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

Abstract: In this chapter, an attempt is made to experimentally verify temperature influence on the evaluation of diesel fuel impedance with the use of electrochemical impedance spectroscopy. Previous test findings showed that this method can be used to detect contamination, such as water, in constant temperature. Tests presented in this chapter show that temperature itself can change electrical properties of diesel fuel similarly to water. Moreover, tested premium diesel, as a function of temperature, behaved oppositely from what hydrocarbons normally do. This makes temperature and additives present in fuel very important factors, which must be taken into consideration in the evaluation of any diesel properties using impedance spectroscopy.

Keywords: diesel, fuel, impedance spectroscopy, temperature

1 Introduction

Diesel is a very common fuel used to drive engines of vehicles, locomotives, ships and even electricity generation plants. It is a result of crude oil distillation and consists of several types of hydrocarbons (about 75 % saturated, 25 % aromatic), as well as various kinds of additives and enhancers added during or after production [1]. A few percent of fatty acid methyl ester (FAME) is also added in many countries to each fuel commercially available, for example, in Poland there is 7 % (V/V) of biocomponents.

Diesel analysis is very difficult in terms of interpreting obtained results. The encountered problems can be divided into two basic kinds. The first is that only very few research institutes are studying electrical properties of fuel, including its impedance. They have to be studied at refinery laboratories but the results are not publicly available. In such a case, information can only be obtained via private communication with people working in those facilities. The publicly available publications are mainly focused on fossil diesel rather than modern commercially sold fuel. The second kind of problems for a researcher is connected to the fact that the precise chemical composition of diesel is never the same. Responsible for this is the distillation, which, like any process, is never performed with 100 % efficiency. Additionally, the crude oil itself is not always the same. There are also a number of additives that make fuel safe to

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transport, improve its lubricity, reduce the risk of freezing in winter, etc. [2]. Used additives are always producers' secrets and may change at any time, even though there is an obvious need for a maintenance of the quality of diesel fuel that is being sold. Within the European Union the EN 590 standard is valid. It contains ranges of physical properties' permissible values and lists the corresponding test methods to verify them [3].

Premium-type diesel fuels are declared by producers as containing engine cleaning substances [4], improving lubricity [5], having a higher cetane number [6, 7] and being sulphur-free [7]. Some are advertised as being capable of protecting engines against corrosion and increasing the driving range in comparison to regular fuel [5]. Winter premium diesel should enable proper functioning of engines in lower ambient temperatures than regular diesel. Due to this fact it has to contain additional substances. Aforementioned characteristics make the analysis of premium-type fuel even more complicated. Nevertheless, premium diesel is believed to have more consistent content and this is the reason why it was chosen to be examined.

The improved efficiency and performance of diesel engines imply an increase in their sensitivity to all kinds of contaminants in the fuel. Very high pressures, exceeding 300 MPa, are featured by modern direct injection systems (called common rail). Such values would not be possible to achieve without rigorous fuel parameters that ensure the absence of substances aggressive towards metal alloys, of which engines are composed. Particularly newer engines' fuel rails are especially sensitive to water content in the fuel; therefore introducing additional contamination measurement methods seems to be necessary. Only 200 mg/kg of water is allowed by the aforementioned standard EN 590. The coulometric Karl Fischer titration method is used for this determination, as it allows obtaining precise results in the range of 0.003–0.100 % (m/m). The solubility limit of water in diesel is reported to be very low (100 ppm at 40°C [8]) but various kinds of additives can make it significantly higher [2]. Although amounts found in fuel can be considered as relatively low, water should still be treated as a dangerous contamination. Coulometric titration is a very precise method, though it cannot be used *in situ* as it needs to be performed in the laboratory and requires preparation of test samples. One of the various methods proposed for the evaluation of diesel fuel properties is impedance spectroscopy [9, 10] but it has not yet been used for water content assessment in any device. Such device, if designed as portable, could be used for example at the gas station to perform a quick preliminary measurement and indicate whether the examined fuel may be contaminated and should be sent to the laboratory for further, more precise studies.

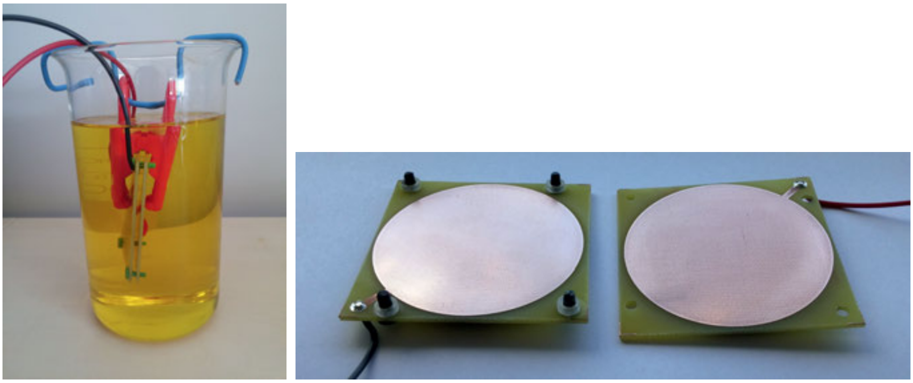
In order to propose a complete method of measuring water content as well as any other contaminant in diesel fuel with the use of impedance spectroscopy, evaluation of the influence of the temperature on diesel impedance is required. Pure diesel fuel can be treated as dielectric [9] but each additive makes its dielectric properties more complex. Hydrocarbons, of which diesel is composed, tend to lower their resistivity with the raise of temperature. Since around 2006 the production of ultra-low sulphur diesel (ULSD) has been growing and this kind of fuel dominates the market nowadays. Processes used to remove sulphur also significantly decrease fuel conductivity [2]. On the other hand, transportation standards require the conductivity of diesel to be above 50 pS/m [11] to allow static charge to dissipate. This is the reason for adding substances that will not noticeably change all fuel properties except conductivity. What kind of additives are added is a secret of the fuel producer. There are many substances available but their composition is also classified in general. It is known that additives are added in very small proportions, of a few tens to hundreds parts per million, and they can raise diesel conductivity tens of times [2]. This implies that additives may alter or overshadow the behavior of hydrocarbons impedance as a function of temperature, thus measurements of diesel impedance at different temperatures are very important to find their correlation. Once this correlation is found, it should be included in the diesel electric equivalent circuit in order to model fuel behavior at different temperatures. Such a model is necessary to assess fuel contamination with the use of a portable device based on impedance spectroscopy in the future.

2 Material and methods

The main objective of this study is to experimentally check the temperature influence on the impedance of premium summer diesel fuel measured with the use of impedance spectroscopy. Fuel samples were obtained from a gas station and were examined at different temperatures in a temperature controlling container. Impedance values were the same during measurement series with increasing and decreasing temperature. Once impedance of samples was measured as a function of frequency, the results were used to fit values of diesel equivalent circuit elements.

2.1 Diesel fuel samples

Diesel samples of 500 ml capacity were examined in glass beakers (shown in Fig. 1 (a)). This rather high capacity was used in previous experiments to prevent unplanned, spontaneous changes of temperature during the 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 (±0.1°C) during each experiment. Measurements were performed at 6.9°C, 9.3°C, 11.1°C, 14.5°C, 16.4°C, 18.4°C, 23°C and 26°C (±0.1°C). These values were chosen arbitrarily as preliminary ones just to cover the basic range. With the equipment the used temperature could be more precisely measured than be set; nevertheless, the measuring conditions were good enough to perform planned studies on the behavior of diesel impedance at different temperatures.



(a) (b)

Fig. 1: (a) Sample with immersed electrodes. (b) Electrodes used in the experiment.

2.2 Electrodes

Measurements were performed using two circular parallel electrodes made of gold-coated copper with a surface area of 25 cm^2 each, that were spaced by 2 mm. During experiments they were immersed in diesel samples. Fig. 1 (b) illustrates both electrodes and four supports providing the planned distance. As can be seen, the actual electrodes were in the form of a copper layer (35 µm) on a laminate, the same that is usually used to build single-layer electronic circuits. Leaving gold-coated electrodes immersed in diesel for long periods of time (up to 14 days) did not reveal any chemical reactions that would take place on their surface. This allowed for the assumption that cleaning electrodes after each measurement is not necessary to maintain repeatability, which was confirmed by later obtained results.

2.3 Impedance spectroscopy

Diesel fuel sample impedance was measured in the frequency range of 0.1–500 Hz with a 700-mV RMS voltage. A laboratory EG&G/Princeton Applied Research electrochemical impedance spectroscopy system was used, consisting of the 263A Potentiostat-Galvanostat, 5210 Dual Phase Lock-In Amplifier and PowerSINE software. The system was calibrated according to the manufacturer's recommendations and 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 arbitrarily and was a compromise between measurement quality and time; each experiment took about twenty minutes. Measured impedance in the form of

$$Z^*(\omega) = Z'(\omega) - jZ''(\omega) \tag{1}$$

was used to fit equivalent circuit element values [12]. The circuit was simple and contained a resistor with parallel constant phase element. Such circuit was already used elsewhere to describe diesel properties [9, 10]. Impedance of such circuit can be described by

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

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

3 Results and discussion

Diesel fuel samples were examined at temperatures listed in Section 2.1. Stray effects can be omitted as several measurement repeats did not reveal values exceeding the measurement error of the system used. Fig. 2 presents the Nyquist plot with the measured impedance of eight diesel samples. It can be seen that measured values form single semi-circles. The right ends of the semi-circles are a bit raised which suggests that within this low-frequency range there may be valuable information. However, further measurements at frequencies down to 1 mHz did not reveal second semi-circles and hence they were not included in the chapter. Although the used frequency range of 0.1–500 Hz may seem to be narrow, it was observed in the evaluation of another dielectric, namely transformer oil, that using a wider frequency range did not reveal more information [13]. The raise may be associated with diffusion phenomena occurring in the dielectric when a metal electrode is used [14] and it is not considered as a primary and dominant phenomenon. The centers of the semi-circles are a bit depressed, which suggests that the calculated capacitance would vary with frequency. It

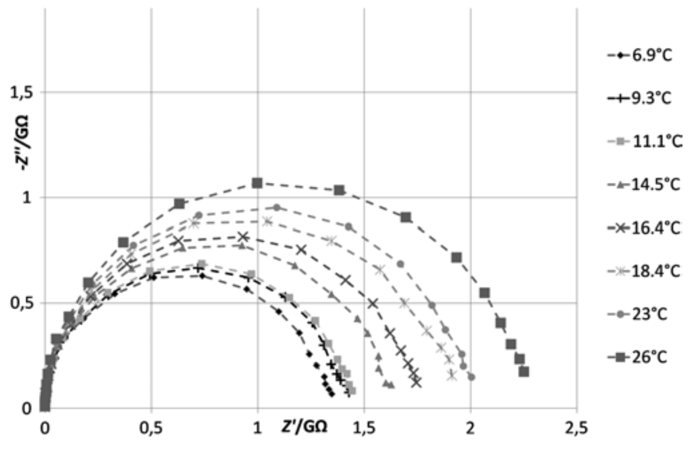


Fig. 2: Nyquist plot of examined diesel fuel samples.

confirms that choosing a simpler equivalent circuit consisting of a resistor and ideal capacitor would lead to greater fitting errors.

Note that with the raise of the temperature, the diesel resistivity increases – semi-circles have larger diameters. The real part of the measured impedance at 0.1 Hz revealed values in the range of 1.35 GΩ at 6.9°C to 2.25 GΩ at 26°C. Increasing resistivity with the raise of temperature is normally encountered in metals, and hydrocarbons should behave in the opposite way; their resistivity decreases with the increasing temperature. This may suggest that additives present in fuel responsible for increasing its conductivity play a leading role in impedance measurements. Electrode material and the fact that we used premium-type fuel were not the reasons for these unexpected results, as experiments with the use of copper electrodes and regular type diesel revealed the same resistivity behavior [15].

Since the diameters of semi-circles from the Nyquist plot were the only visible changes to their shape according to different temperatures, it was decided that overall resistance of the diesel sample can be used to propose the calibration curve that would model the temperature influence on the diesel's electrical properties. As can be seen in Fig. 3, the correlation of the samples' calculated resistance and temperature seems to be linear, with a quite good coefficient of determination ($r^2 = 0.9774$).

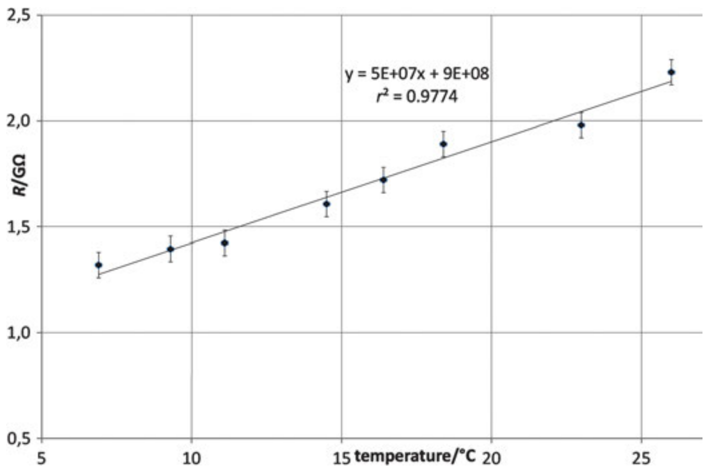


Fig. 3: Temperature dependence of fitted *R* values of studied diesel samples.

Table 1 contains fitted values of equivalent circuit elements and the corresponding χ^2 modeling errors. Relative errors of fitting individual values did not exceed 3.6 % in every examined sample. Note that the most changing value is the parallel resistivity of the equivalent circuit with 1.32 GΩ at 6.9°C and 2.229 GΩ at 26°C. Even though values of *Q* are also varying, it is hard to assess its trend, and therefore their differences are not

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

Temp. (°C)	R (GΩ)	Q (pSs^n)	n	Fitting (χ^2)
6.9	1.320	39.22	0.98216	0.00148
9.3	1.395	39.76	0.98600	0.00074
11.1	1.423	39.92	0.98282	0.00083
14.5	1.606	45.21	0.97990	0.00074
16.4	1.720	45.34	0.98268	0.00069
18.4	1.890	47.94	0.97489	0.00114
23	1.979	44.69	0.98356	0.00052
26	2.229	42.37	0.98278	0.00062

so significant as R values (up to about 20 % raise compared to 69 %) in the investigated temperature range.

A very important and unexpected result of the performed experiments is that the examined diesel fuel had a positive temperature coefficient of resistance. The experiment was repeated with the use of copper electrodes and regular (not premium) diesel. Although the fitted values of the equivalent circuit were a bit different, the examined fuel still had a positive temperature coefficient of resistance. Hydrocarbons do not have such property, thus some other substance present in the fuel caused this phenomenon. The exact chemical compositions of aforementioned additives that are used to increase the fuel's conductivity are unknown, although there is a limited number of possibilities. It is only known that these enhancers are added to fuel in proportions up to one hundred parts per million [2]. A conductivity increase of raw ULSD from about 11 pS/m to required 50 pS/m could be achieved with the addition of conductive polymers during the production. Some of these polymers can have very high conductivity, at the same level as good metal conductors. Thus, it is possible that even a very low proportion of polymers in fuel (below 50 ppm) would change conductivity of the mixture vitally. Moreover, some of the conductive polymers have a positive temperature coefficient of resistance, just like metals do. Given properties incline us to assume that it is possible that some conductive polymers could be present in the examined premium diesel fuel. Confirmation or rebuttal of this thesis will require multiple experiments with the use of different techniques, as diesel has a very heterogeneous composition. Nevertheless, an explanation of what causes diesel fuel to increase its resistivity with the raise of temperature seems to be indispensable.

The encountered behavior of diesel's impedance as a function of temperature does not mean that further studies of its impedance are pointless. Correlation between temperature and diesel's resistance in the examined range seems to be linear. This means that its influence is easy to predict and it definitely should be included in more detailed equivalent circuits that would model diesel's electric properties. Evaluation of different diesel fuel types should answer the question whether all types of diesel behave the same way, such as summer, winter, premium and regular diesel. If the temperature coefficients are, every new study of diesel's electrical properties will be valid.

4 Conclusion

In this chapter, the influence of temperature on impedance of premium summer diesel fuel measured with the use of impedance spectroscopy is presented. Experimental results are discussed and analyzed. A calibration curve as well as fitted values of the equivalent circuit are presented. They together show that temperature has a great impact on the impedance of diesel fuel.

Evaluation of the influence of temperature on diesel impedance is required in order to propose a complete method for measuring diesel contamination with the use of impedance spectroscopy. Given the limitations discussed in Section 3, we can still state that impedance spectroscopy of diesel fuel is reasonable and compares favorably with methods that require preparation of the samples and thus can only be performed in the laboratory. Analysis of the obtained results may be very difficult, as the exact composition of diesel is unknown; nevertheless, impedance spectroscopy can be used as a comparative method. As mentioned before, there does not exist nor will there ever be a reference fuel. However, changing only one property of any diesel and measuring its impedance before and after that change will always be informative. The proposed methodology may not reach the same high level of achieved accuracy as laboratory methods used nowadays; nevertheless, accuracy is not the most important factor in each case. Future studies about diesel impedance behavior in a wider temperature range with and without the addition of other substances should answer the question whether there is a possibility to indicate the harmfulness of fuel based on its measured impedance.

Advantages of using impedance spectroscopy as a measuring technique make 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 the examined diesel fuel can be potentially dangerous to his car. If such a device would be designed to serve an inspector at a gas station, then it would indicate that the examined fuel is somehow different and it definitely should be sent to the laboratory for the whole evaluation of its properties. Plausible relatively low measurement precision of the proposed device could cause sporadic fake alarms. However, we believe that fake alarms are still far better than potentially expensive repairs of the fuel injection system in a modern car.

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