ЕҢБЕК ҚЫЗЫЛ ТУ ОРДЕНДІ
«Ә. Б. БЕКТҰРОВ АТЫНДАҒЫ
ХИМИЯ ҒЫЛЫМДАРЫ ИНСТИТУТЫ»
АКЦИОНЕРЛІК ҚОҒАМЫ

ҚАЗАҚСТАННЫҢ ХИМИЯ ЖУРНАЛЫ

ХИМИЧЕСКИЙ ЖУРНАЛ КАЗАХСТАНА

CHEMICAL JOURNAL of KAZAKHSTAN

АКЦИОНЕРНОЕ ОБЩЕСТВО
ОРДЕНА ТРУДОВОГО КРАСНОГО ЗНАМЕНИ
«ИНСТИТУТ ХИМИЧЕСКИХ НАУК
им. А. Б. БЕКТУРОВА»

4 (72)

ОКТЯБРЬ – ДЕКАБРЬ 2020 г.

ИЗДАЕТСЯ С ОКТЯБРЯ 2003 ГОДА

ВЫХОДИТ 4 РАЗА В ГОД

АЛМАТЫ
2020

UDC 662.749

A. M. IMANGAZY[1,2], B. KAIDAR[2]

[1]Bekturov Institute of Chemical Sciences, Almaty, Republic of Kazakhstan
[2]Kazakh National University named after al-Farabi, Almaty, Republic of Kazakhstan

PROSPECT COAL PROCESSING TECHNOLOGIES

Abstract. A huge amount of coal mined from Kazakhstan deposits requires the development of a waste-free technology based on deep processing . One of the intermediate products of coking coal processing is coal tar. As a product of processing of coal tar, coal tar pitch can be converted into target products with great economic demand. The production of fiber based on them will find wide application in medicine, biotechnology, energy, in treatment facilities, in construction for obtaining composite materials, etc. And to adjust the production of these products, new enterprises are needed near coal deposits. This, in turn, will open up prospects and improvement of new technologies for in-depth processing of domestic raw materials.

Keywords: coal, deepprocessing, coal tar, pitchcomposite materials.

Coal is a raw material for the chemical industry. The most important branch of coal processing is the coke-chemical industry. During coking, which is carried out by heating coal to 900-1100 °C without air access, a number of products are obtained: coke, gas, coal tar, ammonia water, etc. [1].Coal coking is a widespread technological process, consisting of the following stages: preparation for coking, coking itself, capturing and processing volatile products [2].

Coal tar is a mixture of predominantly bi- and polycyclic aromatic hydrocarbons, as well as polycyclic systems with heteroatoms in the rings. The sum of these substances is about 95% of the coal tar components. In addition to them, the coal tar contains 1-2% phenols, 2-3% organic bases, mainly a number of quinoline and acridine. Coal tar is a unique, unparalleled source of raw materials that currently covers more than 95% of the world's demand for condensed aromatic and heterocyclic compounds. The total number of substances in the coal tar is about 10 thousand, of which more than 500 substances have been identified. Approximately 50% of the coal tar is a non-boiling fraction - pitch, which is a mixture of polycondensed polycyclic aromatic hydrocarbons and their polymerization products [3].

The inevitable product of high-temperature destruction of the organic mass of coal coking is coal tar, with a yield of 3-4% of the weight of the coal charge. Coal tar contains up to 10.000 compounds, ~ 300 of whichhave been identified so far. Most of the compounds in tar are contained in amounts of less than 1% [4].

Chemists have long been interested in coal tar. In 1819, naphthalene was found in the coal tar, later anthracene (1833), aniline, phenol, quinoline (1834), benzene (1845), pyridine (1854). For a long time, coal tar was a burdensome by-product and was used as a fuel. The growth in coke production has led to the need to search for new areas of application for coal tar [4].

Julius Rutgers, who built a coal tar distillation plant near Berlin, took the first decisive step in 1860. By distilling the coal tar, they began to obtain coal oils for the impregnation of railway sleepers. By the end of the 19th century and in the 20th century, with the development of the organic chemistry industry, coal tar became the most important source for the production of organic substances [4].

In the second half of the twentieth century, sharp changes took place in the technology of processing coal tar with a widespread rejection of periodic schemes and a transition to continuous ones with the maximum extraction of target products from fractions, both marketable products and as raw materials for the organic synthesis industry [4].

Currently, the decrease in the export potential of coals from Kazakhstan deposits connected with the adoption of the Russian Federation Government decree from January 24, 2012, which provides the consumption replacement of the Ekibastuz coal by Kuznetsk coal from Russian power stations. In addition, some of the Russian thermal power plants switched to natural gas combustion and the new implemented projects moved to Kuznetsk coals[5].

In 2020, Kazakhstan ranked as 10th in the world in terms of proven coal reserves (2.4% of global reserves) and the 9th largest in the world in terms of output (2.08% of world production), according to the BP Statistical Review of World Energy 2020 [6].

Before coal tar processed, considerable attention is given to preliminary preparation for the purpose of its dehydration, desalting and ash removal, including the destruction of dispersed systems and removal of decomposition products - ash,water with salts dissolved in it, as well as salts contained in the coal tar. De-ash removal of the coal tar consists in the removal of the dispersed phase by decanters, vibro-separators, and centrifuges, which can significantly reduce the water content in it. The salts contained in the coal tar and above the coal tar water have a very complex composition. The predominant component (80% by weight of salts) is ammonium chloride. There are also other ammonium salts such as thiocyanates, sulfites, sulfates, cyanides, etc., which necessitates the removal of water without evaporation by other methods: centrifugation, chemical and electrical demulsification [4].

Coal tar is a unique source of raw materials that currently covers more than 95% of the world's demand for condensed aromatic and heterocyclic compounds.It is polyazeotropic-polyeutectic system, where intermolecular interactions of its components lead to the formation of numerous azeotropes, eutectics, mixed crystals. Consideration of coal tar as a physicochemical system opens up new opportunities for studying its properties and improving the technology of its processing. The production of about 350 million tons of coke per year in the world is accompanied by the output of almost 14 million tons of crude coal tar. However, not all of the coal tar is available for recycling, as some coke ovens in the USA and China operate in a non-chemical recovery process and the coal tar is burned directly in the coke production process. The most important features of polycyclic compounds are their thermal stability and stability to oxidation, as well as toxicity to micro-

organisms. This allows the use of technical mixtures based on the products of processing of coal tar for the manufacture of various protective coatings and antiseptic oils that protect wood [3].

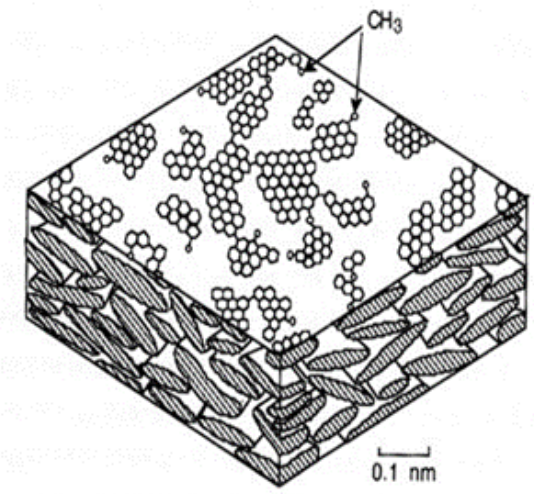

Figure 1 – Schematic model of carbon mesophase

One of the ways to process coal tar is to produce pitch (figure 2). As we know, there are two main types of pitch: isotropic (ordinary non-mesophase) and anisotropic (mesophase). Mesophase pitches are obtained by heat treatment, as a result of which chemical reactions occur with a change in structural characteristics - the formation of mesophases. Heat treatment is carried out in a wide temperature range in an inert atmosphere of nitrogen, argon or helium [7]. The formation of liquid crystal structures (mesophase) occurs in the temperature range 300-500 ºC [8]. Mesophase crystallites are composed of condensed high molecular weight aromatic compounds with an interplanar spacing of 0.35 nm. The course of mesophase transformations depends on the physicochemical characteristics of the feedstock and the temperature regime of processing. An important characteristic of pitch is the content of sulfur and insoluble residues, which determine the quality of the pitch [9]. The preparation of mesophase pitches with a high degree of aromaticity is described in [10]. In this work, the authors presented the results of studies on the production of polyaromatic coal tars by extraction of low-temperature soot. The quality of mesophase pitches and their fiber-forming properties are determined by the degree of aromaticity of the initial coal tar, the presence of highly condensed structures in it [11]. A schematic model of the carbonaceous mesophase is shown in Figure 1 [12]. The transition of carbon pitch to the mesophase structure occurs through the stage of formation of an intermediate istropic-mesophase structure under the influence of temperature. The transition is accompanied by the removal of gaseous products and a change in the H/C ratio [13].

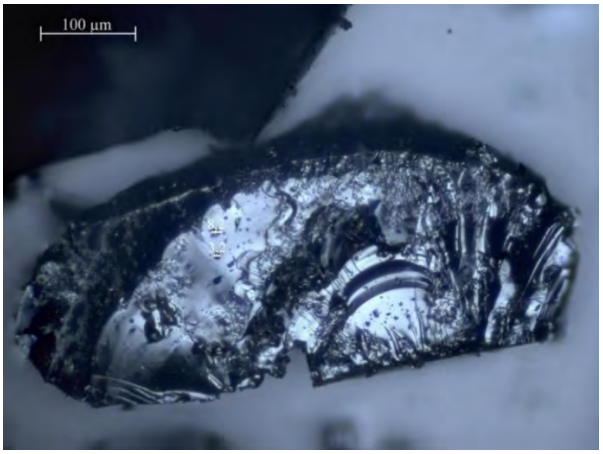

Figure 2 – Micrograph of coal tar pitch

Mesophase pitches are used as raw materials for high-modulus carbon fibers [14, 15]. The work [16] presents the results of studies on the production of carbon fibers by drawing mesophase pitch from melts (figure 3). The fiber diameter was 8-22 μm with an average tensile strength and elastic modulus of 800-1200 MPa and 130-160 GPa, respectively. On the basis of mesophase pitches, monolithic carbon structures with a developed specific surface area and a strict hierarchical pore structure are obtained [17]. In [18], the authors presented the results of industrial testing of the technology for compounding coal tar and oil refined product. The released pilot batch of the compound pitch was characterized by a lower content of benzo(a)pyrene and was used in the production of the pinned anode mass.

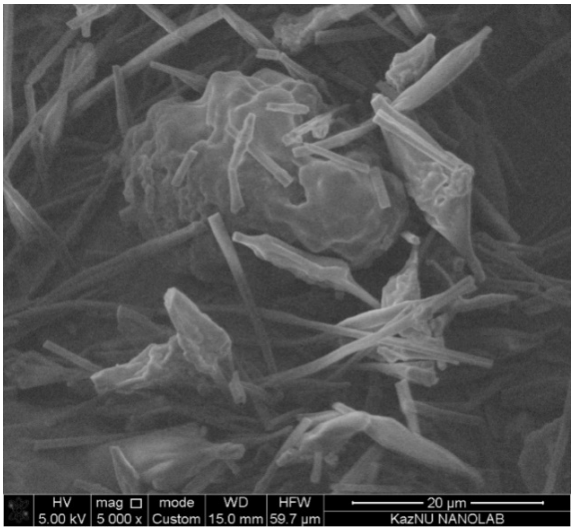

Figure 3 – SEM images of fibers based on coal tar pitch

The most important indicators of the quality of the coal tar from the point of view of its processing are the content of components insoluble in quinoline, moisture content and ash content.

These indicators affect:

1) the number of stages of coal tar purification;

2) the quality of the pitch as a distillation residue.

Over the past 15 years, there have been two major changes in the quality of coal tar. First, the content of components insoluble in quinoline decreased[3]. This is due to the shutdown of old coke oven batteries with poor sealing of the coking chamber doors. Secondly, the solids content of the coal tar has increased due to the use of younger and finer coals. In addition, the latest coke oven batteries are equipped with powerful gas extraction systems to reduce harmful emissions into the atmosphere, which increases the carryover of solids into the tar stream. These changes have caused some difficulties for consumers of coal tar fractionation products, as they require pitch with a high content of components insoluble in quinoline and a low content of unbound carbon. At present, a wide research program has been implemented and new methods have been developed to ensure high binding properties of pitches for the production of electrodes.

Conclusion. Our country, possessing vast reserves of coal, must develop new ways of processing the released reserves of coal. The processing of local coals into coal tar and the further production of coal tar pitch opens up an opportunity for our country to develop new technologies, such as the production of nanofibers. The interest in nanofibers production caused by the fact that the mechanical properties of these materials, such as tensile strength, bending and compression, the elastic moduli increase with decreasing fiber diameter and accomplish a theoretical limit when reaching the nanoscale level.

REFERENCES

[1] Kireev V.A., Vatulyan K.S., Taube P.R., Filippova K.I., FinogenovM.Yu., Khigerovich M.I. Chemistry Course. Part 2 // Higher School Publishing House. 1975. 15 p.

[2] Coke and coking // Encyclopedic Dictionary of a Young Chemist. 2nd ed. / Comp. V. A. Kritsman, V. V. Stanzo. M.: Pedagogy, 1990. P. 117-118.

[3] Pavlovich O.N. Composition, properties and prospects of processing of coal tar: textbook. Yekaterinburg. 2006. 41 p.

[4] Oshchepkov I.A., Chenchenko I.M. Features of formation and processing of coal tar // Scientific journal «Bulletin of the Kuzbass State Technical University». 2009. № 2. P. 78-82.

[5] The official website of government of the Russian Federation // http://archive.government.ru/special /gov/results/18245/

[6] The official website of the British Petroleum oil company // Statistical Review of World Energy // BP Statistical Review of World Energy 2020: 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] Prokhorov V.Yu. Optimization and ways of implementing the reinforcement of carbon fibers in the design and manufacture of carbon-carbon composite materials // Proceedings of the international symposium reliability and quality. 2007. № 2. P. 92-93.

[8] Ozel M.Z., Bartle K.D. Production of mesophase pitch from coal tar and petroleum pitches using supercritical fluid extraction // Turk Journal Chem. 2002. Vol. 26. P. 417-424.

[9] Kiselkov D.M., Moskalev I.V., Strelnikov V.N. Carbon materials based on coal tar pitch // Bulletin of the Perm Scientific Center. 2013. № 2. P. 13-22.

[10] Aldashev R.A., Vasyutinskaya A.G., Tutkabaeva T.T., AmerikYu.B., Mansurov Z.A. Thermopolycondensation of resin for extraction of low-temperature soot // Neftekhimiya. 1995. № 1(35). P. 62-66.

[11] Amerik Y.B., Plate N.A. Deep conversion of heavy oil fractions through mesomorphic structures // Neftekhimiya. 1991. № 3(31). P. 355-378.

[12] Zimmer J.E. and White J.L. Disclination structures in carbonaceous mesophase // Advances in Liquid Crystals. 1982. Vol. 5. P. 157-2013.

[13] Whitehouse S. and Rand B. Pitch-mesophase-carbon transformation diagrams for a variety of pitches // 17th Biennial Conf. on Carbon on Carbon (Amer. Carbon Soc.). Lexington, 1985. P. 159-160.

[14] Patent US 20040096388 A1. Mesophase pitch-based carbon fibers with carbon nanotube reinforcements / OgaleAmod A., Edie Dan D., Rao Apparao M. 2004.

[15] Jiyoung Kim, Ui-Su Im, Byungrok Lee, Dong-Hyun Peck, Seong-Ho Yoon, and Doo-Hwan Jung. Pitch-based carbon fibers from coal tar or petroleum residue under the same processing condition // Carbon Letters. 2016. Vol. 19. P. 72-78.

[16] Yue Zh., Liu Ch., Vakili A. Meltblown solvated mesophase pitch-based carbon fibers: fiber evolution and characteristics // C (Carbon Research Journal). 2017. № 3(26). 14 p.

[17] Adelhelm Ph., Cabrera K. and Smarsly B.M. On the use of mesophase pitch for the preparation of hierarchical porous carbon monoliths by nanocasting // Sci. Technol. Adv. Mater. 2012. № 13. 8 p.

[18] Marakushina E.N., Frizorger V.K., Pingin V.V., Andreykov E.I. Obtaining and industrial testing of a compound oil-and-coal binder at JSC RUSAL KRASNOYARSK // Izvestiyavuzov. Non-ferrous metallurgy. 2016. N 4. P. 17-22.

Резюме

А. М. Иманғазы, Б. Қайдар

КӨМІРДІ ӨҢДЕУДІҢ
ПЕРСПЕКТИВТІ ТЕХНОЛОГИЯЛАРЫ

Қазақстандық кен орындарынан мол өндірілген көмір осы салада қалдықсыз технологияны пайдаланып, отандық көмірді терең өңдеуге негізделген жаңа технологияны дамыту мүмкіндігін қажет етеді. Кокстелетін көмірді өңдеу өнімдерінің бірі – тас көмір шайыры. Тас көмір шайырының қалдығы, яғни қағы экономикалық тұрғыда үлкен сұранысқа ие құндылығы жоғары қосымша өнімдерге айналдыруға болады. Мысалы, тас көмір шайыры қалдығынан талшықтар, медициналық препараттар мен қатар биотехнология, энергетика, тазарту жүйелерінде, құрылысқа қажетті композициялық материалдар және т.б. бұйымдар алуға болады.

Көмір шикізатының көптеп өндірілуіне байланысты, кен орындарының жанынан жаңа кәсіпорындарды дамыту мүмкіндігі ашылады. Бұл өз кезегінде экспорттық шектеулерді реттеп, әлеуметтік шиеленісті төмендетеді және технологияның жаңа саласының Қазақстанда өркендеуіне жол ашады.

Түйін сөздер: көмір, терең өңдеу, көмір шайыры, шайыр, композит материалдар.

Резюме

А. М. Иманғазы, Б. Қайдар

ПЕРСПЕКТИВНЫЕ ТЕХНОЛОГИИ
ПЕРЕРАБОТКИ УГЛЯ

Огромное количество углядобытое из казахстанских месторождений требует развития безотходной технологии на основеих глубокой переработки.. Одним из промежуточным продуктом переработки коксующегося угля является каменноугольная смола. Как продукт переработки каменноугольной смолы, каменноугольный пек может быть преобразован в целевые продукты с большим экономическим спросом, Проозводство волокна на основе их найдут широкое применение в медицине, биотехнологии, энергетике, в очистных сооружениях, в строительстве для получения композитных материалов и т.д. И для наладки производства названных продукций необходимы новые предприятия вблизи угольных месторождений. Это в свою очередь, откроют перспективы и совершенствования новых технологии углубленной переработки отечественного сырья

Ключевые слова: уголь, глубокая переработка, каменноугольная смола, пек, нановолокна.