Solvolytic conversion of softening bituminous coal at 380 °C in solvents derived from the commercial hydrocarbon byproducts and residues from coal and petroleum processing was studied. Hydrogen-donor tetrahydronaphthalene (THN) and non-donor 1-methylnaphthalene (MN) were also used for comparison. The high-boiling solvents of different chemical classes (highly aromatic coal tar, its anthracene fraction, and low-aromatic heavy gas oil of catalytic cracking of the oil residue) and the H-donor THN solvent were found to exhibit high efficiency for coal conversion into quinoline-soluble products. The chemical and molecular compositions of coal, solvents, and dissolved products were characterized in detail by different techniques, including chemical analysis, group analysis, infrared Fourier transform (IRFT) spectroscopy, X-ray diffraction (XRD), liquid chromatography, and thermal analysis to reveal the chemical transformations of the coal–solvent mixture during the dissolution reaction. The solvolytic conversion of coal in the liquid phase of both highly aromatic and low-aromatic solvents was found to involve selective depolymerization of polymer-like coal via breaking of weak linkages between the aromatic units, resulting in the formation of soluble pitchlike products. The effective dissolution of coal in the H-donor THN solvent resulted probably from a combination of the nonselective thermal fragmentation of the coal structure to smaller radical intermediates and their stabilization by hydrogen from THN, producing mainly tar and a few gases. The low-boiling solvents of both predominantly aromatic and aliphatic classes (gas oils from naphtha pyrolysis and delayed coking of the petroleum residue) and MN exhibited poor efficiency for coal dissolution. The concentrations of carcinogenic benzo(a)pyrene (BaP) in the solvents used and in the toluene fractions of the resulting extracts were analyzed. The remarkable result was that coal extracts, compared to solvents, contained much less BaP, probably due to its conversion with coal and/or solvent molecules during coal dissolution.

I. INTRODUCTION
The production of advanced carbon materials and composites is largely based on the use of monocyclic and polycyclic aromatic compounds. The need in the polycyclic aromatics is provided mainly (near 95%) by coal tar, most high-tech carbon materials and composites are produced from its nonvolatile fraction—coal-tar pitch.1,2 Coal tar is a minor byproduct during the production of metallurgical coke, which is an indispensable material in the blast furnace (BF) for iron and steel manufacturing.3,4 In the long term, large-scale switch to competing alternative ironmaking technologies without coke will lead to a dramatic decrease in the demand for metallurgical coke and, consequently, a decrease in the production volume of coal tar and coal-tar pitch. At the same time, the needs for coal tar and coal-tar pitch are steadily increasing in the manufacturing of advanced carbon materials for different applications.5

The opposite trends in the production and consumption of coal tar make it imperative to develop sustainable alternatives for producing aromatic chemicals for the progressively developing carbon industry. The need to solve this challenge is reasoned also by a significant drawback of the commercial coal-tar pitches because of the high content of carcinogenic substances, which are generated under high-temperature coal coking.

Coal processing in the solvent medium, instead of high-temperature coking, can be the best promising alternative for the production of aromatic substitutes for coal tar products. The studies on coal liquefaction have been extensively carried out since the 1970–1980s, and the data accumulated were reviewed in several recent papers.6,7,8 These studies are carried out usually under high hydrogen pressure at temperatures of 420–460 °C and traditionally targeted to produce liquid motor fuels as petroleum substitutes. A large variety of
We studied the thermal dissolution of coals in anthracene oil under mild conditions. The highest yield of the dissolved products was obtained from medium-ranked bituminous coals at 350–380 °C. From the coal extracts obtained, pitch samples were derived. Their chemical composition, molecular and structural characteristics, and empirical properties were compared with those for the commercial coal- and petroleum-derived pitches. It was found that, in terms of the chemical composition and empirical properties, the extractive pitches resembled the commercial pitch sample derived from the blended mixture of coal tar and petroleum feedstock.

Currently, several promising processes for coal dissolution 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 at 350–400 °C in the recyclic aromatic solvent medium. HyperCoal with a low ash content (near 0.04%) can be used as an environmentally friendly fuel for a gas turbine, as an additive in cokemaking, and as a feedstock for manufacturing carbon materials. The coal dissolution process in the United States is targeted to produce pitchlike products that can be used as a binder and a source in the manufacturing of high-grade coke for anode production and also for the synthesis of carbon fibers and other carbon materials. The bench-scale tests have demonstrated the dissolution of bituminous coals (Cdaf of 78–84%) at 400 °C to attain 85%. The process uses anthracene oil as a recycle solvent. 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. If all of the solvent was recovered, the softening point of the resultant product would be too high for the purposes for which it is intended and it would polymerize rapidly.

The dissolution of coal with commercial hydrocarbon residues, from economic considerations, is a promising way because it allows the coprocessing of residues with coal into a valuable product, in addition to significant savings in solvent regeneration. The goal of this paper is to investigate the effect of different available commercial hydrocarbon byproducts and residues from coal and petroleum processing as solvents on the efficiency of bituminous coal dissolution under mild conditions. Tetrahydroanthracene and 1-methylnaphthalene were also used as typical hydrogen-donor and nondonor solvents for comparison. The chemical and molecular compositions as well as the content of carcinogenic benzo(a)-pyrene in the extracts obtained depending on the solvents used were characterized by various techniques.

2. EXPERIMENTAL SECTION

2.1. Coal and Solvents Used. The dissolution experiments were conducted using a 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.

A suite of different coal-derived and petroleum-derived commercial hydrocarbon fractions was chosen for coal dissolution: HCST, heavy coal semicoking tar (provided by Leninsk-Kuznetsk Semicoking Plant); CT, coal tar (Altai-Coke Joint-Stock Company); AFCT, anthracene fraction of coal tar (Coke Joint-Stock Company); HGOC, petroleum-derived feedstock for the production of carbon black (it consisted largely of heavy gas oil from the catalytic cracking of petroleum residues); LGOP, light gas oil from the naphtha pyrolysis...
Table 1. Characterization of Coal and Solvents Used

| element composition (wt %) | C     | H     | N + S + O | H/C atom % | distillation temperature range (°C) | density (g/cm³) |
|---------------------------|-------|-------|-----------|------------|-------------------------------------|-----------------|
| coal                      | 84.7  | 5.5   | 9.8       | 0.78       | 400–600°                            | 1.05            |
| HCST                      | 83.7  | 8.1   | 9.2       | 1.16       | 160–420                             | 1.05            |
| CT                        | 91.5  | 5.3   | 3.2       | 0.69       | 180–550                             | 1.20            |
| AFCT                      | 87.6  | 5.2   | 7.2       | 0.71       | 170–350                             | 1.10            |
| HGOCO                     | 89.9  | 8.3   | 1.8       | 1.11       | 221–508                             | 1.04            |
| LGOP                      | 90.7  | 7.9   | 1.4       | 1.04       | 190–330                             | 1.05            |
| LGODC                     | 89.2  | 8.7   | 2.1       | 1.17       | 240–340                             | 1.11            |
| THN                       | 90.9  | 9.1   |           | 1.20       | 207                                  | 0.97            |
| MN                        | 92.9  | 7.1   |           | 0.92       | 245                                  | 1.02            |

“Determined by the differential scanning calorimetry (DSC) method.

(OMsk petroleum refining Plant, Gas-Prom-Neft Company); and LGODC, light gas oil from the delayed coking of petroleum residue (demonstration unit). Also, H-donor tetraydroanaphthalene (THN) and nondonor 1-methylanaphthalene (MN) of reagent-grade quality were used as reference solvents for comparison.

2.2. Reactor Unit and Dissolution Procedure. The coal dissolution process was carried out following previously optimized conditions using an experimental unit equipped with a 2 L stainless steel autoclave dissolver with a mechanical stirrer (speed 150 rpm). 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 the solvent of 1:2 by weight. The autoclave mixture was heated and allowed to react at 380 °C for a 60 min residence time at autogenous pressure (usually 1.5–2.0 MPa) while continuous stirring. The use of the stirrer provided an effective mass transfer; improved contact between the three-phase reaction mixture of gas, liquid, and solid; and thus gradient-less conditions in terms of temperature and concentration of the reagents. These experimental conditions were especially important to prevent caking when coal softened.

Upon reaction completion, the autoclave was allowed to cool to 250 °C and the vapor-gas products were vented through a refrigerator line where the gases and condensed liquids 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 that consisted of dissolved coal in a solvent + ash coal residue), condensed liquids (termed as naphtha), and gas volume were measured. The mass balance calculated by the weight of coal extract + naphtha + gases was more than 97.5%; the loss accounted for no more than 2.5%.

A representative extract portion of about 20 g was thoroughly dispersed, and 2 g of sample was taken for solubility analysis. Soxhlet extraction was used to determine the toluene-soluble fraction. The toluene-insoluble residue was dried under vacuum at 80 °C, weighed, and then further extracted with hot quinoline until the solution became clear. The quinoline-insoluble residue was washed with toluene, dried under vacuum at 80 °C, and weighed. The analysis was repeated two to three times to confirm the reproducibility. Also, the coal extracts were subjected to control extraction directly with hot quinoline. The data obtained were in good agreement with those resulting from the successive extractions with toluene and quinoline; the average values were used. Coal conversion was determined based on the ash content in the initial coal sample ($A_d^i$) and in the quinoline-insoluble residue ($A_d^f$) using the following equation:

\[
\text{conversion\%} = \frac{1 - A_d^f/A_d^i}{1 - A_d^i/100} \times 100
\]

Coal dissolution experiments were repeated two to three times, and the variations in the conversion of coal were within 2%.

The selected solvents (CT, AFCT, and HGOCO) were exposed to an autoclave treatment at 380 °C for 1 h to check their thermal stability under the dissolution conditions without coal.

2.3. Characterization of Coal, Solvents, and Extracts Obtained. Elemental analysis of coal, solvents, and extract products was performed using a FLASH 1112 elemental analyzer. The gaseous products were analyzed by gas chromatography.

The benzo(a)pyrene (BaP) concentration in the toluene-soluble fractions of the coal extracts was measured using a Shimadzu LC20 high-performance liquid chromatograph. A dispersed extract sample (0.1 g) and 50 mL of toluene were loaded into a flask and refluxed for 30 min. The solution was filtered through a paper filter; the filter cake was washed with small portions of hot toluene. A 1 mL aliquot was taken and evaporated at 40 °C. The residue was dissolved with acetonitrile. Chromatography conditions are as follows: capillary column with a C18 reverse-phase sorbent, diode array detector, and a flow rate of the acetonitrile–water mixture of 1 mL/min. The standard BaP solutions were used for calibration.

Thermal behavior of coal was studied using a Netzsch Jupiter STA 449F1 synchronous analyzer. The coal sample (15 mg) in a corundum crucible was heated (10 °C/min) in an argon atmosphere up to 900 °C. The volatility of the solvents was characterized by the temperature range of boiling on distillation.

The spatial structure of the organic matter of coal was characterized based on the X-ray diffraction (XRD) pattern, which was recorded using a PANalytical X’Pert PRO diffractometer with Cu Kα radiation and step scanning ($2\theta = 0.2°$, 25 s/step) at $2\theta$ from 5 to 55°. The XRD peaks were deconvoluted using a data-processing program assuming the Gaussian shape of bands. The parameters of the structure of organic coal matter were estimated from the (002) and (100) reflections, which were corrected with absorption, polarization,
and atomic scattering factors according to the recommendations described in refs 23, 24.

Fourier transform infrared spectroscopy was used to characterize the molecular groups in the structure of coal, solvents, and products. The samples were prepared in the form of KBr pellets. The finely dispersed sample and KBr were thoroughly mixed (the proportion weight of KBr to the sample was 100:1) and pressed into a KBr pellet. Two to three pellets were prepared for measurements, with the final IRFT spectrum being the average to minimize the effects of any differences in grinding or weight between pellets. The spectra were recorded on a Bruker Tensor-27 IRFT spectrometer for a spectral range from 4000 to 400 cm\(^{-1}\). The specific spectral regions were subjected to curve-fitting analysis, according to the recommendations in refs 25–28. The softening point of the pitchlike extracts produced was determined using a “ring and ball” method.

3. RESULTS

3.1. Coal Characterization. The petrographic composition of coal 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 of coal is presented in Table 1. The contents of the volatile matter and ash were 37.8 and 5.6%, respectively. Thermal analysis of coal showed that the main stage of the pyrolysis of organic matter occurs at the temperature range between 400 and 600 °C (Table 1).

Figure 1 shows a fragment of the XRD pattern for coal in the 2\(\theta\) range from 7 to 34°. The asymmetric reflection centered at about 25° was deconvoluted into three Gaussians assigned to a relatively ordered graphitelike component (C\(_{\text{ggld}}\)) (reflection maximum at 2\(\theta\) = 25°) and to less ordered \(\gamma\)-components (maxima at 2\(\theta\) of 17 and 9°). The graphitelike component is considered usually as a stack of planar polyaromatic molecules. Less ordered \(\gamma\)-components can involve mainly aliphatic fragments including naphthene, alkane, and oxygen-containing groups spatially structured at the periphery of graphitelike stacks.

The XRD pattern shows the structure of the organic coal matter to contain largely \(\gamma\)-components (59%) and less proportion of the graphitelike component (41%). The average polyaromatic stack consisted of 4.4 layers with an interlayer spacing of 3.6 Å. The diameter of the aromatic layer was about 19 Å. The proportion of the graphitelike component in the structure of coal is considered to reflect the degree of coal aromaticity. So, the aromaticity of coal estimated from the XRD pattern is 0.41.

3.2. Solvent Characterization. 3.2.1. Proximate and Ultimate Analyses. The commercial solvents differed significantly in the chemical composition and boiling temperature (Table 1). The petroleum-derived LGODC and HGCC solvents were most enriched with hydrogen. The coal-derived HCST solvent was enriched with hydrogen and oxygen. The volatility of the solvents in terms of the distillation temperature range decreased in the following order: THN > MN > LGOP ≥ LGODC > AFCT ≥ HCST > CT > HGCOCC.

3.2.2. IRFT Data Analysis. Figure 2 shows the IRFT spectra for coal and different solvents. The assignments of the spectral bands were performed according to the recommendations in refs 25–28. All of the solvents show absorbance between 2750 and 3000 cm\(^{-1}\) (stretching vibration of the aliphatic C–H bonds in the CH\(_2\), CH\(_3\), and CH groups), at 1440–1460 cm\(^{-1}\) (bending vibration of CH\(_2\) groups), and at 1376 cm\(^{-1}\) (bending vibration of CH\(_3\)). The petroleum-derived solvents show the highest absorbances at these regions, indicating the highest contents of the aliphatic structures as compared to coal-derived solvents. The bands centered at 3050 cm\(^{-1}\) (stretching vibration of the aromatic C\(-\)H bonds), 1600 cm\(^{-1}\) (stretching vibration of the aromatic rings), and between 900 and 700 cm\(^{-1}\) (out-of-plane bending of aromatic C\(-\)H bonds) are characteristic of the aromatic structures. A shoulder peak at 1650 cm\(^{-1}\) in the spectra for coal-derived HCST, CT, and AFCT solvents indicates a few carbonyls. The broad absorbances centered at 3380 and 1250 cm\(^{-1}\) in the spectrum for HCST indicate a high concentration of hydrogen-bonded phenolic compounds. A weak peak centered at 3430 cm\(^{-1}\) in the spectra for CT and AFCT solvents can be attributed to both hydroxyls and nitrogen-bearing heterocyclic compounds such as carbazole. The spectra for the petroleum-derived solvents show little or no oxygen- and nitrogen-bearing groups.

The IRFT spectra for the thermally treated CT, AFCT, and HGCOCC solvents did not show noticeable changes, i.e., these solvents were fairly thermally stable at the temperature of 380 °C.

The spectrum for coal shows the highest absorbance at 3380 and at 1600 cm\(^{-1}\) but very weak absorbance at 3050 cm\(^{-1}\). The high absorbance in the range of 1300–950 cm\(^{-1}\) centered at about 1040 cm\(^{-1}\) is poorly specific and difficult to assign.
Silicon- and aluminum-containing minerals can also contribute to the absorbance in this region.

The absorbances at 3000−2750, 3100−3000, and 900−700 cm$^{-1}$ were deconvoluted according to the recommendations in refs 25−28 to characterize semi-quantitatively the molecular composition of coal, solvents, and coal-derived products. The spectral profile between 900 and 700 cm$^{-1}$ is sensitive to the extent of aromatic ring substitution, high absorbance at a low frequency of 750 cm$^{-1}$, indicating the preponderance of rarely substituted aromatic rings. The band at about 1600 cm$^{-1}$ can hardly be used to characterize carbon aromaticity because its absorbance is known$^{25}$ to depend on the number and type of the aromatic ring substituents, the oxygen-containing groups, resulting in increased absorbance.

The representative deconvoluted spectra are shown in Figure 3. The spectra for CT and AFCT solvents show the strongest peaks at 750 cm$^{-1}$, which reflect low substituted aromatic rings with four adjacent C−H bonds, i.e., ortho-substituted rings. The relatively strong peaks at 878 cm$^{-1}$ in the spectra for coal and HCST and HGOCO solvents indicate highly substituted aromatic rings with a lone C−H bond. The other peaks at 843, 814, and 783 cm$^{-1}$ can be assigned to two to three adjacent C−H bonds in the aromatic rings.

In the spectra for the petroleum-derived solvents, small peaks at 700 and at 725 cm$^{-1}$ are also observed, besides the peaks noted above. The weak peak at 700 cm$^{-1}$ indicates the least substituted aromatic rings with five adjacent C−H bonds, i.e., monocyclic benzene rings. The peak at 725 cm$^{-1}$ can be referred to the rocking modes of CH$_2$ groups in the long aliphatic chains, rather than to the aromatic C−H out-of-plane bending. The spectrum for LGOP features the strongest absorbance at 784 cm$^{-1}$. A reasonable explanation of this spectral feature can be as follows: this band is a composite that has contributions both from the aromatic out-of-plane bending of three (or two) adjacent C−H bonds and from the aliphatic rocking modes for two adjacent CH$_3$ units.

The following semiquantitative indexes for the molecular characteristics of the solvents and coal itself were evaluated from the deconvoluted spectra: the $H_{ar}$ index for hydrogen aromaticity, i.e., the proportion of the aromatic C−H bonds to total amount of aromatic and aliphatic C−H bonds; the $I_{ort}$ index for ortho-substitution of the aromatic ring; and the CH$_3$/CH$_2$ ratio in the aliphatic structures. The $H_{ar}$ index was assessed from the absorbances between 3100 and 3000 cm$^{-1}$ ($A_{H_{ar}}$) and 3000 and 2750 cm$^{-1}$ ($A_{Hal}$). The degree of the ortho-substitution $I_{ort}$ was assessed from the ratio of the absorbance at 750 cm$^{-1}$ ($A_{750}$) to the total absorbance in the range of 900−700 cm$^{-1}$ ($A_{900−700}$). The CH$_3$/CH$_2$ ratio was determined from the absorbances at 2955 cm$^{-1}$ (assigned to asymmetric stretching in CH$_3$) and 2923 cm$^{-1}$ (assigned to asymmetric stretching in CH$_2$).

In assessing these indexes, we took account of the statistical data$^{25,26,28}$ 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$_3$ groups and CH$_2$ groups is 0.5. The indexes were calculated using the following formulas

$$H_{ar} = \frac{A_{H_{ar}}/0.2A_{Hal}}{1 + (A_{H_{ar}}/0.2A_{Hal})} \quad (2)$$

$$I_{ort} = A_{750}/A_{900−700} \quad (3)$$

The Brown−Ladner $f_a$ index for carbon aromaticity was also estimated according to ref 29 using the elemental analysis data and $H_{Hal}/H_{ar}$ ratios derived from the IRFT spectra.

One can see from Table 2 that CT and its AFCT fraction are highly aromatic in terms of both $f_a$ and $H_{ar}$ indexes (0.97−0.96 and 0.92−0.89, respectively). Their $I_{ort}$ indexes of 0.44−0.49 indicate that the aromatic clusters are rarely substituted. On
the other hand, petroleum-derived HGOCC and LGODC solvents show the least $f_a$ and $H_a$ indexes (0.58–0.61 and 0.26–0.31, respectively) and low $I_{ort}$ indexes (0.24–0.28), indicating the low aromaticity and high degree of the aromatic ring substitution. LGOP solvent differs by fairly high aromaticity, and the aliphatic structures are represented predominantly by CH$_3$ groups. The molecular indexes for THN and MN (calculated based on the molecular formulas) are 0.60 and 0.91 for $f_a$ and 0.33 and 0.70 for $I_{ort}$, respectively.

Coal itself shows low $H_a$, hydrogen aromaticity (0.26) but relatively high $f_a$ carbon aromaticity (0.71). The lowest $I_{ort}$ index indicates that the aromatic rings in coal are highly substituted. It should be noted that the Brown–Ladner aromaticity $f_a$ of coal (0.71) differs significantly from that (0.41) estimated from the XRD pattern. This may imply that only part of the aromatic carbon atoms was in the polyaromatic stacks. The remaining aromatic carbon atoms, possibly, in the low-condensed and/or highly substituted aromatic molecules could be structured with the less ordered $\gamma$-component. From the comparison of the aromaticity estimated from the XRD with $f_a$ aromaticity, it might be said about 60% of all of the aromatic carbon atoms occur in the graphitelike polyaromatic stacks.

### 3.3. Coal Dissolution

The process of coal dissolution in most solvents occurred under an autogenous pressure of about 2 MPa. In the case of the low-boiling THN solvent, the pressure increased to 3.7 MPa.

The ranking of the solvents according to their efficiency for coal conversion is shown graphically in Figure 4. Of all of the solvents used, highly aromatic AFCT showed the highest dissolving efficiency and the LGODC solvent with a predominantly aliphatic nature was least effective.

Coal dissolution in the HCST solvent did not occur at all; even more quinoline-insoluble substances, than in the initial coal–solvent mixture, were found in the reaction product. This may result from the high concentration of oxygen-containing substances both in the HCST solvent and coal, which may play a major role in the regression reactions leading to insoluble matter. Thus, coal semicoking tar itself is hardly suitable for coal dissolution.

Coal dissolution in all of the solvents generated only little naphtha and gases (Table 3). The gaseous products consisted mainly of CO$_2$ (only little CO). The proportions of other gases depended on the solvent type: an enhanced proportion of hydrocarbon gases (mostly methane) was obtained with the petroleum-derived solvents, and more H$_2$S did with CT and AFCT solvents.

The extracts obtained with CT, AFCT, HGOCC, and LGODC solvents represented the typical pitchlike matter with the softening points at 80–127 °C (Table 4). The ash content in the extracts was about 2%. The extracts obtained with light LGODC, THN, and MN solvents represented uniform viscohomogeneous matter when removed from the receiver; however, they showed heterogeneity when heated. Hard and almost nonsoftening products were obtained using HCST as the solvent.

Table 4 presents the group composition of the extracts depending on the solvent used. The content of the quinoline-insoluble $\alpha_i$-fraction in the extracts obtained with CT, AFCT, and HGOCC solvents decreased to 7.1–8.2% (from 33% before reaction), and the contents of the toluene-insoluble $\alpha$-fraction varies in the range 22.4–35.6%. An increase in the reaction time from 1 to 1.5 h further decreased the content of
the $\alpha$-fraction to 5.2%. The extracts obtained with LGOP and LGODC petroleum-derived solvents and with MN had an increased amount of the insoluble $\alpha$-fraction (15–21%).

The data in Tables 5 and 6 and Figure 5 show significant variations in the chemical composition of the extracts obtained depending on the solvent used. One can see from Figure 5 and Table 6 that the extracts obtained with CT and AFCT solvents are represented largely by the aromatic substances ($f_a = 0.87–0.90$ and $H_{ar} = 0.71–0.67$), the aromatic rings being rarely substituted (mostly ortho-substituted, $I_{tot} = 0.37–0.44$, Table 6). The extracts obtained with the petroleum-derived solvents are less aromatic ($f_a = 0.64–0.81$ and $H_{ar} = 0.31–0.65$), the aromatic rings being highly substituted ($I_{tot} = 0.17–0.23$). The product obtained with HCST differs with a high concentration of phenolic hydroxyls and other oxygen-containing groups (absorbance at 3380 and 1000–1300 cm$^{-1}$).

Shown in parentheses in Table 6 are also molecular indexes, which were calculated based on the additive contributions from the indexes for coal and the respective solvents (i.e., for the coal + solvent mixture before the reaction) to reveal the chemical transformations occurring in the coal + solvent mixture during the reaction. One can see that the calculated and experimental $f_a$ and $H_{ar}$ indexes for the extracts obtained with the effective CT, AFCT, and HGOCC solvents practically coincide. However, the calculated and experimental indexes differ significantly for the products obtained with both the effective THN and much less effective for those obtained with petroleum-derived solvents.

The data in Table 7 show the BaP concentrations in coal, solvents used, and toluene-soluble fractions of the coal extracts.

![Figure 5. IRFT spectra for the extracts obtained from coal dissolution in different solvents.](image)

4. DISCUSSION

Coal is considered conventionally as a polymer-like solid with a heterogeneous composition and an irregular structure of the predominantly aromatic carbon matter. Its aromatic units are associated each other by various cross-links, mostly by ether and short methylene linkages, as well as by multiple intermolecular interactions. It is important to note that the strength of the methylene and ether linkages has been shown to depend greatly on the structure and size of the aromatic units bonded; an increase in size results in a dramatic weakening of the linkages.

X-ray diffraction data for coal used showed that only 41% of carbon matter accounts for graphitelike components represented by the ordered polyaromatic clusters. The most part occurred in the poorly ordered and more accessible $\gamma$-component. In addition, a remarkable property of the coal used is that it became plastic at a relatively low temperature of 340–360 °C (just below the reaction temperature).
The data obtained show the yield of the dissolved product to be a complicated function of the solvent used. The efficiency of solvents can be discussed in terms of chemical compositions. In this respect, it should be noted that CT, AFCT, HGOC, and THN are all among the solvents that are most effective for coal conversion; however, they represent different chemical classes: CT and AFCT solvents are highly aromatic, HGOC differs by low aromaticity, and THN is a hydroaromatic H-donor. It is an interesting issue of how these solvents with quite different chemical properties provided a high degree of coal dissolution.

The process of coal dissolution is conventionally considered to proceed via multiple stages. The primary reactions involving the thermolysis of weak bonds generate smaller radical intermediates, which, depending on the reaction conditions, can undergo two kinds of secondary reactions: stabilization to produce substances with lower molecular weights and retrogressive recombination of the fragments and residuals to produce “char”. The high efficiency of THN is clearly due to its active hydrogen atoms capable of stabilizing the reactive radical species and suppressing their regressive (or recombination) reactions. This contributed to the increased yield of soluble products; the THN solvent itself is converted into a dehydrogenated derivate.

The dissolving efficiency of highly aromatic CT and AFCT may be due to their suitable polyfunctional composition consisting of molecules with active hydrogen donation, hydrogen shuttling, and solvating abilities. For example, the AFCT solvent contained 20–25% phenanthrene, 5–6% anthracene, 4–6% pyrene, 5–6%acenaphthene, 2–3% fluorene, 5–6% carbazole, and 0.5% quinoline. Acenaphthene and fluorene molecules have reactive hydrogen atoms located at the α-position of aromatic rings. They can serve as a source of hydrogen for radical stabilization. Polycondensed aromatic hydrocarbons, like pyrene, phenanthrene, and anthracene, are capable to play a role of active shuttling agents to transfer hydrogen from the hydrogen-rich species (both from some solvent molecules and some entities in the coal) to radical species. In addition, the heterocyclic nitrogen-containing compounds, such as carbazole, acridine, quinoline, and oxygen-containing naphthol derivatives, exhibit the solvating ability to dissolve the reaction products.

In this regard, it is rather surprising that the petroleum-derived HGOC solvent of relatively low-aromatic nature proved to be equally effective like the solvents having hydrogen-donating and hydrogen shuttling and solvating abilities. This result may imply that there were some kinds of key parameters of this reaction system, other than discussed above, which affected the performance for coal dissolution. A reasonable explanation may be related to the low volatility of the HGOC solvent, as well as to the ability of coal to pass into a plastic state at a temperature below the temperature of the dissolution reaction. Under the reaction conditions, the distribution of solvent components between the vapor and liquid phases can strongly affect the degree by which they can contact the softened and fusible coal matter. Liquid-phase solvents can contribute to the physical dispersion of the softened coal particles and plastic matter strongly, improving their contacts with the solvent molecules. It is known that many of the chemical moieties present in the bituminous coal matter behave as effective hydrogen donors, which can contribute to radical stabilization. One can suggest that the effective dispersion of the softened coal matter in the liquid-phase solvent prevented the sintering and other regression reactions, and, on the other hand, facilitated the availability of the H-donor moieties to the thermally generated radical species. In this case, polycondensed aromatic molecules present in both the plastic coal matter and the solvent can play the role of shuttle agents for hydrogen transfer from the hydrogen-reach moieties to radical species. The beneficial effect of coal softening on dissolution was reported earlier in ref 16.

On the other hand, all of the highly volatile solvents, like LGOP and MN (of mostly aromatic nature) and LGODC (of mostly aliphatic nature), having no hydrogen-donating activity showed low efficiency for coal dissolution. Under the reaction conditions, these solvents were mostly in the vapor phase so that they had limited contact with the coal matter. As a result, the competing radical recombination and polycoupling reactions led to the formation of charlike matter.

As stated, \( f_p \) and \( H_{\infty} \) molecular indexes reflect the structure of the basic aromatic units. It was found that for the extracts obtained with the effective CT, AFCT, and HGOC solvents, they proved to almost fit those calculated for the solvent + coal mixtures before the reaction. Note that, under these conditions, nearly 80% of the organic coal matter was converted into soluble substances. It seems to be very likely that these solvents differing in chemical properties had, however, a common specific effect together with a mild thermal effect on those coal constituents that had some aliphatic bridges in the polymer-like aromatic coal matter. When considered in conjunction with a few yields of naphtha and gaseous products and the rather mild reaction temperatures, we have every reason to suggest that coal dissolution in the solvents above occurred largely through depolymerization via weakest linkages (ether or/and methylene links) between the polycondensed aromatic units in the polymer-like matter. In these instances, the main structural features of the aromatic units in the dissolved substances remained unaltered. Only a moderate decrease in the aromatic ring substitution and an increase in the CH₃ proportion in the aliphatic groups are observed compared to indexes for the mixtures before the reaction. The latter feature could result from the splitting of the β-methylene or/and ether bonds at the aromatic rings, the methyl groups produced were remained at the aromatic rings.

The molecular indexes for the products obtained with low-boiling solvents (with both the effective THN and much less effective aromatic LGOP and aliphatic LGODC petroleum-derived solvents) are significantly different from the calculated ones. This fact seems to indicate the mechanism of coal dissolution other than described above. It can be assumed that under these solvents, the coal conversion process involved nonselective thermal fragmentation of the coal macromolecular structure producing a variety of reactive radical species. The hydrogen-donor THN solvent played an important role at this stage, blocking radical fragments and preventing their regression and recombination reactions. However, in the presence of light MN and petroleum-derived solvents, which exhibited practically no H-donor abilities and were predominantly in a vapor phase, the regressive reactions of the radicals could occur to a large extent, inhibiting coal conversion into dissolved products.

The content of the carcinogenic BaP in the toluene-soluble fractions of the extracts obtained was found to depend on its content in the solvent used, with the highest concentration being detected in the extract obtained with the CT solvent.
However, a remarkable result is that the BaP concentrations in all of the samples were significantly less than those in the solvents used. The latter may imply that some kind of chemical reactions involving BaP conversion occurred on coal dissolution, thus reducing BaP concentration in the extracts obtained.

5. CONCLUSIONS

The solvolysis of the softening bituminous coal at 380 °C in different solvents derived from the commercial hydrocarbon byproducts and residues from the coal and petroleum processing, in H-donor tetrahydrophenanthrene, and in non-donor 1-methylnaphthalene depending on the solvent properties was studied.

The high-boiling solvents of different chemical classes (highly aromatic coal tar and its anthracene fraction, and low-aromatic gas oil from the catalytic cracking of the oil residue) and the H-donor THN solvent were found to exhibit high efficiency for coal conversion into quinoline-soluble products. Based on the analyses of the molecular composition of the coal—solvent reaction mixture before and after dissolution, the conclusion concerning the reaction scheme was drawn that coal solvolysis in the liquid phase of both highly aromatic and low-aromatic solvents involved the selective depolymerization of polymer-like coal matter via breaking of weak linkages between the aromatic units, resulting in the generation of quinoline-soluble pitchlike products. Coal softening in the liquid-phase solvent medium can have a beneficial effect on the dissolution reaction.

The effective dissolution of coal in the highly volatile H-donor THN solvent resulted probably from a combination of the nonselective thermal fragmentation of the coal structure to smaller radical intermediates and their stabilization by hydrogen from THN to produce tar and a few gases.

The volatile solvents of both predominantly aromatic and aliphatic classes (gas oils from naphtha pyrolysis and delayed coking of the petroleum residue) and 1-methylnaphthalene exhibited poor efficiency for coal dissolution.

Coal extracts obtained, compared to the respective solvents used, contained much less benzo(a)pyrene, probably due to its conversion with coal and/or solvent molecules during coal dissolution.

Notes

The authors declare no competing financial interest.

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