UDC 661.666.1 + 665.6

DOI: 10.15372/CSD2021334

Carbon Materials from Coal Tar and Heavy Oil Residues

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Abstract

The results presented herein were obtained by the scientists from Kazakhstan in research areas concerning the manufacture of carbon fibres by means of electrospinning from coal tar pitch and polyacrylonitrile, making coke from heavy oil residues, investigation of the composition and structures of asphaltenes extracted from the natural bitumen of the Munayly-Mola deposit. The precursor for carbon fibres was coal tar, a by-product of the treatment of coal from the Shubarkol deposit. The physicochemical characteristics and the composition of coke obtained from goudron at the Pavlodar petrochemical plant as a result of preliminary demetallization and desulphuration are demonstrated. It is established that the structure of asphaltenes from natural bitumen is more ordered and non-amorphous.

Keywords: carbon materials, coal tar, bitumen, asphaltenes

INTRODUCTION

Coal is one of the most important representatives of fossil raw materials and has held its value for many years. It is used to generate electricity and serves as the initial material to obtain a number of valuable products. Coal coking is accompanied by the emission of coke gas and coal tar, which is a complicated mixture of aromatic hydrocarbons, heterocyclic sulphur-, oxygen-, and nitrogen-containing compounds [1, 2].

Natural bitumens, along with heavy oil, are non-traditional sources of hydrocarbon raw material. Mining and processing of natural bitumen are difficult because of its high viscosity and increased content of resin-asphaltene components. Much attention is paid to the isolation of natural bitumen by means of extraction, thermal and ultrasonic action, and in a supercritical fluid medium. Prevalence of heavy oil fractions allows using oil-bituminous rocks to prepare bitumen-concrete mixtures [3–5].

Carbon fibres can be defined as fibres composed of carbon atoms by 92 % and more [6]. Due to the unique physicochemical and mechanical properties, carbon fibres and composites based on them occupy a special position among carbon materials. At present, carbon fibres are obtained from various precursors, for example, from oil, coal and mesophase pitch; polymers (polyacrylonitrile (PAN) and polyethylene). Studies are carried out aimed at obtaining carbon fibres from the waste product of plant raw material – lignin. According to the statistical data, the most widespread precursor for obtaining carbon fibres is PAN. In the pre-

sent work, we describe the method to obtain carbon fibres from coal tar.

The main advantages of carbon fibres in comparison with other fibres are in their high tensile strength, thermal stability, high rigidity, low density and high chemical stability. All these advantages may be combined with a suitable matrix material (epoxy resin and so on) to provide good mechanical characteristics of the composite materials. These composite materials based on carbon fibres are characterized by high mechanical properties in combination with low mass, which makes them promising for manufacturing various parts instead of using metals and alloys. These advantages predefine the use of these composite materials in the aerospace and defense industry, automobile and aircraft engineering, civil construction and other branches. The introduction of lightweight structures proceeds most intensively in automobile engineering, which leads to a decrease in energy consumption in this branch of industry.

The first fibres that had been manufactured for commercial purposes were made by thermal treatment of natural fibres (cotton) by Joseph W. Swan in 1860 [7]. In 1879, Th. Edison used carbon fibres based on cellulose as filaments in incandescent lamps. Later on, these filaments were replaced by tungsten ones [8]. Japanese, British and American scientists are considered to be pathfinders on the world market of carbon fibres. For example, the first carbon fibres with high tensile strength were obtained only in the 1960-es. The polymer PAN was used as a precursor of these fibres for the first time [9, 10].

According to the presented data [11] and marketing forecasts, the market of carbon fibres continues growing by 10–15 % every year. For example, the demand for carbon fibres was about 98 thousand tons in 2020. This increase in the consumption of carbon fibres and composites based on them is due to the development of aerospace and military programmes.

Relying on scientifically proven theoretical data, the International Union for Pure and Applied Chemistry (IUPAC) classifies carbon fibres over five types [6]:

1) ultra-high modulus, UHM: carbon fibres with the modulus more than 500 GPa;

2) high modulus, HM: carbon fibres with elastic modulus more than 300 GPa and the ratio of tensile strength to elastic modulus less than 1 %;

3) intermediate modulus, IM: carbon fibres with elastic modulus up to 300 GPa and the ratio of the strength to the modulus more than $1 \cdot 10^{-2}$;

4) low modulus, LM: carbon fibres with elastic modulus up to 100 GPa and low strength; these are fibres with isotropic structure;

5) high tensile strength, HT: carbon fibres with tensile strength more than 3000 MPa and the ratio of strength to modulus from 1.5 to $2 \cdot 10^{-2}$.

The most important precursor on the market of carbon fibres is PAN, while pitch is used to make fibres with specific properties and/or with required characteristics. Previously used viscose precursor has no commercial significance today. The treatment of carbon fibres made from different precursors requires different approaches to obtain high-quality final products. Treatment methods are somewhat similar but differ from each other by the conditions and parameters of specific processes. The main stages of the treatment of precursor fibres are stabilization (oxidation), low-temperature carbonization, high-temperature carbonization (graphitization), and activation.

Coking attracts enormous attention in the world as the process for utilization of heavy residues with the formation of the maximal amount of distillates, production of motor fuel, preparation of the coke of required quality for application in various branches of industry. Petroleum coke is used in nonferrous metallurgy in the production of aluminium, as construction material for manufacturing corrosion-proof devices, and in cement production.

There are several versions of coking process in the industry [12]:

– periodic coking in coke tanks. This process involves coke quenching, and lumpy coke for the production of electrodes is thus obtained;

– continuous coking (or fluid cracking). This process is carried out in the fluidized bed of powdered heat carrier and aims at the maximal yield of distillate fractions;

– a combined process of thermocontact coking followed by steam-oxygen (air) gasification of powdered coke (or flexicoking) to obtain synthesis gas in addition to distillates;

– delayed coking. The raw material heated to 470–510 °C is supplied to coke chambers, where thermal cracking proceeds with the formation of coke and gaseous products. This process is called delayed cracking because the raw material is rapidly heated in furnaces and pumped into a non-heated hollow chamber where it is gradually transformed into coke.

The yield and quality of coke depend on the initial material, but the requirements to it are

controversial: on the one hand, the raw material should provide a high yield of high-quality coke, but on the other hand, it should not coke up the furnace coil to provide the conditions for a maximal run between repairs of the installation for delayed coking [13].

During recent years, coke production has been characterized by the following features: the enterprises note that the coking raw material becomes heavier, and the market for the products of secondary catalytic processes has appeared [14]. It was determined in the studies [15] that coking of petroleum goudron with substantial amounts of asphaltenes and silica gel resins leads to the maximal amount of petroleum coke.

The major methods of raw material preparation are technologies using oil residue hydrodesulphuration, which include hydropurification of straight-run fuel oil (mazut) followed by vacuum fractional distillation to obtain the residue for coking or hydropurification of vacuum cut, with subsequent thermal cracking to obtain low-sulphur cracking residue for coking process [16].

To decrease sulphur and metal content in the coke, preliminary hydrodesulphuration processes were proposed, resulting in a decrease in the concentration of sulphur-containing compounds in the raw material. However, hydrodesulphuration is a complicated and expensive process because it requires the equipment operating at high pressure [17].

A method is known that allows obtaining products in the installation for delayed coking, which includes heating of heavy sulphur-containing oil products to the coking temperature, and coking in the reactor in one stage in the presence of hydrogen [18]. A disadvantage of this method is the explosion and fire danger of the operation of delayed coking installation when hydrogen is used as a reagent.

In another method of obtaining petroleum coke [19], a mixture of heavy oil residues from petrochemical and/or oil processing works (in particular, a mixture of distillate cracking residue and goudron) is supplied into the delayed coking chamber, and then the product is treated with hydrogen at a temperature of 490–550 °C and pressure up to 5 MPa for 8–24 h. A disadvantage of this method is its high net cost due to the use of hydrogen.

Other methods of the preparation of raw material (for example, alkaline washing, thermal and thermochemical methods of coke desulphuration) are characterized by high energy consumption, bring many alkaline or alkaline earth metals as impurities into coke, or require additional thorough investigation [20].

One of the methods of coking oil residues includes heating of the initial raw material, its treatment, preliminary thermopolycondensation with subsequent coking of the secondary raw material and separation of steam-gaseous products of coking [21]. As a result of the application of this method, the yield of coke with respect to the initial raw material was 41 %. Disadvantages of this method are its complicated flowchart, pressure up to 1.5 MPa at which absorption and coking are carried out, and the absence of the data on the reference parameters of coke quality.

A known method leading to the improvement of the quality of petroleum coke is goudron compounding with other products of oil processing and petrochemistry (distillate cracking residues, gas oil from catalytic cracking, products of oil pyrolysis, and extracts from mineral oil production). This method is based on the dilution of raw material with low-sulphur additives. Results reported in [22] showed that the application of four- or five-component compound mixtures decreases the content of impurities in the coke by 10–20 % with the conservation of the yield at a level of 26–29 %.

So, it is necessary to develop a new inexpensive technology improving the quality of coke, in particular, that from high-sulphur raw materials. Obtaining coke with required properties and definite structure, one should take into account the features of the composition and properties of the initial raw material: not only the content but also regular arrangement of aromatic rings in polycyclic structures, the absence of heteroatoms, relatively low coking ability.

Attention to the investigation of asphaltenes was caused by their negative effect on the properties of oil systems. For instance, oil with high asphaltene content is characterized by high viscosity, which requires the application of expensive technologies in order to enhance oil production and provide its transportation [23–26]. Asphaltene molecule is composed of small aromatic clusters connected with each other through methylene, sulphide, ester and oxygen bridges. Peripheral substituents are non-branched and branched aliphatic groups, as well as hydroxyl and carboxyl groups. These structures of asphaltene molecules are called archipelago (Fig. 1) [27, 28].

It was established that asphaltenes might be separated into several fractions. The fraction precipitating from asphaltene solution in the case of

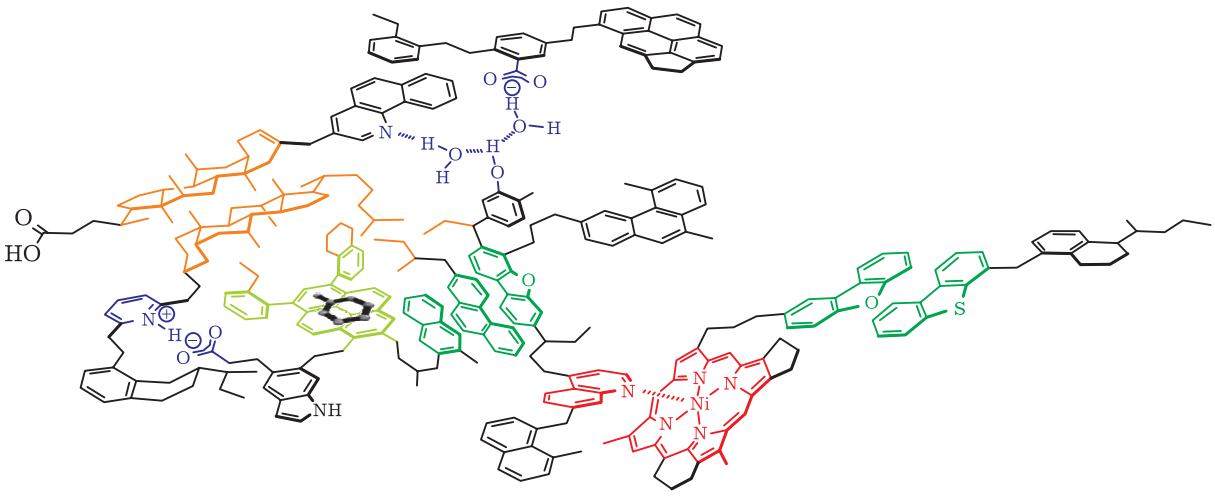

Fig. 1. Archipelago-type asphaltene molecule [26].

the minimal content of *n*-alkanes in a binary solvent or precipitating after the addition of *p*-nitrophenol is called insoluble, while the fraction precipitating from the solution with the maximal content of *n*-alkanes is called soluble [29].

Investigation showed [30] that insoluble fraction, which is composed of dense black lustrous particles, contains highly condensed aromatic compounds with large molecular mass, high aromaticity factor and the low atomic ratio of H/C. Most frequently, this fraction is characterized by the high content of metals (V, Ni, Fe), nitrogen and chlorine, and low solubility in aromatic solvents. After metal removal, the rate of dissolution and solubility increase sharply [31].

The authors of [30] showed that an asphaltene molecule in the majority of cases contains one polycondensed core composed of seven aromatic cycles. This statement was based on the generalization of the results of the studies of molecular diffusion of asphaltenes by means of time-resolved fluorescence detection (TRFD) and fluorescence correlation spectroscopy (FCS), comparative analysis of the optical absorption spectra and fluorescence of extremely diluted solutions of asphaltenes and model compounds, with the application of the method of molecular orbitals, the data of high-resolution transmission electron microscopy (HRTEM), X-ray Raman scattering (XRS). In [32], a group of researchers confirmed the structure of an archipelago-type molecule for asphaltenes from bitumen of the Atabaska deposit (Canada) using the single-molecule force spectroscopy (SMFS). It was shown that under the action of an external force asphaltene molecules from the bitumen of the Atabaska deposit behave like long-chain polymers. Recently, due to the application of new mass spectrometric methods, namely field ionization mass spectrometry (FI-MS), electrospraying ionization Fourier transform ion cyclotron resonance mass spectrometry (ESI-FT-ICR-MS), atmospheric pressure photoionization mass spectrometry (APPI-MS), field desorption and ionization mass spectrometry (FD-FI-MS), and laser desorption ionization mass spectrometry (LDI-MS), generalized in the review by Akbarzadeh *et al.* [33], it has been established that the molecular mass of asphaltenes is within the range 300–1400 g/mol, 700–800 g/mol on average.

It follows from the results reported in [34] that the clusters have fractal structures and are composed of almost 8–10 nanoaggregates. The cluster size for different asphaltenes may be 6 to 30 nm, or even up to 100 nm, according to some data. With further increase in asphaltene concentration in the system, floccules or various nanophases of flocculated nanocolloids are formed; their size may be more than 100 nm, and their aggregation may lead to the loss of sedimentation stability of the solution. The growth of asphaltene aggregates, their flocculation and the loss of sedimentation stability are also observed after the addition of low-molecular *n*-alkanes (precipitators) into the solution of asphaltenes in toluene (benzene). In this case, asphaltene solution will be characterized not by the critical concentration of nanoaggregation (CCNA) by the onset point, that is, precipitator concentration at which asphaltene flocculation starts and their precipitation from the solution takes place. The data on the stability of asphaltene aggregates formed as a result of the addition of precipitators are contradictory [35].

CARBON FIBRES BASED ON COAL TAR PITCH

In the present work, we present the method to obtain carbon fibres by means of electrospinning from coal tar pitch. Coal tar pitch samples were obtained with the help of thermal treatment of coal tar, which is a complicated mixture of the hydrocarbons of aromatic series, heterocyclic sulphur-, oxygen- and nitrogen-containing compounds. Coal tar samples may be divided into three groups according to their properties: neutral, acid, and basic [36]. According to [37], the world production of coke by 2015 was about 700 million t; as a result, 21–35 million t of coal tar was produced, and about 50 % of this amount was further processed. Coal tar processing results in valuable products: benzene, toluene, xylenes and other compounds, as well as sleeper impregnation oil, plastics, electrode pitch, carbon fibres, binding pitch, *etc.*

Preliminary treatment of precursor solution for electrospinning

Coal tar was obtained by processing coal from the Shubarkol deposit (Kazakhstan). The resources of this deposit account for 1.5 milliard t. The consumers of special coke produced from the Shubarkol coal are the largest plants of Kazakhstan (ferroalloy plants Kazkhrom Transnational Company, Kazfosfat, Kaztsink), Russia and Ukraine.

Coal tar is dense black liquid with specific smell. Its major characteristics are listed in Table 1. Mesophase pitch was obtained by thermal treatment of coal tar in the atmosphere of argon within temperature range 200–500 °C. The argon flow rate was 92 cm^3/min. Thermal treatment was carried out in a tubular furnace with a quartz reactor 3 cm in diameter. After thermal treatment, initial coal tar passes from the viscous-flow state to the solid state. Thus obtained

TABLE 1

Characteristics of coal tar from the Shubarkol Komir Plant (Karaganda, Kazakhstan)

Parameter	Coal tar from the Shubarkol Komir Plant	Determination method
Density at 20 °C, kg/m^3	1048	GOST 3900 GOST 11126
Fraction composition, mass fraction (of anhydrous tar), %:		
up to 180 °C	5.1	
180–210 °C	4.4	
210–230 °C	4.8	
230–270 °C	15.8	
Above 270 °C in vapour		
up to 390 °C in tank	19.7	
Above 270 °C in vapour		
up to 405 °C in tank	26.1	
Yield of distillation residue (pitch), %:		
at 390 °C in tank	49.8	
at 405 °C in tank	40.0	
Mass fraction of substances insoluble in toluene (α-fraction), %	1.4	GOST 7847 TU 2543-203-00190437–2005
Mass fraction of substances insoluble in quinoline (α_1-fraction), %	absent	TU 2543-203-00190437–2005
Ash content, %	0.12	TU 2543-203-00190437–2005
Phenol content, %	20.6	Calculated from phenol content in distillate fractions up to 390 °C in tank
Naphthalene content, %	1.6	According to the data of GLC-MS* of distillate fractions

* Gas-liquid chromatography combined with mass spectrometry.

coal tar pitch has a porous structure, which is due to the removal of low-boiling fractions in the form of vapour, which leads to the formation of loose sponge-like material.

Precursor fibres were prepared from coal tar pitch by means of electrospinning using PAN as fibre-forming copolymer. PAN is synthetic semi-crystalline organic polymer resin. In this work, we used commercial PAN (DFL Minmet Refractories Corp., China), with the following technical characteristics: purity – not less than 99 %; density 1.14–1.45 g/cm^3; molecular mass – 150 000 g/mol. To prepare fibre-forming colloid solution, a 7 % polyactylonitrile solution was prepared. PAN dissolution was carried out during heating in a round-bottomed flask 200 cm^3 in volume, equipped with a mechanical mixer. Dimethylformamide was used as a solvent. Dissolution was carried out under continuous mixing at a temperature of 80 °C for 1 h.

Electrospinning process

At first glance, electrospinning is a simple and hence readily controllable process of obtaining fibres. However, actually, it is a complicated system depending on many factors. The use of a necessary precursor and its preparation are the basic operations for obtaining fibres. The experiment on electrospinning was carried out in the Laboratory of Functional Materials at the Institute of Combustion Problems (Almaty).

The use of a rotating collector (for example, a cylinder, wheel or cone) in electrospinning set-up, as shown in Fig. 2, is the most convenient method to obtaine ordered fibres. A research team from the Institute of Combustion Problems developed a rotating cylinder as a collector for fibres with controllable rotation frequency (see Fig. 2, *a*). Electrospinning was carried out as follows: precursor solution was pumped through a thin capping with internal volume not less than 1 mL; resistance was provided by the electric field within 20 kV, and the distance between electrodes was 20 cm; the substrate on which the fibres were collected was in contact with the counter-electrode and was placed in the horizontal position (see Fig. 2, *b*).

It was established that fibre leveling increased with an increase in the surface velocity of the cylinder to a critical level. The process of obtaining fibrous materials may be divided into three stages depending on the frequency of collector rotation:

– rotation frequency is too low to initiate fibre orientation;

– rotation rate initiates fibre leveling with an increase in the frequency to a critical level;

– fibre leveling decreases due to the destruction and formation of a turbulent air flow along the perimeter of the rotating collector, which is caused by the critical rotation frequency.

In addition, the frequency of collector rotation may at the same time affect fibre diameter,

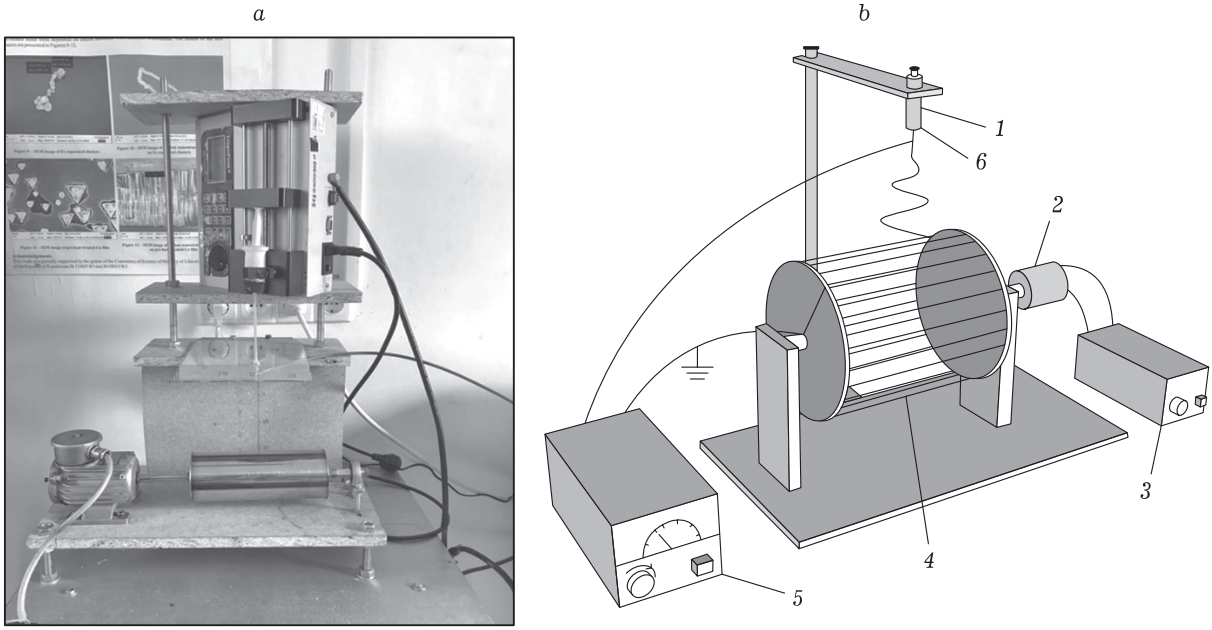

Fig. 2. Photograph (*a*) and a general scheme of electrospinning set-up (*b*): *1* – syringe; *2* – motor; *3* – motor speed controller; *4* – drum collector; *5* – high-voltage power supply unit; *6* – needle.

which is inversely proportional to rotation frequency. An increase in rotation frequency usually leads to a decrease in fibre diameter.

Thermal treatment of precursor fibres

Stabilization (oxidation) is one of the most important stages and has a strong effect on the properties of the resulting fibres. Due to stabilization, the thermal stability of the fibres increases, and the yield of carbon may be enhanced. Optimization of this process is very important for the properties of the resulting carbon fibres, while non-optimized stabilization would lead to larger losses of the material during subsequent carbonization and to worsening of the characteristics of the final product. Stabilization was carried out in a tubular furnace with a quartz reactor. The reactor was heated to 250 °C, and annealing was carried out for 1 h.

After fibre stabilization, low-temperature **carbonization** was performed in the tubular furnace with the quartz reactor. The reactor was preliminarily blown with argon to remove air from it and to exclude the contact with oxygen. The reactor was heated to 600 °C. The heating rate was 2 °C/min, carbonization time was 1 h.

During stabilization, the fibres become dense and rigid; in addition, colour may change. The colour may vary from light yellow to yellow, from brown to gold-brown (Fig. 3).

The resulting fibre samples were studied by means of scanning electron microscopy (SEM) after stabilization and after carbonization. Results of the SEM studies of the morphology of synthesized fibres after stabilization are presented in Fig. 4. Carbon fibres synthesized from the initial fibre-forming polymer solution had smooth surface, without any surface defects, open porosity and cluster joints. However, in spite of the fact that the fibres were gathered on the surface of a rotating collector, they were arranged in a disordered orientation.

As a consequence of chemical and structural transformations, carbonization involves profound changes in physical, mechanical and chemical properties of the fibres; depending on carbonization temperature, the properties change in different manners. Sample morphology after carbonization was also studied by means of SEM (Fig. 5).

It was assumed that carbonization temperature equal to 600 °C is insufficient to observe sharp changes in the diameter of the resulting carbon fibres, which varies within the range from 200 to 1000 nm.

According to the recorded SEM images, thinner fibres are formed from all samples after carbonization, which is due to the evaporation of volatile substances under the action of temperature. All samples were also observed to conserve their fibrous structures.

OBTAINING COKE FROM HEAVY OIL RESIDUES

In the present work, goudron was subjected to coking. Goudron serves as the raw material for the delayed coking unit (DKU) of the facilities for processing heavy oil residues at the Pavlodar Petrochemical Plant (Kazakhstan). Goudron characteristics are: appearance – viscous low-mobile liquid, density at 20 °C – 981.0 kg/m^3; mass fraction of water – up to 0.1 %; ash content – 0.02 mass %; coking capacity – 14 mass %; group composition: aliphatic hydrocarbons – 6.6 %, aromatic hydrocarbons – 45.7 %, resins – 20.5 %, asphaltenes – 27.2 %. After demetallization and desulphuration with various adsorbents at a temperature of 400 °C for 3 h goudron coking was performed to obtain coke with improved physicochemical characteristics.

The yields and physicochemical characteristics of coke obtained from goudron without preliminary treatment and after demetallization with different adsorbents and under different process conditions are shown in Table 2. The mass fraction of volatile substances in coke samples was determined according to GOST R 55660–2013, ash content – GOST 11022–95, total moisture content – GOST 27588–91.

One can see in Table 2 that the yield of coke from goudron without preliminary treatment was 18.9 %, and this coke was characterized by a high mass fraction of total moisture (2.9 %), ash content (0.5 %), mass fraction of volatile substances in the coke (7.9 %). The mass fraction of total moisture decreases substantially (to 1 %) in the coke obtained from goudron after demetallization with zeolite at 400 °C for 3 h, and the mass fraction of volatile substances and ash content decrease insignificantly (to 7.8 and 0.4 %, respectively). Coke yield increases to 27.0 %. With zeolite modified with 1 % xerogel of divanadium pentoxide (V_2O_5) as adsorbent, coke is characterized by low mass fraction of total moisture (1.1 %), the mass fraction of volatile substances also decreases

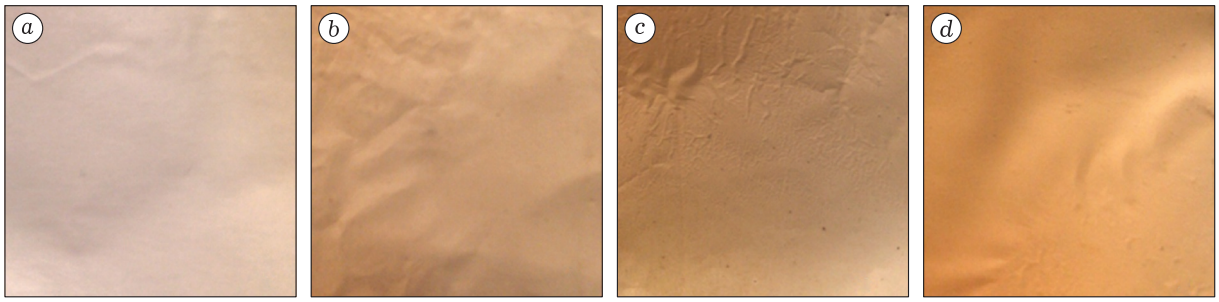

Fig. 3. Photographs of samples after fibre stabilization, obtained from a 7 % solution of PAN (*a*), CT_{100}/PAN (*b*), CT_{150}/PAN (*c*), CT_{200}/PAN (*d*). Here and in Fig. 4, 5: PAN is polyacrylonitrile; CT is coal tar; figures indicate the temperature at which the initial raw material was processed.

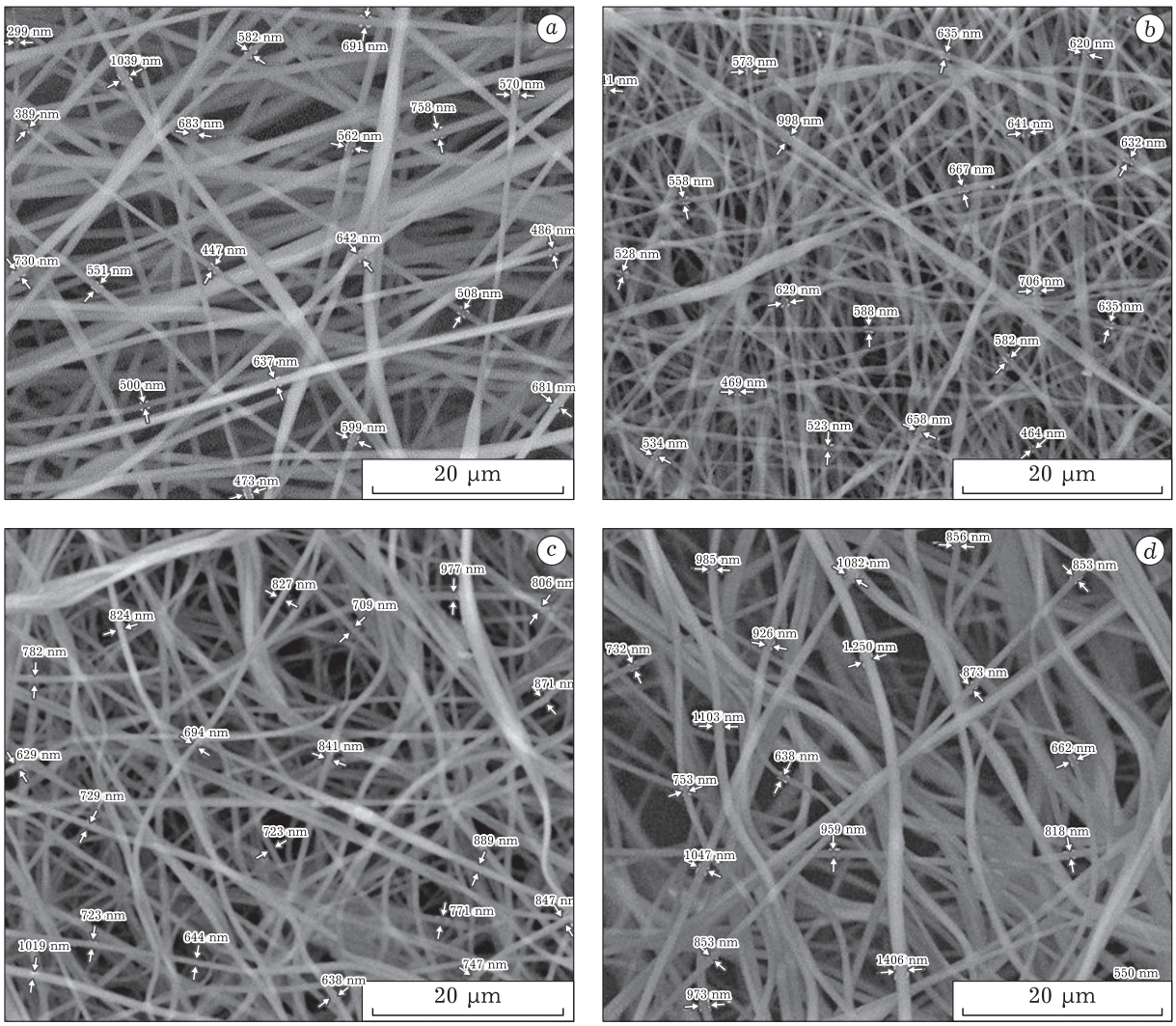

Fig. 4. SEM images of samples after stabilization of fibres obtained from CT_{100}/PAN (*a*), CT_{150}/PAN (*b*), CT_{200}/PAN (*c*), 7 % PAN solution (*d*). For designations, see Fig. 3.

to 6 %, and ash content is 0.25 %. The yield of coke turned out to be maximal: 34.4 %.

The use of serpentine as adsorbent for goudron demetallization allowed us to obtain coke with low mass fractions of total moisture and volatile substances, but ash content was 0.4 %. Demetallization of goudron with the adsorbent based on wollastonite and subsequent coking resulted in the formation of coke characterized by the high mass fraction of total moisture (2.3 %)

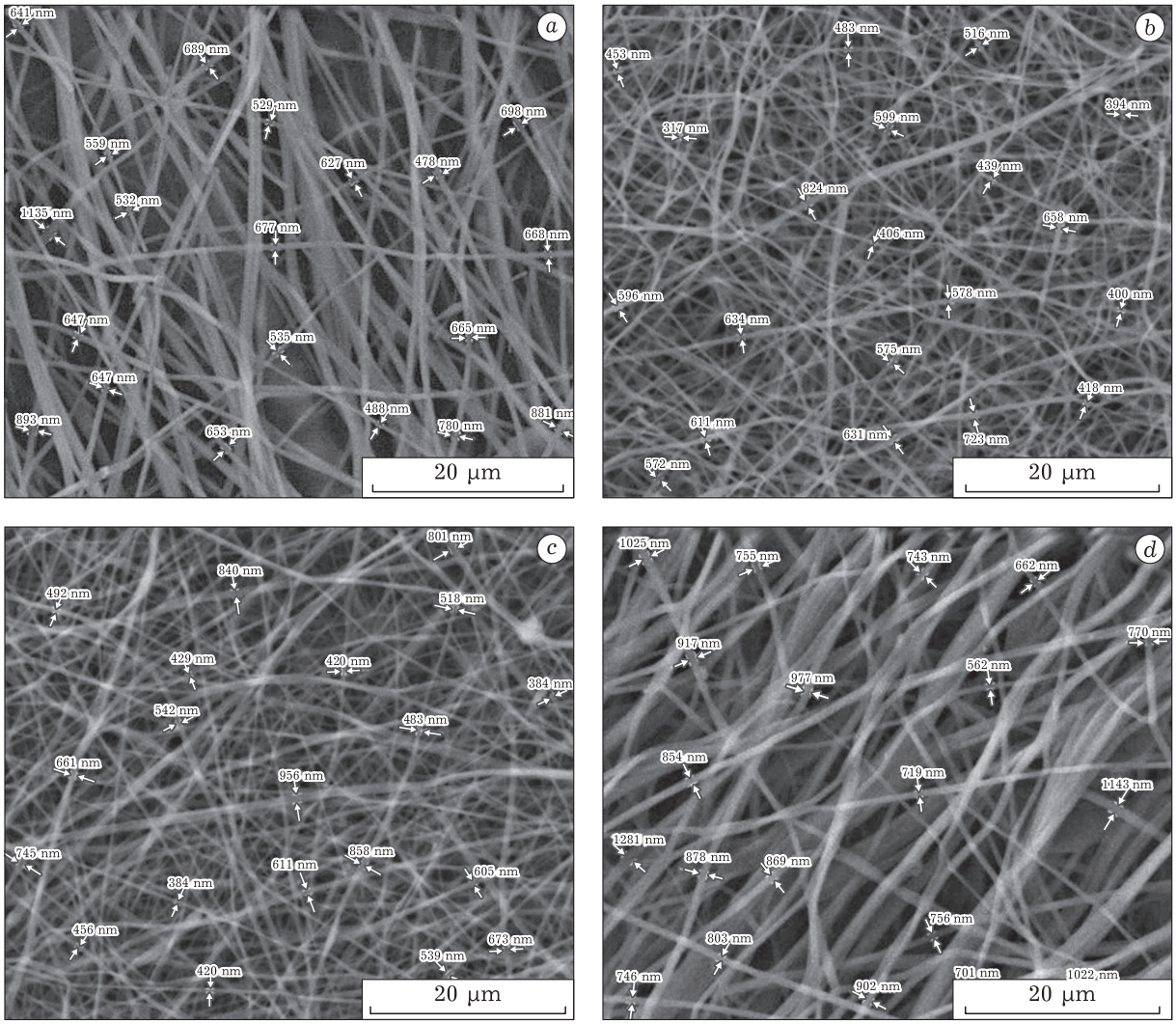

Fig. 5. SEM images of the samples after carbonization of fibres obtained from CT_{100}/PAN (*a*), CT_{150}/PAN (*b*), CT_{200}/PAN (*c*), 7 % PAN solution (*d*). For designations, see Fig. 3.

TABLE 2

Yield and physicochemical characteristics of coke obtained from goudron after demetallization using different adsorbents at 400 °C for 3 h

Raw material to obtain coke	Physicochemical characteristics of coke, %			
	Mass fraction of total moisture	Mass fraction of volatile substances	Ash content	Yield
Goudron without preliminary treatment	2.9	7.9	0.5	18.9
Goudron after demetallization with:				
zeolite	1.0	7.8	0.4	27.0
zeolite modified with V_2O_5 xerogel	1.1	6.0	0.25	34.4
serpentine	1.4	4.6	0.45	32.0
wollastonite	2.3	5.7	0.6	12.0
wollastonite and serpentine	1.3	8.3	0.3	23.2
kaolin clay	2.0	7.2	0.4	32.0
Requirements of GOST 22898–78	not more than 3.0	not more than 9.0	not more than 0.6	–

and ash content (0.6 %), and coke yield decreased to 12 %. Modification of wollastonite with serpentine caused a decrease in the mass fraction of total moisture and ash content of coke, an increase in coke yield, but the mass fraction of volatile substances increased to 8.3 %.

Coke was obtained from goudron after demetallization in the presence of kaolin clay in a yield of 32 %, the mass fraction of total moisture was 2 %, volatile substances – 7.2 %, ash content – 0.4 %.

Among coke samples presented in Table 2, the best physicochemical characteristics are those of coke obtained from goudron after preliminary demetallization with zeolite modified with V_2O_5 xerogel. The main physicochemical characteristics of this coke sample meet the requirements of GOST 22898–78, coke yield is 34.4 %.

Then coke samples were analyzed for metal and sulphur content. Sulphur content in goudron and coke samples was determined according to GOST 8606–2015 "Solid mineral fuel. Determination of total sulphur. Eschka method". The concentrations of metals (vanadium, nickel, iron) in coke samples was determined by means of atomic emission spectrometry with inductively coupled plasma using the atomic emission spectrometer with microwave plasma 4200 MP-AES Agilent Technologies according to GOST 34242–2017.

Results of the analysis of coke samples for metal and sulphur content are presented in Table 3. Vanadium content in coke obtained from goudron without preliminary treatment was 0.031 %, which does not meet the requirements of GOST, according to which vanadium content should be no more than 0.015 %. The product of goudron coking after demetallization with zeolite is characterized by decreased vanadium content (0.019 %). Zeolite modification with V_2O_5 xerogel and demetallization in its presence provide a substantial decrease in vanadium content in coke (to 0.008 %). The use of natural minerals (wollastonite, serpentine, and kaolin clay) as adsorbents for demetallization also causes a decrease in vanadium content in coke, however, its amount was higher than in the case when zeolite modified with V_2O_5 was used.

Nickel content in coke samples also decreases in comparison with its content in goudron; its lowest content (0.0014 %) is observed in coke obtained from goudron after preliminary treatment with zeolite modified with V_2O_5.

Iron content in coke is insignificant (0.003 %) because its content in goudron itself was only 0.0033 %. All coke samples meet the standard requirements for iron content.

Goudron coking after preliminary treatment resulted in a decrease in sulphur content in coke samples. The lowest sulphur concentration (1.45 %) was detected in coke obtained from goudron after demetallization and desulphuration with zeolite modified with V_2O_5 xerogel. The use of zeolite and other natural minerals allowed a decrease in sulphur content in coke to 1.87–2.44 %, while its initial content in goudron was 2.7 %.

Physicochemical parameters of coke samples obtained without preliminary treatment and after preliminary demetallization and desulphuration of goudron at 400 °C for 3 h in the presence of zeolite modified with V_2O_5 are shown in Table 4.

The parameters listed in Table 4 were compared with the standard requirements for defi-

TABLE 3

Metal and sulphur content in coke samples obtained from goudron after demetallization with different adsorbents at 400 °C for 3 h

Sample	Element content, %			
	Vanadium	Nickel	Iron	Sulphur
Goudron	0.054	0.0058	0.0033	2.70
Coke obtained from goudron:				
without preliminary treatment	0.031	0.0022	0.0030	2.50
after demetallization:				
with zeolite	0.019	0.0016	0.0025	1.87
with zeolite modified with V_2O_5 xerogel	0.008	0.0014	0.0011	1.45
with wollastonite	0.021	0.0022	0.0024	2.14
with wollastonite and serpentine	0.011	0.0021	0.0027	2.44
with kaolin clay	0.011	0.0020	0.0025	2.34
Requirements of GOST 22898–78	Not more than 0.015	–	Not more than 0.08	Not more than 1.5

TABLE 4

Physicochemical characteristics of coke obtained from goudron

Parameters of coke quality	Coke from goudron		
	KZA grade, first quality (according to GOST 22898–78)	without preliminary demetallization	with preliminary demetallization
Mass fraction of volatile substances, %	Not more than 9.0	7.9	6.0
Ash content, %	Not more than 0.6	0.5	0.25
Mass fraction of total moisture, %	Not more than 3.0	2.9	1.1
Mass fraction of sulphur, %	Not more than 1.5	2.5	1.45
Mass fraction of impurities, %:			
vanadium	Not more than 0.015	0.031	0.008
nickel	Not standardized	0.0022	0.0014
iron	Not more than 0.08	0.0030	0.0011

nite coke grades (GOST 228989–78). One can see that coke obtained after preliminary demetallization and desulphuration, as compared with the sample obtained without preliminary treatment, is characterized by improved parameters, namely a decrease in the mass fraction of volatile substances and ash content.

The product of goudron coking after preliminary demetallization and desulphuration using adsorption-based method corresponds in its physicochemical characteristics and the concentrations of sulphur and metals to the requirements of GOST 22898–78 for the KZA coke grade, the first quality.

So, the coking of demetallized and desulphurized goudron from the Pavlodar Petrochemical Plant was carried out at process temperature 490–510 °C for 8 h. Experimental results showed the efficiency of goudron coking after preliminary demetallization and desulphuration of the raw material. The result was an increase in the yield of coke (to 34 %) and petrol fractions, and a decrease in the yield of coke distillate.

TABLE 5

Results of X-ray fluorescence analysis of asphaltenes precipitated from natural bitumen of the Munayly-Mola deposit

Element	Relative concentration, %
Fe	42.445
S	28.00
Ca	11.672
Ni	2.640
Zn	6.332
Ti	0.644
As	1.756
K	3.517
V	2.994

INVESTIGATION OF THE COMPOSITION AND STRUCTURE OF ASPHALTENES OF NATURAL BITUMEN

During the present experimental work, asphaltenes were precipitated from the natural bitumen of the Munayly-Mola deposit (Kazakhstan). Organic solvents used for this purpose were changed from pentane, hexane to light petroleum. It has been determined that the efficient yield of asphaltenes is achieved with the mass ratio of light petroleum/bitumen equal to 40 : 1. Asphaltene content was determined in per cent to the weighted portion of the sample.

The elemental composition of the resulting asphaltene samples was determined by means of X-ray fluorescence analysis using a Fokus-2M X-ray fluorescence spectrometer (Russia). The results of the elemental analysis show the presence of a number of elements in the asphaltenes of natural bitumen from the Munayly-Mola deposit (Table 5). According to the data obtained, it may be concluded that bitumen from this deposit, or, more precisely, its heavy residue after various processing operations, may be further used as an alternative resource to obtain essential elements: vanadium, titanium, nickel, and zinc.

The structure and aggregation of the surface of thus obtained asphaltenes were studied by means of SEM. The images of their surface are shown in Fig. 6.

One can see that asphaltenes have partially ordered structures, the main component of the surface is represented by amorphous carbon [28]. The SEM does not give complete data on aggregation processes, so asphaltene samples were studied by means of transmission electron microscopy (TEM).

The investigation was carried out with the help of a transmission electron microscope JEOL

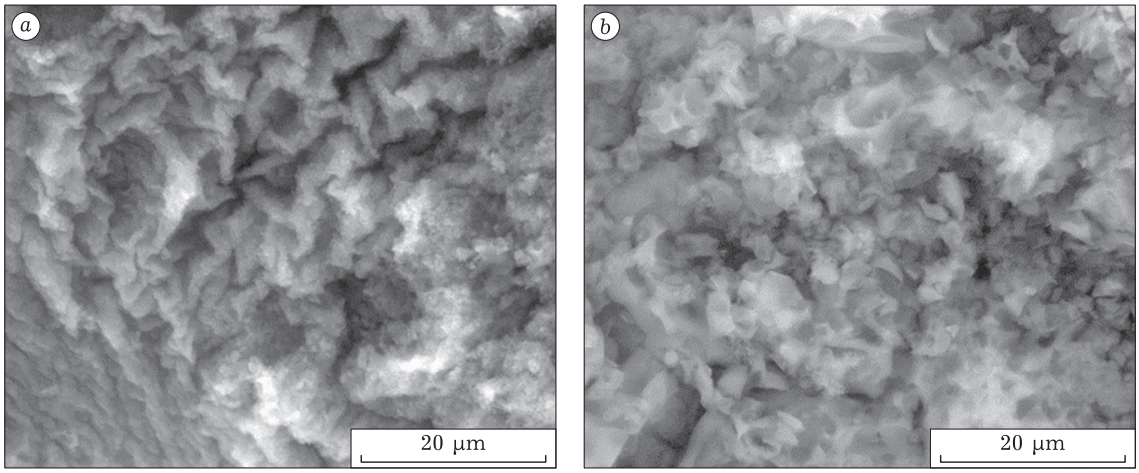

Fig. 6. Electron microscopic images of the surface of asphaltenes precipitated from the petroleum bituminous rock of the Munayly-Mola deposit.

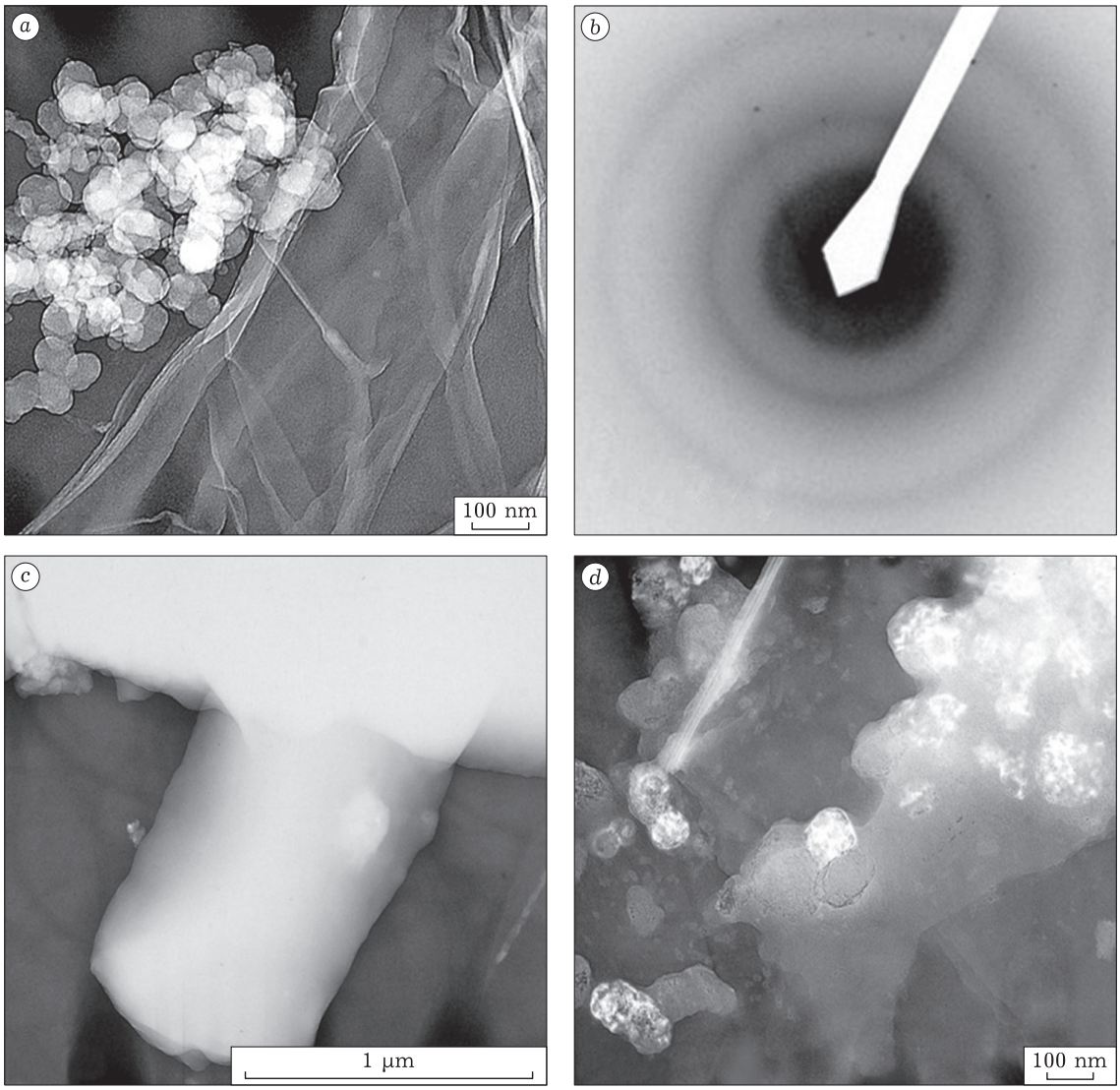

Fig. 7. TEM images of asphaltenes from natural bitumen of the Munayly-Mola deposit.

JEM 100CX (Japan) at the accelerating voltage of 100 kV (vacuum, not very high temperature). The samples were prepared by means of dry preparation. The results of TEM studies are shown in Fig. 7.

A sample of asphaltenes from the natural bitumen of the Munayly-Mola deposit is composed mainly of fragments of a rather dense film. Sample annealing involves film thinning (see Fig. 7, *a*) and its definite structuring (see Fig. 7, *b*). Film edges may contain dense, coarse particles (see Fig. 7, *c*) and less frequently finer ones (see Fig. 7, *d*). Traces of particle transformation are observed in Fig. 7, *d*. Microdiffraction patterns depicting the crystal ordering of the substance provide evidence of the bulk nature of the amorphized substance present in the samples. Sometimes the formations possessing crystal lattice occur in the substance [29].

In general, the results of SEM and TEM studies gave some notions of the structure and aggregation of the asphaltene surface. The major component of the structure is represented by the amorphous phase. However, it was noticed that sample annealing involved film thinning and its structuring. This attracts attention to further studies of asphaltenes and to modification of their structure. This phenomenon may be explained by the destruction of aliphatic bonds during annealing, which leads to structural transformation, structuring due to carbon aromatic rings.

CONCLUSION

Carbon fibres were obtained on the basis of thermally treated coal tar with the addition of PAN by means of electrospinning. The synthesized precursor fibres were thermally stabilized and carbonized at a temperature of 600 °C, which resulted in the formation of carbon fibres 200 to 1000 nm in diameter. It has been established that this method holds a high potential for obtaining ultrathin fibres with required size parameters.

Coke obtained from goudron after preliminary demetallization and desulphuration exhibits improved parameters: the mass fraction of volatile substances (6 %), ash content (0.25 %), sulphur content (1.45 %) and metal content (0.008 % V, 0.0014 % Ni, 0.0011 % Fe). With respect to the indicated parameters, the coke sample corresponds to the requirements to KZA coke grade of the first quality.

The results of the elemental analysis allow us to conclude that bitumen from the Munayly-Mola deposit may be used as an alternative resource for obtaining essential elements – vanadium, titanium, nickel, and zinc. The results of electron microscopic studies provided some knowledge on the structure and the nature of aggregation of the surface in asphaltene structure. It has been established that the structure of asphaltenes in natural bitumen is more ordered and non-amorphous. Asphaltene sample from the natural bitumen of the Munayly-Mola deposit is composed mainly of fragments of a rather dense film. Dense, coarse (or, less frequently, finer) particles may be present on film edges.

REFERENCES

1 Andreikov E. I., Dikovinkina Yu. A., Pervova M. G., Krasnikova O. V., Chemical reactions of coal tar pitch with model organic compounds, *Chemistry for Sustainable Developmen,* 2019, Vol. 27, No. 6, P. 556–560.
2 Buryukin F. A., Safin V. A., Kuznetsov P. N., Kositsyna S. S., Obukhova A. V., Kuznetsova L. I., Ismagilov Z. R., Comparative analysis of the properties of extractive and coal tar pitches, *Chemistry for Sustainable Development*, 2019, Vol. 27, No. 6, P. 568–575.
3 Sozinov S. A., Sotnikova L. V., Popova A. N., Ismagilov Z. R., Coal-tar pitch asphaltene powders as a precursor for the production of carbon graphite nanostructures material, *Chemistry for Sustainable Development*, 2019, Vol. 27, No. 6, P. 651–655.
4 Ongarbayev E. K., Doszhanov E. O., Mansurov Z. A., Processing heavy oil, oil residues and wastes, Kazakh University, Almaty, 2011. (In Russ.).
5 Tileuberdi Y., Mansurov Z., Ongarbayev Y., Tuleutaev B., Structural study and upgrading of Kazakhstan oil sand, *Eurasian Chem.-Technol. J.*, 2015, Vol. 17, No. 2, P. 173–179.
6 IUPAC. Compendium of Chemical Terminology, 2nd ed. (the "Gold Book"). Compiled by A. D. McNaught and A. Wilkinson. Blackwell Scientific Publications, Oxford, 1997. Online version (2019-) created by S. J. Chalk. [Electronic Resource]. URL: https://goldbook.iupac.org/ (accessed 22.01.2021).
7 Pat. GB 4933, 1880.
8 Pat. US 223398, 1880.
9 Donet J. B., Wang T. K., Rebouillat S., Peng J., Carbon Fibers, Marcel Dekker, New York, 1998.
10 Kim J. K., Mai Y. W., Engineered Interfaces in Fiber Reinforced Composites, Elsevier, Amsterdam, 1998.
11 Garside M. Forecast demand for carbon fiber worldwide 2010–2022, 2020 [Electronic resource]. URL: https://www.statista.com/statistics/380538/projection-demand-for-carbon-fiber-globally/ (accessed 22.01.2021).
12 Shakirzyanova G. I., Sladovskaya O. Yu., Sladovskiy A. G., Zimnyakova A. S., Nigmetzyanov N. S., Delayed coking as an efficient technology for deeper oil processing, *Vestn. Kazanskogo Tekhnolog. Un-ta*, 2017, Vol. 20, No. 14, P. 75–78. (In Russ.).
13 Kemalov R. A., Kemalov A. F., Tukhvatullina A. Z., Yusupova T. N., Effect of high-viscosity oils composition on coking process, *Ekspozitsiya Neft Gaz*, 2012, No. 7 (25), P. 22–26. (In Russ.).
14 Khayrutdinov I. R., Akhmetov M. M., Telyashev E. G., State and outlooks for the production of coke from oil raw

material, *Rossiyskiy Khim. Zhurn.,* 2006, Vol. 50, No. 1, P. 25–28. (In Russ.).
15 Kositsyna S. S., Buryukin F. A., Buza A. O., Melchakov D. A., Delayed coking of vacuum residue with a different composition and properties, *Fundament. Issledovaniya*, 2016, No. 6-2, P. 288–293. (In Russ.).
16 Varfolomeev D. F., Stekhun A. I., Raw Material for Coking and the Efficiency of Its Use, TSNIITEneftekhim, Moscow, 1987. (In Russ.).
17 Preparation of raw material and improvement of the technology for the production of oil coke for different purposes (Collection of Research Works), B. M. Ezhov (Ed.), Bashkir Research Institute for Oil Processing; Issue 18, TSNII Inform. i Tekhn.-Ekon. Issled. Neftepererab. i Neftekhim. Prom-sti, Moscow, 1979. P. 38-40. (In Russ.).
18 Pat. RF No. 2260616, 2005. (In Russ.).
19 Pat. RF No. 2079537, 1997. (In Russ.).
20 Pokhodenko N. T., Brondz B. I., Obtaining and Processing Oil Coke, Khimiya, Moscow, 1986. (In Russ.).
21 Pat. RF No. 2277117, 2006. (In Russ.).
22 Kharitonova E. Yu., Karaev A. R., Mordkovich V. Z., Maslov I. A., Kamenev A. A., Mitberg E. B., Kuzora I. E., Elshin A. I., Carbonization of heavy residues of different origin, *Petrol. Chem.*, 2007, Vol. 47, No. 4, P. 288–298.
23 Diyashev R. N., New capabilities of alkaline waterflooding and fire flooding for development of viscous, high-viscosity and heavy oil pools (according to foreign publications), *Neftyanoe Khozyaystvo*, 2009, No. 9, P. 102–106. (In Russ.).
24 Upreti S. R., Lohi A., Kapadia R. A., El-Haj R., Vapor extraction of heavy oil and bitumen: A review, *Energy Fuels,* 2007, Vol. 21, No. 3, P. 1562–1574.
25 Gates I. D., Chakrabarty N., Optimization of steam-assisted gravity drainage (SAGD) in ideal McMurray reservoir, *J. Canadian Petr. Tech.*, 2006, Vol. 45, No. 9, P. 54–62.
26 Gates I. D., Oil phase viscosity behaviour in expanding solvent steam-assisted gravity drainage, *J. Pet. Sci. and Eng.*, 2007, Vol. 59, P. 123–134.
27 Strausz O. P., Mojelsky T. W., Lown E. M., The molecular structure of asphaltene: An unfolding story, *Fuel*, 1992, Vol. 71, P. 1355–1363.
28 Frakman Z., Ignasiak T. M., Lown E. M., Strausz O. P., Oxygen compounds in Athabasca asphaltene, *Energy Fuels*, 1990, Vol. 4, No. 3, P. 263–270.
29 Fossen M., Kallevik H., Jakobsson J., Sjöblom J., A new procedure for direct precipitation and fractionation of asphaltenes from crude oil, *J. Dispersion Sci. Tech.*, 2007, Vol. 23, P. 193–197.
30 Menkovskiy M. A., Yavorskiy V. T., Technology of Sulphur, Khiniya, Moscow, 1985. (In Russ.).
31 Kaminski T. J., Wolf N., Wattana P., Mairal A., Classification of asphaltenes *via* fractionation and the effect of heteroatom content on dissolution kinetics, *Energy Fuels*, 2000, Vol. 14, No. 1, P. 25–30.
32 Mullins O. C., The modified Yen model, *Energy Fuels,* 2010, Vol. 24, No. 4 P, 2179–2207.
33 Akbarzadeh K., Hammami A., Kharrat A., Zhang D., Allenson S., Creek J. L., Kabir S., Jamaluddin A., Marshall A. G., Rodgers R. P., Mullins O. C., Solbakken T., Asphaltenes – Problematic but rich in potential, *Oilfield Rev.*, 2007, Vol. 19, P. 22–43.
34 Tileuberdi E., Sultanov F. R., Ongarbaev E. K., Tuleutaev B. K., Khaseinov K. A., Doszhanov E. O., Mansurov Z. A., Investigation of the structure and composition of asphaltenes precipitated from bitumen, Abstracts, X International Scientific Conference "Promising Technologies, Equipment and Analytical Systems for Materials Science and nanomaterials", Almaty, 2013, P. 342–348. (In Russ.).
35 Gabdullin M. T., Muratov M. M., Nazhipkyzy M., Investigation of the Composition and Structure of Asphaltenes of Natural Bitumen Precipitated from Petroleum Bituminous Rocks, in: White Book on Nanotechnologies, Z. A. Mansurov (Ed.), Almaty, 2018. (In Russ.).
36 Review of the Market of Coal Tar Pitch in FSU Countries (2nd edition), Moscow, 2010. (In Russ.).
37 Gadetskiy A., Technical proposal. Processing coal tar and pitch using low-power delayed coking installations, 2016. [Electronic resource]. URL: https://makston-engineering.ru/f/pererabotka_kamennougolnykh_smol_i_pekov_na_ustanovkakh_zamedlennogo_koksovaniya_maloi_moshchnosti.pdf (accessed 22.01.2021). (In Russ.).