Study of pyrolysis of oil sludge

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Abstract. In this paper, the pyrolysis method of dealing with oil waste (oil sludge) is considered. Presented the mechanism of thermal destruction of hydrocarbons. The conducted study of the processes of non-catalytic pyrolysis of oily waste. At pyrolysis of oil slimes an exit of hydrocarbons was observed C1–C4.

1. Introduction

Oil and gas are the main energy resources that play a key role in the economy of all developed countries of the world. The products of their processing are used in almost all industries, in all types of transport, in construction, agriculture, energy, in everyday life, etc. For several decades, oil and gas have learned to produce various chemical materials: plastics, synthetic fibers, and rubbers, varnishes, paints, detergents, mineral fertilizers and much more.

As is known, the petroleum industry is one of the first among the leading sectors of economic activity on the negative impact of waste on the environment. For the oil industry is characterized by the formation of oil waste, or as they are called - oil sludge. Oil sludge is formed by various industrial processes, such as the construction of oil wells, emergencies, oil refining, cleaning process equipment, etc. [1].

Oil sludge is a complex physico-chemical mixture, consisting of three distinct fractions: water, oil and solid (metals, salts, sand, etc.). Depending on the quality and composition of the initial product, the percentages of these fractions in the sludge change. Produced storage of oil sludge in specially organized places (sludge collectors, settling ponds, and tanks) [2].

2. Pyrolysis of oil waste

Currently used thermal, chemical, biological, physico-chemical, combined methods of processing and disposal of sludge [3]. At the same time, thermal methods for processing oil sludge compared with the others have a number of significant advantages. These include the absence of expensive separation steps; possibility of processing raw materials with high ash content; avoiding the use of consumables (solvents and microorganisms); lack of waste and products requiring disposal (filter elements, hydrophobic encapsulated products, etc.) [4].

Thermal methods involve thermal effects on waste, which leads to the decomposition of the feedstock into its component parts. The main types of thermal methods are combustion, gasification, pyrolysis, heating in air, in vacuum, etc. Also, these methods usually include such stages as sludge preparation for processing, high-temperature treatment, multi-stage gas cleaning, heat utilization, production of organic by-products (gaseous and liquid fuels) and mineral products (oxides, cement, mineral salts) [5,6].
The most promising of the presented methods of utilization of oil sludge is pyrolysis. Pyrolysis is a controlled thermal decomposition of the feedstock into its component parts and is one of the most promising areas for the disposal of oil sludge today. It makes it possible to economically, environmentally clean and technically relatively easy to process oil waste [7].

Depending on the temperature, there are three types of pyrolysis:

- **Low-temperature pyrolysis or semi-coking.** The process takes place at 450-550 °C and is characterized by a minimum gas yield, the maximum amount of liquid product and solid residue (semi-coke). At the same time, the gas formed during this type of pyrolysis has the maximum heat of combustion, and the semi-coke can be used as an energy and domestic fuel. Liquid products (oil condensate) are formed for 29% of the initial mass; the heat of combustion of oil condensate is 9000 kcal / kg [8].

- **Medium temperature pyrolysis or medium temperature coking.** This process takes place at temperatures up to 800 °C and is characterized by an increase in the gas yield (compared to low-temperature pyrolysis), while the yield of liquid and solid products decreases, and the heat of combustion of the gas decreases.

- **High temperature pyrolysis or coking.** The process is carried out at 900-1050 °C. At this temperature, the amount of generated gases is maximum, and the yield of liquid and solid products is minimized, while the gas has the lowest heat of combustion.

According to the types of reactions, oxidative and dry pyrolysis is distinguished. During oxidative pyrolysis, the thermal decomposition of hydrocarbon-containing wastes occurs, with their partial combustion. This method is well applicable to waste (viscous, pasty, etc.) that are difficult to process by incineration or gasification. Dry pyrolysis is the thermal decomposition of carbonaceous waste without oxygen. This method ensures the processing of waste and the production of useful products used as fuel and chemical raw materials. Because of dry pyrolysis, gas (pyrolysis gas), liquid products and solid carbon residue are formed [8].

2.1 The mechanism of thermal destruction

The process of thermal decomposition of hydrocarbons, consisting of many elementary reactions that occur simultaneously and sequentially, can be divided into two successive stages. In the first stage, primary reactions of thermal cleavage of alkanes and cycloalkanes proceed with the formation of olefins, diolefins and alkanes with a smaller or equal number of carbon atoms than the original hydrocarbons, as well as hydrogen. In the second stage, the resulting olefins and diolefins undergo dehydrogenation reactions, further cleavage and condensation with the formation of cyclic unsaturated (cyclopolymenes) and aromatic hydrocarbons. In the further course of the reaction, more and more complex polynuclear aromatic hydrocarbons are obtained. As a result, these compounds, emitting hydrogen and partially absorbed on the surface of the reactors, form a solid film of carbon, the so-called pyrolysis coke. The latter can also be obtained by direct decomposition of hydrocarbons into carbon and hydrogen [9].

Thermal reactions of hydrocarbons can occur both molecular and radical chain or non-valuation. Currently, the most accepted radical-chain mechanism of pyrolysis of hydrocarbons. A radical-chain process of thermal decomposition, like any chain process, consists of three stages: initiation, continuation and termination of the chain [10].

1. Initiation or nucleation of the chain (radicals). The decomposition of hydrocarbons into radicals occurs most often when the C – C bond is broken, for example, during the pyrolysis of ethane:

\[
C_2H_6 \rightarrow 2CH_3
\]

Radicals can be formed not only during monomolecular, but also during bimolecular reactions from olefin molecules in disproportionation reactions or from alkanes and olefins in reactions that are inverse to disproportionation, for example:
2C_3H_6 \rightarrow C_3H_5 + C_3H_7

C_3H_8 + C_3H_6 \rightarrow 2C_3H_7

2. The continuation of the chain. Since the radicals are chemically unsaturated particles, they have a high reactivity and enter into various reactions at a very high rate \[10\]. Below are the main reactions of radicals.

Substitution reaction (detachment of a hydrogen atom), for example:

\[ \cdot \text{C}_3\text{H}_3 + \cdot \text{C}_3\text{H}_8 \rightarrow \cdot \text{C}_4\text{H}_4 + \cdot \text{C}_3\text{H}_7 \]

Joining reactions. Radicals can join molecules of unsaturated hydrocarbons by a multiple bond, for example:

\[ \cdot \text{C}_3\text{H}_3 + \cdot \text{CH}_2 = \text{CH}_2 \rightarrow \text{C}_3\text{H}_3 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \]

Reactions of decay. The decay of radicals is observed in the bond located in the \( \beta \) – position relative to the carbon atom with free valency. Because of the decomposition, an unsaturated hydrocarbon molecule and a radical of lower molecular weight than the initial one are formed \[9\]. For example:

\[ \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3 \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{H} = \text{CH}_2\text{CH}_2\text{CH}_3 \]

Isomerization Reactions These reactions represent the intramolecular detachment of a hydrogen atom by an active carbon atom having a free valency:

\[ \cdot \text{CH}_2 = \text{CHCH}_2\text{CH}_2\text{CH}_3 \rightarrow \cdot \text{CH}_2 = \text{CHCH}_2\text{CH}_2\text{CH}_2\text{CH}_3 \]

3. Open circuit Carried out by the following reactions.

Recombination Reactions (radical recombination). These are the addition reactions of two radicals:

\[ 2\cdot \text{C}_2\text{H}_5 \rightarrow \cdot \text{C}_4\text{H}_{10} \]

Disproportionation reactions (redistribution of hydrogen). Disproportionation occurs because of the interaction of two olefin molecules or two radicals, for example \[9,11\]:

\[ 2\cdot \text{C}_2\text{H}_5 \rightarrow \cdot \text{C}_2\text{H}_6 + \cdot \text{C}_2\text{H}_4 \]

3. Experimental part

To carry out experiments on the study of the process of pyrolysis of oil sludge, an experimental test bench has been developed. Its schematic diagram is shown in figure 1. The experimental test bench consists of the following parts: sectional pyrolysis reactor of 1 periodic action, 100 cm\(^3\) in volume; meter - regulator 2, which allows to monitor the temperature indicator with a limit of relative error of \( \pm 0.5\% \); heat insulating material 3, which provides protection against temperature effects and heat preservation in the reaction zones of the reactor; heating elements 4, necessary for heating sludge; thermocouples 5 that serve to monitor the temperature parameters; fittings for removal of pyrolysis gas 6; pipeline 7 for the transportation of pyrolysis gas; shut-off valves 8 that control the flow of the medium; flow meter 9 to control the amount of final products; sampler 10 for sampling gaseous products; a refrigerator 11 for collecting liquid pyrolysis products; nozzles (mesh type) 12 to ensure uniform heating of the feedstock.
Artificially contaminated oil consisting of crude oil, water and various mechanical impurities was used as the raw material of the reactor. Oil sludge heating temperature $550 \pm 20^\circ$C. The mass of one prepared sample was 30 g. The concentration of oil fraction is 50%. The results of the experiments are presented in figure 2. Data on the yield of gaseous products were recorded every 5 minutes, starting with 15 minutes and ending with 30 minutes.

Figure 1. Experimental installation.

Figure 2. The results of pyrolysis oil sludge.
Thus, based on the data obtained, it can be concluded that the highest yield of gaseous products is carried out at a residence time of 30 minutes, at a pyrolysis temperature of 550 ± 20 °C.

4. Conclusion
In the course of the study, the most effective method of oil sludge utilization was determined, the mechanism of thermal destruction of hydrocarbons was shown. The dependences of the residence time of the raw material on the composition and yield of gaseous pyrolysis products are obtained. The following gases were present in significant amounts in all samples: methane (CH4), ethylene (C2H4), ethane (C2H6), propane (C3H8), butylene (C4H8).

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