Sonocatalytic Oxidative Desulfurization of Oil from the Zhanazhol Oilfield

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Abstract—Sonocatalytic oxidative desulfurization of oil from the Zhanazhol oilfield was investigated. Application of stepwise periodic treatment in an ultrasound field in the presence of a Ni-skeletal catalyst and oxidizer was shown to be an effective procedure for improving the quality of oil and oil-based products, which allowed targeted change of its chemical composition, increasing the yield of light products (gasoline and diesel fractions from 15.6 to 21.9 and from 47.7 to 58.6 wt %, respectively) and decreasing the sulfur content in oil products to 49%.

The main approach for improving for heavy crude oil processing technologies involves the development of catalytic systems that make it possible to conduct processes at lower temperatures and with a higher yield of the target products [1, 2]. The processing of oils and condensates extracted in Kazakhstan, which have a high content of sulfur containing compounds of different classes (hydrogen sulfide, mercaptans, disulfides, sulfides) is of particular significance, especially for environmental protection [3, 4].

Refining requirements on the quality of oil and oil products initiated the search for novel approaches to targeted change of their composition using unconventional technologies. The ultrasound treatment of hydrocarbons is one such technology, which has continued to generate interest for the last 10−15 years [5] due to the potential for hydrocarbon cracking at a relatively low average temperature and pressure compared to conventional oil processing technologies.

Sonocatalytic desulfurization of oil from the Zhanazhol oilfield was investigated in this work with the goal of deeper oil processing and improving the quality of oil products. The Zhanazhol oilfield is located in the Mugodzharskii district of Aktyubinsk oblast 240 km south of Aktyubinsk. It was discovered in 1978. Naphthene-paraffin oil from this oilfield, with geological reserves estimated to be 500 mln t, was marked according to the requirements of the State Standard RK ST 347-2005 as belonging to group 2.0.1.0 based on its hydrocarbon composition.

EXPERIMENTAL

The physicochemical characteristics of diesel fuels before and after desulfurization were determined in a certified (certificate no. KZ.I.02.1572) and accredited laboratory (accreditation no. 03/14) for investigation and comprehensive analysis of fossil fuels and products of their processing at the Scientific-Research Institute of Novel Technologies and Materials, al-Farabi Kazakh National University. The oil fractional composition was determined on an ARN-LAB-02 apparatus intended for assaying the composition of oil fractions according to State Standard GOST 2177-99, ISO 3405, and ASTM D 86. The cloud point, solidification, and freezing point of oil were measured on an INPN Kristall apparatus according to the ISO 9001 standard. The oil density was determined with a pycnometer at 20°C. The sulfur content in the oil composition was determined according to State Standard GOST R1947-2002 and ASTM D 4294-98 on a Spectroscan S apparatus.

A Ni-skeletal catalyst produced from a Ni–Al–Fe−Cr–Ti alloy (51.1% Ni, 46.9% Al, 0.075% Fe, 0.8593% Cr, 0.914% Ti) was used. The Ni-skeletal catalyst was produced by the complete alkaline leaching method. An aliquot of the alloy (1 g) was treated with a 20% NaOH solution under heating in a water bath for 2 h. The sample was washed with distilled water following alkali decantation until a neutral pH of the washing solution was reached.

Table 1. Elemental composition of Ni-skeletal catalyst

Element	Concentration, %	Peak intensities, cps.
Ni	89.18	1661.8
Fe	0.151	5.5
Cr	1.15	33.9
Ti	1.21	21.7
Al	8.31	0.10

Table 2. X-ray diffraction parameters of Ni-skeletal catalyst

Angle 2θ	D, Å	Intensity	Element
44.413	2.0381	1542	Ni
51.407	1.7761	922	Ni
62.401	1.4870	806	Ti
76.160	1.2489	837	Ni
92.462	1.0667	845	Ni

The catalyst was treated at a frequency of 90 Hz in an APFIR ultrasound bath (APC Components, United States).

To study the effect of ultrasound waves on oil, an oil sample (80 mL) was placed in an MLUK 3/22 OL multifunctional laboratory ultrasound complex (U-Sonic, Russia) and subjected to wave treatment with a frequency of 22 kHz (30% power) for 5 min in the presence of the catalyst (0.2% of the oil volume) and an oxidizer (ozone−air mixture), followed by partial removal of the purified oil.

Oil ozonation was carried out on an EUIA 941.711.001 no. 143-94 ozonator with the flow rate of the ozone−air mixture of 0.125 mL/min.

The nickel catalyst was investigated with an H-600 electron microscope (Hitachi, Japan) and a Quanta-3D 200i electron scanner (FEI, United States). X-Ray diffraction patterns of the samples were obtained on a DRON-3M diffractometer in digital form using copper radiation. The X-ray diffraction patterns were preprocessed with the Fpeak program to determine the angles and intensity of peaks from the sample. The PCPDFWIN program with the PDF-2 diffraction database was used for phase analysis.

The IR spectra of oil samples were recorded with a Sectrum-65 Fourier-Transform IR spectrometer (PerkinElmer, United States) over the frequency range 4000−450 cm^{-1}. Crystal samples were prepared as tablets with potassium bromide.

RESULTS AND DISCUSSION

Taking into consideration the literature data [6] on the stimulating effect of ultrasound vibrations on physicochemical and catalytic processes due to acceleration of heat and mass exchange in the cavitation region, we attempted to use ultrasound to stimulate catalytic oxidation of sulfur-containing organic compounds in hydrocarbons to increase the efficiency in desulfurizing oil and oil products.

Oil samples from four wells of the Zhanazhol oilfield were selected for this study. The oil density was 814.5−818.4 kg/m^3, and the kinematic viscosity values were in the range l7.9−5.7 cSt. The content of the fraction from initial boiling to 200°C was 29.8%, and the fraction from 200−350°C was 53.8%. The contents of paraffins, sulfur, water, and mechanical admixtures were 3.3, 0.68, 0.09, and 0.04 wt %, respectively. The concentration of chlorides in the oil was 160 mg/dm^3, the saturated vapor pressure was 41.40 kPa, the total content of hydrogen sulfide and methyl- and ethyl mercaptans did not exceed 40 ppm, and the average amount of chlorinated organic compounds was 3.7 ppm. The yield of the gasoline fraction (40−180°C) containing 0.25 wt % of sulfur was 15.6 wt %. The yield of the diesel fraction (180−320°C) containing 0.84 wt % of sulfur was 47.7 wt %.
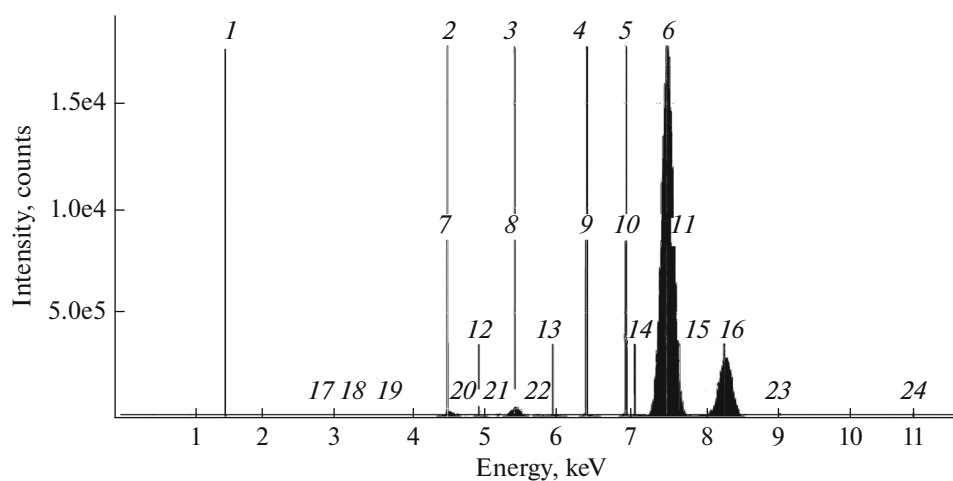
The Ni-skeletal catalyst produced by alkaline leaching of the Ni−Al−Fe−Cr−Ti alloy (51.5% Ni, 46.9% Al, 0.075% Fe, 0.8593% Cr, and 0.914% Ti) was used as the catalyst. Its elemental composition after leaching is shown in Table 1 and Fig. 1.

The X-ray diffraction analysis data (Table 2) indicate that nickel is in a new phase in the sample. This has been corroborated by the observed high background in the diffractogram (Fig. 2), which is characteristic of the nickel-containing phase under copper radiation [7]. A diffraction line ($d = 1.4870$ Å) with a very small crystallite size was observed in the diffractogram. The lattice parameter of nickel crystal was $a = 3.5352$ Å. The halo with 2θ angle maximum of 18.0° was attributed to ebonite cuvette. The size of nickel crystallites (L) was 40 Å.
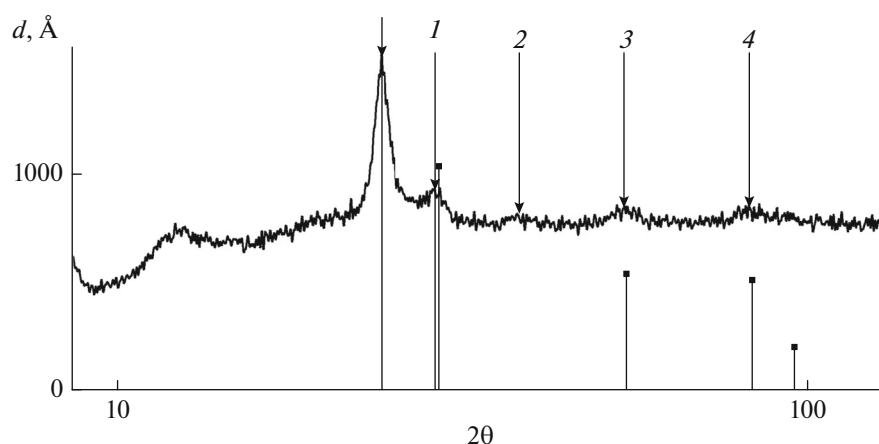
Electron microscopy studies of the catalyst samples before and after ultrasound treatment showed (Fig. 3) that the ultrasound action resulted in the predominance of tiny particles of skeletal Ni in the catalyst; their distribution was close to uniform (2.5−10.0 μm).

It can be seen in the images (Figs. 3a, 3b) that the samples of the initial catalyst and the catalyst treated with ultrasound at 90 Hz show very different morphological features: one sample (Fig. 3a) consists of dispersed grains of various sizes and high-density agglomerations, while the other sample (Fig. 3b) exhibits less dense agglomerations and a lesser grain size. This decrease in particle size in the sample could be caused by cavitation during ultrasound treatment.
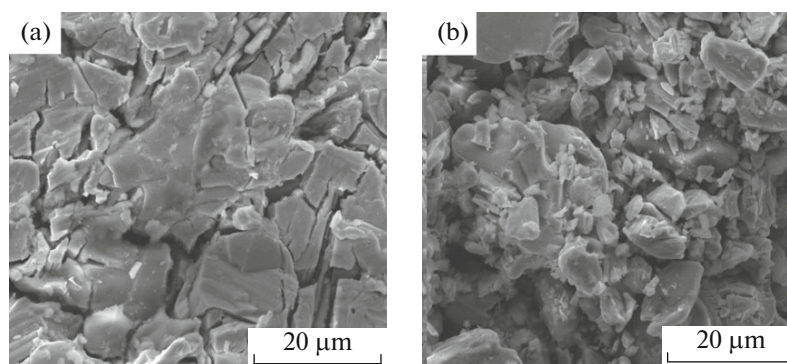
The preliminary experiments demonstrated that stepwise periodic treatment of oil products in an ultrasound field in the presence of the catalyst and oxidizer (ozone−air mixture, 0.125 mL/min) followed by the partial removal of the purified oil shows considerable promise as a technique for purification of oil product from sulfur. The treatment of oil with ultrasound in

Fig. 1. Elemental composition of Ni-skeletal catalyst: *1*, Al:Ka1; *2*, Ti:Ka1; *3*, Cr:Ka1, *4*, Fe:Ka1; *5*, Co:Ka1; *6*, Ni:Ka1; *7*, Ti:Ka1; *8*, Cr:Ka2; *9*, Fe:Ka2; *10*, Co:Ka2; *11*, Ni:Ka2; *12*, Ti:Kb1; *13*, Cr:Kb1; *14*, Fe:Kb1; *15*, Co:Kb1; *16*, Ni:Kb1; *17*, Ti:Esc; *18*, Sum; *19*, Cr:Esc; *20*, Fe:Esc; *21*, Co:Esc; *22*, Ni:Esc; *23*, Ti:Sum; *24*, Cr:Sum.

Fig. 2. X-Ray diffractogram of Ni-skeletal catalyst sample (*d*, Å: *1*, 1.7761; *2*, 1.4870; *3*, 1.2489; *4*, 1.0667).

Fig. 3. Electron microscope images (×5000) of Ni-skeletal catalyst: (a) without ultrasound treatment; (b) with ultrasound treatment.

the absence of a catalyst does not result in a noticeable decrease in the sulfur content. According to the literature data [8], there must be no less than four treatment cycles; after that, the efficiency of sulfur removal from oil products decreases, and the catalyst regeneration in an aqueous medium using ultrasound is required for further purification. In our case, the amount of sulfur in oil decreased to 62% following two treatment cycles

Table 3. Results of analysis of total sulfur in oil

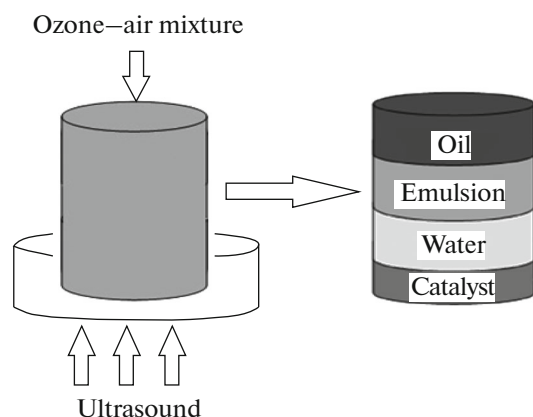| Sample	Phase mass fraction, wt %	Sulfur content, wt %
Crude oil	100	2.645
Aqueous phase	27	0.040
Purified oil	26	1.640
Water–hydrocarbon reverse emulsion	47	3.970

Table 4. Effect of ultrasound oxidative treatment on composition of oil fraction

Parameters	Crude oil		Treated oil	
	gasoline	diesel	gasoline	diesel
Yield, wt %	15.6	47.7	21.9	58.6
Sulfur, wt %	0.25	0.84	0.12	0.61

in the presence of the Ni-skeletal catalyst (Table 3); separation of the treated oil into four layers was observed upon completion of the ultrasound treatment: aqueous phase, purified oil, aqueous hydrocarbon emulsion, and catalyst (Fig. 4). Being a solid compound, the catalyst was located in the bottom layer with a minor amount of oil and water.

The literature data [9] allow the conclusion that the water content in the combined hydrocarbon phase is comparable with the water content in the initial oil. Figure 5 schematically shows the process of removing sulfur-containing organic compounds from oil as a result of ultrasound treatment in the presence of the catalyst and oxidizer.

It can be suggested that diphilic molecules of oxidized sulfur-containing organic compounds formed as a result of sonocatalytic oxidation are adsorbed on the surface of water droplets in the reverse emulsion due to

Fig. 4. Separation of oil into layers after ultrasound and oxidative treatment.

solvation of polar sulfoxide group by the aqueous phase, while nonpolar hydrocarbon radicals face the hydrocarbon phase. When such a reverse emulsion is separated into an aqueous and hydrocarbon phase, the molecules of sulfur-containing compounds are transferred to the aqueous phase, forming micelles.

The sonocatalytic oxidation of oil affects the yield of light products from crude oil. The results of experiments are presented in Table 4.
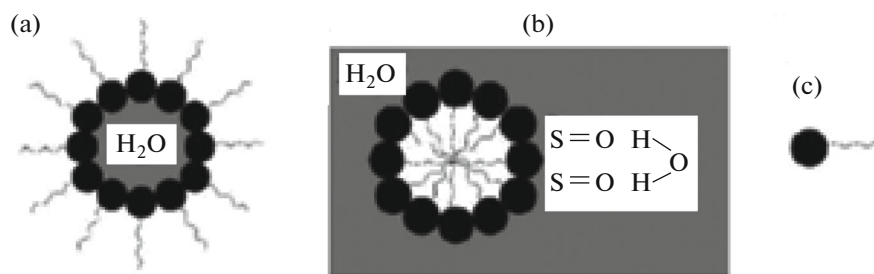
An increase in the yield of light oil fractions is observed following the ultrasound oxidative desulfurization process: the gasoline fraction increases from 15.6 to 21.9 wt % and the diesel fraction increases from 47.7 to 58.6 wt %. A decrease in sulfur content in oil products is also observed: to 0.12 wt % in the gasoline fraction and to 0.61 wt % in the diesel fraction.

According to the IR spectra data, paraffins with a normal and iso-structure are predominant in the samples of crude oil; long paraffin chains are present (absorption bands 1458, 2854, 2924, and 2955 cm^{-1}) together with OH-groups (2341 cm^{-1}) and heterocompounds (2360 cm^{-1}). The absorption bands attributed to oxygen containing organic (1169 cm^{-1}) and aromatic compounds (873^{-1}), as well as to alkyl halogenides (617–693, 726–740 cm^{-1}), are also present in the spectra, but the amounts of these compounds are significantly lower than that of paraffins.

The change in the absorption bands at 2341–2360 cm^{-1} corresponding to OH-groups was observed in the IR spectra of oil treated with ultrasound. The intensities of these peaks decreased significantly. In addition, the new bands occurred in the region 1606–1660 cm^{-1} corresponding to olefin structures as well as bands at 1113 cm^{-1} corresponding to esters. No other bands corresponding to oxygen-containing organic compounds were observed.

A significant decrease of absorption bands characteristic of paraffins (2885, 2871, 2924, 2955 cm^{-1}), heterocompounds (2359 cm^{-1}), and OH-groups (2340 cm^{-1}) is observed in the IR spectra of oil treated with the ozone–air mixture. New low-intensity peaks were observed in the IR spectrum of this oil sample, which corresponded to esters (1108 cm^{-1}) and aromatic compounds (1035 cm^{-1}).

A significant increase in the intensity of absorption bands corresponding to alkyl halogenides (615–697, 725–766, 806–849 cm^{-1}), esters (1107 cm^{-1}), aromatic compounds (873 cm^{-1}), and paraffins (1149, 2854, 2923 cm^{-1}) was observed for the oil samples treated simultaneously with ultrasound and the ozone-air mixture. The occurrence of new absorption bands with moderate and low intensities was observed, which corresponded to olefin structures (1605, 1641, 1658 cm^{-1}), substituted ethylenes (1302–1376 cm^{-1}), and secondary alcohols (1207 cm^{-1}), while the inten-

Fig. 5. Schematic representation of processes of transfer of sulfur-containing organic compounds from hydrocarbons to droplets of reverse emulsion under action of ultrasound: (a) droplet of reverse emulsion with adsorbed oxidized sulfur-containing compounds on the interface; (b) micelle consisting of molecules of oxidized sulfo-organic compounds; (c) diphilic molecule of oxidized sulfo-organic compounds.

sity of absorption bands corresponding to heteroatom compounds decreased significantly.

Hence, it can be concluded from the results of the study that the application of stepwise periodic treatment with an ultrasound field in the presence of a catalyst and oxidizers is very promising for improving the quality of oil products, which allows targeted change in their chemical compositions. Furthermore, the content of sulfo-organic compounds in oil decreases to 62%, the yield of light products increases (the gasoline fraction increases from 15.6 to 21.9 wt %, and diesel fraction, from 47.7 to 58.6 wt %), and the sulfur content in oil decreases to 49%.

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