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STUDY OF PROCESSES INITIATED BY LOW-FREQUENCY EXPOSURE IN DIESEL FUEL OBTAINED FROM PARAFFIN OIL*

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Abstract

The paper discusses the results of a practical experiment on the effect of infrasound on the samples of diesel fuel produced from paraffin oil from the Sarybulak field in Kazakhstan. In the area of environmental protection, the transport sector and, consequently, the production and use of various types of motor fuels play a crucial role. Throughout the world, there is a tendency of increasing the diesel fleet. Environmental parameters of polluting substances emissions of any fuel characterize its ecological and economic efficiency and impact on the environment. Light commercial vehicles with diesel engines are dominant in all the EU countries, Russia, Kazakhstan, and other former Soviet republics. Consequently, automobile traffic, especially in large cities where traffic is heavy, has a huge impact on air quality. The experiment is described and a hypothesis is put forward to explain the results of laboratory measurements.

Keywords: infrasound, paraffin content, sulphur content

1. Introduction

The process of diesel fuel combustion is accompanied by the formation and emission of substances that are dangerous pollutants of the industrial zone and the environment. This is due to the sorption of chemical compounds of organic and inorganic origin. These compounds include, first of all, heavy metals, polycyclic aromatic hydrocarbons that possess carcinogenic and mutagenic properties. In the paper (Dobrzyńska et al., 2020), the authors conducted a study of the effect of diesel fuel emissions on the atmosphere. It was proved that diesel exhaust contributes to air pollution, increased smog, and global warming.

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The chemical composition of the oil is quite complex and depends on many factors, such as the conditions of formation and origin of deposits, their geographical location, stratum depth, etc. The main oil compounds are hydrocarbons with a molecular weight of 220-400 g/mol (sometimes up to 500 g/mol), most of which are in a liquid aggregate state. Associated petroleum gas dissolved in oil also mainly consists of saturated hydrocarbons – mainly propane and isomers of butane. In addition to hydrocarbons, the composition of oil includes heteroatomic compounds that contain in their structure both organic components and inorganic elements, including metals. For example, the specific smell and color are mainly due to the presence of nitrogen-, sulphur - and oxygen-containing compounds.

Sulphuric acid treatment of diesel fuel originates from the mid-50s of the 20th century and consists of mixing the fuel with a small amount of concentrated (more than 90%) sulphuric acid (Grigorov et al., 2014). As a result of the process, refined diesel fuel is formed, and the remainder is naphtha sludge with the sulphur-containing compounds (Chernozhukov, 1978). Utilization of naphtha sludge is a real problem for industrial enterprises, where it is accumulated in large quantities, as to date, no technology has been fully developed that allows it to be processed without harm to the environment.

Today, the desulphurization of diesel fractions on virtually every major oil refinery in our country is carried out by hydrotreating. This method is very energy-intensive and fire-explosive, as it requires high temperatures (420-460 ° C), pressures (3.0–4.5 MPa), and the use of hydrogen-containing gas (50-80% H_2) (Solodova and Terentyeva, 2008). The cost of implementing this method largely determines the net cost of finished diesel fuel.

The authors of paper (Burtnaya et al., 2003) propose a technology that allows the separation of sulphur compounds (mercaptans, sulfides, disulfides, thiophenes, etc.) from diesel fuel, based on mixing the fuel with an active solvent (activator), followed by passing the mixture through membrane devices where cleaning is actually performed. As a result of the process, the sulphur content in diesel fuel makes no more than 0.02 %.

There also is a method of separating sulphur-containing compounds from the diesel fraction by adsorption using pure silica gel of the ASK grade and aluminum oxide in a centrifugal field at 2000-2500 rpm for 30-40 minutes (Kadyrov et al., 2001). Fine purification of hydrocarbon fractions from sulphur compounds is also carried out by their adsorption with zeolites. In this case, the initial hydrocarbon fraction is pre-contacted with a layer of sorbent, hopkalite, that has oxidative properties concerning sulphur compounds (Gimadeev et al., 1999).

There is an attractive method of deep redox-adsorption desulphurization of liquid hydrocarbon fuels, including the preparation of loose sorbent by mixing highly porous adsorbents (bentonite, montmorillonite, activated carbon or highly porous silica) with a metal nitric salt (iron nitrate, nickel nitrate, copper nitrate) and subsequent treatment of liquid hydrocarbons with the specified sorbent. In what connection the treatment is carried out by passing a stream of liquid hydrocarbons through a layer of granular sorbent with a volume speed not exceeding 100 h^{-1} (Krasilnikova et al., 2013).

The paper (Shmal et al., 2020) describes the technology of “smart micro-containers” as a method of adsorption desulphurization of oil. The formation of a special “smart micro-container”, intended directly for desulphurization of oil or oil fractions, takes place by forming a capsule from the corresponding adsorbent, into the structure of which a ferromagnetic particle is embedded. This makes it possible to effectively manage the process – to carry out targeted delivery of the microcontainer with subsequent controlled extraction. The use of adsorbing micro-containers directly in the flow allows providing a huge surface area of contact between the phases of active components and the cleaned medium (and, consequently, high efficiency of adsorbents). Besides, one of the elements of controllability of the process is the ability to use mixing equipment equipped with magnetic stirrers that ensure optimal uniform distribution of micro-containers in the liquid phase, which increases the efficiency of the adsorbent.

Currently, there is no synonymous opinion of which the desulphurization method should be used. The choice of a method for removing sulphur compounds from oil and its fractions is mainly determined by the technological and economic efficiency, as well as the absence of undesirable side processes and the availability of reagents. Research-based development of methods is actively carried out all over the globe. Therefore the search for and development of innovative ways and technologies of desulphurization is a topical research task.

The aim of the work is to conduct an experimental study on the effects of infrasound on diesel fuel samples and their further study in the laboratory to investigate changes taking place in the processed samples.

To achieve the goal, the following tasks were being solved:

- conducting a series of experiments on the effects of infrasound with a frequency of 20 Hz and 26 Hz, the duration of exposure was 20 minutes.
- studying the control sample and processed samples using specialized equipment to determine changes in the content of paraffin and sulphur.
- analyzing the results, formulation of conclusions, and recommendations for further research.

The work was carried out in several stages:

- preparation of crude oil samples and experimenting;
- research of crude oil samples using laboratory equipment, processing of laboratory data;
- analysis of results and formulation of conclusions.

2. Materials and methods

The research was carried out by way of a physical experimental procedure.

The following equipment of "SAT&M" Scientific-production center was used to study diesel fuel samples:

1. "SPECTROSCAN S" – X-ray fluorescence energy dispersion analyzer of sulphur in oil and petroleum products, which is designed to measure the mass fraction of sulphur in oil and petroleum products, such as diesel fuel, gasoline, kerosene, lubricating oils, fuel oil, hydraulic oils, jet fuel, and any distillate oil products.
2. LTN-03 – laboratory high-precision thermostat for determining the viscosity of the oil.

3. Resutls and discussion

Figs. 1-2 show the photos of a control sample that was not subjected to infrasound treatment, and samples that were treated with 20 Hz and 26 Hz infrasound.

Initially, the diesel fuel had a dark color, the sample looked like a mixture of strongly brewed tea with extraneous impurities. After processing, the color of the fuel became much lighter, and extraneous inclusions were no longer observed. The results obtained can be explained by initiated chemical reactions occurring in the fuel under the influence of infrasound.

The research results showed a decrease in viscosity and an increase in sulphur content. The fuel viscosity decreased by 13% compared to the control sample.

Fig. 1 A sample of the fuel BEFORE treatment with infrasound

Fig. 2 Fuel Samples after infrasound treatment, 20 Hz and 26 Hz sound frequencies

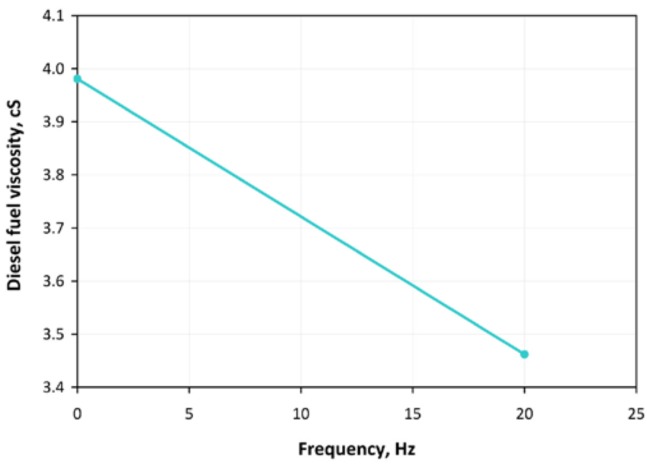

Fig. 3 The diagram of the dependence of .kdiesel fuel viscosity on the frequency of infrasound

At a sound frequency of 26 Hz, a similar result of reducing the viscosity of the fuel was recorded. Under the influence of low-frequency sounds, chemical bonds are broken in hydrocarbon molecules, so the chemical and physical properties of diesel fuel after treatment with infrasound will differ from the chemical and physical properties before treatment (Blinaeva et al., 2019).

The content of sulphur in the treated samples increased in comparison with the control one: at a frequency of 20 Hz, almost by 2 times (by 95.9%), at a frequency of 26 Hz – by 106.2 %.

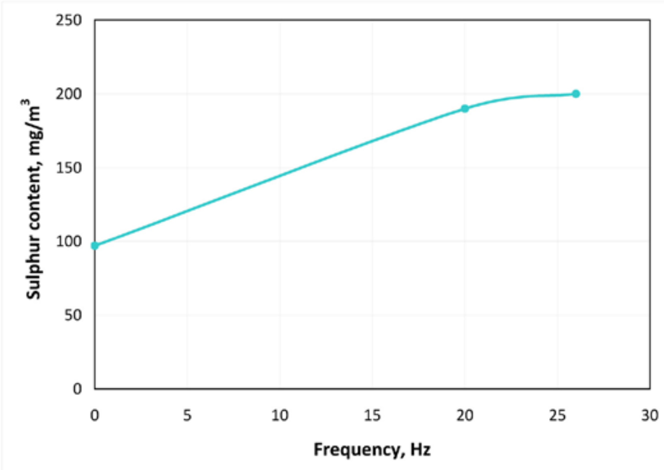

Fig. 4 The diagram of the dependence of the sulphur content in diesel fuel on the frequency of infrasound

The obtained results can be initiated by low-frequency cavitation taking place in the processed fuel samples. According to our hypothesis, the sulphur contained in diesel fuel in the bound state is released under the influence of cavitation processes, which is recorded by laboratory measurements. In the future, the released sulphur can be removed from the fuel using existing technologies used at a refinery. During cavitation, a periodic local concentration of high-density energy takes place, it is associated with pulsations of cavitation bubbles. Due to a local decrease in pressure in the rarefaction phase, cavities (cavitation bubbles) filled with the saturated vapor of the same liquid are formed in the liquid. Under the influence of increased pressure in the compression phase, as well as surface tension forces, the cavity closes, and the steam condenses at the interface of two phases – liquid and gas. The gas dissolved in the liquid diffuses into the cavity and undergoes a strong adiabatic compression. At the moment of the collapse of the cavitation cavity the pressure can reach 100 MPa, and the temperature - up to 10000 K; and at the same time a spherical shock wave begins to spread in the liquid. If periodically pulsed tensile stresses are generated in a liquid, the “center” of cavitation present in it, which are stable steam and gas bubbles of small sizes, begin to grow and form a so-called “cavitation cluster”.

The energy released when the cavern collapses is sufficient to excite, ionize, and dissociate water molecules, gases, and substances with high vapor elasticity inside it. At that, long molecular chains can be converted into light hydrocarbon radicals of gas and distillate fuel fractions. The bond-breaking energy in hydrocarbons varies within 40 ... 400 kJ/mol, while the bond strength in the middle of a normal paraffin molecule is less than at the end. Besides, during high-intensity cavitation and over a long period of time, carbon bonds in paraffin molecules are disrupted. At the same time, when the C-H bond is broken, hydrogen is separated from the hydrocarbon molecule, and when the C-C bond is broken, the hydrocarbon molecule is torn into two unequal parts. As a result, the changes that take place are already of the physical and chemical composition of hydrocarbons – a decrease in the molecular weight, crystallization temperature, etc., which causes changes in the viscosity, density, and flashpoint of the oil product. As a result of micro-cracking at the molecular level, “activated” particles accumulate in the processed petroleum products: radicals, ions, and ion-radical formations.

The elementary composition of diesel fuel consists mainly of three elements: carbon (C), hydrogen (H), and oxygen (O). Diesel fuel contains an average of 85.5...86.0% C, 12.5...13% H, and 1...2% O. During the production of fuel, it is not possible to completely get rid of sulphur.

The average chemical formula for common diesel fuel is $C_{12}H_{24}$, in the range from approximately $C_{10}H_{20}$ to $C_{15}H_{28}$. Diesel fuel contains sulphur compounds – mercaptans (R-SH), sulfides (R-S-R), disulfides (R-S-S-R), thiophenes, thiophanes, etc., but not elemental sulphur as such. The polarity of the S-H bond is much lower than the polarity of the O-H bond, that is why the hydrogen bonds between thiols (mercaptans) molecules are much weaker. As a result of exposure to low-frequency sounds in the range from 10 to 30 Hz with different durations, the covalent bonds in the hydrocarbon are getting broken with the formation of an excessive amount of hydrogen ions. Since the hydrogen ion is in the free state for a fraction of a second, it combines with the sulphur from the S-H bond. If the presence of sulphur was not detected during the study of the control sample, then after infrasound processing the study of samples with the SPECTROSCAN S device made it possible to detect the presence of sulphur in the samples under study.

Accordingly, we can state the fact of a significant change in the structure of diesel fuel under the influence of infrasound vibrations. Despite the seemingly “negative” result – after processing the amount of sulphur in the samples increased, - this result is very important. Modern technologies for sulphur diagnostics have some limitations, which in our case did not allow us to detect the presence of sulphur in the original sample. The exposure to infrasound led to the release of initially “hidden” from diagnostic methods sulphur and its transition to compounds that are easy to identify.

This, in our opinion, is a significant result, since it will prevent the entry into the atmosphere of sulphur compounds that were not diagnosed during the initial check.

4. Conclusions

For the first time, multiple increases in the concentration of sulphur were detected when processing crude paraffin oil with infrasound. This is related to the chemical reactions initiated under the influence of low-frequency cavitation. As a result of these reactions, the bound sulphur passes into compounds that are available for identification.

These results are extremely important because processing allows determining the content of sulphur in such compounds that are not identified by standard methods.

This will significantly improve the purification of oil from sulphur and reduce the burden on the environment.

The results obtained allow us to conclude that there is an undoubted relationship between the infrasonic effect, viscosity, and the process of sulphur release in the studied diesel fuel samples.

The results will serve as the basis for further, more detailed research.

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