Full Length Article

Electrochemical impedance spectroscopy studies of gasoline oxidative stability – Attempt to devise new gasolines chemical stability index

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ABSTRACT

Fuels stored in storage tanks undergo aging processes. In particular, this applies to fuels containing biocomponents. The ability to quickly assess changes taking place in fuel is more and more critical due to the growing resources of fuels stored for a long time. Moreover, it is essential for maintaining the fuel quality. The purpose of this work was to develop a method enabling determination of the stability of gasolines containing biocomponents and allowing for early warning of quality deterioration. For that, the electrochemical impedance spectroscopy (EIS) was tested as it allows for fast, easy, and continuous determination of the gasoline quality. For that, the gasoline electrical parameters were determined by the EIS before and during aging. Then those results were compared with such physico-chemical parameters that change the most quickly during aging. It has been found that selected electrical parameters derived from the impedance spectra, namely, resistance, capacitance, relaxation time, and impedance values at a given frequency decrease with the aging time linearly or exponentially. The changes of those parameters indicate the formation of polar and/or ionic products and decrease of the fuel viscosity, increasing its conductivity. Furthermore, spectral studies of the samples indicate the formation of unsaturated and aromatic hydrocarbons, as well as –OH and C=O group-containing species. These observations are corroborating well with conclusions derived from the EIS studies. Notably, the obtained results indicate the correlation between electrical parameters and critical physicochemical properties of the fuel, thus suggesting possibility of applying the electrical parameters for gasoline quality assessment.

1. Introduction

The constantly growing demand for fuels makes it necessary to increase the strategic reserves of these fuels. Fuels available on the market must meet quality standards, which becomes more difficult because the quality requirements are becoming more and more restrictive. However, gasoline also shows low concentrations of heteroatoms and/or metals, which may introduce instability to it [1,2]. This instability may lead to increase in an oxidation process. This process begins during gasoline production and continues throughout transport and storage. It is causing formation of so called gum (polymeric species) due to reactions of unsaturated hydrocarbons [2]. Anti-oxidizers and metal deactivators added to gasoline delay this process but with only limited effectiveness. After a period of approximately 2 months the fuel is no longer guaranteed to meet the specifications. Therefore it is vital to control its quality,

especially during prolonged storage. For that, fuel properties should be regularly controlled and fuels with properties close to limit values should be released from reserves as soon as possible. If their properties deteriorate below limit values, they would need to be re-processed, thus incurring very high costs.

Gasoline is a mixture of different lightweight hydrocarbons (alkanes, cycloalkanes, alkenes, aromatic) with a carbon number between 4 and 12. Chemical compounds with unsaturated bonds are chemically unstable, and during storage, they can react with oxygen from the atmosphere and with each other, starting oxidation reactions [3,4]. The presence of biocomponents, e.g. monohydric alcohols or ethers in gasoline, can additionally deteriorate the resistance to oxidation of gasoline. Due to the presence of reactive groups, these compounds may react with each other, with oxygen and with water, which causes cloudiness of fuel, as well as the emulsion formation and then breaking, as well as the

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formation of substances with high molecular mass and their sedimentation on the bottom of the tank [1]. Products of oxidation reactions are named gums, and their high content may cause worsening of engine operation (due to deposits in some parts of the engine or supply system) and increasing in harmful substances emissions [5,6].

According to the literature [7], the reactions of gum formation can be explained by the free radical mechanism. During gasoline storage, autoxidation starts and proceeds at ambient temperature and initiates the polymerization of unsaturated compounds. Free radical produced by the breakdown of an unsaturated bond is the initiating factor of such reactions. There is also a second possible mechanism, so-called oxidative degradation. However, this type of oxidation occurs at high temperatures in the engine when the fuel is in contact with the hot surface of the engine's elements [8].

Chemical stability of gasoline depends on its composition, for example, on the type of olefins and their amount in the fuel. This chemical composition is closely related to the origin of the petroleum and the type of refining processes used to produce gasoline components [9,10]. Generally, it is stated that chemical stability decreases in the order of paraffins, naphthenes, aromatics, olefins, and diolefins [4]. Reactions of gasoline components can be promoted by contact with some metals, e.g. copper. During long-term contact of fuel with the surface of tanks, small amounts of metal dissolve and pass into the liquid phase. Metal ions catalyse radical reactions of oxidation that accelerate gums formation [11], such oxidation is higher when gasoline contains higher concentration (20–25%, *v/v*) of anhydrous ethanol [12]. Another factor that may influence the oxidation of fuel is the presence of water. Water can co-exist with gasoline in various forms, for example, as dissolved water, emulsified water, or as a separated phase on the bottom or walls of the tank. The presence of water in storage tanks promotes microbial growth and can cause hydrolysis of some components. Microorganisms degrade chemical compounds with the use of electron acceptors, and thus they favor the deterioration of fuel properties [13].

Due to the sensitivity of gasoline to different oxidative factors during long-term storage, the quality of stored fuel is monitored by periodic checking the values of selected physicochemical parameters e.g. oxidative stability verified with the use of induction period method, vapour pressure, density at 15 °C or gums content. These tests are standardized, and values of particular parameters are determined by the appropriate standard for fuels (for gasoline EN 228 standard). The disadvantage of such tests is that they are laborious and time-consuming and often involve the use of expensive specialized instruments. For this reason, it is necessary to develop new, less complicated, and faster methods for gasoline quality monitoring with time. Considering the previous, in the literature, we can find different studies concerning this problem. Most research works refer to spectroscopic methods like near-infrared (NIR) and middle infrared spectroscopy (MIR) [14,15,16]. Also, alternative techniques have been used for the determination of gasoline properties. For instance, in order to control the quality of commercial gasoline, the Hydrogen Nuclear Magnetic Resonance spectroscopic fingerprinting are coupled with pattern-recognition multivariate Soft Independent Modelling of Class Analogy chemometric analysis has been used [17].

The dielectric spectroscopy and electrochemical impedance spectroscopy (EIS) are both techniques based on the applying sinusoidal alternate voltage of varying frequency to the sample under study [18,19,20]. Then the alternate current resulting from the system excitation is recorded. The change of current signal amplitude and its phase shift in respect to the excitation voltage signal depending on the signal frequency is then analyzed. This leads to the measurement of the complex impedance of the system in the broad frequency range (from mHz to MHz). The analysis of the resulting impedance spectra gives insight into electrical properties and transport processes occurring in the studied samples. This technique is widely used for studying charge transport properties, relaxation effect and charge transfer processes in a wide range of samples, from solids to liquids and from dielectrics to

conductors [18]. Importantly, samples with very low conductivity can be studied via this technique as the broad frequency range of the excitation signal used allows for following not only conductive (charge carrier's migration) but also capacitive effects (dipole orientation and relaxation) [18]. It has been applied to studies of corrosion processes, electron transport in polymers, dynamics in liquid crystals, etc. [17,19]. In the field of fuel research, the dielectric spectroscopy has been employed to determine the octane number of gasoline samples [21]. Use of the piezoelectric resonator with the lateral electric field was reported to develop a method for analysis of the gasoline octane number [22]. Additionally, it has been proposed to use changes in complex permittivity to monitor lubricating oil quality [23]. Furthermore, changes in the capacitance of petroleum products were applied to determine their properties. Such experiments have been carried out [24] to detect the debris in lubricating oil as well as to determine the contamination of engine oil with diesel oil and soot [25]. Moreover, impedance changes were used to study biodiesel water content [26] dielectric property [27,28], biodiesel/diesel blend composition [29], and to characterize the oil and water-in-oil emulsions [30]. Recently studies of the impedance spectroscopy have also been used to study the aging process of biodiesel fuel [31].

Although methods based on changes of impedance are widely used for determining dielectric properties of different materials (solids, colloids, solutions) there is a lack of information about their use as indicators of processes of gasoline aging. The presented research results discuss the influence of the oxidation process of gasoline on its impedance spectra and indicate that impedance measurements can be used as a tool to follow the gasoline aging process. Simultaneously UV–vis and FT-IR spectral studies were performed on the aged gasoline samples. The combination of the techniques indicates the formation of charged/polar species during gasoline aging together with unsaturated and aromatic hydrocarbons. Notably, the obtained results indicate the correlation between electrical parameters and critical physico-chemical properties of the fuel, thus suggesting the possibility of applying the electrical parameters for gasoline quality assessment.

2. Materials and methods

The research was conducted for commercial gasoline with 95 octane number, containing 4.6% of ethyl alcohol and 4.7% of ethyl tertbutyl ether. The physicochemical properties of gasoline were tested in accordance with the PN-EN 228:2013–04 standard [32,33].

In order to determine the changes occurring in gasoline during the oxidation process, the processes of accelerated aging of fuel was carried out. Oxidation of fuel has been carried out with the use of ROFOX Four apparatus (Rofa). This apparatus is used in laboratories to determine the gasoline resistance to oxidation according to EN ISO 7536 standard [34,35].

The gasoline samples of 100 cm³ each were placed in a pressure bomb (Fig. 1). The bombs were filled with oxygen under a pressure of 690–705 kPa at a temperature of 15 °C to 25 °C. The oxidation process has been performed at the temperature 100 ± 2 °C by 3, 6, 12, 18, and 24 h using apparatus described in the EN ISO 7536 standard.

The literature studies and the results of research projects conducted in the Automotive Industry Institute have enabled select key parameters like oxidation stability with the use of PetroOXY method and gums content [2,35]. These parameters are essential to guarantee the quality of stored gasoline. After oxidation, the selected physicochemical parameters and impedance spectra of the aged gasoline were measured. The results were compared with those obtained for a reference sample (fresh gasoline before oxidation). The samples of gasoline were aged under the same conditions, and only aging time was different. Selected physicochemical properties of oxidized samples were then determined, according to standards presented in Table 1.

It is known that the composition of the gasoline and other hydrocarbon mixtures (e.g. lubricants and engine oils) affects its conductivity,
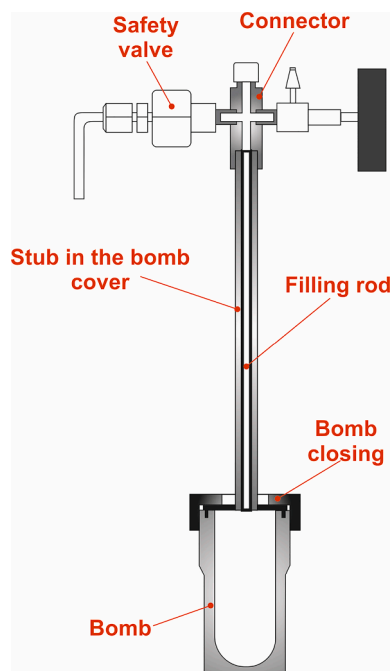
Fig. 1. Schematic view of the pressure bomb for gasoline accelerated oxidation in accordance with [34].

Table 1
Analytical methods used for gasoline analysis.

Parameter	Apparatus	Analytical method
Oxidation stability in small scale (PetroOxy)	Petrotest	EN 16,091
Gums content	Petrotest	EN ISO 6246
Density at 15 °C	DMA 4500 M densitometer (Anton Paar)	EN ISO 12,185
Refractive index at 20 °C	Abbemat 380 refractometer (Anton Parr)	–

especially the presence of more polar and/or charged species would influence this parameter [29,30,36]. The mechanism of this effect is based on faster migration of more polar or charged species in the medium under the applied electric field. Formation of polar or ionic species would also lead to formation of induced dipole moments in the hydrocarbons thus further facilitating charge transport under applied electric field. A similar effect can also be observed if the charged particles (soot, micelles) are present in a non-polar medium [37,38]. Applying an alternating sinusoidal voltage with a given amplitude and frequency to the electrode leads to a system response in the form of current flow in time. The ratio of the excitation signal (voltage) to the response (current) is called impedance. Impedance is a complex value and consists of real (Z_{re}) and imaginary (Z_{im}) parts. Their value depends on the excitation signal frequency. Data obtained during impedance measurements are typically presented in the form of an imaginary part of impedance dependence on its real part, $Z_{im} = f(Z_{re})$. Such a plot is commonly known as the Nyquist plot.

To investigate the influence of the aging process on the gasoline, 5 mL samples of gasoline was aged for different periods. A measuring probe was then placed in the vessel containing a sample. The probe had two parallel platinum plate electrodes with an area of 0.25 cm². These electrodes were separated by 1.5 mm. The measurement system is described in detail elsewhere [31].

EIS spectra (EIS) of the gasoline samples were recorded with the use of the SP-300 potentiostat (Bio-Logic, France) and the EC-Lab v. 10 software (Bio-Logic, France). Measurements were performed in a two-electrode system by applying a sinusoidal potential to the working electrode. This potential amplitude of 0.4 V, open circuit potential, and frequency in the range from 10 mHz to 3 MHz with a total of 50 logarithmically spaced frequency points were used. Recorded spectra for each sample of gasoline were processed and analysed with the use of EC-Lab v. 10 software. The recorded spectra were subsequently fitted to an electrical model consisting of a resistor in parallel with a capacitor. This procedure allowed obtaining of the selected electrical parameters of the studied sample, namely, its resistance, *R*, relaxation time, τ and capacitance, *C*. The results of the EIS measurements are presented in Table 2. The obtained results were then correlated with physico-chemical parameters of the aged gasoline measured with the methods described above (Table 3).

The FT-IR spectra of the gasoline samples have been measured by the Vertex 80v spectrophotometer of Bruker (Ettingen, Germany) with DLATGS detector by using ATR mode with multiple-reflection ATR accessory of the same company with ZeSe prism. The spectra were recorded during 1024 scan with a spectral resolution of 2 cm^{-1}. The spectra were recorded and processed with Opus v 7.2 software of the same manufacturer.

All UV–vis spectra were performed by using UV-2501 spectrophotometer of Shimadzu (Kyoto, Japan) driven by UVProbe software of the same manufacturer. All spectra were recorded with a 1 nm resolution.

3. Results and discussion

EIS spectra of non-aged and series of aged PB95 gasoline samples are presented in the form of Nyquist plots in the Fig. 2. All the plots have the characteristic shape of the semicircle crossing Z_{re} axis in two points, including $Z_{re} \sim 0$ Ω. Furthermore, it illustrates that the impedance values of the non-aged gasoline are very high, reaching gigaohms. This is consistent with the high electrical resistance of the studied liquid and is expected for non-polar liquid such as the gasoline. During the aging process, systematic decrease of both real and imaginary parts of impedance is visible. This leads to a decrease in the diameter of the semicircle on respective Nyquist plots indicating significant changes of electrical parameters of the studied gasoline samples.

The recorded curves well fitted with the described model electrical circuit composed of a resistor in parallel with a capacitor. Such a circuit is often used to describe impedance results of uniform liquids and solids [25,29] following the Debye model [18]. The radius of the observed semicircle corresponds to the resistance of the studied material, while the frequency (f_0) at which maximum of the semicircle is observed corresponds to the relaxation time of the charge carrier or dipoles (τ) in the studied medium [29].

Fitting resulted in obtaining the values of resistance, *R*, of the resistor, as well as capacitance, *C*, of the model circuit capacitor for all non-aged and aged gasoline samples. Furthermore, based on frequency, f_0, relaxation time of the charge carriers, τ, in the studied sample has been calculated by using equation (1):

Table 2
Selected electrical parameters of the gasoline calculated from impedance spectra as a function of the aging time.

Aging time[h]	Resistance [GΩ]	Relaxation time[s]	Capacitance [nF]	Z_{re}at 0.07 Hz [GΩ]	-Z_{im}at 0.15 Hz [GΩ]
0	17.47 ± 0.09	2.27 ± 0.03	0.1154 ± 0.0003	10.19 ± 0.09	7.20 ± 0.07
3	11.67 ± 0.07	1.53 ± 0.05	0.1169 ± 0.0004	8.43 ± 0.08	5.66 ± 0.09
12	4.54 ± 0.01	0.47 ± 0.04	0.1134 ± 0.0003	4.34 ± 0.05	1.83 ± 0.04
24	0.26 ± 0.01	0.03 ± 0.01	0.1121 ± 0.0005	0.26 ± 0.06	0.01 ± 0.01

Table 3
Selected physico-chemical parameters of gasoline as function of aging time.

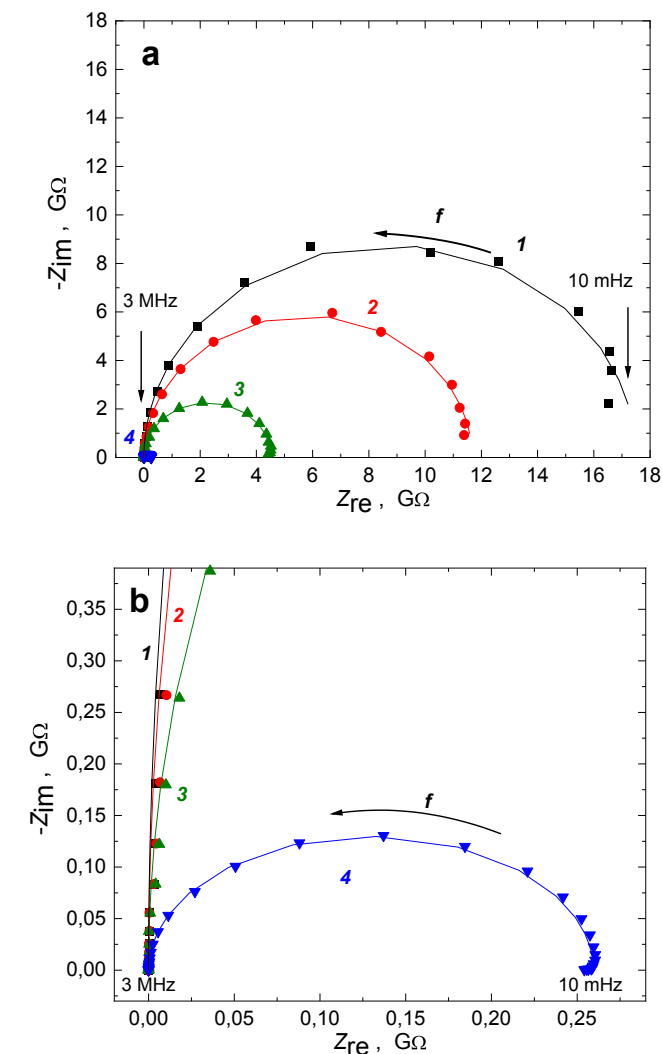| Aging time[h]	Oxidation stability PetroOXY[min]	Gums concentration [mg mL^{-1}]	Refractive index at 20 °C	Density at 15 °C[kg m^{-3}]
0	37.3 ± 0.3	1.0 ± 1.6	1.4118 ± 0.0002	736.9 ± 0.2
3	24.0 ± 0.3	1.0 ± 1.6	1.4138 ± 0.0002	740.8 ± 0.2
12	12.0 ± 0.3	7.8 ± 1.6	1.4193 ± 0.0002	747.8 ± 0.2
24	8.7 ± 0.3	185.0 ± 1.6	1.4223 ± 0.0002	755.8 ± 0.2

Fig. 2. (a) Nyquist plot of the (1) non-aged and aged for (2) 3 h, (3) 12 h, and (4) 24 h gasoline samples recorded at open circuit potential in the frequency range from 10 mHz to 3 MHz. (b) Magnification of the Nyquist plot recorded for sample aged for 24 h. Solid lines show curves obtained through fitting using an equivalent circuit.

$$\tau = \frac{1}{2\pi f_0} \tag{1}$$

The obtained results are summarized in the Table 2.

As shown, the values of capacitance measured for non-aged gasoline were small, equaling to 0.1154 nF. This indicates that the sample contains minimal amount of charge carriers, which is consistent with the non-ionic character sample. During the aging process, a further decrease

in this value was observed (Table 2). This suggests that aging process introduces changes in the charge carrier concentrations.

The value of the τ observed for the non-aged gasoline is relatively high and equals 2.3 s. It dropped rapidly with aging time. A 30% drop was observed after only 3 h of aging. The relaxation time reaches 0.03 s after 24-h of aging. This indicated an important change in viscosity and/or polarity during aging process.

The Nyquist plot does not explicitly show information on excitation signal frequency dependence of impedance. In order to obtain a clearer picture of the observed changes dependence a real, Z_{re}, and imaginary, Z_{im}, parts of impedance were shown as a function of excitation signal frequency (Fig. 3). The obtained results indicated that essential changes in both Z_{re} and Z_{im} during gasoline aging were observed mostly at low frequencies (below 10 Hz). At higher frequencies comparatively much less pronounced changes were observed. This effect indicated that the capacitive behavior of the sample at high frequencies is not much affected by the formation of oxidation products in the samples. On the other hand, gasoline oxidation leads mainly to changes in the resistive behavior of the studied samples.

From the practical point of view, measurement of impedance at a single frequency is much faster than the recording of the full impedance spectrum. We aimed to find an easy and fast way to assess quality changes in gasoline. Thus we concentrated our further discussion on the regions of the impedance spectra where changes to the impedance were the most pronounced. That way, one can follow changes in the electrical parameters of the fuel during aging more precisely. Therefore, all aged and non-aged samples, imaginary and real impedance were measured at constant low frequencies. Real impedance was measured at 70 mHz, and imaginary impedance was measured at 150 mHz. The selected frequencies were located in the regions where changes of the impedance values with aging were most pronounced (Table 2).

The gasoline resistances, R, values extracted from Nyquist plots (Table 2) indicated very high resistance values for non-aged samples reaching 17.5 GΩ. After the forced aging process, the R value decreased. Notably, first to 11.67 GΩ (3 h aging) and finally to 0.3 GΩ for gasoline (24 h aging).

The very high R values observed are expected for non-conducting medium like gasoline containing only small amount of polar additives and charged species. The observed values are in line with values observed for other hydrocarbon liquids such as industrial lubricants or petroleum [29,30,36]. The important decrease of R after aging is most probably indicative of polar and/or ionic product formation. The increased polar compounds concentration would then increase
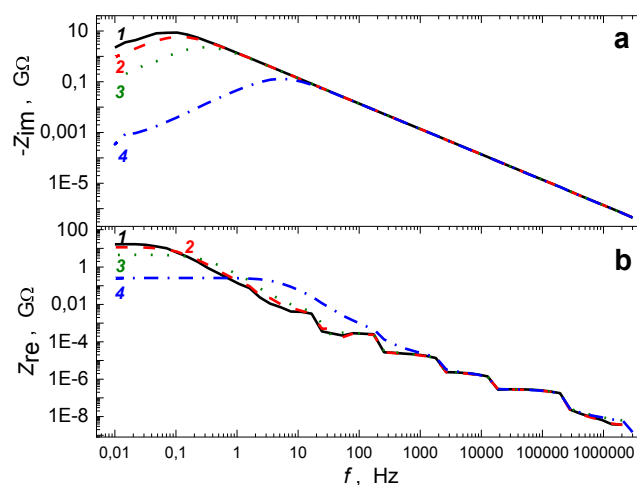

Fig. 3. Plots of (a) real, Z_{re}, and (b) imaginary, Z_{im}, parts of impedance as a function of the logarithm of excitation signal frequency recorded for the (1) non-aged and aged for (2) 3 h, (3) 12 h, and (4) 24 h gasoline samples recorded at open circuit potential in the frequency range from 10 mHz to 3 MHz.

conductivity of the studied gasoline samples through increased migration of the polar/charged species in the applied electric field, as well as through induced dipole formation of the hydrocarbons further facilitating charge transport [29,30,36,39]. Qualitatively similar effect has been observed after addition of polar biodiesel components to the diesel oil [29]. The FT-IR and UV–vis spectral studies confirm formation of such oxygen-containing polar species and detail of those studies are presented below.

In order to better understand the basis of observed electrochemical parameters changes during the gasoline aging process, a series of physico-chemical parameters of the studied samples before and during the aging process were also measured and compared. Those studies were also aimed at establishing the possibility of using electrical parameters obtained from EIS measurements to follow the gasoline aging process in real applications. The measured parameters included: oxidation stability PetroOXY, gums concentration, refractive index at 20 °C, and density at 15 °C. The parameters mentioned are typically used for gasoline quality estimation and were measured according to the respective legal norms. Table 3 summarized selected physico-chemical parameters of the gasoline samples recorded before and during the aging process at times used for impedance studies are reported.

It shows that all studied electrical parameters values decrease with the aging time (Table 2). Values of R, Z_{im}, and τ decrease exponentially with the gasoline aging time, while the character of the Z_{re} dependence on the aging time seems to be more of linear nature. Interestingly, the value of the capacitance first increases with time up to 3 h and then decreases. From the practical point of view, it can be stated that resistance, real and imaginary parts of the impedance at given frequency and relaxation time can be used for evaluation of the gasoline aging in practical situations. On the other hand, capacitance is much less suited for such evaluation.

In the case of the other estimated physico-chemical parameters of the gasoline data shown in Fig. 4a indicated that an increase of the aging time leads to a decrease of the oxidation stability and increase of the gums concentration. While a decrease of the oxidation stability follows an exponential trend, the concentration of the gums increases only slowly for the first 12 h of the process. Then this parameter increased rapidly. On the other hand, density and refractive index values increase in an almost linear fashion with gasoline aging time (Fig. 4b). The observed increase of the gasoline sample density, refractive index as well as gums concentration is caused by the formation of the aging products with higher molecular mass. Lowering of the oxidation stability signifies the formation of products containing unsaturated bonds and/or heteroatoms, which shall be more prone to oxidation than pure hydrocarbons present in the non-aged gasoline samples.

In Fig. 5, a correlation of the sample resistance, real and imaginary part of impedance at a constant frequency, as well as relaxation time with selected physico-chemical parameters of the aged gasoline, is presented.

The correlation results show that electrical parameters Z_{re} and Z_{im}, as well as R and τ calculated from the impedance measurements depend in a similar way on the oxidative stability PetroOXY of the gasoline samples (Fig. 5a). With the decrease of the oxidation stability, the values of all those parameters also decrease. Interestingly, the lower the oxidation stability the faster change of the electrical parameters is observed. Thus accumulation effect is evident from this correlation.

The electrical parameters decrease with an increase in the gasoline density measured at 15 °C (Fig. 5b). The Z_{re} and Z_{im} measured at constant frequency decrease practically linearly with the gasoline density increase, while R and τ decrease follows a rather exponential trend.

Interestingly, all parameters derived from the impedance measurements decrease linearly with an increase of the gasoline refractive index measured at 20 °C (Fig. 5c). The changes of R and τ are more than two times more sensitive to the changes in refractive index than changes of Z_{re}, or Z_{im}. This suggests that they may be especially useful for the estimation of the fuel quality changes.

As can be seen in Fig. 5d, all studied electrical parameters (R, Z_{re}, Z_{im} and τ) decrease drastically with the increase of the concentration of the gums up to a value of ca. 8 mg mL^{-1}. Above this concentration, the decrease of the electrical parameters was much slower. This is in agreement with the observed trend in gums concentration change with aging time (Fig. 5a). This suggests that most essential changes in the electrical parameters of the gasoline sample are connected with the processes occurring at the early stage of the aging process. In this phase, polar products of the gasoline oxidation together with short-chain polymers or cyclic hydrocarbons are formed. Then, the formed species react with each other and form bigger polymeric species. This has a smaller influence on the electrical properties of the sample and, therefore, smaller dependence of the parameters calculated from the EIS measurements on the gums concentrations is observed in this phase. This suggests that electrical parameters of the gasoline are more sensitive to the changes observed at the early stages of oxidation and, therefore, may be used to evaluate the fuel properties at the early stages of the aging.

In order to better understand the results obtained from the EIS studies, we have performed UV–vis and FT-IR spectroscopy measurements of the aged gasoline samples. The results of the spectral studies are summarized in Fig. 6. The UV–vis spectra of the gasoline before aging (Fig. 6a and b) exhibit a strong band below 230 nm and a set of overlapping bands between 235 and 300 nm. The band below 230 nm can be ascribed to transitions originating from unsaturated hydrocarbons, oxygen-containing hydrocarbons, carbonyl group-containing
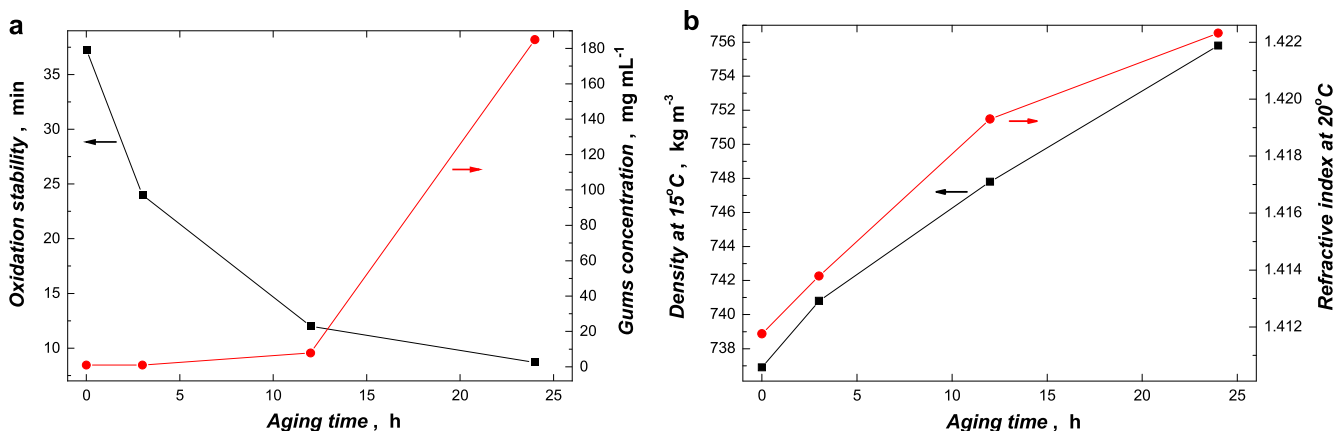

Fig. 4. Dependence of the (a) oxidation stability PetroOXY and gums concentration, as well as (b) density at 15 °C and refractive index at 20 °C as a function of the aging time.
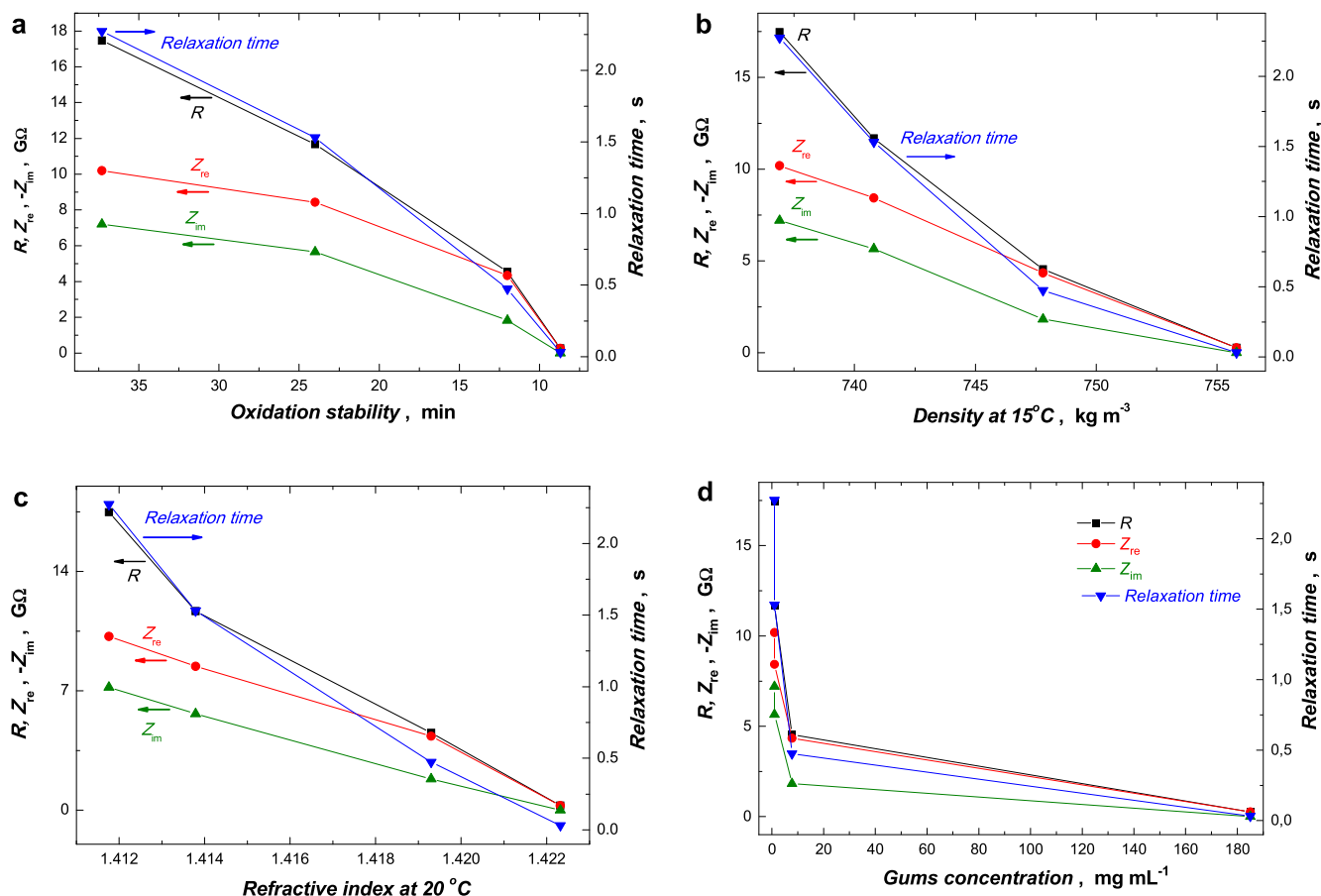
Fig. 5. Dependence of resistance, R, real part of the impedance, Z_{re} at 70 mHz, the imaginary part of the impedance, Z_{im}, at 150 mHz, and relaxation time, τ, determined from impedance measurements on physico-chemical parameters typically used for estimation of the quality of the gasoline: (a) oxidation stability PetroOXY, (b) density at 15 °C, (c) refractive index at 20 °C as well as (d) gums concentration.

compounds, as well as signals from additives (ethyl alcohol and ethyl tertbutyl ether)[40,41]. The multiple bands between 235 and 300 indicate the presence of aromatic systems in the gasoline sample [40,41]. The aging of the samples does not change the general form of the observed spectra. However, a small decrease band below 230 nm can be seen (Fig. 6a) together with a small redshift of the absorption. This indicates most probably saturation of the unsaturated hydrocarbons due to their oxidation leading to the formation of saturated, oxygen-containing species which absorb at lower wavelengths. On the other hand, the formation of carbonyl and carboxyl groups absorbing at higher wavelengths may lead to an observed redshift of the absorption edge of this band.

The intensity of bands observed between 235 and 300 nm increase after 3 h of aging, then decrease and then importantly increases for the samples aged 24 h. Interestingly shape of the bands is not altered during the process. This points to quite the complex formation of aromatic hydrocarbons or conjugated multiple bond systems. This effect is pronounced after prolonged gasoline aging.

The FT-IR spectra (Fig. 6a' and b') of the non-aged gasoline are dominated by hydrocarbon presence. The strong C–H stretching bands between 2800 and 3000 cm^{-1} dominate the recorded spectrum [40,41]. Other bands assigned to CH$_2$ bending vibrations at ca. 1458 and 1378 cm^{-1}, as well as to rocking band at ca. 728 cm^{-1} are also clearly visible. The small bands between 3020 and 3100 cm^{-1}, together with bands at 1495 cm^{-1} indicate the presence of a small amount of aromatic compounds. Furthermore, bands corresponding to unsaturated hydrocarbons C=C stretching vibrations can be observed at around 1607 cm^{-1}. Also, band at ca. 2725 cm^{-1} is characteristic of aldehyde presence. Finally, two overlapping, broad bands at ca. 3342 and 3481 cm^{-1}

originate from –OH group vibration. Those bands are showing the presence of additives and/or the presence of OH-appended hydrocarbons in the gasoline sample.

Oxidation of the gasoline does not show drastic changes in the recorded spectra of the samples after aging (Fig. 6a' and b'). There are only a few changes indicative of the chemical transformation of the gasoline. First of all, band at ca. 1716 cm^{-1} characteristic for C=O stretching vibration of ketones or carboxylic acids appears albeit only after prolonged aging. The amount of unsaturated hydrocarbons also changes as indicated by the intensity variation of the bands centered on 1607 cm^{-1}. Interestingly, the intensity of this band increases after 3 h of aging, then decreases in the samples aged for 12 h and finally increases significantly after 24-h aging process. On the other hand, bands corresponding to –OH vibrations behave differently. The band intensity decreases significantly for samples aged for 3 h and then increases with prolonged aging times.

The observed changes indicate quite complex behavior of the aged gasoline samples. This is understandable in view of complex composition of the gasoline samples. However, few conclusions can be drawn from the performed spectral studies. First of all, prolonged aging leads to an increased content of C=O and –OH containing species as well as unsaturated and aromatic hydrocarbons. The concentration of the various species changes during aging time. It seems that OH-containing species existing in the non-aged samples are first consumed, and then the population of the other OH-containing species is formed. At the same time, unsaturated and aromatic hydrocarbons are being created. Finally, after prolonged aging, carbonyl group-containing species are being formed.

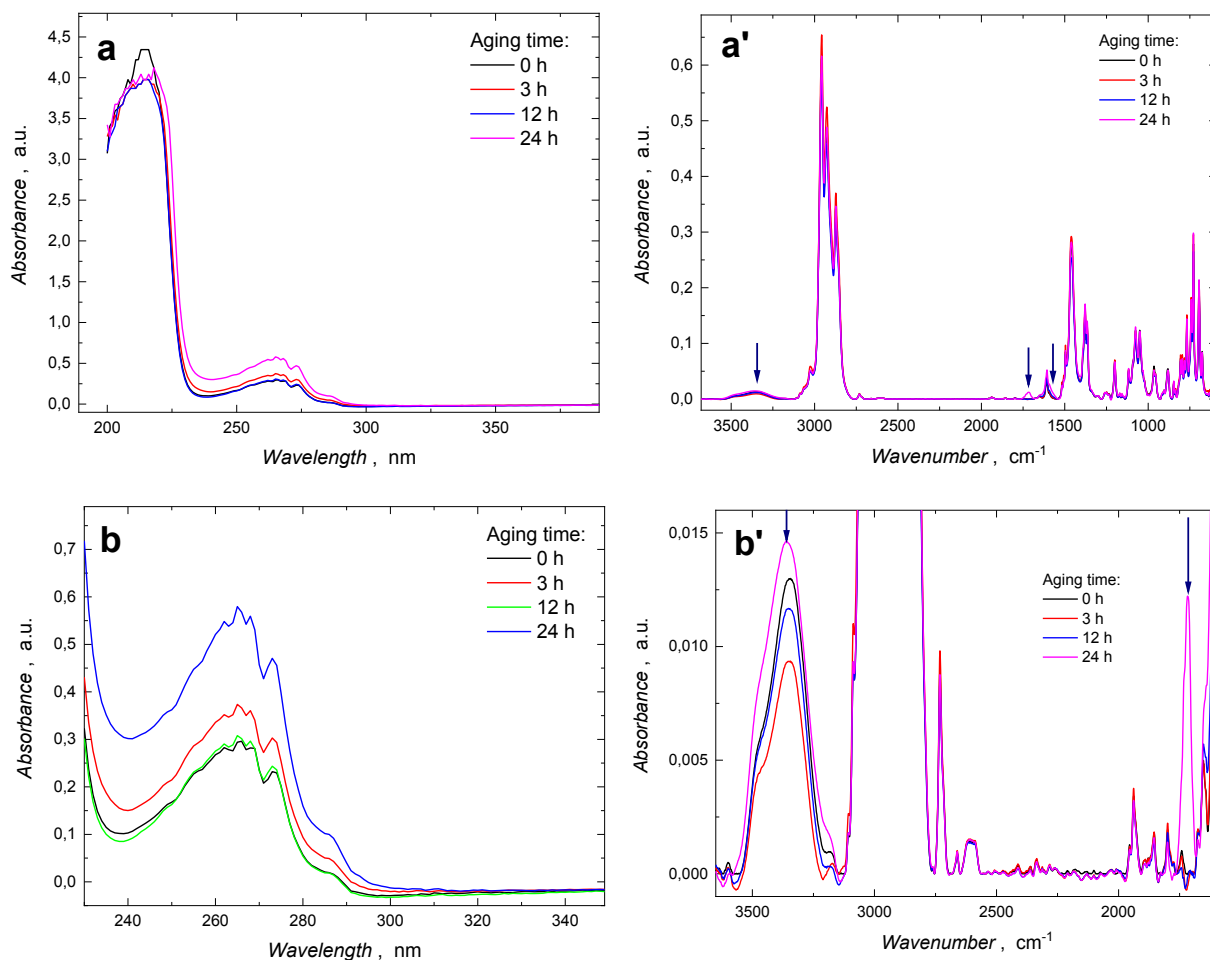The FT-IR and UV–vis studies corroborate that oxygen-containing

Fig. 6. (a, b) UV–vis and (a', b') FT-IR spectra of the aged gasoline samples. Spectra b and b' are showing magnified spectral regions of interest. Arrows on the FT-IR spectra indicate bands showing the biggest changes.

species, with –OH and C=O groups, are being formed during the aging process. Those species are typically more polar than the unsaturated hydrocarbons. As such, they will more readily migrate in the electric field formed during EIS experiments, thus decreasing the gasoline resistance. Furthermore, they point out that unsaturated/aromatic species are also being formed during the process. Similar chemical changes were observed during aging of the ethanol/gasoline blends [1]. In this work increase of total oxygen content, as well as aromatic hydrocarbons content has been observed during aging process. Unsaturated hydrocarbon content has been decreasing during early stages of the aging and then increased.

It has been suggested above that the relaxation time decrease with the aging time (Table 2), indicates a decrease of viscosity of the medium or increase of the diffusion coefficient of the formed species. However, an increase of concentration of aromatic species, as well as hydroxyl and carbonyl group-containing species, shall lead to viscosity increase, as those compounds in the pure form typically show higher viscosity than saturated hydrocarbons [42]. On the other hand, unsaturated hydrocarbons show lower viscosity than corresponding saturated ones [42]. Taking into account the observed evolution of the concentration of unsaturated/aromatic species, as well as hydroxyl and carbonyl group-containing species during the aging, one shall observe a rather slow increase of the relaxation time. In our studies, we have observed relaxation time decrease with the aging time. However, in non-conductive medium important factors may be the migration of the polar species in the electric field generated during EIS experiments. The more polar species shall migrate faster thus, "apparent diffusion constant" considered in relaxation time measurements may increase. This

supposition would explain the observed lowering of the relaxation time observed during gasoline aging as the concentration of more polar species increases during the process. This effect would also lead to a decrease in the gasoline resistance observed in our studies.

The observed capacitance of the gasoline samples depends on electric permittivity, electrode area, and distance between then according to the equation:

$$C = \frac{\varepsilon_0 \varepsilon_r A}{d} \qquad (2)$$

where, A and d are the area of the electrodes and the distances between them, respectively. The ε_0 and ε_r are electric permittivity of vacuum and material, respectively. According to the above equation, the gasoline electric permittivity first decreases after 3 h of aging and then increases continuously (Table 2). In general, the formation of polar, oxygen-containing compounds shall lead to an increase of ε_r of the sample as such compounds exhibit much higher values of ε_r [42]. This agrees well with the general trend observed. On the other hand, unsaturated hydrocarbons exhibit lower values of ε_r as compared to saturated ones [42]. The decrease of ε_r of the gasoline after 3 h of aging indicates then quite complex, multistep oxidation process with the formation of different species at different aging times. Given UV–vis and FT-IR results (Fig. 6, and S1-S4), one can see that the amount of unsaturated/aromatic and carbonyl-containing species increases gradually with aging time, which shall lead the slow increase of the ε_r of gasoline. Interestingly, the amount of hydroxyl group-containing species also decreases after 3 h of the gasoline aging. This would lead to a decrease of ε_r at first, as the slow increase of carbonyl group-containing species concentration would not

compensate for the effect of hydroxyl group-containing species concentration decrease.

It is worth noticing that the gums concentration change with aging correlates well with -C=O absorbance increase observed in the FT-IR spectra (Fig. S1). This indicates that the gums formed contain an important number of –C=O groups. On the other hand UV–vis absorption recorded at 228 nm and 273 nm also correlate with changes in the observed gums concentrations (Fig. S3). This points out also that the gums also contain unsaturated/aromatic units.

Oxidation stability decreases with an increase in the amount of both –OH and C=O group-containing species and unsaturated/aromatic compounds (Fig. S2 and S4).

One of the products of hydrocarbon oxidation is water, which may influence the resistivity of the studied medium. Toward that, samples with known water concentration were also studied by EIS. The results obtained for the water-containing samples showed opposite behavior to the observed for the aged gasoline samples. The diameter of the semicircle observed in Nyquist plot increased with the addition of water (data not shown). However, this observation confirmed that the changes in EIS spectra observed for the aged gasoline samples are not caused by increase in the water content in the sample.

4. Conclusions

The gasoline samples change their physico-chemical properties as a result of their oxidation. With the increased aging time of the gasoline its oxidative stability decreases. On the other hand, the observed concentration of gums, density, and refractive index increases. It is caused by the formation of oxygen-containing products of the aging with higher molecular mass. The formation of the oxygen-containing species has been corroborated by FT-IR and UV–vis spectral analysis. Mostly, hydroxyl and carbonyl group-containing species were observed in FT-IR spectra after samples aging. The performed studies indicate that the observed physico-chemical changes of the fuel are also reflected in the changes of the gasoline electrical parameters. The impedance spectra recorded for the samples show very clear changes with the aging time.

In the studied gasoline samples, systematic changes of both real and imaginary parts of the impedance are observed as a function of the aging time. Also, other electrical parameters derived from the impedance spectra, such as resistance, capacitance, and relaxation time, decrease with the aging time increase. The observed changes of those parameters indicate the formation of polar and/or ionic products, which increase fuel conductivity.

Furthermore, spectral studies performed on the aged gasoline samples support the conclusions regarding mechanistic aspects of the gasoline aging drawn on the basis of the EIS studies. The aging process consists of multiple steps. In the first step, the slow formation of hydroxyl and carbonyl group-containing species, together with an increase of unsaturated/aromatic hydrocarbons content is observed. This leads to a decrease in the sample resistance, capacitance, and relaxation time. It is also noted that the short aging time leads to decrease of hydroxyl group-containing species together with small increase of capacitance.

In the second step of the aging process, compounds with longer chains containing more carbonyl groups and unsaturated/aromatic units are formed, as evidenced by significant increase of the concentration of the gums between 12 and 24 h aging time. This step is accompanied by an increase of carbonyl group signal and signals from unsaturated/aromatic units in FT-IR and UV–vis spectra.

Performed studies indicate that impedance measurements can supplant time-consuming tests routinely used in the evaluation of the gasoline aging process. The electrical measurements are much faster than classical ones and may be also used for continuous monitoring of the fuel quality especially during its long term storage.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.fuel.2020.119620.

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