Application of ferromagnetic nanoparticles and rotating electromagnetic fields for oil desulfurization

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Abstract. An innovative technology for desulfurization of hydrocarbon raw materials, based on the effect of a rotating electromagnetic field of high power and ferromagnetic nanoparticles located in the working area of the device on oil or fuel oil, has been developed and implemented on a pilot scale. The basis of the technology is the device named “electromagnetic process activator”, which is based on the principle of converting the energy of the electromagnetic field into other types of energy. The reduction of sulfur in oil by 2.5 times and fuel oil by 3 times was achieved at energy costs of up to 1.0 kW per ton of processed raw materials, which allows us to conclude that the developed technology is highly efficient and productive.

1. Introduction
Oil production and refining for Russia in the next 10-15 years is and remains one of the main sectors of the economy. For this reason, the business associated with the production and processing of oil in Russia is a sustainable and profitable industry. In the long term, there is a risk of competition with alternative energy sources (gas, etc.), but since the transition to new fuels requires significant capital investments, the market for the production and sale of motor fuels and petroleum products is not expected to shrink in the foreseeable future.

When analyzing the quality of oil produced in Russia in recent years, one can see a noticeable increase in the amount of heavy oils with a high percentage of sulfur in the total production volume. Up to 50 million tons of heating oil are exported from Russia annually. Reducing the total sulfur, density, and viscosity in heating oil already gives an economic effect of up to 5,000 rubles per ton. The same applies to the produced heavy and high-viscosity grades of oil.

In Russia, the technology of tar desulfurization is in demand for the production of low-sulfur petroleum coke, the shortage of which in the domestic market is approximately 2-2.5 million tons per year). A significant part of the missing petroleum coke is imported from China, Japan, and Romania. Thus, the development of technologies for desulfurization of heavy oils, heating oil, and petroleum coke is an important and urgent research task [1].

We have developed and implemented on a pilot scale, an innovative technology for desulfurization of hydrocarbon raw materials using devices for forming spatial polarized electromagnetic effects of rotating electromagnetic fields on hydrocarbon raw materials. Numerous experiments conducted by us have confirmed the effectiveness of the proposed technology in the field of oil refining, which allows
processing oil, fuel oil, shale oil, and petroleum products, with an improvement in their rheological properties (density, viscosity), with a significant reduction in sulfur and an increase in the yield of light fractions in petroleum products. This technology allows cracking at low temperatures, reducing energy consumption, and demetallizing processed raw materials to produce collective concentrates of non-ferrous and rare earth metals.

The technology of desulfurization of hydrocarbon raw materials is based on the effect of a rotating electromagnetic field of high power and ferromagnetic particles located in the working area of the device on oil or fuel oil. The technology is based on the device "electromagnetic process activator", which is based on the principle of converting the energy of the electromagnetic field into other types of energy.

2. Block diagram and operating principle of the equipment

A block diagram of a hydrocarbon desulfurization equipment based on «electromagnetic process activator» (EPA) is shown in figure 1: Flow-through electrolytic cell (1); Container for the ferromagnetic liquid (2); Ferromagnetic liquid feed dispenser (3); Oil and ferromagnetic liquid mixer (4); EPA (5); Separator (6); Pumps (7).

The feedstock (oil, fuel oil) undergoes the primary processing stage in the flow-through electrolytic cell (1), where the process of dissociation in the oil begins. In the mixer (4), the initially processed raw material is mixed with the ferromagnetic liquid and fed to the EPA (5), where the main processing stage takes place. The product then passes through a magnetic separator (6) consisting of a lattice permanent magnet, an electrostatic filter, where the final demetallization process takes place, and then through a centrifuge to release excess water, and then into the product tank. The extracted organometallic precipitate enters a separate container for further processing. The entire process takes place at normal atmospheric pressure and temperatures up to 100 degrees Celsius.

2.1 Ferromagnetic liquid

The proposed technology uses a proven technique for producing a ferromagnetic liquid - a colloidal solution of a fine nanopowder of magnetite Fe₃O₄ in distilled water. The main advantages of magnetite nanoparticles are low susceptibility to oxidation, high magnetic properties and low cost [2]. With a decrease in the size of the magnetite particles to a single-domain level (less than a few tens of nm), they acquire the property of superparamagnetism. Superparamagnetic particles, when the magnetic field is removed, completely lose their magnetization, that is, they return to their original state and can be easily
resuspended in solution. A decrease in the particle size leads to an increase in the share of surface energy in its chemical potential, which makes it able to interact effectively with hydrocarbons.

As a result of our experiments on the processing of oil and fuel oil, we obtained results indicating that magnetite nanoparticles have a catalytic effect and can be successfully used for hydrocarbon raw materials in order to change its rheological properties, reduce its density and viscosity, and desulfurize by forming compounds with sulfur of the FeS type.

The great prospects of nanoparticle catalysis are related to two circumstances. First, a catalyst consisting of nanoparticles has a large specific surface area and can be very active in heterogeneous reactions. Secondly, many properties of nanoparticles depend on their size, so by changing the latter, it is possible to control not only the activity, but also the selectivity of the nanocatalyst.

The feedstock (oil or fuel oil) and the ferromagnetic liquid are mixed in the mixer (4) (figure 1) to form a homogeneous mixture, while the ferromagnetic liquid is added in an amount of no more than 5 wt.%. The homogeneous mixture of oil or fuel oil and ferromagnetic liquid is then fed into the working chamber of the EPA.

2.2 Electromagnetic process activator

The diagram of the electromagnetic process activator is shown in figure 2. The working chamber of the EPA with a diameter of 90 mm is located in the inductor of the rotating electromagnetic field. The EPA working chamber contains ferromagnetic elements in the form of cylinders with a diameter of 1 mm and a length of 5 mm in the number of several hundred pieces (with a total weight of up to 0.5 kg). The rotating electromagnetic field inductor with a cooling system is connected to a three-phase industrial AC network with a voltage of 380/220 V, a frequency of 50 Hz, providing a rotation speed of the electromagnetic field of 3000 revolutions per minute.

![Figure 2](image)

**Figure 2.** Scheme of electromagnetic process activator: 1 - working chamber; 2-inductor of rotating electromagnetic field; 3-cooling system.

The rotating electromagnetic field formed by the inductor in the working chamber is characterized by a high penetrating power, which allows influencing the physical and chemical processes in the processed substance. Multi-level pulsed effects include magnetostriction, cavitation, electrolysis, supercritical effects, as well as mechanochemical, electrophysical, and electrochemical effects on processing objects [3-5]. The hydrocarbon raw materials change their density and viscosity during processing, and the final products acquire qualitatively new properties.

Of the numerous processes that occur in the EPA working chamber, one of the main ones is the process of electrophysical and electrochemical activation of water (which is part of a ferromagnetic liquid) in a rotating electromagnetic field with mechanochemical treatment with ferromagnetic elements [6]. In addition, water is a source of radicals *O, *OH, *H. Oxygen radicals and the longest-lived hydroxyl radical, along with electromagnetic effects, mainly trigger depolymerization reactions of
organic substances. At the same time, due to atomic hydrogen, hydrogenation reactions are carried out, including low-molecular compounds at the time of their formation.

As a result of electromagnetic and electromechanical effects on the mixture of hydrocarbon raw materials and ferromagnetic liquid in the EPA working chamber, water is split according to the scheme: H₂O = *OH + *H. The hydroxyl radical (*OH) mainly oxidizes the sulfur atom to form a sulfone molecule and then eliminate sulfur dioxide [7]. Atomic hydrogen (*H) takes part in the purification process, closing the hydrocarbon residues of the sulfone molecules.

In addition, under the action of extremely high pressures in the region with a spark channel, the direct decomposition of sulfur-containing compounds occurs along the C–S bond, since the energy of breaking such a bond is 138 kJ/mol less than the energy of the C–C and C–H bonds. At the same time, high pressures contribute to the intensification of hydrotreating processes.

In the process of electromagnetic and electromechanical treatment, redox reactions of desulfurization occur in the presence of excess water supplied to the working chamber. Excess water is additional water supplied to the working chamber, the volume of which is up to 20% of the volume of a homogeneous mixture of ferromagnetic liquid and hydrocarbon raw materials.

When processing oil and fuel oil in the working chamber, it is subjected to a complex effect, including ultrasound. These effects contribute to the intensification of mass transfer in the reaction zone. Cavitation, which occurs during the processing of the liquid phase, contributes to the breakdown of liquid droplets that make up the oxidizer/hydrocarbon medium system into submicron and nano-sized parts. This decrease in the diameter of the droplets contributes to the reactions that take place at the interface.

At the first stage, the solvated electrons initiate the precipitation of sulfur-containing compounds. In the second stage, water and heavy sludge with sulfur are coagulated and separated. As a result of the influence of electromagnetic fields, these processes occur under milder conditions than similar reactions under normal conditions. Accordingly, sulfur passes into high-molecular heteroatomic organic compounds, as well as sulfur compounds with metals (sulfides).

The hydrated electron, accepted by the oriented molecules of the water system and the impurity ions, is a very active electron donor. This is the most characteristic reducing agent that provides active electron transfer.

At the same time, the process of oxidation of sulfur-containing compounds with air oxygen takes place in the working area of the reactor. There is a redistribution of sulfur compounds in the volume of processed substances during processing, however, an increase in the sulfur content on the internal surfaces of the equipment does not occur, and the formation of volatile sulfur compounds was not detected.

The compounds obtained as a result of oxidative desulfurization, including sulfones, have properties that distinguish them from the initial sulfur compounds and facilitate removal from the initial substance. The resulting sulfur compounds are carried away from the reaction zone with an excess of water, and also settle as an insoluble precipitate when a colloidal solution of ferromagnetic nanoparticles is added.

2.3 Magnetic separator

From the EPA working chamber, the homogeneous mixture enters a magnetic separator to separate ferromagnetic elements and nanoparticles. The product then passes through an electrostatic filter, where the final desulphurization process takes place in the separation unit. The excess water with the insoluble precipitate is then separated by centrifugation. The composition of the sediment depends on the feedstock and includes solid insoluble particles of sulfur impurities.

The process of separation of processed oil and insoluble sludge is based on an industrial technology for extracting heteroorganic clusters from hydrocarbon-containing raw materials by combined treatment of hydrocarbons, including simultaneous exposure to the feedstock to an electrostatic field, a pulsed magnetic field with simultaneous additional ultrasonic action, which provides deposition on the electrodes of a gel-like concentrate containing clusters V, and/or Ni, and/or Al, and/or Ca, and/or S, and/or Si, and/or P, and/or Co. The technical result is the extraction of chemical elements V, Ni, Al,
Ca, S, Si, P, Co, Na from hydrocarbon raw materials in the form of organometallic clusters consisting of a metal core covered with a layer of thiols, organic sulfides, creating a closed shell. The extracted organometallic precipitate enters a separate container for further processing.

3. Results and discussion
We have conducted many experiments on desulfurization of oils and petroleum products using the technology described above. The following are typical results.

The initial hydrocarbon feedstock is oil processed at the Mari Oil Refinery LLC. The frequency of rotation of the electromagnetic field is 50 Hz, the speed of rotation of ferromagnetic elements in the electromagnetic field is 3000 rpm, the processing time of the mixture is up to 4.5 seconds. The amount of ferromagnetic liquid is up to 1.2 wt.%. The experiments made it possible to reduce the content of the mass fraction of sulfur in oil from 1.2438% to 0.5077%. At the same time, the amount of light fractions in the oil after processing increased by 14.5%.

The initial hydrocarbon feedstock is heating oil M100 produced by LUKOIL–Nizhegorodnefteorgsintez LLC. The speed of rotation of the ferromagnetic elements in the electromagnetic field is 3000 rpm, the processing time of the mixture is up to 6.0 seconds. The amount of ferromagnetic liquid is up to 2.0 wt.%. The content of the mass fraction of sulfur in the heating oil is reduced from 3.50% to 0.50%.

The initial hydrocarbon feedstock is heating oil M100 of the Ryazan Oil Refinery. The speed of rotation of ferromagnetic elements in the electromagnetic field is 3000 rpm, the processing time of the mixture is up to 6.0 seconds. The amount of ferromagnetic liquid is up to 2.0 wt.%. The sulfur content is reduced from 2.62 % to 0.93%.

The above-mentioned indicators of reducing the total sulfur content were achieved at energy costs of up to 1.0 kW per ton of processed raw materials.

It should also be noted that the proposed technology allows to work in a continuous mode, occupies small areas, does not require the construction of capital structures, is characterized by low material and energy costs, is easily integrated into existing technological cycles and is scaled.

This technology at the stage of oil preparation without changing the technological scheme of the refinery increases the profitability of existing refineries by adding another process to the technological chain of oil refining with a valuable product at the output and improves the grade of transported and processed oil.

References
[1] Javadli R and de Klerk A 2012 Appl Petrochem Res 1 3
[2] Gubin S P, Koksharov Yu A, Khomutov G B, Yurkov G Yu 2005 Uspekhi khimii 74 539
[3] Adushkin V V, Andreev S N, Popel S I 2004 Doklady Earth Sciences 399(8) 1153
[4] Adushkin V V, Andreev S N, Popel S I 2007 Geology of ore deposits 49(3) 201
[5] Andreev S, Artem’ev K and Kazantsev S 2020 OSA High-brightness Sources and Light-driven Interactions Congress, OSA Technical Digest (Optical Society of America, 2020) JM3A.29
[6] Lesin V I, Dyunin A G, Khavkin A Ya 1993 Russian Journal of Physical Chemistry A 67(7) 15611562.
[7] Anisimov A V and Tarakanova A V 2008 Russian Journal of General Chemistry 52 32