


Fig. 6 Simulated ASTM distillation curve for the multi-component fuel with and without addition of tracers

Table 2 Composition of the multicomponent fuel by volume

Species	Volume fraction
Butanes	0.304
Isopentanes	
Isooctane	0.550
<i>n</i> -Octane	
Iso-dodecane	0.146
<i>n</i> -Decanes	

The coevaporation ratios obtained from the diffusion-controlled model were generally closer to one than those obtained from the equilibrium model and were within a 10 per cent criterion in all regions of interest.

4 CONCLUSIONS

This paper has, first, for an audience of specialist engineers, outlined the principles of quantitative PLIF as it applies in a linear regime to the measurement of fuel concentration. The underlying theory has been reviewed to show the mathematical background, a prerequisite for justification of quantitative measurements. It has been shown that without careful measurement and understanding of the parameters that contribute to absorption and fluorescence quantum efficiency, quantitative PLIF measurements cannot be justified.

Second, the authors describe the design and characteristics of a six-component three-fraction fuel that may be used with fluorescent tracers to determine quantitatively the distribution of different fuel fractions in an engine. The authors have demonstrated the principal and use of designed fuel fractions tuned to the evaporation characteristics of desirable fuel tracers. This multiphase fuel and its tracers are shown to coevaporate at least as well as existing, accepted, single-component fuel and tracer combinations with negligible effect on overall volatility.

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APPENDIX

Notation

A	Einstein spontaneous emission (fluorescence) rate
B	Einstein stimulated emission rate per unit intensity
c	speed of light
C_{vap}	coevaporation ratio
E	energy
I	intensity
l	length
N	number density
Q	quenching rate
T	temperature
X	cross-sectional area of the exciting laser sheet
λ	wavelength
ξ	quantum efficiency
σ	absorption cross-section