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Capillary Sensor with UV-Forced Degradation and Examination of Fluorescence for Determination of Chemical Stability of Diesel and Biodiesel Fuels

[1] Michal BORECKI, [2] Mateusz GĘCA,
[3] Michael L. KORWIN-PAWLOWSKI and [4] Przemysław PRUS
[1] Institute of Microelectronics and Optoelectronics, Warsaw University of Technology,
75 Koszykowa Str., 00-662 Warsaw, Poland
[2] Institute of Electron Technology, 32/46 Lotników Av., 02-668 Warsaw, Poland
[3] Département d'informatique et d'ingénierie, Université du Québec en Outaouais,
101 rue Saint-Jean-Bosco, J8X 3X7 Gatineau Québec, Canada
[4] Blue Oak Inventions, 31/101 Lwowska Str., 56-400 Oleśnica, Poland
[1] Tel.: +48 22 234 77 49, fax: +48 22 234 60 63
[1] E-mail: borecki@imio.pw.edu.pl

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Abstract: The diesel fuel stability is a function the composition of fuels as it evolved to the modern fuels from the historical ones. There are many different theories describing the mechanism of degradation of diesel fuels linked to various factors that initiate and maintain the degradation process. The instability of modern diesel fuel is mainly the result of chemical conversion of precursors to species of higher molecular weight with limited fuel solubility. The conversion process often involves oxidation of the precursor unsaturated components by reactive chemical compounds, as for example nitrogen and sulfur containing compounds - represented by cetane boosters, organic acids - represented as bio-components, and reactive olefins - resulting from economic distillation. The stability of modern diesel fuel is mainly achieved by reducing the unwanted oxidation processes, by reduction of the unsaturated to saturated hydrocarbons ratio, and by use of antioxidants additives.

Degraded diesel fuel can contribute to rapid wear of the fuel injection system and filter plugging. Therefore, national organizations and fuel producers must test and guarantee the diesel fuel stability under storage conditions and set standards for fuel examinations. Traditional techniques for measuring fuel stability utilize oxygen–assisted degradation of a heated sample. For example, American Society for Testing and Materials (ASTM) in standard D4625 introduces a time of 24 weeks of fuel sample exposition to air atmosphere heated to 43 °C. The evidence of degradation is the appearance of resins and sediments. The contemporary standards are time consuming. Consequently, development of new methods of 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 enabling fast examination of fuel stability as a characteristic of fuel itself not of the gas atmosphere. The examined fuel sample is enclosed in a vessel and the degradation factor is the UV radiation. The fuel samples used to develop the method are compositions of fresh petro-diesel fuels samples with cetane improver, bio-component and antioxidant. The result is a sensor set-up to determine the chemical stability of fuels in 40 min based on two UV light emitting diodes, one used to stimulate degradation, the second used for signal reading.

Keywords: Diesel fuel, Fuel quality, Fuel stability, Capillary sensor, Fluorescence sensor, UV fuel degradation.

1. Introduction

The diesel fuel consists of fuel base and fuel improvers and impurities. On the fuel user's side, diesel fuel quality is direct connected with diesel engine operating characteristics, such as starting ease, low noise, low wear, long life, sufficient power, good economy, low temperature operability, low emissions [1]. On the fuel producer's side, the quality of diesel fuel is defined by quality standards. The most popular standards are ASTM D 975 introduced by the American Society for Testing and Materials and EN 590 introduced by the European Committee for Standardization. In this approach, the quality standard can be described as a set of laboratory measured fuel parameters, like for example:

- The cetane number, which depends on fuel composition and indicates the ignition quality;
- The result of accelerated oxidation stability test, acid number, and result of test for gum content in fuels by jet evaporation, which indicate the stability;
- Pour point, viscosity, density, which describe fuel transfer characteristics;
- Sulfur, nitrogen and oxygen contents of fuel composition, indicating gas emission.

The common feature of both mentioned sets of fuel quality parameters is that they depends on diesel fuel composition, which changes in storage due to some chemical active fuel components [2].

1.1. Classical Versus Modern Diesel Fuels

Classical petro-diesel fuels were made from fuel base that was prepared with stable components of distillation products of crude oil. These products include mostly linear and branched 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.

The base of modern diesel fuels are products of the distillation processes, of the upgrading processes, as well as conversion processes products [3]. The popular upgrading process is hydrogen treating that mainly removes reactive compounds. The conversion process fundamentally changes the molecular structure of the feedstock, usually by "cracking". In this process the hydrocarbons with large molecules are broken down (cracked) into larger number of smaller molecules that carbon atoms number is between 9 and 21 [4].

Modern petroleum-derived diesel fuel base is composed of about 74 % saturated hydrocarbons - primarily alkanes, 25 % aromatic and unsaturated hydrocarbons - primarily alkenes. The modern diesel fuels include also a range of additives, as for example cetane improvers, antioxidants, detergents, corrosion inhibitors, deposit modifiers and lubricity agents, as well as bio-component [5]. This bio-component may be significant from fuel technology, affiliation (bio-diesel) and parameters point of view as it may reach a few percent of fuel volume. Important is that bio-components may be of first or second generation. The first generation of bio-diesel components include fatty acids methyl esters (FAME) that are characterized by the presence of double bonds, while second generation components base on hydro-treated vegetable oils (HVO) that seem to be mainly carbohydrates with saturated carbon atoms bonding [6-8].

At the minimum, the cetane number of modern diesel fuel is 51, therefore the cetane improver additive is required in fuel composition. The most popular cetane improver is 2-ethyl hexyl nitrate (2-EHN), the minor significant improver is di-tertiary-butyl peroxide (DTBP). Both substances include oxygen and are reactive. Cetane improvers 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 [9].

1.2. Diesel Fuel Storage and Stability

The diesel fuel may be in storage as strategic reserves, or as commercial stocks. The fuel storage conditions may include tank walls, air access including oxygen and water vapor, temperature and ambient lighting. The diesel fuel storage seems to be nowadays recognized as a problem even by fuel producers, who recommend the maximum time of diesel fuel storage in function of temperature conditions [10], for example 6-12 months at an ambient temperature higher than 30 ºC.

There are some factors other than temperature and oxygen presence 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 in turn make the fuel unstable;
- Exposure to dust and dirt, which contain trace elements that can destabilize the fuel;
- Fuel composition because some components in diesel fuel naturally age quickly.

There are many different theories describing the mechanism of degradation of diesel fuels as there are various factors that initiate and maintain the process. However, the instability of modern diesel fuel is mainly a results of chemical conversion of fuel base to species of higher molecular weight with limited fuel solubility. The conversion process often involves oxidation of the unsaturated components of fuel base by reactive chemical compounds as for example nitrogen and sulfur containing compounds - represented by cetane improvers, organic acids - represented as bio-components, and reactive olefins - resulted as economic distillation.

Since alkenes are more reactive than alkanes and are susceptible to oxidation modern diesel fuels are more sensitive to oxidation than previous fuels. Oxidation of alkenes may lead to waxy solids or emergence of gums [11]. It is important, because the ignition quality depends on the molecular composition of the fuel.

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 kept for 16 hours at 95 °C in the presence of oxygen, which approximately corresponds to one year's storage at 25 °C. The test result is the measured 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, as for example, microorganisms present in diesel fuel may be also the result of its storage [12].

The effects of FAME instability may be the presence in the fuel tank of a wide variety of alcohols, aldehydes, peroxides, polymers, as well as the previously mentioned insoluble gum and sediments. The FAME component of diesel fuel instability may be determined with the use of oxidation stability of biodiesel fuels and blends using the Rancimat method - accepted by EN14112, and the PetroOXY method [13]. The determination of the oxidation stability according to EN 14112 is an accelerated oxidation test. It lasts over a dozen of hours, up to 48 hours. The sample is held in a sealed reaction tube at a constant temperature of 110°C while a continuous flow of air is passed through the sample. FAME in the sample are oxidized to peroxides as the primary oxidation products. After some time, the fatty acids are completely decomposed, forming volatile organic compounds, like low molecular organic acids. An air flow transports them to a measuring vessel containing distilled water. The conductivity of liquid increases rapidly when acids are mixed with water. The time that passes until a rapid conductivity increase is known as the induction time. This time is a measure of the oxidation stability of the sample of FAME, but due to specific chemical reaction the method is not suitable for petro-diesel examinations [14].

The cetane improvers are a potential source of oxygen for oxidation of hydrocarbons. Therefore, doses of cetane improver to diesel fuels have to be carefully calculated. The reduction of cetane improver's concentration is possible when advanced treating of fuel products is applied. The method of cetane improvers using is preferred due to its low cost. The ASTM D 4046 standard test method is used for determining the amount of 2-EHN to diesel fuel.

The stability of modern diesel fuel is mainly achieved due to the reduction of the unwanted oxidation processes, by reduction of unsaturated to saturated hydrocarbons ratio, and by use of antioxidant additives. The base of diesel fuel antioxidant additives is phenol and its derivatives, like butylated hydroxytoluene (BHT) and butylated hydroxyanisole (BHA). The efficiency of the antioxidants varies depending upon the different types of diesel fuel [15]. The universal petroleum-based fuel antioxidant additive called ETHANOX® contains a phenolic component. As it does not absorb UV light, direct photo-degradation does not take place. It protects fuels against thermo- oxidative and UV degradation.

The result of instability of diesel fuel that was stored in improper conditions is degraded fuel. Foreign particles present in the degraded diesel fuel can damage fuel lines, fuel injectors, and other system components.

Present techniques of measuring fuel stability, like the rancimat methods, are relatively complex, expensive in use and time consuming. Thus, for the diesel fuel user, fast and low-cost sensing of the stability of diesel and biodiesel fuel is important.

1.3. Optical Methods for Diesel Fuel Stability Testing

The optical testing of fuel parameters is performed in laboratory and in-situ conditions of working engine. 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 [16]. 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 [17].

The fuel components concertation may be examined with absorption and fluorescence measurements. The absorption methods using infra-red (IR) are well developed to measure FAME component concentration [18]. Fluorescence examination methods include synchronous reading fluorescence and time resolved fluorescence [19, 20].

The oxidation stability of oils tests with spectroscopy measurements of absorption and fluorescence in VIS and UV bands were reported in the case of baru oil [21]. 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.

Despite the drawbacks of the spectroscopic method of costs of equipment (tunable lasers) and of costs of examination of oils in quartz cuvettes, including costs of cuvettes and reagents for sample dilution, dedicated components for new sensors set-ups are under development [22-24].

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 an inclined capillary [25, 26]. The concentration of 2-EHN may be evaluated with the analysis of fluorescence signal excited with 366nm wavelength light and 2-EHN degradation may be estimated with the 366 nm signal scattering [17].

Dedicated components for sensors set-ups for those methods have been developed [27-30]. Also, some aspects of automatization of sensor with capillary set-ups as data filtering and processing and influence of man operator are under investigation [31, 32]. It is worth mentioning that some capillary experiments are now accessible with commercial capillary holders proposed by GE Healthcare under the name of UV-grade capillary cell.

The new accelerated method of fuel stability testing in which fuel sample positioned in a capillary is aged with UV radiation with simultaneous fluorescence reading has been proposed [33]. Nevertheless, for their routine daily work, the fuel distributors still demand the development of new rapid and low-cost sensing devices at proper technology readiness level 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.

2. Sensor Construction

2.1. The Principle of the Sensor

A simple method of fuel degradation analysis is to use differential visual examination. UV radiation may act as the degradation factor. In the following experiments, the sun light containing UV radiation was used to directly illuminate one sample positioned in a capillary while the second sample was positioned in a glass and after five months the central part of the liquid was downloaded into the capillary. The experiment was performed with CV7087Q capillary the inner diameter of which is 700 µm and with glass of inner diameter of 7 cm.

The results of the experiment, presented in Fig. 1, show that the UV-caused degradation of diesel fuel sample runs faster in the capillary than in a glass, when an external source of light is used. The degradation is visible as honey color of sample. The experiment confirms relatively high attenuation of UV radiation in diesel fuel as a glass walls seem to be covered with honey colored substance. 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 glass. Similar, but not as drastic difference in fuel degradation is present in a case of standard 10 mm quartz spectroscopic cuvette used instead of glass.

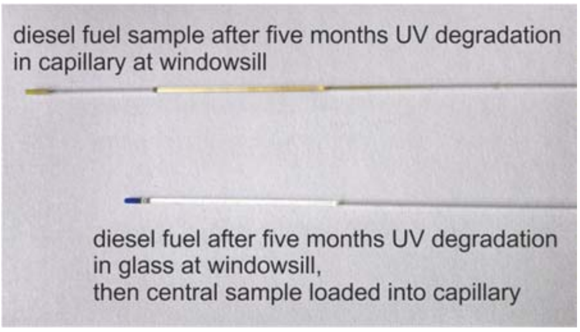

Fig. 1. Visible effects of diesel fuel UV sunlight degradation running in different vessels for five months.

The experiment of atmosphere impact on degradation of diesel fuel has been run in dark conditions, for fuel positioned in the capillary with one end closed for positioning purpose and the second opened to enable the atmosphere – fuel contact. The results of five months storage of samples are presented in Fig. 2. Diesel fuel after five months of atmospheric degradation in dark conditions in a capillary shows a light color change of the sample to honey at the atmosphere-to-sample contact area. The penetration of honey color phase do not enter the entire volume stored in the capillary.

Fig. 2. Visible effects of diesel fuel samples exposed to atmosphere in dark conditions for five months.

The tentative conclusions are that the capillary is an effective vessel to study diesel fuel controlled degradation, while the degradation with the use of natural UV radiation runs faster than natural contact with atmosphere containing oxygen.

Therefore, the idea of a rapid sensor of diesel fuel stability based on forced UV degradation of fuels placed in a capillary vessel seems promising. Furthermore, 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.

2.2. Light Sources for the Sensor

For sensor device applications, one has to consider the light emitted diode (LED) as a source of UV radiation. That radiation could be used for excitation of fluorescence and for the degradation of the sample. As general rule, the power of LEDs increases with wavelength from deep UV to VIS range, but the degradation speeds of samples using equal radiation powers decrease with the increase of the light wavelength. Therefore, two different types of LEDs will be used for the sensor set-up, but both LEDs will be coupled with the same type FG550LEC optical step-index large core fiber.

The UVTOP265 LED emitted 250 µW at 265 nm and was equipped with a ball lens, provided good coupling of radiation to the fiber. The residual radiation of this LED is in the range of 280-320 nm. 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 mentioned fiber. The M365F1 is characterized by a residual radiation in the band of 400-460 nm. The LEDs were controlled with a Thorlabs DC2100 High-Power drivers. Due to LEDs working points set at their maximum ratings, the examination was performed of the stability of radiated power. The M365F1 LED was coupled to Maya 2000 pro spectrometer and PM100D power meter with power divider made from fiber optic bundle. 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 Fig. 3.

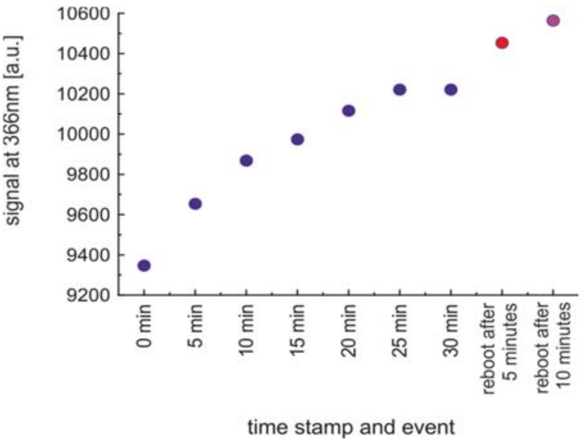

Fig. 3. M365F1 LED optical power at 366 nm coupled into optical fiber in function of time and event.

The fiber-coupled signal of the UVTOP265 LED constantly driven for 30 minutes at maximum current equal to 30 mA is presented in Fig. 4.

The examination of mid-range stability UVTOP265 LED showed similar results as for the high power M365F1 LED. The LEDs experimental examination show that 10 % of variation of maximum signal intensity is to be expected, but the signal's changes are not uniform. Therefore, precise fuel examination requires optical power stabilization of the source or/and mathematical signal correction. Unfortunately, both solutions require source signal monitoring with additional sensing modules. The third solution is LEDs function division, where one LED is used for fuel degradation and the second is used for fluorescence reading. This way the LED used for fluorescence reading can work in relatively short period of time, and the power fluctuation of LED used for fuel degradation are somehow averaged over time.

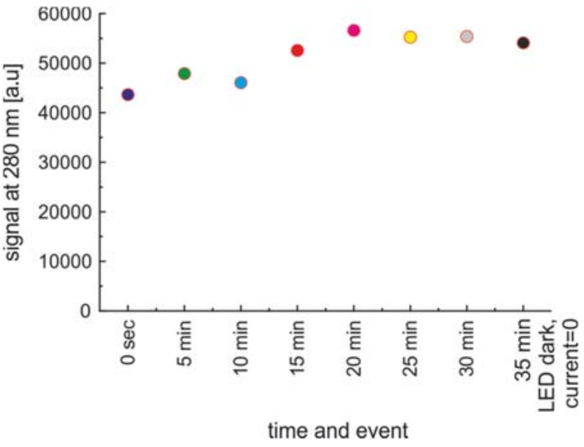

Fig. 4. UVTOP265 LED optical power at 265 nm coupled into optical fiber in function of time and event.

2.3. Sensor Set-up with One UV Source

The sensor head of set-up with one UV source presented in Fig. 5 consists of only two optical fibers.

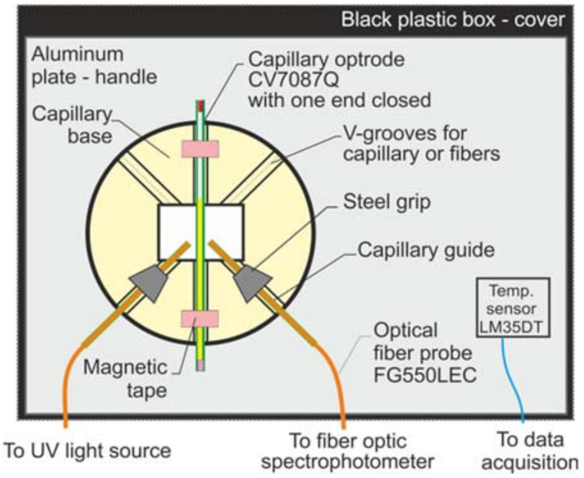

Fig. 5. Scheme of the capillary sensor head with one UV source.

The head is coupled to the optoelectronic sensor set-up for M365F1 LED according to the scheme presented in Fig. 6.

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

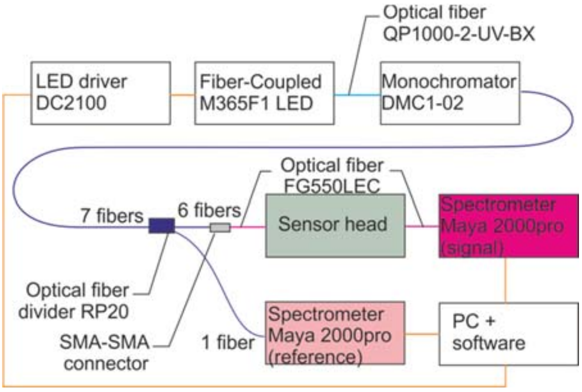

Fig. 6. Scheme of the capillary sensor set-up with one M365F1 LED.

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 M3651F1 LED's optical signal with proper accuracy required by florescence excitation and reading.

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.

The head is coupled to the optoelectronic sensor set-up for UVTOP265 LED according to the scheme presented in Fig. 7.

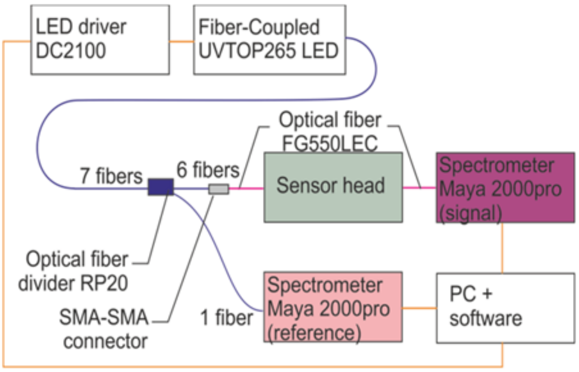

Fig. 7. Scheme of the capillary sensor set-up with one UVTOP265 LED.

The monochromator rejection in this case is possible due to separation of excited signals that are in 350 nm to 650 nm range that is well separated from residual LED radiations present at longer wavelengths than peak. Signals recorded using the sensor head with an empty capillary (see Fig. 5) versus time of measurement is presented in Fig. 8.

The conditions described above were the worst-case examination of fuel from the detection unit point of view, as the received signal was only scattered at the smooth glass surface of the capillary. The received signal was close to the sensitivity of the used spectrometer, therefore spectral characteristics showed fluctuations over time of examinations, and the residual long wavelength signal is not recorded.

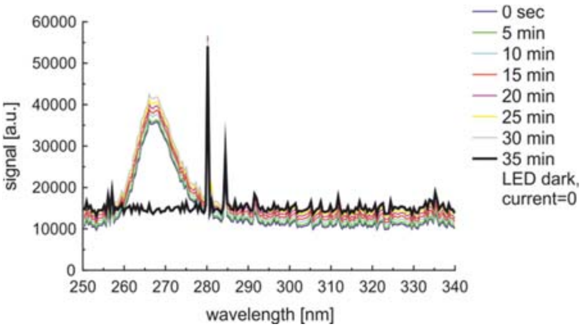

Fig. 8. UVTOP265 LED optical spectra at signal spectrometer in function of time for empty capillary in head.

2.4. Sensor Set-up with Two UV Sources

The sensor's head with two UV sources is presented in Fig. 9.

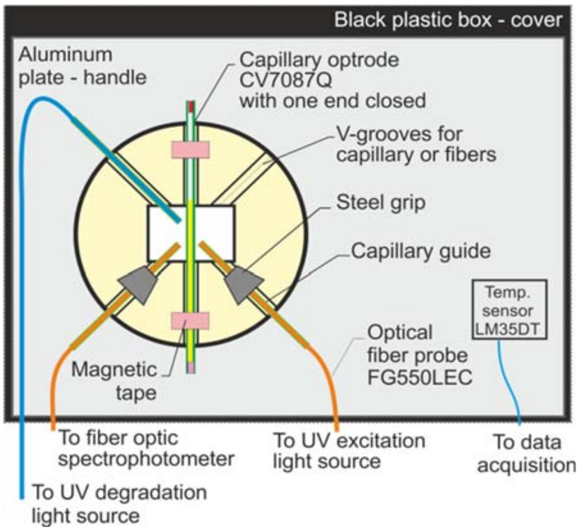

Fig. 9. Scheme of the capillary sensor head with two UV sources.

To make allowance for separate UV degradation from fluorescence examination an additional optical fiber was placed in the test head. The system set-up scheme was changed by the addition of a LED block for UV degradation of the sample as presented in Fig. 10.

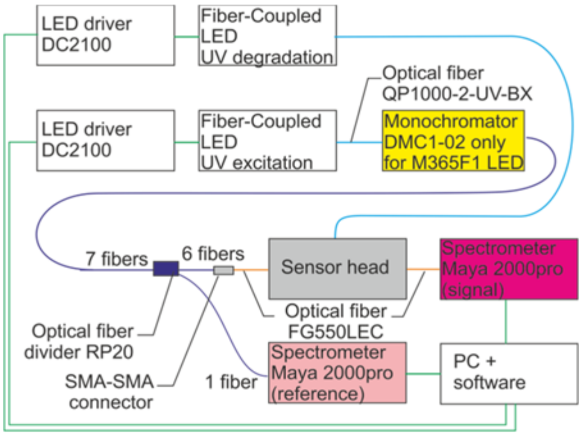

Fig. 10. Scheme of the capillary sensor set-up with two UV LEDs.

The monochromator in this scheme is only for fluorescence reading with the use of M365F1 LED, because, as previously shown, UVTOP265 LED does not require wavelength filtering. The organization of system control was changed compared to one UV source as the LED drivers for UV degradation and UV fluorescence examination were switched alternately. Therefore, the advantage of two UVTOP265 LEDs set-up to one UVTOP265 LED set-up is expected to be in time of life of UV sources. While, the advantage of two M365F1 LEDs set-up to one M365F1 LED set-up is expected to be in time of examinations as analyzed one LED set-up provides much more UV power to sample degradation.

3. Experimental Results of Fuel Examinations

The measurement procedure of experiment consists of a few steps. Step 1: At the initial configuration of the set-up for selected diode is mounted. Step 2: the background signal of for the empty optrode is measured. Step 3: the optrode is directly filled from the middle of a tank and the outer walls of the optrode are wiped. Step 4: the signal of fluorescence is measured with the use of UV fuel sample 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.

3.1. 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 Fig. 11 show similar shapes of characteristics, while the maxima of excited spectra for different excitation are at slightly different wavelengths.

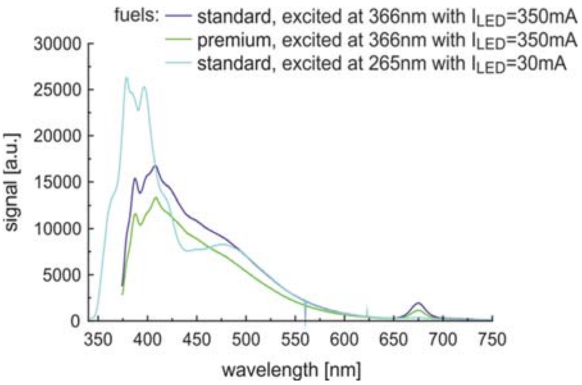

Fig. 11. Spectra of fresh fuels excited with 366 nm and 265 nm wavelengths respectively.

Taking into account LEDs powers, the excitation efficiency at 265 nm looks greater than to run at 366 nm. But, taking into account the fact that the monochromator reduces the optical power of 366 nm peak significantly (as mentioned previously 1000 times), the UV powers at the head's inputs are similar. Therefore the signals exciting the fluorescence are also similar. But then again, the signal of biological fluorescence at 675 nm is readable only for excitation at 366 nm.

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 one M365F1 LED working in set-up from Fig. 6 and are presented in Fig. 12.

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 (Fig. 13).

The constant increase of the signal is adequate to measure the initial stages of fuel degradation. At those stages the degradation is evidenced by the constant presence and the value of the signal of the emitted biological fluorescence at 675 nm.

The spectra of degradation results of standard diesel fuel with the use of UVTOP265 are presented in Fig. 14. The degradation of standard fuel is evidenced as the significant increase of fluorescence signal, which saturates after 5 minutes (Fig. 15).

In both cases of examination the measured speed of the degradation varies, but its course is similar. 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.

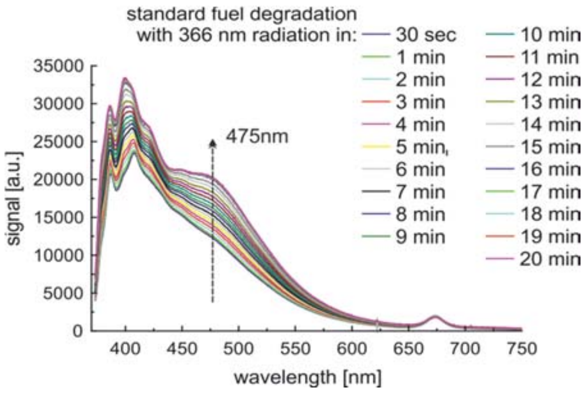

Fig. 12. Spectra of standard fuel degradation examined with the use of one M365F1 LED.

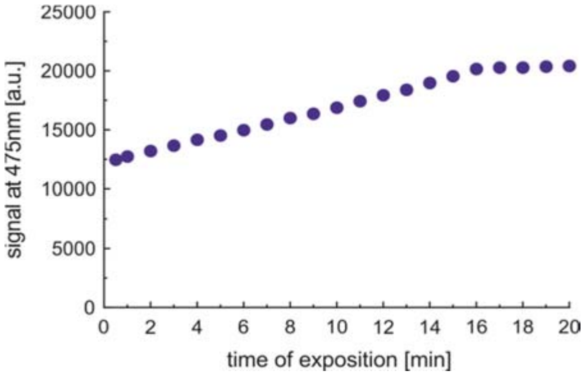

Fig. 13. Signal at 475 nm of standard fuel degradateion examined with the use of one M365F1 LED.

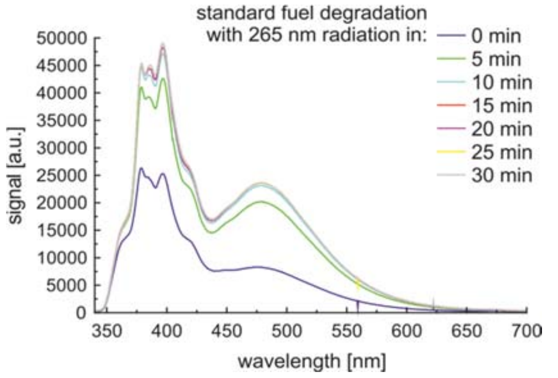

Fig. 14. Spectra of standard fuel degradation examined with the use of one UVTOP265 LED.

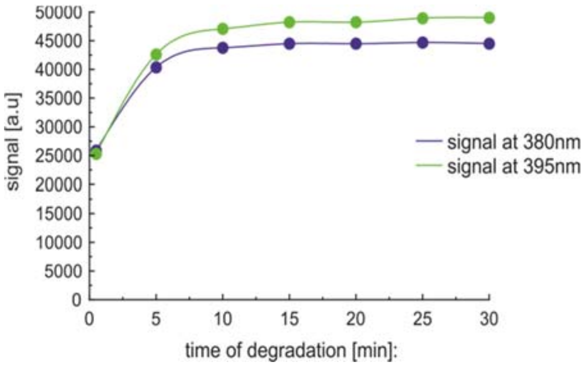

Fig. 15. Signals at peaks 380 nm and 395 nm vs. time of standard fuel degradation and examined with the use of one UVTOP265 LED.

3.2. Set-up with Two M365F1 LEDs

The set-up with two M365F1 LEDs has been used to standard fuel stability examination. The results of standard fuel direct aging and fluorescence reading are presented in Fig. 16.

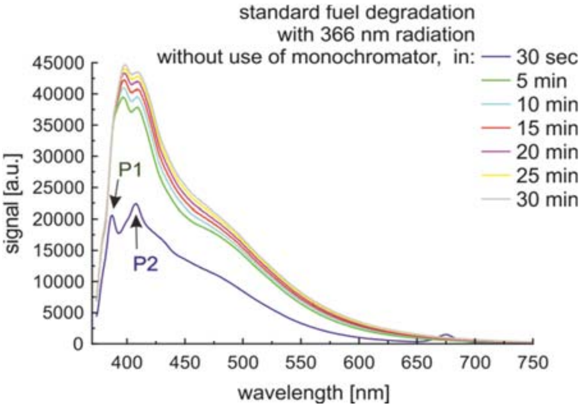

Fig. 16. Spectra of standard fuel degradation examined with the use of two M365F1 LEDs.

The peak at characteristics are marked P1 and P2. Four signs of fuel aging are now present. 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 as presented in Fig. 17.

From this examination it is evident that the increase of UV power results in the increase of the degradation speed as the excited signal at peaks shift saturates after 5 minutes of degradation now compared to 16 minutes (Fig. 13) in the set up with one M365F1 LED. The best resolution of degradation measurement is at peak 1 (P1). But, the signals of peak wavelength shift and amplitude change seems to be similar.

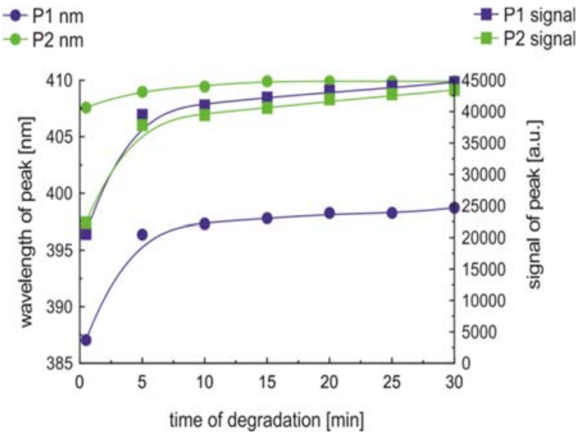

Fig. 17. Peak shifts during standard fuel degradation examined with the use of two M365F1 LEDs.

3.3. Set-up with Two UVTOP265 LEDs

The set-up with two UVTOP265 LEDs was used for the examination of the stability of premium fuel. The results of fresh and clear premium fuel aging and fluorescence reading are presented in Fig. 18.

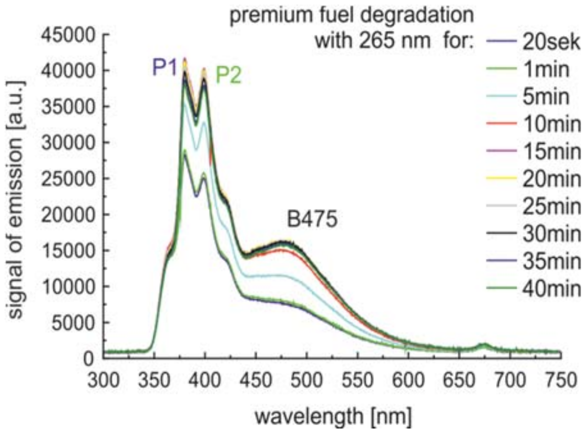

Fig. 18. Spectra of premium fuel degradation examined with the use of two UVTOP265 LEDs.

The premium fuel spectral characteristics are similar to the standard fuel examined in one UVTOP265 LEDs, but difference are better visible in comparison of peak analysis presented in Fig. 15 and Fig. 19.

For premium fuel the peaks are in different wavelengths P1 is at 385 nm instead of 380 nm, the P2 is at 399 nm instead of 395 nm. Moreover, the premium fuel dynamics range of amplitude shift is (40000-25000) of arbitrary units, lower than standard fuel amplitude shift (45000-25000) of arbitrary units. Significant is also that the amplitude shifts at 475 nm that describes the resin's concentration is also lower (17500-7500) of arbitrary units for premium fuel contrary to (25000-7500) of arbitrary units for standard fuel.

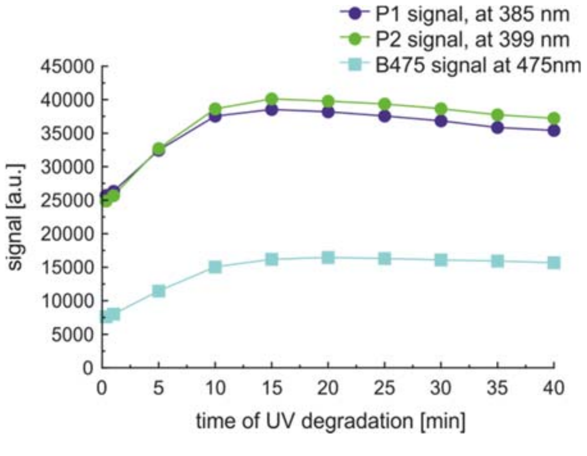

Fig. 19. Signals at peaks 380 nm and 395 nm vs. time of standard fuel degradation examined with the use of one UVTOP265 LED.

4. Summary and Conclusions

We proposed a sensor for diesel fuel stability testing based on the forced by UV radiation fuel degradation with simultaneous 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 366 nm, as well as 265 nm wavelength emitted LEDs are fit for realization of initial and middle states of fuel degradation in time below 40 minutes.

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 an residual radiation removal to enable proper florescence reading of cetane improver. Therefore, set of constructions are proposed and initially examined. Most promising and simple construction possibilities are offered by UVTOP265 LED, as it implementation does not require additional optical filtering of signal. But, the expected time of life of UVTOP265 LED is significantly smaller than M365F1 LED. The second promising set-up is constructed 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 periodically checked for calibration. But, even at the present demonstration of technology level, the proposed construction enables proper classification of fuel stability in time much shorter than presently accepted standards. Moreover the proposed measurement technique seems to be fit for use for diesel fuel with bio-components of different type as FAME and HVO.

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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Authors' contribution: Michał Borecki proposed the method of fuel examination, designed the sensor and analyzed the data from heads and set-ups, Mateusz Gęca proposed the algorithm of fuels examination and performed the tests of fuels, Przemysław Prus developed the methods of data processing, Michael L. Korwin-Pawlowski counseled the design process,

verified the data analysis and the construction specifications.

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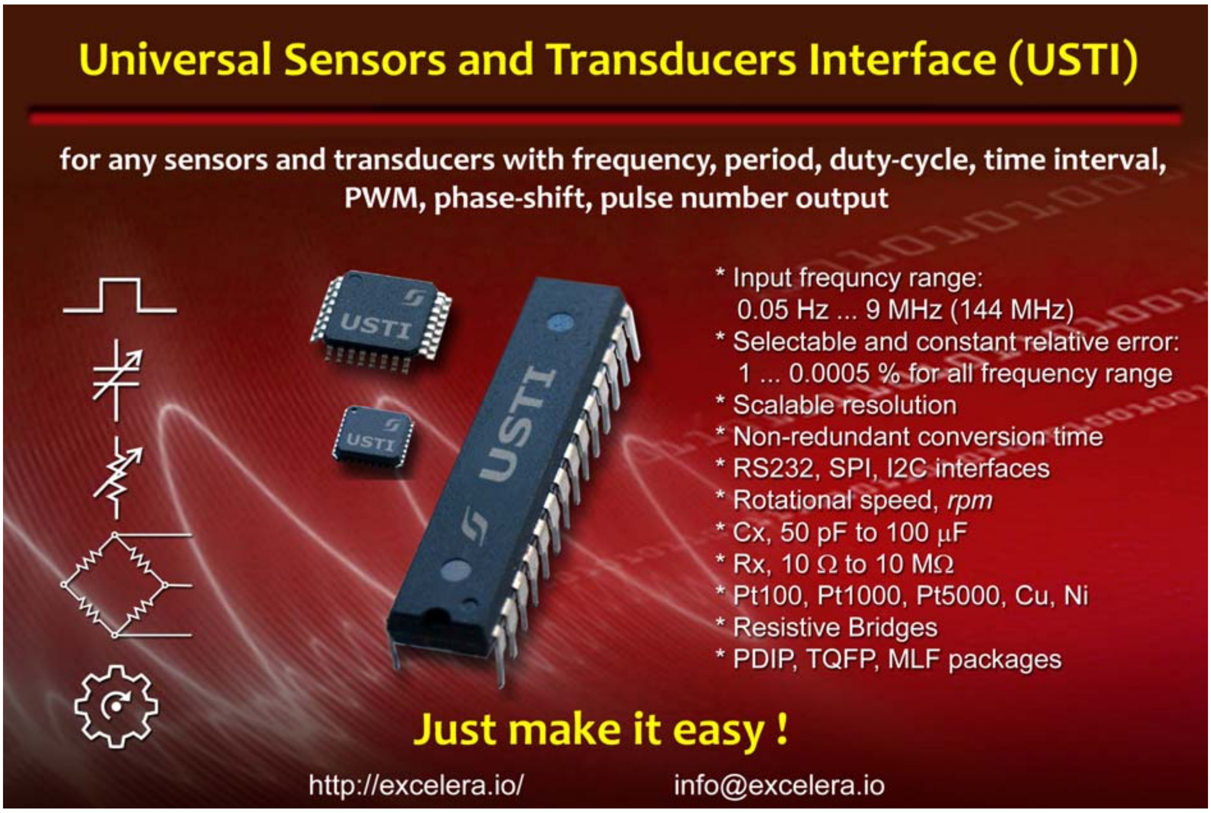

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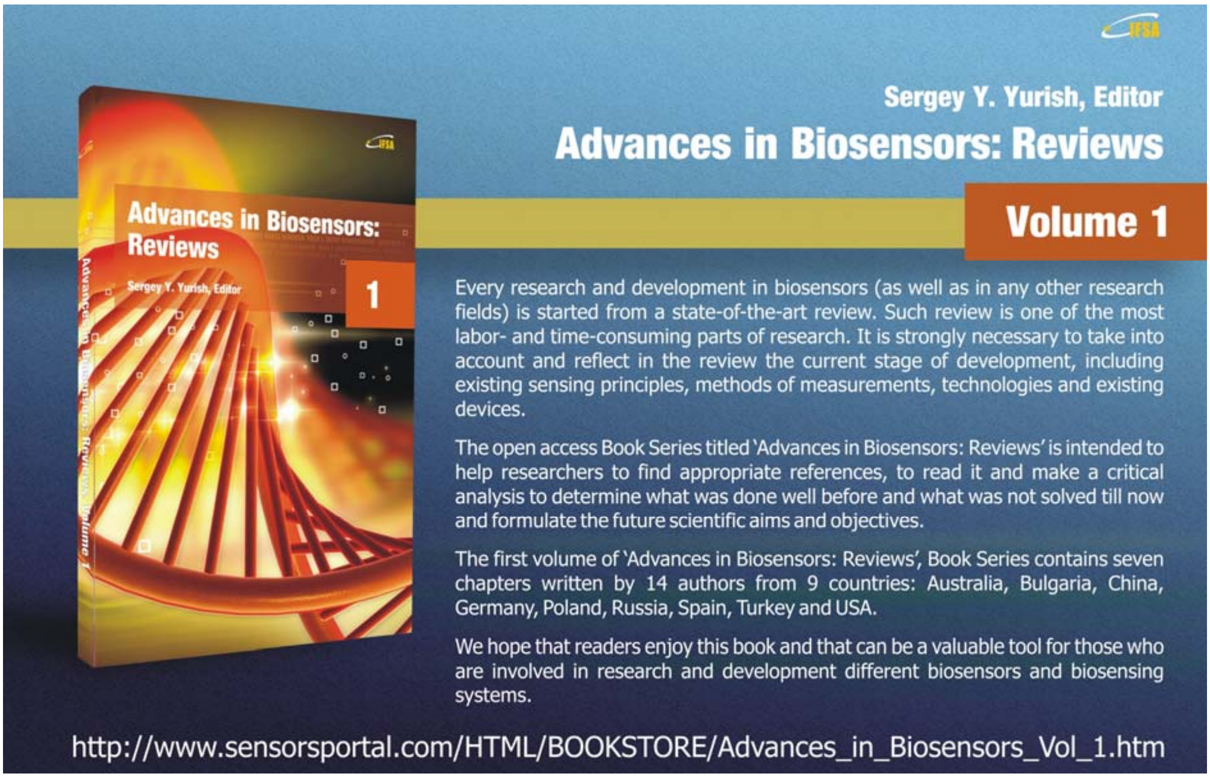

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