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TEMPERATURE MEASUREMENTS USING EXCIPLEX FLUORESCENCE WITH TMPD AND METHYLNAPHTHALENE AS TRACERS

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ABSTRACT
Laser-induced exciplex fluorescence has been used to measure the temperature in a spray of a diesel-like fuel. To a model fuel consisting of 70 % n-decane and 30 % 1-methylnaphthalene, TMPD was added in a concentration of 0.2 %. When excited with UV-light TMPD efficiently forms an exciplex with methylnaphthalene fluorescing with a peak intensity at a wavelength around 505 nm at room temperature. When the temperature of the fuel increases the peak position shifts to shorter wavelengths, and the peak reaches a position of 475 nm at 150 ºC. This shift of the fluorescence spectrum can be used to estimate the temperature of the liquid fuel, by measuring the fluorescence light intensity in two different wavelength intervals and evaluate the ratio between them as a function of temperature. The intensity ratio as a function of temperature was evaluated and calibrated, and subsequently used to determine the temperature of the liquid fuel along the spray axis.

INTRODUCTION

Laser-induced exciplex fluorescence (LIEF) is a method that is well suited for fuel spray diagnostics, in particular as planar LIEF using imaging detectors. The most common application of LIEF is two-phase diagnostics in order to investigate the fuel distribution in liquid and vapour phase, respectively [1]. This application is based on the fact that the fluorescence emitted by molecules in vapour and liquid phases differs spectrally. In the vapour phase the molecules fluoresce as individual molecules, i.e. as monomers, but if fuel components and the fluorescent tracer molecules are selected properly the fluorescence from the liquid is dominated by exciplex emission. Excited complexes, exciplexes, can form as a result of dipole-dipole interaction between an excited molecule and another molecule, and due to the binding energy of the complex the fluorescence emitted by the complex is red-shifted. Exciplexes are normally only efficiently formed in the liquid phase due to the immediacy of the complex-forming molecules and the ability of surrounding molecules to stabilise the complex, and if the concentrations of the exciplex-forming molecules are chosen appropriately the exciplex fluorescence will dominate over monomer fluorescence from the liquid. Thus, by imaging the fluorescence in two wavelength ranges, corresponding to monomer and exciplex fluorescence, the distribution of fuel in vapour and liquid phase can be analysed [2-5].

Another application of LIEF is temperature measurements, which can be performed in two different ways. One method is to measure the ratio between the monomer and exciplex fluorescence from the liquid [6-9]. Since the binding energy of the exciplex is limited, the lifetime of the exciplexes is shorter at a higher temperature resulting in an increasing monomer emission and decreasing exciplex emission with increasing

temperature. The other approach is to use a temperature-induced shift in the wavelength of the exciplex fluorescence. Often the exciplex peak shifts to shorter wavelengths with increasing temperature, and if the fluorescence intensity is recorded at two different wavelength intervals, the ratio is a measure of the temperature [10-13]. The use of the ratio between the monomer and exciplex fluorescence has a higher sensitivity if the tracers and their concentration are appropriately chosen, whereas the use of the exciplex peak shift allows for two-phase diagnostics based on the monomer and exciplex fluorescence intensities in parallel with the temperature measurements.

One combination of model fuel and tracers that has been identified as suitable for both two-phase diagnostics and temperature measurements is a combination of n-decane, 1-methylnaphthalene and N,N,N',N'-tetramethyl-p-phenylenediamine (TMPD) [10,11]. In this study we have investigated and compared two different strategies for the choice of wavelength intervals for the temperature measurements.

EXPERIMENTAL

The diesel-like model fuel used is a combination of 70 % (w/w) n-decane and 30 % 1-methylnaphthalene. To this fuel TMPD is added with a concentration of 0.2 %.

Temperature-dependent fluorescence spectra were recorded in a fluorescence spectrometer equipped with temperature-regulated quartz cell holder in which the liquid samples could be heated to more than 200 ºC.

Spray imaging was carried out in the Chalmers high-pressure/high-temperature spray chamber, which is a constant-pressure chamber with a continuous airflow (velocity 0.1 m/s)
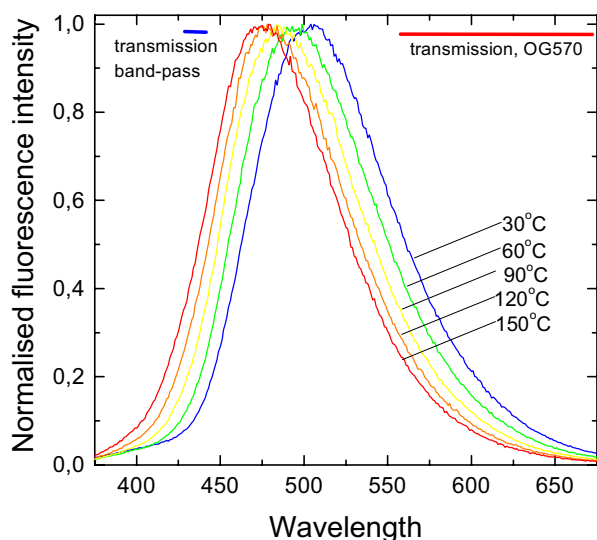
Figure 1. Fluorescence spectra recorded at five different temperatures. The excitation wavelength was 355 nm. Each spectrum is normalised to its peak intensity.

through the chamber. The air in the chamber can be heated to 600 ºC and pressurised to 100 bar. Fuel sprays were generated by a common-rail injection system with a solenoid injector with a single-hole nozzle.

The sprays were illuminated by the third-harmonic light at a wavelength of 355 nm from a Nd:YAG-laser. The light was focused into a 35 mm high sheet passing through the centre of the spray. The chamber could be translated vertically so that several regions of the spray at different distances from the nozzle could be illuminated. The fluorescence light was by a beam splitter directed to two intensified CCD-cameras. In front of each camera filters were placed to transmit a selected wavelength range of the exciplex fluorescence or the monomer fluorescence.

RESULTS AND DISCUSSION

The temperature-dependent fluorescence properties of the used fuel have been presented before [10,11] and are briefly recapitulated here. At a wavelength of 355 nm TMPD is the only of the three fuel components that has a significant light absorption, and in vapour phase it fluoresces with a peak at 380 nm. The liquid phase fluorescence is completely dominated by the exciplex emission with a broad peak at 505 nm at room temperature. As shown in Figure 1, the peak shifts to shorter wavelength when the temperature of the liquid is increased, but without any significant increase in the monomer fluorescence intensity. The shift is practically linear with temperature and the peak moves to 475 nm at 150 ºC. There is also a decrease in fluorescence intensity with increasing temperature, not shown in Figure 1 where the curves are normalised to the highest intensity in each curve.

In previous studies, the applicability of using a combination of two long-pass filters for the temperature measurement was investigated [11]. Here we have also investigated the use of a band-pass filter transmitting in a range on the short-wavelength side of the peak and a long-pass filter transmitting at the long-wavelength side of the peak.

The advantage of taking the ratio between wavelengths on either side of the peak is that the ratio should have a larger sensitivity to temperature changes, and thereby give a better accuracy in the temperature determination. The previously
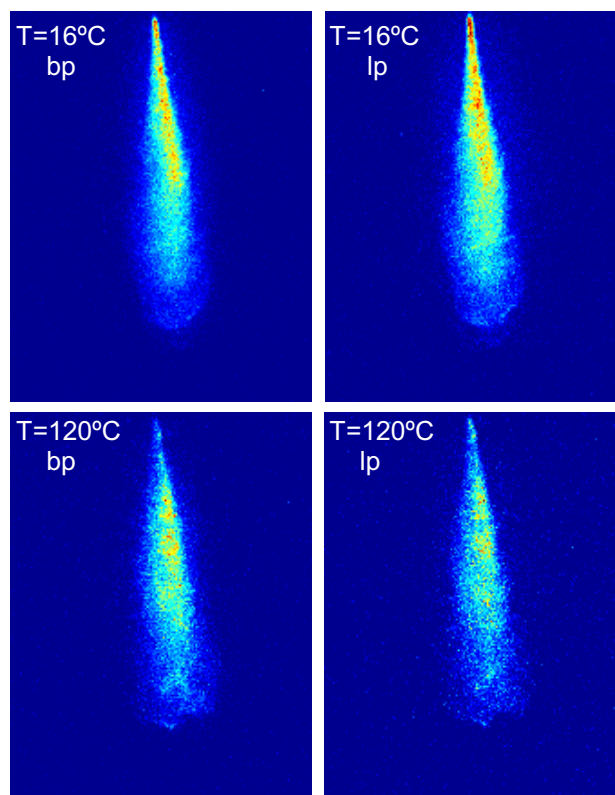

Figure 2. Spray images recorded 0.9 ms asoi at two different chamber temperatures, 16 ºC (top) and 120 ºC (bottom). The chamber pressure was 28 and 38 bar, respectively corresponding to a constant air density. The left image in each pair was recorded with a band pass filter at 436 nm, and the right image with a long-pass filter OG570. The size of each image is 42 mm high and 32 mm wide.

used combination of two long-pass filters, coloured glass filters GG495 and OG550, showed that a change in the ratio between the fluorescence light transmitted by the two filters increased by about 50 % when the temperature was raised from room temperature to 150 ºC. The potential of detecting light in intervals on either side of the peak, should enhance the sensitivity significantly, with a theoretical increase in the ratio to about 400 % using optimum wavelength bands, around 430 and 560 nm respectively. In this study a bandpass filter centred at 438 nm, with a bandwidth of 10 nm was placed in front of one of the cameras. In front of the other camera a long-pass filter, OG570, transmitting wavelengths longer than ~550 nm was placed. The transmission ranges of the filters are indicated in Figure 1.

Figure 2 shows spray images recorded at two different chamber temperatures. In each pair, one image is recorded with the band-pass filter and the other with the long-pass filter. As expected the two images in each pair appear very similar, since they both represent exciplex fluorescence emitted by fuel in liquid phase. However, it can also be seen that the intensity ratio between the two images of each pair is different for the two temperatures, with a higher intensity for the long-pass filter at the lower temperature and a higher intensity for the band-pass filter at the higher temperature, showing that the intensity ratio functions as an indicator of the liquid fuel temperature. To be able to use this ratio for temperature measurements the ratio needs to be calibrated to a temperature scale.

As a first step the same laser, filter and camera set-up was used to image the fluorescence from fuel in the temperature-controlled quartz cell. The relative fluorescence intensity was
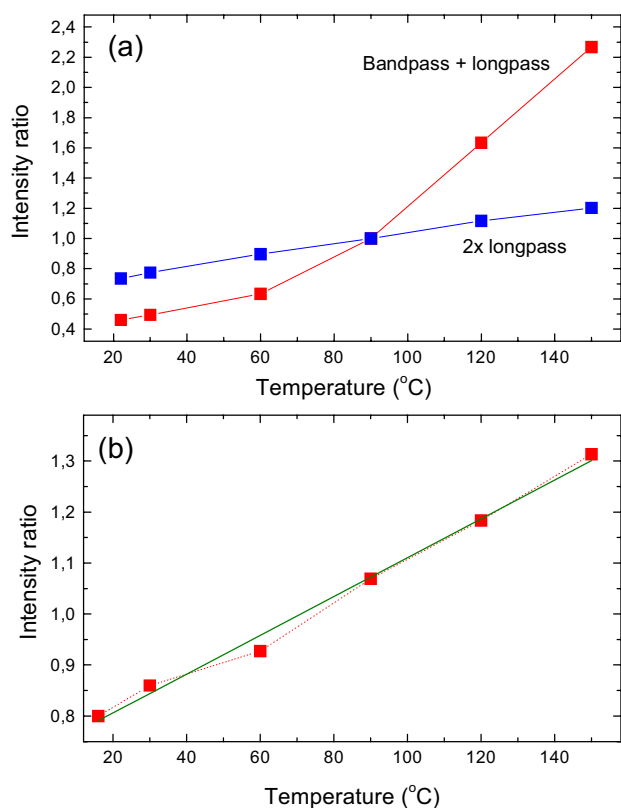
Figure 3. Intensity ratios as a function of temperature for (a) images recorded of a reference cell with a combination of a band-pass and a long-pass filter (red) and two long-pass filters (blue); (b) spray images using a band-pass and a long-pass filter (red) and a linear fit to the data (green line).

recorded at six different temperatures: 22, 30, 60, 90, 120 and 150 ºC, a range in which the evaporation of fuel is negligible during the measurement. The intensity ratio as a function of cell temperature is shown in Figure 3a. In and ideal case this temperature calibration should immediately be applicable to the spray measurements. However, there are a few factors that could induce a difference in the ratio. The reference cell measurements are carried out at atmospheric pressure, but in the spray chamber the fuel drops are surrounded by air at an elevated pressure, typically several tens of atmospheres. This may influence the fluorescence spectrum as indicated by Kadota et al. who observed a shift in the spectrum induced by the oxygen concentration in the surrounding atmosphere [8]. Another factor that differs between the cell and spray measurements is the laser light intensity. In order to obtain a sufficient signal intensity, in particular for the vapour phase signal when two-phase imaging is carried out in parallel with the temperature measurement, a relatively high intensity of the incoming laser light was used, whereas the intensity was kept lower in the quartz cell not to induce damage to the cell. An additional complication using a fuel injection system based on standard components of commercial systems is that there are gaskets and other components leaking trace amounts of large organic molecules, predominantly aromatic molecules, which may fluoresce when excited at 355 nm.

Therefore a calibration of the intensity ratio in the spray chamber was also carried out, in spite of the circumstance that the temperature of the fuel drops could not be determined by an independent method. Instead it was assumed that the fuel drops had attained the temperature of the surrounding air at a sufficiently long distance from the nozzle and at a sufficiently long time after start of injection. The ratio between the
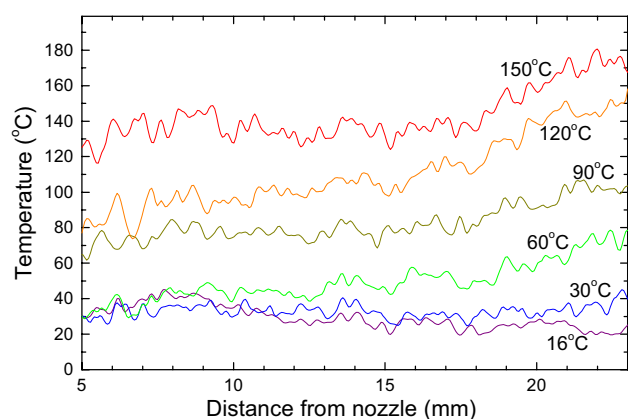

Figure 4. Temperature of the liquid fuel in the spray as a function of distance from the nozzle, 0.5 ms asoi. The corresponding air temperature in the chamber is indicated next to each curve.

fluorescence intensity in images recorded 1.5 and 2.1 ms after start of injection (asoi) was calculated. The intensity in an area 12-30 mm below the nozzle was used for this calculation. A comparable result was obtained when the intensity at a longer distance from the nozzle was used, except for a slight deviation at the higher temperatures at which evaporation of the fuel may have started. When evaporation starts, n-decane evaporates first, and the changes in relative concentration of n-decane and methylnaphthalene induces a shift of the fluorescence peak to longer wavelengths, i.e. in the opposite direction as induced by the increasing temperature. The intensity ratios determined for chamber temperatures of 16, 30, 60, 90, 120 and 150 ºC, are shown in Figure 3b. A straight line fitted to the data is also shown. This calibration line was later used to convert intensity ratios to temperatures

By comparing Figures 3 a and b one can note that there is a clear difference in the evolution of the ratio with assumed temperature. The slope of the curve is much lower for the spray than in the case of the reference cell measurement. One possibility for this could of course be that the temperature of the liquid in the spray has not reached the measured air temperature. There are no steep gradients in the intensity ratio in or around the areas used for the temperature calibration, so it is likely that the temperature of the liquid actually has reached a value close to that of the surrounding air. There is however a possibility that the air in the vicinity of the spray is cooled by the presence of the liquid. An effect that has proven to be difficult to avoid is that molecules from gaskets and other components in the fuel injection system are dissolved in the fuel and modify the fluorescence properties. Spectra recorded of the fuel that has circulated in the system shows some additional fluorescence around 400 nm, so it is possible that some additional fluorescence from the contaminating molecules is transmitted by the band-pass filter. Since this fluorescence is expected to give a contribution that is either constant with temperature or decreasing with higher temperature, it will result in a lower increase in the ratio with increasing temperature. This effect, possibly together with other factors mentioned above as the influence the laser-light intensity and of a high pressure of an oxygen-containing atmosphere, is the likely explanation for the difference in the evolution of the intensity ratio as a function of temperature for the spray and reference cell cases. However, even if the spray case does not represent an ideal case, a temperature scale can be calibrated and used for temperature measurements. The

accuracy is limited by how well known the temperature of the drops can be estimated by the calibration.

The development of the temperature in the spray was investigated by calculating the intensity ratio along the vertical axis. The intensity is for each horizontal pixel row was summed to obtain a vector representing the intensity as a function of the distance from the nozzle.

Figure 4 shows vertical temperature profiles recorded 0.5 ms asoi. To obtain the profiles, the intensity is summed for each pixel row. The profiles represent the average of 10 individual sprays. One should notice that the injector was not kept at a constant temperature. Since it was in contact with the air inside the chamber, it was heated by the flowing air, but also water cooled to limit the maximum temperature. Thus, the initial temperature of the fuel is different for the various air temperatures, and the gradients are accordingly not as steep as they otherwise would have been. Still an increasing temperature with an increasing distance from the nozzle can be observed in most curves. In particular, the area close to the tip of the spray appears to have a higher temperature, which is reasonable since the tip will be more exposed to the surrounding air. For the lowest temperature it actually seems like the fuel initially has a higher temperature and is cooled by the surrounding air.

COMPARISONS AND CONCLUSIONS

It was demonstrated how the exciplex fluorescence can be used for temperature measurement of the liquid part of a spray of diesel-like model fuel. The temperature was determined from calculating the ratio between the intensity of the exciplex fluorescence recorded in two wavelength intervals. The wavelength intervals were selected as one interval on the short-wavelength side of the peak and the other on the long-wavelength side in order to obtain a high sensitivity in the temperature measurements. The change in intensity ratio with temperature was also found to be larger compared to another filter combination selecting two intervals on the long-wavelength side [11]. On the other hand the change in intensity ratio was not as large as theoretically predicted, which is likely due to the fact that the selected filter combination is more sensitive to perturbations and contamination than in the case of using two long-pass filters.

ACKNOWLEDGMENT

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