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Temperature influence on parameters of summer diesel fuel measured with the use of impedance spectroscopy

***Abstract**. In the paper an attempt was made to experimentally verify temperature influence on the evaluation of diesel fuel with the use of impedance spectroscopy. Previous tests' findings showed that this method can be used to detect undesirable substances in constant temperature. Tests presented in the paper show that temperature can change electrical properties of diesel fuel similarly to contaminants. This makes temperature an important factor, which must be taken into consideration.*

***Streszczenie.** W pracy podjęto próbę oceny wpływu temperatury na wyniki badań oleju napędowego metodą spektroskopii impedancyjnej. Wyniki wstępnych badań w stałej temperaturze wskazywały na możliwość użycia metody do wykrycia substancji szkodliwych dla silnika. Badania przedstawione w pracy wskazują zaś na to, że temperatura może zmieniać podobne właściwości elektryczne oleju napędowego co szkodliwe substancje, czyniąc temperaturę ważnym czynnikiem wpływającym. (**Wpływ temperatury na parametry letniego oleju napędowego mierzone metodą spektroskopii impedancyjnej**).*

Keywords: diesel, fuel, impedance spectroscopy, temperature.
Słowa kluczowe: olej napędowy, diesel, paliwo, spektroskopia impedancyjna, temperatura.

Introduction

Diesel is one of the most popular fuels in the world. It is used to drive compression-ignition engines which drive many types of vehicles, locomotives, ships and power generation plants. Diesel is the product of crude oil's distillation and it consists of about 75% saturated and 25% aromatic hydrocarbons [1]. During and after production many types of additives and enhancers may be added to maintain either safety during production and transportation processes as well as high quality of fuel for its consumers. In some regions of the world biocomponents are added to fuel. For example, there are 7% (V/V) of fatty acid methyl ester (FAME) in each type of diesel fuel commercially available in Poland.

Difficulties in analysing diesel fuel properties come from its various composition. Although its general composition may seem to be similar, there is no 100% repeatability of fuel being sold and there is not, nor will be, reference diesel fuel. Main reasons for this are that distillation like any process is never performed with the same efficiency as well as additives and enhancers added to fuel can change in time without any notice. These substances, although added in very small proportions, are able to change different fuel properties vitally and their composition is always a producer's secret.

To maintain all the important properties of automotive diesel fuel on the constant level, the EN 590 standard was developed and is valid within the European Union. It describes the physical properties that all diesel fuels must meet in order to be sold and test methods to verify them. The standard describes cetane index, cetane number, density, viscosity, lubricity, FAME content and more, as well as permissible amounts of undesirable substances such as sulphur, ash, carbon residue, and water.

Growing efficiency of modern diesel engines requires higher fuel purity in terms of lack of harmful for the engine substances. Some of the modern car engine constructions utilize very high fuel pressures exceeding 300 MPa. It is very likely that water contaminated fuel can cause severe damage to fuel rails in such extreme conditions. Although only 200 mg/kg of water in diesel is allowed by the EN 590 standard and this limit is usually fulfilled, it happens that fuel rails are damaged and require expensive repair because of water contaminated fuel. These cases may not occur very often, however they do happen. Furthermore, they prove that fuel filters are not able to stop all contaminants thus fuel quality seems to be the most important factor that provides long engine life.

Test method indicated in the EN 590 standard to determine water content in diesel fuel is the coulometric Karl Fischer titration (ISO 12937). It is a very precise method used in the range of 0.000–0.100% (m/m). However, it needs to be done in laboratory and repeated several times to acquire such high precision. One of the measuring methods that can be used *in situ* is impedance spectroscopy. It is a relatively cheap and fast method compared to titration, although it is not able to ensure equally high precision in each of its many applications. Among others, impedance spectroscopy can be used to either measure the amount or just indicate presence or absence of certain substances in mixtures. Measuring system can be quite simple and deployed as a hand-held device. Given the aforementioned limitations and advantages of impedance spectroscopy, the author decided to study the possibility of using it in the evaluation of water content in diesel fuel. Experimental tests that were performed under constant, well known temperature, showed that this method can be used to assess the water amount in diesel fuel [2]. However, temperature influence on measured impedance values of diesel has not been verified yet.

Diesel fuel can be treated as a dielectric in general. Diesel/biodiesel blends have been already successfully studied with the use of impedance spectroscopy [3], however temperature was not taken into consideration as an affecting factor. It is known that dielectric properties of matter can change significantly in function of temperature and that hydrocarbons have negative temperature coefficient of resistance. However, influence of additives and enhancers present in fuel is not known. Some of them are there to increase lubricity and distance possible to drive, while others are added to increase very low conductivity of diesel. Fuel with too low conductivity may be dangerous during transport because of the static charge that can be accumulated. Thus, transportation standard requires diesel's conductivity of about 50 pS/m. On the other hand there is a need to lower sulphur content in fuel to reduce environment pollution. Processes involved in producing ultra-low sulphur content diesel (ULSD) lower the conductivity of fuel also, therefore there is a need to further increase it to desirable level.

Work presented in this paper is focused on experimental verification of temperature influence on impedance of summer diesel fuel measured with the use of impedance spectroscopy (IS). Studies presented may be used to propose more detailed equivalent circuit of water contaminated diesel fuel in the future.

Material and methods

The main objective of the study was to verify experimentally that impedance of diesel fuel change in the function of temperature. Summer diesel was obtained from a gas station and was examined with the use of IS at the temperatures of: 6.5; 8.5; 11.5; 14; 15.5; 17 and 18.5 °C in a temperature controlling container. Impedance values were the same during measurement series with increasing and decreasing temperature. Once impedance of samples was measured in the function of frequency, the results were used to fit values of diesel equivalent circuit elements.

Diesel fuel samples

Diesel fuels are declared by producers as containing engine cleaning substances, as nearly completely sulphur-free or with a higher than standard cetane number (especially premium type fuels). Others are advertised as being capable of protecting engines against corrosion or improve their lubricity. The lack of full reproducibility of fuel itself combined with the fact that each additive and enhancer added during or after production is a secret of the producer make diesel studies difficult. Pure diesel fuel can be treated as dielectric [3] but each additive makes its dielectric properties more complex. Results presented in the paper correspond to this very examined summer fuel and although its chemical composition may be different than winter fuel because of the another additives and enhancers added. Further experiments will confirm the author's assumption that temperature changes diesel properties the same way despite the fuel type, whether it is regular, summer, winter or premium diesel.

Fig.1. Diesel fuel sample with immersed electrodes

Samples of 500 ml capacity were examined in a glass beakers (shown on Fig. 1). This rather high capacity was used in previous experiments to prevent unplanned, spontaneous changes of temperature during experiment. Although such situations did not take place, it was used again to preserve maximum possible repeatability of experiments. Temperature was monitored all the time and was approximately constant during each experiment.

Electrodes

Two the same circular parallel electrodes made of copper were used in the experiments. Electrodes had a surface area of 25 cm^2 each and were spaced by 1.95 mm and immersed in diesel samples. Figure 2 illustrates both electrodes and four supports providing the planned distance between them. It can be seen that the actual electrodes were in form of single copper layer (about 35 μm) on a laminate, the same that is usually used to build one sided electronic circuits. They were also designed and produced with the same processes as circuits normally are. For performing preliminary measurements electrodes presented in the paper were good enough, although it is obvious that better (in terms of being less chemically reactive) materials that can be used as electrodes exist, such as platinum, stainless steel or gold.

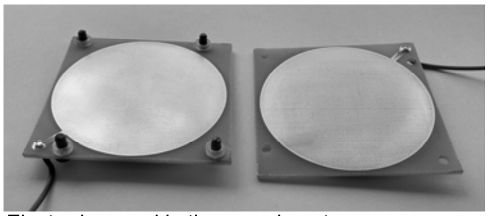

Fig.2. Electrodes used in the experiment

Electrodes were washed after each measurement with the use of water and acetone to clear out all the remains of diesel oil. To maintain reproducibility of the measurements, electrodes were also polished with water emery paper to remove any oxides. Micro-scale properties of copper were changed by this process but in macro-scale it had no negative influence on measured impedance. After such treatment electrodes were dried and used again.

Impedance spectroscopy

Prepared diesel fuel samples' impedance was measured in a frequency range of 0.1 Hz–1 kHz with a 700 mV RMS voltage. Although much lower values of voltage are normally used in electrochemical experiments, the chosen one was the lowest possible to maintain sufficient measuring conditions required by the system used, which was the EG&G/Princeton Applied Research electrochemical impedance spectroscopy laboratory system, consisting of the Potentiostat-Galvanostat 263A, Dual Phase Lock-In Amplifier 5210 and PowerSINE software. The system was calibrated according to the manufacturer's recommendations, moreover self calibration before each measurement was also performed. Each final measuring result was an average of four separate impedance measurements that were performed by the system. This number was chosen arbitrary and was a compromise between measurement quality and time, thus each experiment took about twenty minutes. Measured impedance in form of

$$Z^*(\omega) = Z'(\omega) - jZ''(\omega) \quad (1)$$

was used to fit equivalent circuit elements values [4]. The circuit was simple and contained resistor with parallel constant phase element (CPE). Such circuit was already used elsewhere to describe diesel properties [2, 3]. Impedance of such circuit is described by

$$Z^*(\omega) = \frac{R}{\left(1 + QR(j\omega)^n\right)}, \quad (2)$$

where Q is the admittance $1/|Z|$ at $\omega = 1$ rad/s and real n satisfies $0 \le n \le 1$.

Results and discussion

Examined diesel sample was exposed to aforementioned temperatures and measured using EIS system. It means that the same sample was measured many times to reject at the beginning any differences between samples. In terms of measured impedance, more reactive to temperature than fuel itself can be used additives which are the secret of producer and can be of various types, thus it is hard or impossible to make assumptions of precise electrochemical reactions taking place in diesel.

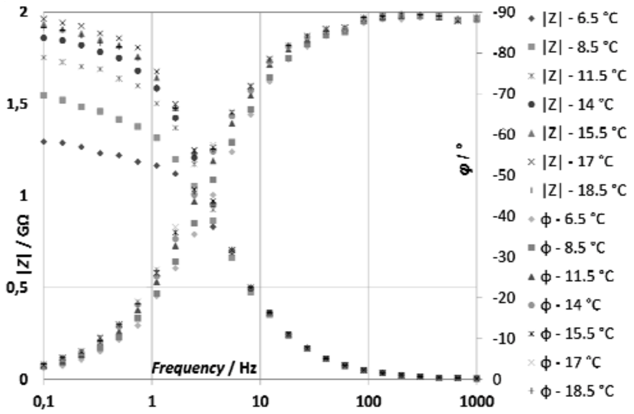

Fig.3. Bode plot of measured impedance modulus (|Z|) and phase angle (φ) of diesel fuel samples

Stray effects can be omitted as several measurement repeats did not reveal results exceeding measurement error of the system used. Figure 3 presents the Bode plot of measured impedance modulus (|Z|) and phase angle (φ) of diesel sample examined at different temperatures. At 0.1 Hz impedance modulus |Z| of diesel takes the value of 1.29 GΩ at 6.5 °C and close to 2 GΩ at higher temperatures. Differences between |Z| values are getting less visible with the raise of frequency and above 10 Hz they become indistinguishable. Further increasing frequency up to 100 kHz did not reveal spots where measured values would be distinguishable again. Similar (low) frequency range seems to be the most informative in case of transformer insulating oil dielectric spectroscopy [5]. Most visible differences between measured phase angle occur for the frequency range of 1–10 Hz, reaching over 12° at 3.67 Hz for the samples examined at 6.5 °C (-45.2°) and 17 °C (-57.4°). Characteristics curvature is similar to that related to circuits with parallel capacitor and resistor.

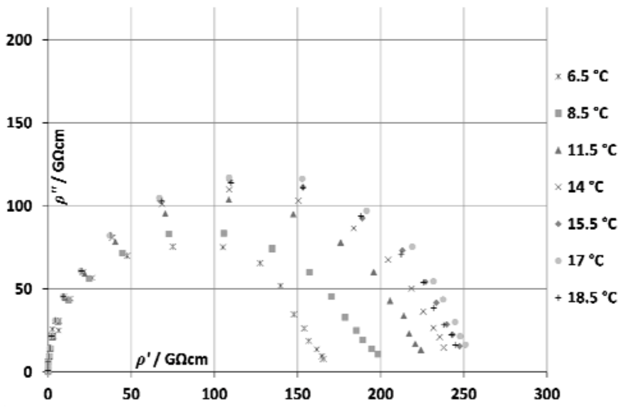

Fig.4. Impedance spectra, presented in terms of ρ'' versus ρ' complex plane plots

For the sake of comparison, impedance of sample measured at seven different temperatures was converted into complex resistivity $\rho^*(\omega)=\rho'(\omega)-\rho''(\omega)=Z^*/L$, where $L=h/A$ represents the measuring cell's geometrical factor with h being electrodes' spacing and A electrodes' surface area. Figure 4 presents calculated complex resistivity of samples at given temperatures. It can be seen that measured values form single semicircles. The centres of semicircles are a bit depressed which suggests that calculated capacitance will vary with frequency. Another approach to that phenomenon is the use of constant phase element instead of ideal capacitor in equivalent circuit that simulates impedance of diesel fuel more accurately. Although the right ends of semicircles are a bit raised, a further decrease in frequency did not reveal additional semicircles or other meaningful shapes (it is not shown in Fig. 4). This raise may be associated with diffusion phenomena occurring in the dielectric when a copper electrode is being used [6] and was not treated as a primary and dominant phenomenon. Dots presenting measurement results become more distant to ideal semicircles on the right side of the plot, despite aforementioned raise. It is related to the highest impedance values measured by the system and corresponding largest measurement error. The biggest semicircle represents resistivity of the diesel sample at 17 °C, close is the one at 18.5 °C, while the smallest one is drown by values of fuel at the lower investigated temperature. Note that as well as in the Fig. 3, with the higher temperature values characteristics are getting less distinguishable.

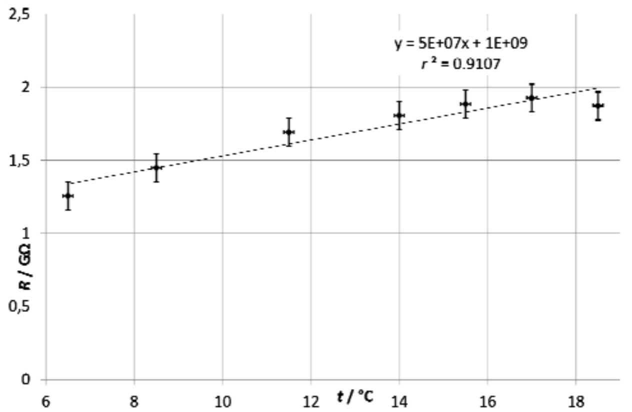

Fig.5. Calculated resistance R in function of temperature

Between impedance of diesel fuel sample at 17 and 18.5 °C is visible change of the trend. During preliminary studies sample was not exposed to higher temperatures than presented in this paper, thus this change is not verified as taking place at higher temperatures also. Nevertheless, measured increasing impedance modulus with the raise of temperature is something abnormal for hydrocarbons of which diesel is composed. It can be seen in three previous figures and the next one, Fig. 5, where calibration curve based on fitted resistance R value is presented. Further experiments should show how much calibration curve coefficients will vary for different examined diesel types, in example interim and winter.

Table 1 contains fitted values of equivalent circuit elements and the corresponding χ^2 modelling errors. Relative errors of fitting individual values did not exceed 5% in every examined sample. Note that the most changing value is the parallel resistivity in equivalent circuit with 1.255 GΩ in sample measured at 6.5 °C and 1.926 GΩ at 17 °C. Values representing the constant phase element Q and n have nearly the same values in each tested temperature. This observation may indicate that in more detailed equivalent circuit of diesel fuel that would include temperature influence on fuel's impedance, resistance would be the best choice to describe temperature coefficient. Future assessment of water content in diesel might require measurement of the fuel's temperature. This however, should not be considered as a serious problem as temperature measurements are very common nowadays.

Table 1. Fitted values of equivalent circuit elements and corresponding modelling errors

Temperature /°C	*R*/GΩ	*Q* /pS·s^n	*n*	Fitting χ^2
6.5	1.255	36.55	0.98417	0.02862
8.5	1.448	39.49	0.98266	0.00140
11.5	1.692	38.97	0.98459	0.00070
14	1.805	38.81	0.98409	0.00077
15.5	1.884	38.64	0.98444	0.00073
17	1.926	38.78	0.98379	0.00073
18.5	1.872	38.54	0.98439	0.00072

Conclusion

In this paper, the influence of temperature on impedance of summer diesel fuel measured with the use of impedance spectroscopy was presented. Experimental results were discussed and analysed. Fitted values of equivalent circuit as well as calibration curve were presented. They together show that temperature has a great impact on the evaluation of diesel fuel properties using impedance spectroscopy.

The most visible and unexpected result of performed experiments is that examined diesel fuel had positive temperature coefficient of resistance. As hydrocarbons do not have such property, some other substance present in fuel causes this phenomenon. Aforementioned additives that are used to increase fuel's conductivity are unknown, but there is a limited number of possible substances. It is known that enhancers are added to fuel in proportions of about several dozens parts per million. To increase conductivity of raw ULSD from about 11 pS/m to required 50 pS/m [7], conductive polymers can be used. Some of them can have conductivity of as high as good metal conductors. It is possible that low proportion of polymers in fuel (below 50 ppm) would change conductivity of mixture vitally. Moreover, some of the conductive polymers have positive temperature coefficient of resistance like metals do. These properties incline the author to assume that it is possible that some conductive polymers could be present in the examined diesel fuel. Future steps that would confirm or deny this thesis will require multiple different experiments as diesel has very heterogeneous composition. However, explanation of what causes diesel fuel to increase its resistance with the raise of temperature seems to be indispensable.

The encountered behaviour of diesel's impedance in the function of temperature does not have to mean that every further studies of its impedance are pointless. More experiments performed on different types of diesel fuel should answer the question whether all types of diesel behave the same way. With known temperature coefficient every other studies of diesel's electrical properties would still be valid.

Although the measuring voltage was relatively low (700 mV RMS) it might be sufficient to start the oxidation of electrodes when higher water contents are present in diesel. The main advantage of impedance spectroscopy as a measuring method is its ability to be used without changing any of the examined matter properties. Oxidation effect can cause the lack of measurement repeatability but also change composition of examined fuel thus the proper electrode materials should be used. Evaluation of the best possible material was not within the scope of this paper but is inevitable. Electrodes presented and used in this paper were just enough to perform preliminary studies. Circular electrodes made of stainless steel were used elsewhere [3] without reports about their oxidation. Experiment was repeated with the use of gold electrodes. Although fitted values of equivalent circuit were a bit different, examined diesel still had positive temperature coefficient of resistivity.

Given the above limitations, the author can still state that impedance spectroscopy of diesel fuel is reasonable and compare favourably with methods that require preparation of the samples and thus can only be performed in laboratory. Analysis of obtained results may be very difficult as exact composition of diesel may be unknown, but then impedance spectroscopy can be used as a comparative method. As mentioned before, there does not exist reference fuel, but changing one property of any diesel and measuring its impedance before and after that change will always be informative. Achieved accuracy of proposed methodology may not reach the same high level as laboratory methods used nowadays, however accuracy may be not the most important factor in each case. Future studies about diesel impedance behaviour in function of wider temperature range as well as other substances added should answer the question whether there is a possibility to conclude the harmfulness of fuel based on its measured impedance. The aforementioned advantages of using impedance spectroscopy makes it possible to build a device that could theoretically work *in situ*. After relatively fast measurements and proper calculations it could warn a user that contamination was found and examined diesel fuel can be potentially dangerous to his car. Even with the plausible low measurement precision of proposed device the author believes that sporadic fake alarms would be better than for example expensive repair of the fuel injection system in a modern car.

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