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Combining Impedance Spectroscopy with Optical Absorption Spectroscopy in the UV for Biofuel Composition Measurement

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Abstract— A capacitive probe is generally used in a flex-fuel engine for measuring the ethanol content in biofuel. However, the water content in biofuel of high ethanol content cannot be disregarded or considered constant and the full composition measurement of ethanol, gasoline and water in biofuel is required. Electrical impedance spectroscopy with a customized capacitive probe operating in the 10 kHz to 1 MHz frequency range is combined with optical absorption spectroscopy in the UV spectral range between 230 and 300 nm for a full composition measurement. This approach is experimentally validated using actual fuels and the results demonstrate that electrical impedance spectroscopy when supplemented with optical impedance spectroscopy can be used to fully determine the composition of the biofuel and applied for a more effective engine management. A concept for a low-cost combined measurement system in the fuel line is presented.

Keywords—fuel sensor, impedance spectroscopy, optical absorption spectroscopy, ternary mixtures, biofuel composition

I. INTRODUCTION

Biofuels have been introduced as a renewable source of energy and as an attempt to reduce our 'carbon footprint'. Biofuels are produced from biomass, such as sugar cane or corn. Biofuel has been made commercially available at fuel stations as ethanol-gasoline mixtures. Although the ethanol/gasoline ratio is strongly varying for different countries, the E85 mixture (containing 85% ethanol) is dominating the international market. Cars that are designed to run on these fuels are called flex-fuel vehicles, and should be able to run on mixtures of gasoline and ethanol in any ratio.

Water is an almost unavoidable additional component in a biofuel/gasoline mixture for different reasons. Firstly, ethanol is hygroscopic and therefore attracts water vapour from the air. The ternary phase diagram reveals that all gasoline in the E85 mixture can in principle be replaced by water, without causing phase separation and water deposition [1].

Secondly, water can be introduced by the production process of the ethanol, which in turn depends on the source of the biomass (organic matter) used. The two main types of crop

used as bio-mass are sugar cane and corn [2]. Ethanol is produced via fermentation of bio-mass in distillation plants. Ethanol production from sugar cane results in hydrous ethanol, also called wet-alcohol or AEHC (Hydrous Fuel Ethanol). The wet-ethanol is mainly produced in Brazil, because of the huge production of sugar cane [3]. According to the ANP (National Agency of Petroleum, Natural Gas and Bio-fuels, Brazil) AEHC must have an ethanol content between 92.6 and 93.8 INMP (which refers to mass content, National Institute of Weights and Measures) [4]. When we translate these values into volume fractions, AEHC must contain between 94.1 and 95 °GL (Degree Gay-Lussac, alcohol by volume at 15 °C (59 °F) [5]), which implies that the maximum water fraction is equal to 5.9%. Dry alcohol (EACA) typically results in case corn is used as organic source, as is the case for bioethanol produced in the USA. After a dehydration step maximally 0.7 INMP of water results, which corresponds to a volume fraction of 99.7 °GL [4].

Thirdly, water can be added by less-trustworthy vendors of car fuels. Obviously, 5% of water can be added to turn EACA into 'illicit AEHC'. The art of adulterating fuel with a few percent of water is also referred to as 'fouling'.

Approaches for fuel composition measurement include optical techniques and impedance measurements. Roy [7] presented an optical fiber sensor to determine the adulteration of petrol and diesel by kerosene. Lima et al. [8] proposed a photo-thermal analysis for the detection of adulterants in gasoline. The fuel in this case is analysed in the vapour phase. The measurement was based on the change of the thermal diffusivity with time, which results from the change in vapour concentration. Continental has been working on a sensor based on infrared absorption [9]. Santos [10] has developed an impedance sensor for determining the concentration of alcohol (ethanol) in Brazilian gasoline. Rocha and Moreira [11] have developed a coaxial sensor using a pair of stainless steel electrodes and the impedance is used as a measure of the mixtures of ethanol and gasoline. Hoffmann et al [12] developed a liquid composition sensor for measuring impedance using inter-digitated electrodes.

Luke Middelburg has contributed to this project within the framework of his M.Sc. Thesis work, which was supported by a grant from the Ford Poling Challenge.

A commercially available dielectric sensor is produced by Continental [13][14]. This sensor measures the capacitance at a constant frequency (~10kHz) and the information is used for determining the ethanol/gasoline fractions in a binary mixture. To compensate for water content, a fixed water concentration is assumed and corrected for. Since the dielectric constant of water ($\epsilon_r= 80$) is much higher than of ethanol ($\epsilon_r= 25$) or gasoline ($\epsilon_r= 2$), a variable water content in the fuel strongly affects the measurement. The measurement of a single property of the mixture fundamentally restricts the approach to application in a binary mixture. Consequently, the simple dielectric measurement is inadequate for measuring the conventional gasoline/ethanol/water composition of biofuel and approaches need to be investigated to obtain the additional information required for solving this ternary mixture problem.

The first approach is to use the same probe over a range of frequencies and to measure both the real and imaginary parts of the impedance (i.e. perform full impedance spectroscopy). As is indicated in the next Section, the resistive part of the impedance is insufficiently reproducible to ensure a reliable measurement of the full composition of the biofuel. However, fouling can be detected using prior information about the fuel.

Optical absorption spectroscopy in the Ultra-Violet (UV) spectral range was found in this work to be a highly suitable technique for deriving the required additional information, as the typical absorbance in the UV spectral range between 230 and 300 nm is highly dominated by gasoline, while ethanol and water are almost transparent. Therefore, the gasoline concentration can be selectively measured, thus leaving it to the electrical impedance spectroscopy to identify the composition of binary ethanol/water mixture, as is discussed in more detail in Section 3.

II. ELECTRIC IMPEDANCE SPECTROSCOPY

A customized probe, as shown in Fig. 1 was designed to meet the special objective of enabling a reproducible measurement at changing biofuel compositions. It was decided to design a coaxial probe with a characteristic impedance of 50Ω in air for flexible use in combination with a HP4294A impedance analyzer. The measurement system is calibrated to correct for parasitic effects. The reproducibility of the measurement relies heavily on the cleaning of the probe after each measurement and the use of fresh fuel at each measurement. Therefore, an additional advantage for a coaxial geometry are that the probe is easy to clean and that the liquid under test will flow in and out of the structure reliably. Brass was chosen as the construction material, which was silver-plated to decrease series resistance.



Fig. 1. Structure of the impedance probe.

The impedance is assumed to comprise of a capacitance in parallel to a conductance. These are measured in air, deionized water, ethanol, gasoline and tap water and the results are plotted in Figs. 2 and 3 in the frequency range from 100 Hz up to 100MHz. The results for the empty (air) and the gasoline-filled dielectric confirm that the medium behaves purely capacitive. Furthermore, deionized water and ethanol have the similar behavior and a scaling of the capacitance proportional to their ϵ_r . Tap-water shows an increasing impedance with decreasing frequency below 100 kHz, which is due to the so called ‘double’ layer capacitance. Tap-water contains many free ions, which diffuse through the liquid as a result of the electric field. At the boundaries (the electrodes) this diffusion causes a charge build-up. When the field is opposite (AC excitation), this process is reversed and the charge builds up on the opposite side. This effect is called electrode polarization and is represented by a series impedance to the probe parallel RC combination, which is comprised of a resistor and a capacitor; the polarization impedance [15][16].

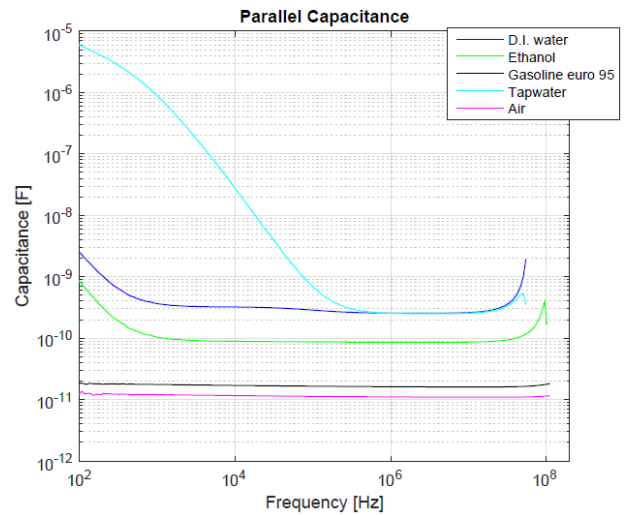


Fig. 2. Parallel capacitance of the three main components and tapwater.

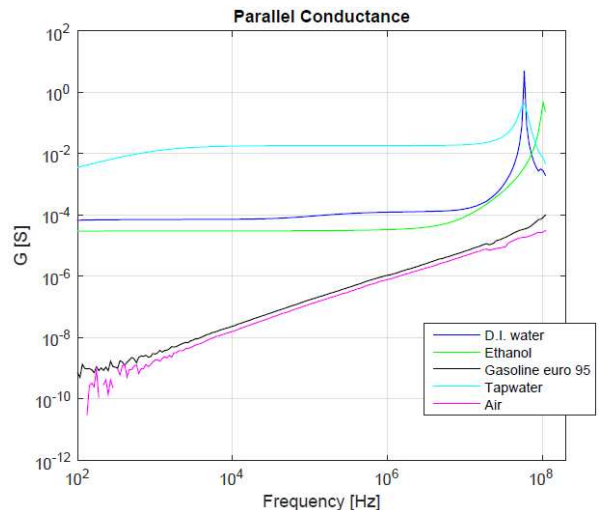


Fig. 3. Parallel conductance of the three main components and tap water.

The measured capacitance provides reliable information and different fuels can be identified. However, the conductivity measurement is limited by a non-linear sensitivity to the ethanol concentration, as shown in Fig. 4 [29].

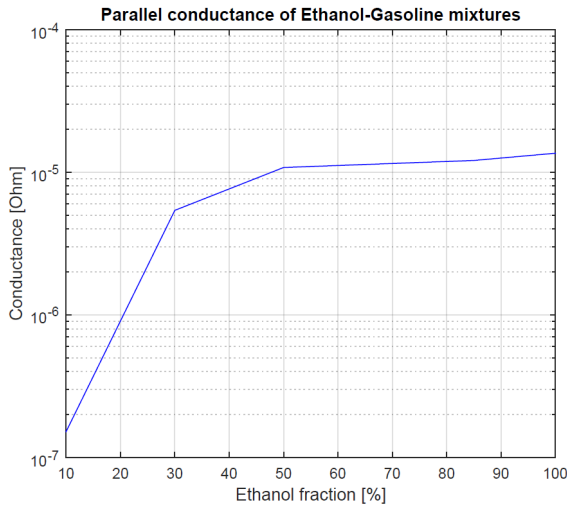


Fig. 4. Non-linear dependence of the conductance to ethanol concentration.

Moreover, the measurements were highly non-reproducible. This observation is consistent with literature and is due to: a complex temperature dependence, an ethanol sample dependency, high sensitivity to free ions/contamination and the influence of static dissipaters which are added to gasoline for safety reasons [10] [18].

III. ELECTRICAL IMPEDANCE SPECTROSCOPY FOR FOULING DETECTION

In this section a method to detect fouling in specific scenario's is described. The starting point is E85, which contains water dissolved in ethanol. This is to be considered prior information (gasoline is 15% - so a binary measurement could be sufficient). There are two scenario's possible. Either the water is part of the ethanol part in the E85 mixture (i.e. wet ethanol is used). When this is not the case, the water is added after production of the mixture (i.e. adulteration of the bio-fuel has taken place, thus fouling). Only in the latter case is the percentage gasoline affected (should be 15%).

Practically, this implies establishing two data-sets by impedance measurements. In the first series of measurements, the non-fouling set, the water content was at the cost of the ethanol content, thereby keeping a constant 15% gasoline. The capacitance and conductance plots are shown in Fig. 5. In the second set, a pure E85 mixture was taken and water was added to it, resulting in adulteration of this fuel. The capacitance and conductance plots are shown in Fig. 6.

If one would like to say something about fouling, without working out the linear mixing models, one can start by looking at the measured capacitance of an adulterated mixture. Suppose an adulterated E85-mixture is measured with 5% water. The parallel capacitance of this mixture is 82 pF (at 100 kHz) and this value corresponds with a legitimate mixture with water content between 5% and 10%.

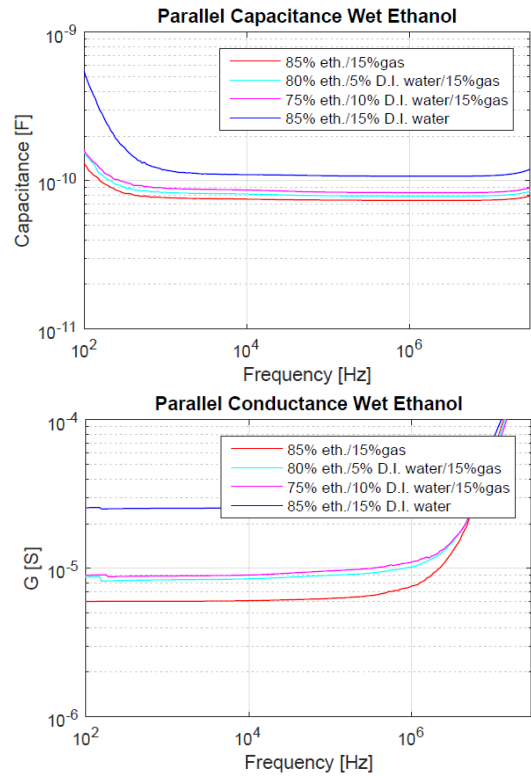


Fig. 5. Non-fouling E85 data-set

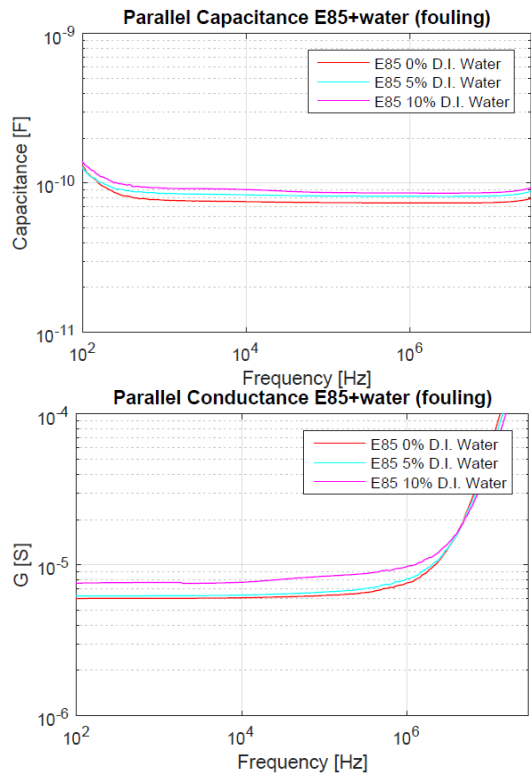


Fig. 6. Fouling E85 data-set

To check whether this mixture could be legitimate, we now look at the conductivity of these legitimate mixtures (figure 5), the corresponding values for this range (water between 5 and 10%) are between 9.0μS and 9.6μS. When we look at the

measured (adulterated) conductance, this value is equal to $6.6\mu\text{S}$, so these measured values do not ‘pass’ this test, and it can be concluded that the measured mixture is adulterated: hence fouling. In other words; there is no linear combination possible of both the capacitance and conductance of a legitimate mixture that would satisfy both the measured conductance and capacitance values of the adulterated E85-mixture. The detection of adulterating in biofuel may be interesting in forensics, but is not a viable approach for a flex-fuel sensor and approaches need to be investigated to provide the required additional information.

IV. OPTICAL ABSORPTION SPECTROSCOPY

Gasoline contains several components with aromatic bonds [19], for example benzene and toluene (methyl-benzene). According to literature [20], benzene shows a strong optical absorption at 180 nm (which is in the vacuum-UV) and more suitable absorption bands at 200 nm and 254 nm [21].

For experimental validation a Varian Cary 500 Spectrophotometer was used in combination with quartz cuvettes. A 1 mm path length was found the most suitable to obtain the spectral information. Since saturation (i.e. reduction of the intensity of a spectral component of the light down to the equivalent noise level of the detector, due to the high absorption coefficient of the gasoline) still occurs with the 1 mm cuvettes, it was decided to dilute the gasoline (mixtures) with a suitable solvent. In this way the absorption behavior of the gasoline (mixtures) would fall into the lower absorption ranges and the measurements would give the best spectral information. Cyclo-hexane was chosen as the solvent, because of the low absorption over the entire UV spectrum and the fact that it dissolves the relevant components well. According to literature [22] the cut-off wavelength in the UV range of cyclo-hexane is 195 nm and is therefore not interfering in the spectral range of interest.

Indolene 50E clear was used in combination with the so-called 200 proof ethanol (>99.98% pure). Indolene is a gasoline that is used in laboratories for testing, because it does not contain the additives and colorants that are routinely added to regular fuels. The dilution ratio of 1/10 is used to enable optimum use the dynamic range of the spectrophotometer. No dilution is applied when measuring pure ethanol to prevent further loss of spectral information. As can be seen in figure 7 two absorption features are present. One local minimum in the absorption at 240 nm and a peak around 265 nm. Despite the dilution ratio of 1/10 and the path length of only 1 mm, saturation at minimum sensitivity occurs at 70% indolene concentration and beyond. On the other hand, no saturation is present and the absorption is dominated by gasoline content at 240 nm.

To investigate if this gasoline-dependent absorption behavior could be utilized in determining the composition of the initial ternary mixture problem, indolene 50E was replaced with a different kind of an ‘off the shelf’ test fuel, namely Unleaded Low Octane gasoline 87RON (Research Octane Number) in a new series of identical measurements. The results are shown in Fig. 7. The absorption behavior closely resemble the measurements of indolene gasoline.

This result can be considered as promising in the final application of a future optical extension of the fuel composition sensor system in flex fuel vehicles. Therefore, the combined capacitive probe/optical microsystem is considered in more detail.

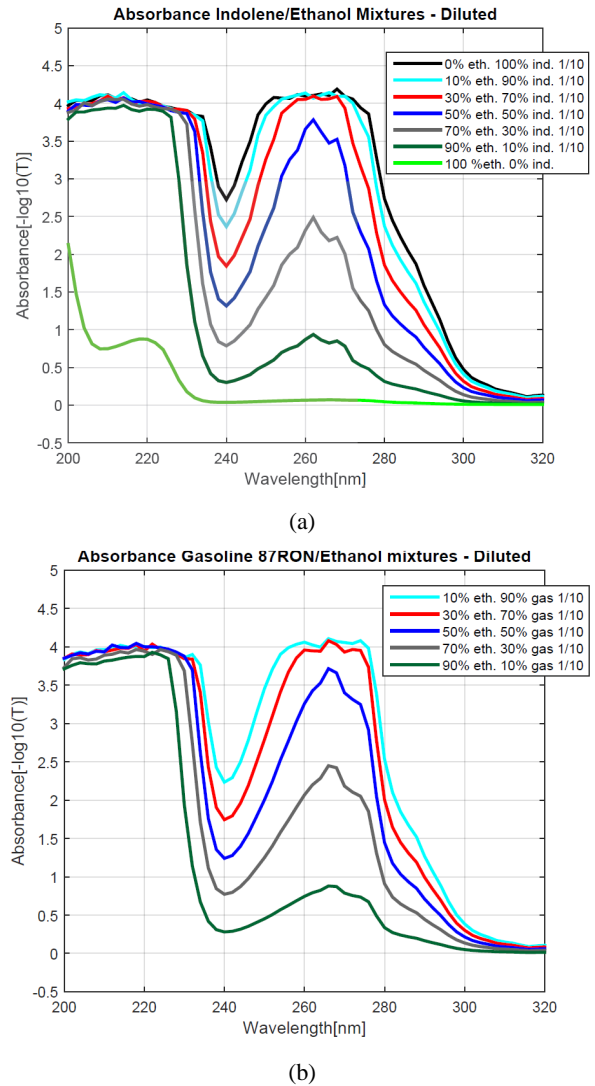


Fig. 7. UV absorption spectroscopy on: indolene 50E (a) and gasoline (b)

V. IMPLEMENTATION

The combined electrical/optical probe should contain both electrical probe and optical path in one unit. The preliminary focus is on the optical part, which is complicated by the short optical path length (< 1 mm) to avoid full absorption at the gasoline absorption lines. The advantage of the measurement of a full spectrum in the measurement range of interest is that more detailed information about the absorption features becomes available. Especially, the peaks and local minima in the absorption behavior provide the kind of additional information that may be useful in the case of interference or stray light. Moreover, the redundancy provided by multi-channel information could be used to improve the quality of the measurement.

A simple implementation is based on a Linear Variable Optical Filter (LVOF) designed for operation over the 230-300 nm band. The three main optical channels of interest (taking into account most interesting ranges of gasoline absorption) are therefore centered at 240 nm, 265 nm, and 290 nm. A value of about $\Delta\lambda = 1$ nm (about 70 channels) is expected to be sufficient. The LVOF is composed of two reflectors separated by a cavity. The depth of the cavity determines the transmission wavelength. The resolution is determined by both the reflectivity and the cavity depth. Figure 8 shows the schematics of the optical sensor design. The structure consists of four main components: 1) a light source, 2) a sample cell, 3) LVOF, and 4) the photo detectors. Further advantages in LVOF-micro spectrometer design are the CMOS compatibility and feasibility of high spectral resolving power as compared to grating-based systems when operated over a relatively narrow band.

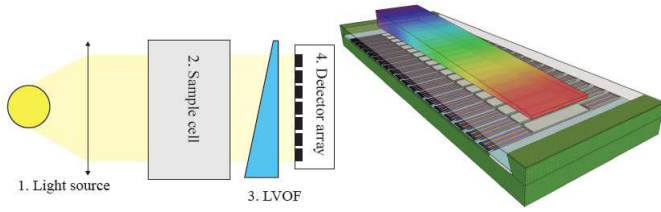


Fig. 8. Principle of the LVOF-based microspectrometer

Therefore, a sensor system based on multiple-LVOFs centered around the intended spectral channels is promising for this application [23].

VI. COMBINING IMPEDANCE SPECTROSCOPY WITH ABSORPTION SPECTROSCOPY

Merging the information provided by low-frequency impedance spectroscopy with that of the optical absorption spectroscopy in the UV spectral range is highly suitable for measuring the biofuel composition. The absorption behavior in the UV range of the optical spectrum is highly selective for gasoline content. The result is a high degree of orthogonality in the matrix.

To compare these two domains further, a quantitative analysis has been made. A first-order linear approximation of the equivalent medium approximation is assumed, see matrices below with α_g, α_e and α_w the volume fractions of gasoline, ethanol and water respectively.

The first row contains the relative permittivity's in the electrical domain of gasoline, ethanol and water respectively, while the second row contains the optical absorption in the UV range at 240 nm (a different wavelength can be chosen). The last row states that the sum of the separate fractions is equal to 100% of the volume.

$$\begin{bmatrix} \varepsilon_{mix} \\ A_{mix} \\ 1 \end{bmatrix} = \begin{bmatrix} \varepsilon_{rg} & \varepsilon_{re} & \varepsilon_{rw} \\ A_g & A_e & A_w \\ 1 & 1 & 1 \end{bmatrix} \begin{bmatrix} \alpha_g \\ \alpha_e \\ \alpha_w \end{bmatrix}$$

After insertion of the measured values in the matrix and matrix inversion, the following solution is found.

$$\begin{bmatrix} \alpha_g \\ \alpha_e \\ \alpha_w \end{bmatrix} = \begin{bmatrix} 0 & 0.367 & 0 \\ -0.0179 & -0.512 & 1.429 \\ 0.0179 & 0.144 & -0.429 \end{bmatrix} \begin{bmatrix} \varepsilon_{mix} \\ A_{mix} \\ 1 \end{bmatrix}$$

Note that the sensitivity of the optical absorption for water and ethanol is below the resolution of the dataset. Hence, zero is used. The orthogonality between the electrical impedance spectroscopy and the optical absorption spectroscopy demonstrate that the two-parameter measurement is a suitable approach for full biofuel composition measurement.

VII. CONCLUSIONS

The measurement of biofuel (ethanol/gasoline/water mixtures) composition by electrical impedance spectroscopy only is not sufficiently accurate, because of the three components, the limited amount of spectral variability and the poor quality of the conductivity measurement. The capacitance measurement remains highly suitable, however should be supplemented by another source of information. If the origin of the biofuel is known, than fouling can be detected. This was demonstrated for E85. However, determining the full composition of the biofuel requires the measurement of an additional property.

Absorption spectroscopy in the UV range between 230 nm and 300 nm was found to be highly representative for gasoline because of the benzene absorption band in this part of the spectrum. Experimental validation has confirmed this conclusion and has demonstrated the viability of the combined electrical impedance/optical absorption spectroscopy for uniquely determining the composition of a biofuel.

On-going work is directed towards a combined probe design and actual implementation. The complication is the short absorption path of smaller than 1 mm to avoid full optical absorption by the gasoline, while ensuring the unrestricted flow of fuel. The matching of the impedance of coaxial probe to the nominal fuel impedance will be abandoned in a next design to enable the functional integration with the optical probe with short absorption path, which is possible because of the relatively low-frequency operation. Multi-line absorption spectroscopy is considered for alleviating the constraints imposed by the short optical absorption path.

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