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Thermoadsorption Demetallization of Heavy Oil Residues

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Abstract

The high content of metal- and sulfur-containing compounds in the composition of heavy oil residues leads to negative impacts during their processing, the use of catalysts and equipment. To solve this problem, various methods of demetallization and deasphalting are proposed. The article provides information on various methods of demetallization, desulfurization and coking of heavy oil residues. The disadvantages of the considered methods are shown, and a thermal adsorption processing method is proposed as an effective method of demetallization and desulfurization. The results of demetallization and desulfurization of vacuum residue from the Pavlodar Petrochemical Plant (Kazakhstan) using various adsorbents: serpentine, zeolite modified with wollastonite and coke, kaolin clay with coke are presented. The maximum degree of demetallization of 81–94% with respect to vanadium and nickel is observed when using kaolin clay modified with coke as an adsorbent and during the process at 400 °C for 4 h. The maximum degree of desulfurization 39.6% is observed during the process using zeolite modified with wollastonite and coke at 400 °C for 3 h. After demetallization and desulfurization, the vacuum residue was subjected to a coking process to produce coke with improved performance and yield. Coke with good yield (32%) and low values of ash and mass fraction of total moisture is obtained by vacuum residue coking after demetallization with kaolin clay modified with coke.

1. Introduction

Sulfur and metal-containing compounds are present in the composition of oil and oil products, which deactivate the catalysts of secondary processes, lead to equipment corrosion, and reduce the quality of oil products obtained. Basically, they accumulate in heavy oil residues, which provides for their preliminary treatment and demetallization.

For the preparation of heavy oil feedstock for deep processing at refineries, preliminary deasphalting and demetallization processes are used, in which the viscosity, density and coking behavior of oil products decrease, the content of metal compounds in it decreases and clarification occurs [1]. The removal of asphaltenes also results in the removal of complexes of vanadium, nickel and organic compounds with heteroatoms, especially nitrogen and sulfur.

Currently, in the oil industry, the demetallization of heavy oil feedstock is carried out by the processes of solvent extraction, deasphalting, hydrogenation and thermal destruction.

Various options for extraction methods of deasphalting are summarized in the paper [2]. The uniqueness of the developed technical solutions lies in the implementation of the features of the multi-stage extraction process in oil refining - contacting oil with solutions (or vapors) of inorganic acids, which allows only by changing the distribution coefficients of inorganic components to separate them from the oil (organic phase) into another phase without changing the physical chemical properties and structural composition of oil supplied for processing.

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Extraction of metal-containing compounds, including metal porphyrins, from petroleum fractions with a boiling point above 300 °C is carried out with a mixture of 90–60 vol.% pyrrolidone-2 and 10–40 vol.% C_1–C_3 alcohol. The content of metals, in particular vanadium, according to the authors of [3], decreases 10–15 times.

However, solvent processes are characterized by high energy intensity, increased operating and capital costs, and lead to the formation of an even heavier asphalt residue than vacuum residue.

Chemical methods include the use of the complexing agent demetallization, thermal processes related to visbreaking and coking, and hydrogenation.

Chemical methods of demetallization involve the destruction of the bond of metals with the organic matrix of oil components, or the transfer of metal-containing components of oils into another chemical form, which is accompanied by a loss of their solubility in the oil environment. A fairly high degree of demetallization of oils and petroleum products is achieved when they are treated with acids. The most widely used acids are sulfuric, various sulfonic acids (methanesulfonic acid, p-toluenesulfonic acid, sulfobenzoic, sulfosalicylic, sulfonyl), hydrofluoric in the presence of hydrogen, polyphosphoric, and phosphorous, hydroxycarboxylic. Reducing and oxidizing agents are used to reduce the content of metals in oil systems [4].

When the metal-containing components of oils interact with some chemical compounds, products are formed that are insoluble in a hydrocarbon medium.

Chamorro et al. [5] studied the removal of metals and sulfur in carbonaceous material under microwave heating, the degree of Ni and V removal reached 80 and 99%, respectively, using an acidic solution during microwave irradiation of 15 min.

Wen et al. [6] used microwave heating to remove Ni and V from Iranian and Shengli crude oils using sodium dimethyldithiocarbonate as a demetallizing agent in the presence of water. The feasibility study has been demonstrated with removal rates of 45–49% for Ni and 70–87% for V, over a temperature range of 80–90 °C, microwave power of 100–800 W and treatment time of 5–60 min.

Organic demetallizing agents such as cationic starches (CS), carboxymethylchitosan (CT) and chitosan Schiff base have been proven high efficiency in conditions of exposure to microwaves. A number of cationic starches with varying degrees of substitution were synthesized by the reaction of soluble starch with NaOH and an esterifying agent consisting of a quaternary ammonium salt. The higher the degree of substitution of CS for cations, the greater the effect of electrostatic adsorption of positive ions of heavy metals. When using carboxymethylchitosan (CT-50) as a demetallization agent, the efficiency of Ni and V removal reached 69.8% and 93.7%, respectively, under mild processing conditions. Microwaves are believed to enhance molecular motion. The structure of organic compounds Ni and V became loose; they were adsorbed in CT-50 and reacted with amino ($-NH_2$) and carboxylic ($-COOH$) groups [7–9].

Although demetallization using microwave radiation has shown influence on the removal of Ni and V, lower thermal efficiency and conversion rate were found, in addition, the mechanism under microwave irradiation is still unclear [10].

Recently, there has been a tendency to develop processes of an intermediate type between thermal and catalytic, the so-called hydrothermal processes, such as hydropyrolysis, hydrocoking, hydro-visbreaking, donor-solvent cracking, however, they are limited by the conversion depth, but are free from restrictions on the content of metals in heavy oil residues [11–14].

The main drawback is the low quality of the products obtained, and for the processes of thermal cracking and visbreaking (these processes are exclusively intended for processing heavy oil residues as well as the process of demetallization and desulfurization), there is also a limited conversion depth.

The hydrogenation process consists in the hydrofining of oil or its fractions on catalysts in the presence of hydrogen under pressure, as a result of which more than 70% of the metals are precipitated. In fact, they are a kind of adsorption-catalytic processes of demetallization of petroleum feedstock, since the destruction of petroleum-containing metal-containing compounds is accompanied by the subsequent adsorption of the liberated metals on the catalyst. A distinctive feature of hydrogenation methods in comparison with adsorption-catalytic methods is that the destruction of the bond of metals with the organic matrix of petroleum components is carried out by hydrogenolysis of the bonds of carbon atoms with heteroatoms (N, S, O), with which petroleum metals are mainly associated.

The most widespread in world practice are the following processes of demetallization and desulfurization of oil residues:

– hydrotreating processes are designed to reduce the content of sulfur, nitrogen, asphaltenes, metal compounds and reduce residual feedstock in order to obtain high-quality boiler fuel or for further processing in hydrocracking, coking, catalytic cracking;

– hydro-visbreaking-aqua conversion allows obtaining hydrogen from water under visbreaking conditions by introducing a composition of two catalysts based on base metals into the feed together with water (steam). In the process of aqua conversion, a significantly greater decrease in the viscosity of the heaviest components of boiler fuels is provided with higher conversion of feedstock [15];

– hydrocracking is intended for catalytic hydrocracking and desulfurization of residual feedstock in reactors with the suspended catalyst to obtain high-quality distillates and refined low-sulfur boiler fuel [16, 17].

Significantly higher parameters of yield and quality of distillate products and gas are characteristic of catalytic and hydrocatalytic processes. However, they have significant capital and operating costs associated with the high consumption of catalyst and hydrogen. In addition, they are adapted to processing only relatively favorable raw materials in terms of sulfur, metals and coking properties; in these processes, heavy oil residues can be processed only after preliminary demetallization by various processes.

To increase the yield of coke obtained from the vacuum residue, a method for producing coke with preliminary demetallization and desulfurization of a heavy oil residue using an adsorbent is proposed. Preliminary demetallization and desulfurization of coking raw materials are carried out according to the method presented in the article [18]. In previous works, for the process of demetallization and desulfurization of vacuum residue, we tested adsorbents based on zeolite modified with xerogel of vanadium (V) oxide and titanium compounds [19]. Preliminary demetallization of the primary coking feedstock – vacuum residue allows to reduce hydrogen consumption, to extract an additional 90% of metals and asphaltene components from petroleum feedstock before the coking process, to increase the yield and improve the quality of coke produced. The process of preliminary demetallization and delayed coking is an affordable way to process oil residues of any type and additionally obtain raw materials for catalytic processes, as well as improve the quality of marketable coke.

In the process of demetallization and desulfurization, structural changes occur in the composition of the tar, leading to a wide variety of high molecular weight compounds, namely the appearance of isomeric forms, as well as various combinations of aliphatic, hydroaromatic, aromatic hydrocarbons and their derivatives [20].

In this regard, the aim of this work is to develop an effective method for thermoadsorption demetallization of heavy oil residues.

2. Experimental part

The raw material for the demetallization and coking processes was vacuum residue – the raw material of the delayed coking unit of the heavy oil residue processing complex of Pavlodar Petrochemical Plant LLP (Kazakhstan). Vacuum residue has the following characteristics: appearance – a viscous inactive fluid, mass fraction of water – up to 0.1 wt.%; the content of vanadium is 0.049–0.054%; nickel content – 0.0049–0.0058%; the iron content is 0.0033%; mass fraction of sulfur – 1.72–2.73%; ash content – 0.02 wt.%; coking ability – 14 wt.%; density at 20 °C – 981.0 kg/m^3; boiling point – 380 °C.

The process of demetallization and desulfurization of vacuum residue from the Pavlodar Petrochemical Plant was carried out in an enlarged installation with two reactors at different temperatures and times at atmospheric pressure [18]. Vacuum residue is passed in the reactor through a fixed adsorbent bed at a temperature of 300–400 °C, at a feed rate of 1–3 l/h, with an exposure of the feedstock in the reactor 0.5–3.0 h at atmospheric pressure. According to results, contacting the feedstock with the hot adsorbent hydrocarbon vapors are formed, which, in a mixture with water vapor, are transported to the vapor line. During the passage through the first section of the pipe, various transformation reactions occur: easy conversion, demetallization and partial desulfurization.

After demetallization and desulfurization, the treatment product is heated in a tube furnace at an initial temperature of 420–460 °C and the temperature of coking is brought to 490–510 °C. The temperature of the vapor exit from the furnace is 440–460 °C, the volume of raw materials is 1 l, the coking time is 8 h.

The batch-type laboratory coking unit is designed to carry out the process of delayed coking of heavy oil residues. The general diagram of the laboratory coking unit is shown in figure.

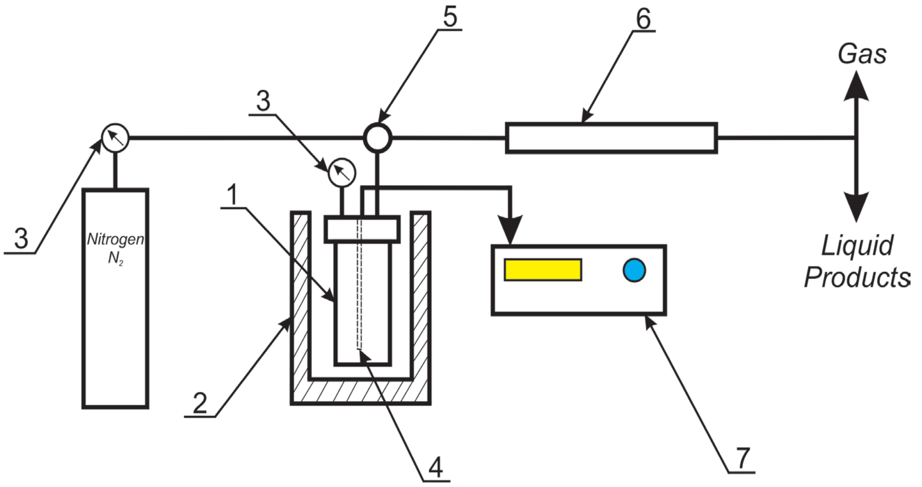

Fig. Scheme of a plant for coking heavy oil residues: 1 – a coking reactor; 2 – an electric furnace; 3 – a manometer; 4 – a thermocouple; 5 – a control valve; 6 – a reflux condenser; 7 – a thermostat.

The vacuum residue sample, after demetallization and desulfurization by the adsorption method, is loaded into the reactor. After the top cover of the reactor is covered and it is installed in its place in the installation, it is checked for tightness by conducting a pneumatic test. For this, the coking gas evacuation system is disconnected and the nitrogen cylinder hose is attached to the connector. With control valve 5, the pressure is set, exceeding the operating pressure by 1.5 times. The valve is closed and the system is tested for leaks for 5 min. The unit is checked for leaks by soaping the flange, threaded and welded joints with soapy water. After checking the tightness, open the valve and release the pressure from the reactor. The detected defects are eliminated. Then the pressure is set back into the reactor. After the pressure is built up, valve 5 is closed, a system for removing gases and liquid coking products is connected to the connector. The temperature rise in the reactor is carried out at a rate of 2 °C per minute. The coking time is the time from the establishment of the operating temperature of the coking reactor to the end of coking. The pressure is measured by a manometer 3. After reaching the required pressure in the reactor, the pressure is manually controlled by slowly opening valve 5 to release vapors and gases that increase the required pressure in the reactor. Hot vapors and gases from the reactor pass to refrigerator 6, part of the vapors, being cooled and condensed, passes into the coking distillate, which is collected in the separator. After cooling, the coking gases are sent to the gasometer, then to be removed from the laboratory unit to the exhaust ventilation system. Discharge of gases and vapors of the coking reactor and gases from the separator is carried out one hour before the end of coking. The pressure is released slowly through the valve. At the end of the process, turn off all electrical appliances at the installation, close the water supply to the refrigerators. The reactor is then cooled by natural ventilation of the air. After cooling the reactor, it is disassembled with the resulting coke unloading.

The sulfur and metal contents were determined by a Xenemetrix X-Calibur energy dispersive fluorescence X-ray spectrometer.

This paper presents the results of testing adsorbents based on serpentine, zeolite and kaolin clay for the demetallization and desulfurization of vacuum residue.

A sample of the serpentinite rock of the Kempirsai massif in the Aktobe region was made at the Don Mining and Processing Plant and is represented by lumpy material, 2–10 cm in size. The chemical composition of the averaged raw material sample (wt.%): SiO_2 – 34.8; MgO – 39.0; Al_2O_3 – 0.9; Fe_2O_3 – 7.3; Cr_2O_3 – 1.5; CaO – 0.8; p.p.p. – 15.7. To increase the strength of the rock, it was crushed to 0.074 cm, followed by firing at a temperature of 1200–1250 °C for 2 h.

3. Results and discussion

When testing adsorbents based on serpentine, oil from the Karazhanbas field was also tested together with vacuum residue. The demetallization temperature was 350–400 °C, the time was 3 h. The test results (Table 1) showed that the content of metals and sulfur in the vacuum residue after the process decreases slightly: the content of vanadium decreases from 0.054 to 0.046%, and the content of iron, nickel and sulfur is practically

Table 1

Results of demetallization and desulfurization of vacuum residue and oil on adsorbents based on serpentine

Raw materials	T, °C	τ, hour	The content of elements in the vacuum residue, %			
			S	V	Fe	Ni
Vacuum residue	-	-	1.72	0054	0.0033	0.0058
Vacuum residue after processing (serpentine unburnt)	350	3	1.70	0.046	0.0033	0.0051
	400	3	1.68	0.054	0.0031	0.0058
Vacuum residue after processing (burnt serpentine)	350	3	1.68	0.053	0.0031	0.0058
Oil	-	-	2.80	0.140	0.021	0.007
Oil after treatment	350	3	2.80	0.013	0.0032	0.0054

does not change. In the case of oil demetallization, a decrease in the vanadium content by an order of magnitude is observed – from 0.14 to 0.013%, iron – from 0.021 to 0.0032, and nickel – from 0.007 to 0.0054. However, the sulfur content remained unchanged.

Due to the low degree of demetallization and desulfurization of vacuum residue on serpentine adsorbents, further experiments were carried out on adsorbents with modified zeolite and kaolin clay.

Zeolite KN-4 (produced by the Novosibirsk Plant of Chemical Concentrates) has the following indicators: specific surface area 329 m^2/g, mechanical strength 5.9 MPa, granule diameter 3.1–4.0 mm, Al_2O_3 mass fraction – 10.13%. During the process of vacuum residue demetallization, the lower reactor of the installation is filled with zeolite activated at 250 °C for 2 h, the upper reactor is filled with wollastonite and coke. The process temperature was 400 °C and the process time was from 0.5 to 3.0 h. As can be seen from Table 2, an increase in temperature led to positive results of demetallization and desulfurization of the vacuum residue. The maximum decrease in the metal content is observed within 2 h of the process: vanadium decreases from 0.049 to 0.0095%, iron – from 0.0033 to 0.0007, nickel – from 0.0049 to 0.0008. At the same time, the sulfur content also decreases from 2.73 to 2.09%. The maximum decrease in sulfur content is observed within 3 h of the process – sulfur decreases from 2.73 to 1.65%.

Table 2

Results of demetallization and desulfurization of vacuum residue on various adsorbents

Raw materials	T, °C	τ, hour	The content of elements in the vacuum residue, %			
			S	V	Fe	Ni
Vacuum residue	-	-	2.73	0.049	0.0033	0.0049
Adsorbent based on zeolite, wollastonite and coke						
Vacuum residue after processing	400	0.5	2.46	0.049	0.0020	0.0049
		1.0	2.24	0.012	0.0012	0.0008
		1.5	1.80	0.015	0.0014	0.0012
		2.0	2.09	0.0095	0.0007	0.0008
		2.5	2.07	0.024	0.0005	0.0019
		3.0	1.65	0.024	0.0033	0.0023
Adsorbent based on kaolin clay modified with coke						
Vacuum residue after processing	350	1	2.58	0.033	0.0033	0.0031
	400	2	2.39	0.034	0.0010	0.0031
		2.5	2.61	0.039	0.0011	0.0035
		3	2.39	0.020	0.0007	0.0021
		4	2.53	0.0027	0.0006	0.0026

Industrial processes of thermal adsorption refinement of hydrocarbon residues: ART (Asphalt Residual Treating) and AKO (adsorption-contact cleaning) are carried out with adsorbents based on kaolin at higher temperatures of 450–520 °C and a pressure of 0.1–0.2 MPa. Therefore, kaolin clay was chosen as the basis of the adsorbent, but the process was carried out at relatively low temperatures.

Test kaolin clay modified 50 wt.% coke as an adsorbent gave even more positive results. In this case, the process temperature was 350–400 °C, time 1–4 h. As can be seen from the tabular data, the metal content in the vacuum residue is reduced as much as possible during the process for 4 h at 400 °C. Under these conditions, the vanadium content decreases from 0.049 to 0.0027%, iron from 0.0033 to 0.0006%, nickel from 0.0049 to 0.0026%. The sulfur content compared to zeolite and wollastonite decreased relatively little – from 2.73 to 2.39%.

Table 3 compares the degree of demetallization and desulfurization of vacuum residue on the tested adsorbents. As can be seen from the tabular data, the adsorbent based on zeolite, wollastonite and coke shows the highest degree of extraction – 39.6%, while the degree of demetallization is 78–83%. The adsorbent based on kaolin clay and coke showed a maximum degree of vanadium demetallization – 94.5%, iron – 81.8%, but the degree of desulfurization is 12.4%.

After the demetallization and desulfurization process, the vacuum residue coking process was carried out to obtain coke with improved physico-chemical characteristics. Table 4 shows the values of the yield and physico-chemical characteristics of coke obtained from vacuum residue without preliminary treatment and after demetallization using various adsorbents and process conditions. As can be seen from the table, the yield of coke from the vacuum residue without pretreatment was 18.9% and it is characterized by low values of the

Table 3

Degree of demetallization and desulfurization of vacuum residue on various adsorbents

Adsorbent	Degree of desulfurization,%	Degree of demetallization, %		
		V	Fe	Ni
Serpentine	2.3	14.8	6.1	12.1
Zeolite with wollastonite and coke	39.6	80.6	78.8	83.7
Kaolin clay modified with coke	12.4	94.5	81.8	57.1

Table 4

Yield and physico-chemical characteristics of coke obtained under various conditions

Raw materials for receiving coke	Physico-chemical characteristics of coke			
	Mass fraction of total moisture, %	Mass fraction of volatiles, %	Ash content, %	Yield, %
Vacuum residue without pretreatment	0.89	7.91	0.53	18.9
Vacuum residue after demetallization with zeolite at 400 °C for 3 h	1.02	7.88	0.40	27.0
Vacuum residue after demetallization with zeolite modified with V_2O_5 xerogel at 400 °C for 3 h	3.0	7.16	0.42	34.4
Vacuum residue after demetallization with serpentine at 400 °C for 3 h	1.39	4.59	0.45	32.0
Vacuum residue after demetallization with wollastonite at 400 °C for 2 h	2.27	5.68	0.58	12.0
Vacuum residue after demetallization with wollastonite and serpentine at 400 °C for 3 h	1.29	8.33	0.31	23.2
Vacuum residue after demetallization with kaolin clay at 400 °C for 4 h	1.14	6.0	0.25	32.0
Requirements State Standard 22898-78	no more than 3.0	no more than 6.0-9.0	no more than 0.6	-

mass fraction of total moisture and ash, but the mass fraction of volatile substances in coke is considered to be high 7.91%. In the composition of coke obtained from vacuum residue after demetallization with zeolite at 400 °C for 3 h, the mass fraction of total moisture slightly increases to 1.02%, the mass fraction of volatile substances and ash content decrease to 7.88 and 0.4%, respectively. The coke yield rises to 27.0%. When using a zeolite modified with a 1% vanadium oxide xerogel as an adsorbent, coke is characterized by a high value of the mass fraction of total moisture of 3%, however, the mass fraction of volatile substances decreases to 7.16%, the ash content is 0.42%. At the same time, the coke yield turned out to be a maximum 34.4%.

The use of serpentine as an adsorbent for vacuum residue demetallization made it possible to obtain coke with low indicators of the mass fraction of total moisture and volatile substances, ash content. Demetallization of vacuum residue with an adsorbent based on wollastonite at 400 °C for 2 h and further coking led to the formation of coke, characterized by a high mass fraction of total moisture (2.27%), but its yield decreased to 12.0. Modification of wollastonite with serpentine led to a decrease in the mass fraction of total moisture and an ash content of coke, an increase in the yield of coke, however, the mass fraction of volatile substances increased to 8.33%.

Coke obtained from vacuum residue after demetallization in the presence of kaolin clay has a yield of 32%, the mass fraction of total moisture is 1.14%, volatiles – 6.0%, and the minimum ash value – 0.25%.

Of the coke samples presented in the table, coke obtained from vacuum residue after preliminary demetallization with kaolin clay has the most improved physico-chemical characteristics. According to physicochemical parameters, the coke sample meets the requirements of State Standard 22898-78 and the coke yield is 32%.

4. Conclusion

Thus, the thermal adsorption process of demetallization and desulfurization of vacuum residue from the Pavlodar Petrochemical Plant was carried out in the presence of various adsorbents and under various conditions. At this stage of research, thermal adsorption treatment on kaolin clay with coke at a temperature of 400 °C for 4 h is recommended to reduce the metal content in the vacuum residue; to reduce sulfur content, heat adsorption treatment on a zeolite with wollastonite and coke at a temperature of 400 °C for 3 h.

Then, after preliminary demetallization and desulfurization, the vacuum residue coking process was carried out to obtain coke. Coke with improved physico-chemical characteristics is obtained from vacuum residue after thermal adsorption treatment with kaolin clay, which showed the highest degree of demetallization. In the future, coke samples will be analyzed to determine the content of metals and sulfur.

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References

[1]. Y.K. Ongarbayev, Y.O. Doszhanov, Z.A. Mansurov. Processing of heavy hydrocarbon raw materials and wastes. Almaty: Qazaq universiteti, 2017, 498 p. (in Russian)
[2]. L.S. Guzei, G.P. Zhmurko, N.Yu. Soboleva, *Russian chemical journal* [Rossijskij himicheskij zhurnal] 5 (1995) 64–74 (In Russian).
[3]. R.M. Fish, J.J. Komlenic, B.K. Wines, *Anal. Chem.* 56 (1984) 2452–2460. DOI: 10.1021/ac00277a043
[4]. S.A. Akhmetov, T.P. Serikov, I.R. Kuzeev, M.I. Bayazitov. Technology and equipment for oil and gas processing. Saint Petersburg: Nedra, 2006, 868 p. (In Russian).
[5]. United States Patent 6068737. Simultaneous demetallization and desulfurization of carbonaceous materials via microwaves. M.De Chamorro, M.C. Romano. Publ. 2000 .
[6]. CN patent 101402878A. Z.C. Wen, J.Y. Yang, X.R. Xu, B.C. Cao, J.S. Gao, Microwave chemistry method removal of nickel and vanadium in crude oil. Publ. 2009.
[7]. S. Wang, J. Yang, X. Xu, *Fuel* 90 (2011) 987–991. DOI: 10.1016/j.fuel.2010.11.036
[8]. S. Wang, X. Xu, J. Yang, J. Gao, *Fuel Process. Technol.* 92 (2011) 486–492. DOI: 10.1016/j.fuproc.2010.11.001
[9]. L. Wang, Q. Peng, S. Li, L. Du, H. Cai, *J. Ind. Eng. Chem.* 19 (2013) 655–658. DOI: 10.1016/j.jiec.2012.10.002
[10]. H. Shang, Y. Liu, J-C. Shi, Q. Shi, W-H. Zhang, *Fuel Process. Technol.* 142 (2016) 250–257. DOI: 10.1016/j.fuproc.2015.09.033

[11]. B.K. Nefedov, *Catalysis in Industry* [*Kataliz v promyshlennosti*] 4 (2007) 31–37 (In Russian).
[12]. D. Nakamura, *Hydrocarbon Processing* 77 (1998) 36–38.
[13]. J. Ancheyta. Modeling of Processes and Reactors for Upgrading of Heavy Petroleum. CRC Press, 2013. DOI: 10.1201/b13879
[14]. D.K. Banerjee. Oil Sands, Heavy Oil & Bitumen: From Recovery to Refinery. Penn Well, 2012. ISBN: 9781593702601
[15]. D. Nakamura, *Hydrocarbon Processing* 76 (1997) 36–39.
[16]. K.M. Jackson, *Hydrocarbon Processing* 85 (2006) 33–38.
[17]. J. Wolff, P. Zuideveld, *Hydrocarbon Processing* 85 (2006) 73–79.
[18]. Y. Ongarbayev, Sh. Oteuli, Y. Tileuberdi, G. Maldybaev, S. Nurzhanova, *Petrol. Sci. Technol.* 37 (2019) 1045–1052. DOI: 10.1080/10916466.2019.1570257.
[19]. Y. Ongarbayev, Sh. Oteuli, Y. Tileuberdi, G. Maldybaev, S. Nurzhanova, *Studia UBB Chemia* LXV:1 (2020) 219–231. DOI: 10.24193/subbchem.2020.1.17
[20]. Ye. Imanbayev, Ye. Tileuberdi, Ye. Ongarbayev, Z. Mansurov, A. Batyrbayev, Ye. Akkazin, E. Krivtsov, A. Golovko, S. Rudyk, *Eurasian Chem.-Technol. J.* 19 (2017) 147–154. DOI: 10.18321/ectj645