XXI IMEKO World Congress “Measurement in Research and Industry”
August 30 – September 4, 2015, Prague, Czech Republic

EVALUATION OF WATER CONTENT IN DIESEL FUEL USING IMPEDANCE SPECTROSCOPY

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Abstract – In the paper an attempt was made to evaluate the water content in the diesel fuel using electrochemical impedance spectroscopy (EIS) to verify experimentally that it can be used as an *in situ*, fast and relatively cheap alternative compared with laboratory method widely used nowadays. Experimental results show that with some limitations EIS method can be used to estimate water content in diesel fuel.

Keywords: impedance spectroscopy, water content, diesel fuel, equivalent circuit

1. INTRODUCTION

Diesel is a very common fuel for engines driving many types of vehicles, locomotives, ships and even electricity generation plants. As a result of crude oil distillation it consists of several types of hydrocarbons (about 75% saturated and 25% aromatic) and various kinds of enhancers and additives added during production [1]. In many countries there is also a few percent of fatty acid methyl ester biodiesel added afterwards. For example, there are 7% (v/v) of bio-components in each type of fuel commercially available in Poland. Distillation, like any process, is never performed with 100% efficiency which is the main reason for that diesel fuels’ exact composition is always a bit different. In response to a demand for repetitive product quality sold within the European Union the EN 590 standard was developed. It describes the physical properties of diesel fuel and lists the corresponding test methods to verify each property.

Increasing engine efficiency implies an increase in their sensitivity to the contaminants in the fuel. Modern direct fuel injection systems (called common rail) feature very high pressures exceeding 300 MPa. Achieving such values would not be possible without rigorous fuel parameters, ensuring the absence of aggressive for metal alloys substances, of which engines are composed. Water content in diesel fuel can be very harmful for fuel rails especially in the newer engines. The aforementioned standard EN 590 allows 200 mg/kg of water content in diesel fuel and indicates coulometric Karl Fischer titration method used for this determination. By using this method we can determine the water content in diesel fuel in the range of 0.003–0.100% (m/m). The solubility limit of water in diesel fuel is very low (100 ppm at 40°C [2]) but various additives increase that limit. Nevertheless, water can still be treated as a contamination in fuel. To prevent an ingress of contaminants into the engine, fuel filters are used. However, their filtration capabilities are not fully effective. Damage to injection system can be very expensive to repair because replacement of damaged parts is often the only solution. With the engines’ increasing sensitivity to fuel contamination it is becoming more important not only to filter but also to detect undesirable substances at every possible stage. Engine failures due to water contamination may occur relatively rarely, nonetheless they really happen creating considerable expenses.

Diesel fuel may contain up to several dozen ppm of water which is normal at the time of production. Higher concentrations are usually caused by a failure either in the refinery, during transport or at a gas station. As water and diesel are immiscible, denser water settles at the bottom where it can be removed over time. This process is well known and used even in the refinery in case of failure for a further use of contaminated batch of fuel. It would not be a problem if the water amount at a solubility limit is fully safe for engines. However, this limit is not constant and depends on many factors, for example temperature and fuel improvers. It’s also not obvious to estimate and there is no certainty that during refuelling it is far enough from the limit permitted by the EN 590 standard.

Although coulometric titration is a well-known and precise method, it needs to be performed in laboratory and requires preparation of test samples. Consequently cannot be used *in situ*. Many different methods were successfully used in evaluation of diesel fuel properties and one of them is the impedance spectroscopy [3, 4] but it has not yet been used for water content determination. It can be a fast, relatively cheap and precise method used for either detection or assessment of various kinds of substances. It’s principles make it possible to be implemented in portable measurement devices. Along with many advantages of EIS method come it’s imperfections. The purpose of presented studies was to examine the possibility of using the aforementioned method for water content assessment in winter diesel fuel.

2. MATERIAL AND METHODS

The main objective of the study was to verify experimentally that different water contents in the diesel fuel are identifiable and thus measurable using impedance spectroscopy. The winter premium diesel fuel samples were obtained from a gas station and were examined before and after water addition.

2.1. *Winter premium diesel fuel*

Premium type fuels are advertised by producers in various ways. They are declared as sulphur-free, with a higher cetane number, containing engine cleaning substances, that protect against corrosion or improve lubricity. Each additive and enhancer added during or after production is a secret of the producer which, combined with the lack of full reproducibility of fuel itself makes the studies more difficult. From the electrical point of view pure diesel fuel can be treated as a dielectric [3] but every additive makes its electric and dielectric properties more complex.

Samples of 500 ml capacity were examined at a temperature of 27.5°C. This rather high capacity was intended to make the samples less sensitive to changes in ambient temperature. Whether with water addition or not samples were stirred with a magnetic stirrer to ensure the same measurement conditions. There are more efficient ways of mixing oil with water, but this particular way was supposed to be close to what can be found in everyday life, for example in car fuel tanks. Demineralized water was added to create samples with concentrations of 0.01, 0.02, 0.03, 0.04, 0.05 and 0.06% (v/v) above the amount already existing in bought fuel. The initial amount has been examined in the laboratory with the use of titration method and the result was 40 mg/kg [5] and corresponds to 0.00332% (v/v). Examined water amounts in diesel fuel samples expressed in terms of weight were equal to 40, 160, 281, 401, 522, 642, 763 mg/kg respectively. This means that from the third sample upwards the limit allowed by the EN 590 standard was exceeded.

2.2. *Impedance spectroscopy*

Impedance of prepared diesel fuel samples was measured in the frequency range of 0.1 Hz–1 kHz with the use of an EG&G/Princeton Applied Research laboratory system consisting of the 263A Potentiostat/Galvanostat, 5210 Dual Phase Lock-In Amplifier and PowerSINE software. Measurements were performed with a 300 mV RMS voltage. Two identical circular parallel electrodes made of copper with the surface area of 25 cm^2 each, spaced by 1.95 mm, were immersed in diesel samples. Equivalent circuit's elements values were fitted to measurement results using the EIS Spectrum Analyser [6].

Integrated circuits that are impedance converters on a single chip [7] exist apart from laboratory electrochemical impedance spectroscopy systems. They make the building of mobile EIS systems even easier. Whether with the use of such ICs or not, only true mobile impedance measurement system would ultimately make the evaluation of water content in diesel fuel using impedance spectroscopy an *in situ* method. Keeping that in mind, the research was performed using the best possible equipment to examine EIS method usefulness in the first place.

For the best possible fitting results, a modified Debye model was used. In place of an ideal capacitor a constant phase element (CPE) was used and a parallel resistor was retained. The resulting circuit has been used elsewhere for high quality fittings of examined real dielectric media [8]. The impedance of the parallel CPE-R network is:

$$|Z|(\omega) = Z'(\omega) - jZ''(\omega) = \frac{R}{1+QR(j\omega)^n}, \qquad (1)$$

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

3. RESULTS AND DISCUSSION

Figure 1 illustrates the measured impedance modulus ($|Z|$) as a function of frequency of 7 diesel samples containing up to 0.06% (v/v) of added water. It can be seen that for higher frequencies (i.e. >1 kHz) the measurement results would be indistinguishable. At the frequency of 1 kHz impedance modulus $|Z|$ is in the range of 5.13–5.26 MΩ. On the other hand, at lower frequencies the measured impedance values are approaching the sensitivity threshold of the measuring equipment, reaching the values from 551.27 MΩ to 1.861 GΩ at 0.1 Hz. Further decrease in frequency did not improve distinguishability between measured impedance moduli but they are already distinct up to about 20 Hz.

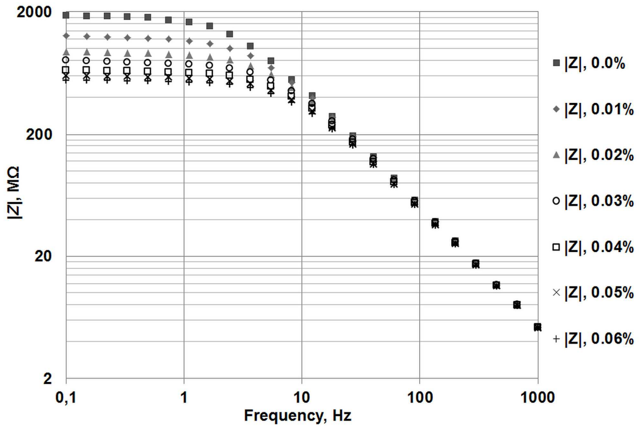

Fig. 1. Measured impedance modulus variation with frequency.

Measurement results are also shown in Fig. 2 which illustrates phase angle (φ) variation with frequency. Values tend to be indistinguishable at both lower and higher frequencies.

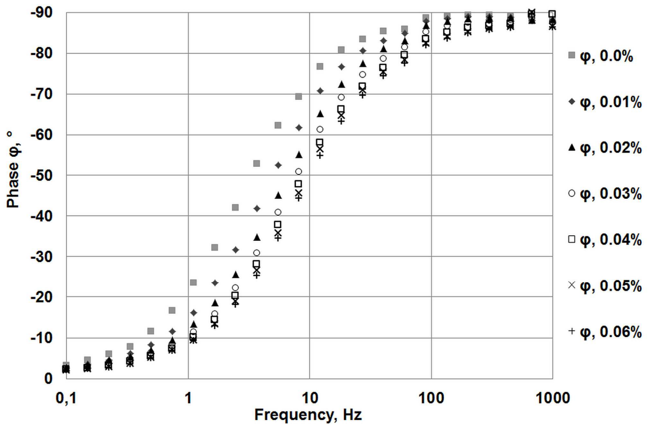

Fig. 2. Measured phase angle variation with frequency.

Phase angle values change along the frequency range the same way for all examined samples but it happens at different frequencies. The more water is added to diesel, the higher frequency it is at which sample’s phase angle decreases.

Another view on the examined samples is presented in Fig. 3, showing a Nyquist plot. Measured impedance values form single semicircles of different diameters. It is distinct from two-semicircle plots corresponding to much higher water content in petroleum water-in-oil emulsions [9] (not exactly diesel fuel). Centres of visible semicircles are depressed, which suggest that an ideal Debye R-C circuit, suitable for dielectrics, could not be used with satisfactory data fitting quality. Although the right ends of semicircles are a bit raised, a further decrease in frequency did not reveal second semicircles (not shown in Fig.3). This raise may be associated with diffusion occurring in the dielectric when a copper electrode is being used [10]. As it is not primary and dominant phenomenon, visible only at the few lowest measure frequencies, it was not considered in the building of an equivalent circuit for the examined diesel fuel samples.

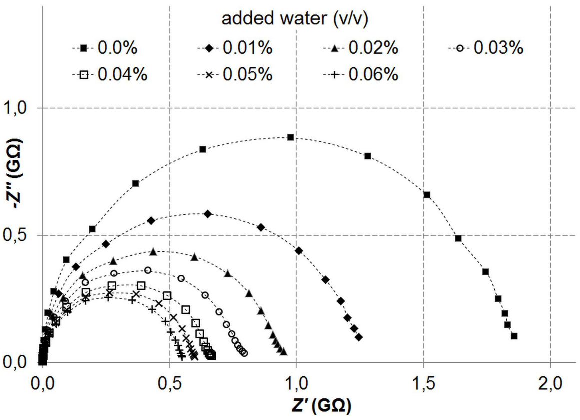

Fig. 3. Nyquist plot of examined diesel fuel samples.

Note that the differences between diesel fuel samples are getting smaller as the amount of water is increasing. Even though water and diesel fuel are immiscible, up to about 0.03% (v/v) of added water samples seemed to be homogeneous. At 0.05% water in diesel was clearly visible as very fine suspended droplets after stopping the stirrer. This order of water content is surely over water solubility limit in the examined winter premium diesel fuel. Much higher (>0.2%) concentrations also resulted in a visible change in transparency of the samples as they were stirred. Complex electrochemical phenomena occur in not homogenous, immiscible liquids. They are studied as an Interface between Two Immiscible Electrolyte Solutions (ITIES) and were not within the scope of this paper.

The impossibility of mixing higher water amounts with diesel fuel is apparent, especially when simple magnetic stirrer is used. Droplets of water are passing the space between electrodes during measurement. The higher water amount, the bigger the droplets are. It is where the space between electrodes should be considered to be an important factor. On the other hand, the longer distance between electrodes results in higher measured impedance values which may be affected by greater measurement error.

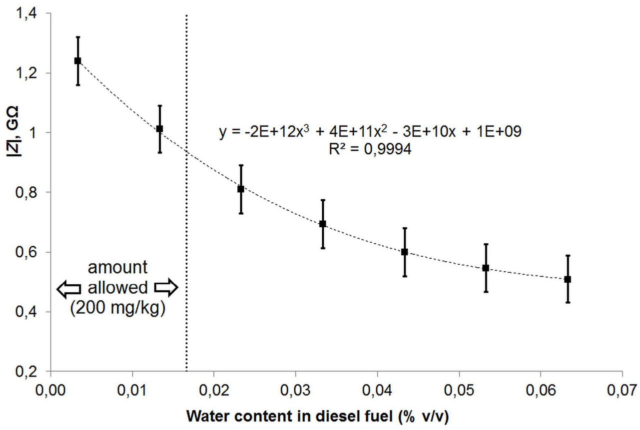

Fig. 4. Calibration curve - |Z| as a function of water content.

Figure 4 illustrates the calibration curve with a limit of detection at about 0.06% (v/v) of water content in diesel fuel. The impedance of samples with water amount up to about 0.1% were examined and the measurement results began to be indistinguishable. This trend is also visible in Fig. 4, in which the calibrations curve flattens out at higher water amounts. It might be considered as the used method’s limit of applicability. Impedance moduli $|Z|$ values taken to create the calibration curve were from the tops of semicircles (Fig. 3) which correspond to frequency of about 2.46 Hz. This choice resulted in the best equation approximation, but it is worth noting that for each different frequency the nature of $|Z|$ changes was similar. The equation of the calibration curve approximates measured values very well. However, it changes it’s slope at around 0.1% which makes extrapolation of calculated water content not possible above the values shown above.

Note that there is a slight change in the characteristics slope at around 0.03% (Fig. 4). It might be related to reaching water in diesel solubility limit. Since then, the differences between further measurements become smaller. Smaller measurement differences often worsen the precision of amount assessment. On the other hand, measuring such $|Z|$ values might strongly suggest that the allowed water amount in examined fuel is surely exceeded. Further change in cells’ geometric might improve the precision and extend the limit of measurability if necessary.

The fitted values of equivalent circuit elements and the corresponding χ^2 modelling errors are presented in Table 1.

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

Water content		R [GΩ]	Q [pS·s^n]	n	Fitting χ^2
[% v/v]	[mg/kg]				
0.00332	40	1.827	33.537	0.98572	0.00077
0.01332	160	1.2333	33.481	0.98645	0.00088
0.02332	281	0.92156	33.914	0.98517	0.00088
0.03332	401	0.77127	35.574	0.97918	0.00083
0.04332	522	0.65148	38.357	0.97222	0.00084
0.05332	642	0.59261	40.748	0.96576	0.00056
0.06332	763	0.54678	41.981	0.96307	0.00058

Relative errors of fitting individual elements did not exceed 1.65% in every examined sample. Note that along the change in characteristic's slope (Fig. 4) there is also a trend change in values of equivalent circuit elements. Until water solubility limit is reached, the only changing parameter seems to be parallel resistance *R*, decreasing significantly with the water content increase. Parameters *Q* and *n* do not vary up to 401 mg/kg of water in diesel, where *n* starts to decrease and *Q* starts to increase.

The oxidation of the copper electrodes was not the subject of research although it is clear that their surface will change especially with higher water amounts. After leaving electrodes immersed in samples containing high water amount (≥0.05%) for a long time (over 72 hours) the repeatability of measurement results was lost. Visible changes in surface colour came with different measurement results with the same water concentrations as with clear electrodes. Decreasing values of impedance modulus $|Z|$ with increasing water amount remained but obtained calibration curve would have flatter shape with smaller detection limit.

Parameter *n* does not change significantly whether water is added or not. Values of about 0.986–0.963 seems to be close to the unity which corresponds to an ideal capacitor. However, such low fitting errors χ^2 would not be obtained once a capacitor was used as the part of equivalent circuit.

4. CONCLUSIONS

In this paper, the use of electrochemical impedance spectroscopy method for water content in diesel fuel assessment was discussed. Experimental results were reported and analysed. Approximated calibration curve with high R^2 parameter as well as good fittings of equivalent circuit elements were presented. They together show that with some limitations EIS method can be used for the evaluation of water amount in diesel fuel.

The first encountered limitation is the top measurable amount of water. It seems to be close to 0.06% (v/v) or 763 mg/kg in terms of weight. Such high concentration is over 3.5 times greater than that allowed by the EN 590 standard. Thus, this limitation may not be an issue if the main purpose of the fuel examination with the use of proposed method would be just exceeded water amount detection. For this purpose, measuring a value of impedance modulus $|Z|$ at 2.46 Hz lower than about 1 GΩ appears to be sufficient to conclude the water content in examined fuel is exceeded dangerously for the modern diesel engine.

The second encountered limitation were electrodes made of metal. Oxidation effect can cause the lack of measurement repeatability. To avoid this problem the proper material should be used. Evaluation of the best possible electrodes to be used in examining diesel fuel water contamination was not within the scope of this paper. Circular electrodes made of stainless steel were used elsewhere [3] without reports about their oxidation. However, they were not exposed to water in addition to rather high measuring voltage that may, but does not have to, accelerate the oxidation process. Nevertheless, it would be worth checking their usability in water content assessment, as well as other kinds of electrodes, with platinum and gold that are popular in electrochemistry.

The third limitation is that within the evaluation an assumption was made that only water addition can change the impedance of diesel fuel in the above presented way. As the exact composition of each fuel commercially available is the secret of producer, it is impossible to define what kind of additional substances were added as improvers during production and what is their effect in electrochemical examination of the product. There are substances that can significantly increase the solubility limit of water in diesel. Examining fuel with such addition would answer the question whether more dissolved water can still be easily detectable and measurable with the use of impedance spectroscopy.

Given the above limitations, we can still state that electrochemical impedance spectroscopy studies of water contaminated diesel fuel are reasonable and compare favourably with other methods, especially these which requires preparation of the samples and can only be performed in laboratory. The greatest advantage of electrochemical impedance spectroscopy is that examination of matter can be performed without changing its properties and composition. This ability makes it possible to build a device that could examine fuel *in situ* and warn a customer or user that it can be potentially dangerous to the engine due to a contamination found. Even sporadic fake alarms would be better than a possible expensive repair of the sensitive injection system.

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