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IMPACT OF THERMO-OXIDATIVE TREATMENT AND HEATING ON CARBONISATION YIELD IN ELECTRODE-GRADE COAL PITCHES

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Abstract. *The paper presents the results of the impact of thermal treatment of electrode pitch category B (JSC Evraz ZSMK, Russia) on the carbonisation yield. The effect of additives from thermo-oxidation products of electrode pitch category C (JSC Altai-Koks, Russia) on the carbonisation yield of electrode pitch category B has been established. The dependencies of the carbonisation yield on the heating temperature of electrode pitch category B were determined. The introduction of additives in the form of high-temperature and high-melting pitch into electrode pitch category B reduces the volatile matter yield and increases the carbonisation yield.*

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Introduction

Coal tar pitch (CP) is a residue of coal tar separation into fractions: light fraction (T < 170 °C); phenolic fraction (T = 170-210 °C); naphthalene fraction (T = 210-230 °C); absorption fraction (T = 230-270 °C); anthracene fraction (270-360 °C); coal tar pitch (T < 360 °C).

Pitch is a multicomponent structure consisting of the following fractions: γ-fraction, soluble in hexane, isooctane; β-fraction, insoluble in hexane but soluble in toluene; α-fraction, insoluble in toluene, divided into quinoline-soluble α_2-fraction and quinoline-insoluble α_1-fraction [1]. According to studies [2-4], the composition of these fractions has been determined:

- the γ-fraction consists of chrysene, pyrene, anthracene, naphthalene, carbazole, phenanthrene, and methylnaphthalene;
- the β-fraction comprises the following polyaromatic compounds: benzo[a]anthracene, benzo[a]pyrene, cyclopenta[ghi]perylene, dibenzo[b,d]thiophene, etc.;
- The α-fraction contains diphenyl oxide, acenaphthene, benzofluoranthene [4], as well as high-molecular-weight compounds: $C_{62}H_{34}$; $C_{60}H_{28}$; $C_{64}H_{24}$; $C_{62}H_{20}$ [2].

The coal tar pitches are binders for the production of electrodes and anode mass [5]. To obtain binders for cathode production in the aluminium industry, according to [6-8], pitches undergo thermal treatment to increase the softening point (T_s), carbonisation yield, and pitch coke yield. Thermal treatment of pitch with T_s = 110 °C at 260 °C for 4-5 days led to an increase in T_s to 157 °C. It is associated with a growth in the α-fraction from 26.4% to 68.6% and an increase in the α_1-fraction from 4.7% to 5.6% [6]. Raising the thermal treatment temperature from 220 °C to 420 °C increased the coke yield from 47.21% to 69.64% [7]. Increasing the pitch thermal treatment temperature to 400°C enhanced the semi-coke and carbonisation yields, and the α_1-fraction content in the final product [8].

Studies [9,10] investigated the effect of thermal treatment on pitch properties in details. Pitches were thermally treated at various temperatures for several hours. The increase in pitch softening point T_s is linked to the growth of the α-fraction. It increased from 30% to 60%; the maximum thermal treatment temperature was raised from 360 °C to 390 °C (duration: 3 hours) [9]. According to the study [10], thermal treatment at 300 °C of medium-temperature electrode pitches leads to an increase in pitch carbonisation yield and a decrease in volatile matter yield for both the carbonizate and the pitch.

In the study [11] medium-temperature electrode pitches were thermally treated at 350 °C for several hours. As a result, an increase in the softening point (T_s) and a decrease in the volatile matter yield (X) were observed. For pitch category B, the increase in T_s occurred faster and reached up to 180 °C compared to pitch category B1 [11]. When mixtures of electrode pitches were thermally treated using both IR and microwave irradiation, products with a softening point T_s > 100 °C were obtained [12].

The thermal treatment of pitches in an air stream (thermo-oxidation) has the greatest fundamental and applied significance for research. Thermo-oxidation (TO) is divided into low-temperature (up to 300 °C) and high-temperature (above 300 °C) processes [13-15]. During low-temperature TO, reactions occur in the gas phase: $\gamma \rightarrow \alpha_2$ [13-15], as experimentally demonstrated in studies [13-17]. During high-temperature TO, in addition to gas-phase reactions, liquid-phase reactions of the following type occur: $\gamma \rightarrow \beta \rightarrow \alpha_2 \rightarrow \alpha_1$ [13-16].

We consider the results of studies on the impact of thermo-oxidation on changes in pitch characteristics and the yield of pitch carbonizates. In study [18] a high-temperature pitch (T_s = 150 °C) was obtained by TO at T = 260-380 °C for 35 minutes (air flow rate 100 L/h (400 L/kg·h)) using electrode pitch category C (T_s = 91 °C). According to the study [19], TO of medium-temperature electrode pitch at T > 400 °C increased the carbonisation yield and reduced the volatile matter yield for both the pitch and the carbonizate. A similar effect was observed during TO of coal tar in study [20]. In [20], coal tar was thermo-oxidized from 260 to 360 °C, resulting in a pitch with T_s = 128 °C, and it was found that TO reduces the volatile matter yield in the pitch carbonizate compared to the volatile matter yield in the carbonizate from pitch obtained by distillation of coal tar.

Of particular interest is the study of the combination of TO and thermal treatment of pitch. In study [21], a pitch with T_s = 114 °C was obtained by TO at T = 260-320 °C of pitch category C (the same initial pitch as in study [18]), followed by heating in a self-gas atmosphere to T = 410 °C for 28 minutes. A high-melting pitch with T_s = 202 °C was produced by TO at T = 260-320 °C (using pitch C, as in study [18]) for 32 minutes with an air flow rate of 100 L/h, followed by heating from 320 to 400 °C for 43 minutes, holding at T = 400 °C for 40 minutes, and TO (air flow rate 40 L/h) from 400 to 430 °C for 50 minutes [21].

It is necessary to consider the prospects of introducing additives in the form of high-temperature and high-melting pitches into electrode pitch to enhance the carbonisation yield and determine their impact on improving the coking properties of binder pitches. To improve the characteristics of electrode pitches, the effect of heating at various temperatures on the carbonisation yield should be examined. Establishing the impact of pitch heating on the carbonisation yield offers the potential for applying this method to enhance the coking properties of binder pitches.

The purpose of the study is to determine the impact of additives in the form of electrode pitch category C and its thermo-oxidation products on the carbonisation yield of electrode pitch category B, and assess the effect of heating electrode pitches category B and C on the carbonisation yield.

Experimental part

As initial samples, electrode pitch category B with a softening point T_s = 71.5 °C (obtained on OOO Evraz ZSMK, Russia) and electrode pitch category C with T_s = 91 °C (obtained from OOO Altai-Koks, Russia) were used. Data on T_s and fractional composition are shown in Table 1.

Table 1. Characteristics of the fractional composition of electrode pitches categories B and C.

Name	Pitch B	Pitch C
T_s, °C	71	91
γ, %	28.0	29.0
β, %	39.8	34.5
α, %	32.2	36.5
α_1, %	10.3	7.5

Additionally, thermo-oxidation (TO) products of electrode pitch C were used: high-temperature pitch (HTP) with T_s = 150 °C, obtained in study [18]; high-melting pitch (HMP) with T_s = 202 °C [21]. The described pitches were carbonized by heating to 800 °C and holding at this temperature for 1 hour.

Thermal treatment of electrode pitches was conducted in a muffle furnace; the pitches were placed in lidded crucibles following the methodology described in studies [10, 11]. The pitches were heated to T = 290 °C, 330 °C, and 400 °C. The yield of pitch W after heating was determined as the percentage ratio of the pitch mass after heating to the mass of the pitch sample before heating. For pitches after heating, the volatile matter yield X was measured (GOST 9951-2023).

Composite formulations based on pitch category B with additives of pitch category C and their TO products (HTP and HMP) were also prepared. The pitches were mechanically crushed and sieved through a sieve with pore size ≤ 200 μm. To the crushed sample of pitch category B, an additive of crushed TO product (40% by mass) in the form of HTP or HMP was added. The mixture was thoroughly stirred with a spatula and placed in a ceramic crucible with a ground-in lid. The mixture was then heated in a muffle furnace to 220 °C and held at this temperature for

10 minutes. Heating ensured the production of a homogeneous product without separation of light pitch components, as evidenced by their absence on the ceramic lid of the crucible.

For thermally treated pitches and composite formulations, carbonisation was performed by heating in a muffle furnace to 800 °C and holding at this temperature for 1 hour. The carbonisation yield K was determined as the percentage ratio of the mass of the resulting carbonizate to the mass of the pitch sample.

Main body

The pitches obtained after thermal treatment in studies [18, 21] and the composite formulations were carbonised in lidded crucibles in a muffle furnace by heating to 800 °C and holding for 1 hour. Table 2 shows data on the volatile matter yield for pitch category C and the products obtained by thermo-oxidation (TO).

Table 2. Characteristics of electrode pitch category C and the resulting thermo-oxidation (TO) products

№	Name	X, %	K, %
1	B	53	50.7
2	HMP	33	78.7
3	HTP	36	62.1

Table 2 shows a decrease in the volatile matter yield from 53% to 33% for HMP (high melting pitch) as a result of thermo-oxidation (TO) combined with thermal treatment of electrode pitch C [21]. The value of K (carbonisation yield) after thermal treatment increased to 78.7%. It can be explained from the following perspectives: TO of electrode pitch category C at T = 260-320 °C, as reported in [21], led to an increase in the α and α_1-fractions. Thermal treatment and TO in the low-temperature carbonisation region (at T ≥ 400 °C) result in a significant growth of the α_1-fraction, as it shown in [22]. This could lead to a noticeable increase in K. In the case of HTP (high-temperature pitch), TO of pitch C in the range of 260-360 °C, according to [16-19], promotes an increase in the α and α_1-fractions. It could contribute to the rise in K.

Table 3 shows the characteristics of electrode pitch B and composite formulations based on it.

Table 3. Characteristics of electrode pitch B and composite formulations based on it.

№	Name	X, %	K, %
1	B	54.4	54.3
2	B+C-40%	48.3	55.7
3	B+HTP-40%	46.8	64.5
4	B+HMP-40%	41.7	68.4

According to the Table 3, the introduction of additives in the form of pitches C, HTP, and HMP into category B pitch led to a noticeable increase in the value of K. The addition of electrode pitch category C to category B pitch increased K to 55.7%. Table 3 also shows a decrease in the volatile matter yield X for all types of additives as a result of the incorporation of additives into category B pitch. It can be assumed that the addition of thermo-oxidation (TO) products with reduced volatile matter yield X to category B pitch also reduces the percentage content of X in the final product. The decrease in X may also be a consequence of preliminary thermal treatment during the preparation of the mixture. Furthermore, it can be hypothesised that the addition of TO products to category B pitch increases the content of α and α_1-fractions in the final product. It leads to a quantitative increase in K.

Table 4 shows the dependence of the volatile matter yield on the heating temperature for category B and C pitches.

Table 4. Data on the volatile matter yield of electrode pitches category B and C depending on the heating temperature

№	For category B pitch				For category C pitch			
	T, °C	W, %	X, %	K, %	T, °C	W, %	X, %	K, %
1	290	98.8	53.8	54.4	290	99.4	52.2	53.3
2	330	95.8	50.0	54.7	330	96.7	48.6	53.8
3	400	89.8	45.5	65.0	400	90.3	43.0	60.0

According to the Table 4, after heating pitches B and C, the volatile matter yield X decreases. After heating to 330 °C, the value of X decreased from 54.3% to 50% for pitch B and from 53% to 48.6% for pitch C. Heating to 400 °C led to a decrease in the volatile matter yield to 45.5% for pitch B and to 43% for pitch C. Moreover, heating to 290 °C does not increase K compared to the original pitch in the case of category B pitch. However, there was a slight increase of 3% for category C pitch (see Tables 2 and 3). Increasing the heating temperature to 330 °C also did not lead to a significant increase in K for both pitch categories. Increasing the temperature to 400 °C resulted in an increase in the carbonisation yield by approximately 10% for both pitch categories.

Based on the data presented in Table 4, the dependence of K on X was obtained. Figure 1 shows the relationship between the carbonisation yield K and the volatile matter yield X.

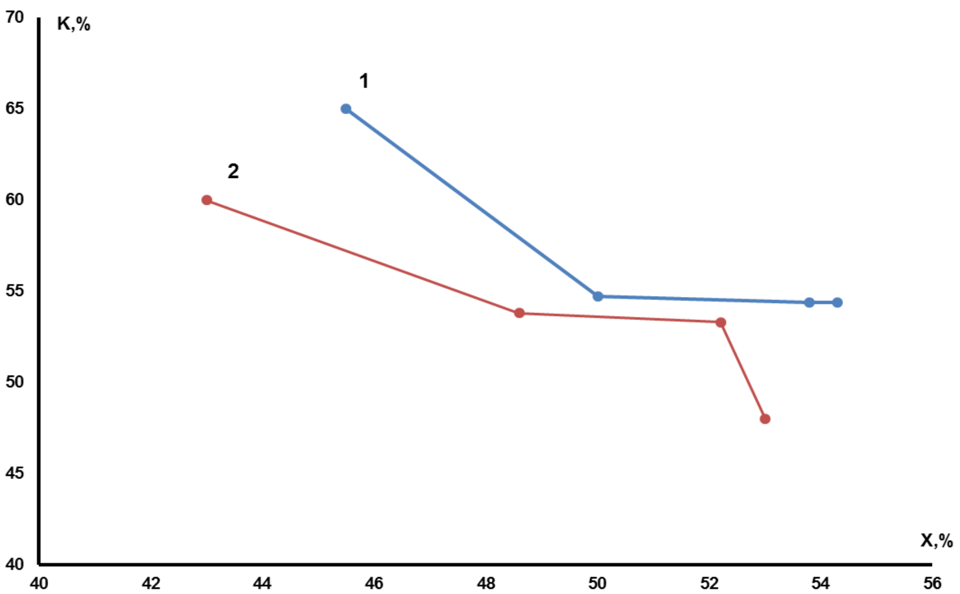

Fig. 1. Dependence of the carbonisation yield K on the volatile matter yield X for category B pitch after thermal treatment: 1 – for pitch B; 2 – for pitch C.

As shown in Fig. 1, the carbonisation yield K increases with a decrease in the volatile matter yield for pitches B and C.

According to the results of studies [9, 16, 17], during thermo-oxidation (TO) the increase in softening point T_s [9] and the growth of the α-fraction [9, 17] in pitch occur faster than during conventional thermal treatment in a self-gas atmosphere. Literature data [23-24] confirm increasing the α_1-fraction in pitches at temperatures above 300 °C. At temperatures of 400-500 °C, mesophase transformations occur [22, 25, 26, 27]. It is accompanied by a significant increase in the α_1-fraction, as reported in [22]. At temperatures above 500 °C, semi-coking and coking processes of pitches occur [7, 8, 26-29]. It can be assumed that the α_1-fraction may influence the carbonisation process and quantitatively increase the final product yield, as experimentally confirmed in [10, 20]. Hence, the increase in the α_1-fraction may play a significant role in enhancing the K value for high-temperature pitch (HTP) and vacuum-distilled pitch (HMP) compared to the original category C pitch (Table 2). It also explains higher carbonisation yield for pitch B than that of pitch C; pitch B has a higher α_1-fraction content (10.3%) compared to α_1-fraction of pitch C (7.5%) (Tables 3 and 4).

Heating to 290 °C led to the separation of light components of the pitches, as evidenced by the decrease in X (Table 3). Heating to 290 °C increased K only for pitch C, from 50.7% to 53.3%. For pitch B, heating to 290 and 330 °C did not affect the carbonisation yield. Increasing the temperature to 400 °C significantly reduced the yield of pitches W after heating, decreased the volatile matter yield X, and increased the carbonisation yield K. It may also be a consequence of the growth of the α and α_1-fractions, as reported in [6, 10, 22].

Conclusions

1. Thermo-oxidation of electrode pitch B increases the carbonisation yield.
2. The introduction of a 40% additive to category B pitch in the form of high-melting pitch increases the pitch carbonisation yield from 54.3% to 68.3%.
3. Increasing the heating temperature of electrode pitch B from 290 to 400 °C raises the carbonisation yield to 65%; for category C electrode pitch it reaches 60%.

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References

1. **Privalov V.E., Stepanenko M.A.** Coal pitch. Moscow: Metallurgiya, 1981. 208 p. (in Russian).
2. **Maltseva L.D., Gaisarov M.G., Mochalov V.V.** Study of the properties of pitches and their group components. *Koks i Khimiya [Coke and Chemistry]*, 1980, 8, 33-36 (in Russian).
3. **Yurkevich Ya., Rosinskii S.** Coal Chemistry. Moscow: Metallurgiya, 1973, 360 p. (in Russian).
4. **Kekin N.A., Stepan A.A.** On the data of chromatographic analysis and the composition of coal tar pitches. *Koks i Khimiya [Coke and Chemistry]*, 1986, 1, 30-34 (in Russian).
5. **Utkin Y.A., Yanko E.A., Soloveichik E.Y., Strakhov V.M.** Assessing coal pitch as a binder in anode production. *Coke and Chemistry*, 2012, 55(**9**), 342-346.

6. **Galiguzov A.A., Malakho A.P., Avdeev V.V., Rogozin A.D.** Comparative characteristics of coal tar pitches: qualitative analysis, stability of properties during storage, and thermal stability. *Izv. Vyssh. Uchebn. Zaved. Khim. Khim. Tekhnol. [Russian Journal of Chemistry and Chemical Technology]*, 2015, 5(**12**), 55-57 (in Russian).
7. **Xiaojun L., Jian X., Yanqing L., Jie L., Zhao F., Yan S., Yexiang L.** Effects of pitches modification on properties of TiB_2-C composite cathodes. *TMS Light Metals*, 2009, 1, 1-5.
8. **Lü X.J., Xu J., Li J., Lai Y.Q., Liu Y.X.** Thermal-treated pitches as binders for TiB_2/C composite cathodes. *Metall. Mater. Trans. A*, 2012, 43(**1**), 219-227.
9. **Chistyakov A.N.** Kinetics of thermal and thermo-oxidative transformation of coal tar pitch. *Koks i Khimiya [Coke and Chemistry]*, 1978, 11, 38-40 (in Russian).
10. **Kovalev R.Yu., Nikitin A.P.** Investigation of the influence of thermal treatment of electrode pitches on carbonization product yields. *Chemistry for Sustainable Development*, 2024, 32(**6**), 839-844. DOI: 10.15372/KhUR2024616. (in Russian).
11. **Kovalev R.Yu., Naimushina T.M., Nikitin A.P.** Thermal treatment of medium-temperature electrode coal tar pitches. Materials in External Fields: Proceedings of the XII International Online Symposium. Novokuznetsk: Publishing Center of SibSIU, 2024, pp. 88-90 (in Russian).
12. **Tolmacheva T.V., Berveno V.P., Grigoriev V.M.** Relationship between the softening temperature of the mixture and components of coal tar binder pitch. *Polzunov. Vestn. (Polzunov Bulletin)*, 2011, 4, 206-208 (in Russian).
13. **Sidorov O.F.** Process of thermal oxidation of coal tar pitches. *Coke and Chemistry*, 2002, 9, 35-43.
14. **Sidorov O.F.** Modern ideas about the process of thermal oxidation of coal pitch. Part 3. Impact of oxidation conditions on the character of thermochemical transformations and structure of pitch. *Koks i Khimiya [Coke and Chemistry]*, 2004, 6, 24-30 (in Russian).
15. **Mochalov V.V.** Structural features of coal tar electrode pitches. *Raw Materials for Electrode Production: Collection of Scientific Papers*. Moscow: NIIgrafit, 1986, pp. 5-19 (in Russian).
16. **Sidorov O.F., Seleznev A.N.** Prospects for production and improvement of consumer properties of coal tar electrode pitches. *Ross. Khim. Zh. (Russian Chemical Journal)*, 2006, l(**1**), 16-24 (in Russian).
17. **Kovalev R.Yu., Gavriljuk O.M., Nikitin A.P., Ismagilov Z.R.** Thermal Oxidation of Electrode Coal Pitch. *Coke Chem.*, 2023, 66(**7**), 351-354. DOI: 10.3103/S1068364X23700941.
18. **Kovalev R.Yu., Gavrilyuk O.M.** Optimizatsiya tekhnologii polucheniya vysokotemperaturnogo peka. *Innovatsionnyi konvent "Kuzbass: obrazovanie, nauka, innovatsii": Materialy XII Innovatsionnogo konventa.* Kemerovo: Kemerovskii gosudarstvennyi universitet, 2024, 356-357 *(in Russian).*
19. **Kovalev R.Yu.** Study of the heat treatment effect of medium-temperature electrode pitch on carbonisate yield. *From Chemistry Towards Technology Step-by-Step*, 2024, 5(**4**), 113-120. DOI: 10.52957/2782-1900-2024-5-4-35-42.
20. **Kovalev R.Yu.** Comparative analysis of fractional composition of pitches obtained from coal tar depending on production technology. *Bulletin of TvSU. Series: Chemistry*, 2024, 4(**58**), 147-158. DOI: 10.26456/vtchem2024.4.15 (in Russian).
21. **Kovalev R.Yu., Naimushina T.M.** Thermal treatment of electrode pitch. *Materials in External Fields: Proceedings of the XII International Online Symposium*. Novokuznetsk: Publishing Center of SibSIU, 2024, pp. 92-94 (in Russian).
22. **Yuan G., Xue Z., Cui Z., Westwood A., Dong Z., Cong Y., Zhang J., Zhu H., Li X.** Constructing the bridge from isotropic to anisotropic pitches for preparing pitch-based carbon fibers with tunable structures and properties. *ACS Omega*, 2020, 5(**34**), 21948-21960. DOI: 10.1021/acsomega.0c03226.
23. **Gaisarov M.G., Maltsev L.D., Mochalov V.V.** On the nature of the α_1-fraction of pitch and its effect on the quality of carbonaceous products. *Koks i himiya [Coke and chemistry]*. 1981. Vol. 10, pp. 37-39 (in Russian).
24. **Twigg A.N.** Relationship between chemical structure and secondary quinoline insoluble for-mation in electrode binder pitches. *Fuel*, 1987, 66(**11**), 1540-1543. DOI: 10.1016/0016-2361(87)90015-9.
25. **Kumari K., Rani S., Kumar P., Prakash S., Dhakate S.R., Kumari S.** Study of mesophase pitch based carbon fibers: Structural changes as a function of anisotropic content. *J. Anal. Appl. Pyrolysis*, 2023, 171, 105961. DOI: 10.1016/j.jaap.2023.105961.

26. **Li L., Lin X., Zhang Y., Dai J., Xu D., Wang Y.** Characteristics of the mesophase and needle coke derived from the blended coal tar and biomass tar pitch. *J. Anal. Appl. Pyrolysis*, 2020, 150, 104889. DOI: 10.1016/j.jaap.2020.104889.
27. **Cheng X., Zha Q., Zhong J., Yang X.** Needle coke formation derived from co-carbonization of ethylene tar pitch and polystyrene. *Fuel*, 2009, 88(**11**), 2188-2192. DOI: 10.1016/j.fuel.2009.05.006.
28. **Svitilova J., Machovic V., Kolar F.** 9,10-bis(chlormethyl)anthracene-curing agent of coal tar pitch. *Acta Geodyn. Geomater.*, 2006, 3(**2**), 57-62.
29. **Montes-Morán M.A., Crespo J.L., Young R.J., Garcıa R., Moinelo S.R.** Mesophase from a coal tar pitch: a Raman spectroscopy study. *Fuel Process. Technol.*, 2002, 77, 207-212. DOI: 10.1016/S0378-3820(02)00079-6.

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