ISSN: 1231-4005
e-ISSN: 23540133
DOI: 10.5604/01.3001.0010.3054

ENGINE FUEL CHARACTERISATION THROUGH ULTRAVIOLET ABSORPTION SPECTRA

Emilia Baszanowska, Zbigniew Otremba

Gdynia Maritime University
Department of Physics at Faculty of Marine Engineering
Morska Street 81-87, 81-225 Gdynia, Poland
tel.:+48 58 5586588, fax: +48586901399
e-mail: eba@am.gdynia.pl, zotremba@am.gdynia.pl

Abstract

In the article, light absorption properties of the fuel oil are considered with a view to create basis for establish optical indicator of the type and quality of this kind of crude oil derivative, in this case the Diesel fuel. The organic solvent – n-hexane – was chosen as a solvent to prepare samples of dilutions of Diesel fuel in several oil concentration. Spectrophotometer Aqualog Horiba were applied to record the absorbance spectra in the ultraviolet and visual range of the light (from 240 to 600 nm) for each previously prepared samples. Obtained results allow concluding that the changes of absorbance occur primarily in the wavelength range from 240 nm to 355 nm. Moreover, the absorbance spectra are characterized by the characteristic sharp peak located at 270 nm for excitation wavelength. Spectra of absorbance were converted to spectra of absorption coefficient based on Lambert-Beer law. Due to the independence the absorption coefficient from the fuel concentration, this parameter could be used as a potential indicator to access composition and quality Diesel fuel used in the diesel engine system. Therefore, preliminary tests allow concluding that absorption coefficient for selected wavelength located at 270 nm could be a sensitive indicator for quick access to fuel quality.

Keywords: *fuel, spectroscopy, absorptivity, diesel engine system*

1. Introduction

Petroleum and most of their derivatives, for example fuel oils or lubricating oils, consists of a complex mixture of hydrocarbons of various molecular weight. Moreover, petroleum as well as its refining products contain specific organic compounds showing the ability to strong fluoresce. These substances are mainly aromatic compounds which can be monocyclic (MAH) or polycyclic (PAH) [5]. The ability to fluoresce manifests itself in the shape of oils fluorescence spectra. On the other hand, every petroleum substance is responsible to absorb light in ultraviolet (UV) range much stronger than the visible (VIS) range. From a physical point of view, this is due to the much greater probability of electron transitions that are caused by high-energy UV photons than the likelihood of rotational and oscillatory transitions induced by VIS photons. Petroleum products, including fuel, in the visible range do not show a clear spectral structure. Furthermore, in visual assessment they appear to be more or less transparent. However, in the short-wave edge zone of the visible spectrum hydrocarbons exhibit light absorbing properties, and the shorter the wave of light is, the stronger absorption is observed. Studies on light absorption in lubricating oils have shown that the absorption spectra exhibit a more diverse variant structure in solutions than in oil-in-water emulsions [3, 4].

To characterise the properties of petroleum products several indicators have been introduced. For description petroleum and its derivatives such us lubricate oils or fuels the basic indicators such as temperature dependence of viscosity-coefficient, water content, total acid number, total base number, rheometric and tribometric characteristics [6, 10, 8] are typically determined.

The question arises as to whether the combustion engine fuel has a spectrum of structure that is sufficiently shaped to identify and even determine the quality of oil. There may be a case, for example, the degree of chemical transformation in aging, falsification at the distribution stage, contamination by water or other oil. The fuel sample cannot be directly placed in the spectrophotometer, as the intensity of light absorption in the oil contained in the sample is too high, especially in the ultraviolet range. Therefore, the fuel sample must first be diluted in the solvent. However, the basic question is whether the spectrum structure will be preserved for any degree of sample dilution. Therefore, the principal purpose of the analysis reported in this article is to prepare a methodological basis for determining the absorption spectra of fuel sampled from a tank or engine installation.

In the article, absorbance measurements were performed for preliminary tests regarding to the composition of fuel used in diesel engine system. Based on dilution method, fuel was dissolved in organic solvent and several fuel concentration was prepared. Obtained absorbance spectra of Diesel fuel were converted to the absorption coefficient spectra to check if they are independent of oil concentration in the previously prepared oil-in-hexane solutions.

2. Method

2.1. Oil samples

Fresh fuel typically used in marine transport was selected for this study: *Diesel* – applied in ship diesel engine. This kind of oil visually shows a transparent yellow liquid.

2.1.1. Samples of fuel dissolved in n-hexane

N-hexane (for analysis, 96.0% purity) was applied as a solvent and a stock solution of oil in n-hexane for Diesel fuel was then prepared. Based on this dilution method, individual concentrations for Diesel fuel were made. The concentrations of individual oil samples were prepared in relation to the weight of the solution (n-hexane) and the weight of oil samples. Those concentrations of oil in n-hexane are presented in Tab. 1.

Tab. 1. Concentration [ppm by weight] of Diesel fuel dissolved in n-hexane

	Diesel
	c [mg/kg]
DO	200
DO	400
3D	450
DO	900

2.2. Measurement

An *Aqualog Horiba* spectrofluorometer was applied to determine the absorbance spectra of oil samples [1, 2, 7]. Absorbance spectra for all solutions in 1×1 cm quartz cuvette were measured.

For absorbance spectra measurements, the following parameters were applied: excitation wavelength from 240 nm to 600 nm with a 5 nm sampling interval, 5 nm slit and a 1s integral time. Moreover, due to the technical features of the spectrophotometer, the absorbance spectra were measured from the longest to the lowest excitation wavelength.

Measurements were made at stabilised temperature of 20ºC.

3. Results

Absorbance spectra $A(\lambda)$ of considered Diesel fuel, samples for each fuel concentration were determined basing on the Lambert-Beer law describes by formula 1 [9]:

$$A(\lambda, c) = -\log\left(\frac{I(\lambda, c)}{I_h(\lambda, c)}\right), \tag{1}$$

where:

$I_h(\lambda,c)$ – describes the intensity of the light that has passed through the reference sample (n-hexane),

$I(\lambda,c)$ – describes the intensity of the light that has passed through the dissolved fuel sample in n-hexane,

c – describes the concentration index of the fuel solution expressed in kilograms of fuel per one kilogram of n-hexane solution (ppm by weight).

The spectra were registered in the range 240-600 nm for various concentrations of dissolved fuel in n-hexane (see Tab. 1). Fig. 1 presents determined absorbance spectra for dissolved Diesel fuel for each concentration.

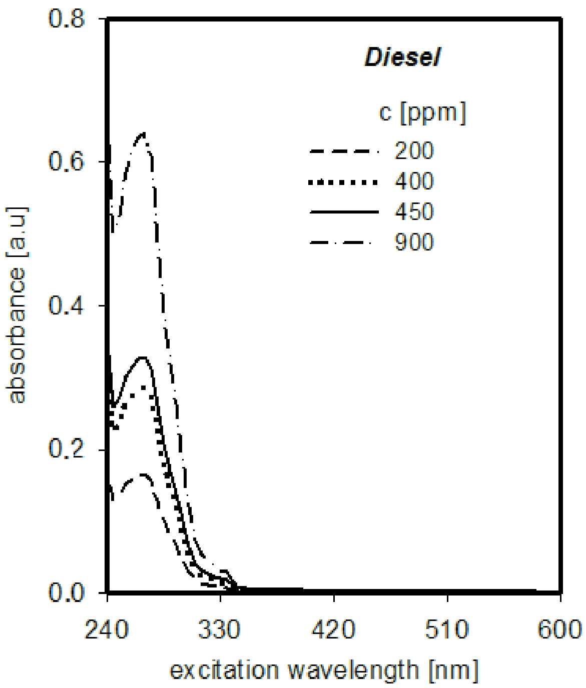

Fig. 1. Absorption spectra of dissolved in n-hexane Diesel fuel for various oil concentrations

In Fig. 1 there is clearly visible that the absorbance spectra change significantly in the wavelength range from 240 nm to 350 nm. However, for the longer wavelengths the absorbance values are closed to zero, it could be caused due to that crude oils and its derivatives such as fuels are relatively transparent in the visual range of the light spectrum. Moreover, in Fig. 1 is visible that the absorbance values and half width of absorption spectra strongly depend on the fuel concentration. However, maximum of absorbance was detected for excitation wavelength at 270 nm and does not shifted in excitation wavelength when fuel concentration in changing.

4. Discussion and conclusions

The aim of this study is to characterise fuel basing on an indicator determined from the measurements of absorbance spectra. Basing on Lambert-Beer law (formula 2) used to determine absorbance spectra of Diesel fuel, the specific indicator of absorption – absorption coefficient $a(\lambda)$ was determined for each Diesel fuel concentration.

$$I((,c) = I_h((,c)\exp[-a\,d\,c], \tag{2}$$

where:
c – describes the concentration index as in formula 1,
d – describes the cuvette length.

The absorption coefficients $a(\lambda)$ for dissolved in n-hexane Diesel fuel for considered fuel concentrations in the whole of excitation wavelengths range from 240 nm to 600 nm were calculated and determined basing on formula 3 (which is determined taking into consideration formulas 1 and 2)

$$a(\lambda) = \frac{2.303\, A(\lambda, c)}{c\, d}, \tag{3}$$

where:
$A(\lambda)$ – describes the absorbance (as in formula 1),
c – describes the concentration index as in formula 1,
d – length of cuvette.

Figure 2 presents the calculated absorption coefficients for dissolved in n-hexane Diesel fuel for considered fuel concentrations. In Fig. 2 is clearly visible that the values of absorption coefficients are changing in the excitation wavelength range from 240 nm to 360 nm and the absorption peak (sharp) is observed at 270 nm.

Taking into account considered results for Diesel fuel in comparison with the calculated absorption coefficients for crude oils [2] and its derivatives such us lubricate oil [3], the absorption coefficient peak for Diesel fuel located at 270 nm is narrower and changes in the wavelength range from 240 nm to 350 nm, while for crude oils changes in range from 240 nm to 420 nm [2]. Moreover, the absorption coefficients increase when excitation wavelength increases and achieve maximum value at 270 nm from excitation wavelength. However, absorption coefficients, starting from 270 nm and decrease when excitation wavelength increases, moreover are close to zero for excitation wavelength above 355 nm. Additionally, absorption coefficients do not depend on the oil concentration in considered range of oil concentration. It allows concluding that absorption coefficient could be a good indicator to oil identification independent from oil concentration.

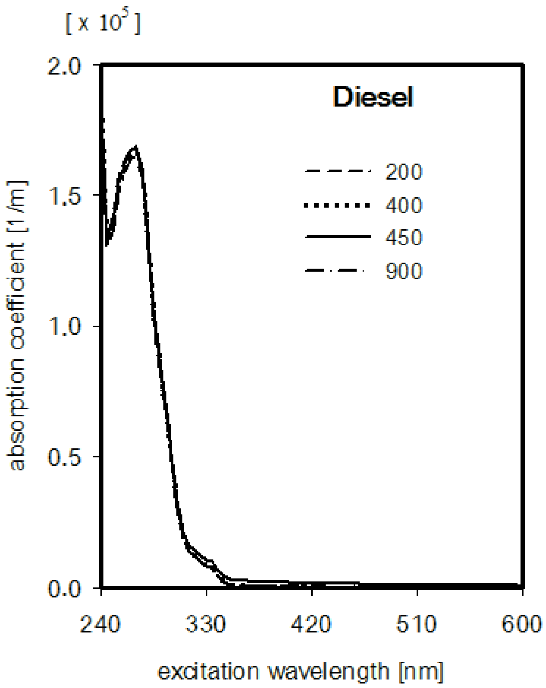

Fig. 2. Absorption coefficient of Diesel fuel dissolved in n-hexane for various fuel concentrations (derived using formula (2) based on the data depicted in Fig. 1)

5. Conclusions

The absorbance spectra for Diesel fuel dissolved in n-hexane were measured to characterize this kind of crude oil derivative. The absorbance measurements were performed for several oil concentration in the range of concentration from 200 ppm to 900 ppm to check the impact of amount of oil on the shape of absorbance spectra and further to define the indicator based on absorption spectra which allow to characterize the spectral properties of this kind of fuel.

Obtained results for Diesel fuel give information those values of absorbance decrease in the range from 240 nm to 355 nm. Moreover, the absorbance spectra are characterized by the presence of sharp peak located at 270 nm for excitation wavelength. Additionally, the absorbance for wavelength higher than 355 nm is practically irrelevant. It is necessary to highlight that determined peak position does not depend on the oil concentration. However, the half-width of determined peak depends on oil concentration. On the other hand indicator – absorption coefficient determined for each excitation wavelength indicate the independence from the oil concentration as well as the half-width of determined peak for absorption coefficient indicator also does not depend on oil concentration.

In conclusion, the absorbance measurements for Diesel fuel dissolved in organic solvent could be useful tool to access the quality of fuel used in diesel engine system, however for the future studies various other Diesel fuels should be analysed.

Acknowledgements

This article was supported by the Gdynia Maritime University grants No. 427/DS/2017.

References

[1] Baszanowska, E., Zielinski, O., Otremba, Z., Toczek, H., *Influence of oil-in-water emulsions on fluorescence properties as observed by excitation-emission spectra*, J. Europ. Opt. Soc. Rap. Public., Vol. 8, No. 13069, pp. 13069-1 – 1369-5, 2013.

[2] Baszanowska, E., Otremba, Z., *Spectral signatures of fluorescence and light absorption to identify crude oils found in the marine environment*, J. Europ. Opt. Soc. Rap. Public., Vol. 9, pp. 14029.1 – 14029.7, 2014.

[3] Baszanowska, E., Otremba, Z*., Light Absorption Spectra for Lubricate Oil Quality Tracking in the Combustion Engine*, Journal of KONES Powertrain and Transport, Vol. 23, No. 1, pp. 55-60, Warsaw, Poland 2016.

[4] Baszanowska, E., Otremba, Z*., Spectrum of Light Absorption as the Indicator of Lubricate Oil Dispsersed in the Natural Water*, Journal of KONES Powertrain and Transport, Vol. 23, No. 1, pp. 61-66, Warsaw, Poland 2016.

[5] Geddes, C. D., Lakowicz, J. R., *Review in fluorescence*, Springer, 2005.

[6] http://www.kittiwake.com/base_number, 2017-05-30.

[7] Meier, D., Voß, D., Zielinski, O., Heuermann, R., Horn, M., Krause, S.-E., Machulik, U., Munderloh, K., Oest, J., Spitzy, A., *Development of an online detection system for determination and characterization of dissolved organic substances in water via fluorescence spectroscopy*, 3rd EOS Topical Meeting on Blue Photonics® – Optics in the Sea (Blue Photonics 3), Texel 2013.

[8] Młynarczak, A., *Investigation of the influence of aftermarket additive on lubricating properties of Titan Truck Plus 15W40 oil used in marine diesel engines*, Zeszyty Naukowe Akademii Morskiej w Gdyni, No. 76, pp. 62-68, 2012.

[9] Operation manual, Aqualog Horiba, rev. A, Horiba Scientific, 2011.

[10] Wierzcholski, K., Miszczak, A., *Algorythm for variable pseudoviscosity coefficients under experimental basis*, Tribologia, Vol. 44, No.4, pp. 125-136, 2013.