Capillary Sensor with UV-Forced Degradation and Fluorescence Reading of Diesel and Biodiesel Fuel Chemical Stability

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Abstract-There are many standards set by national organizations and fuel producers to test and guarantee the diesel fuel stability under storage conditions. Traditional techniques for measuring fuel stability utilize oxygen–assisted degradation of heated sample submit the fuel sample to a relatively high pressure of air, temperature of the sample or a long time of examination. For example, American Society for Testing and Materials (ASTM) D4625 requires a time of up to 24 weeks of fuel exposition to air atmosphere heated up to 43°C. The degradation is evidenced by the appearance of resins and sediments. There are many different theories describing the mechanism of degradation of diesel fuels, as there are various factors that initiate and maintain the process. The stability of modern diesel fuel is mainly due to the reduction of the oxidation processes, the result of the presence of unsaturated components and components with oxygen as organic components and cetane index improvers. Therefore, the diesel fuel stability is related with the fuel composition. As a consequence of all that, fast and low-cost sensing of the stability of diesel and biodiesel fuel is important. The present paper concentrates on the construction of the capillary sensor which enables fast examination of fuel stability as a characteristic of fuel itself not of the gas atmosphere. Therefore, the fuel sample under examination is enclosed in a vessel and the degradation factor is assumed to be the UV radiation. The fuel samples used to develop the method are compositions of a classical mixture of petroleum products and the most widely used cetane improver (2-ethyl hexyl nitrate). The result is a sensor set-up based on two UV light emitting diodes, one used to stimulate degradation, the second used for signal reading.

Keywords-biodiesel fuel stability; diesel fuel degradation; cetane index improvers; capillary sensor; LED excited fluorescence.

I. INTRODUCTION

Diesel fuel stability may be affected by a large number of parameters which can be categorized to describe the effects of oxidation, thermal and storage conditions [1]. The estimated life of a diesel fuel is determined according to the accelerated oxidation stability test ASTM D2274. This test is performed with fuel of 350 mL volume is to be kept at 95 °C in the presence of oxygen for 16 hours, which approximately corresponds to one year's storage at 25 °C. This test measures the ratio of the mass of settled gum and sediment to the mass of the diesel fuel sample. However, this method may not provide a prediction of the quantity of insoluble matter that will form in field storage conditions over any given period of time [2], as for example, microorganisms present in diesel fuel may be also the result of its storage [3]. Therefore, the chemical and biological stability of diesel fuel is under examination.

The storage conditions can be described as exposure to air and/or light at the environment temperature. The diesel fuel storage issue seems to be nowadays recognized as an issue even by fuel producers, who recommend the maximum time of diesel fuel storage in function of temperature conditions [4], for example 6-12 months at an ambient temperature higher than 30 ºC. There are some other factors that accelerate diesel fuel ageing: contact with zinc or copper, as these metals will quickly react with diesel fuel to form unstable compounds; presence of water, which allows the growth of fungus and bacteria producing organic acids, which make the fuel unstable; exposure to high temperatures; exposure to dust and dirt, which contain trace elements that can destabilize the fuel; fuel composition as some components in diesel fuel naturally age quickly.

A. Modern diesel fuels

Classical petro-diesel fuels were made from stable components of straight run distillate products of crude oil (alkanes). The minimum cetane number of such diesel fuel was 40, but it has been determined that such fuel may be kept in storage for prolonged periods. Modern diesel fuels are the composition of petro-diesel products, bio-diesel products with an addition of improvers [5]. Modern petro-diesel fuels include stable components (alkanes) and cracked material, which contains olefins (alkenes) characterized by a double bond chemical and aromatic content. Bio-diesel

components include fatty acids esters that are also characterized by the presence of double bonds. As the minimum cetane number of modern diesel fuel is 51, the cetane number boost of fuel composition is required. Most popular is the application of cetane number boosters in the form of 2-ethyl hexyl nitrate (2-EHN) or di-tertiary-butyl peroxide (DTBP). Both substances include oxygen and are reactive. Cetane boosters decompose rapidly and form free radicals when exposed to temperatures above 100 °C. These radicals increase the rate of main fuel components decomposition, therefore the ignition delay is negatively affected [6]. The use of cetane boosters in diesel fuel of high quality increases the engine durability [7]. On the other hand, cetane boosters are a potential source of oxygen for oxidation of hydrocarbons. For hydrocarbons that are characterized by double bonds the oxidation products are waxy solids and gums. Therefore, doses of cetane number boosters to diesel fuels have to be carefully calculated. The reduction of cetane number booster's concentration is possible when hydro-treating of fuel products is applied. But, the cetane number improving method using mainly cetane boosters is preferred due to its low cost [8]. The 2-EHN is the most popular cetane index additive. The ASTM D 4046 standard test method is used for determining the amount of alkyl nitrate added to diesel fuel.

B. Optical sensors for diesel fuel stability testing

The optical testing of fuel parameters is performed in laboratory and in-situ conditions of working engine [9]. The optical sensors implemented in a working engine (ICOS - Internal Combustion Optical Sensor) – are infrared sensors of air to fuel ratio, CO_2 concentration, and gas temperature. The optical sensors of diesel fuel used in the laboratory enable a wide range of examination. The sequence of visible effects of diesel fuel instability may be described as fuel clouding, fuel clouding disappearance, formation of fuel sediments at the fuel-environment contact area (vessel walls and fuel surface), changes in fuel color (loss of color or darkening) and sediments presence on the bottom of vessel [10].

The fuel components concertation may be examined with IR spectroscopy and UV excitation methods including synchronous reading fluorescence and time resolved fluorescence [11][12]. Despite spectroscopic method drawback of costs of examination of oils in quartz cuvettes including costs of cuvettes and reagents for sample dilution, dedicated components of sensors are under development [13-15].

The examination of diesel fuel fit for use may be performed with capillary measurement methods. These method include measurement of characteristic points of local sample heating of fuel positioned in a capillary and measurement of the dynamical rise of fuel in a inclined capillary [16][17]. Also, for these methods dedicated components have been developed [18][19].

The oxidation stability of oils with spectroscopy measurements in VIS and UV bands were reported in the case of baru oil [20]. The obtained results show that UV absorption from 230 nm to 270 nm during thermal aging increases non-uniformly, while VIS absorption at 475 nm decreases almost linearly down to a threshold value. The fluorescence intensity excited at 405 nm and measured in the range from 450 nm to 750 nm may be a pointer of thermal oil degradation. In particular, the emitted signal at 500 nm that represents oxidation products increases almost linearly and then saturates during thermal aging over a dozen hours at 110 °C.

Nevertheless, for their routine daily work, the fuel distributors still demand the development of new rapid and low-cost sensors for reliable determination of fuel stability.

The rest of this paper is organized as follows. Section II describes the sensor construction development including sensor head with optrode as well as optoelectronics system set-up. Section III addresses the experimental results of the fluorescent signal analysis. Section IV goes into short conclusions.

II. SENSOR CONSTRUCTION

The idea of rapid sensor of diesel fuel stability bases on forced UV degradation of fuels placed in a capillary vessel. In this case, the sample volume is reduced and the surface of sample increases in comparison to the standard cuvette set-up. The inner diameter of the capillary is 700 μm while the diagonal of the cuvette is 1.41 cm. Therefore, UV radiation that is intended to stimulate the sample's degradation penetrates the fuel sample volume more uniformly in the capillary than in the cuvette. Moreover, the use of capillary reduces significantly the costs of the measurement, because the cost of a single CV7087Q capillary is lower than the cost of the quartz cuvette, and is even lower than the cost of a cleaning and washing process of quartz cuvette.

A. Light sources for the sensor

For practical applications one has to consider the light emitted diodes as a source of radiation. For excitation of fluorescence and degradation, two LEDs were used. The UVTOP265 LED emitted 250 μW at 265 nm and was equipped with a ball lens, provided good coupling of radiation to the fiber. It was connected to the set-up with Thorlabs SMA adapters and a SM1 tube. The M365F1 LED equipped with a SMA fiber connector providing about 5mW into a 550 nm diameter fiber was directly implemented into the set-up. This LED is characterized by a residual radiation in the band of 400-460 nm. The LEDs were controlled with a Thorlabs DC2100 High-Power, 1-Channel Driver. Due to LEDs working points set at their maximum ratings, the examination was performed of the stability of radiated power of M3651F1 LED with direct fiber coupling to Maya 2000 pro spectrometer. The M365F1 LED is characterized by an increase of the coupled-to-fiber power when it is driven constantly with the current of 300 mA. Interestingly, the coupled power does not depend on the temperature of the LED as it increases even after LED's resting for 5 minutes and a sequential reboot as presented in Figure 1.
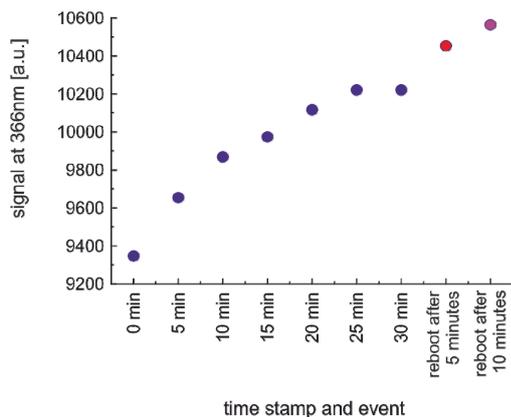
Figure 1.   M365F1 LED optical power at 366nm coupled into optical fiber in function of time and event.

The fiber-coupled signal of the UVTOP265 LED constantly driven for 30 minutes at maximum current equal to 30 mA recorded using the sensor head with an empty capillary (see Fig. 4) versus time of measurement is presented in Figure 2.
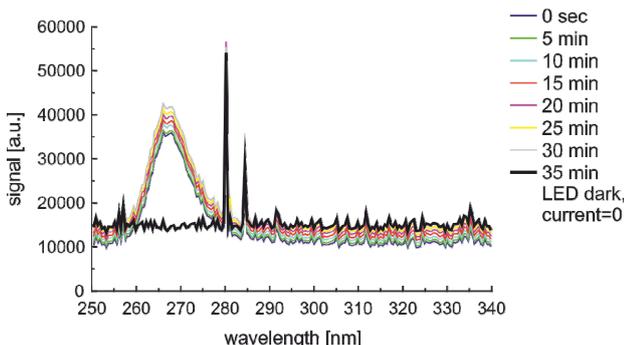
Figure 2.   UVTOP265 LED optical power coupled into optical fiber in function of time.

The conditions described above were the worst case examination from the detection unit point of view, as the received signal was only scattered at the smooth glass surface of the capillary and the received signal was close to the sensitivity of the used spectrometer. Thus, spectral characteristics showed fluctuation due to high sensitivity set on the spectrophotometer. The examination of mid-range stability UVTOP265 LED showed similar results as for high power M365F1 LED. The signal peak present at 280nm represents spectrophotometer error. This signal of error varies versus time as presented in Figure 3.

The experimental results show that 10 % of variation of maximum signal intensity is to be expected, but signal changes are not uniform, and also at some signal sampling rate spectrophotometers are characterized by middle-time drift. Therefore, spectral examination requires optical power stabilization of the source or/and mathematical signal correction. Unfortunately, both solutions require source signal monitoring with additional sensing modules.
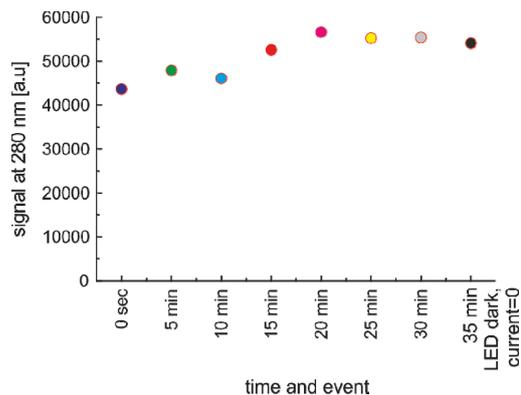
Figure 3.   Spectrophotometer imperfection signal at 280nm in function of time and event.

Therefore, a sensor set-up with one and two UV sources was examined. In the case of one UV source, the source performs functions for both fuel degradation and fluorescence excitation. In the case of the set-up with two UV sources the mentioned functions are separated. In both cases, the sensor head enables the observation of the excited fluorescence in the sample of liquid positioned in a capillary vessel using optical fibers as probes.

B.   Sensor set-up with one UV source

The sensor head of set-up with one UV source presented in Figure 4 consists of only two optical fibers.
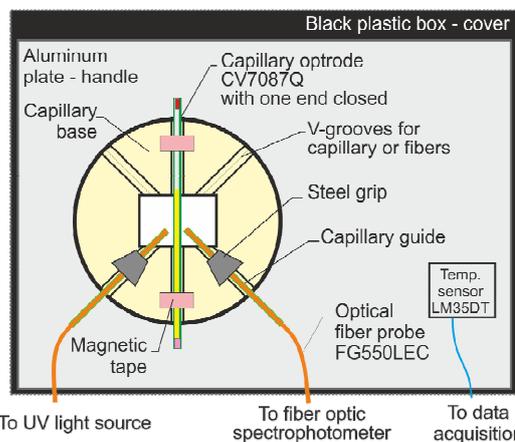
Figure 4.   Scheme of the capillary sensor head with two optical fibers.

The head is coupled to the optoelectronic sensor set-up according to the scheme presented in Figure 5.

The set-up is divided into two functional units, optical and optoelectronic, working in a conjugated manner.

The optical unit consists of the head, the optical fiber divider and the monochromator. The set-up element causing the highest optical signal damping is the DMC1-02 monochromator, the attenuation of which is about 1:1000 at analyzed wavelengths. But, the set-up using the monochromator enables tuning of the LED's optical signal with proper accuracy.
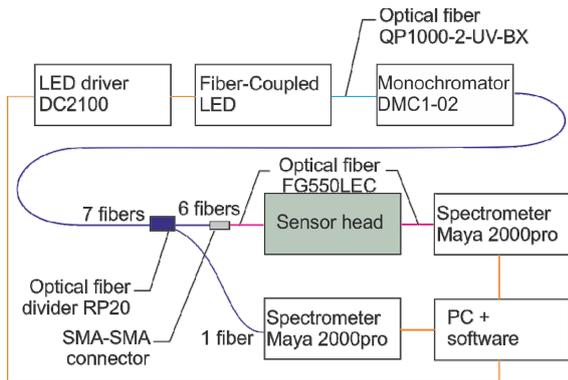
Figure 5.   Scheme of the capillary sensor set-up with one LED.

The set-up is optically powered by a LED controlled with the hardware D2100 driver that is triggered from a PC with the use of software. The fiber optic divider 1:7 is used to produce a reference signal and monitor light source parameters with Maya 2000pro spectrometer connected to the PC. The head output is connected to Maya 2000pro spectrometer which is connected to PC. Both spectrometers are controlled by the PC with Ocean Optics software that enables sequential writing of data recorded for the fluorescence and source signals.

C.   Sensor set-up with two UV source.

The sensor's head with two UV sources is presented in Figure 6.
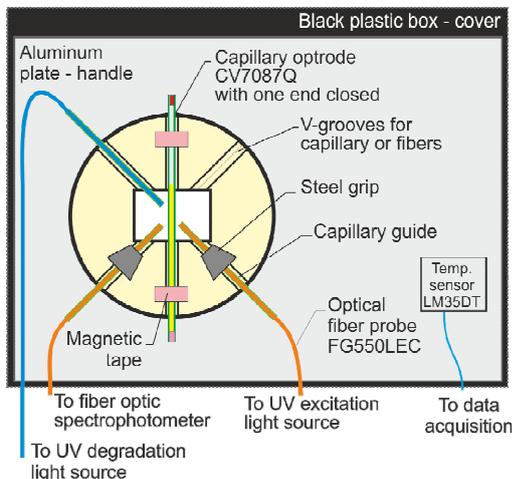
Figure 6.   Scheme of the capillary sensor head with two UV sources and three optical fibers.

To make allowance for UV degradation and fluorescence excitation signals an additional optical fiber was placed in head. The system set-up scheme was changed by the addition of a LED block for UV degradation of the sample as presented in Figure 7.
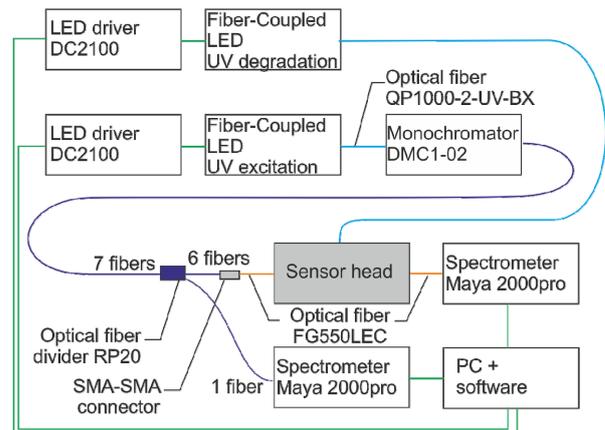
Figure 7.   Scheme of the capillary sensor set-up with two LED-s.

The hardware of the detection units was not modified. The changes of the degradation signal may be observed with the spectrometer during the degradation as a reflected signal from capillary walls. This LED output is directly coupled to the head to avoid any power losses. Also the scheme of system control was changed as the LED drivers for UV degradation and UV fluorescence excitation were switched alternately.

III.   EXPERIMENTAL RESULTS

In this section, there are presented the experimental procedures and the results of examination of different diesel and biodiesel fuels.

The measurement procedure consists of a few steps. Step 1: At the initial configuration of the set-up the selected diode is mounted. Step 2: the background signal of for the empty optrode is measured. Step 3: optrode is directly filled from the tank and the outer optrode walls are wiped. Step 4: the signal of fluorescence is measured with the use of UV ageing procedure. Step 5: the spectra were calculated as the difference between the fluorescence and the background signals.

The operation of the sensor was examined with fuels provided by the Automotive Industry Institute in Warsaw. The fuels were mixtures of petrodiesel with additives including 2-EHN – one with as bio-component 7% of fatty acids methyl esters (FAME) (CN=59.1) considered as the standard fuel, and the second with 7% of hydrogenated vegetable oil (HVO) (CN=59.2) considered as premium fuel.

A.   Set-up with one UV LED

First examination included measurements of the fluorescence of fresh fuels excited with a UVTOP265 LED or a M365F1 LED. Results presented in Figure 8 show similar shapes of characteristics, while the maxima of excited spectra for different excitation are at slightly different wavelengths. Taking into account LEDs currents, and therefore powers, the excitation efficiency at 265 nm is much greater than at 366 nm. The signal of biological fluorescence at 675 nm is readable for excitation at 366 nm.
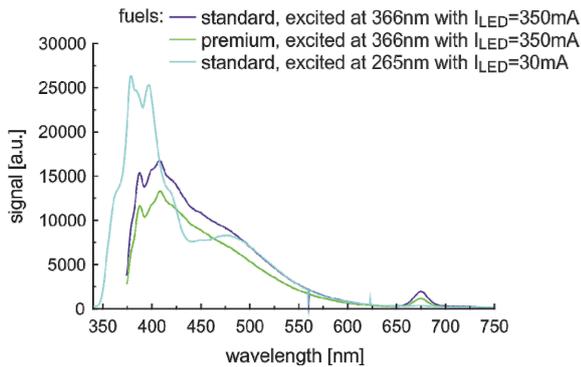
Figure 8. Spectra of fresh fuels excited with 366nm wavelength.

The visible fluorescence emitted signal is caused by the presence of the 2-EHN cetane booster. According to diesel fuel producers' classification, and evidenced by the emission spectra signals recorded at 366 nm excitation, the premium fuel is characterized by a lower concentration of cetane booster than is the case for the standard fuel.

The results of standard fuel degradation with the use of set-up from Figures 4 and 5 and with the use of one M365F1 LED are presented in Figure 9.
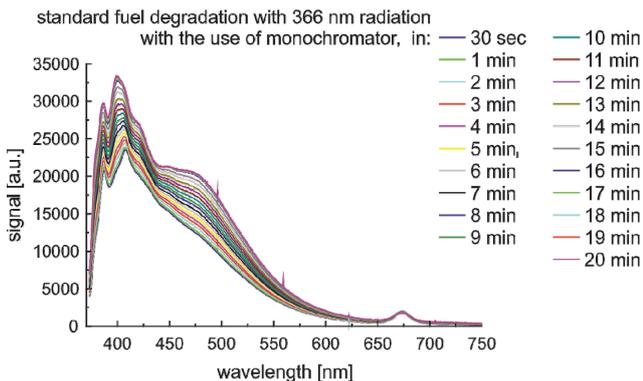
Figure 9. Spectra of fuels degraded and examined with the use of one M365F1 LED coupled to the set-up and with the use of monochromator.

The fuel degradation is evidenced as the increase of the fluorescence signal. The wavelength position of the peak located about 404 nm shifts during measurement. Fortunately at wavelengths of 475 nm the signal increase is almost monotonic. The constant increase of the signal is adequate to measure the initial stages of fuel degradation. At that stage the degradation is evidenced by the constant presence and the value of the signal of the emitted biological fluorescence at 675 nm.

When the UVTOP265 LED is used in one-LED set-up the monochromator can be removed, as the excited spectra of 2-EHN and gums are positioned at a range where there is no residual emission of LED radiation. The direct spectra of degradation results of standard diesel fuel with the use of UVTOP265 are presented in Figure 10.
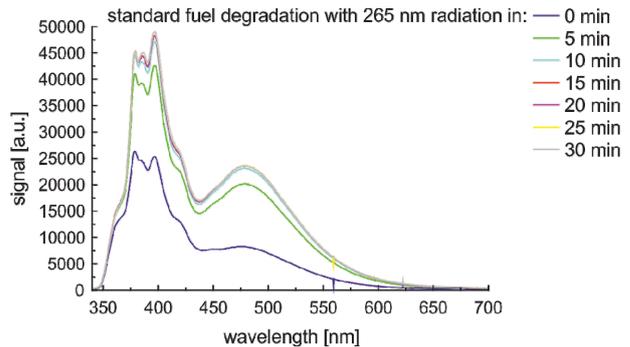
Figure 10. Spectra of fuels degraded and examined with the use of one UVTOP265 LED directly coupled to set-up - without monochromator using.

The degradation of standard fuels is evidenced as the significant increase of fluorescence signal, which saturates after 10 minutes. The measured speed of the degradation varies. For example, the characteristics faster saturate at 380 nm than at 395 nm peak. But, what is most interesting, the peak wavelengths are stable, when fuel is excited with 265 nm, contrary to excitation results performed at 366 nm.

B. Set-up with two UV LEDs

The set-up with two UV LEDs used of two M365F1 LEDs as their expected stable operational life time is much greater than of UVTOP265 LED. The direct results of fuel aging and fluorescence reading are presented in Figure 11.
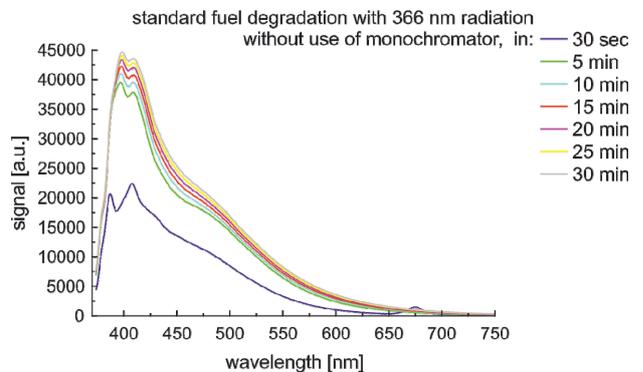
Figure 11. Spectra of fuels degraded and examined with the use of two M365F1 LEDs.

Four signs of fuel aging are now presented. The first sign adequate for initial aging is the increase of fluorescence excited signal emitted by 2-EHN. The second sign is the disappearance of the emitted peak of biological contamination that happens faster than at 5 minutes of aging. The third sign is the shift of 2-EHN local emitted maxima. The last sign is the change of the relation of 2-EHN local maxima amplitudes.

V. CONCLUSIONS

We proposed a sensor for diesel fuel stability testing based on the examination of fluorescence. The key of the method is placing the sample of the fuel in a capillary optrode and using UV radiation for accelerated ageing.

The analysis of the sensor construction showed that 366nm, as well as 265 nm wavelength radiation is sufficient for simulation of initial and middle states of fuel degradation. The conclusion for sensor examination with one LED source is quite obvious; the monochromator decreases significantly the speed of fuel aging. But, the spectra of 366 nm emitted wavelength LED requires positioning at some distance of an optical filter or monochromator to enable proper florescence reading. Therefore, two constructions are proposed. One, with UVTOP265 LED does not require additional optical filtering of signal. The second, with two M365F1 LEDs – one coupled with a monochromator and used for fluorescence reading, – the second directly coupled to the sensor head and used for high power UV fuel degradation. Finally, the power emitted by the LEDs used has to be constantly monitored and its variations taken into account in calculations of aging spectra. The spectral response of the spectrophotometer has to be checked for calibration.

The proposed instrumentation can be further improved by changing the spectrophotometers for dedicated photodetecting devices. It may be a valuable added module to the capillary sensor system for diesel fuel fit-for- use examinations or as an independent device used at petrol station points of use.

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