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Study of Oil Sludge Pyrolysis in the Presence of Calcium Oxide

Vladimir Khaskhachikh[a,*], Gennady Gerasimov[b], Valentina Kornilieva[c], Nadezhda Gubina[a]

[a]Joint Institute for High Temperatures of the Russian Academy of Sciences, Izhorskaya st., 13 Bd.2; 125412 Moscow Russian Federation

[b]M.V. Lomonosov Moscow State University; Institute of Mechanics, Michurinsky Ave., 1; 119192 Moscow; Russian Federation

[c]G.M. Krzhizhanovsky Power Engineering Institute (ENIN), Leninsky Ave., 19; 119071 Moscow; Russian Federation

v.khaskhachikh@ihed.ras.ru

The study of thermal processing of oil sludge from the Ukhta oil field (Russia) was conducted in order to assess the possibility of extracting liquid products and their simultaneous purification from sulfur compounds. Proximate and ultimate analyzes of the feedstock as well as its thermogravimetric study were performed. The data on the yield of pyrolysis products were obtained in the fixed bed retorting system, depending on the process temperature and the addition of calcium oxide (CaO). The presence of calcium oxide allows to clean the pyrolysis gas of oil sludge from hydrogen sulfide (H_2S), as well as to reduce the sulfur content in the liquid products of the pyrolysis.

1. Introduction

The production activities of oil refineries and oil and gas plants inevitably have a technogenic impact on environmental objects, and oil sludge is one of the most dangerous pollutants (Shen et al., 2003). This waste is complex physico-chemical mixture that consists of petroleum products, mechanical impurities, and water (Cheng et al., 2018). Its formation occurs during such technological processes as discharges in the preparation of oil, stripping of oil tanks, discharges of oily waste from drilling operations, discharges during testing or repair of wells, emergency spills during the transportation of oil. In Russia, one ton of produced oil accounts for up to 7 kg of oil sludge (Timoshin et al., 2016).

Existing methods of oil sludge processing can be classified according to the principle of impact on physical, physical-chemical, thermal, biological and complex methods, based on their combination (Gao et al., 2018). The choice of a specific method of processing and disposal of oil sludge should take into account both the environmental and economic aspects of processing, as well as the specifics of a particular raw material. Due to the strong heterogeneity of the sludge composition thermal methods are the most universal, which in turn are divided into incineration, gasification, and pyrolysis (Cheng et al., 2019). Pyrolysis has a number of advantages, primarily because of the possibility of obtaining liquid products, which are raw materials for petrochemical industries (Ma et al., 2014). Pyrolysis is a destruction of organic compounds of the sludge under high temperatures without oxygen access with yield of oil, coke, and gas (Cheng et al., 2017).

Previous studies have investigated the issue of obtaining liquid products from oil sludge (Kaminsky et al., 2001). The purpose of this work is to assess the possibility of extracting liquid products from oil sludge with their simultaneous purification from sulfur compounds.

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2. Experimental

2.1 Materials

Oil sludge used in this work as feedstock was obtained from the Ukhta oil field (Russian Federation). In appearance, the samples are a black and viscous suspension. The results of proximate and ultimate analysis of sludge are presented in Table 1. As an additive for the purification of volatile components from sulfur compounds, a chemically pure calcium oxide reagent (CaO) was used, which was uniformly mixed with the feedstock in predetermined proportions (15 and 25 wt.%). The initial oil product from the sludge for the study of the fractional composition was obtained by extraction with toluene followed by distillation.

Table 1: Analysis of the tested oil sludge.

Proximate analysis (wt.%)^a		Ultimate analysis (wt.%)^a	
Moisture	31.27	C	13.27
Volatile matter	14.65	H	2.24
Ash	52.49	S	0.57
Fixed carbon	1.59	(O + N)^b	0.16
LHV (MJ/kg, dry basis)	6.07		

^{a}As-received basis.

^{b}Calculated by difference

2.2 Analytical methods

The elemental composition of solid and liquid samples was determined using the Vario MACRO cube CHNS-analyzer (Elementar Analysensysteme GmbH). Certified samples of sulfanilic and benzoic acids were used as calibration standards. The standard deviation for CHNS elements did not exceed 0.2 %. The calculation of oxygen and nitrogen was carried out by difference. Calculation of the lower heating value of oil sludge samples was carried out based on the obtained elemental composition.

Proximate and thermal analysis of the oil sludge samples was carried out using the NETZSCH STA 449 F3 Jupiter in the TG-DTG mode with a heating rate of 10 ºC/min to a final temperature of 620 ºC. Nitrogen (N_2) was used as an inert gas and oxygen (O_2) was employed for oxidation. The results of the analysis were corrected using the baseline obtained by measuring the empty crucible.

The component composition of pyrolysis oil was determined on the Thermo Focus DSQ II chromatography-mass spectrometer. To identify the components, the reference mass spectra presented in the NIST/EPA/NIH 17 database were used. The content of the components was calculated on the basis of the total ion current chromatographic peak areas on the chromatogram without correction for ionization efficiency.

The composition of the pyrolysis gas was carried out on the chromatograph LXM-2000M with a thermal conductivity detector of the DTP type. The flow rate of the carrier gas (helium) is equal to 30 mL/min. The chromatograph has the software “Zet-lab” that allows the signal processing. The relative mean square deviation of the output signal (height, peak area and retention time) is not more than 1%.

2.3 Experimental procedure

Thermal decomposition of oil sludge was investigated in the fixed-bed laboratory retorting system (see Fig. 1). The retort was heated using the PID controller at a rate of 10 °C/min. To determine the amount of hydrogen sulfide (H_2S) released, the whole volume of pyrolysis gas was passed through a solution of $Cd(CH_3COO)_2$, after which it was collected in a gas meter. During the experiment, atmospheric pressure was maintained in the condensation system, which was controlled by a differential pressure gauge.

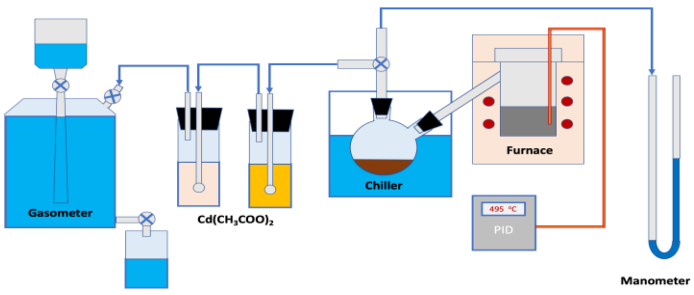

Figure 1: Schematic diagram of the experimental retorting system

3. Results and discussion

3.1 TG and DTG analysis

The results of the TG-DTG analysis are shown in Fig.2. Thermal decomposition of oil sludge occurs in two stages. It can be assumed that at the first stage, in the temperature range from 100 °C to 396 °C, the evaporation of moisture and the release of light components occur predominantly. The maximum mass loss rate is reached at ~ 320 °C. The mass change at this stage is ~ 31.87 %. With further heating of the raw material, the destruction of organic compounds takes place, accompanied by the release of volatile substances. The volatile release process occurs in the temperature range of 396 - 505 °C, and the maximum mass loss occurs at a temperature of 462 °C. This range corresponds to the stage of active pyrolysis, where thermal decomposition of the original oil product that is contained in the sludge occurs. The weight loss at this stage is 13.78 %.

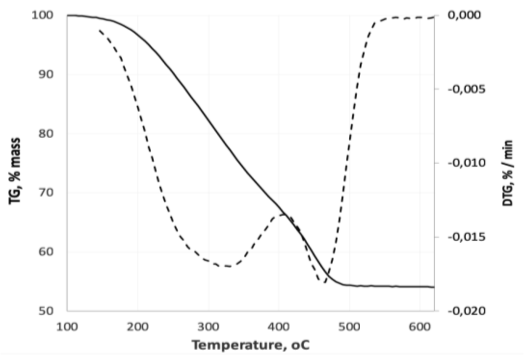

Figure 2: Thermogravimetric and volatile yield rate curves of oil sludge.

3.2 Effect of temperature on yields

The effect of temperature on the distribution of pyrolysis products obtained in the fixed bed reactor is shown in Fig. 3. The temperature of the experiment in this case corresponds to the final temperature of the pyrolysis process. The behavior of semi-coke (COKE) is characterized by a monotonous decrease of its concentration in the pyrolysis products from 54.3 wt.% (daf) at 302 °C to 4.3 wt.% (daf) at 598 °C due to decomposition of the organic mass. This leads to a corresponding increase in the ash content in COKE from 81.3 to 98.7 wt.%. This study did not analyze the mineral components of the ash, but it can be assumed that its composition contains predominantly silicon oxide (SiO_2). It is also possible to find iron sulfide (FeS) and other mineral components (MgO, CaO, etc.) formed during oil production (Chen et al., 2016).

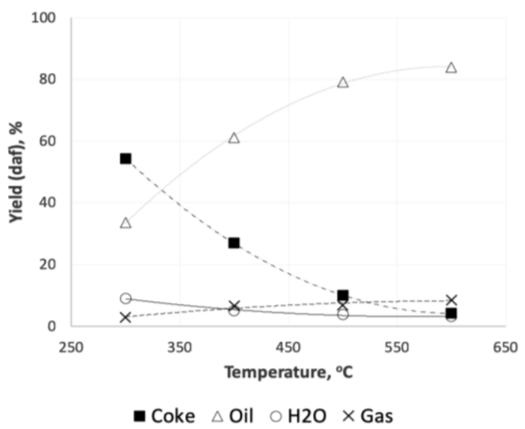

Figure 3: Temperature dependence of the yield of various pyrolysis products in fixed-bed reactor.

Pyrolysis oil (OIL) from thermal decomposition of sludge is of great interest from the point of view of the possibility its return to the production cycle. The results of experiments in the laboratory setup show its increase with increasing temperature with maximum concentration ~ 80 wt.% (daf) at T = 500 °C followed by flattening of

this curve, which is in good agreement with the results of the TG analysis considered earlier. This temperature is optimal for this type of reactors, if the goal of the process requires obtaining a maximum yield of oil.
The yield of non-condensable gases (GAS) in pyrolysis products is characterized by a monotonous increase with increasing temperature. The main components of gases are hydrogen (H_2), methane (CH_4), ethane (C_2H_6), and propane (C_3H_8). In addition to the components listed above, hydrogen sulfide (H_2S) is formed at temperatures above 300 °C, which is absorbed by a solution of $Cd(CH_3COO)_2$ followed by the determination of its concentration by titration.

3.3 Effect of CaO on yields

To assess the possibility of cleaning the volatile components of the pyrolysis products from sulfur compounds, a series of experiments in the presence of calcium oxide (CaO) was carried out with various CaO concentrations. The data received at T = 500 °C are shown in Fig. 4.

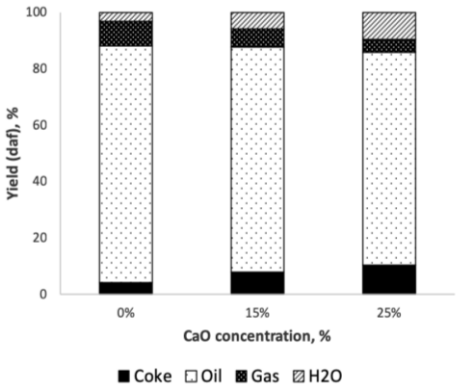

Figure 4: CaO concertation dependence of the yield of various pyrolysis products in fixed-bed reactor.

An increase in CaO concentration in the mixture leads to a decrease in the yield of pyrolysis gas due to the interaction of H_2S with CaO and the subsequent formation of calcium sulfide (CaS) and water as well as due to the reaction of CaO with methane (CH_4) (Yang et al., 2006). The interaction of pyrolysis gas with calcium oxide leads to an increase in the yield of pyrogenic water. The oil yield decreases as the CaO concentration in the mixture increases, which can be explained, firstly, by increasing the specific surface of the solid phase in the reactor, and, secondly, by the interaction of calcium oxide with sulfur-containing oil compounds. The latter indirectly confirms the purification of liquid pyrolysis products from sulfur compounds. At the same time, there is an increase in the yield of semi-coke in proportion to the increase in the concentration of calcium oxide.

Table 2: Elements balance of pyrolysis products of oil sludge.

Products	Concentration of CaO, %	Balance of elements, % mass			
		C	H	S	(O + N)[b]
Coke	0	4.74	0.10	0.18	0.18
	15	7.04	0.16	0.28	0.15
	25	9.23	0.21	0.36	0.14
Oil	0	70.34	11.67	2.98	-
	15	66.22	10.96	2.73	-
	25	62.78	10.38	2.45	-
H_2O	0	-	0.10	-	0.80
	15	-	0.66	-	5.26
	25	-	1.08	-	8.56
Gas	0	6.63	1.94	0.34	-
	15	5.05	1.49	-	-
	25	3.87	0.94	-	-

[b] Calculated by difference

The obtained data on the yield of pyrolysis products for mixture of sludge with calcium oxide allow to determine the elements balance, which is shown in Table 2. One can see, that the addition of calcium oxide leads to a decrease in the sulfur concentration in the oil from 2.98 wt.% during the pyrolysis of the original sludge to 2.45 wt. % during the pyrolysis of the mixture with 25 % addition of CaO. During the pyrolysis of the mixture with a 15 % CaO addition, the sulfur concentration in the pyrolysis gas is completely absent. At the same time, the sulfur concentration in the semi-coke monotonically increases with increasing concentration of CaO in the mixture.

3.4 Pyrolytic oil composition

To assess the possibility of using liquid products of sludge pyrolysis as a raw material for returning to the technological cycle of oil refining, the fractional composition of the original organic matter from sludge was studied, as well as liquid products of pyrolysis of sludge and its mixture with 15 % CaO. The results of the distillation into the gasoline fraction (80 - 180 °C), the kerosene fraction (180 - 250 °C), the gasoil fraction (250 - 305 °C), and the residue from the distillation (more than 305 °C) are shown in Fig. 5. The analysis shows that the pyrolysis of the original sludge and its mixture with calcium oxide makes it possible to obtain the liquid products with a large number of light fractions than in the feedstock. In turn, the addition of CaO leads to an increase in the number of high-molecular compounds in the composition of the liquid pyrolysis products of the mixture compared with the pyrolysis oil of the original oil sludge. The content of light fractions (gasoline and kerosene) in the feedstock as well as in the pyrolysis oil of sludge and its mixture with CaO are 21.6 wt.%, 46.0 wt.% and 35.2 wt.%.

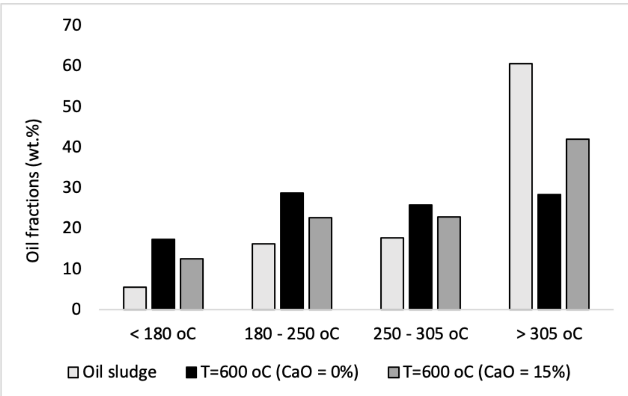

Figure 5: Results of fractional composition of oil

The method of gas chromatography-mass spectrometry (GC-MS) was applied for the qualitative assessment of the composition of the liquid pyrolysis products obtained as a result of thermal decomposition. Fig. 6 shows the results of the analysis of the pyrolytic oil from pyrolysis of the mixture of sludge with 15 % addition of CaO.

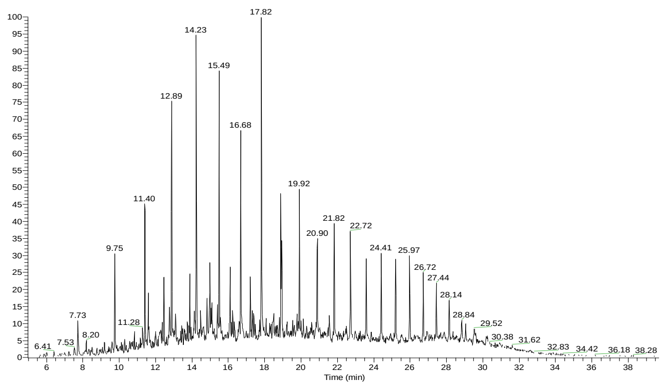

Figure 6: GC-MS chromatogram of pyrolytic oil obtained at 500 °C

The group composition of the pyrolytic oil is shown in Table 3. It represented by paraffin, naphthenic, and aromatic hydrocarbons. The oil obtained as a result of thermal processing of the oil sludge can be attributed to the analogs of oil that can be recycled by standard technologies.

Table 3: Group composition of pyrolytic oil obtained at 500 ℃ (% Area).

Paraffins	Naphthenes				Aromatics
	Mono	Bi	Tri	Tetra	
60.46	23.08	5.75	2.98	0.12	7.61

4. Conclusions

A study of the pyrolysis of oil sludge from the Ukhta oil field in a fixed-bed laboratory retorting system in the temperature range of 300 - 600 °C has been carried out. The results of the experiments show that an intensive increase in the oil yield occurs up to a temperature T = 500 °C, which is in good agreement with the results of the TG-DTG analysis. This temperature is optimal for fixed bed reactors, if it is necessary to obtain the maximum yield of oil. The addition of calcium oxide leads to a decrease in the sulfur content in the oil from 2.98 wt. % during the pyrolysis of the original sludge to 2.45 wt. % during the pyrolysis of the mixture with 25 % CaO addition, and also allows to clean the pyrolysis gas completely from hydrogen sulfide (H_2S). It is necessary to note the negative impact of the addition of CaO, in particular, a decrease in the total yield of oil and pyrolysis gas, as well as an increase in the number of high-molecular compounds in the pyrolysis oil compared to the oil obtained during the pyrolysis of the original sludge. Oil obtained as a result of thermal processing of oil sludge can be attributed to oil analogues that can be recycled by standard technologies.

Acknowledgments

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