Application of Laser-Induced Exciplex Fluorescence with Alternative Diesel Fuels

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Abstract
This study presents a new possibility to investigate diesel fuel injection and mixture formation with the laser-induced exciplex fluorescence (LIEF). Instead of commonly used single component substitute fuels, real diesel fuel alternatives with and without exciplex tracers were analyzed by means of spectroscopy. Especially the Gas-to-Liquid (GTL) Fischer-Tropsch diesel was found to be an applicable fuel for LIEF measurements.

Introduction
In the last decades, laser measurement techniques have played a key role in research for a successful reduction of emitted pollutants from combustion systems. Among different techniques, the laser-induced fluorescence (LIF) was often used to measure and optimize pre-combustion and combustion related phenomena such as spray breakup, fuelspray penetration, spray-wall interaction, fuel-vapour concentration and key-radicals for different phases in the combustion process itself. In 1983, the laser-induced exciplex fluorescence (LIEF) was developed by Melton [1]. This advanced LIF-technique allowed a simultaneous spectrally separated 2D measurement of liquid and vapour phase in spray and combustion systems. With its high time resolution the important evaporation and mixture formation processes can be studied. One drawback of the technique for engine applications is the fact that diesel fuel (EN590) had to be substituted by base fuels like n-Decane [2,3] or n-dodecane [4] for example, due to the broadband fluorescence response of several components of EN590. These substitute fuels have EN590-like properties, but they still show differences in the evaporation and combustion behaviour of real EN590 diesel fuel. In order to compensate this drawback and regarding the fact that Fischer-Tropsch- (FT) and biodiesel are promising alternative diesel fuels, they were both studies for the applicability of LIEF with the tracers naphthalin and N,N,N',N'-tetramethyl-p-phenylenediamine (TMPD).

Materials and Methods
In this study the base fuels n-dodecane, FT-diesel (Winter GTL from Shell) and regular biodiesel (rapeseed FAME) were applied. The pure substances were used as a reference, whereas for LIEF measurements every fuel was doped with an amount of 1 % TMPD and 10 % Naphthalin. A frequency tripled pulsed Nd:YAG Laser (Spectra-Physics) at 355 nm was used for excitation. At this wavelength, only the TMPD Monomer can get excited. Mainly in case of the fluid phase with its high density of tracers the excited TMPD can form an excited state complex together with a naphthalin molecule. Due to the bond energy needed to form such a complex the excitation energy of the complex is reduced by the amount of the bond energy. This behaviour allows a spectral separation of fluid and vapour phase with the TMPD-naphthalin tracer system.

To investigate the fluorescence response of the tracer system in combination with the alternative diesel fuels, an optically accessible high-temperature, high-pressure calibration chamber (Esytec GmbH) for vapour phase studies and quartz cuvettes for liquid phase studies were applied. For a spectral analysis of the fluorescence signal, a spectrometer (HoloSpec, Kaiser Optical Systems) with reflection grating (300 g/mm) and an intensified CCD camera from Princeton Instruments were set up.

For the measurements of the vapour and the liquid phase fluorescence 1 mJ laser energy with a pulse length of 15 ns was used. The signal was detected perpendicular to the laser beam and was filtered with a GG395 edge filter to block reflected laser light. Prior to the signal detection the chamber was scavenged and filled with nitrogen to prevent oxygen quenching. For the measurements presented, the chamber was heated up to 573K before 0.3 ml of the exciplex fuel was injected into the chamber.

Results and Discussion
The exciplex system n-dodecane/TMPD/naphthalin was used as a LIEF reference. The Graph in Figure 1 states the spectrally separated liquid and the vapour phase. Both, liquid and vapour signal are related to the fluo-
rescence of the excited tracers, because n-dodecane without tracers does not show any fluorescence response at all.

The biodiesel-exciplex system in Figure 1 exhibits an extremely low liquid phase fluorescence, which might be due to the stronger polarization of biodiesel compared to the other fuels in this study. This could lead to an inactive fluorescence tracer. With this behaviour it is impossible to separate liquid and vapour phase using this system.

In contrast to regular EN590, the pure FT-diesel has no fluorescence response, most possibly due to its missing aromatic components. The fluorescence signal of the exciplex system FT-diesel/TMPD/Naphthalin is therefore almost similar to the n-dodecane-exciplex system. Only the ratio of the liquid to the vapour fluorescence signal intensities of both systems are different. This, however, is more interesting for quantification [3,4] than for the applicability.

These results have shown, that the FT-diesel-exciplex system is suitable for investigations on diesel fuel sprays and mixture formation. On the one side this is a possible new exciplex system capable of replacing single component substitute fuel LIEF systems used for EN590 because the properties of FT-diesel are similar to EN590. On the other hand the FT-diesel-exciplex system will be extremely helpful for current studies on the effect of FT-diesel on mixture formation, combustion and engine-out emissions.

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References

![Figure 1. Liquid and vapour phase fluorescence spectra for different base fuels with TMPD and Naphthalin as exciplex tracers. Bottom right: Fluorescence signal from EN590 and FT-diesel vapour phase.](image-url)