The object of research is the process of thermal degradation of oil sludge in the presence of heterogeneous catalysts.

The creation of efficient technological processes for processing the organic part of oil sludge into motor fuels, raw materials for petrochemicals and the disposal of microsilicate is an important urgent task, the solution of which will allow to obtain a significant economic and environmental effect. The problem to be solved is to establish the general kinetic laws of the process of thermal degradation of oil sludge in the presence of microsilicate with deposited metals. The advantage of the Ozawa– Flynn–Wall method is that it is possible to determine the kinetic parameters for each value of oil sludge conversion, that is, for different stages of thermal degradation. The activation energy of oil sludge 67.1 kJ/mol, and with a catalyst 59 kJ/mol are calculated for each degree of conversion (α), respectively. The value of the correlation coefficient was ($R^2 \geq 0.997$) provides good convergence with experimental results. Compared with other methods of thermal processing of oil sludge, catalytic thermal degradation has a number of advantages: relatively low process temperatures (400–650 °C), low sensitivity to the composition of raw materials and the processing process, which meets all modern requirements of chemical production.

Regularities of thermokinetic parameters of thermal decomposition of oil sludge were studied using raw materials obtained during the process of oil transportation, in the presence of catalyst with applied metal (nickel, iron, cobalt) to microsilicate. Obtained results of oil sludge decomposition kinetics can be used in creating a database for mathematical modeling of process of heavy hydrocarbon raw materials processing

Keywords: thermal destruction, thermal gravimetric analysis, catalysts, microsilicate, oil sludge

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KINETIC STUDY OF THE THERMOLYSIS PROCESS OF OIL SLUDGE (ATASU-ALASHANKOU) WITH NICKEL, COBALT AND IRON DEPOSITED ON MICROSILICATE

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1. Introduction

Intensive development of oil production, transportation and expansion of the sphere of use of petroleum products causes an increasing impact on environmental pollution. During oil transportation by pipeline and oil storage due to the influence of gravity, oil sludge is formed. Due to the high content of asphalt-resinous substances, water and mineral impurities of oil sludge, it is difficult to process raw materials.

Research aimed at creating scientific foundations for the processing of heavy petroleum raw materials is particularly relevant. Investigation of the kinetic regularity of the process of thermal degradation of oil sludge in the direction of chemical transformation of raw materials, the knowledge of which allows to control the process, obtaining the maximum amount of light distillates from oil sludge. In this regard, the creation of effective technological processes for the complex processing of oil sludge valuable multi-purpose products is an important and urgent task, the solution of which, in addi-

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tion to expanding the raw material base, will allow to obtain significant economic and environmental effects.

Possible solution of the problem of reducing negative impact of oil sludge on the environment is extraction of valuable components from hydrocarbon raw material contained in oil sludge and converting them into finished products when reducing share of waste to a possible minimum.

2. Literature review and problem statement

Over the last years, oil producing enterprises are implementing various technological solutions aimed at the utilization of waste of oil production and processing [1].

Extraction, transportation, storage, and usage of oil and oil products are among the most aggressive industries in terms of the amount of man-made factors affecting the environment. Consequences of such an impact can be emergencies that can cause environmental problems associated with the ingress of pollutants into the soil and aquatic environment [2]. Oil refinery plants produce huge amounts of oil sediments during storage and ongoing operations.

Oil sediments or oil sludge are multicomponent stable aggregative physical and chemical systems, consisting of 5–90 mass % of oil hydrocarbons, 1–52 mass % of water and 0.8–65 mass % of mineral additives (sand, clay, metal oxides, etc.) [3].

Currently, there is no unified method of oil sludge processing. Most of known physical and chemical technologies of processing waste are not flexible, but they can give the maximum result when using waste as a raw material to obtain a useful product [4], so the restructuring of the oil industry should be aimed at the development of waste-free environmental technologies that minimize the amount of oil waste, or reuse them [4].

Organic mass of oil sludge contains various aromatic, heterocyclic compounds. Due to the complex composition of oil sludge it is difficult to choose an effective and selective catalyst for oil sludge processing. Based on the kinetics of decomposition of the organic mass of the oil sludge, a catalyst can be chosen. Method of thermogravimetric analysis (TGA) is widely used when studying pyrolysis kinetics of organic substances [5]. In the work [6], which can be divided into model-fitting and model-free or isoconversion. One of them is model-free method of calculating kinetic parameters of OFU [7, 8] using the approximation [9], which requires construction of kinetic curves at different heating rates. The approximate ratio of the heating rate to the activation energy was obtained by [8]. Later by [7] is used to determine the activation energy the method of thermal analysis allows to obtain this information in a simple and fast way [9]. Previously [10], used an integral method to determine the thermokinetic parameters of primary coal tar [10]. The undoubted advantage of the OFU method [7, 8] is the ability to determine the kinetic parameters for each value of the α conversion of the degree of thermal degradation of the substance, and the integral method [10] does not allow this.

3. The aim and objectives of the study

The aim of the work is to study the kinetics of thermal destruction of oil sludge (Atasu-Alashankou) in the presence of catalyst with metal oxides of nickel, cobalt and iron deposited on the microsilicate using the method of thermogravimetric analysis. In addition, it will solve the practical problem of oil sludge disposal and microsilicate waste.

To achieve the aim, the following objectives were set:

– to determine chemical composition of microsilicate, oil sludge and catalyst with nikel, cobalt and iron oxides supported onto microsilicate;

– to determine the kinetic parameters of thermal dege radation of oil sludge in the presence of a catalytic system.

4. Materials and methods

Raw material obtained during the process of oil transportation by pipeline was used to study the thermokinetic decomposition of oil sludge (Atasu-Alashankou). Physical and chemical description of oil sludge (Atasu-Alashankou): density – 0.87 g/cm^3, viscosity – 30 cSt, ash content – A – 0.36 %, C – 72.3 %, H – 11.1 %, N – 0.1 %, O – 16.1 %. Hydrogen-to-carbon atomic ratio in the oil sludge is 1.8. The microsilicate used acts as an entrainer and catalyst.

Component chemical composition of the initial microsilicate was determined using X-ray spectrum and gravimetric methods. Content of components, %: SiO_2 – 95.5; TiO_2 – 0.02; Al_2O_3 – <0.95; Fe_2O_3 – <1.0; CaO – 0.5; MgO – 0.4; MnO – 0.04; P_2O_5 – 0.06; K_2O – <0.1; Na_2O – 0.3. LDC – 2.5.

LDC – loss during calcination. The gravimetric method is the difference between the mass of the analyzed sample of microsilicate or microsilicate with deposited metal oxides of nickel, cobalt and iron before calcination and after calcination.

Thermogravimetric study was performed using a *Labsys Evo TG-DTA/DSC* 1600 derivatograph (*Setaram*, France) in corundum crucibles in the temperature range from 30 to 600 °C in a nitrogen flow (flow rate of protective and purge gases was 30 ml/min^{-1} respectively). Kinetic parameters of thermal decomposition (rate constant, activation energy, and pre-exponential factor) of oil sludge mixture (Atasu-Alashankou) with catalysts and microsilicate were calculated by the methods presented in works [8, 9]. Kinetic characteristics were determined on the basis of TGA – data at three different heating rates of 5, 10, and 20 deg/min^{-1}. Calculation and report of measurement results was performed using the software package *"OriginLab"* and the Python distribution *"Anaconda3"*.

The model-free Ozawa-Flynn-Wall (OFW) method was used [7, 8] when calculating the kinetic parameters of oil sludge (Atasu-Alashankou) thermodestruction in the presence of a catalyst.

The method for determining the activation energy is based on the dependence of the rate constant on temperature, which is calculated using the Arrhenius equation.

The determination of the activation energy values was based on the generalized value expression (1) for the rate of the solid-phase reaction under non-isothermal conditions:

$$\frac{d\alpha}{d\mathrm{T}}=\frac{A}{\beta}e^{\left(\frac{-E_a}{RT}\right)}f(\alpha), \quad (1)$$

where α is fractional conversion of raw material; β – linear heating rate of samples, °C/min; A – pre-exponential factor, c^{-1}; T – absolute temperature, K; E – activation energy, kJ/mol; R – gas constant, kJ/mol K, $f(\alpha)$ – mathematical model of the dimensionless kinetic function depending on

the type and mechanism of the reaction. The value α in (1) is the relative degree of oil sludge transformation, defined as $\alpha = m_s - m/m_s - m_f$ where m_s and m_f are the initial and final mass of the substance, m is the mass of the substance at the measurement point [5].

Ozawa-Flynn-Walls Method According to the Ozawa-Flynn-Walls method of non-isothermal kinetics, when integrating and then taking logarithm (1), let's obtain expressions (2)

$$\ln G(\alpha) = \ln\left(\frac{AE}{R}\right) - \ln\beta + \ln p(z), \quad (2)$$

$G(\alpha)$ for a first-order reaction is equal to

$$\int_0^a \frac{d\alpha}{f\alpha} = \int_0^a \frac{da}{1-a} = -\ln(1-a);$$

$$p(z) = \frac{e^{-z}}{z} - \int_{-\infty}^{z} \frac{e^{-z}}{z} dz; \quad z = \frac{E}{RT}.$$

Using the Doyle approximation [9] let's obtain (3) for substitution into (2):

$$\ln p(z) = -5.3305 - 1.052z. \quad (3)$$

The OFW method is based on the assumption that the reaction rate at a constant value of α depends only on temperature. When analyzing non-isothermal kinetics, the following equation is used:

$$\ln\beta_i = \ln\left[\frac{A_\alpha E_a}{Rg(\alpha)}\right] - 5.331 - 1.052\frac{E_a}{RT_{\alpha,i}}, \quad (4)$$

substitution (2) and (3) gives the OFW equation (4) to calculate the dependence of the thermal destruction rate of the catalyst mixtures with oil sludge (Atasu-Alashankou) on inverse temperature calculated the activation energy and the pre-exponential multiplier [9].

5. Results of the study of the catalyst and the kinetics of thermal degradation of oil sludge in the presence of catalytic systems

5. 1. Individual chemical composition of microsilicate and oil sludge

The initial microsilicate was preliminarily grinded, then samples with a particle size of 0.1 mm were taken by screen analysis. The initial microsilicate was leached using a 20 % hydrochloric acid solution to remove alkali and alkali earth metals.

The catalyst was produced by method of wet impregnation of leached microsilicate with a 15 % solution of salts Co $(NO_3)_2 \cdot 6H_2O$, Ni $(NO_3)_2 \cdot 6H_2O$, Fe $(NO_3)_3 \cdot 6H_2O$. Catalyst impregnated with nitrate microsilicate solutions (20 g) was dried in drying oven for 2 hrs, at 80–90 °C, and then dried at 105 °C also for 2 hrs. Then the obtained catalyst samples were calcination in a muffle furnace at 650 °C for 2 hrs (applied catalyst).

In the framework of process, it is recommended to use a "calcination" word.

The chemical composition of the microsilicate after leaching was determined using X-ray spectrum and gravimetric methods and is shown in Table 1.

Table 1

Composition of initial microsilicate after leaching

Content of components, %										
SiO_2	TiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	MnO	P_2O_5	K_2O	Na_2O	LDC
97.439	0.023	<0.95	<1.0	0.414	0.304	0.033	0.057	<0.1	0.276	2.7

As can be seen from the data in Table 1 the chemical composition of the initial microsilicate before and after leaching changed almost insignificantly.

Oil sludge is characterized by high density and viscosity (0.88 g/cm^3 and 30 cSt). The oil bottom sediment has the following chemical characteristics: A – 0.4 %, C – 72.4 %, H – 11.2 %, S – 0.21 %, N – 0.12 %, O – 17.2 %. The atomic hydrogen to carbon ratio of the oil sludge is 1.86.

Leaching of the initial microsilicate slightly increased the content of silicon oxide from 95.5 – 97.4 %, respectively. Apparently, an increase in silicon oxide in the microsilicate leads to an increase in acidity.

The metal content deposited on the leached microsilicate is: nickel in sample 2 – 16.2 %; cobalt in sample 3 – 17.3 %; and iron in sample 4 –10.9 %, respectively.

5. 2. Kinetics of thermal degradation of oil sludge in the presence of a catalytic system

The curves dependence of samples mass loss on teme perature are shown in Fig. 1 at heating rates β – 5 °C/min, β – 10 °C/min, β – 20 °C/min at intervals of 140–480 °C using the Ozawa-Flynn-Wells (OFW) method. The reactivity of a substance can be described by the activation energy value.

The section marked by grey have to be relocated to "4. Materials and methods".

Thermogravimetric (TG) curves were formulated to estimate the degree of influence of catalysts with applied metals (iron, nickel, cobalt) on the rate of thermal degradation of oil sludge (Fig. 1).

For this purpose, on the basis of thermogravimetric data of oil sludge and catalyst for their mixtures of known composition let's calculate TG-curves (Table 2), which described the process of thermolysis of oil sludge mixture and with catalyst (Fig. 1). To calculate the TG (Table 2), let's use the Callisto Data Acquisition software designed to control one or more Setaram thermal analyzers via a PC.

Kinetic parameters were determined at the degree of conversion of the samples: the initial oil sludge, mixtures of oil sludge with nickel deposited on the microsilicate, mixtures of oil sludge with cobalt deposited on the microsilicate, mixtures of oil sludge with iron deposited on the microsilicate from 0.1 to 0.9. The results are shown in (Fig. 2).

From the tangents of the slope angles (Fig. 2.) of the lines from the windows of the version, let's calculate the activation energies of the process of thermal destruction of oil sludge and mixture. From the data obtained, the value of the activation energy depends on the degree of loss of their mass. The function of the activation energy from the degree of mass loss shows a complex process of thermal degradation of a mixture of oil sludge with a catalyst. The average particle sizes of SiO_2, NiO, FeO and CoO in the catalyst are from 74 to 211.7 nm. Nowhere it is not proved that there is a "nano"structured catalyst. It does not allow to attribute the prepared catalysts to the nanocatalyst class.

Table 2

Calculated values of thermogravimetric curves of samples 1, 2, 3, 4 obtained at different heating rates (β)

Test mixture	Sample heating rate, °C/min	Degree of conversion, α	Temperature range, °C
Sample 1 Oil sludge (without catalyst), T °C	β – 5 °C/min β – 10 °C/min β – 20 °C/min	0.1–0.9 0.1–0.9 0.1–0.9	189–225 217–396 221–433
Sample 2 (microsilicate+Ni 1.5 %+oil sludge, particles size 0.1 mm), T °C	β – 5 °C/min β – 10 °C/min β – 20 °C/min	0.1–0.9 0.1–0.9 0.1–0.9	194–374 197–398 213–414
Sample 3 (microsilicate+Co 1.5 %+oil sludge, particles size 0.1 mm), T °C	β – 5 °C/min β – 10 °C/min β – 20 °C/min	0.1–0.9 0.1–0.9 0.1–0.9	194–382 195–409 216–449
Sample 4 (microsilicate+Fe 1.5 %+oil sludge, particles size 0.1 mm), T °C	β – 5 °C/min β – 10 °C/min β – 20 °C/min	0.1–0.9 0.1–0.9 0.1–0.9	194–385 201–383 212–406

Note: the degree of conversion of raw materials was determined $\alpha=m_s-m/m_s-m_f$ *where* m_s *and* m_f *are the initial and final* mass *of the substance, m is the* mass *of the substance at the measurement point [5]*

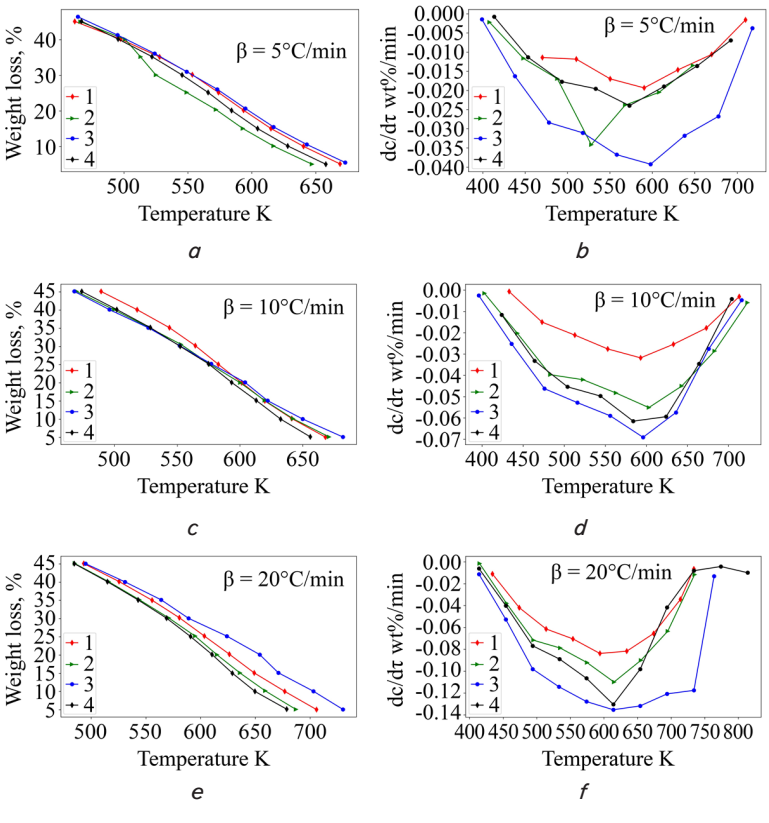

Fig. 1. Thermogravimetric curves of samples: *a* – TG curves of mass loss of initial oil sludge samples, a mixture of oil sludge with nickel, cobalt and iron deposited on the microsilicate; *b* – the rate of mass loss of the samples of oil sludge, a mixture of oil sludge with nickel, cobalt and iron deposited on the microsilicate; *c* – TG curves of mass loss of initial oil sludge samples, a mixture of oil sludge with nickel, cobalt and iron deposited on the microsilicate; *d* – the rate of mass loss of the samples of oil sludge, a mixture of oil sludge with nickel, cobalt and iron deposited on the microsilicate; *e* – TG curves of mass loss of initial oil sludge samples, a mixture of oil sludge with nickel, cobalt and iron deposited on the microsilicate; *f* – the rate of mass loss of the samples of oil sludge, a mixture of oil sludge with nickel, cobalt and iron deposited on the microsilicate

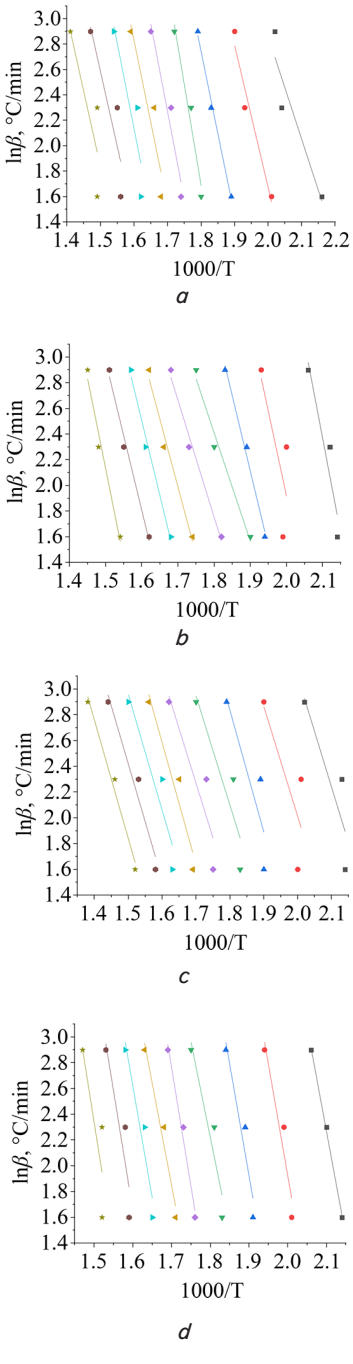

Fig. 2. Samples dependence of the logarithm of heating rate β – 5 °C/min, β – 10 °C/min, β – 20 °C/min oil sludge samples: *a* – initial oil sludge; *b* – a mixture oil sludge with applied nickel on microsilicate; *c* – a mixture oil sludge with applied cobalt on microsilicate; *d* – a mixture oil sludge with applied iron on microsilicate)

Due to the complexity of the chemical composition of the object under study (oil sludge), there are some deviations from linear dependencies. The experimental points were approximated by a straight line using the least squares method. Each point of the conversion degree α on the straight line of Fig. 2 is obtained with the help of three heating rates β.

The activation energy (E) and the pre-exponential multiplier (lnA) obtained by the OFU method are presented in Table 2.

Table 2

Activation energy of thermal destruction of initial oil sludge and oil sludge mixture (Atasu-Alashankou) and microsilicate with deposited catalysts

Degree of conversion, α	Sample 1 Oil sludge (without catalyst)		Sample 2 (microsilicate+Ni 1.5 %+oil sludge, particles size 0.1 mm)		Sample 3 (microsilicate+Co 1.5 %+oil sludge, particles size 0.1 mm)		Sample 4 (microsilicate+Fe 1.5 %+oil sludge, particles size 0.1 mm)	
	E_a, kJ/mol	$\ln Ac^{-1}$	E_a, kJ/mol	$\ln Ac^{-1}$	E_a, kJ/mol	$\ln Ac^{-1}$	E_a, kJ/mol	$\ln Ac^{-1}$
0.1	67.1	19.02	123	33.46	72	20.31	135	36.39
0.2	93	24.04	109	28.19	71	19.03	144	36.53
0.3	107.2	25.95	98	24.45	59	19.86	144	34.80
0.4	131.4	30.15	70	17.57	70	17.34	123	28.87
0.5	115	25.74	76	18.14	70	16.66	153	34
0.6	107.3	23.48	88	19.89	78	17.67	132	28.73
0.7	112	23.60	97	21.07	74	16.44	144	30.30
0.8	98	20.25	97	20.38	70.6	15.87	154	31.32
0.9	99	19.64	117	23.19	76.3	15.62	158	30.83

Table 2 shows the change in the activation energy values from the α degree of thermal decomposition of oil sludge samples and a mixture of oil sludge with a catalyst. For sample 1, the activation energy increases with an increase in conversion from 67.1 to 131.4 kJ/mol, and further increases in the conversion α from 0.4 to 0.9, the curve has an extremum. Samples 2, 3, 4 are characterized by a decrease in the activation energy with an increase in the degree of conversion α from 0.1 to 0.9.

The thermal decomposition of sample 1, 2, 3, 4 is described by more complex curves of the activation energy dependence on the degree of conversion α (Fig. 3). In Fig. 3. In the initial stage of destruction of sample 1, a high value of the activation energy is observed than for samples 2, 3, 4 (Table 2). Apparently, this is due to the destruction of stronger C – C bonds.

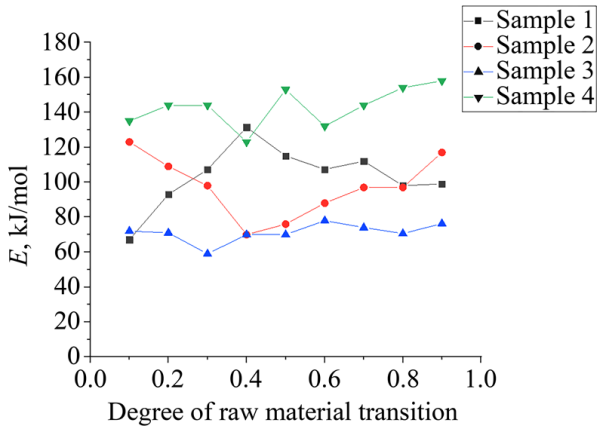

Fig. 3. Dependence of activation energy *E* on degree of transformation α of samples (Ozawa-Flynn-Wall analysis): 1 – initial oil sludge; 2 – a mixture oil sludge with nickel applied on microsilicate; 3 – a mixture oil sludge with cobalt applied on microsilicate; 4 – a mixture oil sludge with iron applied on microsilicate

Fig. 3 depicts the dependence of activation energy on the degree of conversion (α) of a mixture of oil sludge samples with catalyst. Ozawa-Flynn-Wall curve – $E=f(\alpha)$ (Fig. 3) demonstrates complicated process of thermal destruction of oil sludge mixture with catalyst. It is not convenient to analyze this data. The table has to be converted /added plots.

According to the OFU method, it is necessary to build the dependence of the activation energy on the degree of conversion of α oil sludge of thermal destruction. This dependence allows to show the initial stage of destruction of heavy hydrocarbon raw materials. It is not clear the relation between values of "Relative degree of conversion" and activation energy E_a.

The dependence of the activation energy on the degree of conversion (α) of oil sludge and a mixture of oil sludge samples with a catalyst are shown in Fig. 3. The complex dependence of the calculated activation energy value on the degree of conversion of samples 1, 2, 3, 4 (Fig. 3) is due to the fact that many parallel reactions with different activation energy values occur during thermal degradation. It is possible that with an increase in the temperature of thermal degradation of oil sludge, the contribution to the reaction rate of a high activation energy value increases. Therefore, to give a mathematical description of the dependence of the activation energy on the degree of conversion α.

Usually, calculated data has a strong dependency (linear or non-linear), but in the case of authors' data, it is seen data in the random order.

6. Discussion of the results of the study of thermal degradation of oil sludge and mixtures

It follows from equation (4) that for a series of temperature measurements of thermodestruction of the catalyst mixtures with oil sludge (Atasu-Alashankou) obtained at different β heating rates of samples and fixed values of their degree of transformation α, the function graph $\ln\beta=f(1/T)$ gives curved lines (isoconversion lines), the slope ratio of which is $1.052E/R$ directly proportional to activation energy [9] (Fig. 2). Each point on the curve (Fig. 2) was obtained with three measurements at different heating rates (β). There are no straight lines, even so, if to use only three pairs of data (but for making plots it is not enough – minimum 5 pairs of *X*, *Y*) it is seen that they are not lying on the line.

The experimental points satisfactorily lie on straight lines by the entire range of conversion degrees, which indicates the correct choice of the Doyle approximation [9] used in the mathematical processing of thermogravimetric data. The calculated values show a high correlation coefficient ($R^2 \geq 0.997$) Table 3. From the slope ratio of the isoconversion lines (Fig. 2), the activation energy values *E* of the thermodestruction process of the samples were calculated, which depends on the degree of their mass loss.

It can be seen from Fig. 3, for 1 sample, the thermal decomposition stage proceeds with a low activation energy, which may be associated with the destruction of low molecular compounds (oils). Further decomposition of oil sludge with the increasing temperature of its organic part leads to

exhalation of volatile substances with high activation energy 131.4 and 115 kJ/mol, i. e. heavier parts of oil sludge – resin and asphaltenes – are involved in thermal process. The thermal decomposition of oil sludge mixture with nickel, cobalt, and iron applied on microsilicate is described by more complex kinetic curves. The initial stages of the activation energy of sample 2 and sample 4 proceed with a higher activation energy than for sample 3. Apparently it is associated with the fact that organic structure with added metals is formed. The last ones function as a catalyst, i. e. they accelerate the destruction reaction of organic mass of oil sludge and thus the activation energy is dee creased (Table 3, Fig. 3). Of the number of added metals, cobalt and nickel had the greatest effect on the microsilicate, and the addition of iron leads to an increase in the activation energy and the pre-exponential factor.

The data given above about the influence of catalysts on oil sludge destruction demonstrate that the method of thermogravimetry makes it possible to record quickly the influence of applied catalysts on the thermal decomposition of oil sludge. Addition of three catalysts to oil sludge leads to differences in thermal destruction of oil sludge.

Thus, by changing the organic structure of an oil sludge with an applied catalyst through exchange reactions with the metal, it is possible to control the process of thermal destruction, changing its rate and kinetic parameters, as well as to test the selected catalysts for thermal destruction of oil sludge.

The advantage of the non-model OFU method was presented in the paper [5]. The analysis of various methods for determining the kinetic parameters of non-isothermal thermal degradation of heavy hydrocarbon raw materials has shown that kinetic curves should be constructed at different heating rates. This is an undoubted advantage without model methods that allow to determine the kinetic characteristics for each conversion value of a substance, that is, for different stages of decomposition.

The limitation of the differential thermal analysis (DTA) method in our conditions is due to the fact that it is not possible to carry out the process of catalytic thermal destruction of oil sludge in a hydrogen atmosphere. The DTA method does not allow to determine the yield of liquid products from oil sludge during thermal degradation. Kinetic parameters of thermal degradation of oil sludge in the presence of microsilicate with deposited metals were carried out in an inert gas atmosphere.

The results obtained using the DTA method can later be used in the process of hydrogenation of oil sludge in the presence of microsilicate with deposited metals.

7. Conclusions

1. The mass content of the introduced metal in the mikrosilicate was, wt. %: nickel – 1.5, cobalt – 1.5, iron – 1.5, respectively. Oil sludge is characterized by high density and viscosity (0.88 g/cm^3 and 30 cSt). The oil bottom sediment has the following chemical characteristics: A – 0.4 %, C – 72.4 %, H – 11.2 %, S – 0.21 %, N – 0.12 %, O – 17.2 %. The atomic hydrogen to carbon ratio of the oil sludge is 1.86.

2. By changing the organo structure of oil sludge with a catalyst applied due to exchange reactions with metal, it is possible to control the thermal degradation process by changing its speed and kinetic parameters, as well as to test the selected catalyst for thermal destruction of oil sludge. The values of the activation energy of the initial and mixture of oil sludge with catalysts were in the range of 59–158 kJ/mol. At the same time, the free activation energy of the thermal destruction of the mixture at values α 0.6 turned out to be less for nickel and cobalt than in the case of the initial oil sludge, which confirms the assumptions about the active effect of microsilicate with added hydrogenating agents. The addition of iron to oil sludge leads to an increase in the activation energy and indicates the inhibition of the process of thermal degradation of oil sludge.

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