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Characterization of Sulfur Functionalities of Supercritical Extracts from Coals of Different Rank, Using Reductive Pyrolysis

Grażyna Gryglewicz,^{*,†} Piotr Rutkowski,[†] and Jan Yperman[‡]

*Institute of Chemistry and Technology of Petroleum and Coal,
Wrocław University of Technology, ul. Gdańska 7/9, 50-344 Wrocław, Poland, and
Laboratory of Applied Chemistry, CMK, Limburgs Universitair Centrum,
B-3590 Diepenbeek, Belgium*

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The extracts obtained via supercritical fluid extraction (SFE) from three Polish coals of different rank, using toluene, toluene/2-propanol, and toluene/tetrahydrofuran (THF) mixtures, were subjected to reductive pyrolysis to determine their organic sulfur functionalities. The extraction yield was in the range of 11.4–43.1 wt %, depending on the type of solvent and coal. Toluene gave the highest extraction yield for medium-volatile bituminous coal, whereas a toluene/2-propanol mixture was the most effective in the case of lignite. The organic sulfur content in the resultant supercritical extracts amounted to 2.17–3.70 wt %. The atmospheric-pressure-temperature-programmed reduction technique coupled with potentiometric detection of H₂S (AP-TPR) and mass spectrometry (AP-TPR-MS) were applied to monitor the sulfur-containing compounds. During this reductive pyrolysis, these compounds were hydrogenated to H₂S at specific and discrete temperature intervals. The H₂S AP-TPR recovery for supercritical extracts was in the range of 23–65 wt %. The results show that thiols, polysulfides, and/or elemental sulfur have the highest contribution to the detectable sulfur in supercritical extracts by AP-TPR. However, alkyl aryl sulfides, aryl sulfides, and thiophenes are also present in smaller amounts. A toluene/THF mixture, compared to the rest of solvents used, seems to have the greatest extraction ability toward thiols and polysulfides-containing coal fragments. It was proven that the higher rank coal subjected to the SFE, the higher the contribution of thiophenic sulfur into the H₂S AP-TPR evolution profile in the range of 350–900 °C. The use of the AP-TPR setup coupled with a mass spectrometer instead of the potentiometric detection system has revealed the presence of alkanethiols, thiophene, and C₁- and C₂-thiophenes in the gaseous products of reductive pyrolysis. C₁–C₃ dibenzothiophenes, C₁–C₃ benzonaphthothiophenes, and C₁–C₂ dinaphthothiophenes can be observed in the evolved tar.

Introduction

Great progress has been recently achieved in the field of the nature of organosulfur constituents in coal and coal-derived products. The knowledge about organic sulfur compounds (OSCs) is of great importance for their removal, either before combustion of coal or removal of sulfur oxides after combustion. In the past decade, it has been demonstrated that atmospheric-pressure-temperature-programmed reduction (AP-TPR) can be successfully used to determine the sulfur functional groups in the raw coals and their products of chemical and thermal treatment.^{1–5} Attar et al.⁶ were pioneers in applying this method to study organic sulfur groups

in coal. Later, the AP-TPR technique was improved by Majchrowicz et al.⁷ and modified by Lafferty et al.,⁸ who used high hydrogen pressure. For many years, Yperman et al.⁹ have been working on further improvement of the AP-TPR to remove or minimize some drawbacks that still exist.

One of the factors that generates difficulties in the interpretation of the AP-TPR results is the fact that pyrite is present in every coal. This is because the pyrite signal in the kinetogram occurs in the temperature

* Author to whom correspondence should be addressed. E-mail address: grazyna.gryglewicz@pwr.wroc.pl.

[†] Wrocław University.

[‡] Limburgs Universitair Centrum.

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range close to those characteristic of aryl sulfides and thiophenes.¹⁰ To overcome this problem, the best way is to study vitrinite concentrates¹¹ or the coal extracts obtained via solvent extraction.¹²

Extraction of coals with organic solvents is widely used in the investigation of coal structure. Difficulties in the examination of coal result from the fact that coal is a solid that limits the possibilities for the direct use of many advanced instrumental techniques. Investigation of the coal extract will permit one to obtain a deeper knowledge about the constitution of coal, provided that the extracted material is representative for the entire organic coal matrix. Usually, the coal extract, because of its heterogeneity, is subjected to separation into fractions of different classes of compounds. Moreover, improved procedures for isolating sulfur-enriched fractions from complex mixtures have been developed.^{13,14} The most information concerning the nature of organosulfur constituents in coal and coal-derived products has been provided by pyrolysis–gas chromatography–high-resolution mass spectrometry (Py–GC–HRMS),¹⁵ low-voltage high-resolution mass spectrometry (LV–HRMS),^{16,17} and gas chromatography (GC) combined with different detectors such as those for mass spectroscopy (MS), flame photometric detection (FPD), and atomic emission detector (AED).^{14,18,19}

The extraction process of a coal sample is most often conducted in a Soxhlet apparatus. Different organic solvents were used for this purpose, e.g., toluene, pyridine, ethylenediamine, tetrahydrofuran (THF), and others.²⁰ It was found that the mixture of different solvents may give a much higher extraction yield than a single solvent.^{21,22} Particularly, an *N*-methyl-2-pyrrolidinone/CS₂ mixture at ambient temperature was effective for the extraction of medium-rank coals, reaching a yield of 40–65 wt %.²³ A significantly higher extract yield than that produced by conventional Soxhlet extraction can be obtained by extracting coal with organic solvents in the supercritical state (supercritical fluid extraction, SFE), because of better penetration of the solvent molecules into the porous structure of coal. Mild SFE process temperatures (<360 °C) influence the composition of the extracted hydrocarbons only slightly,

Table 1. Characteristics of Coals Subjected to the Supercritical Fluid Extraction (SFE) Process

characteristic	Bełchatów	Siersza	1 Maja
proximate analysis (wt %)			
moisture	29.4	16.9	1.1
ash (db)	23.9	13.2	9.5
volatile matter (daf)	54.5	38.3	29.8
ultimate analysis (wt %)			
C (daf)	61.5	79.4	87.5
H (daf)	5.3	5.4	4.7
N (daf)	1.3	1.3	1.8
S (db)	8.5	1.75	4.3
O _{diff} (daf) ^a	28.2	12.7	4.4
sulfur forms (wt %, db)			
organic	3.74	1.18	1.55
sulfatic	0.59	0.03	0.27
pyritic	4.08	0.52	2.36
elemental	0.09	0.02	0.12

$$^a \text{O}_{\text{diff}}(\text{daf}) = 100 - (\text{C}^{\text{daf}} + \text{H}^{\text{daf}} + \text{N}^{\text{daf}} + \text{S}^{\text{db}}).$$

as compared to their composition from conventional extraction.^{24,25} The SFE yield is related to the type of coal and solvent used. Toluene is the most effective solvent for dissolving the nonpolar component of a coal substance, which predominates in medium-volatile bituminous coal. Lignites and sub-bituminous coal contain a great amount of oxygen functionalities; thus, the mixture of nonpolar and polar solvents is expected to give an enhanced yield of extraction.^{26,27}

The study reported in this paper is a continuation of our work on the characterization of organically bound sulfur of coal extracts by GC–MS^{28,29} and reductive pyrolysis.¹² The objective of this study was to determine the sulfur functionalities of supercritical extracts obtained from coals of different rank, by means of an AP-TPR technique coupled with different detection systems. So far, there has been no report in the literature concerning the distribution of organic sulfur groups of the coal extracts obtained via SFE.

Experimental Section

Coals. Three Polish coals of different rank—i.e., lignite (lignite A) from a Bełchatów deposit, sub-bituminous coal (subA) from a Siersza mine, and bituminous coal (mbv) from the 1 Maja mine—were used in this study; these coals are denoted as B, S, and M, respectively. The detailed characteristics of the coals used was given in Table 1. The organic sulfur content of the initial coals was in the range of 1.18–3.74 wt %.

Supercritical Fluid Extraction (SFE). For raw coals with a grain-size range of 0.315–0.5 mm, a series of SFE runs were performed in an apparatus with a flowing solvent. Toluene (T), toluene/2-propanol (50:50 v/v, TiP), and toluene/tetrahydrofuran (90:10 v/v, TTHF) were used as solvents. All solvents were pure p.a. Pseudo-critical temperature and pressure were calculated for the solvent mixtures, according to Kay's method,³⁰ and are given in Table 2. For the solvents used, the extraction was conducted at 360 °C and 10 MPa in a constant solvent flow of 0.6 dm³ h^{−1}. The extracted material was continuously removed from the extraction cell, cooled, and collected in a collector that was filled with argon. The extrac-

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Table 2. Critical Temperature (T_c) and Critical Pressure (p_c) of Solvents

solvent	T_c (°C)	p_c (MPa)
toluene	319	4.2
toluene/2-propanol, 1:1 (v/v)	275	4.8
toluene/THF, 9:1 (v/v)	312	4.3

Table 3. Temperature Ranges of Reduction/Hydrogenation of Different Sulfur Functionalities in Atmospheric-Pressure-Temperature-Programmed Reduction (AP-TPR)^a

sulfur group	temp (°C)
elemental sulfur	180–220
alkanethiols	180–320
polysulfides	200–250
aryl thiols	300–400
disulfides	400–460
dialkyl sulfides	380–490
alkyl aryl sulfides	430–560
pyrite	480–590
diaryl sulfides	500–640
thiophenes	≥ 600
troilite	> 740

^a From refs 5, 9, and 10.

tion process was continued until the condensate was clear, followed by solvent removal in a rotary evaporator and drying in a vacuum oven at 60 °C until an almost-constant weight was obtained. More details about the SFE apparatus and procedure were published in our previous report.²⁸ For each coal, the extraction with a given solvent was performed in duplicate. The extract samples were stored in an inert gas atmosphere.

The yield of extraction (Y) was calculated on a dry and ash free (daf) basis, according to the following equation:

$$Y(\%) = \frac{m_e}{m_c} \times \frac{100}{100 - M^a - A^a} \times 100$$

where m_e is the mass of extract (given in grams), m_c the mass of coal (given in grams), M^a the moisture content in the coal (given as a percentage), and A^a the ash content in the coal (given as a percentage).

The supercritical extracts were labeled as follows: e.g., Sse-TiP represents the supercritical extract obtained from Siersza coal with the toluene/2-propanol mixture and Mse-T represents the supercritical extract obtained from 1 Maja coal with toluene.

Elemental Analysis. A Perkin-Elmer model 2400 CHN elemental analyzer was used for carbon, hydrogen, and nitrogen determinations. The total sulfur was determined by combusting the sample and absorbing sulfur oxides in a hydrogen peroxide solution.

Atmospheric-Pressure-Temperature-Programmed Reduction (AP-TPR). The apparatus and experimental procedure for AP-TPR analyses are described in detail elsewhere.⁹ For each experiment, 40 mg of finely ground sample ($d < 88 \mu\text{m}$) mixed with 30–40 mg of fumed silica were placed in the reactor under a 100 mL/min flow of pure hydrogen. A linear program of 5 °C/min from room temperature up to 1025 °C was followed. The gaseous H_2S formed was detected potentiometrically as S^{2-} . For each temperature region, peaks are attributed to the presence of specific sulfur functionalities in the analyzed sample. These temperature regions have been established through the use of model compounds^{5,9,10} and are given in Table 3. Samples were analyzed by AP-TPR with and without the reducing solvent mixture. The mixture was composed of 25 mg each of resorcinol, phenanthrene, and 9,10-dihydroanthracene, and 65 mg of pyrogallol. For each sample, all the AP-TPR-pot experiments were performed in duplicate. The AP-TPR sulfur recovery (S_{rec}) was determined, which is

expressed as the ratio of H_2S evolving during the AP-TPR experiment to the total sulfur content of an analyzed sample (see Table 4). The relative deviation in S_{rec} determination was <10%, which is acceptable, taking into account the small sample size (40 mg). All obtained AP-TPR H_2S profiles are normalized; i.e., AP-TPR data are divided by the experimental sulfur recovery (S_{rec}) and multiplied by the total sulfur content of the sample. In this way, kinetograms are independent of S_{rec} and quantitative comparison between different AP-TPR results is possible. The H_2S kinetograms presented in the paper are always the average of two independent measurements. The two recorded profiles always coincide very well with each other.

To follow H_2S , as well as other sulfur compounds that can evolve during reductive pyrolysis, the reactor was also coupled with the mass spectrometer (Fisons-VG model Thermolab MS) through a capillary heated at 135 °C. The mass spectrometer, which was equipped with a quadrupole analyzer, was set at an ionizing voltage of 70 eV with the mass range of $m/z = 15$ –150.

Gas Chromatography–Mass Spectrometry (GC–MS). The tar evolved during reductive pyrolysis was collected and analyzed via GC–MS. A Hewlett-Packard model HP6890 gas chromatograph was equipped with a Hewlett-Packard model HP5973 mass-selective detector and a model HP-5MS capillary column (30 m \times 0.25 mm inner diameter, film thickness of 0.25 μm , cross-linked 5% PH ME siloxane). Helium (purity of 99.999%) was used as a carrier gas. The column temperature was programmed from 40 °C to 280 °C at a rate of 5 °C/min after an initial isothermal period (2 min) and kept at the final temperature for 10 min. The inlet was set at 280 °C. Sample injection was made in the split mode (1:20).

Mass spectrometer was set at an ionizing voltage of 70 eV with a mass range of $m/z = 15$ –400. The identification of OSCs was accomplished by comparing the mass spectra of the resolved components, using electronic library search routines. For the GC–MS analysis, the tar sample was prepared as a 0.1 vol % solution in methylene chloride.

Results and Discussion

Elemental Composition of Supercritical Extracts. The results of the ultimate analysis of extracts obtained using different solvents under SFE conditions are presented in Table 4. A comparison of elemental composition of the raw coals (Table 1) and that of their supercritical extracts shows a marked increase of carbon content for lignite, almost no changes for sub-bituminous coal, and a decrease of carbon content for bituminous coal. For the two latter coals, a pronounced increase of both hydrogen and sulfur, followed by a decrease of nitrogen in the extracts, is observed. Except for the Siersza coal, the highest sulfur content in the extract was reached when TTHF was used for the SFE. It can be observed that an increment of organic sulfur is not related to the coal rank. Nevertheless, the fact that the obtained supercritical extracts for Siersza and 1 Maja coals are richer in organic sulfur (i.e., 2.17–3.70 wt %), compared to the respective raw coals (1.18–1.55 wt %), is not only important in view of the study on organic sulfur functionalities but refers also to the differences found in the organic sulfur present toward its bounding characteristics.

Extractability of Coals. The extraction yields for the studied coals are shown in Table 5. The obtained results indicate a great impact of coal rank and the type of solvent on the supercritical extract yield. The 1 Maja coal (mbv) clearly gives a much higher yield of extraction (23.9 wt %) using toluene, compared to that obtained

Table 4. Ultimate Analysis of Supercritical Extracts

element	content (wt %)								
	Bse-T	Bse-TiP	Bse-TTHF	Sse-T	Sse-TiP	Sse-TTHF	Mse-T	Mse-TiP	Mse-TTHF
C	73.03	75.12	72.87	79.57	79.50	79.34	86.08	83.85	85.48
H	6.83	6.85	6.42	7.12	7.05	6.72	5.62	6.56	6.10
N	<0.10	<0.10	<0.10	0.48	0.26	<0.10	0.81	0.42	0.82
S	3.30	2.62	3.54	2.58	3.65	3.30	2.17	2.97	3.70
O	~16.80	~15.40	~17.20	10.25	9.54	~10.60	5.32	6.20	3.90

Table 5. Yield of the SFE Process

solvent	yield (wt %)		
	Belchatów	Siersza	1 Maja
toluene	14.5	14.4	23.9
toluene/2-propanol	43.1	39.9	11.4
toluene/THF	35.0	17.2	21.9

for lower-rank coals (~14.5 wt %), i.e., Siersza coal (sub A) and Belchatów lignite. These results are consistent with the finding that, for medium- and high-rank coals, toluene is the most suitable solvent for SFE.³¹ An enhanced extraction yield for both Belchatów lignite and Siersza coal was obtained when 10 vol % of THF was added to toluene (35.0 vs 14.5 wt % and 17.2 vs 14.4 wt %, respectively). However, in the case of 1 Maja coal, no improvement in extraction yield with added THF could be obtained. The highest extraction yields for low-rank coal were obtained using TiP: yields as high as 43.1 wt % for Belchatów and 39.9 wt % for Siersza were obtained. In contrast, for the 1 Maja coal, the yield further decreased to only 11.4 wt %. It was previously reported^{26,32} that the mixture of hydrocarbon and polar solvent is the most effective for SFE of lignite, whereas the same finding was observed for sub-bituminous coal. The enhanced ability of the solvents mixture to dissolve the coal matrix is probably related to the synergistic effect that the solvents may have on the coal during the SFE process. Lignite as well as sub-bituminous coal contains a large number of hydroxyl groups, followed by hydrogen bonds, which makes it more difficult for toluene to penetrate the coal. However, 2-propanol breaks these bonds and facilitates an access of toluene to the macromolecular network. On the other hand, toluene can break the π - π interactions between low condensed aromatic systems of coal, leading to an enhanced penetration of coal by 2-propanol. Both factors can make a TiP mixture very efficient for getting a high extraction yield.

Atmospheric-Pressure-Temperature-Programmed Reduction (AP-TPR). Figures 1, 2, and 3 show the H₂S evolution monitored by AP-TPR with potentiometric detection for a series of supercritical extracts obtained from Belchatów lignite, Siersza coal, and 1 Maja coal, respectively. For all studied extracts, the most pronounced peak in their kinetograms is that with a maximum at a temperature range of 195–240 °C. This temperature range corresponds to the hydrogenation/reduction of thiols, polysulfides, and elemental sulfur. For a given coal, the intensity of this signal is different, depending on the type of solvent used for the SFE process. This suggests that the solvent and mixtures used (i.e., T, TiP, and TTHF) differ in terms of their abilities to break coal-coal interactions and dissolve the

coal molecular fragments, which contain thiols and/or polysulfides. Moreover, as shown in a previous paper,²⁸ the new sulfur functionalities may have been formed during the SFE process if elemental sulfur is present in the coal. Monosulfides, disulfides, and trisulfides were detected in the model reaction products of elemental sulfur with iP and TiP, and these observations have been obtained under the same SFE conditions as those used in this work. Figures 1–3 clearly show that, for the three coals studied, their supercritical extracts obtained with TTHF give a signal with the highest intensity at the temperature range of ~195–240 °C. This observation suggests that this solvent mixture is the most effective in the extraction of thiols, elemental sulfur, and polysulfides, compared with T and TiP.

For the Belchatów extracts, the first peak not only refers to the possible original presence of thiols and polysulfides and certainly to elemental sulfur, but it also refers to the formation of secondary polysulfides. The presence of elemental sulfur in the amount of 0.12 wt % in Belchatów lignite was confirmed by GC-MS.²⁸ Because the Siersza coal contains only very small amounts of elemental sulfur (0.02 wt %), the contribution of secondary polysulfides formation²⁸ to the peak at ~200 °C can be neglected for all SFE processes used. Thus, the first peak must be attributed mainly to the possible original presence of thiols. Taking into account that polysulfides and even disulfides probably do not occur in a medium-volatile bituminous coal,³³ the presence of polysulfides in the Mse-TiP extract can only be explained by the reaction of elemental sulfur (0.09 wt %) with 2-propanol during the SFE process.²⁸ Therefore, the first peak in the H₂S kinetogram of the 1 Maja SFE must be attributed to the possible original presence of thiols and certainly to elemental sulfur, as well as to the formation of secondary polysulfides in the case of Mse-TiP extract.

As observed in the H₂S kinetograms presented in Figures 1–3, for a given coal, there are no significant differences between supercritical extracts obtained with different solvents, in terms of the distribution of organic sulfur functionalities giving a response at higher temperature, i.e., 350–900 °C. Furthermore, the H₂S profiles in the temperature range of 350–900 °C are less pronounced, compared to those obtained in the temperature range of 150–350 °C.

For all Belchatów SFEs, a broad signal at ~450–900 °C can be observed, which suggests the presence of small amounts of alkyl aryl sulfides, aryl sulfides, and complex thiophenes with comparable contributions (see Figure 1). Two well-resolved signals, apart from the first signal, with slightly different intensity in the temperature range of 300–900 °C, can be observed in the case of the

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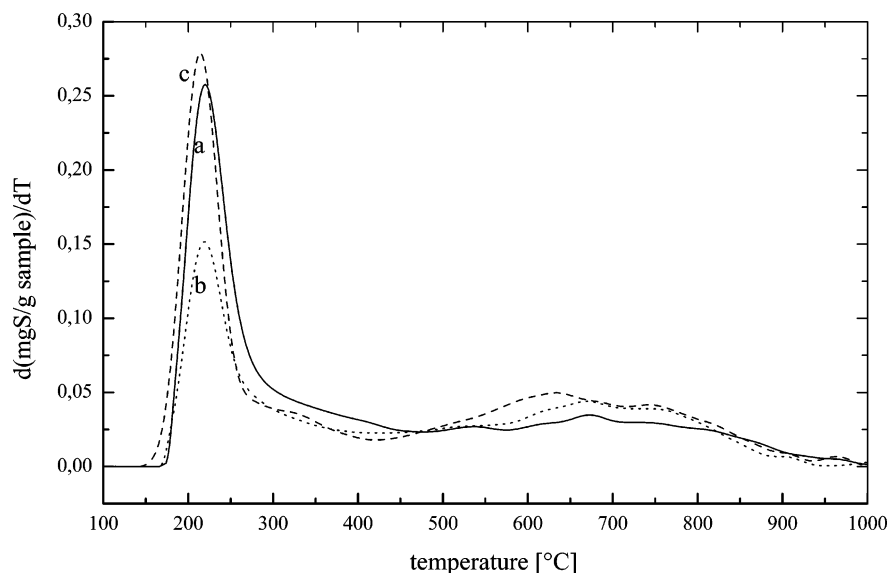


Figure 1. Atmospheric-pressure–temperature-programmed reduction (AP-TPR) kinetograms of supercritical extracts from Belchatow lignite (Bse-T (curve a), Bse-TiP (curve b), and Bse-TTHF (curve c)).

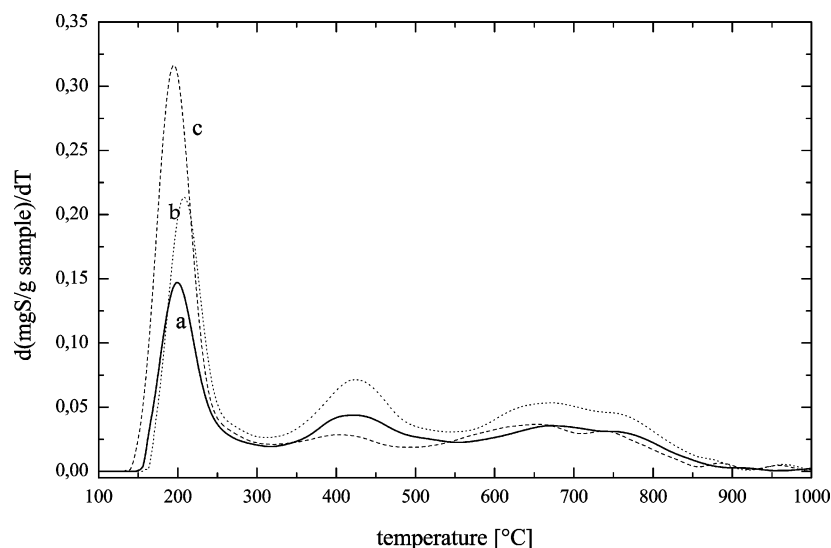


Figure 2. AP-TPR kinetograms of supercritical extracts from Siersza sub-bituminous coal (Sse-T (curve a), Sse-TiP (curve b), and Sse-TTHF (curve c)).

Siersza SFEs (see Figure 2). The peak with a maximum at 400–425 °C corresponds to the hydrogenation/reduction of small amounts of disulfides and dialkyl and alkyl aryl sulfides. The presence of diaryl sulfides and complex thiophenes in the Siersza supercritical extracts is confirmed by a broad peak with a maximum at ~650–750 °C. Similarly to Siersza coal, the SFE extracts from the 1 Maja coal also show, in the temperature range of 400–1000 °C, two distinct signals with apparently different intensity but are less pronounced and also shifted toward some higher temperatures (see Figure 3). The first peak, with a maximum at ~500 °C, can be assigned to alkyl aryl sulfides and the second peak, with a higher intensity at a maximum of ~750–770 °C and a shoulder at ~630 °C, refers to complex and even more complex thiophenic structures and diaryl sulfides, respectively. This confirms the fact that, for a medium-volatile bituminous coal, a higher contribution of complex thiophenes always is observed.^{11,33–35}

More information about organic sulfur functionalities from the low-temperature kinetogram can be provided

when the AP-TPR experiment is performed in the presence of the reducing mixture.⁹ Comparing the AP-TPR experiments, using only pure hydrogen, the addition of this mixture results in a more-efficient reduction/hydrogenation of elemental sulfur, thiols, and polysulfides to H₂S at a lower temperature, and thus, as it should be for the reliability of this technique, before evaporation/degradation of these species can occur.^{5,36} Figure 4 shows the comparison of the results of AP-TPR analysis of toluene supercritical extracts obtained for the three different coals at temperatures up to 400 °C without mix and when mix was added. For all extracts, two separated peaks instead of one peak can be observed using this mix. The first, more-pronounced peak, with a maximum in the range of 180–210 °C, can be attributed to alkanethiols, polysulfides, and elemental

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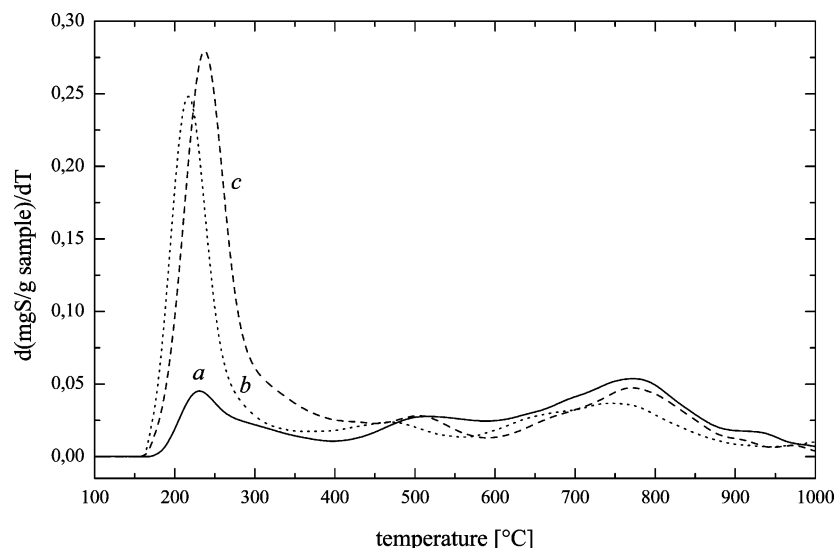


Figure 3. AP-TPR kinetograms of supercritical extracts from 1 Maja bituminous coal (Mse-T (curve a), Mse-TiP (curve b), and Mse-TTHF (curve c)).

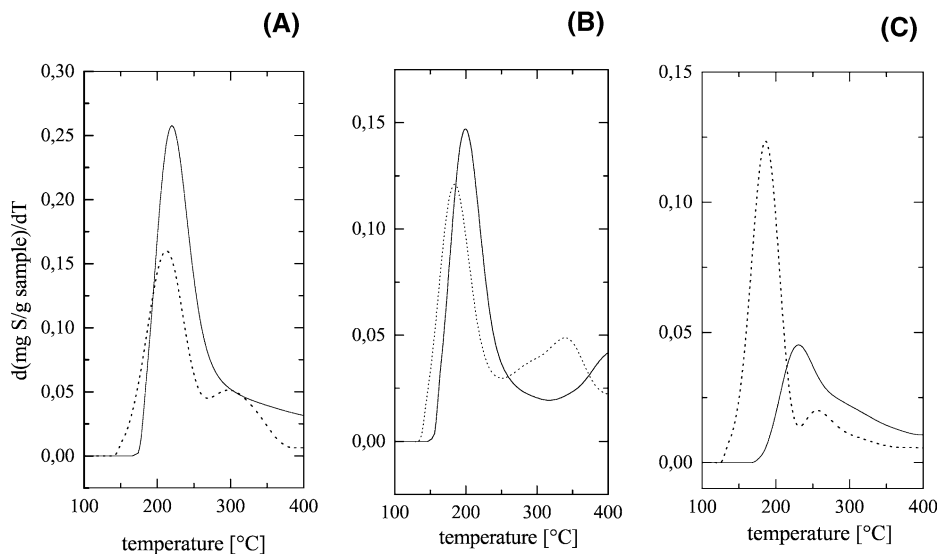


Figure 4. AP-TPR kinetograms of toluene supercritical extracts analyzed (—) without and (····) with a reducing mixture: (A) extract from Belchatów lignite, (B) extract from Siersza coal, and (C) extract from 1 Maja coal.

sulfur, and the second peak, with a much lower intensity and centered at 300–330 °C, can be attributed to aryl thiols. This suggests that the contribution of aryl thiols to total organic sulfur, as found using AP-TPR analysis, is considerable lower, compared to that of alkanethiols, polysulfides, and elemental sulfur. According to the knowledge about the organic sulfur functionalities of different-rank coals, the presence of polysulfides cannot be excluded in the lignite.^{33,36} Indeed, dimethyl disulfides and trisulfides were identified by GC–MS in the Bse-T extract,²⁸ whereas they were not detected in the Sse-T and Mse-T extracts.²⁹ The peak with a maximum at 210 °C observed in the kinetogram of the Bse-T extract (Figure 4A, dotted line) can be an overlapping of signals referred to alkanethiols, elemental sulfur, and polysulfides. Undoubtedly, for the Sse-T extract, the peak with a maximum at 180 °C (Figure 4B, dotted line) can be mainly attributed to the presence of alkanethiols. This conclusion could be drawn because polysulfides are not present in a sub-bituminous coals and, in addition, almost no elemental sulfur was detected in the Siersza coal. For the Mse-T extract, the H₂S evolution with a

maximum at 185 °C refers mainly to elemental sulfur (Figure 4C, dotted line). Alkanethiols are normally not present in a medium-volatile bituminous coal.³³ The extent to which the very small peak at ~250 °C can be attributed to some presence of aryl thiols is doubtful. Although some quantitative trends could be deduced from Figure 4, great differences between the SFE extracts, such as those in AP-TPR sulfur recoveries (which, in addition, are sometimes low) of the different coals makes this impossible. Therefore, only qualitative interpretations can be made.

Table 6 shows the AP-TPR sulfur recoveries (S_{rec}), which are relatively low and range from 23% up to 65%. As can be observed, for a given coal, the extracts obtained via the SFE process with TTHF show the highest sulfur recovery. Moreover, a general trend can be observed for a given solvent: i.e., the higher the coal rank, the higher the sulfur recovery obtained in the AP-TPR experiments for supercritical extracts. From these results, it is also clear that only a portion of the sulfur functionalities of supercritical extracts has been detected using this reductive pyrolysis technique. The

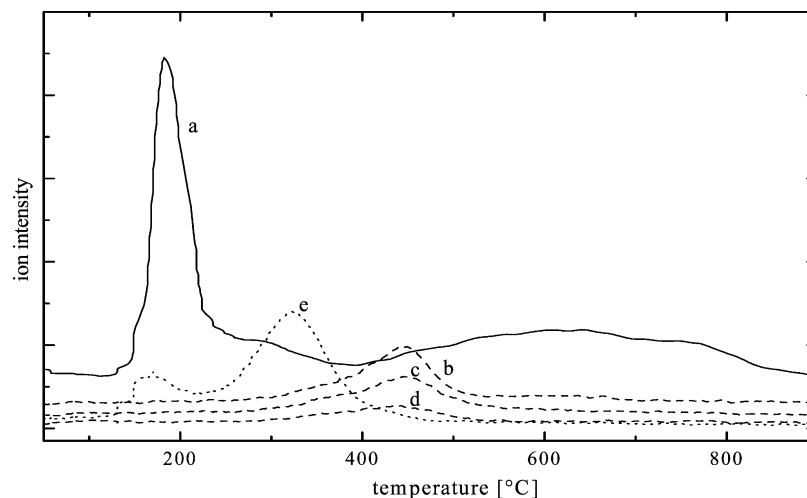


Figure 5. AP-TPR-MS profiles of selected ions formed during analysis of Bse-T extract: H_2S^+ , m/z 34 (profile a); $\text{C}_4\text{H}_4\text{S}^+$, m/z 84 (profile b); $\text{C}_5\text{H}_5\text{S}^+$, m/z 97 (profile c); $\text{C}_6\text{H}_7\text{S}^+$, m/z 111 (profile d); and CH_2SH^+ , m/z 47 (profile e).

Table 6. Sulfur Recovery in AP-TPR Analysis of Supercritical Extracts

sample	amount of sulfur recovered, S_{rec} (%)
Bse-T	31
Bse-TiP	30
Bse-TTHF	44
Sse-T	37
Sse-TiP	23
Sse-TTHF	45
Mse-T	50
Mse-TiP	48
Mse-TTHF	65

reasons for the low sulfur recovery of extracts was extensively discussed in a previous paper.¹² In our case, the AP-TPR results show that the supercritical extracts contain alkanethiols, aryl thiols, polysulfides, and elemental sulfur, which, to some extent, before their hydrogenation/reduction, can already evolve in the lower-temperature range. Moreover, even cyclization and aromatization reactions of nonthiophenic functionalities may occur during this reductive pyrolysis, leading to the formation of condensed thiophenic structures preserved in the solid residue. Also, the extract can contain complex thiophenic compounds that were not hydrogenated and remain in the solid residue. Furthermore, note that, during heat treatment, the sulfur is distributed between solid, liquid, and gaseous products. Not only H_2S but also other volatile sulfur compounds can be released during an AP-TPR experiment. However, the latter compounds cannot be monitored by the potentiometric system.

Analysis of Gaseous Products from Reductive Pyrolysis (AP-TPR-MS). It becomes clear that some of the sulfur compounds may not be reduced/hydrogenated to H_2S but evolve unchanged with the carrier gas, as shown in Figure 5. The AP-TPR-MS analysis of Bse-T, as an example, is presented in this figure. The H_2S profile obtained via AP-TPR-MS (profile a in Figure 5) clearly is very similar to that obtained when a potentiometric detection of H_2S as S^{2-} was applied (see curve a in Figure 1). Moreover, the signals for an m/z ratio of 84, 97, and 111 can be observed, which could correspond, respectively, to thiophene (profile b), C_1 -thiophenes (profile c), and C_2 -

Table 7. Organic Sulfur Compounds (OSCs) Identified in the Tar Obtained during AP-TPR Analysis of Supercritical Extracts from 1 Maja Coal

compound	Mse-T	Mse-TiP	Mse-TTHF
dibenzothiophene (DBT)	●	●	●
C_1 -DBT	●	●	●
C_2 -DBT	●	●	●
C_3 -DBT	●	●	○
benzonaphthothiophene (BNT)	●	●	○
C_1 -BNT	●	●	
C_2 -BNT	●	●	
C_3 -BNT	●	●	
dinaphthothiophene (DNT)	●		●
C_1 -DNT	●		
C_2 -DNT	●		

^a Solid circle (●) denotes abundant content; open circle (○) denotes less-abundant content.

thiophenes (profile d), with a maximum evolution temperature of 420°C. These m/z ratios can also refer to other fragments; however, some clear indication for the first mentioned species is observed, using the GC-MS results (see further discussion). The m/z ratio of 47 (profile e) can refer to the presence of alkanethiols or, again, to other organic compound fragments. Again, GC-MS results in this case also give some clear indications. Here, two maxima, at 180 and 310 °C, can be observed in the profile of the CH_2SH^+ ion. This suggests that, in the case of alkanethiols, their original presence can be explained by their occurrence in different forms in the coal matrix (adsorbed or bound). There are no indications for the presence of oxidized OSCs, because no signals for SO_2 or SO were observed in the MS spectrum.

Analysis of Liquid Products from Reductive Pyrolysis via Gas Chromatography-Mass Spectroscopy. Table 7 shows the OSC identified in the AP-TPR tars from the extracts obtained via SFE using T, TiP, and TTHF. The GC-MS analysis indicates that C_1 - C_3 dibenzothiophenes (DBT), C_1 - C_3 benzonaphthothiophenes (BNT), and C_1 - C_2 dinaphthothiophenes (DNT) occur in the liquid product. The tar from Mse-T extract is the most abundant in thiophenic functionalities. For this sample, selective ion chromatograms are shown in Figure 6. Compared to Mse-T, the tar from Mse-TiP contains less-condensed thiophenic structures

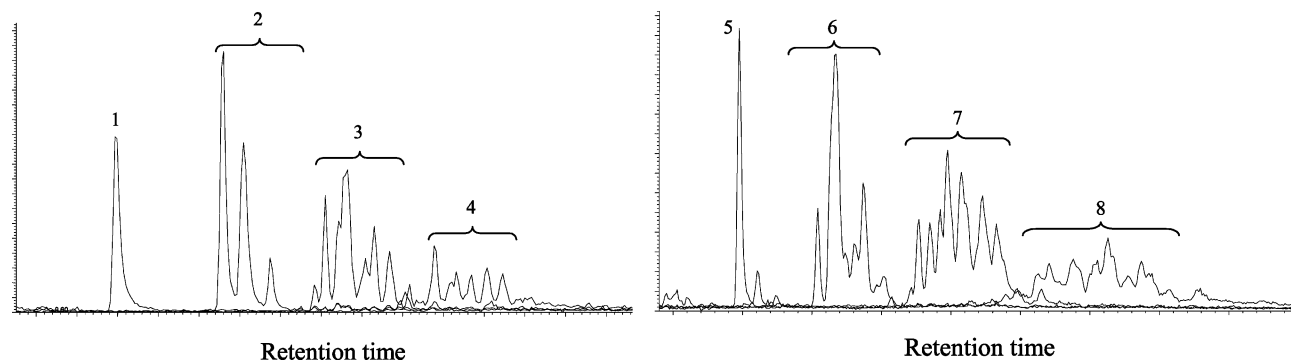


Figure 6. Partial accurate summed ion chromatogram of m/z 184 + 198 + 212 + 226 + 234 + 248 + 262 + 276 of the tar obtained from Mse-T during AP-TPR: (1) DBT, (2) C₁-DBT, (3) C₂-DBT, (4) C₃-DBT, (5) BNT, (6) C₁-BNT, (7) C₂-BNT, and (8) C₃-BNT.

(DBT, BNT, DNT vs DBT, BNT). The smallest spectrum of the thiophenic compounds can be observed for the tar from Mse-TTHF. It seems that the highest AP-TPR sulfur recovery obtained for Mse-TTHF, compared to those of Mse-T and Mse-TiP, can be explained by the lowest amount of sulfur compounds evolved in the tar from Mse-TTHF.

Conclusions

The sulfur in the extracts obtained via supercritical fluid extraction (SFE) from lignite, sub-bituminous coal, and medium-volatile bituminous coal with different solvents, which was determined by atmospheric-pressure-temperature-programmed reduction (AP-TPR), occurs mainly as alkanethiols, aryl thiols, polysulfides, and/or elemental sulfur. The presence of polysulfides in the toluene/2-propanol extract from a medium bituminous coal can only be explained by secondary reactions between 2-propanol and the elemental sulfur present in this extract. Using AP-TPR, alkyl aryl sulfides, aryl sulfides, and thiophenes are observed in small amounts in the SFE extracts. The contribution of thiophenic functionalities is observed to increase as the rank of coal subjected to the SFE process increases. The same relationship was observed for pyridine extracts obtained

from the same coals¹² that were used in this work. Moreover, the SFE conditions favor the extraction of thiols and polysulfides, whereas no such findings are observed in the case of the classical extraction with pyridine.

The AP-TPR sulfur recovery ranges from 23% to 65%, the last being the highest for the extract from a medium-volatile bituminous coal. Therefore, it can be concluded that only a portion of the sulfur present in the supercritical extracts has been determined via AP-TPR. H₂S, as well as alkanethiols, thiophene, C₁-thiophene, and C₂-thiophenes, can be observed in the gaseous products. Moreover, more-condensed thiophenic compounds such as C₁–C₃ dibenzothiophenes, C₁–C₃ benzonaphthothiophenes, and C₁–C₂ dinaphthothiophenes were detected by gas chromatography–mass spectroscopy (GC–MS) in the AP-TPR liquid product.

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