Determination of Ethanol Content in Fuels with Phononic Crystal Sensor

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Abstract

**Introduction.** In-line analysis of ethanol content in gasoline blends is currently one of the urgent needs of the fuel industry. Developing safe and secure approaches is critical for real applications. A phononic crystal sensor has been introduced as an innovative approach to high performance gasoline sensing. Distinguishing feature of proposed sensor is the absence of any electrical contact with analysed gasoline blend, which allows the use of sensors directly in pipelines without the risk of explosion in an emergency.

**Aim.** Investigation of the possibilities of using phononic sensor structures to determine the ethanol content in liquid hydrocarbons.

**Materials and methods.** A theoretical analysis of sensor structure was carried out on the basis of numerical simulation using COMSOL Multiphysics software. For measurement, substances of ordinary gasoline and gasoline 63–80 with ethanol concentrations in the range of 1–10 % by volume in increments of 2 % were prepared. The phononic crystal sensor was designed as a stainless steel plate with cylindrical holes and a resonant cavity, formed as a running across the wave propagation path slit between two lattices.

**Results.** In-line analysis of measuring the concentration of ethanol in alcohol-containing fuels on a phononic crystal structure with a resonant cavity was carried out. Using the Agilent4395A admittance meter, the transmission spectra of longitudinal acoustic waves through the gasoline-filled sensor structure with were obtained. The non-linear correlation between the composition and the speed of sound of the mixture is presented in the article is due to the ability to reduce the speed of sound of the mixture with an increase in ethanol concentration in the range of 0–10 % by volume.

**Conclusion.** A measurement structure on the basis of phononic crystal was created. The measurements of various gasoline-ethanol mixtures show that the sensor has significant sensitivity (0.91 kHz/(ms<sup>-1</sup>) with quality factor of 200) to distinguish between regular fuels, gasoline based blends and the presence of additives in standard fuels. The sensor has prospects for in-line analyzes the composition of liquid hydrocarbons.

**Key words:** gasoline sensor, petroleum sensor, phononic crystal, ultrasonic sensor, ethanol, gasoline


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Introduction. Nowadays, ethanol containing gasoline is widely utilized around the world replacing clear fossil petroleum fuels. Originally gasoline is obtained as a derivative product after oil distillation at the temperature of 60…120 °C (known as still gasoline). It has a sufficiently low octane number
that results in the impossibility of its use as a fuel in modern engines. In order to increase the octane number, various additives such as aromatic hydrocarbons and alcohols became widespread in recent decades [1]. Ethanol is currently one of the most popular additives widely utilized in bio-fuels. It increases the octane number and improves the combustion process. In Brazil since the 1930s, a gasoline with ethanol content of 2–8 % became widespread. Nowadays, there is the E85 brand with ethanol content of 85 % in Sweden and Finland [2].

The usage of ethanol in substandard fuels on the other hand requires a compatibility of the engine. The utilization of ethanol blended gasoline in motors that are not designed to operate with fuels containing high concentrations of alcohol can lead to undesirable effects and can cause a rapid engine wear, decrease its efficiency and a service lifetime. Moreover, due to the incomplete oxidation of the combustible mixture, an increase of environment pollution with CO₂, CO and other emissions can be expected.

The engines with different features require various kinds of fuel. In order to achieve optimal technical and operational results of the petrol engine, it is necessary to control the fuel with respect to content of ethanol. Currently, permanent works are carried out to improve the characteristics of gasoline engines to operate on different mixtures of ethanol and gasoline [1–3]. One of the promising directions in current research field is the development of engines that can operate on pure gasoline, pure ethanol or on a mixture of petrol and ethanol in any proportions (so-called Flex-fuel engines). The optimal ratio of the ethanol content in gasoline was previously discussed and estimated [4–6].

At the present time, a large number of techniques for gasoline and gasoline-ethanol mixtures analysis are developed. Several of them allow the determination of their composition [7] but they are inapplicable for conducting an in-line analysis. Prasad et al. [8] demonstrated the analysis possibility of combining the gas chromatography with Fourier transform infrared spectroscopy which specifies advantages and disadvantages of these methods. Additionally, there are some straightforward methods [9] where the determination of ethanol content was carried out by means of the viscosity measurement of a mixture. Also, there are ways to make express analysis of the ethanol content in gasoline. One of the approaches shown by Pereira [10] to test the gasoline samples injected into the sensor working area using the batch injection by means of a gold electrode. An impact of ethanol concentration on a fuel mixture can also be seen from the distillation curves, as shown in [11]. That is an example of a fairly accurate analysis of the ethanol content in gasoline-ethanol mixtures, but it is cumbersome and time consuming. The determination of ethanol concentration in gasoline-ethanol blends is an important task that leads to the development of different techniques and sensors. Nowadays, the application of acoustic metamaterials for liquid sensor purpose, so called phononic crystal sensors, was proven to be an innovative approach demonstrating certain advantages [12–15]. It allows conducting the analysis with only acoustical coupling to the fuel. In comparison to impedance spectroscopy methods [16, 17], in current approach the analysing gasoline is not part of an electrical circuit. This feature allows minimizing the explosion risk in an emergency case and affords to apply such sensors for in-line analysis directly in pipelines without any danger. The method itself is based on analysis of volumetric properties of fluids, such as speed of sound and density. The measuring system provides integral information about analyte volumetric properties that reflect the intermolecular interaction of complex liquid mixtures.

**Materials and Methods.** The sensor experimental verification was completed with following substances. Gasoline 63–80 and Ethanol 99.5 % were obtained from Carl Roth GmbH and Sigma-Aldrich Chemie GmbH. Gasoline E-5, Gasoline E-10 and Gasoline V-Power were purchased from the local Shell gasoline station as a regular fuel. The measured probes were prepared from regular gasoline and 63–80 fraction of gasoline (gasoline 63–80) with ethanol concentrations in range 0–10 % by volume with increment of 2 %.

The phononic crystal sensor is performed as a periodically structured two-dimensional arrangement. The structure scatters completed as cylindrical scatters (holes) structured in the stainless steel slab. The resonant cavity is formed as a running across the wave propagation path slit between two lattices, Fig. 1, a. The lattice constant of the periodical structure is 3.0 mm, the thickness of the slab is 15 mm. Cylindrical scatters have a diameter of 1.8 mm, and the resonant cavity has a width of 1.5 mm.

Overall phononic crystal sensor layout as well as parameters and dimensions have been defined upon numerical simulations. A robust design of the sensor, including shape and materials were optimized assuming industrial applications. In addition, for practical
reasons, the structure is designed to the wavelength that corresponds to the probing frequency around 1 MHz because of a vast variety of external ultrasonic transducers that can be utilized for the structure probing.

The experimental setup and the phononic crystal sensor are demonstrated in Fig. 1.

The coupling of the phononic crystal sensor to the external measuring circuit is performed only acoustically with a help of external ultrasonic transducers. Panametrics V103-RB clamp-on contact piezoelectric transducers with central frequency of 1.0 MHz have been brought into contact with the sensor utilizing glycerol as a coupling agent (Fig. 1, b). Transducers excite and receive longitudinal acoustic waves orthogonally to the scatter’s axis and resonant cavity. The analysed liquid fills the structure scatters (holes) and a slit cavity. The sensor is an in-line part of a fluidic system that operates in a circle with analysing liquid, Fig. 1, b. The measurement scheme does not include any matching circuits; hence, acoustically coupled ultrasonic transducers are directly connected with coaxial cables to a network analyser. The S-parameter measurements of the PnC sensor filled with analysing fuel were completed with Agilent 4395A network analyser together with S-parameter extension Agilent 87511A (100 kHz…500 MHz).

**Theory.** Phononic crystal sensor utilizing resonant cavity is well known and its basics and applications are well described [13] including gasoline properties determination [12]. Therefore, we used the same design and experimental setup as described in [12] since rheological properties of examined blends are very close. Spectral parameters and expected frequency range of resonances have been determined on the basis of numerical simulation performed with COMSOL™ Multiphysics. The 2D computational domain has been used. We studied both arrangements with finite dimensions along and across acoustic wave propagation and the case with the infinitely long (periodic super-cell) domain in across direction, as well.

Transmission has been computed as the ratio of displacement induced by the incident on the slab acoustic wave and displacement on the opposed side of the slab induced by transmitted wave. The overall transmission has been computed for the frequency range 1.0…1.2 MHz covering the range of expected resonances. The 5 kHz frequency step has been chosen. The liquid domain is represented by the model liquid having rheological properties (density and speed of sound) similar to the low temperature fraction of gasoline (clear gasoline). Computed transmissions corresponding to two different speeds of sound are shown in Fig. 2.

The simulation has been performed for the structure filled with four different model liquids having the same density and different speeds of sound. The density of both liquids was 750 kg/m³. The speed of sound was set as 1080, 1100, 1120 and 1140 m/s respectively. The speed of sound in range 1080…1100 m/s correspond to known data for the low temperature gasoline fraction [18, 19] and the...
The transmission spectra of the PnC sensor filled with equivalent to gasoline liquids provide several well-distinguishing transmission peaks. The variation of speed of sound in the liquid domain significantly affects their position. The shift of transmission peak to lower frequencies for the liquid with lower speed of sound indicates the involvement of the liquid analytic filling the structure. For lower speed of sound liquids (1080 and 1100 m/s) the transmission maximum is rather narrow and well-isolated. Increase of speed of sound of liquid domain shifts the transmission peak to a higher frequency considerably broadening in case of liquid with 1120 m/s speed of sound and splitting to two separate coupled transmission maximums with 1140 m/s. Observed effect can be associated with coupling of transmission modes of liquid cavity and phononic structure separately. In order to get more insides on the transmission behavior of the phononic structure filled with equivalent to gasoline liquid the displacement and a pressure patterns in the structure were analyzed. The structure displacement and pressure distribution obtained at the frequency of maximum transmission for liquid with speed of sound 1080 m/s is shown in Fig. 3.

Shown in Fig. 3 displacement pattern and pressure distribution illustrate the phenomenon behind the transmission peak. An incident from left to right acoustic wave passes through the phononic structure at the frequency of peak transmission. One can see well defined pressure resonance pattern inside the slit cavity that explains the direct speed of sound dependency.

Increase of speed of sound of the liquid domain causes transmission maximum broadening with further separation into two coupled peaks (Fig. 2, speed of sound 1140 m/s). That phenomenon can be vividly explained by analysis of displacement and pressure distribution at two separated maximums appearing with liquid speed of sound 1140 m/s, Fig. 4.

The observed on Fig. 4 displacement and pressure patterns demonstrate splitting of resonant cavity mode and phononic structure transmission mode into two separate frequencies. Fig. 4, a shows the appearance of structure cavity mode at frequency 1.124 MHz, but the transmission through the periodical arrangement of holes is rather weak. On the other hand, for the frequency 1.142 MHz the transmission through phononic structure is more pronounced but it does not coincide with the cavity mode resulting reduction and broadening of transmission maximum. That is an unwanted effect that decreases the sensor resolution that makes it necessary to consider this effect and adjust the sensor for a certain speed of sound range where the effect is avoided.

**Results.** Initial investigations were conducted in a way to determine the ethanol presence in different concentrations in low temperature gasoline fraction with the use of the developed PnC sensor. For that reason, the gasoline 63–80 probes were mixed with

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Fig. 3. Displacement and pressure distribution in phononic crystal sensor structure. Liquid domain density 750 kg/m³, speed of sound 1080 m/s

Fig. 4. Displacement and pressure distribution for the phononic structure filled with analogous to gasoline liquid (density 750 kg/m³, speed of sound 1140 m/s) at frequencies 1.124 MHz (a) and 1.142 MHz (b)
ethanol in a weight concentrations range of 0–10 % with increment of 2 % were measured.

The dependence of sensor $S_{21}$ – parameter magnitude response that is demonstrated in Fig. 5 shows that the shift of the peaks is observed in the selected area depending on the ethanol content in the solution. With an increase of ethanol concentration, peaks gradually shift towards the region of lower frequencies.

Nowadays, most of the fuels contain additives in concentration up to 30 %; for example, aromatic components. Following experimental investigations were conducted in order to receive an experimental verification of the sensor frequency spectrum behavior for different ethanol concentrations in a gasoline mixture containing ethylbenzene as an aromatic additive. As it can be seen in Fig. 6, the experimental results confirm previous findings where increase of ethanol concentration causes a gradual shift of the transmission maximum to lower frequency region. The experiment was conducted utilizing mixtures of Gasoline 63–80 (78 %) and Ethylbenzene (22 %) with a variable concentration of ethanol containing 0, 5 and 10 % of ethanol. The content of ethylbenzene increases the speed of sound of the multicomponent gasoline mixture that shifts the peaks of maximum transmission in a higher frequency range in comparison to light gasoline fraction experiment Fig. 5. An increase of ethanol concentration leads to shifting the peaks towards lower frequencies (Fig. 6) in the same way as it was observed in previous experiment.

In a similar manner several experiments were carried out using regular Gasoline E5, E10 and VP purchased from local gasoline station. The results of experimental investigations are demonstrated in Fig. 7. The representation of the sensor response as a Nyquist diagram allows obtaining more distinct information from measured regular fuels (see Fig. 8).

The demonstrated in Fig. 8 Nyquist plot shows the data in a frequency range of 1.17…1.18 MHz, omitting the higher and lower frequency information in order to make the plot clearer in a frequency range where the dependence on different gasolines is more pronounced. For the case where in magnitude measurements the dependences for E10 and V-power gasoline almost overlap, the Nyquist plot shows significant distinguishability.

Referring to magnitude sensor response Fig. 7, it can be observed that the sensor transmission peak merges two transmission maximums in most cases. That effect is more pronounced for Shell V-power.
gasoline. The effect of transmission double maximum origin is also reflected in Nyquist plot as an interruption of continuous phase change (observed as a bending of curve semicircle on Nyquist plot). Observation of coupled transmission maximums can be explained as an overlapping of separate transmission modes originated by the liquid cavity and phononic structure. The same effect of coupled transmission maximums was also observed theoretically and was shown in Fig. 2 and Fig. 4, a, b.

Due to the influence of aromatic hydrocarbons and to the fact that the composition of regular gasoline is much broader and contains various fractions, the peak of maximum transmission is shifted to higher frequencies as it was observed with respect to similar measurements for a narrow low temperature fraction. Additionally, regular gasoline can contain up to 30% of aromatic additives that have a considerably higher speed of sound than original gasoline. Their presence in a fuel causes an increase of speed of sound of the whole blend. As it can be seen in Fig. 7 and Fig. 8, experimental results demonstrate that the transmission maximum of regular gasoline with a higher ethanol concentration has higher frequency that contradicts to previous findings. We assume that these results can be explained by the variation of composition of E5 and E10 gasolines not only in terms of ethanol content. Presumably, we can conclude that E10 regular gasoline contains more high speed of sound components (such as aromatic additives and others) than E5. Such variation of the hydrocarbon’s composition can diminish the expected downshift of transmission peak caused by increased ethanol concentration. This conclusion can be supported with additional experimental investigation with two different blends. One of them is regular E5 gasoline, which presumably has 5% of ethanol concentration, and another is the same E5 mixed with additional 5% of ethanol. The idea behind the experiment is to keep constant the composition of the initial fuel and observe only the ethanol influence. Experimental results are demonstrated in Fig. 9.

The obtained experimental results confirm previous findings; the increase of ethanol concentration shifts the transmission maximum to a lower frequency range as it was observed in previous experiments where the composition of gasoline in the mixture was kept constant.

**Discussion.** Velocities of sound in hydrocarbon components and their mixtures were previously investigated in [20, 21] showing enough agreement between hydrocarbons liquid mixture composition and speed of sound of their constituents. Predictable reflection of multicomponent composition of hydrocarbons mixtures in velocity of sound provided platform for applying this method for more sophisticated analyses of thermodynamic properties of liquid mixtures [22–27] that in most cases is hardly completed with alternative methods. In adiabatic liquid systems the isentropic compressibility is directly related to the speed of sound [28] that became a convenient method to study molecular interactions occurring in liquid mixtures. Compressibility as a measure of relative volume change under external pressure depends on thermodynamic properties of liquid mixture [29]. The difference between measured and adiabatic compressibility provides an excess compressibility that reflects the interaction between mixture constituents. The sign of excess compressibility shows how strong are the intermolecular interactions in current liquid mixture. For binary mixtures a negative access compressibility defines a preliminary attractive intermolecular interaction and the positive excess compressibility on the other hand advocates to an establishment of a less “rigid” molecular structure [29, 30]. The investigation of the excess compressibility or excess thermodynamic properties of liquid mixtures in general is a widely utilized approach allowing obtaining the information from intermolecular interactions in multicomponent liquid systems.

The observed behavior of ethanol–gasoline mixtures demonstrates a non-linear correlation between composition and speed of sound of the blend. Even though ethanol has a higher speed of sound than gasoline, the increase of its concentration (in range 0–10% by volume) causes lowering of mixture speed of sound that is observed as a shift of transmission maximum to a lower frequency region. This behavior of gasoline-ethanol blends was already
previously observed [13]. Due to alcohol contains a special functional group R–OH, its presence leads to a very big difference in the ability to attract and retain electron pairs between atoms of oxygen, carbon and hydrogen that are included in the hydroxyl group of alcohol molecules. C–O and O–H interconnections have significant polar properties: an oxygen atom has an unshared electron pair and a partial negative charge that leads to occurrence of a significant positive charge on a hydrogen atom inside hydroxyl group. The charge difference between a hydrogen atom of a hydroxyl group and other hydrogen atoms gives the opportunity to form intermolecular hydrogen bonds and stable clusters of molecules as a result. The mechanism of formation and interaction of clusters formed with ethanol and other liquids can lead to abnormal fluctuations [31, 32] that was observed in current work.

**Conclusion.** Current contribution describes the development and experimental verification of the phononic crystal based in-line fuel sensor. The distinguishing feature of demonstrated sensor is its conceptual difference from those that are currently utilized. The application of acoustic metamaterials, so called phononic crystals, allows build conceptually different measuring scheme that does not require the fuel to be a part of the electrical circuit (as it is in impedance – based methods); hence, the gasoline is only acoustically coupled. The presented sensor design and its theoretical investigation demonstrate an ability of the sensitive integral analysis of complex hydrocarbon mixtures. Numerical calculation results underline the necessity for the phononic structure to be optimized for certain speed of sound range of analyzing liquid to keep the sensor high resolution. The experimental investigations confirmed theoretical predictions. The speed of sound variation reflects the fuel composition and indicate the existence of intermolecular interactions causing non-linear response. Demonstrated results of the in-line ethanol concentration analysis provide distinguishing and explainable results. The measurements of various gasoline-ethanol mixtures demonstrate that the sensor has a significant sensitivity to distinguish regular fuels, gasoline – based blends and presence of additives in standard fuels. The demonstrated for a first time results of measuring with phononic crystal sensor the regular fuels and ethanol containing gasoline can be valuable for applications in a fuel industry.

**Authors’ contribution**

Nikolay V. Mukhin, numerical calculation of phononic crystals; comparison of theory with experiment; preparation of the final manuscript.

Aleksandr Oseev, measuring setup preparation; writing the basic draft; data validation.

Mykhailo M. Kutia, gasoline-ethanol mixtures preparation and experimental measurements.

Ekaterina S. Borodacheva, design and data processing.

Pavel G. Korolev, measuring system control.

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