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Measuring Systems and Instruments Based on Acoustic, Optical and Radio Waves

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Thiophene Determination in Liquid Hydrocarbons by In-line Acoustic Measurements

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Abstract

Introduction. Petroleum is a complex mixture of hydrocarbons. Sulphur is the most common heteroatom in pe-troleum and petroleum products. Its content in oil can reach 14 %. The determination of sulphur in oil and its removal is of great importance, since sulphur compounds adversely affect the quality of petroleum products and pollute the environment. Desulphurization of hydrocarbons is important in the processing of petroleum products, which needs in usage of accurate and simple methods for the sulphur-containing components determination. Most of developed methods are difficult to apply for flow online analysis, which can create difficulties in using them to monitor the content of sulphur-containing heteroatomic components in real time. Acoustic sensors are one of the possible solutions. In term of sensing of flammable liquids, the use of the acoustic methods is attractive since the analyte is not a part of an electrical measuring circuit and it is only acoustically coupled that prevents an occurrence of a spark.

Objective. The purpose of the work is to study the possibilities of online flow analysis of sulphur-containing heteroatomic components using acoustic measurements. The challenge is the development of a resonator system integrated with the pipe.

Materials and methods. Thiophene and oil fraction with the boundary boiling point of 100–140 °C were used to prepare the mixtures. Thiophene is a representative of sulphur-containing components, which may be included in the composition of petroleum and its derivatives. Experimental measuring equipment includes impedance analyzer, a developed sensor structure integrated with a liquid-filled pipe, a pump and a tank with a measured liquid. A theoretical analysis of sensor structure was carried out on the basis of numerical simulation using COMSOL Multiphysics software.

Results. The sensor structure was designed as a combination of 2D and 1D pipe periodic arrangements to achieve high Q-factor of acoustic resonance in the flow system. The eigenmodes of the sensor structure with a liquid analyte were carried out. The characteristic of sensor structure is determined. The sensor shows good sensitivity to the thiophene content with high resolution in-line analysis. This result is achieved by limiting the energy losses of acoustic resonance in radiation along the pipe by creating a periodic structure.

Conclusion. The study of acoustic properties of solutions prepared on the basis of thiophene and oil fraction with boundary boiling point 100–140 °C was performed. It shows that methods based on acoustic spectroscopy make it possible to accurately determine the concentration of heteroatomic components in gasoline mixtures, since the presence of heteroatomic components leads to a change in mechanical properties of liquid hydrocarbons mixtures. Possible applications for developed acoustic sensor are flow analysis for monitoring the quality of oil products.

Key words: acoustic sensor, liquid hydrocarbons, thiophene, periodic structures

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Introduction. Petroleum is a complex mixture of hydrocarbons that includes paraffins, naphthenes, aromatic compounds, unsaturated hydrocarbons, and heteroatomic compounds in the form of components containing atoms of sulphur, oxygen or nitrogen. There are sulphur compounds thiols, sulphides, cyclic sulphides, disulphides, thiophenes, benzothiophenes, dibenzothiophene and naphthobenzothiophenols in petroleum. Compounds containing oxygen may be present as alcohols, phenols, ethers, carboxylic acids, esters, ketones and furans. Compounds containing in their composition a nitrogen atom in petroleum mixtures, are represented as molecules of pyrrole, indole, carbazone, benzocarbazone, pyridine, quinoline, indoline and benzoquinolines and their metal components. Detection and determination of the exact concentration of these components is necessary for the entire petroleum production and processing cycle: to set the initial data for the design of petroleum inflow, for petroleum preparation for transport, and for deep petroleum refining [1–3]. To create a qualitative mathematical model of the inflow, it is necessary to know the exact composition of petroleum. Heteroatomic components can significantly affect to the properties of the hydrocarbon mixture, so determining their content is an important task for petroleum engineers [4].

Sulphur is the most common heteroatom in petroleum and petroleum products. Its content in oil can reach 14 %. Oil, committed devoid of sulphur, does not exist. The determination of sulphur in oil and its removal is of great importance, since sulphur compounds adversely affect the quality of petroleum products and pollute the environment. There are different methods of analysing oil and oil products to control heteroatomic components that can be used to determine the concentration of sulphur compounds.

One of the most effective laboratory methods for analyse of petroleum component composition are gas and high-performance gas chromatography. Gas-liquid chromatography is also demonstrating high measurement accuracy and can separate components that are very similar in their physical and chemical properties. However, preparation and preliminary separation of the sample into narrower fractions requires a big period of time. Separation of analytes occurs in columns (tubes) filled with a solid porous sorbent, with a liquid non-volatile stationary phase on the surface of the sorbent. A vapours of analytes that are mixed with carrier gas are move through the column. In this case, multiple equilibrium is established between the mobile gas and liquid stationary phases due to repeated repetition of the dissolution and evaporation processes. Substances that dissolve in the stationary phase better have retained longer in the column. As a next step an analysed mixture is divided into separate components and all of them are leave a column separately and registered at the output. As a result it can be concluded that with the help of these methods it is possible to achieve high resolution of the analysis [5–8]. However, the high cost of equipment, large dimensions and complexity of the analysis process limit the industrial application of chromatographic methods in industry.

Methods of spectral analysis are also widely used to determine the properties of liquids hydrocarbons and gases. Raman spectroscopy makes it possible to obtain spectra with characteristics for different components in complex mixtures. This method has been successfully used to measure a suspension of carbon particles in an aqueous solution of carbohydrates [9]. In addition to Raman spectroscopy, IR spectroscopy and NIR spectroscopy are also widely used. A comparison of NIR, IR, and Raman spectroscopy for analysing the component composition of petroleum was carried out in work [10]. The results of the study showed that IR spectroscopy provides an acceptable analysis of fractions of heavy oil. The use of Raman spectroscopy is limited due to fluorescence due to fractions of heavy oil. However, Raman spectroscopy can be used for narrow fractions of oil with a low boiling point.

Most of the methods listed above are difficult to apply for flow online analysis, which can create difficulties in using them to monitor the content of sulphur-containing heteroatomic components in real time.

However, perhaps the simplest and most effective method to control heteroatomic oil products is to measure impedance, evidenced by a large number of works devoted to the study of various types of fuel by the methods of impedance spectroscopy [11–13]. In [14], the authors show the possibility of using a sensor system with an impedance component to study complex three-component mixtures of gasoline, ethanol and water. Similar work on the study of bioethanol fuels by the method of impedance spectroscopy is described in [15]. Another important advantage of impedance spectroscopy is the ability to use it to create microfluidic sensory systems [16]. Impedance spectroscopy can exploit electromagnetic or acoustic measurement methods. Acoustic spectroscopy looks more perspective. In term of sensing of flammable liquids, the use of the acoustic methods is attractive since the analyte is not a part of an electrical measuring circuit and it is only acoustically coupled that prevents an occurrence of a spark. Sound velocity is closely linked to Gibbs Free Energy and related values [17], hence ultrasonic velocimetry allows for detecting molecular interactions [18], for example in enzyme catalysis [18, 19], or microstructural transitions [20]. Ultrasonic methods can even be applied to optically non-transparent systems [19].

Therefore, in this work, we used acoustic spectroscopy method and studied its acceptability for flow online analysis.

Materials and Methods. The purpose of the work is to study the possibilities of online flow analysis of sulphur-containing heteroatomic components using acoustic measurements. The challenge is the development of a resonator system integrated with the pipe.

To achieve the goal, the measuring system shown in Fig. 1 was prepared. Measuring equipment includes impedance analyzer (*1*); a sensor structure (*2*) integrated with a liquid-filled pipe (*3*); a pump (*4*) and a tank with a measured liquid (*5*).

The Agilent4395A network analyzer was used as a measuring instrument along with an Agilent 87511A S-parameter extension.

During the experiment, the measured solution circulates through the system with a flow rate of

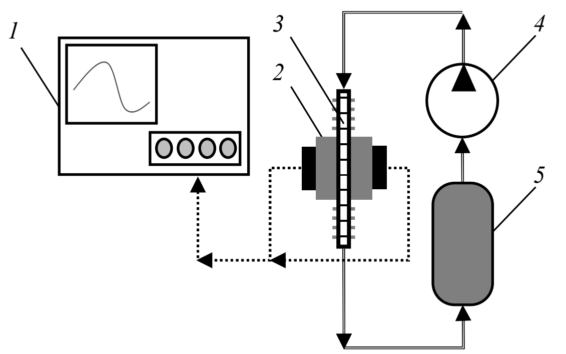

Fig. 1. Measuring equipment layout

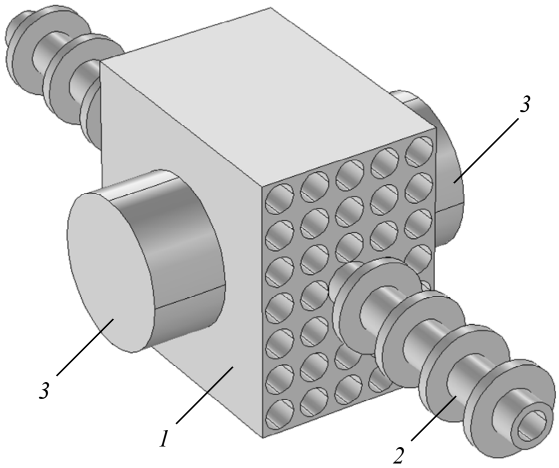

Fig. 2. Measuring structure

5 ml/min. Using connecting tubes, the pump is connected to a container with a solution and measurement structures. The liquid, after passing through the measurement structures, returns to its original capacity. The experiment was carried out at a constant ambient temperature of 22 degrees Celsius.

The sensor structure (Fig. 2) was designed as a combination of 2D and 1D pipe periodic arrangements to achieve high Q-factor of acoustic resonance in the flow system. The acoustic measurement device consists of a steel matrix with a periodic system of cylindrical holes (*1*). The diameter of the cylindrical holes is 4 mm; the distance between them is 4.9 mm. Liquid is supplied through a central cylindrical steel channel with a periodic system (period length is 12 mm) of rings along the axis (*2*). Piezoelectric transducers (*3*) made of PZT are placed on the right and left of the contact to the perforated steel plate (*1*). A longitudinal acoustic wave is excited on the left side and received on the right one by measuring the s21 parameter. The 2D periodic system of cylindrical holes is designed to excite high-Q liquid resonance in the central cylindrical cavity, then the system of periodic rings along the channel axis is made to prevent acoustic energy losses due to radiation along the pipe.

A theoretical analysis of the eigenmodes of sensor structure was carried out on the basis of numerical simulation using COMSOL Multiphysics software.

The narrow oil fraction was taken as a basic solution. The boundary boiling point of the fraction is 100–140 °C. Thiophene was used to prepare the mixtures. Thiophene is a representative of sulphur-containing components, which may be included in the composition of petroleum and its derivatives.

Results and Discussion. When designing the sensor structure, calculations of its resonance modes were performed. The propagation of acoustic waves in an elastic medium can be determined by the equation:

$$\rho_S \frac{\partial^2 u_i(\mathbf{r}, t)}{\partial t^2} = \sum_{j,m,n} \frac{d}{dx_i}\left[C_{ijmn}\frac{\partial u_n(\mathbf{r}, t)}{\partial x_m}\right], \quad (1)$$

where ρ_S is the density of solid medium; u_i are the components of the elastic displacement field; C_{ijmn} is the elasticity tensor components; *i*, *j*, *m* and *n* are indices running from 1 to 3; $\mathbf{r} = (x, y, z)$ is the coordinate vector; *t* is time. To search for the eigen resonant solutions, Bloch's theorem was used, according to which the displacement vector can be represented as the product of the propagating wave and the periodic function of the sonic crystal:

$$\mathbf{u}(\mathbf{r}, \mathbf{k}) = \mathbf{u}_k(\mathbf{r})\exp(-i\mathbf{kr}),$$

where $\mathbf{u}_k(\mathbf{r})$ is the periodic function of **r**; **k** is the wave vector.

Fig. 3 shows calculation results of the sonic crystals behaviour. Fig. 3, *a* shows an acoustic band diagram (the dependence of the frequency of the structure eigenmodes on the wave vector close to high symmetry points (Γ, *K* and *M*) in the first Brillouin zone) for a two-dimensional infinite cubic symmetry 2D sonic crystal made of steel with a periodic arrangement of cylindrical empty holes.

The size of the holes is 4 mm, the distance between the holes is 4.9 mm. The sonic crystal, as seen from Fig. 3, *a*, has a bandgap in the frequency range from 352 to 420 kHz. It is highlighted by a gray stripe. Fig. 3, *b* shows an acoustic band diagram for a one-dimensional infinite pipe sonic crystal made of steel with a periodic arrangement of rings. The inner diameter of the pipe has the same size as holes of the 2D sonic crystal. Rings repetition period (*L*) is 12 mm. This pipe periodic structure has a narrow bandgap in the frequency range from 360 to 367 kHz, which falls into the forbidden frequency band of 2D sonic crystal. In this frequency range, both structures work as perfect reflectors of acoustic waves. For structures of finite size, the penetration depth of acoustic waves is 2 lattice periods for the 2D crystal (Fig. 3, *c*) and 3 periods for a pipe sonic crystal (Fig. 3, *d*).

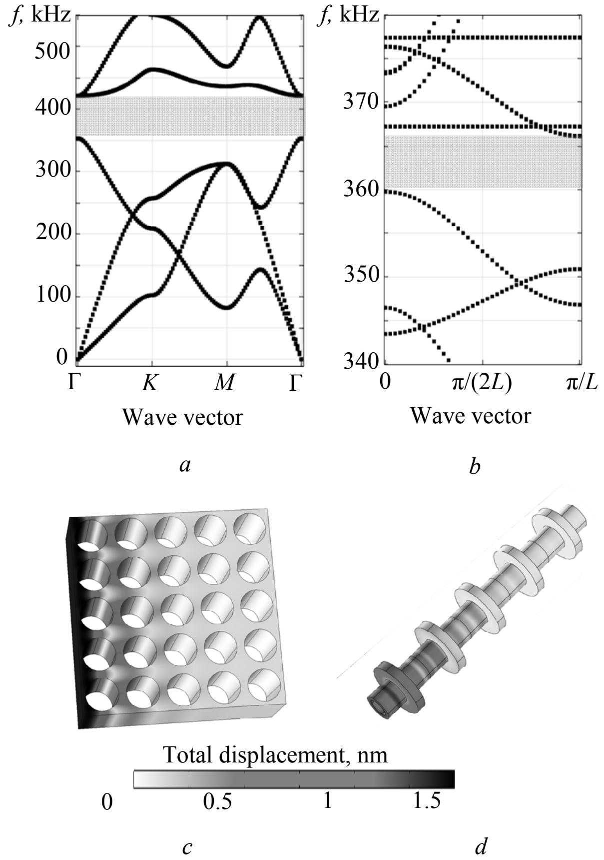

Fig. 3. Band diagrams of infinite 2D cubic (*a*) and 1D pipe (*b*) sound crystals and the reflection of an acoustic wave from finite structures (*c*, *d*) in its forbidden frequency ranges

The most interesting features of the spectra of the sensor structure must be associated with the liquid pressure resonances in the pipeline. The pressure changes can be described as a wave equation for given boundary conditions. Resonance modes can be found by solving the eigenmode problem for acoustic modes in a cylindrical cavity. The basic equation for the pressure wave with harmonic solutions is the Helmholtz equation, which can be represented as follows:

$$\nabla\left(-\frac{1}{\rho_L}\nabla p\right) - \frac{\omega^2 p}{\rho_L V_L^2} = 0, \quad (2)$$

where ρ_L is the density of liquid; *p* is pressure; ω is circular frequency; V_L is speed of sound in a liquid.

Conditions at the boundaries of the "solid–liquid" section are as follows:

$$\mathbf{F} = -\mathbf{n}_S p; \ (\mathbf{n}_f \bullet \mathbf{u})\omega^2 = -\mathbf{n}_f\left(-\frac{1}{\rho}\nabla p + \mathbf{q}\right), \quad (3)$$

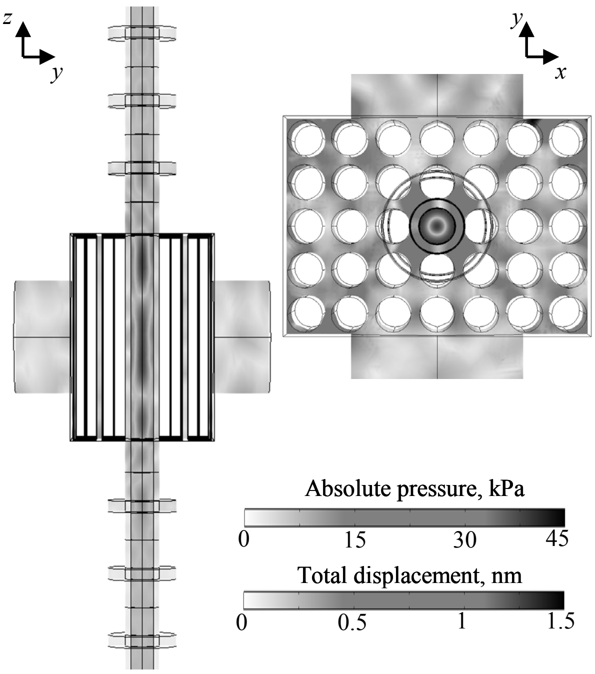

Fig. 4. Simulation of resonance conditions in the pipe of the sensor structure

where **F** is the force per unit area representing the load on the cylinder walls; $\mathbf{n}_\mathrm{S}$ is the normal vector directed from a solid; $\mathbf{n}_\mathrm{f}$ is the normal vector directed from the fluid volume; **u** is the mechanical displacement vector in a solid; **q** is the acceleration vector reported by the fluid.

On the basis of the equations (1–3) computation results of eigenmodes for the sensor structure (Fig. 2) were carried out. Fig. 4 shows the liquid resonance in the pipe embedded in the measuring acoustic system.

Here the liquid-filled pipe works like a structural defect in a 2D sonic crystal. By creating a replacement-type defect in the regular structure of a sonic crystal by filling one of the holes with a liquid, we can create an isolated localized state if the resonance frequency of the liquid-filled pipe falls into the bandgap.

For typical values of the gasoline speed of sound (about 1200 m/s [21–23]), axisymmetric mode is in the centre of the bandgap (Fig. 3). A cylindrical liquid-filled resonator is surrounded by a periodic structure that provides high acoustic contrast at the edges of the resonator and, as a result, a high Q-factor of the resonant peaks can be achieved. In this case, the resonance peak turns out to be isolated, since there are no other vibrational modes of the solid-state structure within the bandgap. When the composition of the fluid changes (more precisely, the speed of sound changes), the resonant frequency of the defect mode shifts. This fact allows to use the shift of the resonant frequency to detect the composition changings.

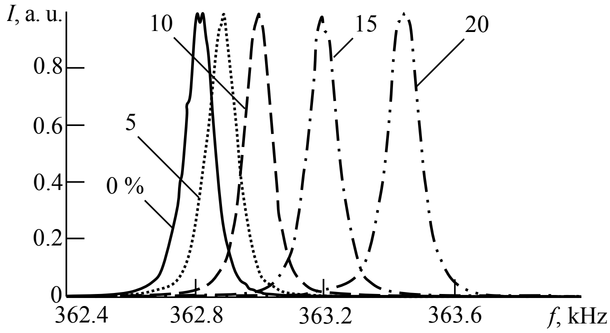

Fig. 5. Experimentally measured frequency spectra of the sensor structure for different gasoline-thiophene mixtures

The dependence of the resonant frequency (f_r in kHz) of the structure on the speed of sound in a liquid (V_L in m/s) is described by the following equation:

$$f_\mathrm{r} = 0.3049 V_\mathrm{L} + 0.02.$$

Fig. 5 depicts an eexperimental dependence of the intensity (*I*) of the acoustic signal passing through the structure on the frequency (*f*) for various volumetric concentrations of thiophene in gasoline.

The quality factor of the resonance peaks is limited by the viscosity of the fluid and imperfection of the manufactured structure.

The sensor shows good sensitivity to the thiophene content with high resolution in-line analysis. This result is achieved by limiting the energy losses of acoustic resonance in radiation along the pipe by creating a periodic pipe structure. Secondly, the structure of a 2D sonic crystal allows to excite axisymmetric eigenmodes of liquid pressure in a pipe that have reduced viscosity losses compared to o spining modes that would be excited by direct contact with piezoelectric transducer.

Possible applications for developed acoustic sensor are flow analysis for monitoring the quality of oil products.

This work extends the field of sonic crystal liquid sensors with novel results that have a high potential in a field of liquids properties evaluation in flow analysis.

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