Study of pyrolysis process of different types of oil-containing wastes

V V Khaskhachikh¹, G Y Gerasimov², V F Kornilieva³, and S G Avtamonov⁴

¹ Joint Institute for High Temperatures of the Russian Academy of Sciences, Izhorskaya st., 13 Bd.2; 125412 Moscow, Russian Federation
² M.V. Lomonosov Moscow State University; Institute of Mechanics, Michurinsky Ave., 1; 119192 Moscow; Russian Federation
³ G.M. Krzhizhanovsky Power Engineering Institute, Leninsky Ave., 19; 119071 Moscow; Russian Federation
⁴ Ukhta State Technical University, Pervomayskaya st., 13, 169300 Ukhta, Russian Federation

v.khaskhachikh@gmail.com

Abstract. The study of pyrolysis process of different types of oil-containing wastes was conducted in order to evaluate the possibility of extracting liquid products. Proximate and ultimate analysis 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. The resulting products of pyrolysis of oil-containing wastes were investigated to draw up a balance of elements.

1. Introduction

The production activities of oil refineries and oil and gas producing companies sure have a technogenic impact on the environment, and one of the most dangerous pollutants is oil-containing wastes (OCW) [1]. This waste is a complex mixture, which consists of petroleum products, solid particles and water [2]. Their formation occurs during such technological processes as: discharges in the preparation of oil, cleaning of oil tanks, discharges of oily waste drilling operations, discharges during well testing or repairing, and emergency spills during oil transportation [3]. Depending on the origin, the OCW differ significantly in their composition and physicochemical properties. In Russia, one ton of produced oil accounts for up to 7 kg of oil sludge [4]. Threatening growth of annually accumulated hazardous oil-containing wastes in the absence of the necessary level of their utilization and processing leads to confiscation of land resources for long periods.

The utilization methods implemented at most enterprises do not allow recycling of OCW without formation of secondary waste. In this regard, their utilization is one of the priorities of oil refineries in activities aimed at improving the efficiency of the use of hydrocarbons and reducing the negative impact on the environment [5]. At the moment, for disposing of oil-containing wastes, thermal methods are preferred, which make the most of the energy potential of these wastes. From the existing thermal methods, incineration or pyrolysis is used to dispose OCW [6].
Incineration is a process of oxidizing organic mass of the waste at a temperature of 800-1000°C in the presence of oxygen [7]. The OCW contains heavy metal compounds, some of which (Hg, Cd and As), even with the most advanced low-temperature technologies (700-800°C), become volatile and lead to the use of an expensive flue gas cleaning system. The burning of OCW is accompanied by the release of toxic dust-gas emissions containing SO\(_x\) and NO\(_x\), as well as benzopyrene and chlorine-containing compounds that can form polychlorinated dibenzo-p-dioxins (PCDDs) and dibenzofurans (PCDFs) - groups of hazardous chemicals known as persistent organic pollutants.

Thermal decomposition (pyrolysis) is the destruction of organic compounds under the action of high temperatures without oxygen [8]. In the process of pyrolysis, liquid, solid and gaseous products are formed. This method allows the most complete conversion of hydrocarbons from the OCW, in order to return them to the production cycle, as well as to control emissions of heavy metals.

In the earlier works, the fundamental possibility of obtaining liquid products from oil sludge was investigated [9-11]. The purpose of this work is to determine the operating parameters of the pyrolysis process for the extraction of liquid products from various types of OCW.

2. Experimental

2.1. Materials

In this study, three types of OCW were studied: oil sludge from spillage (sample No. 1), sludge from cleaning of fuel oil tank (sample No. 2), and sludge from cleaning the pipelines and tanks from oil (sample No. 3). Samples No. 1, 2 are the black and viscous suspensions; sample No. 3 is a black paste-like mass. The results of proximate and ultimate analysis of the studied samples are presented in table 1.

| Sample No. | Proximate analysis, wt.% a | Ultimate analysis, wt.% a | LHV, MJ/kg |
|------------|----------------------------|--------------------------|------------|
|            | M  | ASH | FC  | VM  | C   | H   | S   | (O+N) b |            |
| 1          | 31.27 | 52.49 | 1.59 | 14.65 | 13.27 | 2.24 | 0.57 | 0.16 | 6.85 |
| 2          | 0.15  | 0.42  | 5.93 | 93.50 | 84.36 | 12.34 | 2.42 | 0.43 | 41.51 |
| 3          | 1.82  | 5.69  | 1.09 | 91.40 | 79.03 | 13.98 | 0.82 | 0.49 | 41.21 |

a As-received basis.

b Calculated by difference

2.2. Analytical methods

The elemental composition of the initial samples, solid and liquid pyrolysis products was determined using a Vario MACRO cube CHNS analyzer (Elementar, GmbH). The sample weight did not exceed 20 mg, and certified sulfanic and benzoic acid samples were used as calibration standards. Oxygen was measured by difference. Calculation of the lower heating value of oil sludge samples was carried out based on the obtained elemental composition.

Technical analysis of the samples was carried out using a TA Instruments SDT Q600 synchronous thermal analysis instrument in TG-DTG mode with a heating rate of 10°C/min to a final temperature of 620°C. Nitrogen (N\(_2\)) was used as an inert gas, and oxygen (O\(_2\)) was used for oxidation. The results of the analysis were adjusted for the baseline obtained by measuring the empty crucible.

The composition of the pyrolysis gas was determined using a Vario Plus Industrial flow type gas analyzer (SYNGAS), which allows identification of the following gases: H\(_2\), CO, CO\(_2\), N\(_2\), C\(_n\)H\(_m\), and H\(_2\)S. The hydrocarbon composition of the pyrolysis gas was determined on the chromatograph LXM-2000M with a thermal conductivity detector of the TCD type.
2.3. Experimental procedure
Pyrolysis of oil-containing wastes was investigated in a modified Fisher retort, which differs from the standard one by the fact that it was made of steel AISI 321, and its volume was increased to ~ 200 ml. The schematic diagram of the installation is shown in figure 1. Heating of the retort was carried out using the PID controller OWEN TRM 251 at a rate of 10°C/min. During the experiment, atmospheric pressure was maintained in the condensation system, which was controlled by a manometer. The implementation of the above-mentioned technical solutions allowed the expansion of the temperature range of studies in the retort, as well as obtaining additional information on the amount and components of the pyrolysis gas.

![Figure 1. Schematic diagram of the experimental retorting system.](image)

3. Results and discussion

3.1. Thermogravimetric analysis
The results of the TG-DTG analysis are presented in figure 2. Thermal decomposition of all samples occurs in two stages. Sample No. 1 contains a significant amount of water (initial moisture content of 31.27 wt.%) and at the first stage, its evaporation occurs predominantly and a small amount of light components is released. Samples 2 and 3 contain less moisture: 0.15 wt.% and 1.82 wt.% and already at the first stage there is an intensive loss of organic mass due to the release of volatile substances. The temperature range of the first stage of thermal decomposition is from ~ 100 to 396°C for sample No. 1, to 385°C for sample No. 2, and to 390°C for sample No. 3. The maximum mass loss rate for samples No. 1 and 2 is reached at 320°C, and for sample No. 3, it is reached at 315°C. The mass change at the first stage is 31.87 wt.%, 61.53 wt.% and 72.03 wt.%, respectively. Upon further heating of sample No. 1 in the temperature range of up to 505°C, volatile substances are released, with a maximum mass loss at a temperature of 462°C. This range corresponds to the stage of active pyrolysis of the original petroleum product contained in the sludge, and the mass loss is 13.78 wt.%. For samples 2 and 3, the second stage is associated with the release of heavier hydrocarbon fractions and occurs up to 501°C for the second sample and up to 490°C for the third, with the greatest intensity of mass loss at 440°C. Mass loss is 30.04 wt.% and 19.38 wt.%, respectively. The residual mass for all three samples contains fixed carbon and ash.
3.2. The effect of temperature on the yield of pyrolysis products

The effect of temperature on the distribution of pyrolysis products is shown in table 2. The temperature of the experiment in this case corresponds to the final temperature of the pyrolysis process.

| Sample No. | T, °C | Coke | Oil | H₂O | Gas |
|------------|-------|------|-----|-----|-----|
| 1          | 302   | 54.35| 33.74| 9.07| 2.84|
|            | 405   | 26.95| 61.21| 5.12| 6.71|
|            | 501   | 10.01| 79.31| 3.87| 6.80|
|            | 598   | 4.21 | 83.99| 3.18| 8.61|
| 2          | 513   | 7.17 | 88.65| 0.07| 4.10|
|            | 600   | 6.81 | 88.54| 0.14| 4.51|
| 3          | 495   | 8.70 | 86.97| 0.69| 3.64|
|            | 602   | 6.37 | 90.58| 0.32| 2.73|

For sample No. 1, the semi-coke yield (COKE) is characterized by a decrease in its concentration in the pyrolysis products from 54.3 wt.% (daf) at 302°C to 4.3 wt.% by mass (daf) at 598°C due to decomposition of the organic mass and leads to a corresponding increase in its ash content. For samples No. 2 and 3 in the range of the temperatures studied, the change in the yield of semi-coke is not significant, which indicates that by this time the decomposition process has already been completed. The results for semi-coke obtained for all samples match with the TG-DTG analysis data very well.

Pyrolysis oil (OIL) from thermal decomposition of oil-containing wastes causes an increased interest in terms of the possibility of its return to the production cycle. The results of experiments in a retorting system show that for sample No. 1 the maximum yield is reached at T=501°C and amounts to 79.31 wt.% (daf). For other samples, the maximum is also reached at a temperature of ~ 500°C, followed by a flattening of the curve and amounts to 88.65 wt.% (daf) and 86.97 wt.% (daf), respectively, for samples No. 2 and 3. Unlike the original raw materials obtained as a result of pyrolysis, liquid products are easily separated from water and do not have solid particles. For sample No. 1 this is most noticeable, since the content of the initial oil product in the sample is only 16.24 wt.% Pyrolysis oil samples No. 1 and 2 are represented by a black viscous liquid with a characteristic...
hydrogen sulfide odour. The pyrolysis oil of sample No. 3 at room temperature solidifies, has brown color, which indicates that paraffins prevail in the composition. As a result, a temperature of ~ 500˚C is optimal for the fixed bed reactors, if the goal of the process is to obtain the maximum yield of liquid products. However, co-processing of various types of oil-containing wastes, in particular, with sludges from stripping pipelines and tanks, can lead to a negative result because such a combination increases substantially the viscosity of the resulting raw material and makes it impossible to use liquid products as the boiler fuel.

The yield of non-condensable gases (GAS) for all samples in the pyrolysis products is characterized by a monotonous increase with increasing temperature. The main components are hydrogen (H₂), methane (CH₄), ethane (C₂H₆), propane (C₃H₈), and hydrogen sulfide (H₂S).

The resulting products of OCW pyrolysis, obtained at a temperature of ~ 600˚C, were investigated to draw up a balance of elements. The greatest interest is the sulfur content (S) in various products of pyrolysis. As it can be seen from Table 3, pyrolysis reduces the sulfur content (S) in the oil for all samples. The sulfur content on a mass (daf) in the original substance of sample No. 1 was 3.51 wt.% and after pyrolysis, it was 2.98 wt.%, for sample No. 2 this value decreased from 2.43 wt.% to 1.74 wt.%, and for sample No. 3 it decreased from 0.87 wt.% to 0.34 wt.%. This is connected to the fact that part of sulfur during pyrolysis is released together with the gas in the form of hydrogen sulfide (H₂S), and part remains in a bound state in coke. This fact, together with the fact that in the course of processing there is a separation of liquid products from water and solid particles indicates a positive effect achieved in the processing of oil-containing wastes.

Table 3. Elements balance of pyrolysis products of oil-containing wastes.

| Product | Sample No. | Balance of elements, wt.% |  |
|---------|------------|---------------------------|---|
|         |            | C  | H  | S  | (O + N) |
| Coke    | 1          | 4.74 | 0.10 | 0.18 | 0.18 |
|         | 2          | 6.21 | 0.21 | 0.26 | 0.13 |
|         | 3          | 5.27 | 0.63 | 0.44 | 0.03 |
|         | 1          | 70.34 | 11.67 | 2.98 | -   |
|         | 2          | 75.54 | 11.25 | 1.74 | -   |
|         | 3          | 77.43 | 12.81 | 0.34 | -   |
| Oil     | 1          | -  | 0.10 | -  | 0.80 |
|         | 2          | -  | 0.02 | -  | -   |
|         | 3          | -  | 0.04 | -  | 0.28 |
| H₂O     | 1          | 6.63 | 1.34 | 0.34 | -   |
|         | 2          | 6.63 | 1.34 | 0.34 | -   |
|         | 3          | 1.10 | 1.34 | 0.09 | 0.20 |

*Calculated by difference

4. Conclusions
A study of the pyrolysis of various types of oil-containing wastes in an experimental retorting system with a fixed bed in the temperature range of 300-600˚C was conducted. The results of the experiments show that for all samples an intensive increase in the oil yield occurs up to a temperature T=500˚C, which matches with the results of the TG analysis. This temperature is optimal for fixed bed reactors, if it is necessary to obtain the maximum yield of liquid products. Co-processing of various types of oil-containing wastes, in particular with sludge from cleaning pipelines and tanks can lead to a negative result due to a significant increase in the viscosity of the resulting liquid products. The positive effect is that during processing the separation of liquid products from water and solid particles contained in the feedstock occurs. Another equally important result of pyrolysis for all samples of oil-containing wastes is the reduction of sulfur content in liquid products, due to its redistribution into
pyrolysis gas and solid residue. Liquid products resulting from the pyrolysis of oil-containing wastes can be used as a boiler fuel or a raw material for the petrochemical industry.

Acknowledgments
Research has been conducted with financial support from the Russian Science Foundation (Project No18-79-00282).

References
[1] Hu G, Li J, Zeng G Recent development in the treatment of oily sludge from petroleum industry: A review Journal of Hazardous Materials 2013, 261, 470-90
[2] Zhang J, Li J, Thring R, Hu X, Song X Oil recovery from refinery oily sludge via ultrasound and freeze/thaw Journal of Hazardous Materials 2012, 203-204, 195-203
[3] Lin B, Wang J, Huang Q, Chi Y Effects of potassium hydroxide on the catalytic pyrolysis of oily sludge for high-quality oil product Fuel, 2017, 200, 124–133
[4] Timoshin A, Nikolaev A, Nityagovsky A, Lozhkina D Analysis method of disposal of oily waste and developing a new integrated process for sludge disposal tank-type International journal of applied and fundamental research 2016, № 6, 209-213
[5] Shen Y, Chen X, Wanga J, Ge X, Chen M Oil sludge recycling by ash-catalyzed pyrolysis-reforming processes Fuel 2016, 182, 871–878
[6] Johnson O, Affam A Petroleum sludge treatment and disposal: A review Environmental Engineering Research 2019, 24(2), 191-201
[7] Cheng S, Zhang H, Chang F, Zhang F, Wang K, Qin Y, Huang T Combustion behavior and thermochemical treatment scheme analysis of oil sludges and oil sludge semicokes Energy 2019, Volume 167, 575-587
[8] Cheng S, Wang Y, Fumitake T, Kouji T, Li A, Kunio Y Effect of steam and oil sludge ash additive on the products of oil sludge pyrolysis Applied Energy 2017, 185, 146-157
[9] Chen L, Zhang X, Sun L, Xu H, Si H, Mei N, Study on the fast pyrolysis of oil sludge and its product distribution by PY-GC/MS, Energy & Fuels 2016, 30, 10222-10227
[10] Cheng S, Chang F, Zhang F, Huang T, Yoshikawa K, Zhang H Progress in thermal analysis studies on the pyrolysis process of oil sludge Thermochimica Acta 2018, 663, 125-136
[11] Ma Z, Gao N, Xie L., Li A Study of the fast pyrolysis of oilfield sludge with solid heat carrier in a rotary kiln for pyrolytic oil production Journal of Analytical and Applied Pyrolysis 2014, Volume 105, 183-190