Determination of Calorific Ability of Fuel Briquettes on the Basis of Oil and Oil Slimes

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Abstract. Utilization and neutralization of oil slimes is one of important environmental problems of the oil-extracting, oil-processing and petrochemical industry. The easiest and economic way of utilization of oil slimes is their use as a part of the bricketed boiler fuel. In this work the highest calorific ability of crude oil, the oil slimes and fuel briquettes made on their basis is defined. A research problem was carrying out the technical analysis of oil fuels on the content in them analytical moisture, the cindery rest and volatiles. It is established that in comparison with oil slimes crude oil possesses bigger highest calorific ability, has smaller humidity and an ash-content. The highest calorific abilities of the boiler briquettes made of samples of crude oil, oil slimes and peat made 14 – 26 MJ/kg.

1. Introduction
Environmental pollution by oil and oil products which have negative effect on the soil, a surface water and the geological environment [1 - 4] became one of the most important environmental problems of our country and the whole world. World and domestic experience of development of oil fields showed that modern technologies of oil production don't exclude its flood. It is counted that about 16.5 % of oil are lost at its production, preparation, transportation and processing. Now at the enterprises of the oil-extracting, oil-processing and petrochemical industry about 4.5 million tons of oil slimes [5, 6] are saved up. Oil slimes represent the liquid, pastelike or solid waste consisting of oil or oil products, water and firm particles (sand, clay, oxides of metals) [7]. They are formed during the drilling of wells, preparation of oil for transportation, in system of reverse water supply, at sewage treatment, repair of the equipment and cleaning of tanks. Oil slimes classify on three main groups: soil, benthonic and reservoir. Soil slimes are formed at hit of oil products on the soil, benthonic – at subsidence of oil on a bottom of reservoirs, reservoir – at storage and transportation of oil products in capacities. Crude oil contains soil particles, water, salts and gases. These impurity cause corrosion of the equipment therefore clear oil before transportation. Water after removal from oil is pumped in oil layer, and mechanical impurity form soil oil slime with oil. Reservoir oil slimes are formed as a result of physical and chemical interaction of oil products with water, air oxygen, mechanical impurity and walls of the tank. As showed researches of many authors [8, 9], the composition of reservoir oil slimes changes over a wide range: hydrocarbons – 5-90 %, water – 1-52 %, solid impurity – 0.8-65 %. Respectively density (830 - 1700 kg/m³), hardening temperature (270 – 353 K) and flash temperature (308 – 393 K) oil slimes change. Now in Russia there are in operation more than 40 thousand horizontal and vertical cylindrical tanks of various capacity for storage of oil and oil products. At long storage reservoir oil slimes are divided into the separate layers having various properties. The top layer represents the flooded oil product with the content of fine mechanical impurity to 5 %. It belong to the class of emulsions "water in oil". 70-80 %
of oils, 6-25 % of asfalten, 7-20 % of pitches, 1-4 % of paraffin, 5-8 % of water are its part. The organic part of the top layer of oil slime on properties and structure is close to the initial oil product which is stored in tanks. The center contains 70-80 % of water and 1.5-15 % of mechanical impurity. It represents an emulsion like "oil in water". The following layer completely consists of water solution of salts. The benthonic layer represents the firm phase consisting of organic chemistry – to 45 %, water – to 25 %, solid mechanical impurity and a rust – 52-88 %.

There are some directions of use of oil slimes. At dehydration and drying of this waste their return to production for the subsequent processing according to the existing schemes in target products is possible [10]. Perhaps also use of oil slime in drilling as an additive to boring solutions, in production of construction materials (a front tile, concrete, a brick, expanded clay, waterproofing and heat-insulating materials), road construction, the fuel industry (receiving fuel oil, the bricketed solid fuel materials), an igneous metallurgy (extraction of V, Li, B, Sr, Sc, Ge, etc.) [11, 12].

Here is an opinion that burning of oil slimes is ecologically dirty way of their utilization. However, experimental data according to the contents benzo(a)pyrene in emissions of various enterprises of Kurgan showed that in emissions of the boiler rooms working at natural gas benzo(a)pyrene it is more, than in the boiler rooms using oil and mix of coal with gas [13]. So, emissions benzo(a)pyrene of the boiler rooms working at gas make 1341 ng/m³, working at gas and coal – 594.7 ng/m³, working at oil – 718.9 ng/m³, working at fuel oil – 1219.1 ng/m³, burning coal – 2633.1 ng/m³. On the basis of these data it is possible to conclude that use of oil slimes as an additive in the bricketed boiler fuel is ecologically proved. Oil slimes can be applied in mixes with peat, coal dust, sawdust or other cheap combustible substances. Their contents in briquettes shouldn't exceed 30-40 % of masses. As binding material it is possible to use a lignin – lignosulfonate, 3,4- polyisoprene, epoxy, etc.

In the real work for production of fuel briquettes peat was used. It well absorbs the polynuclear, unsaturated and aromatic hydrocarbons containing in oil slimes and possesses high calorific ability.

2. Problem Definition
Determination of the highest calorific ability of the fuel briquettes made of mixes of oil fuels and peat was the purpose of our work. A research problem was carrying out the technical analysis of samples of crude oil, soil and reservoir oil slimes on the contents in them analytical moisture, the cindery rest and volatiles. Samples of oil fuels were taken on the Pioneer field of the Tyumen region.

3. Theory
The highest calorific ability of samples of oil fuels was counted according to the technical analysis with use of a formula of Gutal:

\[ Q_B = 82 \cdot K + \alpha \cdot V_G \]

where K is the maintenance of the nonvolatile ashless rest, %; \( V_G \) is the content of volatiles in relation to the combustible mass of fuel, %; \( \alpha \) is the coefficient depending an exit of volatiles.

The technical analysis of fuel included definition in tests of analytical moisture on a method Dyne and Starck, the content of ashes and an exit of volatiles at long and short-term heating of tests at 1073±25 K respectively [14].

The content of analytical moisture in fuel test (in %) was calculated on a formula:

\[ W_a = \frac{V_0}{V} \cdot 100 \% \]

where V is the volume of test of fuel, cm³; \( V_0 \) is water volume in the receiver trap, cm³.

The content of volatiles in relation to the combustible mass of fuel (in %) was determined by a formula:

\[ V_G = V_A \cdot \frac{100}{100-W_a-A_a} \]

where \( V_A \) is the content of volatiles in relation to analytical test of fuel, %; \( A_a \) is the maintenance of the cindery rest in test of fuel, %.
\[ V_A = \frac{G_2}{G_1} \cdot 100 - W_A; \]
\[ A_a = \frac{G_2}{G_1} \cdot 100 \%, \]

where \( G_1 \) is the mass of a hinge plate of fuel; \( G_2 \) is the mass of ashes.

The maintenance of the nonvolatile ashless rest in fuel test (in \%) was found from expression:
\[ K = 100 - (V_G + A_a). \]

4. Results of Experiments

Results of the technical analysis of oil fuels are presented in tab. 1

| Oil fuel          | Crude oil | Reservoir oil slime | Soil oil slime |
|-------------------|-----------|--------------------|---------------|
| Content of analytical moisture \( W_a \), \% | 0.84      | 8.40               | 2.44          |
| The content of volatiles in relation to analytical test of fuel \( V_A \), \% | 42.19     | 58.55              | 27.56         |
| The content of volatiles in relation to the combustible mass of fuel \( V_G \), \% | 42.90     | 70.38              | 29.90         |
| The maintenance of the nonvolatile ashless rest \( K \), \% | 56.98     | 33.04              | 67.04         |
| Maintenance of cindery rest \( A_a \), \% | 0.83      | 8.41               | 5.40          |
| Coefficient \( \alpha \) | 76        | 50                 | 93            |
| The highest calorific ability \( Q_{bi} \), MJ/kg | 33.19     | 26.06              | 23.27         |

The highest calorific abilities of the oil fuels and fuel briquettes made of samples of oil fuel and peat are presented in tab. 2.

| The highest calorific ability \( Q_{bi} \), MJ/kg |
|-------------------|-----------|--------------------|
| Crude oil | Reservoir oil slime | Soil oil slime |
| 33.19     | 26.06     | 23.27              |
| Mix: 30 \% of oil fuel + 70 \% of peat | 16.96 – 26.76 | 14.82 – 24.62 | 13.98 – 23.78 |

5. Discussion of results

The comparative analysis of oil fuels (tab. 1) showed that reservoir oil slimes contain the greatest number of water (8.40 \%) and the cindery rest (8.41 \%). These slimes have the highest exit of volatiles (70.38 \%). This indicator for soil oil slimes and crude oil makes 29.90 and 42.90 \% respectively. Unlike oil slimes, crude oil possesses the greatest calorific ability – 33.19 MJ/kg, a smaller ash-content and humidity. Considering that availability of water in oil slimes and crude oil reduces formation of soot at their burning, the studied oil fuels can be used for production of the bricketed boiler fuel. As a filler of briquettes peat as it well adsorbs organic substances was chosen and possesses high calorific ability (10-24 MJ/kg). In the tab. 2 results of determination of the highest calorific ability of the boiler briquettes made of samples of oil fuel and peat are presented (70 \% of mass of peat + 30 \% of mass of oil fuel). The received values of the highest calorific ability of briquettes made 14 – 26 MJ/kg.

Thus, sharing of peat and oil fuels in the form of briquettes is a perspective and economic way of utilization of oil slimes of various type as slurry moisture replaces the water vapor added to a burning zone at smokeless burning of fuel.
6. Conclusion
With use of data of the technical analysis on Gutal’s formula the highest calorific ability of oil fuels is defined. For crude oil it made 33.19 MJ/kg, for oil slimes – 23-26 MJ/kg. Calorific abilities of the boiler briquettes made of oil fuels and peat made 14 – 26 MJ/kg.

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