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Possibilities for producing secondary materials from hydrocarbon waste

Możliwość produkcji materiałów wtórnych z odpadów węglowodorowych

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ABSTRACT: The utilisation and processing of crude oil sludge is one of the major global challenges. Therefore, it is necessary to justify the following scientific solutions in the field of oil sludge utilisation and processing worldwide: the study of the physicochemical properties of oil sludge in order to obtain construction grade bitumen; detection of dispersion of solid particles in the composition of oil sludge; development of the optimal technological parameters for the process of obtaining construction grade bitumen from oil sludge; establishing a correlation dependence between process efficiency and the environment, the content of light fractions in the sludge composition, the process temperature. In this work, oil sludge was diluted with a solvent in a ratio of 70:30, with light naphtha used as a solvent. A laboratory distillation column was used to separate the sludge into fractions, and the chemical composition of the oil sludge was investigated. Oil sludge consists of asphaltenes up to 4.2–4.5%, resins up to 21.0%; paraffin-naphthenic hydrocarbons up to 41.2%; monocyclic aromatic hydrocarbons up to 4.6%; bi- and tricyclic aromatic hydrocarbons up to 5.8%; polycyclic aromatic hydrocarbons up to 9.7%. The paper also presents the results of the change in the viscosity and density of the distillate fractions separated during the distillation of diluted oil sludge. Density and viscosity were measured using an areometer and a VPZh-4, respectively. One of the main components of the oil sludge is water. A series of experiments were conducted to determine the water content using the Dean and Stark method. In addition, the sulphur content in oil sludge diluted with solvents – light and heavy naphtha, heavy gas oil – was determined.

Key words: distillation column, light naphtha, heavy naphtha, heavy gas oil, oil, oil sludge, distillate, fraction, density, viscosity, bitumen.

STRESZCZENIE: Utylizacja i przetwarzanie odpadów ropopochodnych to jedno z głównych globalnych wyzwań. W związku z tym konieczne jest uzasadnienie rozwiązań naukowych w zakresie utylizacji i przetwarzania szlamu naftowego na całym świecie, w tym: badanie właściwości fizykochemicznych szlamu naftowego w celu uzyskania asfaltu budowlanego; wykrywanie dyspersji cząstek stałych w składzie szlamu naftowego; opracowanie optymalnych parametrów technologicznych procesu wytwarzania asfaltu budowlanego; ustalenie zależności korelacyjnych pomiędzy wydajnością procesu a środowiskiem, zawartością frakcji lekkich w składzie szlamu naftowego, temperaturą procesu. W niniejszej pracy szlam naftowy rozcieńczono rozpuszczalnikiem w stosunku 70:30, przy czym jako rozpuszczalnika użyto benzyny lekkiej. Do rozdzielenia osadów na frakcje użyto kolumny destylacyjnej dostępnej w laboratorium, a także zbadano skład chemiczny szlamu naftowego. Zawiera on asfalteny w ilości 4,2–4,5%, żywice do 21,0%; węglowodory parafinowo-naftenowe do 41,2%; jednopierścieniowe węglowodory aromatyczne do 4,6%; dwu- i trójpierścieniowe węglowodory aromatyczne do 5,8%; wielopierścieniowe węglowodory aromatyczne do 9,7%. W artykule przedstawiono również wyniki badania zmian lepkości i gęstości frakcji destylatów wydzielonych podczas destylacji rozcieńczonego szlamu naftowego. Gęstość i lepkość mierzono odpowiednio za pomocą areometru i VPZh-4. Jednym z głównych składników szlamu naftowego jest woda. Przeprowadzono serię eksperymentów w celu określenia zawartości wody metodą Deana i Starka. Dodatkowo określono zawartość siarki w szlamie naftowym rozcieńczonym rozpuszczalnikami – benzyną lekką i ciężką oraz olejem opałowym ciężkim.

Słowa kluczowe: kolumna destylacyjna, benzyna lekka, benzyna ciężka, olej opałowy ciężki, ropa, szlam naftowy, destylat, frakcja, gęstość, lepkość, asfalt.

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Introduction

The oil industry is one of the top industries in terms of environmental impact producing a significant amount of heterogeneous waste. One such waste is oil sludge – a colloidal system composed of high-molecular compounds of crude oil, mineral particles of various compositions, and water (Levitskiy, 1987; Petrovskiy et al., 2018).

Most projects aimed at disposing of such sludge fail to achieve the desired outcomes due to improperly selected equipment, chemical reagents (demulsifiers, flocculants), or insufficient understanding of the nature of the waste being processed (Shlepkina, 2009; Aminova et al., 2015).

Special attention should be paid to such oil-containing waste as oil-contaminated soils from accidental oil spills. Their main difference between these soils and oil sludge is their lower hydrocarbon concentration. The reduced viscosity of spilled oil causes it to form a monomolecular film layer on the ground surface. If its thickness does not exceed 10 mm, oxygen penetration is reduced by about 5–10%, which does not significantly affect the vital activity of microorganisms (Lesueur, 2008; Timofeyeva and Timofeyev, 2009).

Methods and materials

Determination of the chemical composition of the mixture

The experiment was carried out in a laboratory setup. Waste oil sludge and light naphtha solvent were used for the experiment. They were diluted in a ratio of 70:30, respectively. The mixture was then fed into a distillation column and separated into fractions. After studying the chemical properties of oil sludge from the Bukhara oil refinery, it was determined that its chemical composition includes asphaltenes up to 4.2–4.5%, resins up to 21.0%, paraffin-naphthenic hydrocarbons up to 41.2%, monocyclic aromatic hydrocarbons up to 4.6%, bi- and tricyclic aromatic hydrocarbons up to 5.8% and polycyclic aromatic hydrocarbons up to 9.7% (Schmets et al., 2010; Hafeez et al., 2012; Xurmamatov et al., 2021).

Determination of the physical properties of the obtained fractions

A series of experiments were conducted to determine the density and viscosity of the distilled fractions during the process of obtaining construction grade bitumen from oil sludge. First, the density of the fraction was measured using an areometer, and the viscosity was measured using a VPZh-4 capillary glass viscometer (for the viscosity of clear liquids). To measure the flow time of the fraction, a funnel was placed on the elbow, and the lower part of the viscometer was filled to 1/3–1/2 of its volume. The viscometer was placed in a thermostat so that the expansion was below the liquid level in the thermostat. The correct installation of the viscometer was checked with a plumb line in two mutually perpendicular planes. After stabilising in the thermostat for at least 15 minutes to establish thermal equilibrium, the fluid was drawn into the elbow with a rubber tube attached to the elbow and a bulb, approximately 1/3 of the expansion height. The rubber tube was then removed from the elbow, and a stopwatch was used to measure the time taken for the liquid meniscus to move from M_1 to M_2 during the free flow of the fraction, with an accuracy of 0.2 seconds. The results of three successive measurements should not differ by more than 0.02% (Khurmamatov et al., 2023a; Shomansurov et al., 2024).

The viscosity coefficient depends on the nature and composition of the liquid, i.e. its chemical composition, chemical structure, and molecular weight. The kinematic viscosity of the distilled fraction in the process of obtaining bitumen from oil sludge was determined using the known formula:

$$v = \left[\frac{g}{9.8}\right] \cdot T \cdot K \qquad (1)$$

where:

K – viscometer constant [mm /s^2],

T – arithmetic mean time of fractional flow [c],

g – acceleration of gravity at the point of kinematic viscosity determination [m/s^2],

9.8 – normal acceleration of gravity [m/s^2].

The dynamic viscosity (Schmets et al., 2010) of the investigated oil product (μ) in mPa·s was calculated using the formula:

$$\mu = \mathrm{v} \cdot \rho \qquad (2)$$

where:

v – kinematic viscosity [mm^2/s],

ρ – density at the same temperature at which the viscosity was determined [g/cm^3].

Determining the water content

A series of experiments were conducted to determine the water content using the Dean and Stark method. The experiment lasted for 45 minutes. The condensed solvent and water were continuously separated in the trap until the water volume ceased to increase. The water remained in the graduated compartment of the trap while the solvent returned to the distillation vessel. The sample was thoroughly mixed by shaking in a vial for 5 min. Highly viscous products were preheated to 40–50°C. A 100 g sample was taken from the stirred mixture into a clean, dry flask. The flask was pre-weighed, then 100 ml of solvent was added to the flask and the contents were stirred. Several

glass capillaries or a few pieces of pumice or porcelain were added to the flask to ensure even boiling. The flask was then connected to the outlet tube of the receiver trap, and a condenser was attached to the top of the receiver trap on the slip. Both the receiver trap and the condenser were clean and dry. In order to avoid condensation of water vapor and air, the upper end of the condenser was covered with cotton wool. The contents of the flask were heated on an electric hotplate. The distillation was carried out at a rate of 2–4 drops per second falling from the condenser tube into the receiver trap. Heating was stopped when the water volume in the receiver trap stopped increasing and the upper solvent layer became completely transparent. After cooling of the test product to room temperature, the apparatus was dismantled. When the amount of water in the trap was less than 0.3 ml and the solvent appeared turbid, the trap was placed in hot water for 20–30 minutes to clarify it, and then it was cooled back down to room temperature. After cooling, the water volume in the receiver trap was measured to the upper limit (Khurmamatov et al., 2023b; Auesbaev et al., 2024).

The mass fraction of water V_w [%] was calculated according to the formula (Hafeez et al., 2012):

$$V_w = \left[\frac{100 \cdot V}{G}\right] = \frac{100 \cdot 0.1}{100} = 0.1\% \quad (3)$$

where:
V – volume of water collected in the trap [ml],
G – sample weight of oil sludge taken for the test [g].

An amount of water in the receiver trap of 0.1 ml or less is considered to be trace. Discrepancies between two parallel determinations of water content shall not exceed one upper division of the part of the receiver-trap occupied by water.

Determination of the content of mechanical impurities

Mechanical impurities in oil sludge negatively affect the quality of the resulting product.

A series of experiments were conducted to determine the content of mechanical impurities in oil sludge after dilution with oil fractions and stirring for 30–60 minutes (Khurmamatov et al., 2023c).

The mass fraction of mechanical impurities [%] was calculated using the following formula:

$$M = \left[\frac{m_1 - m_2}{m_3}\right] \cdot 100 \quad (4)$$

where:
m_1 – mass of the beaker with the filter after filtration [g],
m_2 – mass of the beaker with the clean filter [g],
m_3 – mass of the oil sample.

The content of mechanical impurities was calculated as the arithmetic mean of the results of two parallel determinations. If the content of mechanical impurities does not exceed 0.05%, it is considered that no mechanical impurities are present. First, the initial mechanical impurity content of the oil sludge was determined. The paper filter was dried to a constant weight at 105°C. A sample of oil sludge was preheated in a water bath to 40°C due to its high viscosity. A 2 g sample of oil sludge was then diluted with 25 g of petrol. The hot suspension solution was filtered through a dried paper filter placed in a glass funnel. After filtration, the filter was transferred to a beaker and dried in the thermostat for 1 hour. After drying, the beaker was cooled in a desiccator for 30 minutes, then weighed on an analytical scale. The weight of the beaker with a clean filter was 19.5498 g (Edwards et al., 2006).

According to GOST 6370-83 (*Petroleum, petroleum products and additives Methods for determination of mechanical admixtures*), the content of the mass fraction of mechanical impurities in oil sludge was determined by extracting the sludge in a Soxhlet apparatus. The Soxhlet apparatus was equipped with a round-bottom flask containing the extraction solvent and a reflux condenser. In the center of the apparatus was a tank holding a paper sleeve filled with a solid sample for extraction. The solvent was heated to its boiling point, evaporated, and passed through a side to a return cooler, where it condensed and flowed into the sleeve. As the sleeve was filled with solvent, extraction of the target substance into this solvent took place.

When the liquid level in the thermowell reached the upper level of the siphon, the thermowell was emptied, draining the solution into the original flask, and the cycle was repeated again. In this way the apparatus allows multiple extraction by reusing a relatively small volume of solvent, while the substance to be extracted accumulates in the main flask. Extraction efficiency is further enhanced by the fact that the sleeve is located directly above the flask and is heated by the vapors of the boiling solvent.

To easily separate mechanical impurities from oil sludge, the sludge was mixed with diluents (reformate, light and heavy naphtha) at a 30:70 ratio of diluent to sludge for 30–60 minutes at 60°C. The diluted oil sludge was then fed into a hydrocyclone to separate solid particles in centrifugal field.

Results and discussions

The physico-chemical properties of the distillate obtained after distillation of diluted oil sludge at various process temperatures were determined. The results are shown in Figure 1.

From Figure 1, it is evident that as the distillation temperature of the distillate fraction increases between 105 and 200°C,

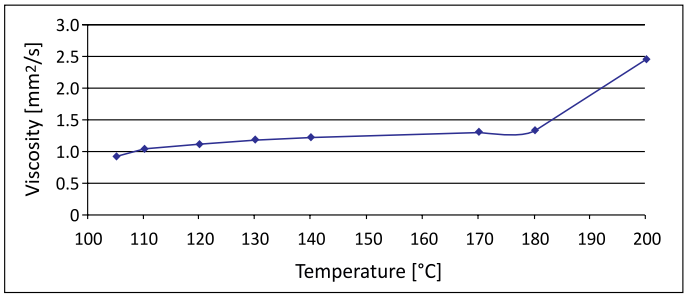

Figure 1. Variation of viscosity of the fraction obtained from oil sludge recycling as a function of the distillation temperature

Rysunek 1. Zmiana lepkości frakcji uzyskanej z recyklingu szlamu naftowego w funkcji temperatury destylacji

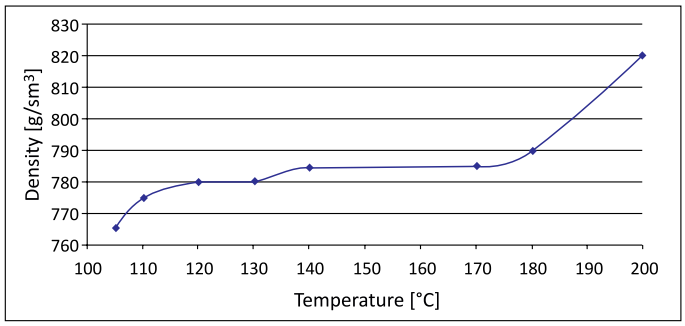

Figure 2. Variation in the density of the fractions obtained when distilling a mixture of oil sludge as a function of the lower column temperature

Rysunek 2. Zmiana gęstości otrzymanych frakcji podczas destylacji mieszaniny szlamu naftowego w funkcji temperatury dolnej kolumny

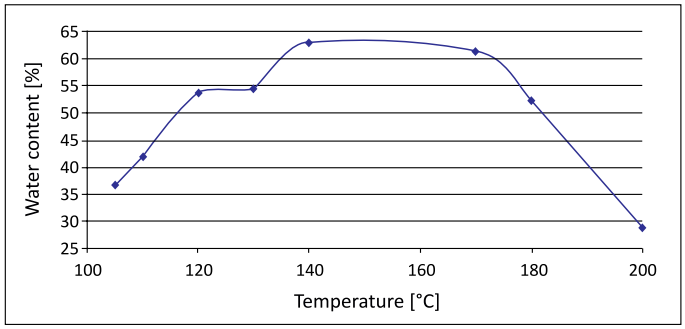

Figure 3. Water content of the oil sludge under study

Rysunek 3. Zawartość wody w badanym szlamie naftowym

its viscosity gradually rises from 0.93 to 2.47 mm^2/s. In the course of our experimental studies, the density of researched fractions was also determined. The results of these studies are shown in Figure 2.

As shown in Figure 2, the density of the studied fraction obtained at a temperature of 105°C is 765 kg/m^3, increasing to 775 kg/m^3 at 110°C. At 170°C, the density changes to 785 kg/m^3, and further increasing the temperature to 200°C results in a maximum density of 820 kg/m^3. From the data in Figures 2 and 3, it is clear that both the density and viscosity of investigated fraction change depending on the process temperature. The sulphur content in the fractions obtained from the distillation of the oil sludge mixture was also determined (Khurmamatov and Auesbaev., 2023; Ismaylov et al., 2024).

Table 1. Sulphur content of distillate fractions obtained from the distillation of a mixture of oil sludge (ratio of oil sludge to solvent: 70% oil sludge – 30% solvent (light naphtha, heavy naphtha and heavy gas oil))

Tabela 1. Zawartość siarki we frakcjach destylatu otrzymanego z destylacji mieszaniny szlamu naftowego (stosunek szlamu do rozpuszczalnika: 70% szlam naftowy – 30% rozpuszczalnik (benzyna lekka, benzyna ciężka i ciężki olej opałowy))

The resulting fractions	Sulphur content [%]	
Light naphtha	0.027	0.029
Heavy naphtha	0.030	0.031
Heavy gas oil	0.035	0.039

Table 1 shows that the sulphur content in light naphtha ranges from 0.027 to 0.029%, in heavy naphtha from 0.03 to 0.031%, and in heavy gas oil from 0.035 to 0.039%.

From Figure 3 it can be seen that the water content in the structure of the fraction obtained by distillation of a mixture of oil cuttings at a temperature of 120°C is 53.75%, while the water content in the structure of the distillate obtained at temperature of 140°C is 63.16%. As the process temperature rises further to 200°C, the water content decreases to 28.89%. This reduction is explained by the fact that the amount of water decreases with increasing temperature of the distillation process. Water was separated from the obtained fractions using the Dean and Stark method, and the amount of water was calculated. Thus, based on our experimental studies for determining the water content in oil sludge according to GOST 2477-65 (*Crude oil and petroleum products. Method for determination of water content*), it was found that oil sludge contains 26% water.

The results of the research on the content of solid mechanical impurities are given in Table 2.

Table 2 shows that when cleaning oil sludge diluted with 30% heavy naphtha (stirring time was 30 min), the content of mechanical impurities decreases from 0.12% to 0.132%. When the temperature increases to 60°C, this index decreases to 0.12%, and when using 30% reformate, the content of mechanical impurities significantly decreases markedly, i.e. this indicator reaches its maximum value – 0.06%. With 30% light naphtha, the content of mechanical impurities in oil sludge decreases to 0.05%. Based on the studies conducted to determine the suitable hydrocarbon solvent for dilution of oil sludge and to study the content of mechanical impurities in it, the optimal diluent ratio is 30% light naphtha and 70% oil sludge, with a stirring time of 60 min, resulting in a mechanical impurity

Table 2. Results from the cleaning of oil sludge from mechanical impurities

Tabela 2. Wyniki oczyszczania szlamu naftowego z zanieczyszczeń mechanicznych

Indicators	Names of diluents					
	30% light naphtha		30% heavy naphtha		30% reformat	
Stirring time [min]	30	60	30	60	30	60
Concentration of solids [%]	–	0.050	0.132	0.120	0.060	0.100

Table 3. Fractional composition of the distillate obtained from oil sludge disposal

Tabela 3. Skład frakcyjny destylatu uzyskanego z utylizacji szlamu naftowego

Oil sludge density at 20°C [g/sm^3]	1,2
Water content in oil sludge [%]	35.0
Content of mechanical impurities [%]	19.0
Fractional composition of oil sludge	
Oil sludge distillation start temperature	93.0
at 95°C is distilled [% vol.]	1.0
105	4.0
110	11.0
120	13.0
130	15.0
140	20.0
170	25.0
180	35.0
200	45.0
210	60.0
230	75.0
240	86.0

content of 0.05% after purification. The results of the research on the fractional composition of the distillate obtained from oil sludge recycling are shown in the Table 3.

Table 3 shows that the density of oil sludge at 20°C is 1.2 g/cm^3, with a water content of 35% and mechanical impurities at 19%. The initial temperature of oil sludge distillation is 93°C. At 95°C, 1% was distilled, and at 105°C – 4%, at 110°C – 11%, at 120°C – 13%, at 130°C – 15%, and in this form the experiment was continued up to 240°C, at which 86% of the total oil sludge was distilled.

Conclusion

A series of experiments were conducted to study the change in viscosity of the distillate fraction obtained from the distillation of diluted oil sludge at temperatures ranging from 105 to 200°C. The results showed that the viscosity increased gradually from 0.93 to 2.47 mm^2/s. Experiments were also carried out to investigate the change in density of the studied fraction as the temperature increased within the range of 105°C to 200°C, with the density of the distillate fractions obtained changing from 765 kg/m^3 to 820 kg/m^3.

Experimental studies to determine the water content according to GOST 2477-65 in the oil sludge composition indicate that the water content in the oil sludge is 26%. Based on the studies conducted, a suitable hydrocarbon solvent and the optimum mixing time were determined, namely: 30% light naphtha and 70% oil sludge, with a mixing time of 60 minutes, resulting in a mechanical impurity content of 0.05% after cleaning.

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