

Complex Technology of Oil Sludge Processing

A.V. Anisimov, V.I. Frolov, E.V. Ivanov, E.A. Karakhanov, S.V. Lesin and V.A. Vinokurov

Abstract The technology of processing sludge includes electromagnetic activation of raw materials, catalytic cracking, hydrocracking, and oxidative desulfurization. Preliminary activation reduces electromagnetic temperature catalytic processes at 60–80 °C, increasing the yield of light products, reduce sulfur content in liquid products at 13–19% by weight, coke formation, and reduces gassing.

Keywords Oil sludge · Electromagnetic activation · Catalytic cracking
Hydrocracking · Oxidative desulfurization

At present, the refineries, the acute problem of recycling and disposal of sludge (PS) as well as available technological solutions aimed at processing of oily waste, cannot be the basis of a uniform method of processing sludge [1–3]. In the

A.V. Anisimov
Department of Petroleum Chemistry and Organic Catalysis,
Lomonosov Moscow State University, Moscow, Russia
e-mail: anis@petrol.chem.msu.ru

V.I. Frolov (✉) · V.A. Vinokurov
Gubkin Russian State University of Oil and Gas (National Research University),
Moscow, Russia
e-mail: fvi209@mail.ru

V.A. Vinokurov
e-mail: vinok_ac@mail.ru

E.V. Ivanov · S.V. Lesin
Department of Physical and Colloid Chemistry, Gubkin Russian State University
of Oil and Gas (National Research University), Moscow, Russia
e-mail: ivanov166@list.ru

S.V. Lesin
e-mail: lesinsv@gmail.com

E.A. Karakhanov
Lomonosov Moscow State University, Moscow, Russia
e-mail: kar@petrol.chem.msu.ru

© The Author(s) 2018

K.V. Anisimov et al. (eds.), *Proceedings of the Scientific-Practical Conference
“Research and Development - 2016”*, https://doi.org/10.1007/978-3-319-62870-7_65

development of technologies for processing and disposal of the NS the most important is the maximum possible extraction of hydrocarbons, so special attention is paid to methods aimed at obtaining a variety of commercial products, such as components of the engine and boiler fuel, secondary hydrocarbon feedstock of various technological processes of oil refining, secondary petrochemicals, road-building materials [1].

In recent years, proposed technologies for processing crude oil and oil waste using non-standard physical, chemical, and physical influences on them. In this case, the raw material is pretreated using acoustic energy, ultrasound, high-frequency (HF) and ultrahigh frequency (UHF) electromagnetic fields, ionizing radiation, exposure to plasma-chemical and electric current [1–17]. Efficient processing and recycling of the PS will solve the environmental problems in the storage of waste oil. Conducting such research confirms the global level of the project.

It is very promising for fuel products represented PS recycling technologies through their pre-wave treatment in combination with conventional catalytic methods. Using such technology would lead to the maximum recovery of liquid hydrocarbons with high destruction and subsequent conversion to fuel products. The most promising techniques using high-frequency electromagnetic emissions, which contribute to the effective separation of simultaneous PS phases, reduce the temperature of catalytic thermal processing, increase the depth of oil refining up to 85% and the production of high-quality fuel products. In carrying out this project developed a complex technology of processing raw materials nefteshlamosoderzhashego including several processing steps as follows:

- Activation of the sludge by means of an electromagnetic field
- Catalytic cracking activated PS
- Hydrocracking PS
- Oxidative desulfurization activated PS.

Experimental Part

The raw material for the implementation of pilot studies on the impact of various external factors on the process of recycling the activated PS were selected sediments buffer ponds biological sewage treatment plants, having the following phase composition: 20.9% by weight of oil, water—69% by weight, fur impurity—10.1% by weight. After the separation of water and solids component of the oil extracted from the sediment buffer ponds, had an initial boiling temperature of—83.5 °C, final boiling point—680.4 °C. For the experiments, the oil component used was obtained after separation of water and solids extraction averaged sediment samples carbon tetrachloride with a water content of 1.5 ÷ 2.0 mass %. Pre by simulated distillation was determined factional and group composition of the oil component of the bottom sediments, according to which they contain 40% by weight. paraffins; 32.5% by weight. mono-, bi-, tri-, and tetradenia naphthenes; 27.6% by weight

aromatics. Electromagnetic activation watered sediment was carried out under optimal conditions found for the catalytic cracking process activated the oil component of dewatered sediment (frequency of electromagnetic radiation—50.5 MHz, power—0.55 kW, Activation time—6 h, activation temperature of—50 °C. Pilot studies activated the catalytic cracking process of petroleum PS conducted at 400–500 °C component, the mass hourly space velocity of 15 h^{-1} in order to reduce its viscosity PS preheated before entering the reactor to 70 °C. Liquid products were analyzed by GC and GC-spectrometry. The sulfur content in the raw compounds and the reaction products were determined by fluorescence spectrometer at a wave ARL PerformX2500. The catalyst used cracking catalyst NS brand “Grace” with an average particle size of 72 microns, a BET surface area of $350 \text{ m}^2/\text{g}$ mass fraction of rare earth oxides 0.2% the masses, the mass fraction of Al_2O_3 , 43% by mass, the mass fraction of Na_2O , 0.29% by weight. For identification of the main regularities of catalytic cracking, hydrocracking, and oxidative desulfurization activated PS oil component was the varied frequency of the electromagnetic radiation of electromagnetic power and time of activation to assess the effects on the composition and the total yield of the products of catalytic cracking, hydrocracking, and oxidative desulfurization.

The Discussion of the Results

Sludge processing technology development was carried out with pre-electromagnetic activation of raw materials on the basis of three processes—catalytic cracking, hydrocracking and oxidative desulfurization. For the selection of the optimal conditions of the electromagnetic activation sludge mathematical models were developed separately for the process of catalytic cracking, hydrocracking and oxidative desulfurization. For catalytic cracking in the presence of a catalyst 40% mass. LUX-2 (Russia)+60% mass. DA-250 (Grace, USA) under 500 °C temperature, the feed rate of 15.6 h^{-1} was obtained regression equation and calculated parameters OLS regression equation separately for a total yield of light oil for diesel and gasoline yield fractions. Optimization of electromagnetic activation of the catalytic cracking activated PS was carried out by a steep ascent on the response surface (for a total yield of light oil) and the optimum conditions of the electromagnetic activation PS process were found: the frequency of electromagnetic radiation—50.5 MHz, power—0.55 kW and activation time—6 h.

To carry out the catalytic cracking of heavy oil wastes was developed catalyst comprising a medium—mixture of the ordered mesoporous silica MCM-41 (17 wt %) Gamma alumina (49 wt%) and zeolite-Y (30 wt%) with the addition of lanthanum nonzero valence state in an amount of 3% by weight. ($\text{La}_2\text{O}_3/\text{MCM-41} + \gamma\text{-Al}_2\text{O}_3$). In the catalytic cracking of a mixture of activated PS and non-activated vacuum gas oil (HS) HS conversion component in 520 °C more than 90%, the selectivity of the gasoline fraction in a MAT of 63.7%, a decrease in the sulfur content of broad fraction of light oil occurred at 37%.

Catalytic cracking was PS after preliminary treatment of the wave electromagnetic radiation with a frequency of 50.5 MHz (for the control of the characteristic frequencies of groups and individual frequencies of electromagnetic radiation signal generator parameters used data collector and signal analyzer VIBXPART II and digital oscilloscope Agilent Technologies) and a capacity of 0.55 kW at 50 °C, pressure 0.4 MPa, treatment time clock 6. Catalytic cracking of feedstock was carried out in a continuous-flow reactor at a temperature of 500 °C and the mass feed rate of 15 h⁻¹. PS catalytic cracking results with and without activation of the activation of the pilot sample developed catalytic cracking catalyst are given in Table 1

As shown in Table 1 preactivation sludge followed by catalytic cracking catalyst on La/MCM-41/ γ -Al₂O₃ allows cracking in comparison with the process without activating the lower sulfur concentrations in liquid products of 29.8%, cracking gas 4.4 wt% coke on the catalyst 1.0% wt; increase the yield of the gasoline fraction at 8.0% by weight of the diesel fraction to 4.0% by weight, the processing depth (the residue reduction) 7.6% by weight.

For hydrocracking of heavy oil and waste sludge was developed catalyst of general formula NiO–MoO₃/Al-HMS/ γ -Al₂O₃, which is a support based on mesoporous aluminosilicate Al-HMS/ γ -Al₂O₃ coated with a hydrogenation promoter NiO (5.1 % by weight) and MoO₂ (18.0%), the specific surface area of the catalyst—955 m²/g. For the process of hydrocracking, PS activated in the presence of said catalyst at T = 400 °C, p = 5 MPa, t = 3 h were obtained regression equation and calculated parameters OLS regression equation separately for the total output of light oil, to exit gasoline and diesel fractions. Carried out optimization of the electromagnetic activation process hydrocracking PS activated by a steep ascent on the response surface (for a total yield of light oil) allowed for this process to find optimal conditions for electromagnetic activation NS: frequency electromagnetic radiation—47.5 MHz, power—0.35 kW activation time—3.5 h.

Hydrocracked oil sludge after it is subjected to a preliminary treatment by electromagnetic wave radiation at a temperature of 50 °C, 0.4 MPa pressure, 3.5 h treatment time. hydrocracking process was carried out in a steel autoclave of 45 ml, equipped with a magnetic stirrer. The autoclave was placed a sample hydrocracking catalyst NiO–MoO₃/Al-HMS/ γ -Al₂O₃ amount of 0.2–1.5 g of 3 ml Hereinafter

Table 1 Results of sludge on the catalytic cracking test specimen developed catalytic cracking catalyst La/MCM-41/ γ -Al₂O₃

Products	Un.	Output change		Change
		Before	After	
Light petrochemicals, including:	wt%	60.0	73.0	+13.0
Gasoline fraction	wt%	41.0	50.0	+9.0
The diesel fraction	wt%	19.0	23.0	+4.0
Coke	wt%	8.0	7.0	-1.0
Gases	wt%	17.1	12.7	-4.4
Balance	wt%	14.9	7.3	-7.6
The sulfur content	ppm	8790	6171	-29.8

feedstock after the electromagnetic activation, heated to 30–40 °C beforehand to obtain a liquid consistency. The autoclave was filled with hydrogen to a pressure of 9 MPa. And placed in an oven heated to 340 °C with vigorous stirring. For complete extraction fraction hydrocracking transmitted to the autoclave were added 4.0 ml of n-C₇H₁₆ and stirred vigorously for 5 min. After centrifugation, the clear liquid in it an equal volume of 10% NaOH solution to remove the hydrogen sulfide dissolved therein. Thereafter, the aqueous phase was separated and the organic phase was washed with water, dried and analyzed by GLC. The sulfur content of the feedstock and the reaction products were determined on an analytical-based complex energy dispersive spectrometer JEOL JED-2300T. PS hydrocracking results with and without activation of the activation of the pilot pattern designed hydrocracking catalyst are given in Table 2.

As shown in Table 2 preactivation sludge followed by hydrocracking of the pilot sample developed catalytic cracking catalyst NiO–MoO₃/Al-HMS/ γ -Al₂O₃ allows versus hydrocracking process without activating the lower sulfur concentrations in liquid products of 41.2%, lower cracked gas yield of 3.6% by weight, to increase the yield of light products to 19% by weight.

To remove the sulfur from the sludge along with hydrocracking can be used and the process of oxidative desulfurization for those cases where there are no available and cheap sources of hydrogen. For oxidative desulfurization of heavy oil and waste, sludge was developed catalyst comprising molybdenum peroxy, preparing directly in the same reactor, where the process is conducted by mixing desulfurizing sodium molybdate, sulfuric acid, and triethylbenzylammonium chloride.

Before desulfurization slime subjected to electromagnetic radiation with a frequency of 47.5 MHz, the power of 0.35 kW at 50 °C, under atmospheric pressure for 3.5 h. Validating oil sludge and activated oxidative desulfurization was then contacted with a catalyst system which is prepared mixing the dihydrate of sodium molybdate, 50% aqueous solution of hydrogen peroxide and a phase transfer agent in the form of quaternary ammonium salts—cetyltrimethylammonium bromide, combined in amounts to provide the following molar ratios: metal: sulfur contained in the oil sludge of 1:100, hydrogen peroxide: the sulfur contained in oil sludge 2:1, phase transfer: the sulfur contained in the oil sludge 1:20. The catalyst can withstand at least 6 cycles of continuous operation without substantial loss of activity and reduces the sulfur content in the resulting desulfurized sludge sample by 43%.

Table 2 Results of the pilot hydrocracking sludge sample developed hydrocracking catalyst NiO–MoO₃/Al-HMS/ γ -Al₂O₃

Products	Un.	Output Change		Change
		Before	After	
Light petrochemicals, including:	wt%	22.0	39.0	+19.0
C ₅ -C ₁₁	wt%	2.0	6.0	+4.0
C ₁₂ -C ₁₆	wt%	20.0	33.0	+13.0
Gases	wt%	14.3	10.7	-3.6
Balance	wt%	63.7	50.3	-13.4
The sulfur content	ppm	85	50	-41.2

Table 3 Results of laboratory tests of experimental sample of oxidative desulfurization catalyst in the desulfurization sludge, initial sulfur content of 6500 ppm of, a catalyst—Sodium molybdate

№	The sulfur content in the experiment after the PS desulfurization ppm	
	Validating slime	Slime activated
1	4830	3700
2	4850	3800

In quantitative terms, using 25 g of sludge, 1.73 ml of a 50% aqueous solution of hydrogen peroxide, 0.264 g of cetyltrimethylammonium bromide and heated at 80 °C for 8 h with stirring the reaction mass at a speed of 35,000 rev/min. After the reaction, the water formed is distilled off, the remaining product was heated to 360 °C for 3 h, then cooled and analyzed for total sulfur content on the device “Atomic Emission Spectrometer microwave plasma AGILENT MP-AES 4100.” The results of the process of liquid-phase oxidative desulfurization sludge are shown in Table 3.

As can be seen from Table 3, after the oxidative desulfurization of activated sludge in the presence of sodium molybdate content of sulfur in the final product is 22.5% lower compared to unactivated sludge. The desulfurized activated slime can then be used for further processing thermocatalytic.

Conclusions

The developed technology for processing oil sludge using electromagnetic treatment of raw materials, followed by catalytic cracking, hydrocracking, and oxidative obessrivaniem provides conversion of heavy oil waste into liquid hydrocarbon products. Preliminary activation reduces electromagnetic temperature catalytic processes, increasing the yield of light products, reduce sulfur content in liquid products, coke formation and reduce gassing.

The developed technology of catalytic oxidative desulfurization of petroleum residues and waste can reduce the sulfur content of two or more times and can be used for further catalytic thermal processing of oil residues and waste.

Acknowledgments Research is carried out (conducted) with the financial support of the state represented by the Ministry of Education and Science of the Russian Federation. Agreement (contract) no/ 14.577.21.0106, September 22, 2014. Unique project Identifier: RFMEF157714X0106.

References

1. Mazlova, E.A., Meshcheryakov, S.V.: Problems of waste sludge and methods of their processing. M.: Publishing House of the “noosphere”, (2001). 56 p
2. Gridina, M.S.: The influence of the components of oily waste on the quality of products hydrotreating hydrocarbon fractions: dis... cand. tehn. Sciences. Samara, (2010). 135 p

3. Silva, L.J., Alves, F.C.: F.P.F. A review of the technological solutions for the treatment of oily sludges from petroleum refineries. *Waste Manag Res.* **30**(10), 1016–1030 (2012)
4. Chang, C., Shie, J.L., Lin, J.P.: Major products obtained from the pyrolysis of oil sludge. *Energ. Fuels* **14**(6), 1176–1183 (2000)
5. Khaydarov, P.R., Kudratova, S.K.: Development of engineering and technology of waste oil disposal. Publishing house “Young scientist», **11**, 125–127 (2014)
6. Hayrudinov, I.R.: Methods of processing of oil waste and sludge. M.: Publishing house “Chemistry”, (1989). 425 c
7. Mazlova, E.A., Meshcheryakov, S.V.: Ecological characteristics of oil sludges. *Chem. Technol. Fuels Oils* **35**(1), 49–53 (1999)
8. Krestovnikov, M.P., Snegotsky, A.L.: The process of degradation of organic compounds and petrochemicals processing plant waste. RF patent **2246525**, (2005)
9. Aristarkhov, D.V., Krestovnikov, M.P., Snegotsky, A.L.: Method for processing of rubber products and high. RF patent **2273650**, (2005)
10. Kurochkin, A.K., Kurochkin, A.V.: Thermal non-catalytic cracking of hydrocarbon oils, in the absence of hydrogen. RF patent **2375409**, (2009)
11. Vinokurov, V.A., Frolov, V., Krestovnikov, M.P.: The study of the thermal cracking of used lubricating oils when wave action. *Refining and Petrochemicals* **12**, 8–16 (2011)
12. Vinokurov, V.A., Frolov, V., Krestovnikov, M.P.: Investigation of the effect of wave action on oil. *Refining and Petrochemicals* **3**, 3–8 (2012)
13. Vinokurov, V.A., Frolov, V., Krestovnikov, M.P.: Properties of the thermal cracking of heavy petroleum feedstock in the electromagnetic field. *Ind. service* **4**, 2–5 (2012)
14. Vinokurov, V.A., Kolesnikov, I.M., Frolov, V.I.: Influence of electromagnetic radiation on the thermal cracking of the activated sludge. *Chem. Techno. Fuels Oils* **1**(593), 34–39 (2016)
15. Lyubimenko, V.A., Frolov, V.I., Krestovnikov, M.P.: Mathematical modeling of the thermal cracking of oil sludge, activated by electromagnetic radiation. *Chem. Technol. Fuels Oils* **2** (594), 12–16 (2016)
16. Minnigalimov, R.Z., Nafikova, R.A.: Improving the technology for processing oil sludge. *Oil Ind.* **4**, 105–107 (2008)
17. Yagafarova, G.G., Nasyrova, L.A., Shakhov, F.A.: Environmental engineering in the oil and gas industry: a textbook for graduate students and researchers studying the ecology. Ufa. Publishing house UGNTU, (2007). 334 p

Open Access This chapter is licensed under the terms of the Creative Commons Attribution 4.0 International License (<http://creativecommons.org/licenses/by/4.0/>), which permits use, sharing, adaptation, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons license and indicate if changes were made.

The images or other third party material in this chapter are included in the chapter's Creative Commons license, unless indicated otherwise in a credit line to the material. If material is not included in the chapter's Creative Commons license and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder.

