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Co-processing of Bituminous Coal with Heavy Hydrocarbon Fractions of Coal and Petroleum Origins into Pitch-Like Products

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Abstract

The efficiency of the dissolution of bituminous coal at moderate temperature to produce quinoline-soluble substances was studied using commercially available coal tar (CT), its anthracene fraction (AFCT), heavy coal semicoking tar (HCST), heavy gas oil from catalytic cracking of petroleum (HGOCC), their binary blends, as well as tetralin (for comparison) as solvents. The chemical and molecular compositions of the coal, solvents, and the extracts obtained were characterized in detail by chemical and group analyses, FTIR spectroscopy, liquid chromatography, analysis by means of gas chromatography–mass spectrometry. The highly aromatic CT, AFCT, low aromatic HGOCC solvents, binary blends of these solvents and hydrogen donor tetralin showed high performance for coal dissolution at 380 °C in the quinoline-soluble substances, the yields of gases being no more than 0.6 %. The extracts obtained with CT and AFCT solvents represented highly aromatic pitch-like matter with rarely substituted aromatic rings. The extract obtained with the HGOCC solvent was characterized by lower aromaticity, the aromatic nuclei being highly substituted with fairly large alkyl fragments. The blended solvents yielded more extracts whose structural parameters were intermediate between those obtained with each solvent separately. Heavy semi-coking HCST tar showed no dissolving ability because of the high content of phenolic hydroxyls. The concentration of benzo(a)pyrene (BaP) in the toluene-soluble fractions of the extracts obtained was much lower than that in the solvents used, and decreased as the coal dissolution time increased, thus indicating BaP conversion.

Keywords: coal, solvents, residues, coal dissolution, aromatics

INTRODUCTION

The high-temperature coal coking to produce metallurgical coke is the second large-scale process of coal utilization (after combustion for energy generation). This process is an inherent part of the integrated production of iron and steel where both at present and centuries ago traditional blast furnace technology using indispensable metallurgical coke dominates [1]. Currently, world crude steel production is dynamically developing [2], the major part (more than 65 %) accounting for hot metal from blast furnace. The key challenge of the blast furnace technology development is a radical decrease in the specific consumption of coke because of its high cost (its production accounts for almost half of all costs for metal production), significant CO_2 emissions and limited resources of high-quality coking coals [3]. During the last decades, the specific coke consumption in blast furnace has been reduced tremendously due to technological innovations [1].

In the long term, an increase in the number of blast furnaces with injection of pulverized coal, oil fractions and natural gas (for partial replacement of coke), and also large-scale development of the alternative steelmaking technologies without coke, such as direct reduction, smelting reduction, Corex process, and smelting in electric arc furnaces with graphite electrodes, will lead to further decrease in demand for metallurgical coke and, consequently, to decrease, most likely irreversibly, in the production of coal tar (CT) and coal-tar pitch (CTP) if an alternative way of large-scale use of metallurgical coke is not found.

However, the high temperature coal coking yields also CT as a minor byproduct (3–5 %) which is a valuable indispensable feedstock for the polyaromatic compounds needed in the production of advanced carbon materials and composites [4–6]. Most high-tech carbon materials such as electrodes, pitch coke, graphites and graphite-based construction materials, diamond, fullerenes, carbon foams and various anodes including anodes for aluminium electrolysis and advanced batteries, carbon fibers, mesocarbon microbeads, activated carbons, molecular sieves, electrical products, refractory and roofing materials, various carbon materials for mechanical engineering, for chemical apparatus and nuclear and rocket equipments, are produced from a non-volatile fraction of CT – CTP which consists of polycondensed aromatic and heterocyclic compounds. The needs for CT, particularly, for CTP are steadily increasing in manufacturing the advanced carbon materials for various purposes. Currently, the predominant part (more than 70 %) of CTP produced is consumed as a binder agent in anode manufacturing for the increasingly developing aluminium electrolysis, significant shortage in the pitch availability taking place in most countries (except for China). It is appropriate to add here that the most progressively developing steelmaking technology with the electric arc furnaces also needs CTP for graphite electrode manufacturing.

The opposite trends in production and in consumption of CT are a growing concern to the availability of the polyaromatic chemicals for manufacturing carbon materials. The need to solve this challenge is reasoned also by a significant drawback of the commercial CT and CTP because of serious environmental and health issues, since some polycyclic aromatic hydrocarbons massively present in CTP are carcinogenic and mutagenic. They are generated inevitably on high-temperature coal coking. These are the reasons why the development of methods for the production of environmentally friendly substitutes for CT bypassing the coal coking process is of considerable current issue.

The recent decade, coal dissolution at mild conditions has attracted much attention because the dissolved coal products of the polyaromatic nature can find wide application as a feedstock of both the ecologically friendly liquid fuels and the aromatic chemicals for manufacturing valuable carbon materials [6–9]. The efficiency of the dissolution process depends on the properties of both solvent and coal, the solvent is considered to play a critical role. The dissolution of different coals was shown to occur effectively at 350–380 °C using polar aprotic N-methyl-2-pyrrolidinone (NMP) as a solvent [7, 9]. According to Japanese researchers [10–12], the extraction yields of 84.6 % can be obtained from the bituminous coals using the CS_2/NMP blend. However, significant loss of NMP was shown to take place during the reaction due to its chemical bonding with the molecules of dissolved products [10]. The aromatic 1-methylnaphthalene (1MN) was much less effective [10, 12, 13], the highest extract yield of 50–60 % was obtained at the optimal temperature of 360 °C. Commercial crude 1-methylnaphthalene oil (CMNO) which contained some polar molecules was found [13] to be more effective, and the addition of polar methanol further improved coal dissolution.

Shui *et. al.* [13] and Schobert *et. al.* [14] used light cycle oil as a solvent for coal dissolution. The extract yields of more than 60 % were obtained from the bituminous coals. Rahman *et. al.* [7] studied the dissolution of coals using heavy aromatic commercial hydrocarbon fractions from the CT industry and its hydrotreated derivatives as solvents. The extract yield of 73 % was obtained at 400 °C using hydrotreated heavy aromatic solvent. The high dissolution performance was considered to be due to the presence of both polar components and hydrogen donor species in the hydrotreated derivatives of the solvent. The extracts obtained with the commercial solvents contained more aromatics with mainly condensed and pericondensed structures than with 1MN solvent.

Currently, several promising technologies for coal dissolution at moderate temperature are at different levels of development. The Japanese technology for the production of the ash-free coal called HyperCoal is based on coal dissolution at 350–400 °C in the medium of recycle two-ring aromatic solvents [10–12]. The HyperCoal with low ash content (less than 0.1 %) can be used as an environmentally friendly fuel, for example, directly in a gas turbine, as an additive in cokemaking and as a feedstock for manufacturing carbon materials. The goal of the coal dissolution process in the USA [15] is to produce pitch-like products which can be used as a binder and as a source in the manufacture of high-grade coke for anode production, and also for the synthesis of low-cost carbon fiber and other carbon materials. The process is conducted with the anthracene oil as a recycle solvent. However, the experiments showed that it was not possible to quantitatively recover the anthracene oil solvent because it was retained by heavy viscous process products. So, continuous unit operation requires the addition of fresh solvent from some kind of other source.

It should be noted that despite fairly high level of demonstration projects developed, further efforts are undertaken to find highly reactive coals and more available cost-effective and efficient solvents to maximize the extract yield. The coal dissolution process involving the use of the available commercial coal- and petroleum-derived hydrocarbon residues as solvents without recycling can be a promising way because it allows the co-processing of petroleum residues simultaneously with coal into high value added demanded products, in addition to significant saving in solvent regeneration. In our recent papers [16–18], commercial hydrocarbon byproducts and residues derived from coal- and petroleum processings were used for thermal dissolution of coals to produce quinoline-soluble extracts. It was shown that the highest extract yields in the anthracene oil as a solvent at 380 °C were obtained from the medium-ranked coals of fat and gaseous-fat grades. The empirical properties and molecular and structural characteristics of the coal extracts and pitches isolated from the extracts were comprehensively studied in comparison with commercially available pitch samples, including typical CTP, petroleum-derived pitch, and compounded pitch derived from the blend of CT with petroleum feedstock [18, 19]. In terms of the technical specifications, the extractive pitches resembled commercial blended petro-coal-tar pitch. A significant merit of the extractive pitches compared to CTP was low carcinogenicity (two to three times lower).

This paper aimed to investigate the effect of blending of commercial coal- and petroleum-derived heavy hydrocarbon byproducts and residues of different compositions on the conversion of bituminous coal into the quinoline-soluble substances. Co-processing of petroleum residues with coal can be considered as a way to involve coal into chemical processing, as well as to increase the depth of petroleum utilization into valuable products – an actual petroleum processing issue.

EXPERIMENTAL

Coal and solvents used

The dissolution experiments were conducted using bituminous coal from the Chadan deposit (Tyva Mining Company). It was ground to a fraction of <1 mm (the average particle size of 0.4 mm) and dried in a vacuum oven at 85 °C.

Three types of commercial hydrocarbon byproducts and residues were used for coal dissolution: i) coal-derived solvents, namely, HCST – heavy coal semi-coking tar provided by the Leninsk-Kuznetsk Semicoking Plant; CT – coal tar, Altai-Coke Joint-Stock Company; AFCT – the anthracene fraction of coal tar, Coke Joint-Stock Company; ii) HGOCC – petroleum-derived residue consisting largely of heavy gas oil from catalytic cracking of petroleum; iii) binary blends of these commercial solvents. Also, H-donor tetrahydronaphthalene (THN) of reagent grade quality was used as a reference solvent for comparison.

Reactor unit and dissolution procedure

Coal dissolution was carried out following previously optimized procedures [17, 18] using an experimental unit equipped with a 2 L stainless steel autoclave dissolver with a mechanical stirrer (speed 150 rpm). The autoclave was charged with coal/solvent slurry, purged carefully with nitrogen and hermetically sealed. Unless otherwise stated, the reactor was loaded with 900 g of coal-solvent slurry with the proportion of 1 : 2 by the weight, respectively. The autoclave was heated to 380 °C, and the coal-solvent mixture was allowed to react at this temperature for 60 min residence time and at autogenous pressure under continuous stirring. The use of the stirrer provided effective mass transfer, improved contact between the phases in a three phase reaction mixture of gas, liquid and solid, and thus less-gradient conditions in terms of temperature and concentration of the reagents. These experimental conditions were important for multi-phase reaction system, and especially important to prevent caking when coal softened.

At reaction completion, the autoclave was allowed to cool to 250 °C, the vapour-gas products were vented through a refrigerator line where the gases and condensed liquids (naphtha) were separated and measured. Finally, the valve at the bottom of the autoclave was opened, and the molten digested product was drained off into a cylinder receiver. The product in the receiver was allowed to cool with continuous stirring for homogenization and then pushed out of the cylinder by a piston. The weights of the digested product (termed as an extract which consisted of dissolved coal in a solvent + ash coal residue), condensed liquids (termed as naphtha), and gas volume were measured. The composition of gaseous products was analyzed with a gas chromatograph.

The representative extract portion 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 or three times to confirm the reproducibility.

Analytical techniques

The elemental analysis of the coal, solvents and extract products was performed with a FlashEA 1112 elemental analyzer (Thermo Fisher Scientific, Netherlands). Thermal decomposition of coal was studied using Jupiter STA 449F1 synchronous analyzer (Netzsch, Germany). The volatility of the solvents and products was characterized by temperature range of boiling on distillation.

The FTIR spectra were recorded using KBr pellets prepared by a conventional technique. The spectra were recorded on a Tensor-27 FTIR spectrometer (Bruker, Germany) within the spectral range from 4000 to 400 cm^{-1}. The concentration of benzo(a)pyrene (BaP) in the solvents and in the toluene-soluble fractions of the coal extracts was measured using LC20 high-performance liquid chromatograph (Shimadzu, Japan). The softening point of the pitch-like extracts produced was determined using a “ring and ball” method.

RESULTS AND DISCUSSION

Coal and solvent characterization

The coal used represented typical coking coal with a plastic layer thickness of 21 mm, vitrinite content of 85 % and vitrinite reflectance coefficient of 0.77 %. The yield of the volatile matter was 37.8 mass %, ash – 5.6 mass %. Coal softening commenced at around 350–360 °C. Thermal decomposition with the weight loss started at 400 °C, the main decomposition stage occurred in the temperature range of 400–550 °C with the maximum rate of weight loss at 465 °C.

Table 1 shows the chemical and group compositions and other characteristics of coal and solvents. The petroleum-derived HGOCC solvent was most enriched with hydrogen. The coal-derived

TABLE 1

Characterization of coal and solvents used

Sample	Element composition, mass %				Distillation temperature range, °C	Density, cm^3/g	Toluene insolubles, mass %	Quinoline insolubles, mass %
	C	H	N + S + O	H/C at.				
Coal	84.7^a	5.5^a	9.8^a	0.78	400–550^b	–	–	–
Solvents:								
HCST	83.7	8.1	9.2	1.16	160–420	1.05	7.9	1.9
CT	91.5	5.3	3.2	0.69	180–550	1.20	11.6	1.7
AFCT	87.6	5.2	7.2	0.71	170–350	1.10	0.1	0.1
HGOCC	89.9	8.3	1.8	1.11	221–508	1.04	0.1	0.1
THN	90.9	9.1	–	1.20	207	0.97	Not	Not

Note. Here and in Tables 2–5: HCST – heavy coal semi-coking tar; CT – coal tar; AFCT – anthracene fraction from CT; HGOCC – heavy gas oil from catalytic cracking of petroleum; THN – tetrahydronaphtalene.

[a] Based on daf coal.

[b] Determined by TG/DTG analysis.

HCST solvent differed by an enhanced concentration of oxygen. The CT and HCST solvents contained 11.6 and 7.9 % of toluene-insolubles, and 1.7 and 1.9 % of quinoline-insolubles, respectively. In the AFCT and HGOCC solvents, the content of toluene-insolubles was as small as 0.1 mass %. The volatility of solvents decreases in the following order: THN >> AFCT > HCST > CT ≥ HGOCC.

FTIR analysis

The spectrum of 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) [20–23] (Fig. 1). 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 presence of the aromatic fragments. The largest absorbance centered at 3400 cm^{-1} indicates hydrogen-bonded hydroxyls.

The spectra for the solvents show different spectral pictures depending upon the sample. The HCST solvent shows high absorbance centered at 3400 cm^{-1} due to the presence of a large amount of hydrogen-bonded hydroxyls. The bands within 3000–2750 and 1450–1300 cm^{-1} indicate aliphatic groups of different configurations, and large absorbance centered at 1600 cm^{-1} and weak absorbance between 3100–3000 cm^{-1} due the aromatic groups. The CT and AFCT solvents exhibit the highest absorbances between 3100–3000 and 900–700 cm^{-1} (out-of-plane bending of the aromatic C–H bonds). A weak shoulder at 1650 cm^{-1} in the spectra of the coal-derived HCST, CT, AFCT solvents indicates few carbonyls. The weak peak centered at 3430 cm^{-1} can be attributed to both hydroxyls and nitrogen-bearing heterocyclic compounds such as carbazole. The petroleum-derived HGOCC solvent was distinguished by the highest absorbances between 3000–2750, 1460–1440 cm^{-1} and at 1376 cm^{-1}.

The spectral regions within 3100–2750 and 900–700 cm^{-1} characteristic of the aromatic and aliphatic structures were subjected to deconvolution according to recommendations [20] to characterize semi-quantitatively the molecular structure of the solvents and coal. The representative curve-resolving results are shown in Fig. 2. The subpeak at 750 cm^{-1} in all the spectra indicates low-substituted aromatic rings with four adjacent C–H bonds, *i.e. ortho*-substituted rings, and a subpeak at 878 cm^{-1} indicates highly substituted aromatic rings with lone C–H bond. The subpeaks at 843, 814, and 783 cm^{-1} can be assigned to two-three adjacent C–H bonds in the aromatic rings. In the spectrum of the petroleum-derived HGOCC solvent, the weak subpeak at 700 cm^{-1} indicates aromatic rings with five adjacent C–H bonds, *i.e.* monocyclic rings, and that at 725 cm^{-1} should be assigned to the rocking modes of CH_2 groups in the aliphatic chains with more than 4 carbon atoms, rather than to aromatic C–H out-of-plane bending vibrations [20].

The following semi-quantitative indices for molecular characterization of the solvents and coal were estimated based on the deconvoluted spectra: H_{ar} index for hydrogen aromaticity, *i.e.* the proportion of the aromatic hydrogen atoms to the total amount of hydrogen atoms in an 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_{ar}) and at 3000–2750 cm^{-1} (A_{al}). 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} index of *ortho*-substitution was assessed from the ratio of the absorbance at 750 cm^{-1} (A_{750}) to total absorbance in whole range of 900–700 cm^{-1} ($A_{900-700}$).

In assessing these indices we took account of the statistical data [23] that the ratio of the extinction coefficient for the stretching vibrations

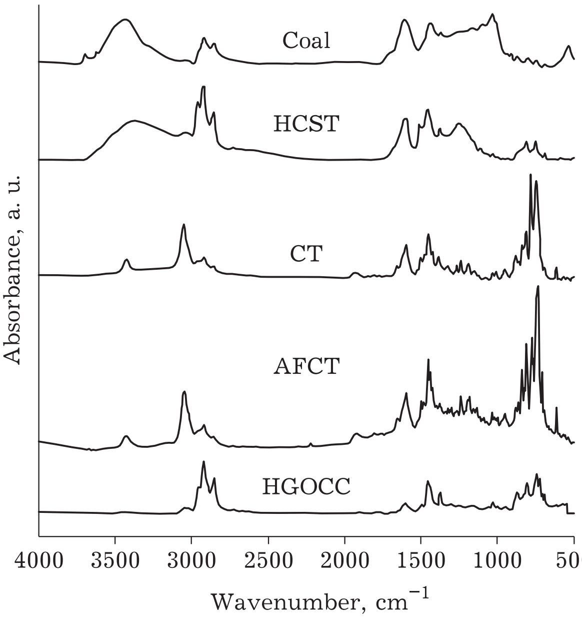

Fig. 1. The FTIR spectra for coal and solvents. Here and in Fig. 2: HCST – heavy coal semi-coking tar; CT – coal tar; AFCT – anthracene fraction from CT; HGOCC – heavy gas oil from catalytic cracking of petroleum.

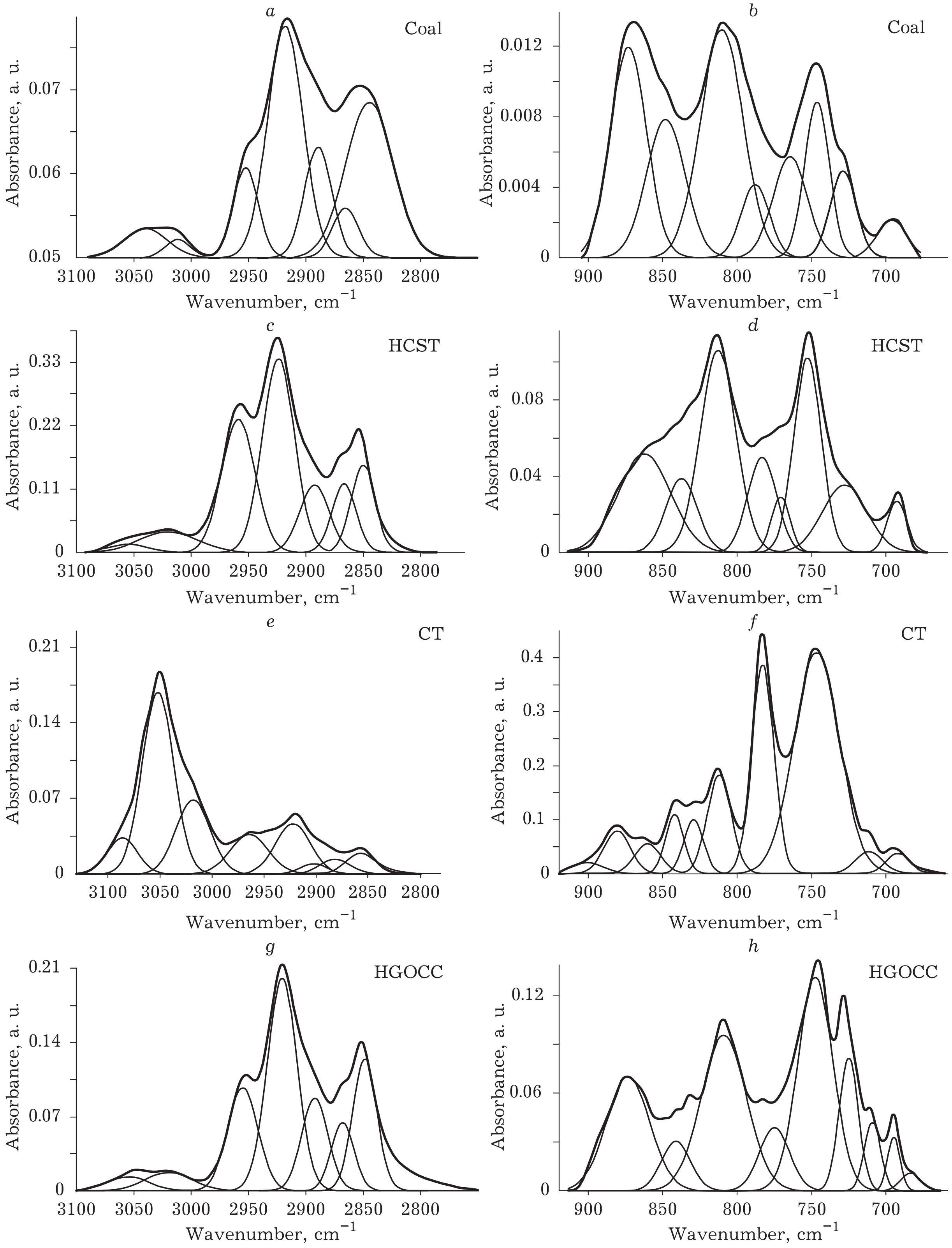

Fig. 2. The examples of deconvoluted FTIR spectra for coal (*a*, *b*) and solvents (*c*–*h*). For designations, see Fig. 1.

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 and CH_3 groups is 0.5. The molecular indices were calculated using the following formulas:

$$H_{ar} = \frac{A_{ar}/0.2A_{al}}{1 + (A_{ar}/0.2A_{al})} \quad (1)$$

$$I_{ort} = A_{750}/A_{900-700} \quad (2)$$

$$CH_3/CH_2 = 0.5(A_{2955}/A_{2923}) \quad (3)$$

Brown-Ladner f_a index for carbon aromaticity was also estimated according to [24] using the elemental analysis data and FTIR data for the proportion of aliphatic hydrogen atoms to the total amount of hydrogen atoms in an average molecule.

Shown in Table 2 are the molecular indices thus estimated. One can see that coal 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 CT and AFCT solvents are highly aromatic in terms of both f_a and H_{ar} indices (0.97–0.96 and 0.92–0.89, respectively). Their relatively high I_{ort} indices indicate aromatic rings to be rarely substituted. On the other hand, the petroleum-derived HGOCC solvent shows the least f_a and H_{ar} indices (0.61 and 0.31, respectively), low I_{ort} index (0.28) indicates a high degree of the aromatic ring substitution. HCST is characterized by relatively low aromaticity, the aromatic rings being highly substituted.

Coal dissolution

Coal dissolution with low-volatile solvents occurred under autogenous pressure of near 2 MPa. In the tests with THN as a solvent, the pressure increased to 3.7 MPa. The main digested reaction product was coal extract representing dissolved coal in solvent + coal residue with the ash content of about 2.0 mass % based on extract. The extracts obtained with the CT, AFCT, HGOCC solvents and with binary blends represented pitch-like solid matter with the softening points of 73 to 125 °C depending upon the solvent used. The THN extract represented viscous heterogeneous matter. Hard and almost non-softening product was obtained with HCST.

Little naphtha and a little gases (no more than 0.6 %) which were released during the autoclave depressurization at 250 °C were obtained with all solvents. The gas consisted mainly of CO_2 (50–70 %), the concentration of H_2 ranged from 5 to 15 %, and H_2S – 5 to 21 % depending on the solvent type. An enhanced proportion of hydrocarbon gases (28–37 mol %, mostly methane) was obtained when the petroleum-derived HGOCC solvent was used.

Shown in Table 3 are the data on the group composition of the extracts obtained with different solvents. The performance of the individual solvents at 380 °C for coal dissolution into quinoline solubles decreased in the following order: AFCT > THN > HGOCC > CT. Coal dissolution in the HCST solvent did not occur at all. Moreover, even more quinoline-insoluble α_1-fraction (55 %) than in the initial coal-solvent mixture (33 %) was found in the reaction product. Most likely, this was due to too high concentration of the oxygen-containing species (phenols, in particular) both in coal and solvent, which initiated regression reactions. Of all the individual solvents, highly aromatic AFCT was the most effective for coal dissolution. An increase in the reaction time to 1.5 h further reduced α_1-fraction from 7.1 to 5.2 %. The reaction occurred fairly effectively at reduced temperature of 350 °C. The HGOCC solvent of predominantly aliphatic character proved to be as effective as highly aromatic CT solvent and typical hydrogen donor THN solvent, the extract featuring less toluene-insolubles.

TABLE 2

The molecular indices of the coal and solvents based on the FTIR data

Sample	Aromaticity index		*Ortho*-substitution degree, I_{ort}	CH_3/CH_2 ratio
	f_a	H_{ar}		
Coal	0.71	0.26	0.15	0.14
Solvents:				
HCST	0.62	0.29	0.20	0.54
CT	0.97	0.92	0.49	0.52
AFCT	0.96	0.89	0.44	0.45
HGOCC	0.61	0.31	0.28	0.30
THN[a]	0.60	0.33	–	0

Note. For designations, see Table 1.

[a] Calculated from the molecular formula.

TABLE 3

Characterization of the extracts obtained, depending on the solvents used (380 °C, 1 h)

Solvent	Content of insolubles, mass %, based on daf extract		Softening point, °C
	α-fraction	α_1-fraction	
HCST	–	55.0	–
CT	35.6	8.2	86
AFCT	26.0	7.1	78
AFCT[a]	27.2	5.2	84
AFCT[b]	28.0	10.1	–
HGOCC	22.4	7.9	88
THN	24.0	7.8	–
HCST + AFCT	30.9	8.4	125
CT + HGOCC	27.0	7.1	82
AFCT + HGOCC	26.3	5.7	104
AFCT + HGOCC[c]	29.9	10.9	73

Note. 1. α – toluene-insolubles; α_1 – quinolone-insolubles. 2. For designations, see Table 1.

[a] 1.5 h reaction time.

[b] 350 °C reaction temperature.

[c] 425 °C reaction temperature.

The CT + HGOCC and AFCT + HGOCC binary blends contributed to some increase in the efficacy of coal dissolution. Blending of HCST with AFCT (with 1 : 1 proportion) allowed the solvent composition to be optimized and thus relatively low content of the quinoline-insolubles (8.4 %) to be obtained. The extract obtained represented pitch-like matter with the softening point of 125 °C.

Chemical composition of the extracts depended upon the solvents used: the AFCT and CT extracts had rather low hydrogen concentration (5.4–5.5 %), and the HGOCC one had an enhanced hydrogen concentration (7.4 %). The concentrations of nitrogen, sulphur and oxygen were 0.6–1.3, 0.8–1.3 and 0.8–2.7 %, respectively, depending on the solvent used. The molecular indices estimated from the deconvoluted FTIR spectra of the extracts are shown in Table 4. One can see that the CT and AFCT extracts are highly aromatic (f_a = 0.87–0.90 and H_{ar} = 0.71–0.67), the aromatic rings having little substituents (mostly *ortho*-substituted, I_{ort} = 0.41–0.44). The HGOCC extract is less aromatic (f_a = 0.64 and H_{ar} = 0.31), the aromatic rings being highly substituted (I_{ort} = 0.33) with fairly large alkyl fragments. Binary solvents give extracts whose molecular indices are almost average compared to those obtained with each solvent separately.

The analysis by means of gas chromatography–mass spectrometry showed the 210–300 °C fraction derived from the AFCT extract to contain mainly naphthalene (25.4 %), alkylnaphthalenes (12.4 %), acenaphthene (10 %), dibenzofuran (11.4 %), fluorene (11.2 %), anthracene (12 %) and their derivatives. A small amount (2.5 %) of partially hydrogenated anthracene and phenanthrene was also present in this fraction. So, light distillate fractions of the pitch-like extracts can be used as a feedstock for bi- and tricyclic aromatic chemical compounds. Heavy fractions with polycondensed aromatic substances can serve as a raw material for the production of pitch binders for various applications.

The data obtained show coal dissolution and composition of the extracts obtained to be a com-

TABLE 4

Characterization of the molecular composition of the extracts obtained, depending on the type of solvents

Solvent	Aromaticity index		*Ortho*-substitution degree, I_{ort}	CH_3/CH_2 ratio
	f_a	H_{ar}		
AFCT	0.90	0.71	0.37	0.41
CT	0.87	0.67	0.44	0.42
HGOCC	0.64	0.31	0.20	0.33
CT + HGOCC	0.76	0.46	0.35	0.34
CT + HGOCC[a]	0.78	0.50	0.32	0.41
AFCT + HCST	0.78	0.47	0.34	0.44
AFCT + HGOCC	0.76	0.33	0.35	0.34
AFCT + HGOCC[b]	0.87	0.60	0.34	0.53
THN	0.75	0.52	0.33	0.27

Note. For designations, see Table 1.

[a] 3 h reaction time.

[b] 425 °C reaction temperature.

plicated function of the solvent used. AFCT, CT, HGOCC, their binary blends and THN all turned out to be among the effective solvents which, however, represent different chemical classes: CT and AFCT are highly aromatic, HGOCC is low-aromatic, binary solvents are of moderate aromaticity, and THN represent typical hydroaromatic H-donors. It is an interesting issue how these solvents with quite different chemical properties all ensured high extents of coal dissolution.

The high efficiency of THN solvent is clearly due to its hydroaromatic cycles capable of donating reactive hydrogen to radical species and thus preventing regression reactions, the solvent itself being converted into the respective dehydrogenated derivatives. The performance of highly aromatic CT and AFCT solvents consisting of various polycondensed aromatics and heteroatomic molecules [25] can be due to an appropriate balance between different functionalities. For example, fluorene and acenaphthene molecules (7–8 % in AFCT) can exhibit hydrogen donating ability due to reactive CH_2 groups at the α-position to the aromatic rings. Polycondensed aromatics, like pyrene (4–6 %), phenanthrene (20–25 %), anthracene (5–6 %), though not hydrogen donors, however, can play a role of the active hydrogen shuttlers and accelerate hydrogen transfer from some hydrogen-rich moiety to thermally generated radicals. Carbazole (5–6 %), quinoline (0.5 %), other nitrogen-containing compounds and oxygen-containing naphthol derivatives exhibit solvating properties, and can improve dissolution of the components of the reaction mixture.

In light of the results obtained, it was rather surprising to find that the HGOCC solvent alone of low aromatic nature proved to be almost equally effective as the highly aromatic solvents with hydrogen shuttling, hydrogen donating, and solvating abilities. A reasonable explanation may lie in conjunction of the properties of coal and solvent and of the liquid-phase reaction conditions (because of low solvent volatility). The coal used in this study is a bituminous coking coal having the plastic layer thickness of 21 mm and low softening point of 350–360 °C. Its thermal decomposition with the noticeable weight loss started at 400 °C, the main decomposition stage occurred in the temperature range of 400–550 °C with the maximum rate of weight loss at a temperature higher than 465 °C. Thus, the liquid-phase dissolution reaction took place when the coal matter had already been transformed into a plastic state, but before the active thermal destruction of covalent bonds began.

Coal is known to be a cross-linked aromatic polymer-like matter where aromatic units are coupled with each other mainly by methylene and ether linkages. The strength of these linkages has been shown [26, 27] to depend greatly upon the structure and size of the aromatic units, the larger the size of these units, the weaker the linkage between them, difference in the thermolysis rates attained 5–6 orders of magnitude. The primary dissolution reactions at low temperature commence thus with a cleavage of the most weak linkages.

Bituminous coals are known also [28] to have some fragments, like hydroaromatic cycles, as well as fluorene-type CH_2 groups, which contain active hydrogen and can behave as effective hydrogen donors. One can suggest that polycondensed aromatics of the plastic coal matter dispersed in the liquid-phase solvent as well as some polyaromatics present in the HGOCC solvent itself could play a role of shuttlers to transfer these active hydrogen atoms to radical species generated as a result of the cleavage of the weakest linkages. Taking into account rather low reaction temperature, lower than that of thermal destruction, and also low yields of distillates and gases, it may well be that liquid-phase dissolution reaction proceeded selectively through a depolymerization of the coal matter by a thermally activated solvolysis of the weak ether and/or methylene linkages between the large polycondensed aromatic units. The disruption of these linkages results in disintegration of the coal matter, in peptization and dissolution of the monomeric (oligomeric) substances in the solvent media.

Shown in Table 5 are the data on the BaP concentrations in the toluene-soluble fractions from the extracts obtained and in the starting solvents for comparison. Coal itself (tetrahydrofurane extract from coal in Soxhlet apparatus) was found to have almost no BaP (less than 0.01 mg/g). The BaP concentrations in the starting commercial solvents decreased in the following order: CT > CT + HGOCC > AFCT > AFCT + + HGOCC >> HGOCC >> HCST. The concentrations in the toluene-solubles derived from the coal extracts decreased in the same solvent order, however, they were much less than in the respective solvents and also less than 2/3 of their values (taking account of the coal/solvent proportion in the starting mixture). Importantly, the increase in coal dissolution duration from 1 to 3 h

TABLE 5

Benzo(a)pyrene (BaP) concentration (mg/g) in the solvents used and in the toluene-soluble fractions of the coal extracts

Solvent	Starting solvent	Coal extract	
		actual	calculated[a]
HCST	0.10	0.05	0.07
AFCT	4.14	2.16	2.76
CT	8.10	4.92	5.40
HGOCC	0.59	0.29	0.39
AFCT + HSCT	2.12[b]	1.18	1.41
AFCT + HGOCC[c]	2.37[b]	1.50	1.42
CT + HGOCC	4.35[b]	1.84	2.89
CT + HGOCC[d]	4.35[b]	1.48	2.89
THN	0	0.04	0.03

Note. For designations, see Table 1.

[a] Determined as 2/3 of the BaP concentration for the respective solvent taking account of the coal/solvent proportion in the starting mixture.

[b] Calculated based on the additivity for solvent blends with the proportion of 1 : 1.

[c] The mass proportion of coal to solvent in the slurry was 1.0 : 1.5.

[d] The reaction time was 3 h.

resulted in a decrease in the BaP concentration (from 1.84 to 1.48 mg/g). Thus, these data may mean that: i) organic coal matter hardly contained BaP molecules, and ii) BaP was not generated under coal dissolution conditions, in contrast, its consumption (but not generation as at high-temperature coking) took place as coal dissolution progressed.

CONCLUSION

The solvents of different chemical nature such as highly aromatic coal tar, its AFCT fraction, low-aromatic HGOCC, their binary blends, as well as hydroaromatic THN were found to exhibit high performance for coal dissolution at moderate temperature, the yields of the gaseous products being no more than 0.6 %. The blends of commercial coal-derived and petroleum-derived solvents improved extract yields.

Coal dissolution in the liquid-phase commercial hydrocarbon solvents occurred *via* depolymerization of the polymer-like coal matter by selective thermally activated solvolysis of the weak linkages between the polycondensed aromatic units.

Unlike solvents above, HCST showed practically no ability to dissolve coal, which may be due to too large amount of phenolic hydroxyls which play a major role in the regression reactions. However, blending with highly effective AFCT solvent allowed HCST to be involved for coal dissolution.

The extracts obtained with the CT and AFCT solvents represented highly aromatic pitch-like matter with rarely substituted aromatic rings and with softening points of 78 to 86 °C. The distilled fraction of 210–300 °C from the pitch-like product consisted predominantly of the aromatic hydrocarbons with two and three rings. The extract obtained with the petroleum-derived HGOCC solvent was characterized by lower aromaticity, the aromatic nuclei being highly substituted with fairly large alkyl fragments.

The concentration of BaP in the toluene-soluble fractions of the extracts obtained depended on its concentration in the solvents used, however, it was much lower. BaP was not generated during the coal dissolution reaction, quite contrary, the BaP concentration decreased as the coal dissolution progressed indicating its chemical reaction with coal and products.

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