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OBTAINING CARBON FIBERS BASED ON COAL TAR BY ELECTROSPINNING METHOD

Abstract. This research discusses the use of coal-processing wastes of the Shubarkol Deposit (Karaganda region, Kazakhstan) to produce valuable materials such as carbon fibers. Annually «Shubarkol Komir» JSC alone produces up to 35,000 tons of coal tar as byproduct. In this experiment, mesophase pitch was obtained by coal tar heat treatment at 200 ^oC. By cracking mesophase pitch into the pieces with the addition of poly (methyl methacrylate) as fiber-forming material and 1,2-dichloroethane as solvent, the spinnable solution was prepared. The elemental analysis of the mesophase pitch showed that the heat treatment up to 200 ^oC does not contribute to the full elimination of sulfur containing components that influence the forming of mesophase. From the Raman spectra of the pitch, the D peak appearance at ~ 1370 cm^{-1} and G peak at ~ 1600 cm^{-1} responsible for carbon products. Carbon fibers with an average diameter of 2.5-3.3 μm were obtained by electro-spinning technique in laboratory settings.

Keywords: coal tar, pitch, electrospinning, carbon fibers.

Coal is primarily used and has been known for thousands of years as a fuel. Moreover, the invention of the steam engine also increased the coal consumption. As of 2018, coal remains an important fuel resource as it supplied about 25% [1]. The product of coal pyrolysis - coal coke - for its excellent efficiency in adsorption and process ability has found application in chemical industry, steel and cast-iron manufacturing, *etc*. During coal coking process, coal gas, aromatics mixture, ammonia water and coal tar are extracted. Coal tar pitch is a possible precursor for carbon fiber production [2,3]. By further coal tar processing, valuable products such as benzene, toluene, xylenes, *etc*., as well as sleeper impregnation oil, plastics, pitched-based electrodes, binding pitch, carbon fibers, *etc*. might be produced [4,5].

Republic of Kazakhstan, according to the British Petroleum Statistical Review 2020, in terms of proven coal reserves, ranked as 10^{th} in the world (2.4% of global reserves) and the 9^{th}among countries in terms of coal output (2.08% of world production) [6]. The production of this huge amount of coal requires the development of a waste-free technology based on its deep processing. Spinnable mesophase pitch could be converted into target products with high economic demand such as carbon fibers. The production of carbon fibers finds a wide application in medicine, biotechnology, energy, in treatment facilities, in construction to obtain composite materials, aerospace *etc*. [7].

A product of coal tar processing is pitch. The two basic types of pitch are anisotropic (mesophase) and isotropic (non-mesophase). The commonly used method for converting isotropic pitch into mesophase pitch by pyrolysis. Manufacture of mesophase by pyrolysis involves heating it under an inert gas such as nitrogen for approximately 40h. The optically isotropic material is transformed into an optically anisotropic liquid stage mesophase by the heat treatment [8].

Carbon fibers are promising materials that outperform other materials in their unique characteristics such as high chemical resistance, high tensile strength, light weight and low coefficient of thermal expansion [9-11]. These fibers could be obtained by electrospinning method. The technique of electrospinning is a complex physicochemical process that depends on many factors and, primarily, on the choice of the precursor and its preparation [12,13]. Polymers are the most widely used fiber-forming materials. In our research we used poly (methyl methacrylate) as fiber-forming material as common and available polymer. The main goal of this work was to obtain fibers from coal-processing wastes such as coal tar using electrospinning method [14].

The physicochemical characteristics of the feedstock and the temperature regime of its processing affect the occurrence of mesophase changes. The quality of the pitch is determined by the presence of sulfur-containing components and insoluble residues [15,16].

In this research, carbon fibers were produced with the thinner diameters of 2.5-3.3 μm by electrospinning method. The transition of carbon pitch into the mesophase structure occurs through the formation of an intermediate isotropic-mesophase structure under the influence of temperature. Coal tar heat treatment up to 200°C led to the complete removal of sulfur content in mesophase pitch. The process of the mesophase formation is influenced by the initial composition of the original pitch and also by the presence of heteroatoms in the pitch content. The heteroatoms in the molecule of the resulting pitch affects the formation of the mesophase itself. An increase in the content of oxygen and sulfur in obtained pitch affects the graphitability of the system, which sharply decreases, for example, with a sulfur content of 5-9%, the formed carbon does not form a graphite structure. This effect of sulfur is explained by the occurrence of reactions of dehydrogenation and crosslinking of layers of macromolecules in crystallites and, as a result, by a decreese in their mobility [17].

Carbon fibers are an extremely important carbon material, which are mostly used for the production of composite, heat-shielding, chemically resistant and other types of carbon fiber reinforced plastics. Fibers based on poly(acrylonitrile) are relatively expensive. The solution to the problem is to develop a technology for the production of mesophase pitch as a raw material for the production of high-modulus, high-strength carbon fibers based on cheap raw material as coal tar for producing carbon fibers with high physical and mechanical properties.

EXPERIMENTAL PART

Materials. Coal tar formed during the coking of Shubarkol deposit coals was used. Some characteristics of coal tar: viscosity at 80 °C – 3.0 conventional degrees, density at 20 °C – 1060 kg/m^3, coking capacity – 2.0-3.5%; flash point – 115 °C; softening temperature – 65 °C. As a solvent, we used 1,2-dichloroethane(Sigma-Aldrich, Germany). Poly (methyl methacrylate) (Sigma-Aldrich, Germany) was used as a binder.

Methods of Analysis. To determine the surface structure and morphology of the obtained carbon fibers we used Quanta 200i 3D scanning electron microscope (FEI Company, USA); accelerating voltage 30 kV (provided by the National Nanotechnology Laboratory at the al-Farabi Kazakh National University). For registration of Raman spectra, we used an Integra Spectra probe-scanning microscope by a laser with a wavelength of 473 nm. The sample was supported as a thin replica on a glass substrate. The CCD3spectral detector had the wavelength of K = 632.8 nm (20 mV) with the spectral line width of 2.08 cm^{-1}. Device parameters: power 35 mW, solid-state laser, grating600/600 (provided by the National Nanotechnology Laboratory at the al-Farabi Kazakh National University).

Preparation of mesophase pitch. Mesophase pitch was obtained by coal tar heat treatment at 200 °C with a heating rate of 15 °C/min by holding at 200 °C for 3 hours in an argon medium. Argon consumption was 80 cm^3/min.

The heat treatment was conducted in a quartz reactor (figure 1) with diameter of 30 mm. Then the reactor was cooled and coal tar pitch was removed.

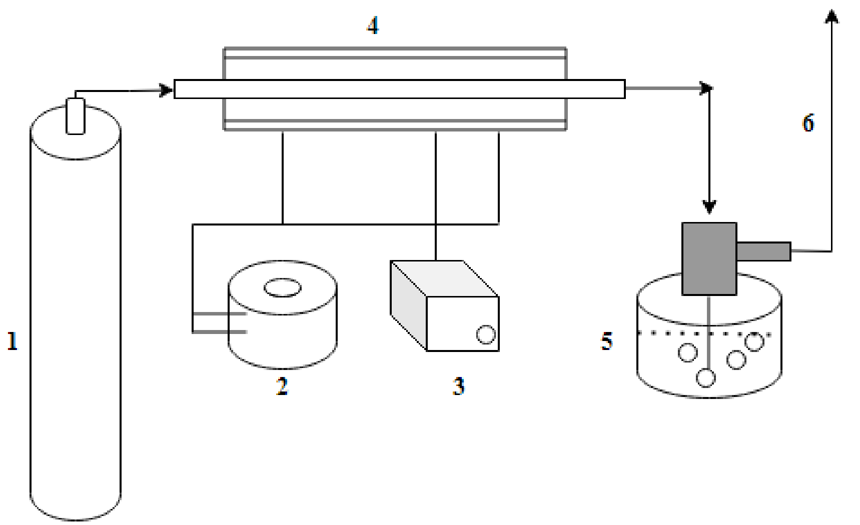

Figure 1 – Schematic diagram of laboratory installation for coal tar pitch obtaining:
1 - gas cylinder with argon; 2 - laboratory autotransformer; 3 – thermostat;
4 – quartz reactor; 5 – gas outlet flask controller; 6 – gas outlet

Heat treatment of the original coal tar turned it from a viscous state to a solid one, and the final product increased in volume. Removal of low-boiling fractions in the form of vapours led to the formation of mesophase pitch with a porous structure as a friable spongy material.

Preparation of carbon fibers. The electrospinning method as a complex physicochemical process depends on many factors and, largely, on the choice of the precursor and its preparation. Polymers are the widely used fiber-forming materials. In our research we used poly(methyl methacrylate) as a binder.

The technological scheme of carbon fibers production from coal tar consists of the following stages: preparation of raw materials at 200 °C; dissolving of pitch and poly (methyl methacrylate) in 1,2-dichloroethane; electrospinning process; stabilization of the obtained fibers in an oxygen atmosphere, carbonization in an inert atmosphere.

For the process of electrospinning, the obtained pitch was crushed and 1,2-dichloroethane was added. For uniforming, the resulting mixture was placed for 25 minutes in an ultrasonic bath. Poly (methyl methacrylate) as a binder was also mixed with 1,2-dichloroethane and put in an ultrasonic bath for 25 minutes. Their common mixture in 1:1 ratio was placed in an ultrasonic bath for 35 minutes.

The process of electrospinning (figure 2) occurs when the electric field among the electrodes and the electrostatic forces between the charges accumulated in the spinning solution overcome the surface tension of the solution. The action of the repulsive force between the same charges stretches the viscoelastic flow of the

Figure 2 – Electrospinning installation

molding solution. Figure 6 shows the obtained fibers with a diameter of 2.5-3.3 μm, where the structural elements take the form of filamentary formations with some defects.

RESULTS AND DISCUSSION

A sample of coal tar before and after the heat treatment process was weighed to determine the post-treatment mass loss. It was found that the weight loss during heat treatment at 200 °C was 50% of the original weight. This is because heat treatment leads to the removal of volatile fractions from coal tar.

The results of the elemental analysis showed the elemental composition of obtained coal tar pitch composed by weight percentage (wt.%): C – 91,04%; O – 8,72%; S – 0,24%. Figure 4 shows the optical microscopy image of coal tar pitch after the heat treatment at 200 °C.

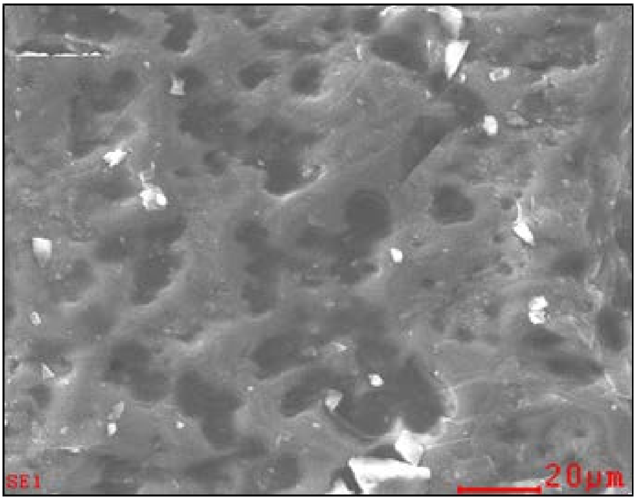

Figure 4 – Optical microscopy image of coal tar pitch after heat treatment at 200 °C

The process of mesophase formation depends not only on the initial pitch composition, but also on the presence of heteroatoms in pitch molecules. An increase in the content of oxygen- and sulfur-containing compounds in pitch reduces the graphitability of the system and the resulting carbon does not form a graphite structure. This effect of the sulfur-containing component is explained [16] by the occurrence of dehydrogenation and cross-linking of macromolecule layers in crystallites and, as a result, by a decrease in their mobility.

Figure 5 shows a Raman spectrum, which makes it possible to evaluate the effect of heat treatment on the degree of graphitization of the initial coal tar, where the peaks D and G characterize the carbon materials [17]. The peak position of G (~1600 cm^{-1}) with the I_G intensity of 600 units indicates the formation of nano-crystalline mesophase centers; the D peak at ~1370 cm^{-1} with the I_D intensity of 393. The intensity of G is higher than D indicating the less disorder due to defects.

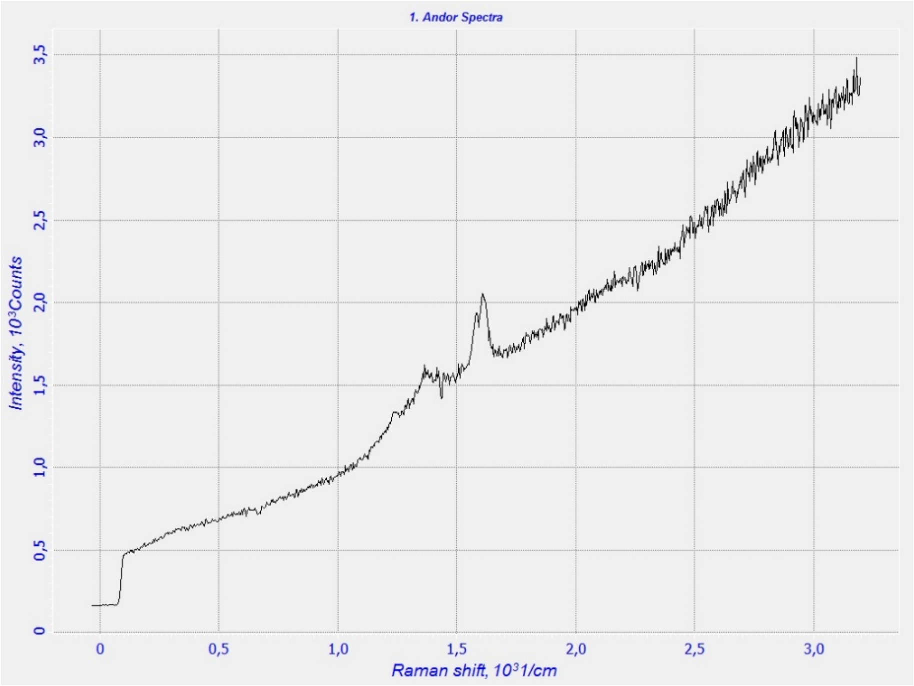

Figure 5 – Raman spectrum of coal tar pitch pyrolyzed at 200°C

SEM image analysis of carbon fibers (figure 6) obtained from coal tar pitch showed that the diameters of the obtained short carbon fibers were in average 2.5-3.3 μm.

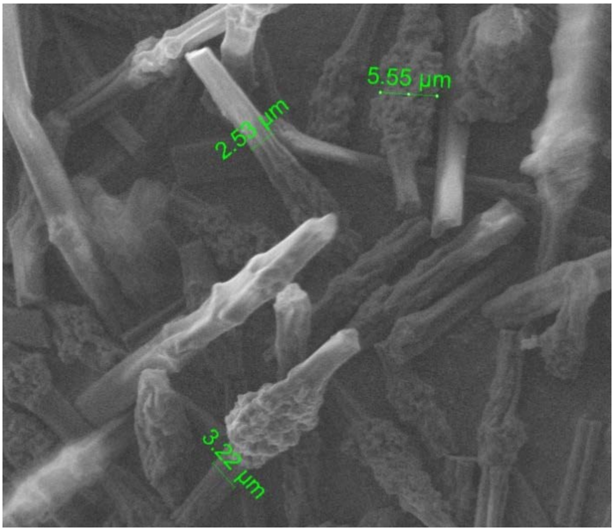

Figure 6 – Electron microscopic images of carbon fibers

To improve the strength characteristics, the resulting fibers were subjected for oxidation in the air stream at 200 ºC for 1 hour. The carbonization of the obtained fibers was carried out in a nitrogen atmosphere. The carbonized fibers were then graphitized under tension by passing the electric current through them while electrical heating occurred.

The interest in the manufacture of carbon fibers is due to the fact that the mechanical properties of these materials, such as tensile strength, bending and compression, increase the elastic moduli with a decrease in fiber diameter and achieve a theoretical limit when the nanoscale level is reached[18].

Conclusion. Our research confirms the possibility of using Shubarkol Deposit coal-processing wastes to manufacture useful materials of high added value, such as carbon fibers, by means of electrospinning. Finally, we have obtained carbon fibers with a diameter of 2.5-3.3 μm in laboratory settings.

This technique allows useful materials to be produced from waste from coal mining. It would be possible to obtain useful materials for further use in the manufacture of carbon fibers outside laboratory conditions through the processing of Shubarkol coals into pitch. Further process changes are needed for industrial-scale applications.

REFERENCES

[1] The official web site of the International Energy Agency (IEA) https://www.iea.org/

[2] Kim B.J., Kil H., Watanabe N., Seo M.H., Kim B.H., Yang K.S., Kato O., Miyawaki J., Mochida I., Yoon S.H. // Curr Org Chem. 2013, 17, 1463. http://doi.org/10.2174/13852728113171300l3

[3] Zhu J., Park S.W., Joh H.I., Kim H.C., Lee S. // Carbon Lett. 2013, 14, 94. http://doi.org/10.5714/CL.2013.14.2.094

[4] https://www.erg.kz/ru/news/693

[5] Derbyshire F., Andrews R., Jacques, D. Jagtoyen M., Kimber G., Rantell T.. // Fuel. 2001, 80, 345. http:/doi.org/10.1016/S0016-2361 (00)00099-5

[6] https://www.bp.com/content/dam/bp/business-sites/en/global/corporate/pdfs/energy-economics/statistical-review/bp-stats-review-2020-full-report.pdf

[7] Forintos N., Czigány T. Composites Part B: Engineering, 2019, 162, 331. https://doi.org/ 10.1016/j.compositesb.2018.10.098

[8] Aldosari S.M., Khan M., Rahatekar S. // Journal of Materials Research and Technology. 2020, 9(4), 7786. http://doi.org/10.1016/j.jmrt.2020.05.037

[9] Doshlov O.I., Kondrat'ev V.V., Ugap'ev A.A. et al. // Coke Chem. 58, 32-38 (2015). https://doi.org/10.3103/S1068364X15010020

[10] Frank E., Steudle L.M., Ingildeev D., J. M. Spörl, M. R.:Buchmeiser, AngewChemInt Ed., 2014, 53, 5262. http://doi.org/10.1002/anie.201306129

[11] Yang K.S., Kim B.H., Yoon S.H. // Carbon Lett. 2014, 15, 162. http://doi.org/10.5714/CL.2014.15.3.162

[12] Mochida I., Toshima H., Korai Y., Matsumoto T. // J Mater Sci. 1988, 23, 670. https://doi.org/10.1007/BF01174704

[13] Zhiyuan C., He J., Fengwen Z., Yuexing L., Yong L., Huilin Y. // J. Serb. Chem. Soc. 2014, 79, 587. http://doi.org/10.2298/jsc130702150z

[14] Yoo M.J., Ko H.J., Lim Y.S., Kim M.S. // Carbon Lett. 2014, 15, 247. http://dx.doi.org/10.5714/CL.2014.15.4.247

[15] Yermagambet B., Kazankapova M., Nauryzbaeva A., Mansurov Z., Smagulova G., Kaidar B. // News of the NAS of RK. Ser. of Geo. Tech. Sc. 2019, 4, 436. https://doi.org/10.32014/2019.2518-170X.101

[16] Park S. Carbon Fibers, Springer Netherlands, Incheon, Republic of Korea (South Korea). 2015, 337. http://dx.doi.org/10.1007/978-94-017-9478-7

[17] Filippov M.M. Ramanovskaya spektroskopiya kak metod izucheniya gluboko ugleficirovannogo organicheskogo veshchestva // Russia, Petrozavodsk, 2014, 1, 115. http://igkrc.ru/assets/publication/trudy-2014-1-p115-134.pdf

[18] Severyuhina A.N., Svenskaya Yu. I, Gorin D.A. // Izvestiya Saratovskogo universiteta. Novaya seriya. Seriya Fizika. 2013, 13(2), 67.

Резюме

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КӨМІР АШЫҒЫНДА ЭЛЕКТРОСПИНДЕЛУ ӘДІСІ МЕНЕН КӨМІРТЕК ЖИБАСЫН ӨНДІРУ

Бұл зерттеуде Шұбаркөл кен орнының (Қарағанды облысы, Қазақстан) көмір өндірісінің қалдықтарын көміртекті талшықтар сияқты құнды материалдар өндірісінде қолдану мүмкіндігі қарастырылған. «Шұбаркөл Көмір» АҚ жыл сайын қосымша өнім ретінде 35 мың тоннаға дейін көмір шайыр өндіреді. Біздің зерттеуімізде мезофаза қадамы көмір шайырларын 200 °C температурада өңдеу арқылы алынды. Алынған мезофаза қадамын талшық түзуші материал ретінде поли (метилметакрилат) және еріткіш ретінде 1,2-дихлорэтан қосып фракцияларға бөлшектеу арқылы электрошығуға арналған ерітінді дайындалды. Мезофаза қадамының элементтік талдауы көрсеткендей, 200°C дейінгі термиялық өңдеу мезофазаның түзілуіне әсер ететін күкірті бар компоненттердің толық кетуіне ықпал етпейді. Шайырдың Раман спектрлерінен D шыңы 1370 см$^{-1}$-де, ал G шыңы шамамен 1600 см$^{-1}$ деңгейінде байқалатынын көруге болады, бұл көміртек компоненттерінің бар екендігін көрсетеді. Зертханалық жағдайда көміртекті талшықтар орташа диаметрі 2,5-3,3 мкм болатын электрлі іиру арқылы алынды.

Түйін сөздер: көмір шайыры, шайыр, электроспиринг, көміртекті талшықтар.

Резюме

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ПОЛУЧЕНИЕ УГЛЕРОДНЫХ ВОЛОКОН НА ОСНОВЕ КАМЕННОУГОЛЬНОЙ СМОЛЫ МЕТОДОМ ЭЛЕКТРОСПИННИНГА

Рассматривается возможность использования отходов угледобычи месторождения Шубарколь (Карагандинская область, Казахстан) в производстве ценных материалов, таких как углеродные волокна. Ежегодно АО «Шубарколь Комир» производит до 35 тыс. т каменноугольной смолы в качестве побочного продукта. В иссле-

довании мезофазный пек был получен термообработкой каменноугольной смолы при 200 °С. Путем дробления полученного мезофазногопека на фракции с добавлением поли (метилметакрилата) в качестве волокнообразующего материала и 1,2-дихлорэтана в качестве растворителя приготовлен раствор для электроспиннинга. Элементный анализ мезофазного пека показал, что термообработка до 200°С не способствует полному удалению серосодержащих компонентов, влияющих на образование мезофазы. Из спектров комбинационного рассеяния смолы видно, что пик D наблюдается при 1370 см$^{-1}$, а пик G – около 1600 см$^{-1}$, что указывает на присутствие углеродных составляющих. Углеродные волокна в лабораторных условиях были получены со средним диаметром 2,5-3,3 мкм методом электроспиннинга.

Ключевые слова: каменноугольная смола, пек, электроспиннинг, углеродные волокна.

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