# CONTROL OF THERMOCHEMICAL TRANSFORMATIONS
# OF COMPONENTS OF COAL-BASED BINDERS

*Olexandr Borisenko[1,✉], Fedir Cheshko[1], Leonid Bannikov[1], Natalia Holik[1],*
*Natalia Ponomarenko[2]*

**Abstract.** The possibility of considering coal pitch as a material suitable for research modeling the processes of thermochemical transformations of the plastic mass of coal carbonization and their interaction with the solid carbon phase is analyzed. The possibilities of controlling the properties of coal pitch and blast furnace coke during its production with the help of aprotic acid additives in the presence of a co-catalyst are shown.

**Keywords:** coal pitch, coal plastic mass, binder, filler, thermochemical transformations.

## 1. Introduction

It is well known that electrode pitch, obtained from the non-boiling residues of thermal fractionation of coal tar, is used in the production of a wide range of conductive and structural materials. These materials include, for example, anodes and anode masses for aluminum production, graphite electrodes for steelmaking, materials for sliding contacts, *etc*. The main purpose of pitch in these industries is to act as a binder for solid carbon fillers. High-temperature and, in some cases, ultra-high-temperature processing (from 1173 to 1773–2273 K)[1] is a mandatory processing step for filler and binder mixtures.

Specific technological requirements for electrode and other binder pitches are determined by the requirements for the quality indicators of the final product and the peculiarities of the technology of its manufacture at specific enterprises. In general, the pitch used as a binding material for high-tech electrodes and carbon structural materials should have optimal binding properties and sinter well with crushed fillers, firmly

binding their grains and providing a high yield of coke residue. Oil, pitch and shale coke, artificial or natural graphite, thermoanthracite and charges based on these materials can be used as fillers. The main requirements to the final carbonized products are high mechanical strength, homogeneity of the carbonized matrix, chemical inertness, *etc*.

Both at present and according to forecasts for the short and medium term, coal pitch binders remain scarce and practically unavailable. For several years, one of the ways to expand the raw material base of electrode binders has been to search for additives to coal pitch based on heavy oil residues, pyrolysis resins, cracking residues, and other oil products. However, these materials are characterized by a much lower content of high molecular weight aromatic components, a lower C/H ratio, and, as a result, a much lower coke residue yield compared to their coal counterparts[2,3].

At the same time, high consumer requirements for the properties of binders based on coal tar often contradict the actual properties of coal tar. This is not least due to the impossibility of purposefully shaping the quality indicators of the latter directly at the stage of their formation, *i. e.*, in the process of coal coking. Despite its high demand in the global market, coal tar is only a by-product of a process aimed at producing high-quality metallurgical (primarily blast furnace) coke, which is a disproportionately larger product and whose quality characteristics are also subject to very stringent requirements. These include high mechanical strength, homogeneity of the carbonized matrix, and chemical inertness.

All of the above arouses a broad research interest in developing new opportunities for more efficient control of thermal transformations of the initial coal pitch at the stage of binders production for high-tech electrodes and structural carbon materials. One of the most promising areas in this regard, in our opinion, is the thermal treatment of pitch in the presence of chemically active materials that selectively intensify the course of various processes of accumulation of the most technologically valuable group composition components in the produced

---

[1] State Enterprise "Ukrainian State Research Institute for Carbochemistry" (SE "UKHIN"), 7, Vesnina str., Kharkiv, 61023, Ukraine
[2] National Technical University "Kharkiv Polytechnic Institute", 2, Kyrpychova str., Kharkiv, 61002, Ukraine
✉ *zd@ukhin.org.ua*

binder or inhibit the accumulation of undesirable components[4, 5]. Such studies help, among other things, to clarify the understanding of the mechanisms of thermochemical transformations of the original pitch in the process of producing high-tech binders from it.

It should be noted that studies of the possibility of targeted influence on thermochemical processes occurring at the stages of both obtaining a binder from the initial pitch and further thermal exposure to the molded electrode or other workpiece (*i. e.*, when pitch turns into semi-coke and coke) are important not only from the point of view of achieving the required quality of the binder pitch and, accordingly, the products manufactured with its participation. In our opinion, the results of such studies can also be used to optimize the metallurgical coke production process.

It is known that the key role in the coking process is played by the so-called coal plastic mass, which is responsible for sintering coal grains. It consists of coking coal components that, at a certain temperature, turn into a plastic state and play a role in the formation of coke cake, almost similar to the role of coal pitch in the production of electrodes and structural materials. The temperature at which the coal plastic mass begins to release (form) (the initial coal softening temperature) depends on the coal grade and a number of technological factors. For example, according to Yan Wang *et al.*[6] based on the Gieseler fluidity analysis, this indicator can vary between 663 and 733 K. Characteristically, the initial coal pitch, a raw material for the production of binders, is formed as a non-boiling residue when fractions boiling at temperatures $\leq 653$–673 K are separated from coal tar.

Determining the composition of coal plastic mass is complicated by the peculiarities of its formation. For the laboratory extraction of plasticizing components in the process of heating a coal sample, researchers use, for example, the thermal filtration method, also known as the KhPI method (Kharkiv Polytechnic Institute, Kharkiv, Ukraine)[7]. The method involves centrifugation of a coal sample (class 0–3 mm) in a special heated glass with a mesh bottom, through which the resulting liquid-solid products are separated. Centrifugation is carried out by controlled heating of the sample without air access from room temperature to 873 K.

Despite all the possible tricks, some of the dusty solid particles are still carried to the collector of liquid non-volatile components of the coal plastic mass. This is evidenced, for example, by the group composition of the separated liquid products[7], shown in Table 1.

Table 2 presents some properties of high-temperature coal electrode pitches used as binders for the production of electric coal products and construction materials according to Ukrainian technological standard TU U 24/1-00190443-084-2001. These pitches are produced by prolonged thermal treatment of the initial pitch formed by distillation of coal tar.

The differences in the values of the indicators given in Tables 1 and 2 can be caused by both the ingress of fine coal particles and solid products of its destruction into the plastic layer separated from coal, as well as the higher separation temperature of the coal plastic mass (the temperature of heat treatment when producing binder pitch without the use of vacuum or increased pressure rarely exceeds 673 K). The first assumption is supported, for example, by the ash content of pitch: for plastic mass separated from coal, this indicator can vary within 1.4–2.0 %[7].

**Table 1.** Group composition of liquid non-volatile products extracted from different coal charges

| Content, wt. % | Coal charge number | | | |
|---|---|---|---|---|
| | 1 | 2 | 3 | 4 |
| Malthenes (substances soluble in petroleum ether) | 7.9 | 7.7 | 10.2 | 10.8 |
| Asphaltenes (substances insoluble in petroleum ether but soluble in chloroform) | 5.5 | 6.0 | 5.1 | 6.0 |
| Carbenes (analogue of β-resins = $TI - QI$) | 42.0 | 27.3 | 46.4 | 39.8 |
| Carboids (analogue of quinoline insolubles, $QI$) | 44.7 | 59.0 | 38.3 | 44.4 |
| Carbenes + carboids (analogue of toluene insolubles, $TI$) | 86.7 | 86.3 | 84.7 | 84.2 |
| Yield of liquid non-volatile components of plastic mass from coal mass | 30.3 | 27.0 | 19.4 | 16.7 |

**Table 2.** Some properties of high-temperature binder pitches

| Indicators | Values | |
|---|---|---|
| | 1 | 2 |
| Softening point, K | 383–408 | 408–418 |
| Ash yield, % | $\leq 0.2$ | $\leq 0.2$ |
| Coke residue yield, % | 52–57 | 54–60 |
| Mass content of the toluene insolubles, % | 43–48 | 46–54 |
| Mass content of the quinoline insolubles, % | 16–18 | 20–30 |

The carbon content in the plastic mass extracted from different coals varies from 80 to 92 % and hydrogen content – from 4.4 to 7.7 %[7]. According to our data, for coal pitch, these indices are 92–93 % and 4.4–4.6 %, respectively.

Some authors believe that the cohesive ability of coal plastic mass is related to the aliphatic structure of coal and hydrogen bonds containing hydroxyl group (-OH) or amino group (-NH₂)[6]. According to the works[8–10], coal pitches contain hydroxy-, sulfur- and nitrogen-containing compounds, as well as aliphatic fragments (-CH₃) and (=CH₂), (-OCH₃), and other functional groups.

The components of both coal pitch and liquid non-volatile products of coal coking are capable of undergoing the stage of formation of liquid crystalline structures (mesophase)[11, 12] when heated, the amount and thermal transformations of which have a significant impact on the properties of the carbonized product of co-carbonization of a binder with a carbonaceous filler.

Finally, as can be seen from Table 1, the yield of liquid non-volatile products from an industrial charge during their coking can be 16–31 %. And the share of binder pitch in the processed charge in the production of graphitized electrodes can be about 20 % and 25–30 % in the production of high-strength carbon-carbon composites[13]. Naturally, these are only approximate figures, since the optimal amount of binder in all of the above cases depends on the properties of the materials used and a number of technological factors. The data are provided only to demonstrate the comparability of the amount of binder to filler in the production of both blast furnace coke and carbon electrode and construction materials.

Thus, it may be stated:
– the similarity of origin of coal pitch and coal plastic mass;
– the ability of both materials to combine the role of binder and coke-forming component, forming a strong "pie" at co-carbonization with similar solid disperse materials;
– relative similarity of their composition, mechanism of thermochemical transformations and their share in the carbonized mixture.

All of the above gives grounds to treat coal pitch as a material suitable for simplified research modeling of the processes of thermochemical transformations of liquid-mobile non-volatile products of coal carbonization and their interaction with the solid carbonaceous phase during co-heating.

Let us return to the possibility of controlling the properties of a coal pitch binder during its manufacture by introducing chemically active additives into the treated raw pitch. For example, it has been shown[4] that during heat treatment, an increase in the amount of β-resins in coal pitch is a consequence of ionic (cationic) processes, and secondary *QI*s are mainly products of radical polymerization. From this point of view, it is of interest to carry out thermal treatment of the pitch in the presence of an initiator of β-resins formation, which is also an inhibitor of radical processes of molecular weight increase. This would contribute to a change in the group composition of the resulting binder by the accumulation of components with both binding capacity and high yield of coke residue (β-resin) due to the final *QI* content. The latter, although characterized by the highest coke residue yield, do not possess cohesive properties[8, 9].

The most promising in this respect are Lewis acids (aprotic acids) and, in particular, iron (III) chloride (FeCl₃), which is able not only to initiate polycondensation reactions during the co-pyrolysis of coal pitch with carbonaceous filler but also to inhibit radical polymerization reactions by entering into polymer chain breaking reactions with radicals[14–16]. The possibility of increasing the ash yield by introducing iron into the reaction melt is not dangerous in the case of using the resulting binder in the production of graphitized electrodes for steelmaking furnaces. In addition, the increase in ash yield within such limits will not be important when using coal pitch as a binder in the production of less specific products, such as fuel briquettes based on coal fines[17].

However, the use of iron trichloride as a chemically active additive to pitch and pitch-like materials, especially in production conditions, is very difficult due to the increased ability of this reagent to absorb atmospheric moisture. This complicates not only the dosage of the additive into the pitch melt, but also the maintenance of its required concentration in the reaction volume.

The search for ways to solve this problem has become the subject of our research.

# 2. Experimental

## 2.1. Materials

As a processed raw material in our research, we used coal pitch obtained by one-time evaporation of coal tar at an industrial continuous operation plant under the following conditions:
– the dehydration temperature (the first heating step) is 403–408 K;
– the one-time evaporation temperature (the second heating step) is 663–683 K;
– the consumption of dehydrated coal tar at the second heating stage is 14 t/h.

The properties of the original coal tar were as follows:
– density, kg/m³ – 1210;
– ash yield, % – 0.098;
– mass content of quinoline insolubles (*QI*), % – 5.8;
– moisture, % – 4.0.

Characteristics of a representative sample of a coal tar pitch are presented in Table 3.

**Table 3.** Characterization of coal pitch

| Quality indicators | Unit of measurement | Numeric value |
|---|---|---|
| Softening point (according to "Ring & Rod" method) | K | 328.0 |
| Volatiles yield at 1123 K | % | 61.3 |
| Mass content of toluene insolubles (*TI*) | % | 23.3 |
| Mass content of β-resins (*TI – QI*) | % | 12.7 |
| Mass content of quinoline insolubles (*QI*) | % | 10.6 |

Iron (III) chloride was chosen as the main catalyst. This substance is characterized by almost complete solubility in water, melting point of 579 K, and boiling point of 588 K[18]; when heated to the melting point it decomposes slowly according to Eq. (1):

$$2FeCl_3 \rightarrow 2FeCl_2 + Cl_2\uparrow. \qquad (1)$$
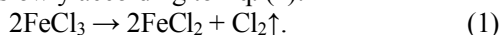
Due to its hygroscopic nature, iron trichloride in air transforms into $FeCl_3 \times 6H_2O$ hydrate and continues to absorb water, forming a black-brown liquid.

Table 4 presents the results of our study on the ability of iron trichloride to absorb atmospheric moisture. Samples of $FeCl_3 \times 6H_2O$ crystallohydrate were kept in open bins in a closed room under normal conditions, after which the dissolved moisture content was determined. Determination was carried out by dehydration over concentrated sulfuric acid according to the method of obtaining chemically pure crystalline iron (III) chloride hydrate. From the given data it follows that the content of absorbed moisture at the level of 25–26 % approximately corresponds to the saturation of iron (III) chloride crystalline hydrate with water.

**Table 4.** Dynamics of iron trichloride saturation with atmospheric moisture

| Exposure time, min | Mass fraction of absorbed moisture, % |
|---|---|
| 10 | 24.7 |
| 20 | 25.4 |
| 30 | 25.6 |
| 40 | 25.7 |

It is known that iron trichloride and water can catalyze ionic polymerization reactions through the formation of hydrogen ion[13, 19]:

$$FeCl_3 + H_2O \leftrightarrow H^+[FeCl_3OH]^- \leftrightarrow H^+ + (FeCl_3OH)^-. \qquad (2)$$

Based on the totality of the above circumstances, we used a mixture of $FeCl_3 \times 6H_2O$ crystalline hydrate and water as a chemically active additive in our studies.

## 2.2. Methods

It seems that at temperatures above 588 K, the modifying effect on pitch should be mainly exerted by vapors and decomposition products of this reagent: iron (II) and iron (III) chlorides are initiators of ionic polymerization, and gaseous chlorine is more effective than air oxygen, which is widely used as a heat treatment intensifier in the production of electrode and other pitch. Based on this, it was decided to heat the coal pitch in the presence of iron chloride in a laboratory heating cube reactor with a reflux condenser. The reactor was heated using electricity, and the total single loading of the starting materials was 300 g.

The refusal to remove distillate products from the reaction medium and their return to the reaction zone (especially when the heat treatment temperature is higher than the vaporization temperature of the catalyst additive) not only prevents the loss of part of the catalyst with vapors but also increases the specific weight of reactions occurring in the vapor phase. Vapors of the additive interact with vapors of low molecular weight components, and with an increase in the molecular weight (and, accordingly, the boiling point) of the reaction products, the latter can condense and pass into the liquid phase, where the intensity of the polymerization processes is lower since the concentration of the chemically active additive is lower. All this should play the role of a kind of fuse and lead to a decrease in the rate of Cl accumulation.

## 3. Results and Discussion

The influence of the $FeCl_3 \times 6H_2O$ to water ratio in the additive on the formation of the group composition of coal pitch during heat treatment under comparable conditions was studied. Heat treatment was carried out under continuous stirring. The temperature of the liquid phase was 603 K, the duration of isothermal holding was 3 h, and the content of $FeCl_3$ crystalline hydrate was 1.31 % of the pitch mass. For the purpose of better averaging, the additive was added to the pitch in the form of a solution in acetone with the 1:1 ratio (*w/w*). The results are presented in Table 5.

As can be seen from Table 5, the mass ratio of iron (III) chloride crystallohydrate to water in the additive at the level of (3:1)–(4:1) provides a significant increase in *TI* and β-resins with almost complete inhibition of the formation rate of secondary quinoline insolubles. The upper boundary of the detected optimum interval of the additive water content corresponds to the maximum saturation of iron trichloride crystallohydrate with atmospheric moisture under normal conditions. This

should considerably simplify storage and dosage of the additive in industrial conditions, as it allows not taking special additional measures at these stages to prevent contact of the additive with atmospheric air. Further increase of water share in the composition of the additive is undesirable due to the increase of thermal effects during its boiling and condensation.

Table 6 shows the effect of the mixed additive concentration on the quality of the obtained pitch. In the experiments the temperature of the liquid phase was

603 K; the water-acetone solution introduced into the pitch contained crystallohydrate and water in the ratio of 3:1; the duration of isothermal holding was 3 h.

Table 7 shows the results of determining the optimum temperature regime of thermal treatment of furnace in the presence of water-acetone solution of iron trichloride crystalline hydrate (mass ratio of crystalline hydrate and water in the additive – 3:1, duration of isothermal holding – 3 h, the amount of the additive in terms of crystalline hydrate – 1.5 % of the pitch mass).

**Table 5.** Heat treatment of initial pitch in the presence of mixed additive on the basis of $FeCl_3$

| Mass ratio $(FeCl_3 \times 6H_2O)$ : water | Mass fraction of group composition fractions, %; | | |
|---|---|---|---|
| | *TI* | *QI* | β-resins |
| 5.0 | 30.0 | 11.7 | 18.3 |
| 4.0 | 37.1 | 10.4 | 26.7 |
| 3.5 | 38.8 | 11.0 | 27.8 |
| 3.0 | 37.0 | 10.8 | 26.2 |

**Table 6.** Effect of the mass fraction of the mixed additive on the quality of the produced pitch

| Pitch quality indicators | Mass fraction of the additive in terms of crystalline hydrate, % | | | | | |
|---|---|---|---|---|---|---|
| | 0 | 0.75 | 0.8 | 1.3 | 1.5 | 1.9 |
| Softening point, K | 343.0 | 350.0 | 352.5 | 355.0 | 360.0 | 373.0 |
| Volatile substance yield, % | 58.3 | 54.9 | 53.2 | 52.3 | 50.2 | 48.1 |
| Ash yield, % | 0.2 | 0.5 | 0.6 | 0.7 | 0.9 | 0.9 |
| Mass content of *TI*, % | 28.6 | 32.6 | 35.0 | 37.0 | 37.7 | 42.0 |
| Mass content of *QI*, % | 12.5 | 11.4 | 10.7 | 10.8 | 10.7 | 11.7 |
| Mass content of β-resins, % | 16.1 | 21.2 | 24.3 | 26.2 | 27.0 | 30.6 |

**Table 7.** Dependence of coal pitch quality parameters on the temperature of thermocatalytic treatment

| Pitch quality indicators | Liquid phase temperature, K | | | | | |
|---|---|---|---|---|---|---|
| | 543 | 573 | 603 | 623 | 633 | 673 |
| Softening point, K | 345.0 | 348.0 | 360.0 | 374.0 | 383.0 | 393.0 |
| Volatile substance yield, % | 56.2 | 54.0 | 50.2 | 46.5 | 45.0 | 42.5 |
| Ash yield, % | 0.8 | 1.0 | 0.9 | 1.3 | 1.3 | 1.4 |
| Mass content of *TI*, % | 32.1 | 35.8 | 37.7 | 39.5 | 48.0 | 51.0 |
| Mass content of *QI*, % | 11.6 | 10.6 | 10.7 | 11.2 | 18.3 | 24.9 |
| Mass content of β-resins, % | 20.5 | 25.2 | 27.0 | 27.3 | 29.7 | 26.1 |

Data given in Tables 5–7 show that the optimal conditions for thermocatalytic treatment of coal pitch in the presence of water-acetone solution of iron (III) chloride crystalline hydrate are as follows:

– mass ratio of water and crystal hydrate in water-acetone solution – (3:1)–(4:1);

– content of the additive in terms of crystalline hydrate, % of the pitch mass – 0.8–1.5;

– processing temperature, K – 603–623.

Subject to the listed parameters, the additive under study allows almost complete inhibition of the secondary quinoline insolubles formation and the accumulation of *QI* exclusively at the expense of valuable β-resins, the content of which can be increased by more than 2 times compared to the initial pitch (from 12.7 to 27.3 %). At the

same time, when more than 1.5 % of the additive is added to the pitch in terms of crystalline hydrate and/or when the processing temperature is increased above 623 K, the *QI* content in the final product increases significantly.

An additional positive factor is the reduction of volatile matter yield in the resulting pitch and, as a result, an increase in the coke residue yield.

From the above data, it is clear that the principles of controlling thermochemical transformations of coal pitch proposed by us are applicable to the production of a fairly wide range of electrode pitch grades. A significant (above the requirements set by the vast majority of consumers) increase in ash yield, undoubtedly caused by the introduction of iron into the matrix of the processed charge, should not lead to a deterioration in the quality of

electrode products intended for electromelting of steel. However, for binders intended for use, for example, in aluminum production, this nuance is a serious obstacle.

The use of iron chloride is also problematic in terms of controlling the thermochemical transformations of the plastic mass of hard coal in the process of blast furnace coke production.

It is known[20, 21] that one of the most important characteristics of blast furnace coke is the reactivity index (*CRI*) and the coke residue strength after reaction with $CO_2$ (CSR). Their values are largely determined by the chemical composition of the mineral part of coal and charge, for the quantitative assessment of which complex indicators are introduced: the basicity index $B_b$ in relation to coke and the base / acid ratio $I_b$ in relation to coke residue[20].

$$B_b = [100 \times A^d \times (Fe_2O_3 + CaO + MgO + Na_2O + K_2O)] \, / \, [(100 - V^{daf}) \times (SiO_2 + Al_2O_3)]; \quad (3)$$

$$I_b = (Fe_2O_3 + CaO + MgO + Na_2O + K_2O) \, / \, (SiO_2 + Al_2O_3), \quad (4)$$

where $A^d$ is an ash yield, wt. %, $V^{daf}$ is a yield of volatile substances from charge, wt. %, $Fe_2O_3$, $CaO$, $MgO$, $Na_2O$, $K_2O$, $SiO_2$, $Al_2O_3$ are mass fractions of corresponding metal oxides, %.

According to known data, for the production of blast furnace coke with actual CRI and CSR indicators, the values of $B_b$ and $I_b$ should be as low as possible, in particular, the $B_b$ of the feedstock coal should be less than $2.5$[21]. At the same time, as follows from Eqs. (3) and (4), an increase in iron content contributes to the growth of both indicators.

Based on the above, iron (III) chloride cannot be recommended as an agent for controlling thermochemical transformations of the plastic (liquid-fluid) mass of coal charge in blast furnace coke production. However, the general principles of using aprotic acids for this purpose, discussed above, are also applicable in this case. As for a specific catalyst, it is permissible to be guided by Eqs. (3) and (4) for its selection.

# 4. Conclusions

Thus, the following conclusions can be drawn from the above:

1. Coal pitch is quite acceptable to consider as a material suitable for simplified research modeling of thermochemical transformations of liquid-mobile non-volatile products of coal carbonization and their interaction with the solid carbonaceous phase during joint heating.

2. It is of interest to carry out heat treatment of coal binders in the presence of an initiator of β-resin formation, which is also an inhibitor of radical processes of molecular weight increase. This helps to change the group composition by accumulating components with both binding properties and high coke residue yield (β-resins) due to the final *QI* content. Lewis acids (aprotic acids) appear to be the most promising in this regard in terms of combining properties.

3. The absence of removal of distillation products from the reaction medium and their return to the reaction zone increases the proportion of reactions occurring in the vapor phase. This leads to a decrease in the rate of *QI* accumulation.

4. The thermal treatment of coal pitch in the presence of a mixture of $FeCl_3 \times 6H_2O$ crystallohydrate and water as a co-catalyst was investigated.

5. The optimal conditions for the thermocatalytic treatment of coal pitch in the presence of an water-acetone solution of iron (III) chloride crystallohydrate are as follows:

– mass ratio of water and crystallohydrate in water-acetone solution – (3:1)–(4:1);

– content of the additive in terms of crystalline hydrate, % of pitch mass – 0.8–1.5;

– processing temperature, K – 603–623.

At the same time, iron trichloride, as the basis of a catalytic additive, can be recommended only for the production of electrodes for electric steel melting furnaces.

6. The general principles of using aprotic acids to improve binder properties discussed in this article are also applicable to control the properties of the plastic (liquid-liquid) mass of hard coal during the coking process, provided that a catalyst is selected that will not adversely affect the mineral composition of the final product.

# References

[1] Arani, H.F.; Mirhabibi, A.R.; Collins, S.; Daroughegi, R.; Khalife Soltani, A.; Naghizadeh, R.; Riahi-Noori, N.; Aghababazadeh, R.; Westwood A. Enhancement in Graphitization of Coal Tar Pitch by Functionalized Carbon Nanotubes. *RSC Adv.* **2017**, *7*, 5533–5540. https://doi.org/10.1039/C6RA25441A
[2] Chesko, F.F.; Borisenko, A.L.; Martynova, A.Yu.; Shmalko, V.M.; Zelenskii, O.I. The Possibility of Reducing the Carcinogenicity of Coal Tar Electrode Pitches. *Pet. Coal* [Online] **2018**; *60*, 584–591. https://www.vurup.sk/wp-content/uploads/2018/06/PC_4_2018_Chesko_29.pdf (accessed May 31, 2018).
[3] Kovalev, E.T.; Cheshko, F.F.; Ponomarenko, N.V. The Use of Coke–Chemical Materials to the Regulation of the Electrode Coal Tar Pitch Quality. *Pet. Coal* [Online] **2021**, *63*, 317–323. https://www.vurup.sk/wp-content/uploads/2021/03/PC-X_Chesko 227-002.pdf (accessed May 31, 2018).
[4] Cheshko, F.F., Shustykov, V.I. Katalitychnyy vplyv na hrupovyy ta khimichnyy sklad kam'yanovuhil□noho peku. In *Problemy katalizu u vuhlekhimiyi*; Zbirnyk naukovykh prats AN Ukrainy; Naukova dumka: Kyiv, 1992; pp. 289–291.

[5] Crespo, J.L.; Arenillas, A.; Vina, J.A.; García, R.; Snape, C.E.; Moinelo, S.R. Effect of the Polymerization with Formaldehyde on the Thermal Reactivity of a Low-Temperature Coal Tar Pitch. *Energy Fuels* **2005**, *19*, 374–381. https://doi.org/10.1021/ef0498768

[6] Wang, Y.; Zhou, Q.; Zhao, Q; Qu, S.; Zhang, Y. Study on Relationships between Coal Microstructure and Coke Quality during Coking Process. *Processes* **2023**, *11*, 724. https://doi.org/10.3390/pr11030724

[7] Nesterenko, L.L.; Biryukov, Yu.V.; Lebedyev, V.A. *Osnovy khimii ta fizyky horyuchykh kopalyn*; Vyshcha shkola: Kyiv, 1987.

[8] Liu, Yu.-Ch.; Hung, Yu.-H.H.; Sutarsis, Ch.-Ch. H.; Ni, Ch.-Sh.; Liu, T.-Yi.; Chang, J.-K.; Chen, H.-Y. Effects of Surface Functional Groups of Coal-Tar-Pitch-Derived Nanoporous Carbon Anodes on Microbial Fuel Cell Performance. *Renew. Energy* **2021**, *171*, 87–94. https://doi.org/10.1016/j.renene.2021.01.149

[9] Sarkar, A.; Kocaefe, D.; Kocaefe, Y.; Bhattacharyay, D.; Sarkar, D.; Morais, B.; Chabot, J. Coke-Pitch Interactions During Anode Preparation. *Fuel* **2014**, *117A*, 598–607 https://doi.org/10.1016/j.fuel.2013.09.015

[10] Lee, S.-H.; Roh, J.-S. Changes in Functional Groups and Crystal Structure of Coal Tar Pitch with Respect to Carbonization Temperature. *Crystals* **2024**, *14*, 1–13. https://doi.org/10.3390/cryst14020122.

[11] Imangazy, A.; Smagulova, G.; Kaidar, B.; Mansurov, Z.; Kerimkulova, A.; Umbetkaliev, K.; Zakhidov, A.; Vorobyev, P.; Jumadilov, T. Compositional Fibers Based on Coal Tar Mesophase Pitch Obtained by Electrospinning Method. *Chem. Chem. Technol.* **2021**, *15*, 403–407. https://doi.org/10.23939/chcht15.03.403

[12] Marsh, H.; Neavel, R.C. Carbonization and Liquid-crystal (Mesophase) Development. 15. A common Stage in Mechanisms of Coal Liquefaction and of Coal Blends for Coke Making. *Fuel* **1980**, *59*, 511–513. https://doi.org/10.1016/0016-2361(80)90179-9

[13] Kim, J.-H.; Hwang, H.-I.; Im, J.-S. Coal Carbonization: Formation, Properties and Relevance of Microstructures in Resultant Cokes. *Materials* **2023**, *16*, 4084. https://doi.org/10.3390/ma16114084

[14] Bégin, D.; Alain, E.; Furdin, G.; Marêché, F. Pyrolysis of Coal Tar Pitch and its Mixtures with a Graphite-FeCl₃ Intercalated Compound. Influence of Heating Rate and GIC Concentration. *Fuel* **1995**, *74*, 139–146. https://doi.org/10.1016/0016-2361(95)92646-N

[15] Odian, G. *Principles of Polymerization*, 4th ed.; Wiley-Interscience: Hoboken, NJ, 2004.

[16] Chen, L.; Guo, F.; Wu, J.; Li, P.; Zhang, Y. Research on Coal Tar Pitch Catalytic Oxidation and Its Effect on the Emission of PAHs during Co-Carbonation with Coal. *Catalysts* **2021**, *11*, 1–15. https://doi.org/10.3390/catal11121428

[17] Tulepov, M.; Sassykova, L.; Kerimkulova, A.; Tureshova, G.; Abdrakova, F.; Zhapekova, A.; Sultanova, Z.; Spanova, G.; Tolep, D.; Gabdrashova, Sh.; Baiseitov, D. Preparation of Briquettes on the Basis of Sub-Standard Coal of Kazakhstan Fields. *Chem. Chem. Technol.* **2022**, *16*, 118–125. https://doi.org/10.23939/chcht16.01.118

[18] Greenwood, N.N.; Earnshaw, A. *Chemistry of the Elements*; Elsevier, 2012.

[19] Chemist's Handbook; V. II; STPH of Chem. Lit, 1951.

[20] Kaftan, Yu.S; Drozdnik, I.D.; Miroshnichenko, D.V.; Bidolenko, N.B.; Ryshchenko, A.I. Relationship between Organic and Mineral Parts of Coal Blend and "Hot" and "Cold" Coke Strength. *Journal of Coal Chemistry* **2007**, *3–4*, 3–13.

[21] Galushko, A.A.; Lysik, N.A.; Miroshnichenko, D.V.; Litvinenko, O.V. Spectrometrical Analysis for the Determination of the Chemical Composition of Ash of Coal Concentrates (Blends) at PJSC "EVRAZ YUZKOKS". *Journal of Coal Chemistry* **2017**, *4*, 3–11.

**КЕРУВАННЯ ТЕРМОХІМІЧНИМИ ПЕРЕТВОРЕННЯМИ КОМПОНЕНТІВ ЗВ'ЯЗУЮЧИХ МАТЕРІАЛІВ КАМ'ЯНОВУГІЛЬНОГО ПОХОДЖЕННЯ**

\

**Анотація.** *Проаналізовано можливість розглядати кам'яновугільний пек як матеріал, придатний для дослідницького моделювання процесів термохімічних перетворень пластичної маси карбонізації вугілля та її взаємодії з твердою вуглецевою фазою. Показано можливості керування властивостями кам'яновугільного пеку та доменного коксу під час його виготовлення добавками апротонової кислоти в присутності співкаталізатора.*

**Ключові слова:** *кам'яновугільний пек, кам'яновугільна пластична маса, зв'язуюче, наповнювач, термохімічні перетворення.*