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Hydroconversion of Oil Sludge in The Presence of Ultradisperse Slurry Catalyst.

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ABSTRACT

The article describes the results of oil sludge hydroconversion in the presence of ultradisperse particles of Mo-containing catalyst. The composition of hydroconversion products has been analyzed, physical and chemical properties of hydrogenate fractions have been determined, along with the conversion degree of heavy fraction 520°C+ of oil sludge. The structure and properties of Mo-containing catalyst of hydroconversion discharged from the reaction system with heavy products have been studied. It has been shown that in hydroconversion conditions, about 80 wt% of 520°C+ organic fraction of oil sludge is converted. It has been established that in the heavy fraction of hydroconversion product, mineral impurities of initial feed and nano-size and ultradisperse catalyst particles (molybdenum sulfide) are concentrated.

Keywords: oil sludge, reservoir sludge, hydroconversion, nanoparticles, ultradisperse catalyst, molybdenum.

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INTRODUCTION

Extraction, transportation and refining of oil stock is associated with the appearance of oil residues of various types, which results in significant environmental pollution by heavy wastes, such as oil sludge of various type, tars, heavy residual fractions, bottoms, oil storage tank residues, etc. Heavy aromatic contained in oil sludges show pronounced carcinogenic and mutagenic properties, and they are extremely resistant to decomposition in environment and can be accumulated in living organisms, plants, soil and water, which destroys the balance of environmental systems and makes the environment unsuitable for life [1-5].

At the same time, oil residues can be regarded as one of oil stock types that can be involved in refining to obtain various fuel products and petrochemical products. In relation to the decreasing amount of light and medium oils and the need to start refining heavy high-viscosity oils, the formation of the above wastes becomes an extremely urgent issue. To solve these issues, intensive studies are undertaken. As a rule, oil sludges represent heavy oil residues of complicated structure, containing significant amounts of emulsion water and mechanical impurities, which makes it impossible to effectively separate hydrocarbons. The presence of high number of asphalt-resinous compounds, metals and sulfur in the hydrocarbon part of heavy oil residues does not allow refining them by using currently existing industrial technologies. Development of oil residues refining technologies is extremely urgent due to the possible increase of additional production of fuel products, reduced losses in extracted hydrocarbon stock and increased depth of hydrocarbon stock refining.

This article gives the results of studying the effectiveness of catalytic hydroconversion of oil residues to obtain fuel products. The hydroconversion process suggests using reverse emulsions of ammonium paramolybdate water solution in hydrocarbon medium. Small catalyst particles can be synthesized both in-situ and ex-situ in relation to the hydroconversion reaction medium. Optimal concentrations of nano-size hydroconversion catalyst in the reaction mixture do not exceed 1000 ppm of Mo. This process is intended to get the maximum of distillate fractions and it has been successfully used in refining of heavy hydrocarbon and organic feedstock: bitumens, tars, heavy residues of atmospheric and vacuum oil rectification, timber-milling wastes, polymeric wastes (tires, plastic package, etc.) [6-8].

The study was aimed at investigating the peculiarities of converting the oil sludge organic part in the conditions of catalytic hydroconversion and in establishing the properties of molybdenum-disulfide-based catalyst formed in situ in the hydrocarbon medium in the reaction area. The results of this work can be used to develop an efficient technology of no-residue disposal of heavy oil residues. Refining of bottom sediments in tanks, residues of atmospheric and vacuum oil distillation, reservoir sludges formed in oil storage, transportation and refining will allow increasing the efficiency of subsoil management and reducing the environmental impact.

EXPERIMENTAL

Experiments of hydroconversion of the oil sludge organic part were carried out in the presence of in-situ synthesized nano-size and ultradisperse particles of molybdenum-containing catalyst [9]. This approach allows obtaining small catalyst particles evenly distributed in the reaction media by means of preserving the highly dispersed condition achieved when nano-particles are directly formed in the oil disperse media during hydroconversion by applying water-soluble catalyst precursors.

In studies, an organic part of oil sludge was taken as initial feedstock from the tank after its preconditioning in accordance with the methodology previously described [10]. Physical and chemical characteristics of feed were preliminary determined by using a number of methods as described below.

Density of the sample was determined by pycnometric method according to GOST Standard 3900. The method is based on comparison of the mass of oil product in predetermined volume with the mass of distilled water in the same volume and at the same temperature.

Coking property of the sample was determined according to GOST Standard 19932 (the Conradson method), based on determination of the mass of coke residue obtained at high-temperature heating and decomposition of the tested oil product.

Content of solid (mineral) impurities was determined using modified procedure of determination of mechanical admixtures (GOST Standard 6370-83). A sample of tested product was placed into a beaker and dissolved in preset amount of toluene. Then the solution was filtrated via moisture-proof smooth pre-dried filter for slow filtration (grade MN 1640 de, thickness: 0.17 mm, filtration rate: 140 ml/cm^2•s, paper density: 85 g/m^2, complete retention of particles with the sizes of ≥ 2 µm). After drying the filter together with the sample was weighed, the content of insoluble in toluene was determined.

Sulfur content in a sample was determined according to GOST Standard 1437-75, and in distillate fractions – using Spectroscan-S energy dispersive X-ray fluorescent analyzer in accordance with GOST Standard R 51947-2002, ASTM D 4294-98.

Fractional composition of the petrochemicals was determined by distillation results at ambient pressure and under vacuum according to GOST Standard 11011-85.

Group composition of petrochemicals was determined using the method of SUE Oil Refining Institute of the Republic of Bashkortostan and a laboratory liquid chromatograph "Gradient-M" intended for determining group chemical composition of heavy oil residues and petrochemicals boiling above 300°C (bitumens, tars, cracking residues, asphaltites, etc.). The method is based on the principles of liquid-adsorption chromatography with gradient displacement and separation into seven groups: paraffinic-naphthenic hydrocarbons, light, medium, heavy aromatic hydrocarbons, resins and asphaltenes.

Elemental analysis of petrochemicals was performed using the method of atomic emission spectroscopy with inductively coupled plasma (AES-ICP) and mass spectrometry with inductively coupled plasma (MS-ICP). Previously, samples were prepared for placing them into a water-acid solution. For this purpose, the samples were decomposed in an autoclave, and subsequently dissolved in nitric acid.

Hydroconversion experiments were performed in an autoclave reactor described in [8] with loading feed up to 100 g at (T) of 450°C, (P) of 7.0 MPa, hydrogen consumption of 18-20 nl/l, and duration of 2 h.

The oil sludge was pre-fractioned to separate a heavy fraction boiling away above 350°C (hereinafter – 350°C+) (HF) that was used as feedstock in experiments for catalytic hydroconversion.

As a catalyst precursor, water-soluble salt of molybdenum- ammonium paramolybdate $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ was used. The precursor water solution of specified concentration was preliminary prepared in a water bath at 80°C and subjected to mechanical dispersion in HF at -95°C, 15,000 rpm for 20 minutes. The precursor water solution was charged into the feed at 0.05 wt% (on molybdenum basis) and 2 wt% of water. A result was a feed emulsion stabilized by surface-active components contained in HF (resins and asphaltenes). The emulsion disperse phase in the HF-based feed emulsion stays in the low-mobility medium where ultradisperse water globules with a precursor (microreactor) are slightly subjected to movements and collision with each other, e.g., high medium viscosity and presence of resinous-asphaltenic stabilizers in the disperse medium promote sedimentation and aggregative stability of feed emulsions with precursors. This is an apparent advantage of oil media when producing nano-size catalysts based on reverse emulsions on their basis.

Thus prepared emulsion was charged into an autoclave and conditioned under the specified hydroconversion conditions. After the experiment, the liquid product of reaction was taken (hydrogenate) that was subjected in laboratory conditions to atmospheric vacuum distillation to determine the output of individual fractions and their qualitative characteristics.

The efficiency of converting organic part of oil sludge during catalytic hydroconversion was evaluated by the degree of feed conversion as determined by the content of 520°C+ fraction in the hydrogenate and by coke formation as determined by the content of insolubles in toluene.

During hydroconversion, the catalyst is sulfided in situ directly in the reactor as a result of interaction between precursor destruction products (molybdenum oxides) with hydrogen sulphide [11-12] formed during the thermal cracking of sulfur-containing feed components in the hydrogen atmosphere.

To study the structure and properties of catalyst particles discharged from the reaction system, the heavy residue 520°C+ of hydrogenate was taken. The catalyst was obtained by filtration from 520°C+ fraction diluted with toluene. Toluene-insoluble residue obtained after filtration and containing catalyst particles was dried in vacuum at 50°C (hereinafter – TIR).

The structure and properties of catalyst particles were studied by using Tecnai G^{2}30ST electronic microscope by TEM methods (transmission electron microscopy), EDX (energy dispersion analysis), HAADF STEM (high-angle annular dark field scanning transmission electronic microscopy) and diffraction analysis at acceleration voltage of 300 kV. For studies, a TIR suspension was used after pre-dispersion by ultrasound in acetone for 5-10 minutes. Molybdenum content in TIR was determined by means of atomic-adsorption spectroscopy (AAnalyst 400). The sample preparation method suggested sample solving in mineral acids and incineration at 450°C.

The thermal analysis was performed by using STA 449 F1 Jupiter synchronous thermal analyzer in the inert gas dynamic atmosphere at the heating rate of 15 K/min.

RESULTS

Primary characteristics of the studied oil sludge determined by using the methods described above are given in Table 1. The results show that the organic part of oil sludge taken for study represents a mixture of organic and mineral components, and the boiling point of hydrocarbons in this sample is 180°C and more.

Table 1. Properties of initial oil sludge

Name of parameter	Measurement unit
Density, kg/m^3	934.7
Coking property, wt%	7.81
Mineral impurities, wt%	0.49
Sulfur, wt%	1.35
180-350°C fraction, wt%	27.1
350-520°C fraction, wt%	26.8
Paraffins and naphtenes, wt%	62.3
Aromatics, wt%	30.7
Resins, wt%	7.0
Asphaltenes, wt%	0
520°C+ fraction, wt%	46.1
Paraffins and naphtenes, wt%	27.4
Aromatics, wt%	46.1
Resins, wt%	21.3
Asphaltenes, wt%	5.3

The study of hydrocarbon fractions included into the sludge showed that distillate fractions are characterized by high content of paraffinic-naphthenic hydrocarbons. The naphthenic hydrocarbons of the 180-350°C fraction are mainly represented by mono-, bi- and tri-naphtenic compounds. The 350-520°C fraction contains 7.0 wt% of resins. Converting of these fractions is not an issue, because their hydrocarbonaceous composition is similar to that of petroleum fractions, and they can be processed in the existing refinery schemes. The content of the heaviest components in 520°C+ fraction is 46.1 wt%. This fraction contained 5.3 wt% of asphaltene components, as well as oils and significant amount of aromatics.

The feed contained a wide variety of elements, mainly Fe, Ni, V, Al, Ba, Ca, Si, Zn (Figure 1). Iron has the highest concentration in all samples. Apparently, the prevailing part of solids in oil sludge is particles of iron oxide, i.e. rust, which is drawn from reservoirs with oil sludge [13].

The boiling above 350°C residue of initial oil sludge has been selected for testing as feed for hydroconversion. The content of 520°C+ fraction in the feed prepared for hydroconversion was 63.2 wt%.

According to Table1 it can be noted that the hydroconversion feed is characterized by high content of asphaltene-resinous compounds that may serve as surface-active stabilizers of water solution $(NH_4)_6Mo_7O_{24}\cdot4H_2O$ in hydrocarbon feed [14-17].

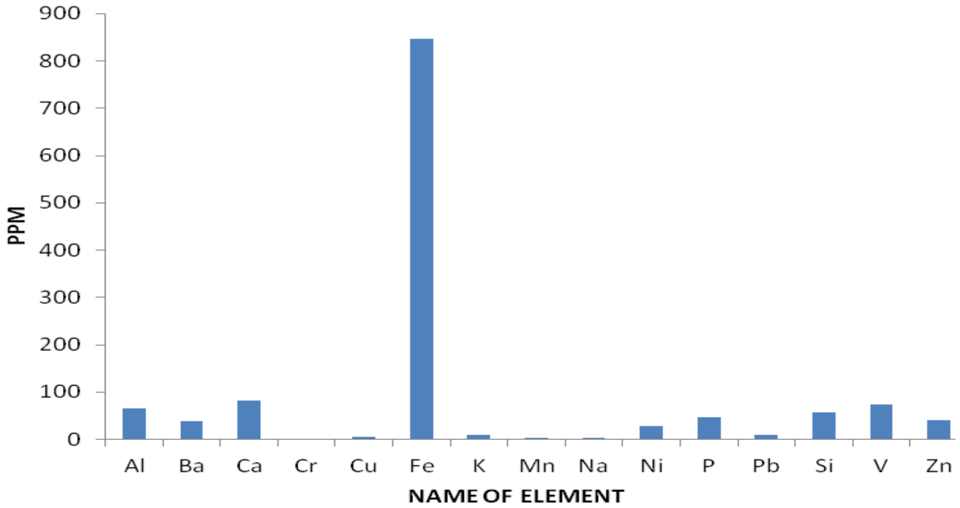

Figure 1. Elemental composition of initial oil sludge

Results of hydroconversion experiment, composition and properties of products are described in Table 2.

The conversion of 520°C+ fraction in initial oil sludge was 78 wt%. Heavy fraction 520°C + was converted into lighter products accompanied by the formation of gas, IBP-180°C, 180-350°C and 350-520°C fractions containing paraffins, naphtenes and aromatics.

Table 2. Results of hydroconversion and properties of products (feed: 350°C+ fraction of the oil sludge organic part containing 63.2 wt% of 520°C+ fraction)

Name of parameter	Value
Product yield, wt%	
Gaseous products	**10.5**
Liquid hydrocarbons	56.9
Heavy residue	32.6
Fractioned composition of mixture of liquid products and heavy residue, wt%	
IBP-180°C fraction	**22.8**
Iodine number (I_2 g/100 g)	41.8
Sulfur	0.26
Fr. 180-350°C	**47.0**
Iodine number (I_2 g/100 g)	11.6
Sulfur	0.96
Fr. 350-520°C	**16.4**
Sulfur	1.97
Paraffins	39.7
Naphtenes	50.0
Resins	10.3
Asphaltenes	0.0
Fr. 520°C+	**13.8**
Paraffins and Naphtenes	4.6
Aromatics	39.0
Resins	29.3
Asphaltenes	27.1
Toluene insolubles	19.4
Conversion of 520°C+, wt%	**80.4**

Non-converted heavy fraction 520°C+ contains a catalyst, mineral impurities of the feed and non-converted polycyclic hydrocarbons.

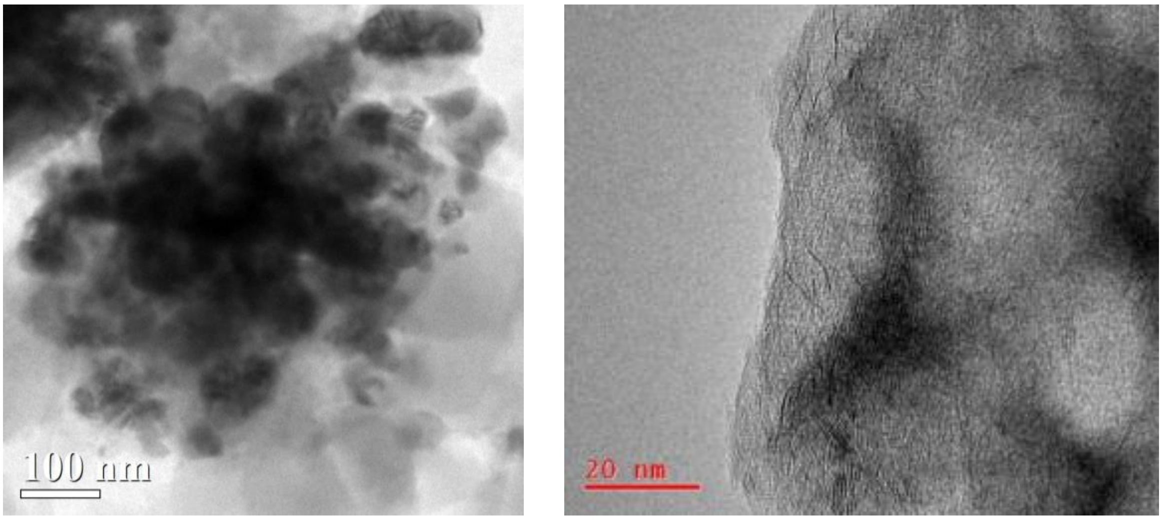

Figure 2. TEM images of particles in TIR sample

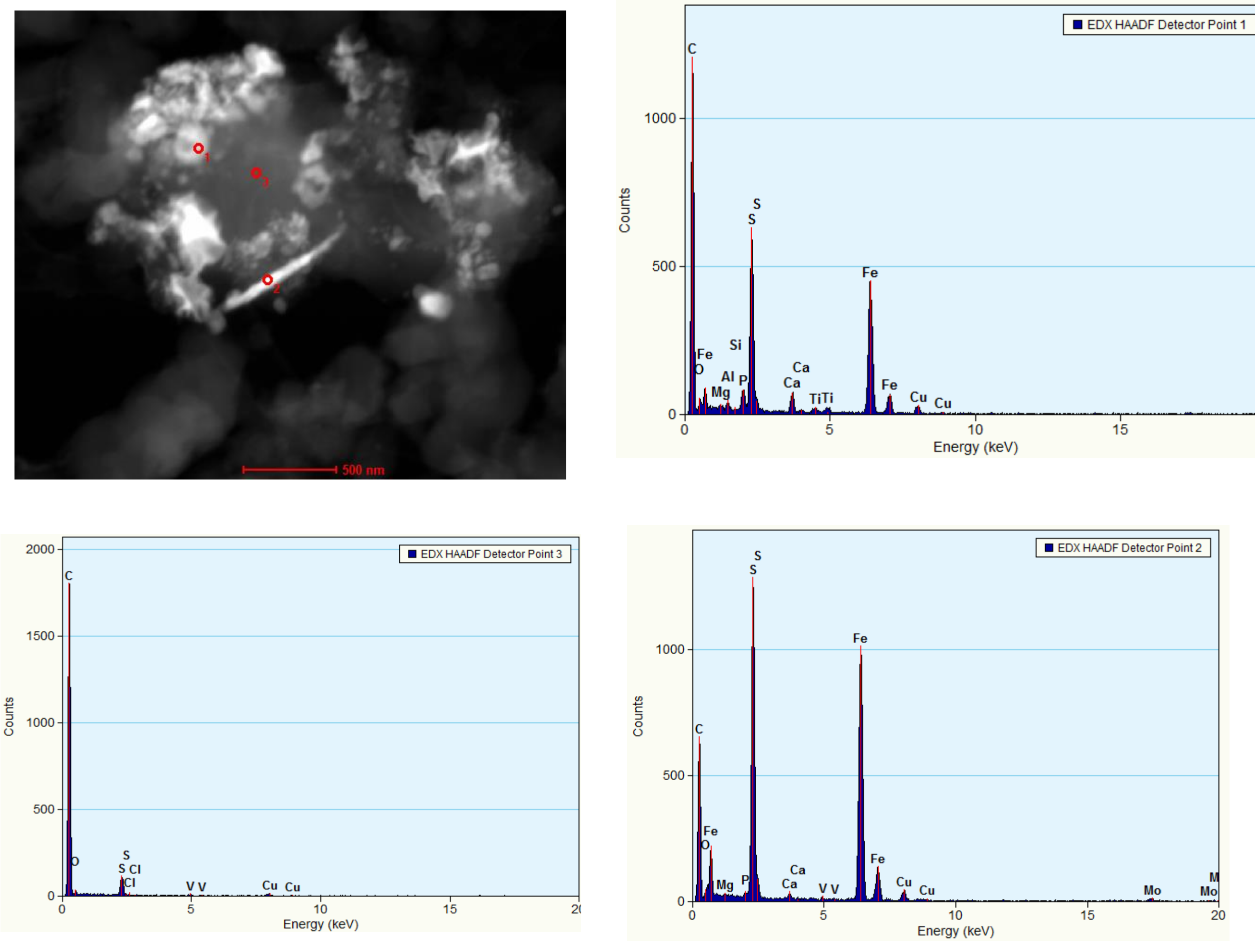

Figure 3. STEM HAADF-image and particle spectra in TIR sample

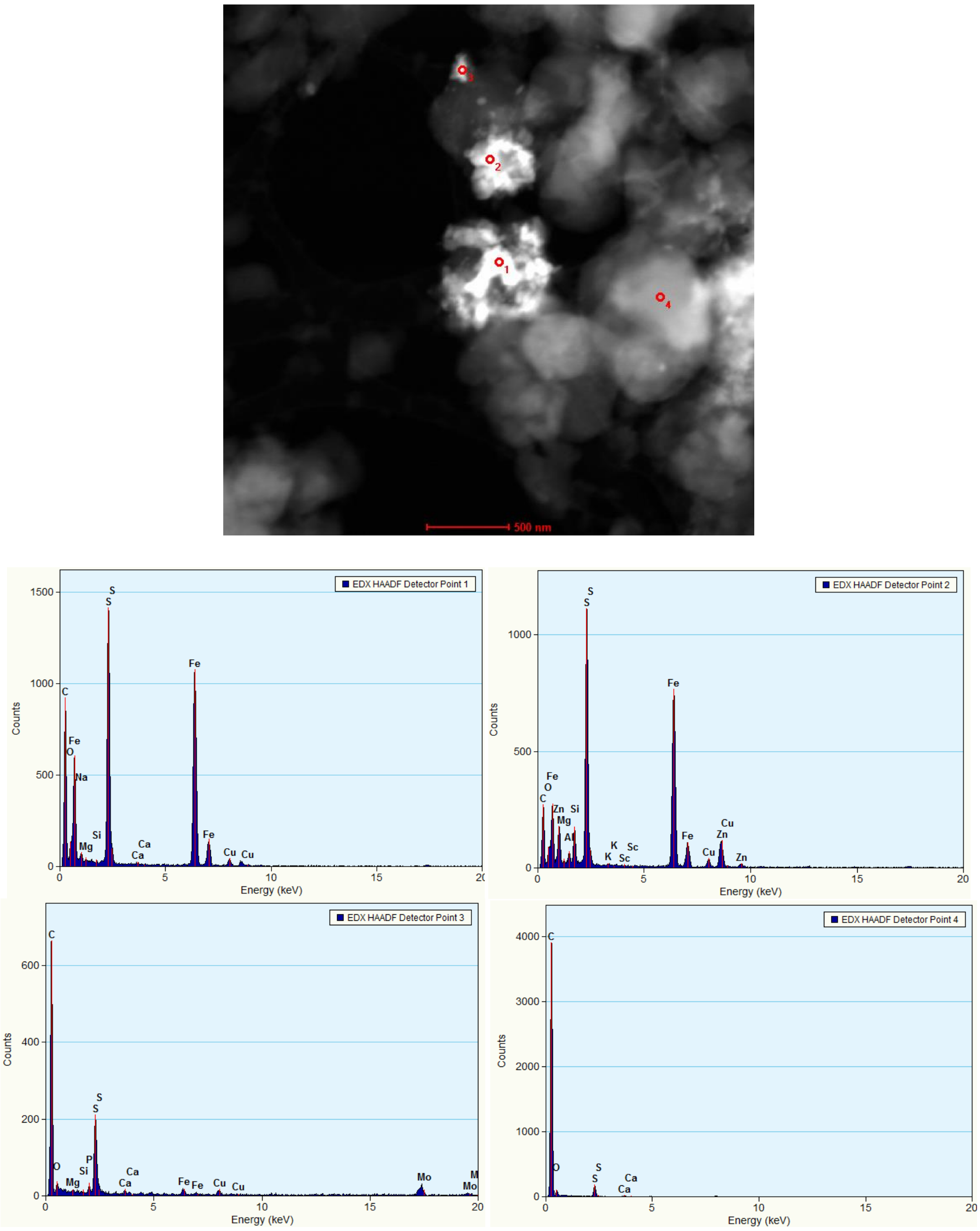

Figure 4. STEM HAADF-image and particle spectra in TIR sample

Table 3 gives data for elemental CHNS-composition of fraction 520°C+ (initial sludge), fraction 520°C+ (hydroconversion product), and a TIR sample obtained from 520°C+ fraction of hydroconversion product. Apart from C, H, N and S, the TIR sample contains a molybdenum-containing catalyst. For comparison, the table gives data for theoretic contents of molybdenum in the residue. We can see that the experimental value of molybdenum contents in the TIR sample is significantly lower than the theoretic one.

To determine the size and structure of catalyst particles of a TIR sample obtained from 520°C+ fraction of hydroconversion products, the TEM method and energy dispersion analysis were used. Figures 2-4 give the results of TIR sample study; in particular, Figure 2 contains bright-field TEM images, Figures 3 and 4 contain dark field images of various sites of the sample and energy dispersion spectra.

Table 3. Elemental composition of 520°C+ fraction of feed, hydroconversion product and toluene insolubles from hydroconversion product

wt%	fr. 520°C+ (from initial oil sludge)	fr. 520°C+ (from hydroconversion product)	TIR from fr. 520°C+ (from hydroconversion product)
Mo	-	-	0.84
N	0.5	0.4	2.8
C	84.0	83.8	77.7
H	10.5	11.0	4.3
S	4.6	4.0	7.2
Mo (theoretic)	-	0.36	1.87

Figure 5 gives the results of thermal studies of the TIR sample and 520°C+ fraction of hydroconversion products. Data for 520°C+ fraction (Figure 5(a)) indicate that the sample is decomposed within 350-850°C. Decomposition products were removed with the carrier gas (argon). The final weight of the sample at 850°C was 54 wt% of the initial sub-sample. The TIR sample weight changed (Figure 5(b)) within 100-850°C at several steps: at 100-300°C the weight loss was 3.27%, 300-850°C – 10.42%. The total TIR sample weight loss did not exceed 14.07%.

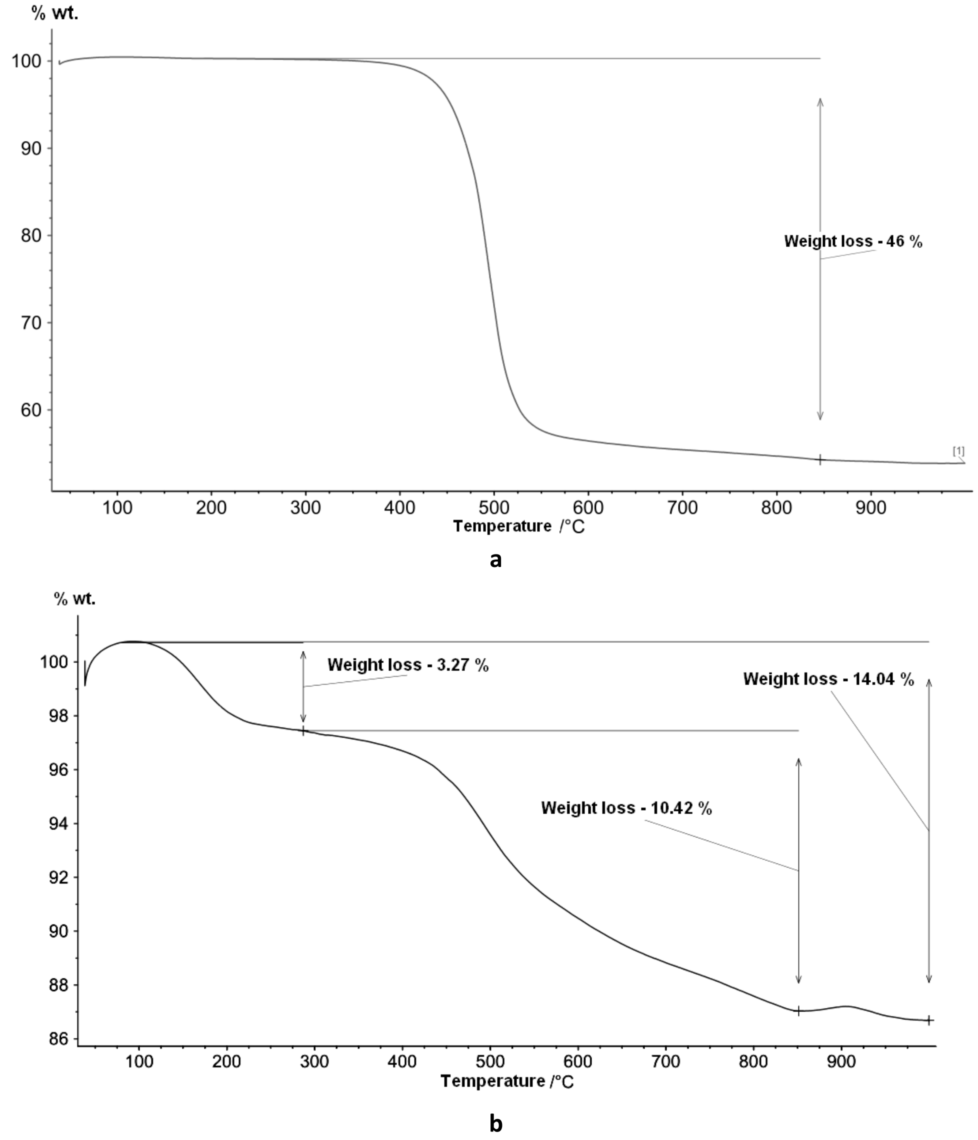

Figure 5. The results of thermal study of 520°C+ fraction from hydroconversion products (a) and a TIR sample obtained from 520°C fraction of hydroconversion product (b)

DISCUSSION

The results of studying the initial feed show that the oil sludge organic part represents a mixture of organic and mineral components (metals and solid impurities). The boiling point of hydrocarbons in the oil sludge organic part according to Table 1 is 180°C and higher. The contents of heavy residue where mineral impurities and oil high-molecular component are transferred during distillation, e.g., the fraction that boils away above 520°C, is below 46.1 wt%. The coke property of the sample characterizing the quantity coke precursors was 7.8 wt%. The sulfur content in the oil sludge was 1.35 wt%, which allows considering the sample as a high-sulfur feed [18].

The result of elemental analysis of the initial oil sludge given in Figure 1 indicate the presence of a wide range of elements, mainly Fe, as well as Ni, V, Al, Ba, Ca, Si, Zn, that may serve as a precursor of sediments on the surface of catalysts during refining of the oil sludge organic part by applying conventional catalysts.

As a result of decomposition of the heavy fraction that boils away above 350°C, hydrocarbon gases, IBP-180°C, 180-350°C and 350-520°C fractions were obtained during hydroconversion (Table 2), which are potentially suitable for producing sales fuel components by conventional methods of further refining. On the hydroconversion feed basis, the yield of IBP-180°C and 350-520°C fractions was 14.6 and 10.9 wt%, respectively, and the yield of 180-350°C fraction (with respect to the fraction contained in the initial oil sludge) was 57.8 wt%. So the total output of distillate fractions on HF-basis was 83.4 wt%.

Non-converted heavy fraction 520°C+, the yield of which on the oil sludge organic part basis after hydroconversion was 9.0 wt%, contains the catalyst, mineral impurities and more than 50 wt% of resinous-asphaltenic components that can't be converted in the study conditions (Table 3).

The elemental analysis of the solid phase insoluble in toluene obtained from the non-converted heavy fraction 520°C and hydroconversion has shown that the sample (along with molybdenum and other metals) (Figures 3-4) contains a significant amount of carbon, as well as hydrogen, nitrogen and sulfur. The S/Mo ratio (atomic) calculated according to Table 3 was 25.8, which is much higher than the stoichiometric ratio for MoS_2. Apparently, it is associated with the fact the studied sample also contains sulfur related to hydrocarbon components in the form of coke. Table 3 shows that the theoretic content of molybdenum in the sample was significantly higher than the experimental one. This can be related to partial losses of Mo-containing components due to their low size and limited retaining capability of the filter applied in filtration of 520°C+ fraction of hydroconversion products at the stage of obtaining toluene insolubles.

The TIR sample includes particles of various sizes, morphology and chemical composition. There are particles of arbitrary shape in the form of agglomerates up to 1 μm (Figure 2). Most particles in agglomerates have the size of 50-300 nm (Figures 2-4). There are particles in agglomerates, containing Fe, Ca, Mg, Zn, Al, Si, Ti, V, P, S, O. Molybdenum is included in small agglomerates (less than 100 nm) and in particles of elongated shape. The latter represents packages of plates as described in literature [20-22]. Most often, particles include iron, which is most probably related to sulfur (iron sulfide).

The comparison of thermal analysis data for the TIR sample and 520°C+ fraction of hydroconversion products (Figure 5) has shown that the TIR sample contains significantly less components that decompose in the study conditions. When toluene insolubles are produced, the most active paraffin-naphtene and oily hydrocarbons are removed during the cracking reaction, and the TIR retains condensed hydrocarbons and coke of low content. The total weight loss of the TIR sample at 850°C was ~14 wt%, which is much less than in case of 520°C+ residue of hydroconversion products (~46 wt%). The reduction of TIR sub-sample weight can be caused by oxidation of hydrocarbon-containing components with the formation and removal of gaseous products, and by conversion of MoS_2 into Mo_3S_4 with further formation of molybdenum oxides [19]. In general, the TIR sample contains less hydrocarbons as compared to 520°C+ residue of hydroconversion products used to obtain the sample.

CONCLUSIONS

As a result of hydroconversion of heavy fraction (boiling away above 350°C) separated from reservoir oil sludge, the conversion of 520°C+ fraction was achieved at the level of 80.4 wt%. The process goes in the presence of nano-size and ultradisperse particles of molybdenum disulfide formed from the precursor in the reaction medium. Microelements contained in the initial oil sludge go to high boiling fractions of hydroconversion products in the form of nano-size and highly disperse particles of converted compounds. Possible presence of impurities of feed microelements in the samples of hydroconversion heavy products shall be considered in the future when studying samples with the hydroconversion catalyst.

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REFERENCES

[1] Shperber, E.R. (2011). Some Types of Wastes of Oil Refineries and Their Classification. Environmental Protection in Petroleum Industry, 2, 27-32.

[2] Hu, G., Li, J., & Zeng, G. (2013). Recent Development in the Treatment of Oily Sludge from Petroleum Industry: A Review. Journal of Hazardous Materials, 261, 470-490.

[3] Elektorowicz, M., & Habibi, S. (2005). Sustainable Waste Management: Recovery of Fuels from Petroleum Sludge. Can. J. Civil. Eng., 32, 164-169.

[4] Shailubhai, K. (1986). Treatment of Petroleum Industry Oil Sludge in Soil. Trends in Biotechnology, 4(8), 202-206.

[5] Gron’ V. A., Korostovenko V. V., Shakhrai S. G.,et al. Problem of generation, reprocessing and disposal of oil sludges. Advances of modern natural science. 2013; 9: 159-162.

[6] Khadzhiev, S., & Kadiev, K. (2009). Budushchee glubokoy pererabotki nefti: sdelano v Rossii [The Future of Advanced Oil Refining: Made in Russia]. Khimicheskiy zhurnal, 9, 34-37.

[7] Kadiev, Kh.M., Khadzhiev, S.N., Zekel’, L.A., Temirsultanova, Z.A., & Gyul’maliev, A.M. (2012). Gidrokonversiya drevesnoy biomassy v srede gudrona v prisutstvii nanorazmernykh katalizatorov [Hydroconversion of Wood Biomass in Oil Tar in the Presence of Nanosized Catalysts]. Khimiya tverdogo topliva, 46(6), 378-388.

[8] Kadiev, Kh., Dandaev, A., Gyul’maliev, A., Batov, A., & Khadzhiev, S. (2013). Gidrokonversiya polietilena i shinnoy reziny v smesi s tyazhelymi neftyanymi ostatkami [Hydroconversion of Polyethylene and Tire Rubber in a Mixture with Heavy Oil Residues]. Khimiya tverdogo topliva, 47(2), 132-138.

[9] Khadzhiev, S.N., Kadiev, Kh.M., & Kadieva, M.Kh. (2014). Sintez i svoystva nanorazmernykh sistem - effektivnykh katalizatorov gidrokonversii tyazhelogo neftyanogo syr''ya [Synthesis and Properties of Nanosized Systems as Efficient Catalysts for Hydroconversion of Heavy Petroleum Feedstock]. Neftekhimiya, 54(5), 323-346.

[10] Oknina, N.V., Kadiev, Kh.M., Maksimov, A.L., Batov, A.E., Kadieva, M.Kh., & Dandaev, A.U. (2015). Studies on Preprocessing of Reservoir Oil Sludges for Further Hydroconversion. Biosciences Biotechnology Research Asia, 12(Spl. Edn. 2), 473-483.

[11] Hanafi, Z.M., Khilla, M.A., & Askar, M.H. (1981). The Thermal Decomposition of Ammonium Heptamolybdate. Thermochimica Acta, 45(3), 221-232.

[12] Chukin, D., & Nefedov, B.K. (2009). Mekhanizmy sul'fidirovaniya alyumonikel'molibdenovogo katalizatora i ego aktivnost' v reaktsii gidroobesserivaniya tiofena [Mechanisms of Sulphidizing the Aluminium-Nickel-Molybdenum Catalyst and Its Activity in the Reaction of Thiophene Hydrodesulfurization]. Khimiya tverdogo topliva, 43(6), 400.

[13] Shlepkina, Yu.S. (2009). Analiz metodov utilizatsii nefteshlamov. Preimushchestva i nedostatki [Analysis of Oil Sludge Disposal Methods. Advantages and Disadvantages]. Zashchita okruzhayushchey sredy v neftegazovom komplekse, 12, 32-34.

[14] Jones, T.J., Neustadter, E.L., & Whittingham, K.P. (1978). Water-In-Crude Oil Emulsion Stability and Emulsion Destabilization by Chemical Demulsifiers. Journal of Canadian Petroleum Technology, 17(2).

[15] Mohammed, R.A., Bailey, A.I., Luckham, P.F. et al. (1994). The Effect of Demulsifiers on the Interfacial Rheology and Emulsion Stability of Water-In-Crude Oil Emulsions. Colloids and Surfaces, 91, 129-139.

[16] Eley, D.D., Hey, M.J., & Symonds, J.D. (1988). Emulsions of Water in Asphaltene-Containing Oils. 1. Droplet Size Distribution and Emulsification Rates. Colloids and Surfaces, 32, 87-101.

[17] Kralova, I., Sjöblom, J., Øye, G., Simon, S., Grimes, B.A., & Paso, K. (2011). Heavy Crude Oils/Particle Stabilized Emulsions. Adv. Colloid Interface, 169, 106-127.

[18] BBC News. (2003, July 14). Oil Markets Explained. Retrieved July 6, 2016, from http://news.bbc.co.uk/2/hi/business/904748.stm.

[19] Wang, H.W., Skeldon, P., & Thompson, G.E. (1998). Thermogravimetric-Differential Thermal Analysis of the Solid-State Decomposition of Ammonium Tetrathiomolybdate during Heating in Argon. Journal of Materials Science, 33(12), 3079-3083.

[20] Wang, S., An, Ch., & Yuan, J. (2010). Synthetic Fabrication of Nanoscale MoS2-Based Transition Metal Sulfides. Materials, 3(1), 401-433.

[21] Panariti, N., Del Bianco, A. et al. (2000). Petroleum Residue Upgrading with Dispersed Catalysts: Part 2. Effect of Operating Conditions. Applied Catalysis A: General, 204(2), 215-222.

[22] Afanasiev, P. (2008). Synthetic Approaches to the Molybdenum Sulfide Materials. Comptes Rendus Chimie, 11(1-2), 159-182.