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ASSESSMENT OF THE PROSPECTS FOR USING THERMO-OXIDATION OF ELECTRODE PITCH TO OBTAIN HIGH-TEMPERATURE BINDING PITCH

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Keywords:
coal tar pitch, thermal oxidation, softening temperature, pitch yield, high-temperature pitch, binding pitch, pitch carbonatate, pitch-coke mixture

Abstract. *The paper analyses the products of thermal oxidation of grade B electrode pitch. The research presents the results of analysis of high-temperature pitch production by thermal oxidation of grade B electrode pitch in a reactor with a large gas space. The dependence of the softening temperature and volatile matter yields on the air flow rate for this type of thermal oxidation has been determined. During the experiment, the dependence of the carbonisate yield on the duration of thermal oxidation of grade B electrode pitch has been obtained. Carbonisation was conducted by heating the initial grade B electrode pitch and the pitches obtained by its thermal oxidation. The research establishes criteria for the special type of thermal oxidation to increase the category of coke and shows the results of carbonisation of a pitch-coke mixture containing various types of coke.*

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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).

Coal tar pitch is used as a binder in the production of carbon materials. Specifically, pitch has practical applications as a binder in the production of electrodes, in the manufacture of anode paste, and in the production of electrocarbon products. According to [1], electrode pitch grades B1 and B are used as binders for anode paste. Of particular interest is the use of pitch with a softening temperature T_p > 100 °C and high-temperature pitch as binders. In [2], the practical significance of using high-temperature pitch as a binder is assessed. In [3-5], it is established that pitches with a softening temperature T_p = 100-110 °C reduce the destructibility of anode paste. According to [6], density, viscosity, and surface tension values of high-temperature pitch are higher than those of electrode pitches. It determines its prospects for use as a binder.

We consider technologies for producing binding pitch with T_p > 100 °C and high-temperature binding pitch. In [7], coal tar was distilled by heating it at a rate of 5 °C/min to a temperature of 430 °C, followed by holding it at this temperature for 1 hour, to obtain a pitch with T_p = 139.5 °C (α content = 51.7%; α_1 content = 17.3%; ash content of 0.09%). In [8], high-temperature binding pitch was obtained by thermally dissolving coal in the anthracene fraction. For example, by thermally dissolving a mixture of GZh+Zh coals in the anthracene fraction (coal/solvent ratio ~1.5), a pitch with T_p = 139 °C was obtained. In [9], a technology for obtaining high-temperature petroleum pitches from heavy pyrolysis tar was developed. In [10], liquid thermal cracking pitch was subjected to distillation to a vacuum column temperature of 363 °C at a vacuum column pressure (P = 1.6 kPa), resulting in pitch with T_p = 133 °C. High-temperature pitch with T_p = 135 °C (α = 48.5%, α_1 = 11.6%) was obtained by adding furfuryl acetone with a mass fraction of 7% to high-temperature pitch. This pitch T_p = 145 °C (α = 52%, α_1 = 26%) has furfuryl acetate with a mass fraction of 7%. It was further heat treated at 150 °C for 30 min with cooling of the mixture; the heat treatment was repeated at the same temperature for 25-30 min [11].

The method of obtaining high-temperature binding pitch by thermo-oxidation of the raw material is of particular interest for research. In [12], coal tar pitch was thermally oxidised by supplying air to the pitch through a 9 mm diameter tube at temperatures of 260-360 °C (process duration t = 73 min, air flow rate ν = 100 l/h) to obtain pitch with T_p = 128 °C. The thermal oxidation leads to an increase in the α and α_1 fractions in the final product. In [13], by the method of thermal oxidation (T = 260-360 °C, ν = 63 l/h) of a mixture of styrene rectification bottom residue (SBR) and coal tar resin in a 1:1 ratio with preliminary ultrasonic treatment of the mixture, a pitch with T_p = 104 °C was obtained (pitch yield is 25%, thermo-oxidation duration t = 40 min). For the obtained pitch, the coke residue was 40.5%; the content of binder fractions was $\beta+\alpha_2$ = 60.5%; the ash content was 0.25%. In [14], by the thermal oxidation method (T = 260-360 °C, ν = 63 l/h, t = 25 min) of the anthracene fraction with the addition of grade G coal (6.3%), a pitch with T_p = 135 °C was obtained A pitch yield is 29%; coke residue is 46.5%; ash content is 0.96%. In [15], by the thermal oxidation method (T = 260-360 °C, ν = 63 l/h, t = 135 min), coal tar with the addition of rubber crumbs (5%); yielded pitch with T_p = 184 °C; pitch yield is 37%; coke residue is 75.2%; ash content is 0.5% was obtained. In [16], by the thermal oxidation method (T = 260-360 °C, ν = 63 l/h, t = 91 min), coal tar with the addition of polycarbonate (5%) was used to obtain pitch with T_p = 131 °C. The pitch yield is 29%; binder fraction content is $\beta+\alpha_2$ = 74.3%; coke residue is 40.6%; ash content is 0.06%.

In addition, examples of obtaining binding pitch with T_p = 110-120°C and high-temperature binding pitch by thermo-oxidation of electrode pitch should be considered. In [17], by the low-temperature thermo-oxidation method (T = 260-300 °C, ν = 40 l/h, t = 90 min) of electrode pitch grade B (T_p = 91 °C), pitch with T_p = 107 °C was obtained. The resulting pitch has high content of binding fractions: their content increased from 63.8% to 70% compared to the initial pitch [17]. In [18], low-temperature thermo-oxidation of grade B electrode pitch (T_p = 91 °C) was used to obtain pitches with T_p = 110-120 °C. Similar experiments were conducted in [19]. In [20], high-temperature pitch with T_p = 136 °C was obtained by thermo-oxidation (T = 260-360 °C, ν = 80 l/h, t = 110 min). Thermal oxidation of electrode pitch in [20] was conducted in a reactor with a large gas space.

This paper evaluates the use of thermal oxidation of grade B electrode pitch in a reactor with a large gas space to obtain high-temperature binder pitch. A comparative analysis of the composition of the initial grade B pitch and the pitch products obtained by thermal oxidation in a reactor with a large gas space is made, and the thermal oxidation parameters at which grade B1 pitch can be obtained are determined. Model experiments were also conducted on the effect of grade B electrode pitch obtained by thermo-oxidation on the yield of carbonised pitch-coke mixture. High-temperature pitch obtained by thermo-oxidation of B-grade electrode pitch was used as the test one. The data obtained on the yield of carbonised pitch-coke mixture will allow assessing the prospects of using these pitches as a binder in the production of carbon materials. The above arguments determine the practical significance of this study. The study is a continuation of studies [12, 17, 18, 20-24] on the use of thermal oxidation and heat treatment of raw materials to obtain high-temperature binder pitch.

The purposes of this study are to determine the dependence of the softening temperature and volatile matter yields of pitch products of thermal oxidation in a reactor with a large gas space on the air flow rate; assess the prospects for using low-temperature thermo-oxidation of grade B electrode pitch in a reactor with a large gas space to improve the grade of electrode pitch; establish the effect of thermo-oxidation of grade B electrode pitch in a reactor with a large gas space on the yield of pitch carbonatite and carbonatite of the pitch-coke mixture.

Materials and methods

The paper analyses the effect of thermal oxidation of grade B electrode pitch on the characteristics of the resulting pitches and on the yield of carbonisation products. The experiment on thermal oxidation of grade B electrode pitch was conducted in a reactor with a large gas space (Fig. 1) in [20].

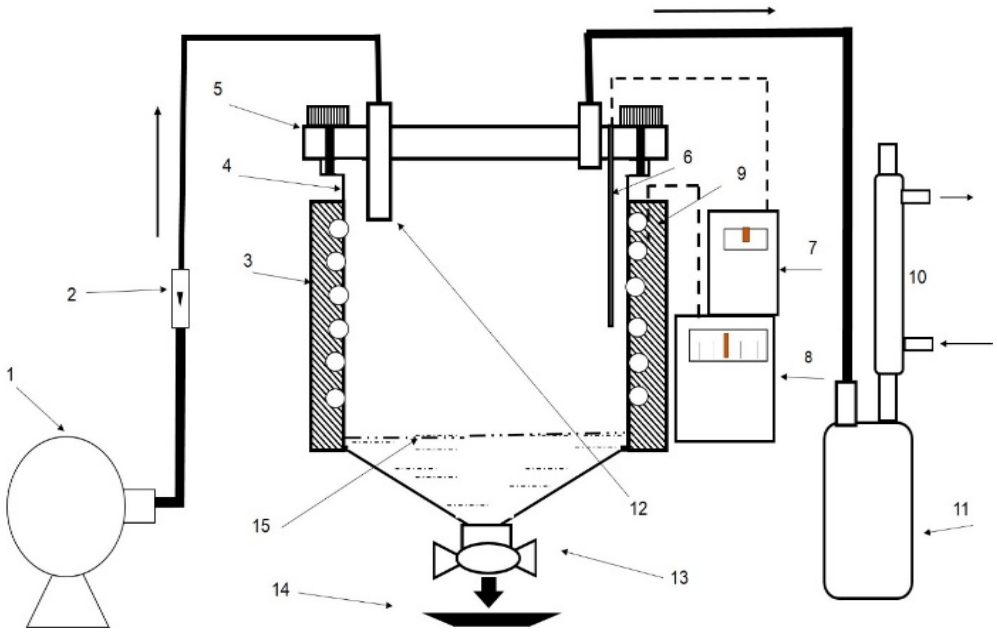

Fig. 1 Diagram of the electrode furnace installation: 1 – compressor; 2 – rotameter; 3 – electric heating system; 4 – reactor body; 5 – reactor cover; 6 – thermocouple for measuring the temperature in the reactor; 7 – secondary element; 8 – temperature controller; cylindrical oxidation tube; 9 – heating thermocouple; 10 – refrigerator; 11 – distillate collector; 12 – oxidation tube (10 mm); 13 – drain valve; 14 – baking tray; 15 – pitch [20].

We conducted the air treatment process for pitch oxidation through a tube with a diameter of 10 mm, length of 5.7 cm (12), with a distance of 24.3 cm from the tube to the bottom of the reactor. A pitch sample weighing m = 100 g was used (15). The height of the reactor and the location of the oxidation tube, allow us to conduct a reaction with a large volume for the gas phase. Air was supplied by a compressor (1); the air flow rate was regulated by a rotameter (2).

Thermal oxidation was conducted at the following temperatures: T = 260-300 °C (low temperature) and T = 260-360 °C (high temperature). The raise in T_p was facilitated by an increase in the duration of high-temperature thermal oxidation at T = 300-360 °C. Table 1 shows the distribution of the durations of high-temperature thermal oxidation of electrode pitch grade B.

Table 1. Distribution of thermal oxidation durations at T = 260–360 °C [20] (t is total thermal oxidation time, t_n is thermal oxidation duration at T = 260–300 °C, and τ is duration at T = 300–360 °C).

№	t	t_n	τ
1	20	10	10
2	48	23	25
3	63	30	33
4	110	32	78

Fig. 2 shows the dependence of T_p during the thermal oxidation of grade B electrode pitch in a reactor with a large gas space.

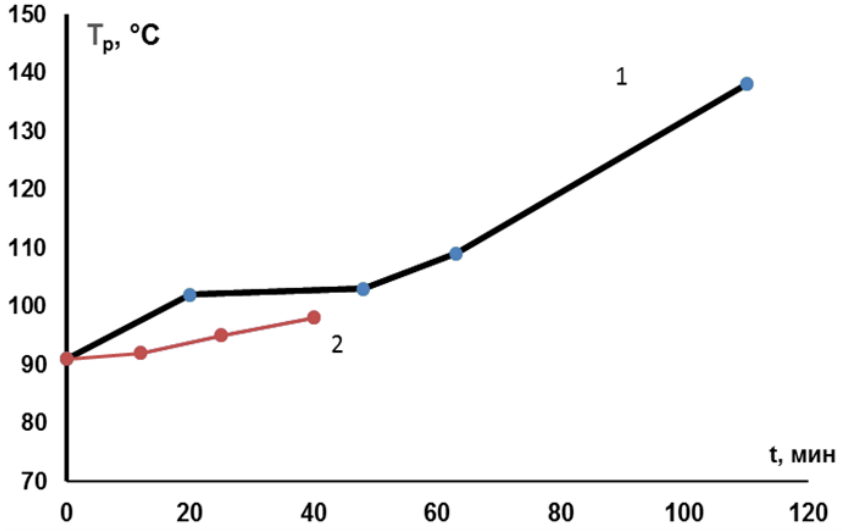

Fig. 2. Dependence of T_p growth on the duration of thermal oxidation of grade B electrode pitch in a reactor with a large gas space [20]: 1 – high-temperature thermal oxidation; 2 – low-temperature thermal oxidation.

Fig. 2 shows the intensive growth of T_p occurring at t ≥ 50 min. During low-temperature thermal oxidation with a maximum duration of t = 40 min (during low-temperature thermal oxidation, t = t_n), T_p increased to 98 °C. The maximum value of t_n = 32 min has a significant effect on the value of T_p during thermal oxidation in a reactor with a large gas space. Fig. 3 shows the dependence in the form of a graph $T_p = f(\tau)$.

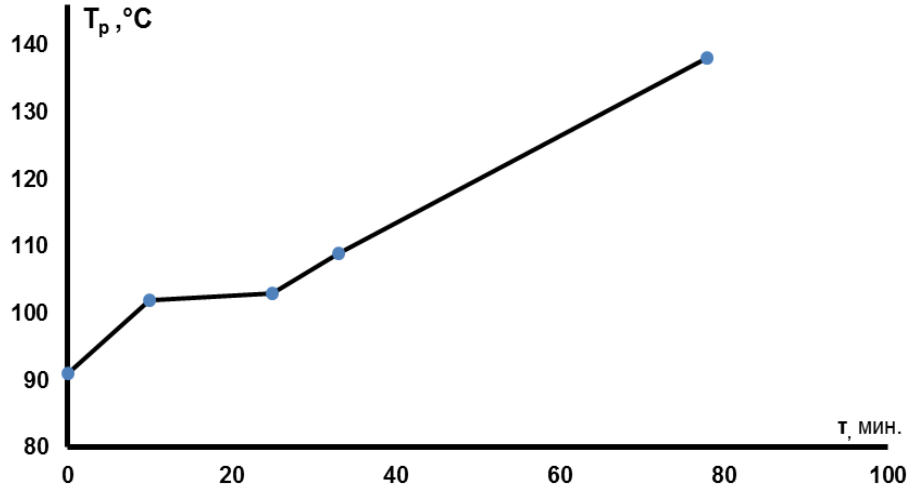

Fig. 3. Dependence of T_p growth on duration τ during high-temperature thermal oxidation of grade B electrode graphite in a reactor with a large gas space.

According to Fig. 3, a rapid increase in T_p occurred at τ ≥ 25 min during high-temperature thermal oxidation of grade B electrode pitch in a reactor with a large gas space. Based on the data obtained in [20], the pitch yield decreased with increasing τ. Fig. 4 shows the approximate dependencies of pitch yields on durations t and τ.

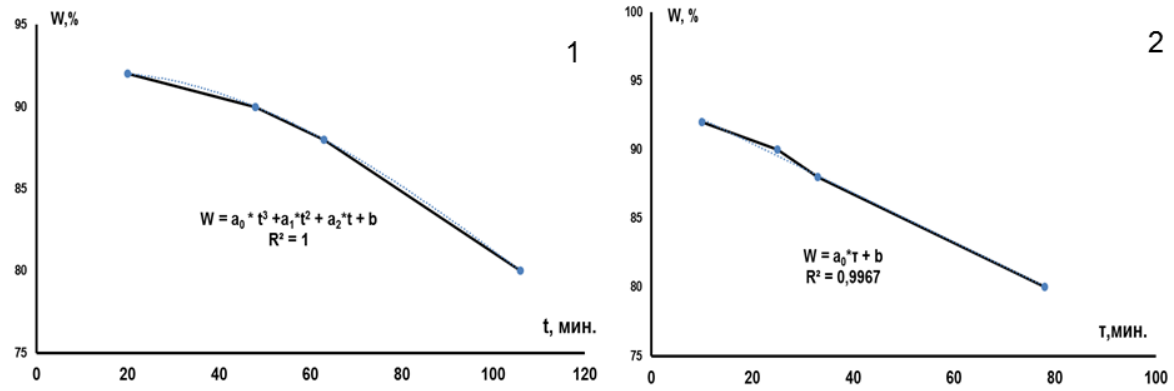

Fig. 4. Dependence of the decrease in pitch yield W on duration t (1) [20] and τ (2) during high-temperature thermal oxidation of grade B electrode pitch in a reactor with a large gas space.

Fig. 4 shows that, when approximated, the dependence W = f(t) is expressed by a polynomial function of the following type:

$$W = a_0 \times t^3 + a_1 \times t^2 + a_2 \times t + b,$$

where a_0 = 6*10^{-6}, a_1 = –0.0022, a_2 = 0.0588 are the coefficients at t^3, t^2 and t, respectively, and the coefficient b = 91.673 is a free term.

When approximating the dependence W = f(τ), the dependence is linear. It is evidenced by the square of the linear correlation coefficient $R^2 \approx 1$. According to it, it is possible to determine the rate of decrease in pitch yield $\Delta W/\Delta\tau \approx 0.18$ %/min during thermal oxidation of grade B electrode pitch in a reactor with a large gas space. The value b ≈ 92% in the case of curve 1 corresponds to the value W at t_0 = 20 min; curve 2 corresponds to the value W at t_0 = 10 min.

Table 2 presents a comparison of the characteristics of the initial B-grade electrode pitch and the high-temperature pitch obtained from it.

Table 2. Characteristics of B-grade electrode pitch and high-temperature pitch obtained from it [20].

№	Name	W, %	X, %	T_p, °C	α, %	α_2, %	α_1, %	Ash content, %
1	Pitch B (initial)	–	53	91	34.3	26.8	7.5	0.15
2	HTP	80	32	136	45.4	37.4	8.0	0.15

We determined the softening temperature T_p of the obtained pitches by the method 'Ring and rod' (GOST 9950-83). The content of α-fraction insoluble substances in toluene was determined in terms of GOST 7847. That of α_1-fraction insoluble in toluene and quinoline was determined according to GOST 10200 by centrifugation. The α_2-fraction content was determined using the following formula: $\alpha_2 = \alpha - \alpha_1$. We performed technical analysis according to known methods. Indeed, we determined the yield of volatile substances X according to GOST 9951-73; ash content of pitch was determined according to GOST7846-73. Table 2 shows a significant reduction in the yield of volatile substances during the thermal oxidation of grade B electrode pitch in a reactor with a large gas space. The content of the binding α_2 fraction in the final product increases by 8%. However, there is a slight increase in the α_1 fraction by 0.5%; it determines the prospect of using the obtained pitch as a high-temperature binding pitch.

This study evaluates the yield of gaseous and liquid products of thermal oxidation in a reactor with a large gas space of grade B electrode pitch. During thermal oxidation, liquid and gaseous products were separated. During low-temperature thermal oxidation, mainly gaseous products were separated. We introduce the value of the yield of gaseous products of thermal oxidation V_{lG}:

$$V_{lG} = \frac{m - \mathrm{M_{TO}}}{m} \times 100\ \%,$$

where m is the mass of the initial pitch; $\mathrm{M_{TO}}$ is the mass of the thermal oxidation pitch product.

Fig. 5 shows the dependence of V_{lG} on the duration t.

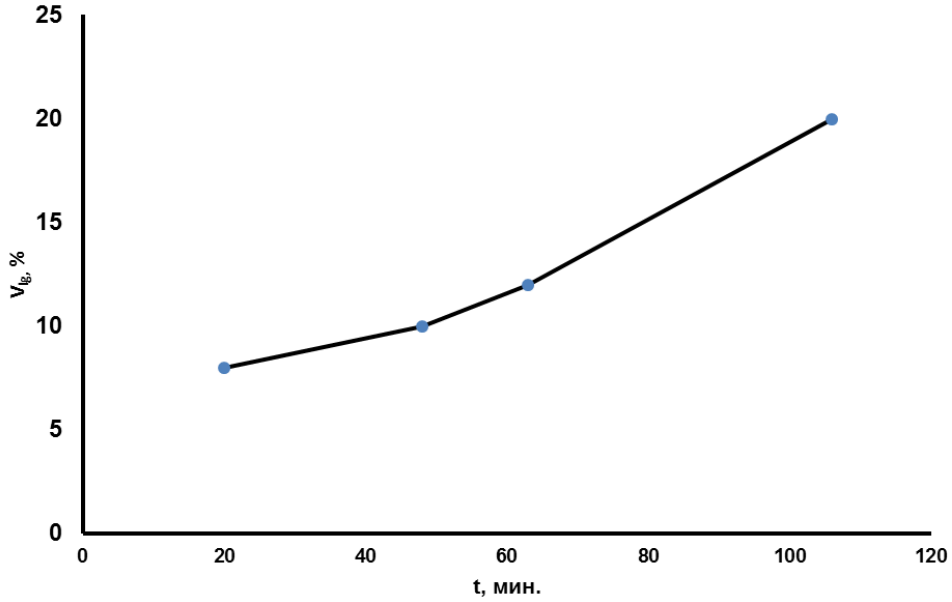

Fig. 5. Dependence of V_{lG} during thermal oxidation on the process duration.

According to Fig. 5, the duration of thermal oxidation increases from 20 to 110 minutes; the values of V_{lG} increase from 5 to 20%. This fact explains the decrease in the yield of volatile substances.

We introduce the concept of air consumption q and show formulas for its calculation from the determined values of air flow rate Q. The air consumption was calculated using the following formulas:

$$q_\tau = \frac{Q}{\tau^{-1} \times m},$$

where q_τ is the air consumption at T > 300°C, where τ is the duration of thermal oxidation at T > 300°C; m is the mass of the pitch sample.

$$q = \frac{Q}{t^{-1} \times m},$$

where q is the air consumption during thermal oxidation at T = 260-360°C; t is the duration of high-temperature thermal oxidation.

Moreover, we also conducted an experiment to determine the influence of pitch carbonisation on the duration of thermal oxidation. We carbonise a pitch by heating at a rate of 6.5 °C/min, with the pitches held at 1000 °C for 1 hour. We determined the carbonisate yield K_{1000} as the percentage of the mass of carbonisate obtained to the mass of pitch. Carbonisation was conducted by putting the pitch in ceramic crucibles and heating in a muffle furnace according to the methodology described in [21]. The final product was cooled in the furnace for 17-20 hours to room temperature.

The ready-made and crushed pitch carbonates were mixed as follows: 1 – carbonates of heat-treated electrode pitches of grades B and B1. Their heat treatment duration is 2 hours. They were obtained in the study [21]. Their maximum particle size is 5 mm. The proportion of B1 grade carbonates in the mixture is 2.16%; B grade carbonates is 8.7%. 2 – carbonates obtained from high-temperature pitches by heating to 950 °C at a rate of 6.6 °C/min. They are held at T = 950 °C for 1 hour. The proportion of carbonate obtained from pitch with T_p = 148 °C is 38.03%. The maximum particle size is 10 mm. Carbonate obtained from pitch with T_p = 150 °C is 10.56%. Its maximum particle size is 5 mm [22]. 3 – carbonate. Its maximum particle size is 10 mm. It was obtained by heating a mixture of grade B electrode pitch with 4.76% high-temperature pitch added to 850 °C and held for 1 hour [23]; 4 – carbonate. Its maximum particle size is 5 mm. It was obtained by heating bauxite with T_p = 140 °C to a temperature of T = 850 °C with a holding time of 1 hour; the additive content in the mixture is 14.72% [24]; 5 – carbonate. Its maximum particle size is10 mm. The high-melting pitch with T_p = 202 °C is 20.78%. It was obtained by carbonisation at 850 °C with a holding time of 1 hour [23].

The obtained mixtures were heated to T = 1050°C and held for 30 minutes; the resulting carbonisates can be considered pitch coke obtained under laboratory conditions. The pitch coke was crushed to sizes of ~1 mm; mixed with crushed (to sizes of 0.2 mm) pitch, followed by carbonisation at 1000°C. The pitch and cokes were ground separately in a mortar and sieved separately through a sieve with specified mesh sizes. The yield of the pitch-coke mixture carbonisate (CP) was determined as the percentage ratio of the carbonisate mass to the mass of the pitch and coke mixture. Carbonisation of the pitch-coke mixture was also conducted in a

muffle furnace according to the methodology described in [21]. After carbonisation, the obtained product was cooled in the furnace to room temperature for 17-20 hours.

Discussion of the results of the study

Dependence of the characteristics of pitch thermal oxidation products on air consumption.

Fig. 6 shows the dependences of the yields of thermal oxidation products of grade B electrode pitch in a reactor with a large gas space on air consumption.

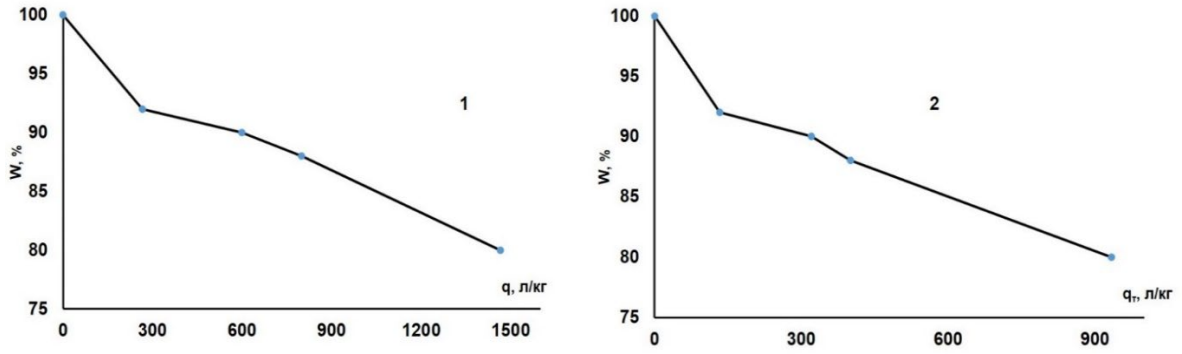

Fig. 6. Dependence of the yield of thermal oxidation product of grade B electrode pitch on air consumption, where 1 is the dependence of W on q; 2 is the dependence of W on q_τ.

According to Fig. 6, there is a sharp drop in W from 100 to 90% for curve 1 as q increases to 300 L/kg due to the increase in duration t from 0 to 20 min. Subsequently, the values of W monotonically decreased from 90 to 80% as q increased from 300 to 1500 L/kg due to the increase in duration t from 20 to 110 min (Fig. 4). For curve 2 (Fig. 6), a sharp drop in W values from 100 to 90% was also observed as q_τ increased from 0 to 133 L/kg due to the increase in duration τ from 0 to 10 min (Fig. 4). Subsequently, the values of W monotonically decreased from 90 to 80% as q_τ increased from 133 to 933 L/kg due to the increase in duration τ from 10 to 78 min (Fig. 4).

Fig. 7 shows the dependence of T_p values for pitch products on air consumption during the thermal oxidation of grade B electrode pitch in a reactor with a large gas space.

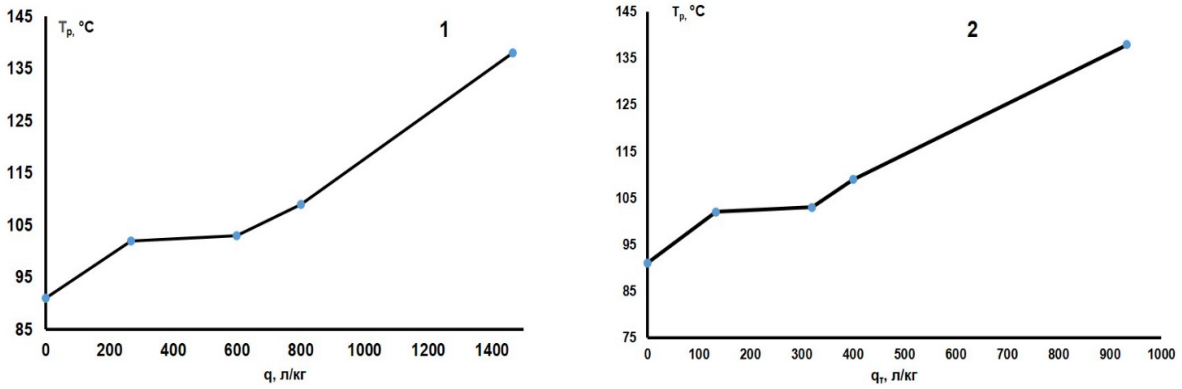

Fig. 7. Dependence of the softening temperature T_p of thermal oxidation pitch products of grade B electrode pitch on air consumption, where 1 is the dependence of T_p on q; 2 is the dependence of T_p on q_τ.

According to Fig. 7, there is a sharp increase in T_p from 91 to 102 °C for curve 1 as q increases to 300 L/kg due to the increase in duration t from 0 to 20 minutes. Subsequently,

the value of T_p remained almost unchanged as q increased from 300 to 600 L/kg. Then, the values of T_p monotonically increased from 103 to 138 °C as q increased from 600 to 1500 L/kg due to the increase in duration t from 40 to 110 minutes (Fig. 2). For curve 2 (Fig. 7), a sharp increase in T_p from 91 to 102 °C was also observed as q_τ increased from 0 to 133 L/kg due to the increase in duration τ from 0 to 10 minutes. The rate of increase in T_p also slowed as q_τ increased from 133 to 333 L/kg with the increase in duration τ from 10 to 25 minutes. The values of T_p monotonically increased from 103 to 138 °C as q_τ increased from 133 to 933 L/kg due to the increase in duration τ from 25 to 78 minutes (Fig. 3).

Fig. 8 presents the dependences of the volatile matter yield X of thermal oxidation products of grade B electrode pitch in a reactor with a large gas space on air consumption.

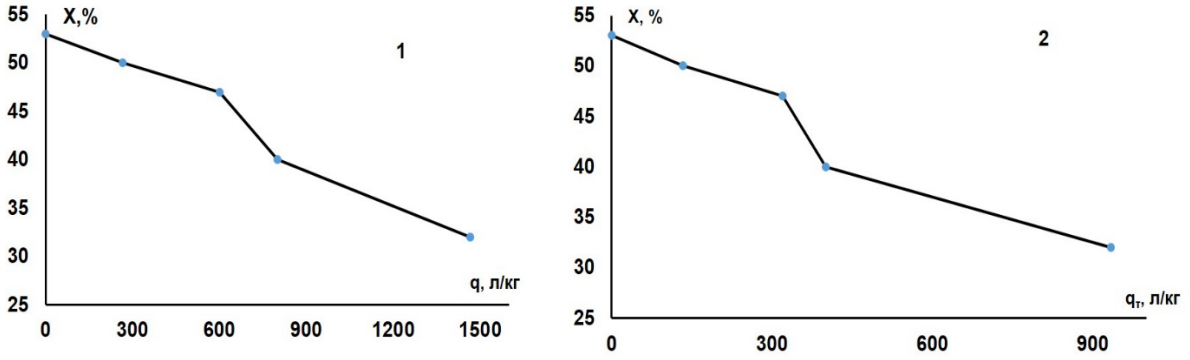

Fig. 8. Dependence of the yield of volatile substances X for pyrolysis products of electrode pitch grade B on air flow rate, where 1 is the dependence of T_p on q; 2 is the dependence of T_p on q_τ.

According to Fig. 8, the decrease in X from q and q_τ is associated with a decrease in the yield of volatile substances from t and τ (Fig. 9).

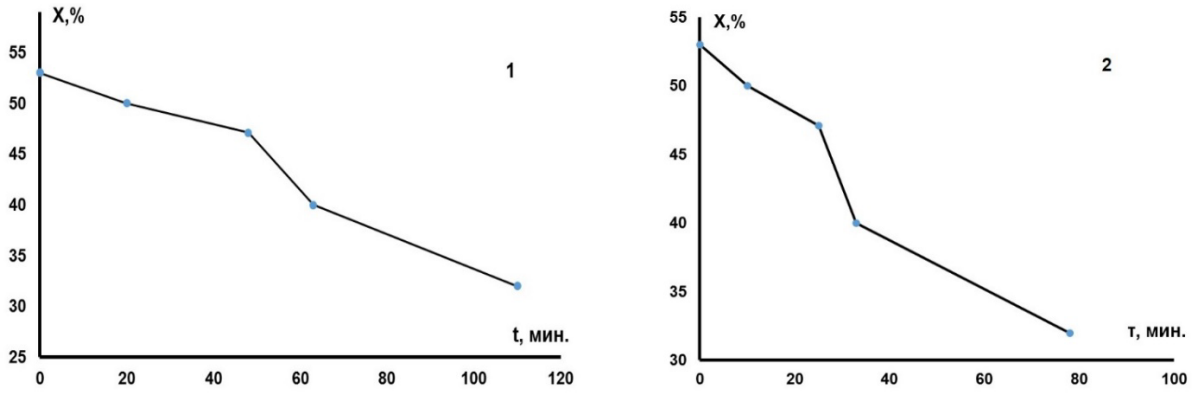

Fig. 9. Dependence of the yield of volatile substances of thermo-oxidation products of electrode pitch grade B in a reactor with a large gas space on duration: 1 – dependence of X on t [20]; 2 – dependence of X on τ.

According to Fig. 9, X decreases due to an increase in t and τ during the thermal oxidation of grade B electrode pitch. It determines the decrease in X due to an increase in q and q_τ.

2. The effect of thermal oxidation on improving the category of electrode pitch.

In [18], low-temperature thermal oxidation was used to increase the grade of pitch from grade B to grade B1. This paper considers the use of low-temperature thermal oxidation of grade B electrode pitch in a reactor with a large gas space to increase the grade.

Table 3. Characteristics of B-grade electrode pitch and pitch obtained from it

№	Name	Obtaining mode	T_p, °C	X, %
1	Electrode pitch B		91	53.1
2	P-1	T = 260-300 °C, t = t_n = 12 min, Q = 80 l/h	92	52.9
3	P-2	T = 260-300 °C, t = t_n = 25 min, Q = 80 l/h	95	52.6

According to Table 3, P-1 and P-2 pitches obtained by low-temperature thermal oxidation of B-grade electrode pitch in a reactor with a large gas space correspond to B1-grade pitches and GOST 10200-2017 in terms of their T_p and volatile matter yield X. The ash content for these pitch grades was ~0.15%. According to studies conducted in [17-18], during low-temperature thermal oxidation, the α_1 fraction content remains identical to the initial pitch α_1 = 7.5%. We evaluate the α fraction content according to the results of [20] (presented in Table 2): the α-fraction content in P-1 and P-2 pitches is in the range 34.3% ≤ α <45.4%. Therefore, P-1 and P-2 pitches correspond to B1 pitches according to T_p, technical analysis and fractional composition.

3. Carbonisation of pitch and pitch-coke mixture.

Pitch carbonates were obtained by heating pitch at a rate of 6.8 °C/min to 1000 °C with a holding time of 1 hour. Fig. 10 shows the dependence of K on the duration of thermal oxidation of grade B electrode pitch in a reactor with a large gas space.

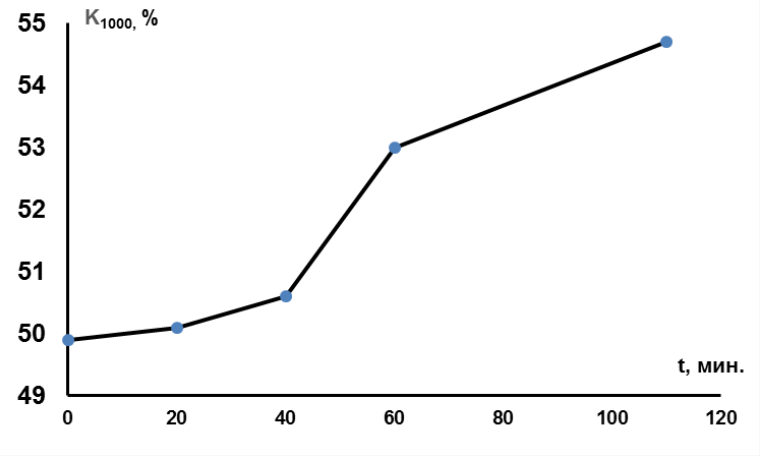

Fig. 10. Dependence of K_{1000} on the duration of the thermal oxidation process of electrode pitch grade B

According to Fig. 10, the duration of thermal oxidation of electrode pitch grade B increases; the carbonised product yield increases from 50 to 55%. A sharp increase in K_{1000} was observed at a thermal oxidation duration of t ≥ 40 min. A similar increase in K_{850} was observed at t > 20 min in [20]. In [20], the increase in K_{850} was from 48 to 59%. The differences in the values of K_{850} and K_{1000} and their increase depending on t may be associated with the difference in the heating rate. In work [20], the pitches were heated at a rate of 9-10 °C/min. There also was the difference in the final carbonisation temperature. Indeed, during the thermo-oxidation process, reactions of atmospheric oxygen with the molecular structure of the pitch occurred lead to the enlargement of molecules [25], thereby increasing the carbonisation yield. This result correlates with the data from [12, 21]. In [12, 21], the increase in carbonisation yield is associated with an increase in the α-fraction in the pitch.

We will consider the impact of various pitches on the yield of carbonised pitch-coke mixture. The following pitch samples were used: a pitch sample with T_p = 138 °C (HTP-1). It was obtained in [20] by thermal oxidation in a reactor with a large gas space; high-temperature pitch with T_p = 150 °C (HTP-2). It was obtained by thermo-oxidation of electrode pitch in [26]; high-melting pitch (HMP) with T_p = 202 °C. It was obtained by alternating thermal oxidation and heat treatment in a reducing environment at T ≥ 400 °C in [27]. All of the above-listed pitch types were obtained by thermo-oxidative treatment of electrode pitch grade B. The crushed HTP-1, HTP-2, HMP, and B pitch types were mixed with pitch coke and carbonised in a muffle furnace. The drop index was determined as the percentage ratio of the cumulative mass, i.e. the mass of the carbonised pitch-coke mixture remaining after discharge on sieves with a nominal hole size of 10 mm to the total mass of the test sample. The drop test was conducted by dropping samples of carbonates from a metal box onto a steel frame fixed to a concrete base. The drop test was conducted from a height of 1.8 m. The drop index characterises the strength characteristics of the carbon material obtained.

Table 4. Characteristics of pitch-coke mixture outputs after carbonisation

№	Name (coke/pitch ratio, %)	CP, %	Carbonisation mode	Drop index, %
1	C/HTP-1 (60/40)	76.4	T = 1000 °C, 2 h	98.6
2	C/HTP-1 (66/34)	82.6	T = 1000 °C, 1 h	97.3
3	C/HMP (40/60)	80.1	T = 450 °C, T = 1120 °C, 1 h	99.4
4	C/HTP-2 (62/38)	80.1	T = 1000 °C, 1 h	98.5
5	C/B (60/40)	76.01	T = 1000 °C, 1 h	96.6

According to Table 4, the maximum CP value was observed for sample No. 2. The coke-pitch ratio was 66/34. However, this pitch had a minimum drop index of 97.3%. Based on the data in Table 4, HTP-1 pitch is a product of the thermal oxidation of HTP-1 pitch in a reactor with a large gas space. It could be used as a binder in the production of carbon structural materials. For sample No. 1, increasing the proportion of HTP-1 pitch from 34 to 40% and carbonisation time from 1 to 2 hours reduced the CP from 82.6% to 76%. However, it increased the drop index from 97.3% to 98.6%. When using HMP pitch and preparing a pitch-coke mixture in a 40/60 ratio, followed by carbonisation, a heterogeneous product consisting of powder and a solid mass was obtained. Therefore, to obtain a high-strength and homogeneous material, the HMP content and carbonisation temperature were increased, additional aging at 450 °C was introduced. The resulting product (sample No. 3) using HMP had a high CP value and drop index. According to Table 4, B-grade electrode pitch-coke mixture, the CP value, and drop index are lower than for its thermally oxidised products. For HTP-1 pitch, this is associated with an increase in K_{1000} after the thermal oxidation of B-grade electrode pitch (Fig. 10). It is also associated with an increase in the carbonisation yield for HTP-2 pitch according to the results of [25].

Thermal oxidation of electrode pitch in a reactor with a large gas space leads to an increase in the α fraction from 34.3% to 45.4% (Table 2) with a minimal increase in the α_1 fraction.

In [28], an experiment was conducted on thermal oxidation in a reactor with a large gas space at 350 °C with an air flow rate of 1200 l/kg*h. The increase in the α fraction was accompanied by an increase in the α_1 fraction. Moreover, in [28], air was supplied closer to the molten pitch than in our study.

The dependencies for W (Fig. 6), T_p (Fig. 7) and X (Fig. 8) on the air flow rate q show these values changing with an increase in q due to an increase in t. Thermal oxidation of grade B electrode pitch in a reactor with a large gas space significantly reduces W. The increase in T_p occurs mainly due to an increase in the duration τ. With this type of thermal oxidation, gas-phase ($\gamma \rightarrow \alpha_2$) and liquid-phase ($\beta \rightarrow \alpha_2$) reactions mainly occur at T > 300 °C. It leads to an increase in the α_2 fraction, based on [29, 30]. Also, with this type of thermal oxidation, volatile substances are presumably blown off, as evidenced by the dependencies (Fig. 5 and Fig. 9).

The increase in the K_{1000} value is due to the accumulation of the α-fraction as a result of thermal oxidation. It quantitatively increases the carbonisation yield. During carbonisation at temperatures above 300 °C, the α_1 fraction in the pitch increases according to studies [31, 32]. Indeed, at temperatures of 400-500 °C mesophase transformations occur. The enhanced increase in the α_1 fraction can be observed in this temperature range [33]. Thus, the α fraction participates in the carbonisation process of pitch.

Thermal oxidation increased the CP and strength characteristics of the resulting carbon material. Increasing the carbonisation time reduced the CP value and increased the strength characteristics of the carbon material. The possibility of using high-melting pitch as a binder for obtaining carbon material has been experimentally demonstrated. To increase CP, it was necessary to increase the content of HMP pitch and double the exposure time. HMP pitch carbonate has a high yield of K = 80.2% (carbonisation mode, Table 4) and a discharge index of 96.1%.

Conclusions

1. The softening temperature T_p increased from 91 to 136 °C when the air flow rate was increased to 1400 l/kg. It is due to the increase in the duration of thermal oxidation of grade B electrode pitch in a reactor with a large gas space.

2. The yield of volatile substances X decreased from 53 to 32% when the air flow rate was increased to 1400 l/kg. It is due to an increase in the duration of thermal oxidation of grade B electrode pitch in a reactor with a large gas space.

3. The conditions for low-temperature thermal oxidation of grade B electrode pitch in a reactor with a large gas space, under which grade B1 electrode pitch was obtained, were determined.

4. Thermo-oxidation of grade B electrode pitch in a reactor with a large gas space increases the yield of pitch carbonatite and carbonatite of the pitch-coke mixture.

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References

1. **Utkin Y.A., Yanko E.A., Soloveichik E.Y., Strakhov V.M.** Assessing coal pitch as a binder in anode production. *Coke Chem.*, 2012, 55(**9**), 342-346. DOI: 10.3103/S1068364X12090098.
2. **Sherryuble V.G., Seleznev A.N., Apalkova G.D.** Viscoplastic properties of masses based on pitches with different softening point. *Chemistry of Solid Fuel*, 2003, 5, 17-21 (in Russian).
3. **Yanko E.Ya.** Investigation of quality of anode mass prepared on high-temperature pitches. *Tsvetmet*, 1981, 12, 73-76 (in Russian).
4. **Itskov M.L., Svoboda R.V., Frolov V.I.** Impact of softening temperature of binding materials on operational characteristics of anode mass. *Tsvetmet*, 1983, 12, 33-35 (in Russian).
5. **Itskov M.L., Dyblina N.P., Denisenko V.I., Wegner A.A., Sergin E.I.** About the impact of alpha-fraction of coal pitch on operational characteristics of anode mass. *Tsvetmet*, 1986, 8, 51-54 (in Russian).
6. **Nazarenko N.A.** Research of the quality of anodic mass prepared on high-temperature furnaces. *Vestnik har'kovskogo nacional'nogo tekhnicheskogo universiteta HPI,* 2011, 43, pp. 25-31 (in Russian).
7. **Nevedrov A.V., Papin A.V., Bobrova I.V., Makarevich I.A.** Research of the characteristics of samples used as a binder for the electrode industry. *Vestnik Kuzbasskogo gosudarstvennogo tekhnicheskogo universiteta*, 2025, 1, 94-101. (in Russian). DOI: 10.26730/1999-4125-2025-1-94-101.
8. **Bazegsky A. E., Shkoller M. B.** Research of the process of thermal dissolution of coal in order to obtain a binder for refractory masses. Message 1. Obtaining a binder. *Izvestiya vysshih uchebnyh zavedenij. Chernaya metallurgiya*, 2016, 59(**8**), 517-522 (in Russian). DOI: 10.17073/0368-0797-2016-8-517-522.
9. **Mukhamedzyanova A.A., Khaybullin A.A., Panov I.I., Iskhanov I.A.** Patent Ru. No. 2647735. Publ. 3/19/2018. (in Russian).
10. **Frizorger V.K., Mann V.Kh., Anushenkov A.N., Khramenko N.A.** Patent Ru. No. 2288938. Publ. 10/12/2006. (in Russian).
11. **Lapina N.A., Starichenko N.S., Lane E.S., Ostrovsky V.S., Averina M.V., Lipkina N.V.** AC. USSR. No 1772130. Publ. 30/10/1992. **(In Russian).**
12. **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).
13. **BarnakovC.N., Vershinin S.N., Khokhlova G.P., Usov O.M., Samarov A.P., Kozlov A.P.** Benefits of ultrasound in pitch production from coal tar and its mixtures with styrene distillation residue. *Coke Chem.*, 2016, 59(**5**), 192-195. DOI: 10.3103/S1068364X16050021.
14. **Barnakov C.N., Vershinin S.N., Khokhlova G.P., Samarov A.P., Kozlov A.P.** Production of coal pitch by the oxidation of coal extracts in anthracene. *Coke Chem*., 2016, 59(**8**), 313-315. DOI: 10.3103/S1068364X16080020.
15. **Barnakov C.N., Khokhlova G.P., Usov O.M., Naymushina T.M.** Pitch Production from Mixtures of Coal Tar and Rubber Crumbs. *Coke Chem*., 2018, 61(**8**), 305-307. DOI: 10.3103/S1068364X18080033.
16. **Barnakov C.N., Khokhlova G.P., Usov O.M.** New Materials for Binder-Pitch Production. *Coke Chem*., 2019, 62(**10**), 464-467. DOI: 10.3103/S1068364X1910003X.
17. **Kovalev R.Yu., Nikitin A.P.** Study of the Properties of Products of Low-Temperature Thermal Oxidation of Carbon Black Electrode Pitch. *Trudy Kol'skogo nauchnogo centra RAN. Seriya: Tekhnicheskie nauki*, 2025, 15 (**1**), pp. 221-227. DOI: 10.37614/2949-1215.2024.15.1.035. (in Russian).
18. **Kovalev R. Yu.** Impact of thermo-oxidation of electrode furnace on changes in its composition and properties. *From Chemistry Towards Technology Step-by-Step*, 2025, 6(**1**), 55-64 (in Russian). DOI: 10.52957/2782-1900-2025-6-1-55-64.
19. **Petrovykh A.P., Moskalev I.V., Kisel'kov D.M., Valcifer V.A., Strelnikov V.N.** Analysis and comparison of properties of air-blown and of thermally treated pitches. *Coke Chem.*, 2015, 58(**1**), 23-31. DOI: 10.3103/S1068364X1501007X.
20. **Kovalev R. Yu., Nikitin A. P.** Study of the Products of Thermoxidative Treatment of Coal-Based Electrode Tar in a Reactor with a Large Gas Space. *Koks i khimiya*, 2025, 1, 19-24 (in Russian). DOI: 10.52351/00232815_2025_1_19.

21. **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, 839-844. DOI: 10.15372/KhUR2024 (in Russian).
22. **Kovalev R. Yu.** Carbonization of high-temperature pitches. Khimiya i himicheskaya tekhnologiya: dostizheniya i perspektivy: materialy I mezhdunarodnoj VII Vserossijskoj konferencii. Kemerovo: Kuzbass State Technical University named after T.F. Gorbachev, 2025, pp. 221.1-221.3. (in Russian).
23. **Kovalev R. Yu., Nikitin A.P.** Thermal Treatment of Carbon Black Electrode Tapes and Mixtures Based on Them. *Vestnik Sibirskogo gosudarstvennogo industrial'nogo universiteta*, 2025, 1(**51**), pp. 63-71. DOI: 10.57070/2304-4497-2025-1(51)-63-71 (in Russian).
24. **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**), 35-42. DOI: 10.52957/2782-1900-2024-5-4-35-42 (in Russian).
25. **Choi K.H., Lee S.Y., Hong I., Son S., An J.C., Kim S.** Molecular-level investigation of coal-tar pitch treated by air blowing: Revealing the restructure of aromatic compounds via radical reactions. *Carbon*, 2023, 203, 377-385. DOI: 10.1016/j.carbon.2022.11.022.
26. **Kovalev R.Yu., Gavrilyuk O.M.** Optimization of technology for obtaining high-temperature pitch,Innovacionny`j konvent "Kuzbass: obrazovanie, nauka, innovacii": Materialy` XII Innovacionnogo konventa. Kemerovo, Kemerovo State University, 2024. pp. 356-357.(in Russian).
27. **Kovalev R. Yu., Naimushina T. M.** Thermal Treatment of Electrode Tar. Materialy vo vneshnih polyah: trudy XIII Mezhdunarodnogo onlajn-simpoziuma, Novokuznetsk: Siberian State Industrial University, 2024, pp. 93-94 (in Russian).
28. **Martın Y., Garcıa R., Keating P., Snape C.E., Moinelo S.R.** A Study of the Polymerization and Condensation Reactions during the Heat Treatment of Pitches under Gas-Blowing Conditions, *Energy Fuels*, 2000, 14, 380-392. DOI:10.1021/ef9901443.
29. **Sidorov O.F.** Modern ideas about the process of thermal oxidation of coal pitch. 1. Mechanism of interaction of oxygen with hydrocarbons of pitch. *Koks i Khimiya [Coke and Chemistry]*, 2002, 9, 35-43 (in Russian).
30. **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).
31. **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).
32. **Twigg A.N.** Relationship between chemical structure and secondary quinoline insoluble for-mation in electrode binder pitches. *Fuel*, 1987, 66(**11**), 1540-1543.
33. **Cao Y., Zang C., Zhang J., Gao F., Liu Y.** High thermal-conductivity mesophase pitch-based graphite fiber with circular cross-section through a spinneret with a Y-shaped spinning hole. *Carbon Trends*, 2023, 10, 100244. DOI: 10.1016/j.cartre.2022.100244.

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