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Desulfurization of Liquid Hydrocarbon Fuels Applying Adsorption Method

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***Abstract*—The article is devoted to the study of an adsorption method for desulfurization of oil products during their processing, purification from admixtures of sulfur-containing compounds by adsorption on the surface of the sorbent material. The article presents the results of experimental studies of properties and efficiency of sorbents and their compositions, resistance and stability of sorption properties, as well as methods of their activation.**

Keywords—desulfurization; oil matrix; ash structures of natural materials; metals; nanoparticles.

I. Introduction

Due to the limitation of oil production volumes, today there is an increase in the share of low-quality raw materials with a high content of sulfur and its compounds involved in the production of motor fuels. Sulfur-containing oil compounds include hydrogen sulfide, mercaptans, sulfides, disulfides, thiophenes, etc. In the process of oil fractionation uneven distribution of sulfur-containing compounds in the oil fractions is carried out. Thus, the smallest share of sulfur-containing compounds is contained in oil gases, which include hydrocarbons with the number of carbon atoms from 1 to 4. As the boiling point of the oil fraction increases, the sulfur content in them increases in proportion to the temperature increase. Thus, the maximum concentration of sulfur compounds is seen in heavy oil residues (masuts, tars).

As a result of oil fuels use, sulfur oxides are released into the environment, which are products of combustion of sulfur-containing oil compounds. Sulfur oxides have toxic effects on air, soil and water [1-3].

The presence of sulfur-containing compounds in automotive fuels causes corrosion of process equipment in contact with chemically aggressive sulfur-containing oil products. The phenomenon of corrosion in the presence of sulfur-containing compounds is enhanced in case water is contained in the oil product [4, 5].

Desulfurization of oil products is carried out by extraction, alkaline treatment, characterized by high technological complexity and water consumption. Thus, the research and development of adsorption methods for purification of oil products from sulfur-containing compounds is a promising direction.

II. Results and discussions

Experimental studies were carried out to determine the effectiveness of the adsorption method for purification of oil products (gasoline, diesel fuel, oil) from sulfur - containing compounds, for which matrices of oil products (gasoline, diesel fuel, oil), catalysts (metal nanoparticles-Fe, Co, Cu, W, etc.) and auxiliary components of natural origin were produced.

Matrices of oil products were made on the basis of elemental composition of their ashes obtained by combustion in a muffle furnace EXP-10 at the temperature of 600 °C for 50 minutes. To activate the metal nanoparticles, i.e. to remove the oxide film from their surface, the metals were placed in a coal bed in a muffle furnace, heated to the temperature of 300 °C for 15 minutes. Ash of oil and oil products was used as the basis to create the matrix. The oil product was combusted seven times with the addition of fresh product in a muffle furnace at a temperature of 600 °C until ash was obtained.

The mass of the product to create the matrix was calculated in such a way that during the last combustion it did not exceed 15 grams. Before combustion the oil product was stirred for 3 minutes to average the fractional composition, after which the mixture was placed in a crucible. Combustion was carried out in a crucible with the lid closed for 95% to exclude ash structure ablation.

The product was combusted until the cessation of smoke formation, and then kept in the oven for another 2 minutes. Then the crucible with an ash structure was cooled, and fresh oil was added to it. Thus, seven combustions of oil products were carried out. The calculation of the required mass is given in Table I.

TABLE I. CALCULATION OF OIL PRODUCTS MASS FOR ADSORPTION MATRIX CREATION

Number of combustions	Amount of a fresh oil product (grams)		
No.	**Gasoline**	**Diesel fuel**	**Oil**
1	5.04	5.11	5.07
2	5.52	5.47	5.36
3	6.11	6.16	6.04
4	6.73	6.62	6.84
5	7.47	7.38	7.51
6	8.13	8.01	7.99
7	8.94	8.89	9.01
8	9.86	9.79	9.79
9	10.83	10.80	10.87
10	11.95	11.94	11.89
Total	80.58	80.17	80.37

Determination of granulometric composition and morphology of the particles of the sorption filter components is carried out by means of electronic inverted metallographic microscope Axiovert.

The analysis showed that: the composition of oil products matrices (gasoline, diesel fuel, oil) includes particles of various shapes with a size of 10 to 150 nm; metal nanoparticles (Fe, Cu, Co, Ni, W) had a size of 10 to 50 nm; particles of auxiliary materials — sorbents based on minerals of natural origin (soil, clay, sand) had a wide range of particle sizes from 10 to 700 microns.

To determine the elemental composition and concentration of elements in the components of the sorption filter, a complex x-ray fluorescence spectrometer was used, which included a measuring unit and an analytical unit. The results of determining the elemental composition of the matrices of gasoline, diesel fuel and oil are presented in Tables II—IV. While studying the properties and process of water-oil emulsions separation, it was found that with the introduction of sea salt ash into the emulsion, the intensity of its separation significantly increases [4, 5].

To study the kinetics of water-oil emulsions separation the following products were used:

A. Oil products:

- Oil of JSC "Lukoil"
- Fuel oil

B. Water structures:

- Artesian water
- River water (River “Polnoy Voronezh”)
- Sea water (the Black Sea)

Chemical and ionic compositions of water of various structures used for the preparation of emulsions are analyzed. The results of studies of the composition of sea, river and artesian water are presented in Tables I—IV.

TABLE II. ELEMENTAL COMPOSITION OF GASOLINE MATRIX

Gasoline					
Element	**Amount (%)**				
Ni	3.16	3.09	3.25	3.18	2.98
Cu	2.14	2.21	2.27	2.36	2.10
Fe	7.21	7.16	8.01	7.15	7.06
S	15.10	15.00	14.50	17.11	16.40

TABLE III. ELEMENTAL COMPOSITION OF DIESEL FUEL MATRIX

Diesel fuel					
Element	**Amount (%)**				
Ni	16.47	16.54	16.53	16.47	16.5
Co	10.19	10.19	10.17	10.21	10.19
Cu	7.62	7.61	7.61	7.59	7.61
Fe	13.16	13.16	13.22	13.16	13.18
W	4.51	4.50	4.57	4.52	4.52
S	14.15	14.12	14.15	14.13	14.14

TABLE IV. ELEMENTAL COMPOSITION OF OIL MATRIX

Oil					
Element	**Amount (%)**				
Ni	15.23	17.51	15.08	14.93	16.75
V	18.56	17.96	18.37	18.19	20.42
Mn	11.23	12.91	11.12	11.01	12.35
Cr	8.14	7.98	8.06	7.98	8.95
Co	7.53	7.16	7.45	7.38	8.28
Cu	9.24	10.63	9.15	9.06	10.16
Fe	7.15	8.22	7.08	7.01	7.87
W	6.23	5.26	6.17	6.17	6.85
S	25.16	28.93	24.49	6.11	26.59

Composition of nanoparticles of similar structured metals, designed to maximize the effect of the components of oil and oil products matrices in the process of adsorptive desulfurization was chosen on the basis of analysis of elemental composition of oil products matrices.

To increase the efficiency and functional purpose of the obtained oil and oil products matrices, the following components of natural origin, which are part of the filter, were used to manufacture the adsorption filter: soil, sand, clay. Activation of filter elements was carried out as follows. The filter component pre-ground in a mortar was taken and sieved on a vibrating table. A fraction with particle sizes from 10 to 100 μm was selected for the experimental study. The mixture of selected components weighing 2 g was alternately treated in a metal crucible at the temperature of 600 °C in the muffle furnace.

The matrices of oil products and components of natural origin were analyzed for elemental and granulometric compositions and morphology of particles applying an x-ray fluorescence technique.

As a result of x-ray fluorescence analysis, the content of the following elements in ash structures was determined (Tables V–VIII).

TABLE V. CONTENT OF SOIL ASH STRUCTURE

Soil						
Element	O_2	Si	Fe	Ni	Ca	S_2
Amount (%)	25.9	15.13	32.08	1.8	1.54	2.91

TABLE VI. CHEMICAL COMPOSITION OF SAND

Sand						
Chemical compounds	SiO_2	Fe_2O_3	Al_2O_3	MgO	CaO	SO_2
Amount (%)	69.40	6.82	7.05	0.25	1.79	0.1

TABLE VII. CHEMICAL COMPOSITION OF CLAY

Clay						
Chemical compounds	SiO_2	Fe_2O_3	Al_2O_3	MgO	CaO	KO_2
Amount (%)	54.61	6.3	15.22	3.14	5.36	5.91

TABLE VIII. IRON OXIDE COMPOSITION

Iron oxide					
Elements	**Amount (%)**				
Fe	49.25	49.21	49.21	49.24	49.23
O2	49.17	49.09	49.16	49.11	49.13

The concentration of sulfur-containing compounds in oil and oil products before and after their adsorption purification was determined in order to identify the effectiveness of each of the components presented above in the process of sorption desulfurization.

Fig. 1 shows the graphical dependence of the concentration of sulfur-containing compounds in diesel fuel before and after filtration using various components as a filter filler.

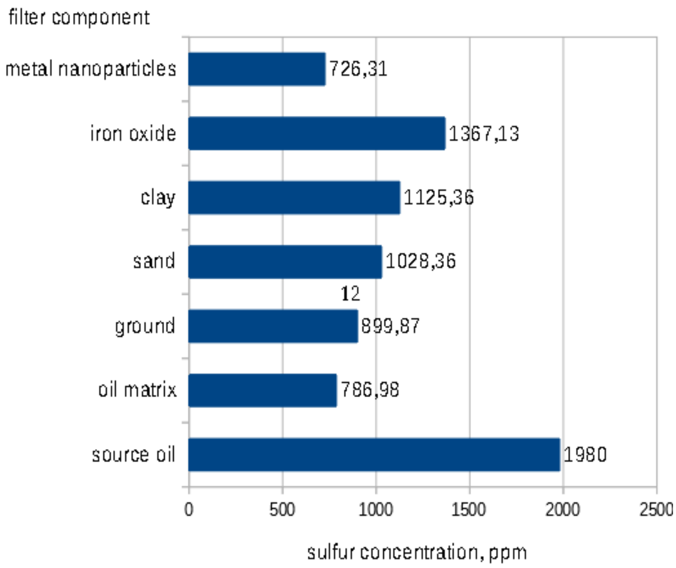


Fig 1. Sulfur concentration in diesel fuel before and after filtration through various sorbent components

Determination of efficiency of adsorption purification of oil products by means of matrices of oil and oil products (gasoline, diesel fuel, oil), components of natural origin and composition of metal nanoparticles was carried out by filtration of oil and petroleum products through a filter composed of sorbents and catalysts of adsorption desulfurization. The structure of the filter composition is shown in Fig. 2.

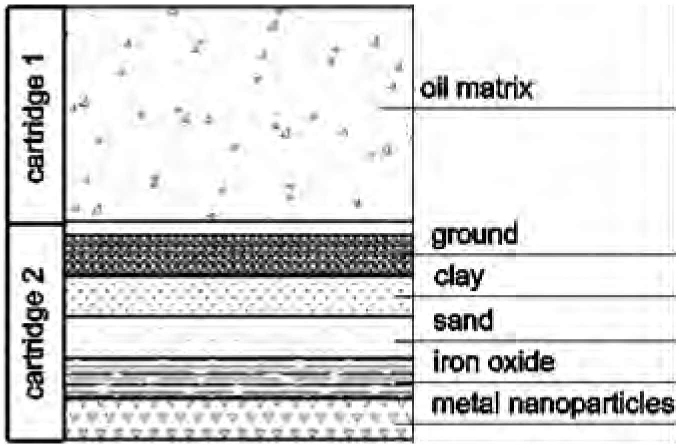


Fig. 2. Structure of adsorption filter for the process of desulfurization of oil and oil products

Each layer of the filter components was separated by a grid with a cell size of 0.04 mm.

Determination of sulfur-containing compounds concentration before and after filtration was carried out: in gasoline and diesel fuel — by gas chromatography, in oil — by x-ray fluorescence energy dispersion analysis.

Sulfur-containing oil and oil products were filtered through composed multi-component adsorbent. After each filtration cycle, a certain amount of the obtained filtrate was selected and a matrix of desulfurized product was made on its basis. The resulting structure of desulfurized oil matrix was added to the filter (top layer filling) and filtration process was repeated. Part of the following filtrate was also used to make the matrix of desulfurized oil product. To determine the sulfur sorption capacity and absorptive potential of the filter, the filtration cycle was repeated 9 times without regeneration. After each filtration cycle, oil product samples were analyzed by chromatographic and energy dispersion methods to determine the concentration of sulfur-containing compounds in them. On the basis of experimental studies, diagrams describing the content of sulfur compounds in oil products are compiled. The diagrams are shown in Fig. 3-5.

The analysis of the presented results of experimental studies shows that the multiple cycle of filtration of oil and oil products through the filter layers, using the matrix structures after each cycle significantly reduces the sulfur content and its compounds. The eighth and ninth filtration cycles showed a decrease in the filter efficiency, which indicates the need for its regeneration. Regeneration of the filter components was carried out by calcining and holding them in a muffle furnace at a temperature of 300 °C. The filter after the regeneration was assembled again, and the matrices of desulfurized oil products obtained after cycles 1-8 of filtration were additionally introduced.

The decrease of sulfur concentration in oil products occurs due to their adsorption on the surface of solid-phase filter components.

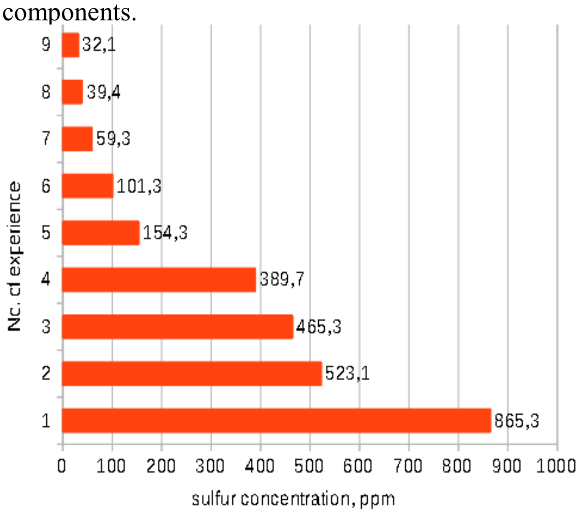


Fig. 3. Concentration of sulfur-containing compounds in gasoline

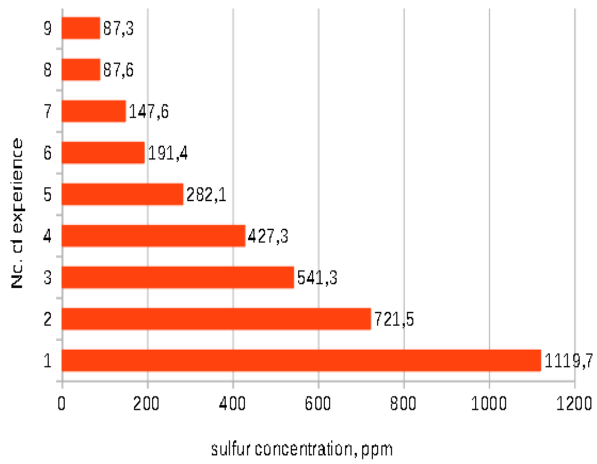


Fig. 4. Concentration of sulfur-containing compounds in diesel fuel

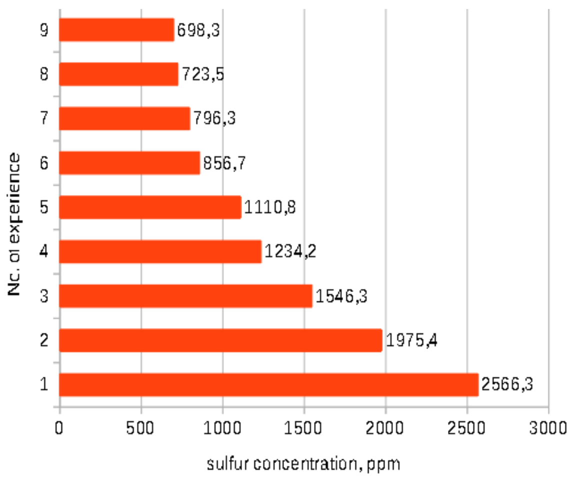
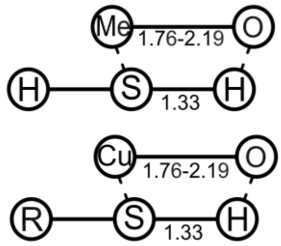


Fig. 5. Concentration of sulfur-containing compounds in oil

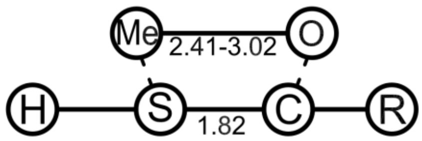
According to the principle of geometric correspondence, a solid body can become an adsorbent if the location of the active centers on its surface geometrically corresponds to the location of atoms in the molecules of reacting substances. In addition, the distance between the atoms in the multiplet must correspond to the distance (length of the chemical bond) between the atoms in the reacting molecules forming a multiplet complex on the surface of the sorbent [6-8].

The mechanism of sorption of organic sulfur compounds is realized by filter components (metal oxides) from petroleum products [9-10].

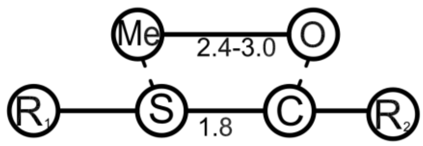
1. Sorption of hydrogen sulfide and mercaptans by S-H bond by metal oxides (Cu, Si, Al, W, Mg, Cr, Zn, Co)



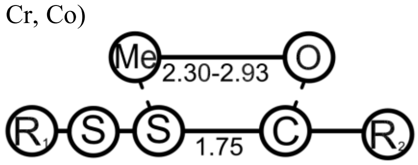
2. Sorption of the mercaptans by S-C bond by metal oxides (Ni, Fe, Ca, Cr)



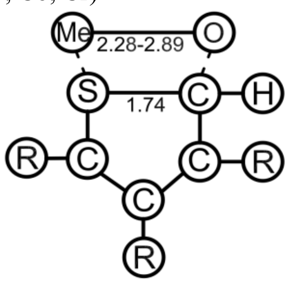
3. Sorption of sulfides by S-C bond by metal oxides (Ni, Fe, Ca, Cr)



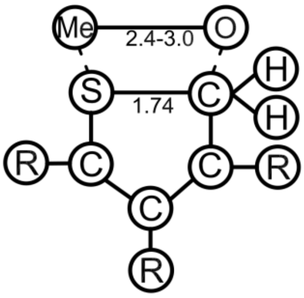
4. Sorption of disulfides by S-C bond by metal oxides (Ni, Fe, Ca, Cr, Co)



5. Sorption of thiophenes by S-C bond by metal oxides (Fe, Ca, Pb, Co, Cr)



6. Sorption of thiophanes by S-C bond by metal oxides (Fe, Ca, Cr, Ni)



III. CONCLUSIONS

The influence of elements of oil and oil products matrices and sorbing components of the natural origin filter on concentration of sulfur-containing compounds was determined. A decrease in concentration of sulfur-containing compounds in the process of desulfurization was found.

It is proposed to use the mechanism of organic sulfur compounds sorption from oil products by metal oxides included in the matrix of oil and oil products and filter components of natural origin, based on the principle of geometric correspondence of atoms bond lengths in the molecules of sulfur-containing compounds and sorbent components.

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