

The Composition and Properties of Soluble Products from the Coal ThermoSolvolysis with Hydrocarbon Residues and Blends as Solvents

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Abstract

The dissolution of bituminous coal at mild temperature was studied using a variety of commercially available coal- and petroleum-derived hydrocarbon fractions, hydrorefined derivatives and blends as solvents. The chemical and molecular composition of the coal, solvents and extracts were characterized by chemical and group analyses, and by IRFT, ¹H NMR, GC-MS and liquid chromatography. Low volatile solvents like highly aromatic coal tar (CT), its anthracene fraction (AFCT), petroleum-derived solvent (HGOCC) and binary blends were found to exhibit high performance for coal dissolution into quinoline solubles (to 79–82%), and the yields of gases being no more than 0.5%. The extracts obtained using CT and AFCT solvents represented pitch-like matter consisting of rarely substituted aromatic molecules with 4–5 condensed rings. HGOCC extract was much less aromatic, the aromatic rings being highly substituted with fairly large alkyl substituents. The blended solvents yielded more extracts, and their molecular indexes were average between those obtained with each solvent separately. A remarkable finding was that the extracts obtained were characterized by significantly lower content of benzo(a)pyrene (BaP) compared to solvents used, its content further decreased as the time of coal dissolution increased.

1. Introduction

Most of the high-tech carbon materials and composites are manufactured currently using polyaromatic coal tar and its non-volatile fraction – coal-tar pitch. Coal tar is a minor by-product (3–5%) of the high-temperature coal coking into metallurgical coke required for steel production. Coal tar provides currently a wide range of aromatic chemicals including polyaromatics which cannot be produced directly from petroleum [1, 2]. However, the future of coal tar availability is dim due to a steady and irreversible decrease in its production because of decreasing demand for coke for blast furnaces,

as well as due to advanced development of steel-making technology without coke [3].

Contrasting trends in production volume and demand for coal tar are a growing concern to the availability of the polyaromatic chemicals for rapidly developing production of carbon materials. The need to solve this challenge is reasoned also by a significant drawback of the commercial coal-tar pitches because of a high content of carcinogenic polycyclic aromatic hydrocarbons (PAH).

Natural humic coals are an ideal and reliable raw material for the production of polyaromatic substances, since their fragments, linked to each other by intermolecular and relatively weak covalent bonds, are initially present in the organic coal matter (OCM) [2]. A promising way to obtain demanded polyaromatic substances from coal is its

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treatment with solvents at moderate temperatures to convert OCM into a soluble form and to separate from the mineral substances [4–8]. The efficiency of coal dissolution was shown [4–6, 9–11] to depend on the properties of both the solvent and coal, the solvents appear to play a critical role. The main properties conceptually important for solvents are as follows: chemical compatibility with the aromatic constituents generated from the coal matter to be able to retain them in solution; the ability to act as hydrogen donor or hydrogen shuttling agents.

Shui et. al. [6] studied the dissolution of Chinese coals with N-methyl-2-pyrrolidinone (NMP), 1-methylnaphthalene (1MN) and methanol as solvents. The extract yield from the subbituminous coal in the 1MN solvent was found to increase as temperature increased, the highest yield of 56% was obtained at 360 °C. Commercial 1-methylnaphthalene oil (CMNO) which contained some polar molecules was more effective, and the addition of polar NMP and methanol further improved coal dissolution. Rahman et. al. [4] used heavy aromatic hydrocarbon fraction from the coal tar industry and its hydrotreated derivatives as solvents for coal dissolution. The improved extract yield of 73% was obtained using hydrotreated heavy aromatic fraction due to the presence of both polar components and hydrogen donor species. The extracts contained more aromatics with condensed and pericondensed structures compared to that obtained with 1MN solvent.

A large body of data on the dissolution of coals in the 1-methylnaphthalene and CMNO solvents was obtained by Japanese researchers [7, 9, 10, 12]. Kobe Steel Co. Ltd. and Mitsubishi Chemical Co. are jointly developing a coal dissolution process to produce a deashed product called Hypercoal [7, 12]. This product contains mainly polycondensed aromatic substances, has good plasticity and coking properties. It can be used as a raw material for the production of chemicals of various classes, carbon materials for a wide range of applications, as well as an environmentally friendly energy carrier, including for direct combustion in gas turbines.

The use of commercial hydrocarbon residues as the non-recycling solvents for coal dissolution can be a promising way because it allows co-processing of the hydrocarbon residues with coal into high value added demanded chemicals and fuels, in addition to significant savings in solvent regeneration. We studied recently [13–16] the dissolution of various coals at mild temperature to produce quinoline-soluble substances using a variety

of commercially available coal- and petroleum-derived hydrocarbon fractions as solvents. The dissolution of bituminous coals in the liquid-phase solvent medium at a mild temperature of 350–380 °C was supposed to occur through depolymerization via weak linkages between the aromatic units. The extracts obtained using CT and AFCT solvents represented pitch-like matter with a low concentration of benzo(a)pyrene (BaP) [15, 16].

The goal of this paper is to study the dissolution of bituminous coal at a mild temperature using a suite of hydrocarbon fractions of coal and petroleum origins, their hydrotreated derivatives, and binary blends as solvents. The chemical and molecular composition and properties of the extracts obtained, and benzo(a)pyrene concentration depending on the solvent used are characterized by different techniques.

2. Experimental

2.1. Coal and solvents used

The dissolution experiments were conducted using a bituminous coal from Chadan deposit in Russia. Three types of commercial hydrocarbon fractions of different origins were used as solvents: heavy coal semi-coking tar (HCST) provided with Leninsk-Kuznetsk Semicoking Plant; coal tar (CT) from coal coking, Altai-Coke Joint-Stock Company; anthracene fraction of coal tar (AFCT), Coke Joint-Stock Company; petroleum-derived fraction consisting largely of heavy gas oil from the catalytic cracking of the petroleum residues (HGO-CC); binary blends of these solvents. Also, HCST and CT tars were subjected to catalytic hydrorefining pretreatments and used as solvents (HCST_h and CT_h, respectively).

2.2. Reactor unit and dissolution procedure

The coal dissolution was carried out according to [13, 16] using an experimental unit equipped with a 2 l stainless steel autoclave with a mechanical stirrer. The autoclave was charged with a coal/solvent slurry (900 g with a proportion of 1:2 by the weight), and the reaction was carried out at 380 °C for 60 min at autogenous pressure. At reaction completion, the gases were collected, and a hot digested product (termed an extract that consisted of dissolved coal in a solvent + ash coal residue) was discharged from the autoclave. The extract produced was subjected to Soxhlet extraction to determine the toluene-soluble fraction. Toluene insoluble residue was further extracted with hot quinoline.

Quinoline insoluble residue was washed with toluene, dried under vacuum at 80 °C and weighed. Coal conversion was calculated based on the amount of the quinoline insoluble organic matter.

Hydrotreating pretreatment of the HCST and CT tars (without coal) was performed at 380 °C under a hydrogen pressure of 5 MPa for 2 h using the same autoclave reactor and a commercial Co/Mo/Al₂O₃ hydrotreating catalyst.

2.3. The methods for characterization of coal, solvents and extracts obtained

The infrared Fourier transform (IRFT) spectra were obtained using Bruker Tensor-27 IRFT spectrometer. The ¹H NMR spectra were recorded for the chloroform-d dissolved fractions using a Bruker Avance III Fourier spectrometer with a proton resonance frequency of 600 MHz. TSQ 8000 Trace 1310 gas chromatography-mass spectrometer was used for identifying and quantifying organic compounds contained in the hexane soluble fractions. The benzo(a)pyrene (BaP) concentration in the solvents and the toluene soluble fractions of the coal extracts were measured using Shimadzu LC20 high-performance liquid chromatography. The gaseous products were analyzed by gas chromatography.

3. Results

3.1. Chemical composition of coal and solvents

The coal used in this study was bituminous vitrinite-type one with a vitrinite reflectance of 0.77%. Its chemical composition was as follows, wt.% on daf: C 84.7; H 5.5; heteroatoms 9.8. It showed softening point at 350–360 °C and a layer thickness of 20 mm.

The solvents used showed large variation in the chemical composition. The CT and AFCT had 91.5 and 87.6% of carbon and 5.2–5.3 wt.% of hydrogen, respectively. HGOCC solvent differed with an enhanced hydrogen concentration (8.3%) and least heteroatoms (1.8% in total). HCST differed with an enhanced content of oxygen. Catalytic refining of HCST and CT increased the content of hydrogen and decreased oxygen content.

3.2. Characterization of the molecular structures of coal and solvents by IRFT

The IRFT spectra for the solvents showed significant variation in the spectral profiles in the regions at 3400 cm⁻¹ (hydrogen-bonded hydroxyls),

3100–3000 cm⁻¹ (stretching vibrations of the aromatic C-H bonds), 3000–2750 cm⁻¹ (stretching vibrations of the aliphatic C-H bonds), 1600 cm⁻¹ (stretching vibrations of the aromatic C-C bonds), 1460–1370 cm⁻¹ (bending vibrations of aliphatic C-H bonds), and 900–700 cm⁻¹ (out-of-plane bending of the aromatic C-H bonds). The assignments were made according to the literature [17, 18].

The specific spectral regions between 3100–3000 cm⁻¹ and 3000–2750 cm⁻¹, and between 900–700 cm⁻¹ were subjected to deconvolution and the following semi-quantitative molecular indexes were evaluated based on the areas of the deconvoluted subbands: H_{ar} index for hydrogen aromaticity; C_{ar} index for carbon aromaticity; I_{os} index for ortho-substituted aromatic rings; CH₃/CH₂ ratio in the aliphatic structures. In assessing the H_{ar} and CH₃/CH₂ indexes we took account of the statistical data for bituminous coals [28] that the ratio of the extinction coefficient for the stretching vibrations of the aromatic C–H bonds to that for the aliphatic C–H bonds is 0.20; while that the ratio for CH₂ and CH₃ groups is 0.5. Carbon aromaticity C_{ar} index was estimated according to ref. [19] using the ultimate analysis data and IRFT data for the proportion of the aliphatic hydrogen atoms to the total amount of hydrogen atoms in an average molecule. The indexes were calculated using the following formulas:

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

$$C_{ar} = 1 - \frac{C_{al}}{C}; \quad \frac{C_{al}}{C} = \frac{\left(\frac{H_{al}}{H} \times \frac{H}{C}\right)}{\left(\frac{H_{al}}{C_{al}}\right)} \quad (2)$$

$$I_{os} = A_{750}/A_{900-700} \quad (3)$$

$$CH_3/CH_2 = 0.5 \times (A_{2955}/A_{2923}) \quad (4)$$

H_{al}/C_{al} in Eq. 2 is the atomic ratio of hydrogen to carbon for aliphatic groups, usually set to 2 [19].

The diagram displayed in Fig. 1 shows a large variation in the molecular characteristics of the solvents. The CT and AFCT solvents show high C_{ar} and H_{ar} aromaticities, the aromatic rings being rarely substituted (high I_{os} indexes). Petroleum-derived HGOCC solvent has least C_{ar} and H_{ar} aromaticities (0.61 and 0.31, respectively), the aromatic rings having high degree of substitution (I_{os} index of 0.28). HCST tar is characterized by relatively

low aromaticity, and the aromatic rings are highly substituted. In this series of samples, coal shows low hydrogen aromaticity ($H_{ar} = 0.26$), however, relatively high C_{ar} carbon aromaticity (0.71), the least I_{os} index indicates the aromatic rings to be highly substituted.

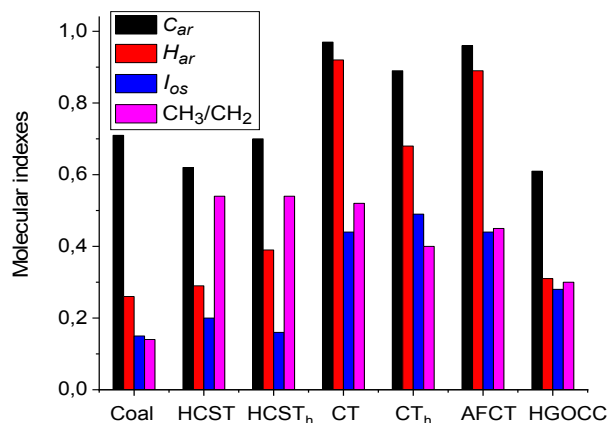


Fig. 1. The molecular IRFT indexes for coal and solvents.

Catalytic hydrotreating of CT significantly reduced C_{ar} and H_{ar} aromatic indexes and also CH_3/CH_2 ratio, probably, due to partial hydrogenation of the aromatic rings into hydroaromatic ones or/and into acyclic aliphatic hydrocarbons. The hydrotreated HCST_h solvent had a higher H_{ar} index compared to the parent one due to hydrogen substitution for phenolic hydroxyl.

3.3. 1H NMR spectra

Shown in Fig. 2 are the 1H NMR spectra of the CT, AFCT and HGOCC solvents, and the distribution of protons between different structural positions is shown in Table 1. The Brown-Ladner molecular characteristics [20] for the average molecule calculated based on the 1H NMR data and ultimate analysis data are also shown in Table 1.

A comparison of the data in Table 1 and Fig. 1 show the molecular indexes calculated from the IRFT and NMR spectra to be in good agreement.

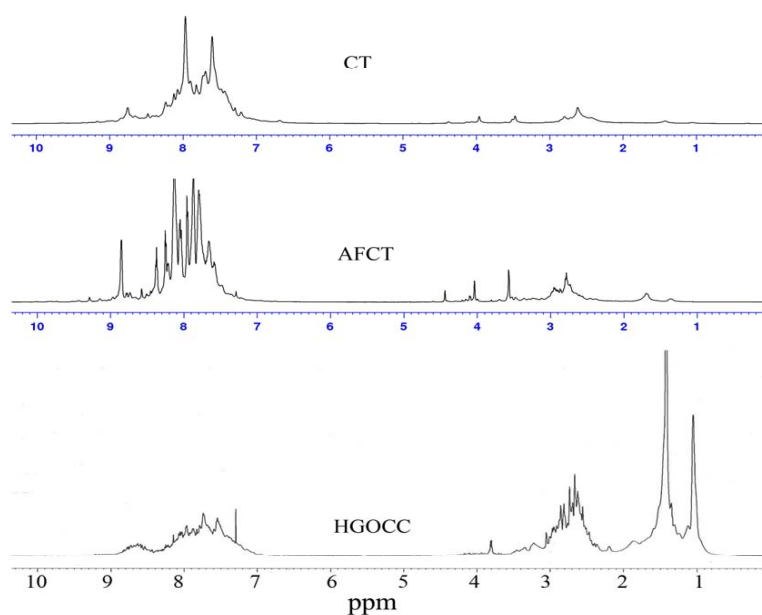


Fig. 2. The 1H NMR spectra of the CT, AFCT and HGOCC.

Table 1

The characterization of the solvents based on the 1H NMR spectra

Solvent	Hydrogen distribution					Structural parameters*			
	H_{ar}	H_o	H_α	H_β	H_γ	f_a	H_{aru}/C_{ar}	σ	n
CK	0.85	0.01	0.13	0.01	0.001	0.95	0.68	0.11	1.08
AFCT	0.83	0.01	0.14	0.02	0.001	0.94	0.74	0.15	1.15
HGOCC	0.28	0.004	0.29	0.34	0.09	0.60	0.79	0.35	2.46

* f_a – carbon aromaticity; σ – degree of aromatic ring substitution; n – average number of carbon atoms in the substituents; H_{aru}/C_{ar} – degree of the aromatic ring condensation.

Compared to CT and AFCT solvents, the HGOCC solvent was less aromatic, with aromatic rings being substituted with longer alkyl groups. Taking account of $H_{\text{aru}}/C_{\text{ar}}$ indexes, one can suppose the chloroform soluble molecules of the CT solvent to have nearly 3–4 condensed aromatic rings, AFCT – 2–3 rings, and HGOCC – 2 rings.

3.4. Coal dissolution

Coal dissolution at 380 °C with low volatile solvents occurred under autogenous pressure of near 2.5 MPa. The major digestive reaction product was coal extract representing dissolved coal in solvent + insoluble ash residue (ash content of near 2.0 wt.% based on extract). Under the conditions studied, the yields of gases were no more than 0.5%. They consisted of mainly CO_2 , the proportions of other gases depended on the solvent type, an enhanced proportion of the hydrocarbon gases (mostly methane) was observed with HGOCC and CT_h solvents. A small amount of H_2S was detected when CT and AFCT solvents were used.

The extracts obtained with CT, AFCT and binary blends with HGOCC represented pitch-like solid matter with softening points of 78 to 125 °C. The CT_h extract showed a lower softening point of 72 °C. Hard non-softening product was obtained with the parent HCST tar, and the product obtained with HCST_h showed plasticity with a softening point of near 104 °C. The extract produced with HGOCC represented viscous matter.

The distillation of the extracts yielded some amounts of liquid fractions (12.6–28.0%) with the boiling point up to 350 °C and 72.0–87.4% of pitch-like residues (Table 2).

The diagram in Fig. 3 shows the group composition and softening points of the extracts obtained with different solvents. The highly aromatic AFCT solvent provided the highest degree of coal

Table 2

The fractionation of the extracts into distillate fraction (before 350 °C) and nonvolatile pitch-like residue

Solvent used for coal dissolution	Yield, wt.%	
	distilled liquid	residue
Anthracene oil	27.5	72.5
Coal tar	16.0	84.0
Heavy gas oil	18.7	81.3
Coal tar + heavy gas oil	14.7	85.3
Heavy semicoking tar	12.6	87.4

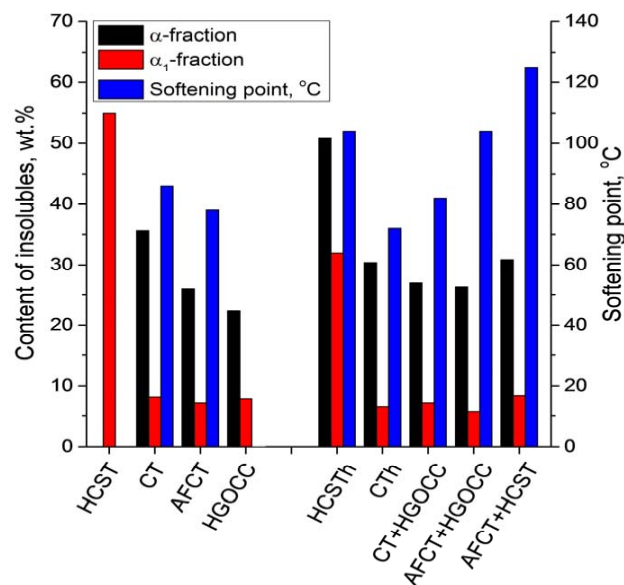


Fig. 3. The group composition and softening points of the extracts obtained on coal dissolution with different solvents.

conversion into quinoline-soluble substances, the content of the quinoline-insoluble α_1 -fraction was 7.1%, and toluene-insoluble α -fraction of 26%. The extract obtained with CT solvent contained slightly more α_1 -fraction (8.2%) and more α -fraction (35.6%). The HGOCC petroleum derived solvent proved to be as effective for coal dissolution as the highly aromatic CT solvent, the extract featuring the least toluene-insolubles (22.4%). Contrasted to this, coal dissolution in the HCST solvent did not occur at all. Moreover, the reaction product contained more α_1 -fraction (about 55%) than the initial coal-solvent slurry (33%), probably, because of regression reactions between the oxygen-containing groups in the coal and solvent. Hydrorefined HCST_h solvent showed specificity, although coal dissolution hardly occurred, however, the resulting product acquired plastic properties with the softening point of 104 °C.

The binary blends of CT + HGOCC and AFCT + HGOCC showed improved coal dissolution and product composition. The blending of HCST with the most effective AFCT (with 1:1 proportion) led to fairly high coal dissolution, the content of the quinoline insoluble α_1 -fraction decreased to 8.4%.

3.5. Characterization of chemical and molecular composition of the extracts

The CT and AFCT extracts had 5.4–5.5 wt.% of hydrogen, HGOCC extract had an enhanced hydrogen concentration (7.4%). The concentrations

of nitrogen, sulfur and oxygen were 0.6–1.3%, 0.8–1.3% and 0.8–2.7%, respectively, depending on the solvent used.

The IRFT spectra of the selected extracts are displayed in Fig. 4 as examples, and the molecular indexes estimated for all the extracts obtained are given in Fig. 5. The diagram shows that the composition of CT and AFCT extracts are represented by highly aromatic substances ($C_{ar} = 0.87$ – 0.90 and $H_{ar} = 0.71$ – 0.67), the aromatic rings having little substituents ($I_{os} = 0.44$ – 0.37). The HGOCC extract is less aromatic ($C_{ar} = 0.64$ and $H_{ar} = 0.31$), and the aromatic rings are highly substituted with fairly large alkyl substituents (CH_3/CH_2 ratio of 0.33). The extracts obtained with binary solvents show molecular indexes which are almost average compared to those obtained with each solvent separately.

3.6. The NMR spectra

Displayed in Table 3 are the Brown-Ladner molecular indexes for the chloroform solubles of three coal extracts obtained with different solvents. One can see that the average molecule of the chloroform solubles of the CT extract contains 4–5 rarely substituted condensed aromatic rings, and HGOCC extract does 3–4 rings with more substituents. The extract obtained with a blended solvent shows

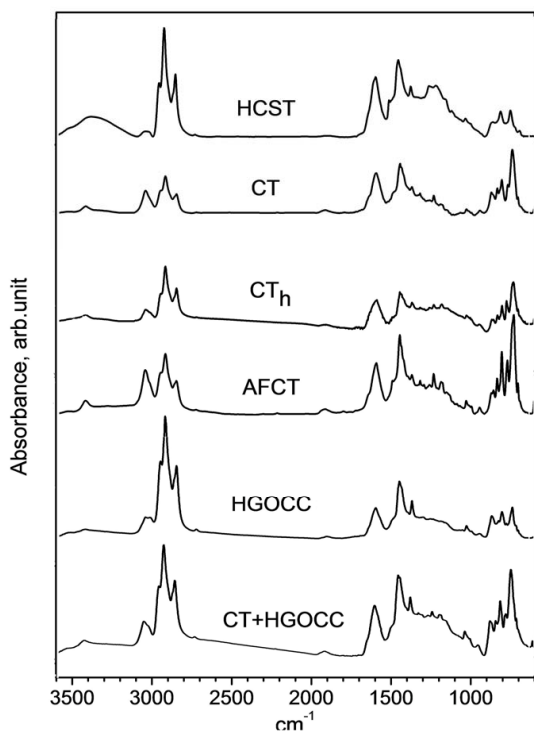


Fig. 4. The FTIR spectra for the extracts obtained in coal dissolution with the parent, hydrorefined, and blended solvents.

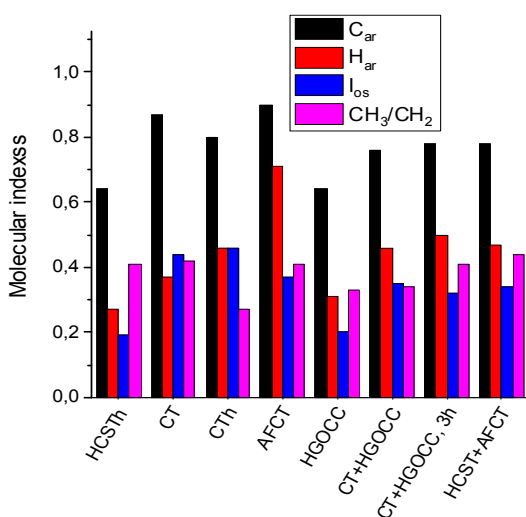


Fig. 5. The characterization of molecular composition of the extracts based on the IRFT spectra.

Table 3

Brown-Ladner indexes of the average molecules of the chloroform-solubles from the extracts obtained with different solvents

Solvent used	Structural parameters			
	f_a	H_{aru}/C_{ar}	σ	n
CT	0.87	0.62	0.17	1.75
HGOCC	0.64	0.68	0.37	2.57
CT+HGOCC	0.74	0.64	0.28	2.65

intermediate molecular indexes. Comparing the data in Tables 1 and 3, it should be noted that the extracts differed from the initial solvents with lower H_{aru}/C_{ar} indexes. This may indicate the aromatic molecules extracted from the coal matter to have highly condensed structure.

In total, the results on the characterization of the molecular structures of the chloroform solubles by 1H NMR spectra corroborate the IRFT characterization, and the NMR f_a carbon aromaticity coincides well with the respective IRFT C_{ar} aromaticity. This comparison is fairly correct since the chloroform-solubles were the major part of the whole extracts in all cases.

3.7. GC-MS analyses

Table 4 shows the GC-MS analyses data on the content of the main components in the hexane-soluble fractions (maltenes) derived from the extracts obtained with CT solvent and with CT + HGOCC blend. The composition of maltenes was dominated by polycyclic aromatic hydrocarbons. The main

Table 4
The chemical substances identified by the GC-MS in the maltene fractions of CT and CT + HGOCC extracts

#	Compounds	Mol. %	
		CT extract	CT + HGOCC extract
1	Indene and derivatives	7.4	12.3
2	Naphthalene and derivatives	0.9	2.2
3	Acenaphthene	5.1	4.3
4	Fluorene and derivatives	5.4	5.1
5	Anthracene and derivatives	12.7	12.2
6	Benz[a]anthracene	4.1	3.8
7	Phenanthrene and derivatives	5.2	8.4
8	Benzo[c]phenanthrene	2.6	2.0
9	Fluoranthene and derivatives	8.6	7.9
10	Benzo[k]fluoranthene	8.9	6.4
11	Pyrene and derivatives	11.5	8.8
12	Triphenylene	5.4	2.9
13	Perylene (5)	3.1	2.4
14	Carbazole	3.4	1.5
15	Dibenzofuran	3.2	2.5
16	Benzo[b]naphtho[2,1-d]thiophene	1.4	-
17	C ₁₆ -C ₂₆ alkanes	-	2.6

components of the CT maltenes were represented by anthracene, fluoranthene, pyrene and their derivatives, as well as indene. Compared to CT maltenes, the CT + HGOCC maltenes contained less polycondensed aromatic hydrocarbons such as fluoranthene, benzofluoranthene, pyrene, triphenylene derivatives, and an enhanced amount of indene and phenanthrene derivatives, also C₁₆-C₂₆ alkanes were observed. The heterocyclic substances were represented mainly by carbazole, dibenzofuran and benzo[b]naphtho[2,1-d]thiophene, CT maltenes had more concentration of these heterocyclic substances compared to CT + HGOCC maltenes.

3.8. Benzo(a)pyrene analysis

The diagram in Fig. 6 shows benzo(a)pyrene (BaP) content in the toluene-soluble fractions from the extracts obtained and in the initial solvents used. BaP contents in the solvents varied from

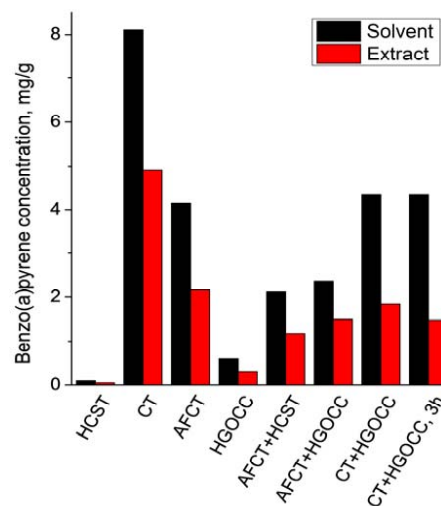


Fig. 6. Benzo(a)pyrene concentration (mg/g) in the toluene-soluble fractions of coal extracts and of solvents used.

8.1 (for CT) to 0.1 mg/g (for HCST). The extracts had much less BaP content compared to respective solvents, it decreased in the following order depending of the solvent used: CT >> AFCT > CT + HGOCC > AFCT + HGOCC ≈ CT + HGOCC (3 h) > AFCT + HCST >> HGOCC >> HCST. The extract obtained with HGOCC solvent showed little BaP concentration (0.29 mg/g). It is noteworthy that an increase in the duration of the dissolution reaction (from 1 to 3 h) led to a significant decrease in the concentration of BaP because of its conversion, this contrasted with the coal coking process which results in BaP generation.

4. Conclusions

The dissolution of bituminous coal at mild temperature was studied using a variety of commercially available coal- and petroleum-derived hydrocarbon fractions, hydrorefined derivatives and blends as solvents. The chemical and molecular composition of the coal, solvents, and extracts were characterized by chemical and group analyses, and by IRFT, ¹H NMR, GC-MS and liquid chromatography techniques.

Low volatile solvents like highly aromatic coal tar (CT), its anthracene fraction (AFCT), petroleum-derived solvent (HGOCC) and binary blends were found to exhibit high performance for coal dissolution at a mild temperature of 380 °C (the yield of quinoline solubles of 79–82%), the yields of gases being no more than 0.5%.

The extracts obtained with CT and AFCT solvents represented pitch-like matter with softening points of 78 °C to 86 °C. They consisted of rarely

substituted aromatic molecules with 4–5 condensed rings. HGOCC extract was much less aromatic, the aromatic rings being highly substituted with fairly large alkyl substituents.

The blended solvents yielded more extracts, and their molecular indexes were average between those obtained with each solvent separately.

The heavy coal semi-coking tar (HCST) exhibited no ability for coal dissolution due to the large number of phenolic hydroxyls, which contributed to regressive polycondensation reactions. However, partially hydrotreated HCST tar showed specificity, although coal dissolution still did not occur, the resulting product acquired plastic properties with the softening point of 104 °C. The HCST + AFCT blend showed a rather high efficiency for coal conversion into quinoline soluble pitch-like product.

A remarkable finding was that all the extracts obtained were characterized by significantly lower content of benzo(a)pyrene (BaP) compared to solvents used. An increase in the duration of the dissolution reaction resulted in a significant decrease in the concentration of BaP because of its conversion, this contrasted with the coal coking process which results in BaP generation.

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