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IPOCC INNOVATION R&Ds IN THE FIELD OF COAL CHEMISTRY

The paper presents a brief historical review and innovation R&Ds of the IPOCC Department for Coal Chemistry. These R&Ds deal with coal mine exploitation problems, prevention of spontaneous combustion, dust control in mines, structural chemical features of coal with different genesis and stages of metamorphism and new methods for their modification and rational use. The methods for obtaining inexpensive sorbents from Ukrainian raw materials (including carbon containing waste) have been proposed. The problems of modern coal chemistry science studied in the IPOCC have been outlined.

Keywords: coal, structure, modification, thermolysis, nanoporous sorbents, and coke.

The fundamental coal chemistry in Donbas started with the establishment of the L.M. Litvinenko Institute of Physical, Organic and Coal Chemistry of the NAS of Ukraine (IPOCC) and the elaboration of physical and chemical theory of dust purging of the air when developing and operating the coal mines and deposits [1, 2]. The results of the abovementioned research have been successfully used for preventing contamination with other dusty aerosols. The mathematical models designed by *V. Saranchuk, V. Kachan, V. Rekun, and A. Maslov* have proved themselves to be fitting for filtration of wide range of dusty aerosols. Their results have been generalized in several monograph studies and applied widely.

The schools of *R. Kucher* and *V. Saranchuk* under the Institute deal with fundamental research of oxidation and self-ignition of coal and natural dumps in order to find a way to prevent and to remedy these negative phenomena [3, 4, 5].

Extension of scope of coal chemistry research initiated by *Litvinenko* resulted in the formation of specialized research teams including the Department for Power and Chemical Coal Processing (headed by *V. Saranchuk*). They continued to study the oxidation and self-ignition of natural coal, started to research structure and properties of combustible fossil fuels, and defined the role of genesis and stage of metamorphism [6, 7]; developed a technique for forecasting potential liability of coal mass to spontaneous ignition [8] and recommendations on prevention of its heating when extracting coal at low stages of metamorphism [9].

The Department initiated studying the chemical modification of coal by chemical agents of various classes; designed methods for agglomerated smoke-free solid fuel made of low metamorphic coal [10, 11]. The researches dealt with chemical transformations of oxygen- and sulfur-containing coal groups during its thermal conversion (thermolysis), which materially influence the results of the process [12]. It should be noted that the mentioned researches were based on the coal from Kansk-Achinsk deposit (Siberia, RF).

At the end of the 1980s, the Department started to research alternative source of energy (from 10 to 20 billion tons), the so called *salt* coal produced in Ukraine. The deposits of coal with a high content

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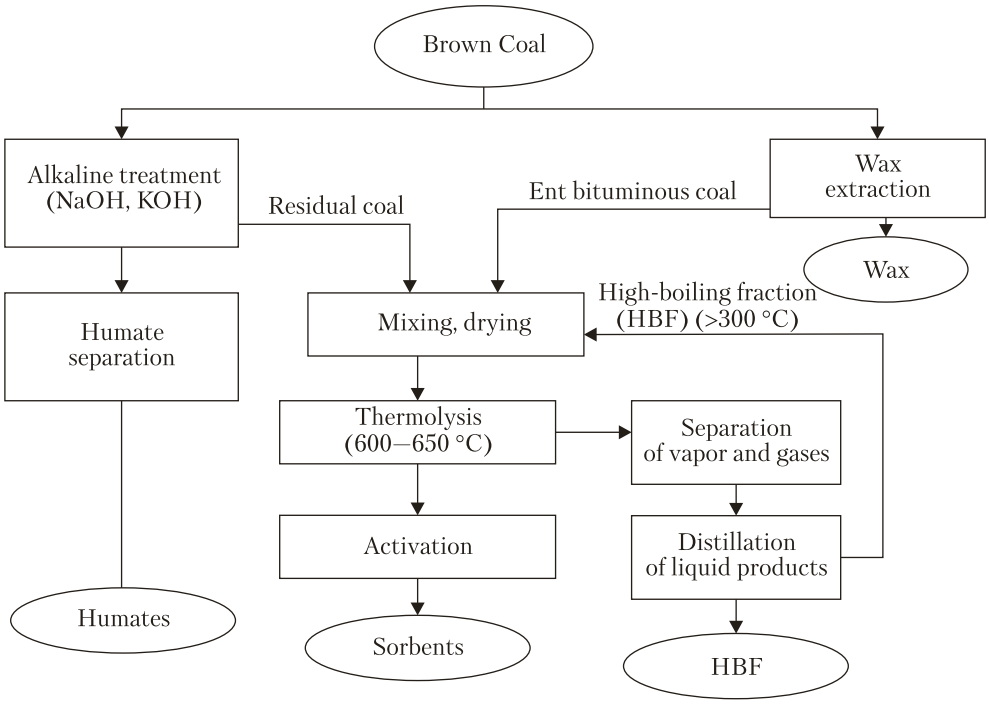


Fig. 1. Flow chart of complex processing of brown coal

of alkali metal salts (namely, NaCl) are located in Northern (Bohdanivske Deposit) and Western (Novomoskovske Deposit) Donbas. On the basis of specific content, molecular and supra-molecular structure of salt coal the principles of environment friendly use of this raw material have been elaborated. Techniques for consecutive conversion of salt coal into humic products, reducing gases, synthetic fuels, and adsorbents have been proposed. Upon request of the Novomoskovsk Geological Survey Expedition, the practical guidelines on possible use of salt coal from Western Donbas have been prepared [13]. Inventor's certificate on the practical use of native (non-processed) salt coal for effective extraction of silver from the film and cinema industry waste has been obtained [14].

In 1990s, the researchers of the Department for Power and Chemical Coal Processing focused their efforts on studying the complex processing of coal, in particular, low-energy brown coal produced in Ukraine, into a wide range of products, such as mineral wax, humic acids, components of motor and boiler fuels (including high-boiling fraction (ICC)), solvents, synthetic and energy gases, sorbents, and smokeless solid fuel [15] (see Fig. 1). Unique results related to the composition and properties of coal organic mass macerals (components of various genesis) have been obtained [16]. These results are of paramount importance for selecting methods for the use of anthracides.

At the beginning of the 2000s, in cooperation with OJSC *Opytnoe Proizvodstvo*, the Department made researchers on selecting agents (based on coke and chemical waste) for beneficiation of coke feed and improvement of carbonization conditions. The results have been presented in monograph study [17]. The designed method for processing of coke waste into flotation agents and their use in flotation processes have been widely used at the *Avdiivka Coking Plant*, OJSC.

At the end of 1990s, as a result of global environment problems, in particular, material problems in Donetsk industrial region, the researchers focused their efforts on designing methods for managing a huge amount of carbon-containing waste (from manufacture of polymer, timber, pe-

troleum, coke products, etc.). Since that time, the Department has been dealing with methods for joint conversion of 2- and 3-component systems: coal (mainly, brown coal from Oleksandrivske deposit) and wastes from petroleum and timber industries (lignin, wood chips) as well as coal and wastes from coking industry to get products of various aggregate state (gaseous and liquid fuel, solid residual) having new composition and properties and to reduce wastes that occupy a large space and contaminate the environment.

Within the period from 1998 through 2002, the Department was engaged in international project within the framework of INCO-COPERNICUS (PL №978009) *Wood Biomass and Wastes Upgrading: Development and Application of Clean Processes for Chemicals, Oils and Carbon Production*. The idea of simultaneous recycling of different type of carbon-containing materials (low-quality coal, timber, petroleum wastes), which was partially implemented within the framework of INCO-COPERNICUS project, has been developed due to NATO Science for Peace and Security program (project «New Approach to Waste Processing into Selective Adsorbents of Heavy Metals» SfP no.977984 (2002–2006)). The projects deliverables are joint publications, Advanced Research Workshop (ARW), and monograph study «Recent advances in adsorption processes for environmental protection and security. Ed. by J.P. Mota, S.B. Lyubchik. — Springer: 2006». Also, the researchers proposed methods for joint recycling of liquid (petroleum industry wastes) and solid (low-quality coal, lignin, sunflower shelling) wastes that enable getting high-porous materials with required properties (given ratio of meso- and micro-pores and absorption characteristics) by varying raw components and activation regime [18,19].

The importance of problem stimulated successful implementation of the project that, in addition to the scientific accomplishments, brought more than UAH 1 million extra-budget revenues for carrying out further research and purchasing equipment and allowed them together with partners (*Electrode*, CJSC, Donetsk) to create a pilot plant for producing sorbents from fossil coal. Now, in the view of military actions in Donetsk, the fate of this plant is uncertain.

Due to the mentioned projects, general principles of thermochemical combination of carbon-containing wastes and coal have been established for obtaining super-strong and effective sorbents and liquid products (coal oil) with a high content of valuable light fractions. In addition, technologically important effects (non-additivity of target product output, acidic and alkaline promoting of condensation reactions and development of porosity of solid products) have been discovered for the combination processes [20, 21].

In 2006–2012, the Department cooperated with Institutes of Siberian Department of the Russian Academy of Sciences (RAS) within the framework of integration project implemented by the NAS of Ukraine and the Siberian Department of the RAS «Analysis of Problems and Development of Technologies for Complex Competitive Use of Coal for Power Engineering Purposes», in particular, «Thermochemical Compatible Conversion of Coal and Carbon-Containing Wastes into Coal Oil and High-Porous Materials». Upon the completion of project, the Siberian Department of RAS published joint monograph study «Deep Processing of Brown Coal for Obtaining Liquid Fuels and Carbon Materials» and more than 20 research papers prepared in collaboration with researchers of SD of RAS [22, 23].

Among national projects in which the Institute researchers have been engaged, there are preparation and publication of *Mining Encyclopedia* and *Mining Encyclopedic Dictionary* in 2001–2014 (Fig. 2).

At the beginning of 21st century, the Department launched systemic research of conversion of fossil coal into nano-porous materials (NPM) that are of high demand for advanced techniques of purification of aqueous solutions and industrial gases and for separation of gaseous mixtures. A new technique for alkaline activation has been developed. It foresees a heat shock of solid humic components (SHC) and alkali mixture and enables obtaining

an adsorbent with highly developed surface at lower alkali/SHC ratio, which can be widely used (see Fig. 3). A patent of Ukraine has been received for obtaining nano-porous carbon material from brown coal [26, 27]. New carbon adsorbents with developed nano-porosity and specific surface area ranging within 1000–2000 m^2/g have been synthesized. Their absorption properties with respect to gaseous hydrogen, some eco toxicants (heavy metal ions, phenol, chlorophenols) and test compounds (krypton, xenon, gaseous iodine, and iodomethyl), which model air contamination by operating NPP have been studied [28, 29].

The important practical results related to effectiveness of NPM in various absorption processes as compared with commercial analogues are showed in Figs. 3, 4, 5, and 6.

The NPMs synthesized from pyrolysed wood chips using the designed method have been tested (together with the Tugan-Baranovskyi Donetsk National University of Economics and Trade) in the production of alcoholic beverages. The proposed method enables obtaining active carbon from timber wastes as a result of smoking foodstuffs. This carbon is adapted to the alcoholic beverage production technologies and enables improving the taste of beverages, speeding up the aging of cognac alcohols, and cheapening the finished goods. Upon the test results, patent applications have been made for the use of these NPMs in the food industry.

The NPMs synthesized by alkaline activation of brown coal have been tested in electro-sorption processes as well. The obtained results allow the researchers to expect further improvement of electro-sorption properties of brown-coal NPMs to be used for creation of ionistores (2-layer super-capacitors) [30] (Fig. 7).

Methods for improving the metrological properties of electro-thermal sorption-atomic-absorption detection of Pb(II) and Cd (II) in aqueous solutions are based on the results of research related to absorption of heavy metals (obtained by the Department and the Analytical Chemistry Chair of the Donetsk National University) [31, 32].

Fig. 2. Publications of researchers of the Department for Coal Chemistry

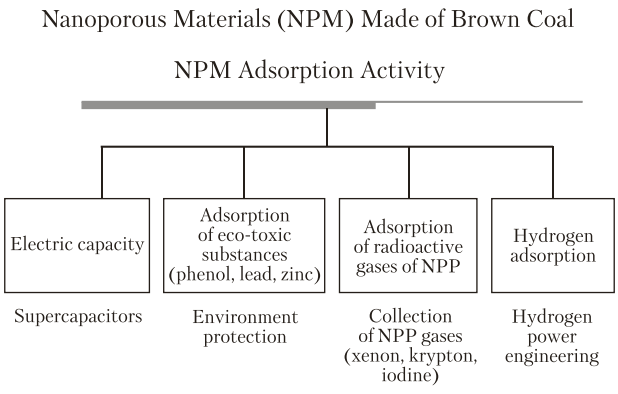


Fig. 3. Application of porous nanomaterials based on brown coal

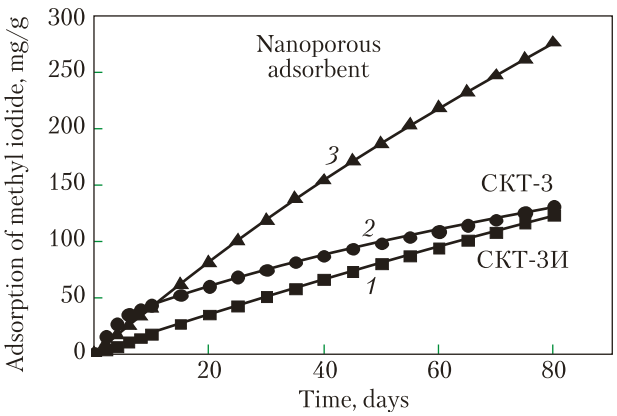
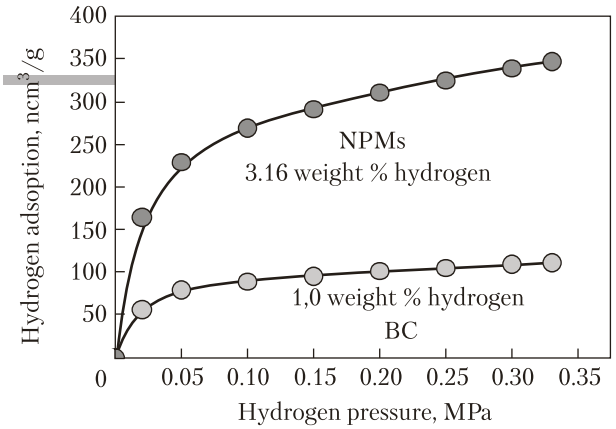


Fig. 4. Absorption of iodomethyl by various sorbents: Ukrainian-made nanoporous sorbent (IPOCC) (3), industrial sorbents СКТ-3 (2) and СКТ-3И (1) made in Russia



In cooperation with the Kharkiv Institute for Physics and Engineering

Fig. 5. Absorption of hydrogen by raw coal and synthesized NPMs

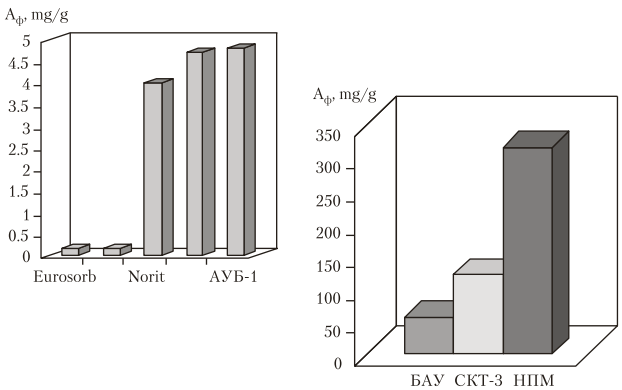


Fig. 6. Absorption of phenol by various sorbents

The method has been used in laboratory tests at UkrNDISil for comparative analysis of culinary salt, natural salt brines, and waters; also, it is recommended for inclusion into the international standard no.13685 «Edible Salt. Test methods». The method has a significant social impact, since unlike the traditional techniques it uses only nontoxic chemical agents, is more rapid and has better metrological characteristics.

Due to close cooperation with industrial corporations of Donetsk Region the Department has managed to focus its research capacity on solving problems of coking industry. The researchers have studied influence of some boron compounds on reactivity and strength of metallurgical coke in order to get parameters typical for Premium type coke widely exported to foreign countries. A technique for after-furnace treatment of metallurgical coke with reagents has been designed for improving its hot mechanical strength (CSR) and reducing reactivity (CRI). The methods for obtaining metallurgical coke with indices that comply with international standards (CSR: 56–70%, CRI: 25–30%) have been patented. The method is realized by chemical modification of ready coke surface by borate solutions with various surfactants [33, 34, 35].

The method for improving quality of metallurgical coke has been put in practice (PrJSC Makiivkoks) with a significant economic effect and expanding raw material base.

The Institute, as a whole, and the Department, in particular, has played an important role in coordination of researches concerning chemistry of solid fossil fuels. Within 1984–1991, the Department regularly participated in all-Union conferences and workshops on the SHC structure, effective methods of use of low-quality coals, and obtaining of liquid fuels from SHC and humic substances, as well as catalysis in coal chemistry. These forums played an important role in raising the level of utilization of chemical potential of solid fossil fuels in Ukraine and abroad. In addition, the Department researchers attended international forums (*Coal Science* – 95, 97, CARBON – 96, 98, 2000, 2002, New Carbon and Composite Materials – 2000, 2003, 2004, etc.).

Upon initiative of the Institute, in 1993, a long-term program for international cooperation PICS-119 CNRS–ECOTECH *Carbon Adsorbents. Coal Chemistry. Environment Protection* was developed within the framework of *The Fuel* priority program. Due to this program the Institute researchers carried out relevant investigations at research centers of Bulgaria, Poland, France and so on. Despite the current challenges, the cooperation with researchers from Russia, Poland, Portugal, Spain other countries continues.

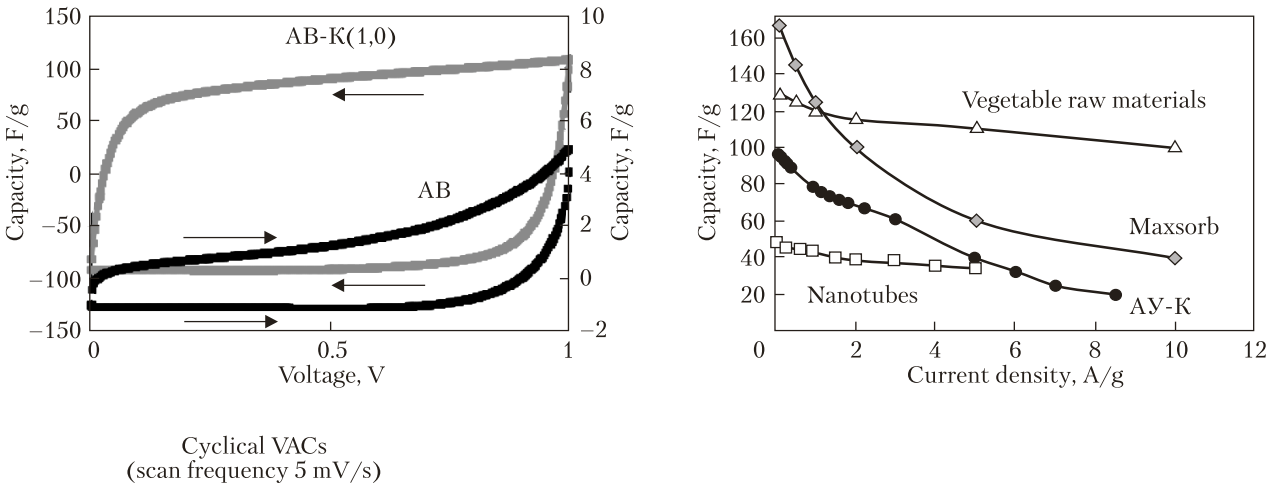


Fig. 7. Electro-sorption properties of NPMs based on brown coal

Recently, the Department has enhanced cooperation with state-owned corporation *Ukrvuhleiakist* in the sphere of coal quality stored in the mine warehouses and ore processing plants and supplied to TPS. Unfortunately, because of war actions this fruitful cooperation (that enabled to prevent corruption and improper use of solid fossil fuels in power engineering) has been suspended.

The Department's plans for the future is to preserve its intellectual capacity due to relocating leading experts in coal chemistry to Kyiv and ensuring working conditions for them. The most pressing tasks are connected with impossibility to carry out experimental studies because the lack of spaces and facilities. The Institute hopes for a help of foreign colleagues who have agreed to pre-owned equipment.

Currently, the leading experts of the Department are working in Kyiv and feel the lack of space and equipment. However, they hope that due to joint efforts (together with researchers of adjacent institutes, with support of the Presidium and Department of Chemistry of the NAS of Ukraine) the Department of Coal Chemistry and the Institute itself can restore and utilize its scientific potential for the sake of independent Ukraine.

Fig. 8. Patents and methods for improving the coke quality and obtaining porous materials

Taking into account the fact that Ukraine (according to the data of 2008) was ranked eighth among leading importers of absorbent coal [35], the organization of sorbent production from raw coal in Ukraine is very expedient and feasible. The Department's R&D results in this field can be very useful to this end. Another important aspect is to extend the list of materials that can be absorbed by coal NPMs. These are the main problems to be studied in the near future.

REFERENCES

1. Saranchuk V.I., Kachan V.N., Rekun V.V. i dr. *Fiziko-himicheskie osnovy gidroobespylivanija i preduprezhdenija vzryvov ugol'noj pyli*. Kyiv: Nauk. dumka, 1984 [in Russian].
2. Saranchuk V.I., Zhuravlev V.P., Rekun V.V. i dr. *Sistemy bor'by s pyl'ju na promyshlennyh predprijatijah*. Kyiv: Nauk. dumka, 1994 [in Russian].
3. Saranchuk V.I. *Okislenie i samovozgoranie uglja*. Kyiv: Nauk. dumka, 1982 [in Russian].
4. Saranchuk V.I., Ruschev D., Semenenko V.K. i dr. *Okislenie i samovozgoranie tverdogo topliva*. Kyiv: Nauk. dumka, 1994 [in Russian].
5. Kucher R.V., Kompanec V.A, Butuzova L.F. *Struktura iskopaemyh uglej i ih sposobnost' k okisleniju*. Kyiv: Nauk. dumka, 1980 [in Russian].
6. Saranchuk V.I., Ajruni A.T., Kovalev K.E. *Nadmolekuljarnaja organizacija, struktura i svojstva uglej*. Kyiv: Nauk. dumka, 1988 [in Russian].
7. Kachan V.N., Saranchuk V.I., Danilov A.T. *Preduprezhdenie vzryvov pyli v ugol'nyh shahtah*. Kyiv: Tehnika, 1990 [in Russian].
8. *A.s.№1132026. SSSR.* Sposob prognoza samovozgoranija iskopaemyh uglej. V.I. Saranchuk, K.E.Kovalev [in Russian].
9. *A. s. № 1615390. SSSR.* Sostav dlja profilakticheskoj obrabotki uglej protiv samovozgoranija. V.I. Saranchuk, L.Ja. Galushko, A.G. Galushko, V.A.Hazipov [in Russian].
10. *A. s. №1333699. SSSR.* Sposob poluchenija aglomerirovannogo uglerodsoderzhashhego topliva. V.I. Saranchuk, V.A. Tamko [in Russian].
11. *A. s. № 1663015. SSSR.* Sposob poluchenija koksa. V.A. Tamko, V.I. Saranchuk, V.N. Shevkopljas [in Russian].
12. Saranchuk V.I., Butuzova L.F., Minkova V.N. *Termohimicheskaja destrukcija uglej*. Kyiv: Nauk. dumka, 1993 [in Russian].
13. Shendrik T.G., Saranchuk V.I. *Solenye ugli*. Donec'k: Shidnij vidavnichij dim, 2003 [in Russian].
14. *A. s. 1681549 SSSR, MKI3, S22 11/00*. Sposob izvlechenija serebra iz kinofotorastvorov. Ivanova L.S., Grabchak S.L., Shendrik T.G. [in Russian].
15. Saranchuk V.I., Tamko V.A., Shevkopljas V.N. i dr. Bezothodnaja pererabotka burogo uglja Aleksandrijskogo mestorozhdenija. *Ugol' Ukrainy*. 1996, N 9: 16–20 [in Russian].
16. Macenko G.P., Bilec'kyj V.S., Shendrik T.G. *Korotkyj slovnyk z petrografii' vugillja*. Donec'k: Shidnyj vydavnychyj dim, 2011 [in Ukrainian].
17. Saranchuk V.I., Arovin I.A., Galushko L.Ja. *Flotirovanie uglej reagentami iz produktov koksohimii*. Donec'k: Vidavnichij dim «Kal'mius», 2006 [in Russian].
18. Shendrik T.G. Pashchenko L.V., KhabarovaT.V. et al. *Porous carbon materials from wood wastes and blends.* Proc.4 International Sympos «Catalytic and thermochemical conversions of natural organic polymers». Krasnoyarsk, RF, 2000. P. 104–113.
19. Shendrik T.G., PashchenkoL.V., SimonovaV.V. et al. Adsorbents from Lignin and Washed-off Petroleum Waste. *Solid Fuel Chemistry*. Allerton Press, Inc. 2007, N 2: 114–118.
20. Shendrik T.G., Tamko V.A., Bovan L.A. Sovmestnaja konversija uglja i zhidkih uglerodsoderzhashhih othodov v produkty vysokoj potrebitel'skoj cennosti. *Jekologija i promyshlennost'*. 2014, N 3: 61–66 [in Russian].
21. Simonova V.V., Kucherenko V.A., Shendrik T.G. Himicheskaja modifikacija smesej uglja i nefte ot hoda kak podhod k povysheniju vyhoda letuchih produktov. *Voprosy himii i him. tehnologii*. 2012, N 4: 95–100 [in Russian].
22. *Glubokaja pererabotka buryh uglej s polucheniem zhidkih topliv i uglerodnyh materialov.* B.N. Kuznetsov, T.G. Shendrik, M.L. Shhipko, N.V. Chesnokov, V.I. Sharypov, A.M. Osipov. Novosibirsk: Izd-vo SO RAN, 2012 [in Russian].
23. Simonova V.V., Shendrik T.G, Chesnokov N.V., Kuznetsov B.N. Properties of active carbons produced by thermochemical transformation of lignin, brown coal and oil slim mixtures. *J. of Siberian Federal University*, Ser. Chemistry. V.4. N 1: 336–343.
24. *Girnychyj encyklopedychnyj slovnyk*. Zag. red. Bilec'kogo V.S. Donec'k: Shidnyj vydavnychyj dim, 2001 [in Ukrainian].
25. *Mala girnycha encyklopedija*. Za red. Bilec'kogo V.S. Donec'k: Donbas, 2004 [in Ukrainian].
26. *Pat. Ukrai'ny na korysnu model' № 61059, MPK S01V 31/08 (2006.01)*. Sposib otrymannja poruvatogo vuglecevogo materialu z burogo vugillja. Tamarkina Ju.V., Habarova T.V., Shendryk T.G., Kucherenko V.A. [in Ukrainian].
27. KucherenkoV.A., ShendrikT.G., TamarkinaYu.V. Nanoporosity development in the thermal – shock KOH activation of brown coal. *Carbon*, 2010. N 48: 4556–4558.
28. Shendrik T.G., Isaeva L.N., Bovan D.V. Burougol'nye adsorbenty dlja ochistki stochnyh vod ot fenola. *Trudy Mezhdun. nauch.-prakt. konferencii «Chistaja voda – 2009»*, Kemerovo (RF), 20–21 oktjabrja, 2009: 209–214 [in Russian].
29. Tamarkina Ju.V., Kolobrodov V.G., Shendrik T.G., Kucherenko V.A. Svojstva adsorbentov, poluchennyh shhelochnoj aktivaciej aleksandrijskogo burogo uglja. *Himija tverdogo topliva*. 2009, N 4: 46–50 [in Russian].
30. Tamarkina Ju.V., Mysyk R.D., Kucherenko Ju.V., Shendrik T.G. *Himicheski aktivirovannye burye ugli kak jelektrody dlja superkondensatorov s organicheskim jelektrolitom*. Kyiv: Izd-vo IHP NANU, 2009. Vyp. 1(16): 147–154 [in Russian].

31. Alemasova A.S., Belova E.A., Trofimchuk A.K.i dr. Sorbcionnoe koncentrirovanie svinca (II), kadmija (II) i ih jelektrotermicheskoe atomno-absorbcionnoe opredelenie v suspenzijah sorbentov. *Ukr. him. Zhurnal*. 2008, 74 (1–2): 106–111 [in Russian].
32. Simonova V.V., Tamko V.A., Tamarkina Ju.V. i dr. Adsorbcija tjazhelyh metallov uglerodnymi sorbentami razlichnogo proishozhdenija. *Jekologija i promyshlennost'*. 2012, N 3: 32–36 [in Russian].
33. *Pat. Ukrainy UA №31186* Sposob uluchshenija kachestvennyh pokazatelej domennogo koksa. Tamko V.O., Saranchuk V.I., Zbykovskij E.I., Zolotarev I.V., Shendrik T.G. i dr. [in Russian].
34. *Pat. RF RU 2336297 S1* Sposob obrabotki domennogo koksa. Tamko V.A., Zbykovskij E.I., Saranchuk V.I., Zolotarev I.V., Shendrik T.G. i dr. [in Russian].
35. Gordienko A.I. Perspektivy organizacii otechestvennogo proizvodstva aktivnyh uglej na osnove malometamorfizovannyh uglej i antracitov. *Uglehimicheskij zhurnal*. 2008, N 3–4: 3–7; 80 [in Russian].

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ІННОВАЦІЙНІ РОЗРОБКИ ВУГЛЕХІМІЧНОЇ НАУКИ В ІНСТИТУТІ ФІЗИКО-ОРГАНІЧНОЇ ХІМІЇ І ВУГЛЕХІМІЇ ІМ. Л.М. ЛИТВИНЕНКА НАН УКРАЇНИ

Наведено короткий історичний нарис і розробки відділу хімії вугілля Інституту фізико-органічної хімії і вуглехімії ім. Л.М. Литвинука НАН України, пов'язані з проблемами експлуатації вугільних шахт, пошуком рішень щодо запобігання самозапаленню вугільних пластів, пилопридушенню у гірських виробках, встановленню структурно-хімічних особливостей вугілля різного генезису і стадій метаморфізму для розробки нових способів їх модифікації і раціонального використання. Запропоновано способи отримання дешевих сорбентів з української сировини (у т.ч. вуглецевмісних відходів). Окреслено проблеми сучасної вуглехімічної науки в Україні.

Ключові слова: вугілля, структура, модифікація, термоліз, нанопористі сорбенти, кокс.

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Институт физико-органической химии и углехимии им. Л.М. Литвиненко НАН Украины, Киев

ИННОВАЦИОННЫЕ РАЗРАБОТКИ УГЛЕХИМИЧЕСКОЙ НАУКИ В ИНСТИТУТЕ ФИЗИКО-ОРГАНИЧЕСКОЙ ХИМИИ И УГЛЕХИМИИ им. Л.М. ЛИТВИНЕНКО НАН УКРАИНЫ

Представлен краткий исторический очерк и разработки отдела химии угля Института физико-органической химии и углехимии им. Л.М. Литвиненка НАН Украины, связанные с проблемами эксплуатации угольных шахт, поиском решений по предупреждению самовозгорания угольных пластов, пылеподавления в горных выработках, установления структурно-химических особенностей углей разного генезиса и стадий метаморфизма для разработки новых способов их модификации и рационального использования. Предложены способы получения дешевых сорбентов из украинского сырья (в т.ч. углеродсодержащих отходов). Очерчены проблемы современной углехимической науки в Украине.

Ключевые слова: уголь, структура, модификация, термолиз, нанопористые сорбенты, кокс.

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