DOI 10.18454/PMI.2016.6.833

UDC 665.637.3

EFFECT OF CHEMICAL COMPOSITION AND QUALITY OF HEAVY YAREGA OIL ON SELECTION OF APPROPRIATE PROCESSING TECHNOLOGY

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The paper explores physical and chemical properties and composition of heavy oil from Yarega field and its vacuum residue, i.e. the tar. The capillary chromatography and gas chromatography-mass spectrometry were used to identify specific group hydrocarbon composition of heavy Yarega oil and components extracted therefrom, which has proven its belonging to highly resinous sulfurous naphthenic and aromatic oils. Based on the comparative analysis of composition and quality of feedstock a possibility has been assessed to produce a high-quality needle coke with low content of sulphur and metals from the heavy oil of Yarega field and its vacuum residue. An integrated process flow diagram for heavy Yarega oil refinement has been proposed, including preliminary deasphalting and demetallization, hydrotreatment, delayed coking and thermodestructive processes or gasification.
Key words: heavy oil, Yarega oil, vacuum residue, needle coke, deasphalting, demetallization, chemical composition, delayed coking.

How to cite this article: Kondrasheva N.K., Jorge Anchita. Effect of chemical composition and quality of heavy yarega oil on selection of appropriate Processing Technology. Zapiski Gornogo instituta. 2016. Vol. 222, p. 833-838. DOI 10.18454/PMI.2016.6.833

Introduction. A major challenge of the present-day oil industry is the growing production levels of heavy oil, which contains a significant amount of impurities (asphaltenes, sulphur, metals), and distillation yields more heavy residue, than lights distillates, thereby reducing the practical value of such hydrocarbons. The main difficulties in the use of heavy oil are associated with its low mobility both in the reservoir conditions and on the surface. Its production, transportation and distillation at the oil refineries are meant to solve a large number of unconventional tasks complicated from technical and technological standpoint and entail considerable capital and operational costs [3].

One of the most efficient and cost-effective heavy oil processing methods is the delayed coking. The purpose of this process is the deepening of oil refining in order to produce petroleum cokes and distillate products. According to [2] the petroleum coke output in 2012 yr. comprised: 60 mln tons globally, 26 mln tons in USA, and 1 mln tons in Russia. Other leaders in coke output besides USA are China (15.4 mln tons), Venezuela (8.8 mln tons) and Germany (5.7 mln tons). Based on records for 2011-2013 yr. 59 out of 134 american refineries have coking units producing from 15 to 30 % of coke from 1 barrel of heavy oil, which comprised 61.5 mln tons.

In Russia until recently the main purpose of a delayed coking process was to obtain a low-sulfur petroleum coke in accordance with the requirements of GOST 22898-78 Low-Sulfur Petroleum Coke [6], which establishes the eight grades of petroleum coke depending on the production technology and field of application (production of carbon engineering materials, graphitized product, abrasives and applications in the aluminum industry). The properties examined to assess the petroleum coke quality include: content of moisture content, volatile matter, sulfur, silicon, iron, vanadium, ash content, friability and actual density after calcining.

In order to increase the output of petroleum coke the units were run at high pressure, with high recirculation ratio and long cycles of coking chambers filling, and in order to comply with the standards regulating the quality of produced coke, the coking feedstock has been thoroughly selected and prepared, while sulphurous and low-sulphur oils were even processed separately [3, 7, 11]. Due to this delayed coking units were built only at those refineries which have access to the local low-sulphur oil (Baku, Krasnovodsk, Guriev, Herson, Volgograd, Fergana) or the low-sulphur oil supplied from the Western Siberia (Angarsk, Omsk, Pavlodar).

Presently the oil is transported to the Russia plants over a system of Transneft trunk pipelines, where oils of varying composition and physical-chemical properties, especially sulphur content, are mixed together. In order to reduce sulphur content in the resultant oil products certain methods can be used for its preliminary removal from the oil (hydrodesulfurization, hydrocracking, extraction), but this will significantly complicate the process flow and implies high capital and operational expenses.

The cokes produced from the sulphurous oil residues cause equipment corrosion, increased cracking of electrode products, destruction of refractory brickwork of calcination furnaces, thus limiting the scope of possible use.

The analysis of changes in the quality of coke produced by domestic refineries revealed elevated levels of sulfur, as confirmed by the data presented in World Energy Outlook (2014 yr.), according to which production of heavy sulfurous and high-sulfur high-viscosity oils is increasing every year and based on estimated by 2035 yr. it will exceed 50 %.

In foreign countries thermal processes, in particular delayed coking, are especially popular for processing of heavy oils, most of which are exported from Mexico, Venezuela and Canada.

The Russian Federation also has considerable reserves of heavy oils and natural bitumens, mostly concentrated in Volga-Ural, West Siberian and Timan-Pechora oil and gas provinces.

This paper examines a possibility to produce high-quality petroleum coke from the vacuum residue (boiling above 530°C) of the heavy oil from Yarega field located in Timan-Pechora province.

Methodology and Methods. The target of research is the heavy oil from Yarega field and vacuum residue separated therefrom (boiling above 530°C) by oil running through the vacuum distillation analyzer MP 632 Herzog. The main physical and chemical properties of the explored systems were determined by standard methods in accordance with GOST requirements.

Dynamic viscosity was studied in the laboratory with the help of a rotary viscometer Rheotest RN 4.1 in a thermostated cell within the temperature range from 10 to 80°C. The operating principle of the viscometer is based on the measurement of shear stress in the sample placed between two coaxial cylinders. The metal content was identified using X-ray fluorescence energy dispersive spectrometer Elipson 3.

Capillary chromatography was carried out under the well-known method, which stages include oil sample dissolving in 40-fold volume of hexane, filtering after 16 hours, filling the chromatographic column with silica gel of SGC brand, adsorption of oil maltenes from the hexane solution to silica gel, extraction of paraffinic-naphthenic hydrocarbons fraction from silica gel by elution with hexane, aromatic substances extraction with hexane and benzene mixture, tarry matter extraction with benzene and ethyl alcohol mixture with a solvent volumetric ratio of 1:1. Then the chemical composition of components separated from Yarega oil was examined using gas chromatography-mass spectrometry based on the ionization of the organic compound molecule with its subsequent identification.

Research Results and Interpretation. The main physical and chemical properties of heavy oil from Yarega field and vacuum residue separated therefrom are presented in Table 1.

It should be mentioned that the initial boiling point of the Yarega oil is 220°C (Fig. 1), and the oil itself contains a small amount of diesel fractions (30 % by volume) and no gasoline fractions at all.

Exploration of dependency of the dynamic viscosity on the temperature revealed its sharp decrease from 5,000 to 100 mPa·s at a temperature from 10 to 80°C (Fig. 2) [4].

Since the quality of resultant petroleum products largely depends on the oil chemical composition, especially the content of hydrocarbon and non-hydrocarbon components, including in heavy oil residue, and their composition, there were substantive reasons to identify and analyze the chemical composition of the Yarega oil (Table 2), and for this purpose preparative chromatography and gas chromatography-mass spectrometry were used [8, 12]. Due to the low content of paraffinic hydrocarbons the distillate fractions of the Yarega oil have low pour and crystallization points.

DOI 10.18454/PMI.2016.6.833

Table 1

Properties of Yarega Oil and Its Vacuum Residue

Property	Yarega oil	Vacuum residue of Yarega oil
Distillate wt of crude, % wt	–	61.2
Density, kg/m^3, at 20°C	944	984
Sulphur content, % wt	1.23	1.18
Pour point, °C	–18	35
Flash point, °C:		
open cup	–	296
closed cup	142	–
Condradson coking ability, % wt	–	16.8
Content of saturated components, % wt	24	24
Content of aromatic compounds, % wt	36	33
Resin content, % wt	23	21
Asphaltene content, % wt	17	22

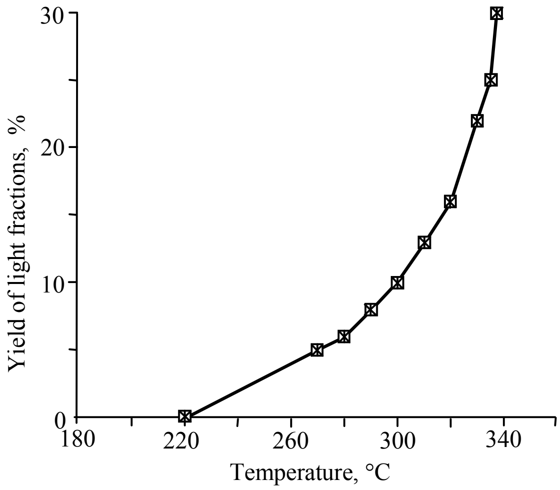

Fig. 1. Temperature dependence of yarega oil light fractions yield

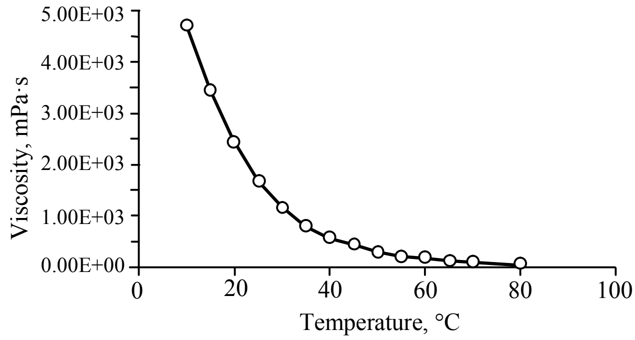

Fig. 2. Temperature dependence of yarega oil dynamic viscosity

Table 2

Chemical Composition of Yarega Oil

Compound	Content, % wt
Linear paraffins	3.78
Iso-paraffines	8.97
Aromatic compounds (benzene derivatives)	12.58
Aromatic compounds (naphtalene derivatives)	7.59
Aromatic compounds (benzene and naphtalene hybrid derivatives)	6.57
Anthracene, phenanthrene	9.85
Heteroatomic compounds	10.39
Isoprenoid compounds	9.95
Naphthenic compounds with 1 ring	5.97
Naphthenic compounds with 2 rings	10.56
Naphthenes with spiral structure	10.89
Naphthenic compounds with 3 rings	2.9

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Based on Tables 1 and 2 a conclusion can be made that the oil from the Yarega field belongs to naphthenoaromatic type.

As is generally known, aromatic hydrocarbons exhibit high tendency to condense and form coke. Saturated or paraffine hydrocarbons are only capable of decomposition reactions and do not undergo condensation reactions. Naphthenes are somewhere in the middle. Unsaturated hydrocarbons play a significant role in coking processes, especially due to addition reactions between them and aromatic hydrocarbons. While in high temperature zone the condensed aromatic compounds continue to condense, producing more macromolecular compounds, such as resins, asphaltenes, and finally, carbenes and carboids (coke). Due to the significant content of aromatic compounds in the feedstock, it is expected that the coke produced from the Yarega oil will be of a rather high quality.

It should be noted, that not only the asphaltenes are precursors of coke formation. It has been revealed [4, 12], that the coke produced from heavy gas oil contains more oxygen and nitrogen, than the coke produced from bitumen. This can be explained by the presence of heterocyclic structures in heavy gas oil, containing O and N, which could be precursors of coke.

Comparison between physical and chemical properties of the major types of feedstock used for production of needle coke [12] and the properties of Yarega oil vacuum residue (Table 3) has shown that after minor reduction of sulphur content the vacuum residue separated from Yarega oil can become a good feedstock for production of high-quality petroleum coke. The density of proposed feedstock is lower than the density of petroleum products, specified in Table 3, while asphaltene content is almost the same, which confirms that the Yarega oil vacuum residue can be used as a feedstock for production of high-quality petroleum coke.

Table 3

Comparison between the properties of major types of feedstock used for production of needle coke by foreign plants and the properties of yarega oil vacuum residue

Property	Distillate cracking residue	Decant oil	Heavy pyrolysis resin	Soft pitch of refined coal tar	Vacuum residue of Yarega oil
Density, g/sm^3	1.044-1.076	1.014-1.044	1.044-1.085	1.17-1.28	984
Coking ability, % wt	15-20	3-4	15-20	20-35	–
Sulphur content, % wt	0.4-0.6	0.3-0.6	0.1-0.4	0.2-1.0	1.18
Nitrogen content, % wt	0.05-0.1	0.05-0.1	0.1-0.15	0.2-1.0	–
Ash content, % wt	< 0.02	0.03-0.05	< 0.01	< 0.03	–
Asphaltene content, % wt	10-20	1-6	8-18	10-20	22

Metals present in Yarega oil (vanadium, nickel, etc.) after high temperature treatment are almost completely converted into the end product, i.e. the coke. Exploration of organometallic compounds content in the Yarega oil and vacuum residue (Table 4) and comparison of results with the requirements to metal content in the petroleum coke have shown that iron and silicon content in the vacuum residue is far below the standard, while the vanadium concentration is above the standard.

Table 4

Metal content in yarega oil and its vacuum residue

Concentration, ppm	Yarega oil	Yarega oil vacuum residue
Sulphur	1.23	1.1857
Aluminium	0.007	0.0063
Silicon	0.007	0.008
Vanadium	0.016	0.032
Iron	0.0047	0.0092
Nickel	0.0047	0.0102

Since macroparticles of asphaltenes, particularly in metal-bearing oils similar to the Yarega oil, are especially rich in organometallic trace elements, the question of preliminary deasphalting and demetallization of coking feedstock is the most important for the reduction of vanadium concentration in the final product, which,

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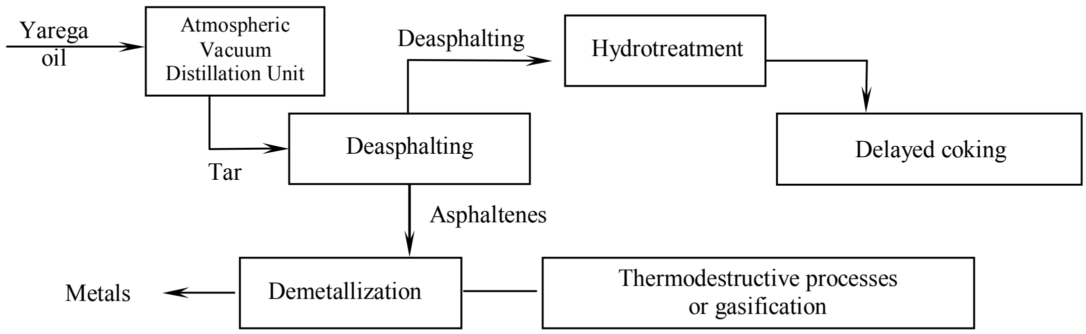

Fig. 3. Process flow diagram for yarega oil refinement

in its turn, will lead not only to the production of high-quality petroleum coke for the aluminum industry, but also of the metal concentrate, followed by isolation of high-quality components, such as vanadium, titanium, etc.

Separation of metals from oil and its residues is an important task of oil refining procedures [5, 9]. Different modern methods are used today to address this task [1]:

– extraction (removal of metals contained in the resin-asphaltene compounds by separation from petroleum feedstock using coagulants);

– adsorption (separation of metals from petroleum feedstock using adsorbents, accompanied with heat treatment);

– catalyst method (destruction of metal-bearing compounds in the presence of resolving catalyst and metal deposition thereon);

– hydrogenation (destruction of metal-containing compounds by hydrogenation treatment and metal deposition on the catalyst);

– thermal treatment (heat-induced decomposition of metal compounds and metal concentrating in thermolysis residues, in coke);

– combined treatment (destruction of metal-bearing compounds by hydrogenation without catalyst).

Based on the conducted research a process flow diagram for heavy Yarega oil refinement (Fig. 3) has been developed in order to produce high-quality petroleum coke for the aluminum industry, which includes the oil preliminary vacuum distillation followed by tar deasphalting and demetallization. Then the resultant deasphalted oil after preliminary hydrotreatment can be subjected to delayed coking, and the separated asphaltenes can be used as a feedstock for further isolation of metals and products of thermodestructive treatment (thermal cracking, pitching, coking and oxydation) or gasification.

Conclusions

1. The current state and future prospects of the integrated use of heavy oils have been explored through an example of oil from Yarega field of Timan-Pechora oil and gas province of Russia, including the oil vacuum residue.

2. Chemical composition and quality of Yarega oil and vacuum residue separated therefrom have been thoroughly studied, the findings are as follows:

• the oil from Yarega field belongs to aromatic-naphthene type of sulfurous highly resinous oils due to high content of aromatic (36.59 % by weight) and naphthenic (30.32 % by weight) hydrocarbons, resins (2 3 % by weight) and asphaltenes (17 % by weight);

• the initial boiling point of the Yarega oil is 220°C, it contains no gasoline fractions and a small amount of diesel fractions (30 % by volume);

• due to the low content of linear paraffinic hydrocarbons (3.78 % by weight) the distillate fractions of the Yarega oil have low pour and crystallization points;

• asphaltenes and metals present in Yarega oil (vanadium, nickel, etc.) after high temperature treatment are almost completely converted into the end product, i.e. the coke, that's why delayed coking process has been selected as one of the most efficient chemical treatment methods for heavy (vacuum) residues of the Yarega oil;

• comparative analysis between the quality of the main types of feedstock used for production of needle coke by the foreign plants and the vacuum residue of Yarega oil has confirmed the principal possibility of its use in this direction;

• exploration of asphaltenes and organometallic compounds content in the Yarega oil and its vacuum residue and comparison of results with the existing requirements to metal content in the petroleum coke have shown that silicon (0.008 ppm) and iron (0.0092 ppm) content in the vacuum residue is far below the standard, while the vanadium concentration (0.032 ppm) is above the standard.

3. Based on the conducted research a process flow diagram for heavy Yarega oil refinement has been developed in order to produce high-quality petroleum coke for the aluminum industry, which includes the oil preliminary vacuum distillation with preliminary deasphalting and demetallization of the Yarega oil vacuum residue, i.e. the tar; the resultant deasphalted oil after preliminary hydrotreatment can be subjected to delayed coking, and the separated asphaltenes can be used as a feedstock for further isolation of metals and products of thermodestructive treatment (thermal cracking, pitching, coking and oxydation) or gasification.

Acknowledgment. *The authors would like to express their gratitude to A.A. Boytsova, the postgraduate student of the Department of Chemical Technology and Energy Carriers Processing at St. Petersburg Mining University for carrying out experimental studies. The research was conducted within the frames of a grant provided by the Russian Science Foundation* (*Project N 15-17-00017*).

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The paper was accepted for publication on 28 September, 2016.