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Thermal Dissolution of Bituminous Coal in Heavy Coal Semicoking Tar and in Binary Blends with the Anthracene Oil

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Abstract. The effect of hydrorefining of heavy coal semicoking tar on its composition and efficiency for bituminous coal dissolution was studied. It was found that the concentration of the oxygen-bearing compounds decreased as a result of catalytic hydrotreating with hydrogen or with hydrogen donors. This resulted in improved dissolving power. However, best result in coal dissolution was achieved when heavy semicoking tar was blended with the anthracene oil. The products obtained represented at ambient temperature solid pitch-like matter with the softening points of 124 to 138 °C ("ring and ball" method). It was composed of mainly bi- and three-cyclic aromatics, the content of quinoline-insolubles being less than 6 %, and the ash content less than 0.5 %.

Keywords: semicoking tar, bituminous coal, anthracene oil, hydrorefining, pitch-like product.

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Термическое растворение битуминозного угля в тяжелой смоле полукоксования и бинарных смесях с антраценовым маслом

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Аннотация. Изучено влияние гидроочистки тяжелой каменноугольной смолы полукоксования угля на ее состав и эффективность в растворении битуминозного угля. Показано, что концентрация кислородсодержащих соединений в смоле снижается в результате каталитической гидроочистки водородом или донорами водорода, что приводит к улучшению растворяющей способности. Лучший результат в растворении угля достигнут при смешении тяжелой каменноугольной смолы с антраценовым маслом. Полученные продукты при температуре окружающей среды представляли собой твердую пекоподобную массу с температурами размягчения от 124 до 138 °С (метод «кольцо и шар»), состоящую в основном из би- и трициклических ароматических соединений. Содержание нерастворимых в хинолине веществ было менее 6 %, содержание золы – менее 0,5 %.

Ключевые слова: смола полукоксования, каменный уголь, антраценовое масло, гидроочистка, пекоподобный продукт.

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1. Introduction

Russia, China and Mongolia are among the countries which are rich with different coals. Currently, the coals are utilized mainly as a fuel for electricity generation. Large proportion of coal in China and Russia is used also for the production of metallurgical coke which is an indispensable material in traditional blast furnace (BF) technology for iron and steel manufacturing. Smelting of iron and steel is growing rapidly mainly due to BF technology. However, this technology produces large amount of environmentally harmful emissions. On the other hand, there is quite limited amount of high quality coal, and “metallurgical” coke is too expensive (almost half of all metal production costs). For these reasons, more advanced coke-less metallurgical technologies are being developed more faster [1]. Large-scale switch to competing alternative coke-less technologies will lead to a dramatic decrease in demand for metallurgical coke and, consequently, to decrease in its production.

Meanwhile, the coking process, beside targeted metallurgical coke, also produces small amount of valuable coal tar, which is an important source of the aromatic chemicals. The latter are widely used for the manufacture of carbon materials and composites for various purposes [2]. Most high-tech carbon composite materials such as electrodes, graphite and structural materials, semiconductors, carbon fibers, integrated circuits, materials for chemical apparatus and machine building, electrochemistry, nuclear energy, and aircraft and rocket engineering are produced from a non-volatile fraction of coal tar – coal-tar pitch. Currently, the largest amount of coal-tar pitch is used for the production of carbon anode for the progressively developing aluminium electrolysis. In most countries (except for China), the aluminum electrolysis has been faced with the problems of a shortage of pitch and poor quality. The progressively developing technology for smelting high-quality steels in electric arc furnaces may also face the same problem because the preparation of the graphite electrodes will require significant amount of the same coal-tar pitch. In this context, there is growing interest in the production of the coal tar substitutes that are not dependent on the coking process [3–5]. The need to solve this challenge is reasoned also by a significant drawback of the commercial coal tar because of high content of the carcinogenic substances.

Coal processing in the solvent medium at lowered temperature conditions (less than 400 °C), instead of high temperature coking (900 °C), is considered to be the best promising alternative for the production of aromatic substitutes for coal tar. During the last decade, thermal dissolution to produce ash-free soluble coal matter (AFC) has attracted much attention because AFC can find wide applications as a valuable feedstock for both environmentally friendly fuels and chemicals [6–8]. Currently, several promising processes for coal dissolution at moderate temperature are at different levels of development. Japanese technology for the production of ash-free coal called HyperCoal is based on the dissolution of medium-ranked coals in the recyclic aromatic solvent [9, 10]. The coal dissolution process in the USA uses anthracene oil derived from coal tar as a recycle solvent [11]. However, some amount of the process solvent is retained by the pitch product so that the addition of about 15–20 % of a fresh solvent is required for continuous operation.

The dissolution of coal with available commercial hydrocarbon residues of coal and petroleum processing, from economic considerations, is a promising way because it allows the co-processing of residues with coal into a valuable product, in addition to significant savings in solvent regeneration. It is tempting to use an available heavy coal semicoking tar as a solvent for coal dissolution. However, our recent study reported [12] that this tar itself showed poor ability for coal dissolution because of high content of the oxygen-containing substances which initiate polycondensation reactions with coal.

In the present paper, we aimed to study how hydrorefining pretreatment of the heavy coal semicoking tar and its blending with the hydrogen donors affect the yield of dissolved products and their properties when used for the thermal dissolution of bituminous coal.

2. Experimental methods

Bituminous coal from Chadansk deposit (Tyva Republic) was used in this study. The heavy coal semicoking tar (HCST) was supplied by Plant of Carbon Materials (Leninsk-Kuznetsk), anthracene oil by OJSC Altai-koks.

Two methods were used for the hydrorefining of HCST: 1) catalytic hydrotreating with hydrogen at 5 MPa; 2) the treatment with hydrogen donors tetralin (THN) or anthracene oil (AO). Catalytic hydrotreating was carried out using commercial Al–Co–Mo catalyst at 400 °C for 2 h.

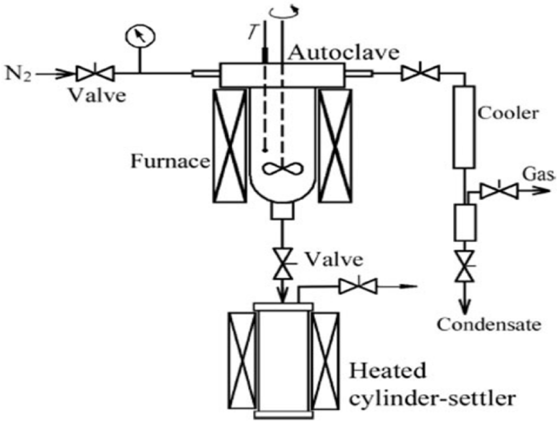

Fig. 1. Scheme of the experimental autoclave installation

The hydrorefining treatments of HCST and coal dissolution tests were carried out using the experimental installation equipped with 2 L stainless steel autoclave dissolver with a mechanical stirrer (Fig. 1).

The coal dissolution process was performed following previously optimized procedures [13] at 350 and 380 °C for 1 h without hydrogen and catalyst. The autoclave was loaded with coal/solvent slurry, purged carefully with nitrogen and hermetically sealed. Unless otherwise stated, the reactor was loaded with 900 g of slurry with the proportion of coal to solvent of 1:2 by the weight. The autoclave mixture was heated and allowed to react at 380 °C for 60 min residence time at autogenous pressure (usually of 1.5–2.0 MPa) while continuous stirring. The use of the stirrer provided effective mass transfer, improved contacts in three phase reaction mixture of gas, liquid and solid, and thus gradient-less conditions in terms of temperature and concentration of the reagents. At the reaction completion, the autoclave was allowed to cool to 250 °C, the vapor-gas products were vented through a refrigerator line where the gases and condensed liquids were separated and measured. The product in the receiver was allowed to settle for 3 h at 250 °C. After settling and cooling, the product was pushed out of the cylinder by a piston. The solid product with little ash was obtained by separation of the bottom ash-containing coal residue.

A representative extract portion was thoroughly dispersed, and 2 g of sample was taken for the solubility analysis. Soxhlet extraction was used to determine toluene-soluble fraction. Toluene insoluble residue was dried under vacuum at 80 °C, weighted and then further extracted with hot quinoline until the solution became clear. Quinoline insoluble residue was washed with toluene, dried under vacuum at 80 °C and weighted. The analysis was repeated two-three times, the average values were used. Hydrotreating of the HCST (without coal) was performed using the same autoclave unit.

The product composition was analyzed by a chromatography-mass-spectrometry using an Agilent Technologies 7890 instrument with an Agilent Technologies 5975 °C mass spectrometric detector. The elemental analysis of the coal, solvents and reaction products was performed on a FLASH^{TM} 1112 elemental analyzer. Fourier transform infrared spectroscopy (FTIR) was used to characterize the molecular groups in the structure of the coal, solvents and products. The FTIR spectra from the KBr pellets were recorded on a Bruker Tensor-27 spectrometer for a spectral range from 4000 to 400 cm^{-1}. The softening point of the pitch-like extracts produced was determined using a "ring and ball" method.

3. Results and Discussion

The coal used contained 37.8 % of volatile matter and 5.6 % of ash. The petrographic composition was represented mainly by vitrinite macerals (85 %), the vitrinite reflectance coefficient was 0.77 %. The plastic-layer thickness and the softening point were 17–20 mm and 350–360 °C, respectively. The chemical composition and properties of coal and solvents are shown in Table 1.

Shown in Fig. 2 are the FTIR spectra for coal and solvents. The assignments of the spectral bands were performed according to refs [14]. The spectrum for coal shows absorbance between 3000–2750 cm^{-1} (stretching vibration of the aliphatic C-H bonds), at 1460–1440 cm^{-1} (bending vibration of CH_2 groups), and at 1376 cm^{-1} (bending vibration of CH_3) which are characteristic of the aliphatic CH_3, CH_2 and CH molecular groups. Large absorbance at 1600 cm^{-1} (stretching vibration of the aromatic rings) and weak absorbance at 3050 cm^{-1} (stretching vibration of the aromatic C-H bonds) indicate the

Table 1. The Characterization of Coal and Solvents Used

Coal, solvent	Element composition, wt. %			Distillation temperature range, °C	Density, g/cm^3
	C	H	N+S+O		
Coal	84.7*	5.5*	9.8*	400–550**	-
HCST	83.7	8.1	9.2	160–420	1.05
AO	87.6	5.2	7.2	170–350	1.10
THN	90.9	9.1	-	207	0.97

*based on daf coal;
**temperature range of decomposition determined by thermal DTG analysis.

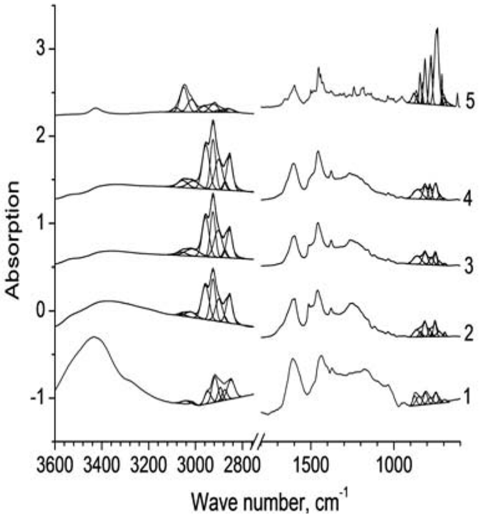

Fig. 2. FTIR spectra of coal (1); HCST before (2) and after catalytic hydrogenating treatment (3) and heat treatment with a hydrogen donor tetralin (4); AO (5)

presence of the aromatic fragments. Largest absorbance centered at 3400 cm^{-1} shows large amount of hydrogen-bonded hydroxyls.

The FTIR spectrum for the parent HCST shows considerable quantity of oxygen-bearing compounds: phenols, ether and esters which were indicated by strong absorption bands at 3375 $cm^{–1}$ and 1000–1300 $cm^{–1}$ (Fig. 2). The absorption bands at 3032 $cm^{–1}$, 1597 $cm^{–1}$, and 700–900 $cm^{–1}$ (out-of-plane vibrations of the C–H bond in aromatic rings) indicate aromatic compounds. Judging from the strong absorptions at 2800–3000 $cm^{–1}$ and 1376–1458 $cm^{–1}$, the hydrocarbons in the HCST were predominantly aliphatic. The AO spectrum features with strong absorbances between 3100–3000 cm^{-1} and 900–700 cm^{-1} reflecting highest AO aromaticity, the strongest peak at 750 cm^{-1} indicating low substituted aromatic rings with four adjacent C-H bonds, i.e. ortho-substituted rings. Weak absorption centered at 3430 cm^{-1} can be attributed to both hydroxyls and nitrogen-bearing heterocyclic compounds such as carbazole. A shoulder at 1650 cm^{-1} in the spectra for the HCST and AO solvents indicates few carbonyls. The spectra for HCST subjected to catalytic hydrotreating with hydrogen and to treatment with tetralin donor indicate reduced absorbance at 3400 cm^{-1} reflecting partial removal of phenolic hydroxyls, the catalytic hydrotreating being more effective compared to tetralin treatment.

The spectral regions between 3100–2750 $cm^{–1}$ and 900–700 $cm^{–1}$ were subjected to deconvolution to characterize the molecular groups in more detail. The following semi-quantitative indexes for molecular characterization of the solvents and coal were evaluated based on the deconvoluted spectra: H_{ar} index for hydrogen aromaticity, i.e, the proportion of the aromatic hydrogen atoms to total amount of hydrogen atoms in average molecule; I_{ort} index for ortho-substitution of the aromatic ring; and CH_3/CH_2 ratio in the aliphatic structures. H_{ar} index was assessed from the absorbances at 3100–3000 cm^{-1} (A_{Har}) and at 3000–2750 cm^{-1} (A_{Hal}). The CH_3/CH_2 ratio was determined from the absorbances at 2955 cm^{-1} (asymmetric stretching in CH_3) and at 2923 cm^{-1} (asymmetric stretching in CH_2). The I_{ort} ortho-substitution index was assessed from the ratio of the absorbance at 750 cm^{-1} (A_{750}) to total absorbance in the whole range of 900–700 cm^{-1} ($A_{900–700}$).

In assessing these indexes we took account of the statistical data [15] that the ratio of the extinction coefficient for the stretching vibrations of the aromatic C–H bonds to the extinction coefficient for the aliphatic C–H bonds is 0.20; while the ratio for the extinction coefficient for the stretching vibrations of the CH_2 groups and CH_3 groups is 0.5. The indexes were calculated using the following formulas:

$$\mathrm{Har}=\frac{A_{Har}/0.2A_{Hal}}{1+\ A_{Har}/0.2A_{Hal}}, \tag{1}$$

$$I_{ort}= A_{750}/A_{900\text{-}700}, \tag{2}$$

$$CH_3/CH_2 = 0.5 \times A_{2955}/A_{2923}. \tag{3}$$

Brown-Ladner f_a indexes for carbon aromaticity were also estimated according to ref. [16] using the elemental analysis data and FTIR ratio for H_{Hal}/H.

Shown in Table 2 are the molecular indexes thus calculated. One can see that coal itself shows low hydrogen aromaticity ($H_{ar} = 0.26$), however, relatively high f_a carbon aromaticity (0.71). The lowest I_{ort} index indicates the aromatic rings in coal to be highly substituted. The composition of the molecular groups in HCST reminds that of coal, except for much more higher CH_3/CH_2 ratio, that indicates more shorter alkyl groups which can be represented mainly by methyl substutuents in the aromatic

Table 2. Characterization of the molecular composition of the coal, and solvents based on the FTIR data

Sample	Absorption ratio, $A_{3375}/A_{2800\text{-}3000}$	Molecular indexes			
		f_a	H_{ar}	I_{ort}	CH_3/CH_2
Coal	-	0.71	0.26	0.15	0.14
AO	-	0.96	0.89	0.44	0.45
HCST	0.35	0.65	0.29	0.20	0.54
HCST (hydrotreating with tetralin)	0.06	0.71	0.42	-	0.41
HCST (hydrotreating with hydrogen)	0.03	0.70	0.39	0.16	0.54

rings. The AO is highly aromatic in terms of both f_a and H_{ar} indexes (0.96 and 0.89, respectively). The relatively high I_{ort} index indicate aromatic rings in AO molecules to be rarely substituted.

The hydrorefining of HCST significantly reduced the absorption at 3375 cm^{-1} due to removal of OH groups. According to $A_{3375}/A_{2800\text{-}3000}$ absorption ratio, catalytic hydrorefining with hydrogen was more efficient deoxygenation procedure as compared to that of hydrorefining with H-donor tetralin. The increased f_a and H_{ar} aromatic indexes in the hydrorefined HCST resulted from both phenolic OH group substitution for hydrogen and naphnalene generation from tetralin.

The composition of light distilled fractions obtained as a result of the reactions of HCST hydrorefining with tetralin was analyzed using chromatography-mass spectrometry. It was found that the 140–240 °C fraction from the tetralin hydrorefining of HCST was mainly bicyclic hydrocarbons with some amounts of phenol derivatives. The conversion of tetralin to naphthalene was about 50 %, some dihydronaphthalene was also observed.

The reaction of coal dissolution with AO as a solvent effectively occurred at 350 and 380 °C, the content of quinoline insoluble substances decreased from 33 % (in the initial slurry) to 7–10 %. The product obtained represented solid (at ambient temperature) pitch-like matter (softening point of near 76 °C) which contained 27–28 % of toluene insoluble substances and 0.25–0.35 % of ash (Table 3).

The effectiveness of AO for thermal dissolution of coal can be related to its composition which contained the active hydrogen-donors (dihydroanthracene, fluorene and fluoranthene, etc),

Table 3. The characteristics of the thermal dissolution of coal in different HCST containing solvents for 1 h

Solvent (HCST: AO)	Reaction temperature, °C	Ash content in pitch, wt. %	Content (wt. % on daf) of materials insoluble in		Softening point, °C
			toluene	quinoline	
0 : 1	350	0.35	28.0	10.0	-
0 : 1	380	0.25	27.0	6.8	76
1 : 0	380	-	-	70.0	-
1* : 0	380	0.72	50.8	33.8	104
1 : 1	380	0.45	30.9	5.0	138
1 : 1	350	0.45	31.9	9.5	124
4 : 1	350	0.34	29.6	5.5	135

*HCST catalytically hydrorefined.

polycondensed aromatics with hydrogen-transfer properties (pyrene, phenanthrene, anthracene, etc.), and also compounds with solvating properties (carbazole, quinoline, etc.).

On the other hand, the reaction of coal with the parent HCST resulted in increased amount of the quinoline insolubles (to 70 %) in the reaction product as compared to the initial coal-solvent slurry (33 %), the product being lacking in plasticity. It follows from this that HCST underwent polycondensation with the coal's organic matter into insoluble product due to too large amount of oxygen containing substances, phenols in particalar. Polycondensation was much less extensive when catalytically hydrorefined HCST was used as solvent, the product obtained showed plasticity with the softening point of 104 °C (Table 3), though actually coal dissolution hardly occur.

The best results in coal dissolution were obtained when the blends of the parent HCST with the AO were used as solvents. At temperatures of 350 and 380 °C, the content of quinoline insolubles reduced to 5.0–9.5 when HCST-AO blends were used, and the pitch-like products had the softening points of 124–138 °C. Thus, one can suggest that the use of the AO and HCST blend for coal dissolution allowed i) polycondensation reaction to be prevented due to HCST hydrorefining with AO, and ii) coal to be effectively converted into a pitch-like soluble matter.

The product obtained with the hydrorefined HCST had an enhanced content of hydrogen (7.5 %) and oxygen (5.8 %) and reduced content of carbon and sulfur compared to pitch product obtained with AO (Table 4). The products of the intermediate compositions were obtained with the blended solvents.

The FTIR spectra of the products from coal dissolution with catalytically hydrorefined HCST, with HCST+AO blend and with AO are shown in Fig. 3, and the molecular indexes of the products in Table 5.

Table 4. Composition of the products obtained by thermal dissolution of coal with different solvents for 1 h

Solvent (HCST:AO)	Reaction temperature, °C	wt. % on daf				
		C	H	N	S	O
0 : 1	380	90.0	5.5	1.4	0.8	2.3
1 : 0 *	380	85.0	7.5	1.4	0.3	5.8
1 : 1	380	88.4	6.3	1.3	0.3	3.8
1 : 1	350	88.0	6.6	1.2	0.3	3.9
4 : 1	350	86.2	7.2	1.4	0.3	4.8

* HCST catalytically hydrorefined.

Table 5. Characterization of the molecular composition of the products of coal dissolution with different solvents

Solvent used	Absorption ratio, $A_{3375}/A_{2800\text{-}3000}$	Molecular indexes		
		f_a	H_{ar}	CH_3/CH_2
HCST + H_2 (with Al–Co–Mo catalyst)	0.06	0.64	0.27	0.39
HCST+AO	0.04	0.78	0.47	0.44
AO	-	0.92	0.79	0.45

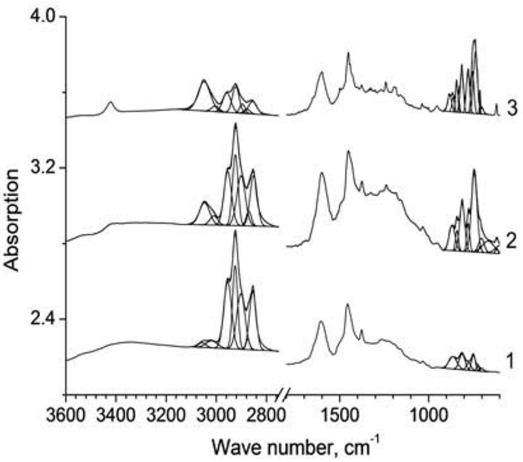

Fig. 3. FTIR spectra of the products from coal dissolution with HCST catalytically hydrorefined (1), with HCST+AO blend (2) and with AO (3)

Pitch-like product obtained with AO solvent was represented predominantly by aromatics. The FTIR spectrum showed little phenolic substances, the weak absorption band at 3420 cm^{-1} in Fig. 3 was, probable, due to mainly nitrogen-bearing compounds rather than to hydroxyls.

The condensate fraction from the reaction of coal dissolution with AO according chromatography-mass spectrometry data consisted mainly of two- and three-ring condensed aromatic compounds.

4. Conclusions

The effect of hydrorefining treatment of HCST on its composition and on the ability for thermal dissolution of bituminous coal was studied. It was found that catalytic hydrorefining with hydrogen at 400 °C and 5 MPa and treatment with hydrogen-donors lead to partial deoxygenation of HCST and to increase in its aromaticity. However, the ability for coal dissolution remained poor. The blends of the parent HSCT with AO were found to behave high efficacy for coal dissolution at 350 and 380 °C. The products obtained represented at ambient temperature the solid pitch-like matter with the softening points of 124 to 138 °C, the content of quinoline-insolubles being less than 6 %, and the ash content less than 0.5 %.

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