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Getting an Alternative Pitch Binder by Thermal Dissolution of Coal

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Abstract: The process of thermal dissolution of medium metamorphosed coals in anthracene oil to produce an alternative pitch binder was studied. The process was carried out at temperatures from 350 to 400°C and pressure not higher than 2.5 MPa, without the use of hydrogen and catalysts. It was determined that during thermal dissolution hard coal of gaseous-fat grade demonstrated a higher activity compared with less metamorphosed gaseous coal. Under optimal conditions at a temperature of 350-380°C yields of pitch tar containing product are 63-75%. With regard to their composition and the main technical characteristics the isolated pitches are at the level in the middle between the coal-tar and oil pitches. Based on the yield data analysis, technical and environmental characteristics of the isolated pitch products a conclusion was made on the prospects of thermal dissolution process as an alternative method for preparing extractive pitch- a substitute for coal-tar pitch produced by coking process.

Keywords: Anode, Binding Matter, Coal, Tar Pitch, Thermal Dissolution

Introduction

Binding substances based on coal tar pitch are the most important component in the production of the majority of carbon products. A favorable combination of their high coking capacity and low viscosity in the molten state is largely responsible for the high level of physical and mechanical properties of the produced anode paste, electrodes, pitch coke, carbon-graphite construction materials, carbon fibers, electrical-coal articles, tap-hole mix, refractory materials, roofing materials, electrical products, various carbon materials for nuclear and missile equipment.

Currently, the main source of pitches is the resin of coal carbonization, which is a by-product in the metallurgical coke production. Demand for coal-tar pitch and requirements to its quality are continuously increasing, particularly in the aluminum industry. At the same time the process' upgrading measures in the ferrous steel industry aimed to reduce metallurgical coke consumption result in the reduced production of coal tar (Rudyka and Malina, 2010). Furthermore, the coking-chemical industry in all countries lacks high-quality coking coal resources. The imbalance between the declining production of coal tar pitch and growing demand for it contributes to the rise in prices. Together, these factors indicate the pressing issue of finding alternative sources for receiving coal tar pitch substitutes from coal.

The polycyclic aromatic nature of coals is a key consideration in making coals attractive feedstocks for pitch-like products and direct thermal coal dissolution in an appropriate solvent to extract these naturally occurring polycondensed aromatics would be one of the most effective and selective. The thermal dissolution of coal can be best interpreted on the basis of three types of chemical reactions. Primary reactions involving thermolysis of weak bonds generate smaller reactive fragments in conjunction with reactive sites within the coal residua. These reactive intermediates can then undergo two kind of secondary reactions: Stabilization to produce liquids and light gases; and retrogressive recombination of the fragments and residua to produce refractory char. Obviously maximum liquid yield can be obtained under conditions which promote stabilization reactions and inhibit retrogressive char-forming reactions. The former objective is accomplished generally by introducing a hydrogen-donor co-solvent into the conversion mixture. Importantly, in the case of non-volatile tar pitch production, the thermal dissolution can be carried out at mild conditions, i.e., with no hydrogen, catalysts and at rather low temperatures, because there is no need for deep destruction of organic matter.

Research of the coal thermal dissolution processes to produce coal-tar pitch-like products was carried out in a number of papers by various authors (Shkoller and Proshunin, 2008; Cheng *et al*., 2012). It was determined that hard coals at the middle stage of metamorphism are most suitable for coal thermal dissolution processes that aim to produce coal-tar pitch-like products (Rahman *et al*., 2013; Takanohashi *et al*., 2008a; Sharma *et al*., 2008a). Japanese companies Kobe Steel Co. Ltd. and Mitsubishi Chemical Co. designed a process of obtaining ashless Hypercoal through a process of coal thermal dissolution and ash content of such Hypercoal is less than 0.01 wt.% (Yoshida *et al*., 2004; Takanohashi *et al*., 2008a; Li *et al*., 2004; Okuyama *et al*., 2005). The process takes place at temperatures of 360-380°C, using a mixture of bicyclic aromatic hydrocarbons as solvent. It is shown that Hypercoal has good ductile and sintering properties with a softening point of 240 to 270°C. Apart from the designated use as an environmentally friendly fuel (Sharma *et al*., 2008a; 2008b; 2009), it can be used as a coking additive to coking charge (Takanohashi *et al*., 2008b) to get needle coke (Cheng *et al*., 2012), other carbon materials (Roberto *et al*., 2004). Mono- and polycyclic aromatic hydrocarbons and their mixtures with different active additives are mostly used as solvents for coal thermal dissolution (Shui *et al*., 2013; Yoshida *et al*., 2004; CAERNCLLC, 2005; Miura *et al*., 2004), as well as various low-boiling solvents, which under reaction conditions are in the supercritical gas state (Roberto *et al*., 2004; Torrente and Galan, 2010; Sun *et al*., 2014; Sangon *et al*., 2006).

This paper presents the results of the research of gas coal thermal dissolution processes in anthracene oil medium and the properties of the products obtained in order to determine whether it is possible to obtain pitch binder on their basis.

Materials and Methods

We used samples of coals from Chadan and Kaa-Khem Tyva fields as raw materials. The samples were ground to a fraction of less than 1.0 mm and dried in a vacuum oven at 80°C. The process of thermal dissolution was performed in anthracene oil medium, which contains in its structure both active hydrogen donors (acenaphthene, dihydroanthracene, fluorene, carbazole) and hydrogen carriers (phenanthrene, fluoranthene, pyrene), as well as compounds with solvating properties (quinoline, indole, phenol).

The coal thermal dissolution experiments were performed in a rotating digester of 80 mL (rotation speed of the digester is 80 rpm) and a 2-liter digester with a mechanical stirrer (rotation speed is 120-160 rpm). The rotating digester was loaded with 4 g of coal and 8 g of anthracene oil. For products in high quantities required for determining technical parameters of the pitch a 2-liter digester was used with 200 g of coal and 400 g of anthracene oil. The digesters were purged with nitrogen to remove air, sealed and checked for leaks. The process was carried out at temperatures in the range of 350-400°C at a pressure produced by the solvent and product vapors, starting at 1.0-2.5 atm. The heating rate was 4-5°C per min, isothermal time was 1 to 3 h.

The reaction products from the rotating digester were transferred to a paper filter and extracted in a Soxhlet extraction apparatus first with heptanes and then with toluene. The residue insoluble in toluene was extracted with quinoline. The coal conversion was determined by changes in the ash content of the source coal and quinoline-insoluble residue. In the experiments on thermal dissolution in a 2-liter digester, after the reaction completion vapor gases were throttled into a special receiver-separator where the vapor gases were separated from condensate. Hot contents of the digester were poured out through a bottom nozzle to a heated cylindrical receiving-settler for separating solids from the free-running mass. The product in the settler was kept for 3 hours at a temperature of 220-280°C. After settling the bottom ash sediments were separated and the main ashless product underwent consecutive extraction with toluene and quinoline.

At room temperature the resulting decalcified pitch-containing products were a solid black mass. Vacuum stripping of distillate fractions was performed in a nitrogen atmosphere at a pressure of approximately 6.7 kPa and temperature of 350°C (corresponding to normal conditions).

Technical characteristics of obtained pitch products were determined according to standard procedures. Mass fraction of substances insoluble in toluene (α-fraction) was determined in accordance with GOST 7847 and the proportion of substances insoluble in quinoline (α_1-fraction) -according to GOST 10200, substances soluble in quinoline, but insoluble in toluene (α_2-fraction) were calculated as the difference of α-α_1. Ash content of coal extracts and pitches was determined according to GOST

7846, volatile substances-according to GOST 9951 and the yield of coke residue by ISO 6998 standard. The softening point was measured according to GOST 9950 (ring and ball method).

Analysis for benz(o)pyrene and other Polycyclic Aromatic Hydrocarbons (PAH) content was carried out for toluene-soluble portion of the coal tar pitch by using high-performance liquid chromatography method on a liquid chromatography by Shimadzu LC20.

Results and Discussion

Characteristics of the Original raw Material Properties

Table 1 shows the technical and elemental analysis of samples of coal from Kaa-Khem and Chadan fields. The coal contained a small amount of ash substances (10.4 and 5.2%), low sulphur, yields of volatile substances were 47.2 and 35.8%, the plastic layer thickness (γ) was 10 and 21 mm, respectively. According to the combination of the technical analysis data, Kaa-Khem coal was consistent with gaseous (G) grade and Chadan coal with gaseous fat (GZh) grade.

Anthracene oil was used as a solvent and paste-former, which is a mobile high-boiling liquid with carbon content of 91.0%, 5.8% hydrogen and heteroatoms 3.2% in total (Table 1). Figure 1 shows the curves of oil thermal analysis TG and DTG. Isolation of volatiles began at about 150°C, the maximum rate of weight loss was observed at 291°C. At 350°C almost complete volatilization of the oil was reached, a small coke residue of 2-3% remained in the crucible.

Determining Optimal Conditions for Thermal Dissolution Process

At the first stage, experiments were performed in an 80 ml digester to determine the indicators of coal thermal dissolution against the temperature and time of isothermal time. The data presented in Table 2 show that at 350°C the dissolution rate of the Chadan and Kaa-Khem coals for 1 h were 49 and 31%, respectively. The greatest conversion of both types of coal was achieved at 380°C. Yield of toluene-soluble substances (recalculated as oil-charcoal paste) in for GZh grade coal was 77%, for 2G coal -74%; yield of quinoline-soluble substances was 88 and 83%, respectively. For the more active 1GZh grade coal, the share of quinoline-insoluble residue at the temperature of 380°C was only 12% and increase in temperature led to deterioration in the process.

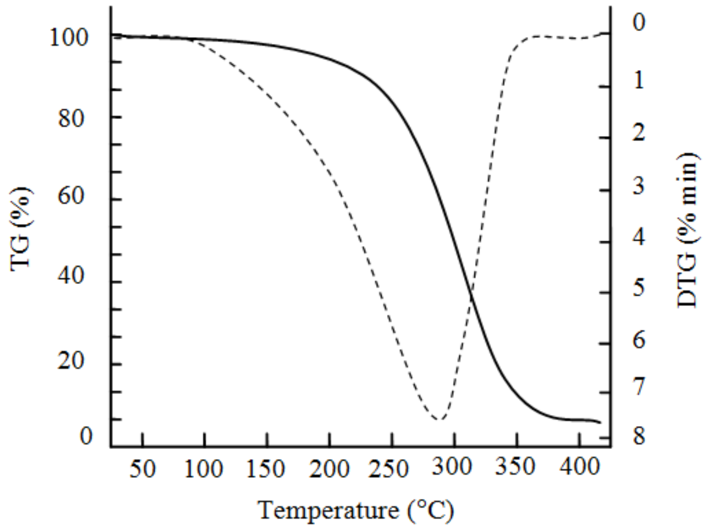

Fig. 1. TG curve (solid line) and DTG curve (dotted line) of anthracene oil thermal analysis

Table 1. Characteristics of coal and solvent and paste-former properties

				Elemental composition, wt% by daf, %				
Coal, solvent	A^d, %	V^{daf}, %	γ*, mm	C	H	N	S	O_{dif}
Kaa-Khem	10.4	45.2	10	78.0	6.2	1.2	0.3	14.3
Chadan	5.2	35.8	21	84.0	5.4	1.1	0.6	8.9
Anthracene oil	-	-	-	91.0	5.8	3.2		

Note: *plastic layer thickness

Table 2. Temperature impact upon the process of coal thermal dissolution in anthracene oil (reaction time 1 h)

Coal grade	Reaction temperature, °C	Coal conversion, mass %	Product yield, wt.% recalculated as paste		
			Toluene-soluble	Quinoline-insoluble	Insoluble residue
GZh	350	49	68	84	16
	380	62	77	88	12
	400	24	69	76	24
G	350	31	70	79	21
	380	46	74	83	17
	400	28	71	78	22

Table 3. The process of coal thermal dissolution process in anthracene oil with the isothermal time of 2 h

Coal grade	Temperature, °C	Coal conversion, wt.%	Product yield, mass % recalculated as paste		
			Toluene-soluble	Quinoline-insoluble	Insoluble residue
GZh	350	73	71	91	9
	380	51	72	84	16
G	350	47	69	84	16
	380	51	74	85	15

Process indicators largely depended on the isothermal time. For Kaa-Khem coal the increase in the reaction time to 2 h resulted in the increased conversion and yield of soluble products both at a low temperature of 350°C and at a higher temperature of 380°C (Table 3). For higher metamorphosed Chadan coal the duration of exposure had different effects on the dissolution performance depending on the temperature. At low temperature of 350°C and by increasing the reaction time to 2 h we received a significant increase in coal conversion (from 49 to 73%) and yield of quinoline-soluble products (up to 91%). At higher temperature of 380°C the increase in reaction time had the opposite effect.

Thus, as a result of digester test the conditions for effective thermal dissolution process were established. Sufficiently high indicators of conversion and product yield were achieved at a temperature of 350-380°C and reaction time of 1-2 h. The observed deterioration of the thermal dissolution with increasing temperature and duration of thermal dissolution for the most active Chadan coal is due to the complex kinetics of the process conditioned by the simultaneous occurrence of competing reactions of depolymerization and destruction and reverse reactions of polycondensation of reactive molecules that produce less soluble products with higher carbon content.

Getting Representative Samples of Pitch-Containing Extracts

In view of the received results, we conducted experiments on thermal dissolution of coal in a 2-liter digester with a mechanical stirrer to get pitches in the amount required to determine their technical characteristics.

Table 4 summarizes the balance thermal dissolution indicators at different temperatures. During the experiments the pressure in the digester did not exceed 2.5 MPa. Table 4 shows that in these conditions only a small amount of distillate fraction (not more than 2%) and gaseous products (not more than 0.5%) was formed. Mass balance was 90-94%. Losses amounted to 6-10%, which is explained by the pitch product sticking to the walls of the reactor, settler, in the isolation valves and connecting fittings.

The composition of gaseous products was predominated by carbon dioxide; hydrogen sulphide, molecular hydrogen were formed in smaller quantities, including only negligible amounts of carbon monoxide. It should be noted that there was virtually no methane or other hydrocarbons. The data on the product yield and composition mean that during coal thermal dissolution in the anthracene oil medium in the given conditions predominantly selective depolymerization reactions were taking place that formed high-boiling and non-volatile soluble products that are the basis of pitches, without any significant contribution from destruction reactions.

De-ashing of the extracts was performed by settling them in a cylindrical clarification tank at 230-280°C for three hours. After cooling and extraction of the product from the tank and separating the bottom ash residue we obtained a hard decalcified pitch-containing extract with ash content of 0.2-0.5 wt.% and the softening temperature of 76 to 96°C. According to elemental analysis, extracts received at 380°C had the following average composition, in weight %: C 89.8; H, 5.5; 4.8% N + S + O.

Results of determining the properties of pitch-containing extracts are given in Table 5. The proportion of toluene-soluble substances ($\gamma + \beta$-phase) varied from 60 to 75 wt.%, toluene insolubles (α-fraction) -25-40%, including 2-8 wt.% substances insoluble in quinoline ($\alpha 1$-fraction).

Table 4. Results of experiments on coal thermal dissolution in anthracene oil in a 2-liter digester with a stirrer Reactor feed: 200 g of coal, 400 g of solvent, reaction time 1 h

			Unloaded from reactor, g			
Coal	$T_{reaction}$, °C	Pressure, MPa	Ash extract	condensate	gas	losses
G	380	2.4	525.7	9.9	1.8	62.4
G*	380	2.2	528.0	11.1	1.9	59.0
GZh	350	0.9	538.3	4.2	0.7	56.8
GZh	380	1.2	531.8	5.6	1.0	61.7
GZh	400	1.7	533.3	8.0	1.3	57.5
GZh	380	1.5	554.9	7.1	1.1	36.9

*reaction time 3 h

Table 5. Characteristics of the properties of ashless pitch-containing extracts received from coal thermal dissolution for 1 hour

		Fraction content, wt.%					
				Incl.			
Coal	$T_{reaction}$, °C	$\gamma + \beta$	α	α_2	α_1	Softening point, °C	Ash content, wt.%
GZh	350	75	25	17	8	76	0.2
GZh	380	70	30	22	8	76	0.3
GZh	400	60	40	33	7	78	0.2
G	380	70	30	22	8	96	0.3
G*	380	72	28	25	3	77	0.5

* isothermal time 3 h; α-substances, insoluble in toluene; α_1-substanbces,inbsoluble in quinoline

Table 6. Pitch content

Pitch	Coal	Reaction temperature	Ash, %	Sulphur content, wt.%	α, %	α_{1}, %
UP-5	GZh	350	0.1	-	34.9	-
UP-6	GZh	380	0.5	0.3	38.6	7.8
UP-7	GZh	400	0.2	0.3	35.7	6.8
UP-8	G	380 (3 h)	0.8	0.3	35.7	3.6

Isolation of Pitch, Characteristics of its Properties

Isolation of the pitch product received from ashless extract was performed by vacuum stripping of distillate fractions up to 350°C. We received representative samples of extractive pitches with a yield of 60-70 wt.%. Their properties are characterized by basic indicators that describe the requirements for coal binder: By ash content, softening temperature, group composition, volatile substances and carbon residue.

Table 6 sets forth the composition of extractives pitches. The content of ash substances was 0.2-0.8 wt.%, sulphur -0.3 wt.% only. The group composition is mainly represented by toluene-soluble fraction, the quantity of substances insoluble in toluene (α-fraction) was 35.5-38.6%. Quinoline-insolubles (α1-fraction) determine the caking ability of pitches and good caking requires an optimal content of such fraction. In traditional hard coal pitches of different grades its content is at a level of 6-12%, the minimum amount should be at least 2%. The determined content of α_1-faction in the extractive pitches ranged from 3.6 to 7.8%, i.e., corresponded to the optimum values for this indicator.

The softening temperature characterizes the plastic properties of pitch. For different extractive samples it varied from 98 to 108°C (Table 7), i.e., by this indicator the received pitches can be attributed to high-temperature grades. Pyrolytic properties are also important for the electrode quality pitches as they are characterized by the output of volatile substances, as well as “coke residue” that acts as a bridge between the filler particles. It is established that the received pitches have a higher- in comparison with industry standards-volatile matters output (59 to 73.4%) and lower coke residue yield (35 to 42%). The formation of a significant amount of volatile substances can be associated with an increased content of heteroatomic compounds, in particular oxygenated ones, which are characterized by a low thermal stability.

In the industry, in order to optimize thermal properties of coal tar pitch one uses methods for their further processing by thermal conditioning at a temperature of 400-430°C, oxidation in controlled conditions at a temperature of 300-350°C or by vacuum distillation (Andreikov *et al*., 2009). It was established that a brief low-temperature oxidation treatment of the UE-8 pitch sample allowed to reduce the volatile content by about 7% and to increase the yield of coke residue by 2.5% (Table 7). The softening temperature went up from 105 to 119°C.

Table 7. Quality indicators of coal pitch tar

Pitch	Softening point, °C	Volatile matters, wt.%	Coke residue, wt. %	Benzapyrene, mg/g	BE, mg/g of pitch
UP-5	98	73.4	35.4	5.7	16.0
UP-6	115	59.0	40.1	5.0	14.6
UP-7	108	62.9	41.6	4.6	13.6
UP-8	105	67.3	41.8	5.4	15.7
UP-8*	119	60.5	44.3	5.8	16.0

*received by oxidation of pitch UP-8 by air at 200°C for an hour; Benzapyrene-Benzapyrene content; BE-Benzapyrene equivalent, calculated in accordance with (Eidet and Sorlie, 2004)

An important pitch quality parameter is the content of carcinogens such as benz(o)pyrene and other PAHs. In some countries, at the urging of environmental protection specialists the information on their content is included in the specifications for electrode pitches. In all extracted pitches we determined a reduced levels of benz(o)pyrene (4.6-6.4 mg g^{-1} of pitch), which is two to three times less than for coal tar pitches with a similar softening point (8 to 21 mg g^{-1}) (Eidet and Sorlie, 2004; Boenigk *et al*., 2002). Other PAH identified by chromatographs (16 PAH) are mainly low molecular weight substances, such as phenanthrene, anthracene, fluorantenom, pyrene, which according to the European and North American standards (Boenigk *et al*., 2002), have relatively low toxicity coefficients. The benz(o)pyrene equivalents of extracted pitches calculated using an appropriate method (Table 7) are also lower than for coal tar, for which the figure is 25 to 45 mg g^{-1} (Eidet and Sorlie, 2004; Boenigk *et al*., 2002).

Conclusion

The process of thermal dissolution of moderately metamorphosed coals in anthracene oil was examined to obtain a binder pitch- a substitute for coking coal tar pitch. The process was carried out at temperatures from 350 to 400°C and pressure not higher than 2.5 MPa, without the use of hydrogen and catalysts.

The efficiency of thermal dissolution of coal in mild conditions at a temperature of 350-380°C was established by means of experiment. The process is characterized by high selectivity for the formation of high-boiling hydrocarbon fractions. The higher amounts of coal conversion (up to 73%) and output of quinoline-soluble products (up to 91%) with the gas yield of not more than 0.5 wt.% were obtained for gaseous-fat coal.

The softening temperature of isolated pitches varies from 98 to 115°C, their composition and basic technical characteristics are consistent with high-temperature coal tar pitches.

It is shown that the received pitches are different from the traditional coking pitches as their contents of benz(o)pyrene and other environmentally hazardous polycyclic hydrocarbons is 2 or 3 times lower.

Based on the group composition and technical parameters a conclusion was made on the prospects of the thermal dissolution process as an alternative method of producing coal tar pitch- a substitute for coking coal tar pitch.

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Author’s Contributions

Peter Nikolayevich Kuznetsov: Designed the plan of experiments, supervised the research.

Elena Nikolaevna Marakushina: Participated in all experiments of the thermal dissolution of coals, analyzed the products of thermal dissolution and extract pitch, have contributed to the writing of the manuscript.

Anastasia Valerievna Kazbanova and Svetlana Mikhaylovna Kolesnikova: Participated in all experiments of the thermal dissolution of coals, analyzed the products of thermal dissolution and extract pitch.

Ludmila Ivanovna Kuznetsova: Executed analysis of experments data, have contributed to the writing of the manuscript.

Fedor Anatolyevich Buryukin: Developed methods of allocation of extractive pitch from the products of thermal dissolution of coals, executed analysis of experimental data.

Svetlana Sergeevna Kositcyna: Analyzed the products of thermal dissolution, developed method of allocation extractive pitch from the products of thermal dissolution of coals.

Ethics

The authors have no conflicts of interest in the development and publication of current research.

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