Articles

Atmospheric-Pressure Temperature-Programmed Reduction Study of High-Sulfur Coals Reduced in a Potassium/Liquid Ammonia System

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Two high-sulfur coals have been subjected to an atmospheric-pressure temperature-programmed reduction study (AP-TPR). The studies were performed on both raw and potassium/liquid ammonia reduced samples. The reduction of coals in the potassium/liquid ammonia system was shown to induce conversion of sulfide and disulfide groups into thiol groups. AP-TPR studies performed with addition of the reducing mixture provided evidence for the presence of different types of thiols. The possibility of cleavage of the C−S bonds in thiophenes was indicated. A favorable effect of the reducing mixture on sulfur recovery was observed in the AP-TPR method, while the calcium compounds occurring in coal were found to be responsible for significant deformation of the kinetograms obtained. The effect of extraction with dichloromethane on sulfur compounds in coal was established, leading to a supposition of sulfur being mainly bonded with the macromolecular part of coal.

Introduction

Recently much attention has been given to the investigation of sulfur compounds occurring in coals[1,2] as this problem is directly related to the quality and protection of the natural environment. Although quantitative and qualitative determinations of inorganic sulfur pose no problem, analysis and determination of the organic sulfur content proved much more difficult.

Among the methods used in the study of organic sulfur in coals, the most interesting are X-ray absorption near-edge structure (XANES),[3,4] X-ray photoelectron spectroscopy (XPS),[5,6] temperature-programmed oxidation (CATPO),[7] temperature-programmed pyrolysis (TPP),[8] high-pressure temperature-programmed reduction (HP-TPR)[9] and atmospheric-pressure temperature-programmed reduction (AP-TPR).[10] The latter has been successfully used by our group for a couple of years in the investigation of coals,[11−15] rubber,[16] and clay.[17]

Unfortunately, signals due to different sulfur groups laying in a partially overlapping temperature range may superimpose in AP-TPR kinetograms, which makes

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Table 1. Proximate and Elemental Analyses of Raw Coals (wt %)

coal	moisture	ash (dry coal)	VM^{daf}	C^{daf}	H^{daf}	N^{daf}	S_{org}^{daf}	$O^{daf\ a}$
Mequinenza coal	4.9	21.9	51.0	62.3	5.5	0.6	9.8	21.8
Illinois No. 6 coal	6.7	10.7	40.4	71.9	4.5	1.3	3.0	19.3

[a] By difference.

their analysis more difficult.[12,13] This problem can be avoided thanks to a controlled chemical modification of the samples, leading to transformation of certain sulfur groups into other groups that are well-resolved in the AP-TPR kinetograms. Such a modification can be rather successfully achieved by reduction in the potassium/liquid ammonia system.[18] This process involves, among others, cleavage of C—S bonds in sulfide and disulfide groups with a simultaneous formation of thiol groups.[19,20] On the basis of this process, Angelova et al.[21] proposed a method of quantitative determination of sulfides in coals. Having analyzed the results of the above reaction in a number of model compounds, Ignasiak et al.[19] concluded that the effect of the alkali metal in liquid ammonia on the other groups of organic sulfur is insignificant. However, results obtained for model compounds cannot always be extrapolated for coals, in which side reactions can occur. In view of this result, the main aim of this paper was to check the effect of reduction in the potassium/liquid ammonia system on sulfur compounds in coal and to determine the viability of this kind of coal modification in AP-TPR studies.

In our earlier work[22] devoted to inorganic sulfur compounds in coal, the results obtained by the classical chemical methods were in a good agreement with those achieved from AP-TPR studies; therefore, in this work, the main subject of interest was organic sulfur groups.

As follows from our earlier works,[23,24] the multiple processes run in the potassium/liquid ammonia system cause deeper transformations in the coal structure than the processes run only once. That is why the effect of repeating the process on the sulfur compounds in coal is also investigated in this study.

Experimental Section

The coals to be studied were selected to have a high content of sulfur of which the dominant form was that of organic origin. These requirements were met by the Spanish coal Mequinenza and American coal Illinois No. 6. The samples were grounded to the grain size of ≤0.06 mm and stored in a vacuum. The process of coal polyanion formation was conducted using potassium in liquid ammonia, and ethyl alcohol was applied as a protonating agent. The reactions were run according to the procedure described earlier,[25] and reduction of the coals was repeated twice. The products were extracted with dichloromethane in a Soxhlet apparatus for 48 h, and then the solvent was removed in a rotary evaporator. The sulfur forms in the coals were determined according to the Polish standard methods. The total content of sulfur was determined by a high-temperature combustion method.[26] Sulfate sulfur was extracted from the samples with hydrochloric acid and determined gravimetrically as barium sulfate.[27] The contribution of pyritic sulfur was assessed in the residue by nitric acid

Table 2. Content of Different Forms of Sulfur in Raw and Modified Coals (wt %, Dry Coal)

	sulfur			
coal	total	pyritic	sulfate	organic
Mequinenza Coal				
raw	9.67	1.22	0.81	7.64
reduced 1×	9.15	1.43	0.21	7.51
reduced 2×	8.08	1.15	0.19	6.74
Illinois No. 6 Coal				
raw	3.91	0.35	0.92	2.64
reduced 1×	2.89	0.33	0.09	2.47
reduced 2×	2.46	0.23	0.11	2.12

extraction and measured gravimetrically as above.[28] In this study, we introduced some modifications to the methods used; the most important modification was removal of all cations on a column with an ion exchanger.[29] Elemental sulfur was extracted from the samples with benzene, transformed into thiosulfate, and determined iodometrically.[30] No elemental sulfur was detected in the samples investigated. The accuracy of the determination of these forms of sulfur was approximately ≤0.05 wt %. The contribution of organic sulfur was found by subtracting that of inorganic sulfur from the total sulfur content. The results of the proximate, elemental, and sulfur analyses are presented in Tables 1 and 2.

The apparatus and experimental procedure of the atmospheric-pressure temperature-programmed reduction (AP-TPR) are described elsewhere.[11] In each experiment, approximately 40 mg of coal sample and 60 mg of fumed silica were placed in the reactor under a 50 cm^3 min^{-1} flow of pure hydrogen. A linear temperature program of 5 °C min^{-1} from room temperature up to 1000 °C was followed. The H_2S gas formed was potentiometrically detected as S^{2-}. Some of AP-TPR measurements were conducted with the addition of a special reducing mixture (mixture of 9,10-dihydroanthracene, phenanthrene, resorcinol, and pyrogallol)[14] to the sample in the reactor. Each AP-TPR experiment was repeated 3 times, and average values were calculated. The reproducibility of the results was quite high, and differences in sulfur recovery data in most cases did not exceed 3%. Identification of particular forms of sulfur was made on the basis of the measurements on model compounds (Table 3).[12,13] The kinetograms obtained are shown in Figures 1—6.

Analysis of the ash obtained from the coals studied was performed according to ASTM standards,[31] and the content of

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(30) Polish Standard PN-80/G-04514.15.

Table 3. Overview of Characteristic Reduction Temperature Regions of Sulfur Functionalities Present in Coal for AP-TPR[12,13]

temp (°C)	sulfur functional group
180−400	thiols
∼250	elemental sulfur
400−450	disulfides
380−475	dialkyl sulfides
440−550	aryl−alkyl sulfides
470−600	pyrite
550−600	iron sulfate
500−630	diaryl sulfides
600 and higher	thiophenes
740 and higher	troilite
800 and higher	other sulfates
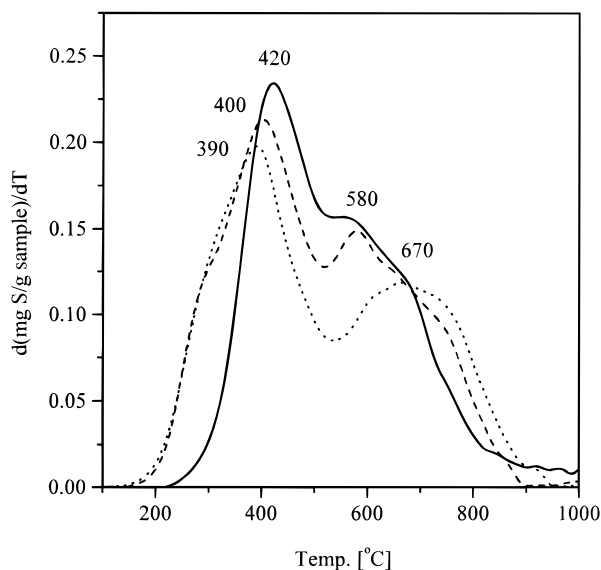
Figure 1. AP-TPR kinetograms of Mequinenza coal: (—) raw coal; (- - -) raw coal once reduced; (···) raw coal twice reduced.
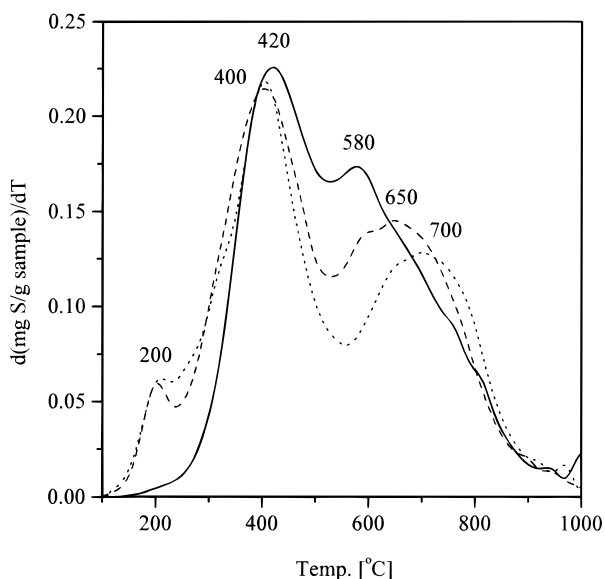
Figure 2. AP-TPR kinetograms of Mequinenza coal with reducing mixture: (—) raw coal; (- - -) raw coal once reduced; (···) raw coal twice reduced.

individual elements was determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES).

(31) ASTM Standard D 3682. *1979 Annual Book of ASTM Standards*; Part 26 p 433.
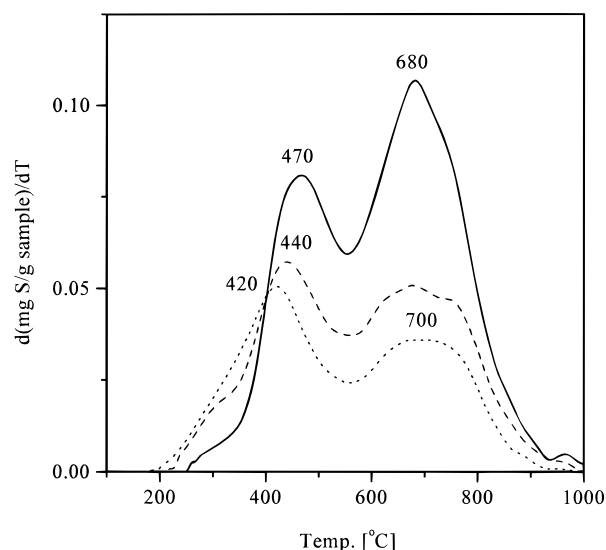
Figure 3. AP-TPR kinetograms of Illinois No. 6 coal: (—) raw coal; (- - -) raw coal once reduced; (···) raw coal twice reduced.
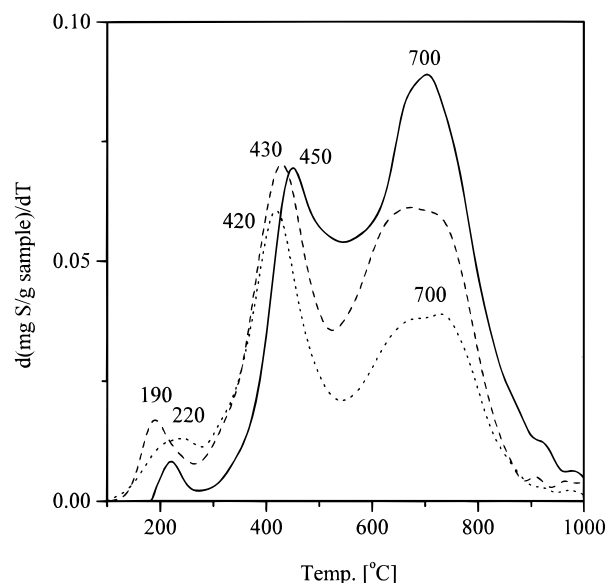
Figure 4. AP-TPR kinetograms of Illinois No. 6 coal with reducing mixture: (—) raw coal; (- - -) raw coal once reduced; (···) raw coal twice reduced.

Results and Discussion

The results of the proximate and elemental analyses of the initial Mequinenza and Illinois No. 6 coals are collected in Table 1. A comprehensive list of the chemical and spectral characteristics of the reduction products of these coals in the potassium/liquid ammonia system is given in our earlier work.[32]

Table 2 specifies the percent contribution of the particular forms of sulfur in the coals and products of their reduction. The Mequinenza coal is characterized by a greater total sulfur content than Illinois No. 6, and in both coals, the dominant form is organic sulfur. With repetition of the reduction process, the content of practically all sulfur forms decreases. This decrease is the most pronounced for sulfate sulfur, whose content diminishes about 4 times in Mequinenza and about 8 times in Illinois No. 6 coal. This fact can be accounted

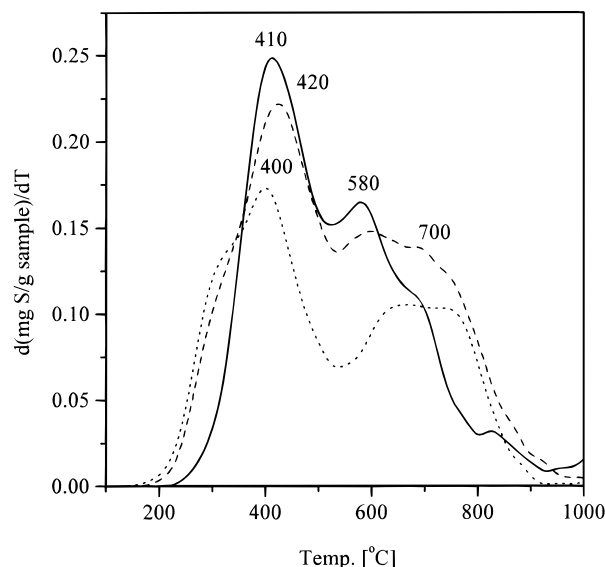(32) Kozłowski, M.; Wachowska, H. Submitted for publication.

Figure 5. AP-TPR kinetograms of CH_2Cl_2 residues of Mequinenza coal: (—) raw coal; (- - -) raw coal once reduced; (···) raw coal twice reduced.
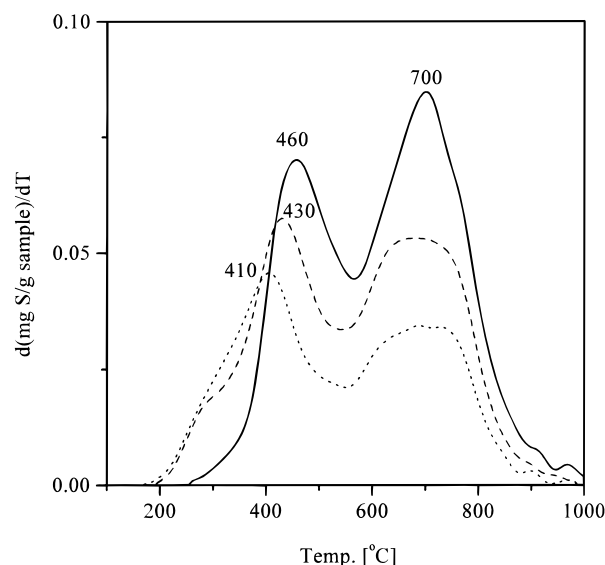

Figure 6. AP-TPR kinetograms of CH_2Cl_2 residues of Illinois No. 6 coal: (—) raw coal; (- - -) raw coal once reduced; (···) raw coal twice reduced.

for by the acid treatment conducted each time during isolation of the reaction products. Moreover, a small decrease of the content of organic sulfur is observed as a consequence of the cleavage of C−S bonds in the potassium/liquid ammonia system, which in some cases leads to elimination of sulfur.[19]

Analysis of the kinetograms obtained by AP-TPR requires the knowledge of hydrogenation temperatures of the particular forms of sulfur. Such temperatures obtained from the studies of model compounds[12,13] are given in Table 3, while the values of AP-TPR sulfur recovery for the samples studied in this work are listed in Table 4.

AP-TPR measurements were performed both with and without the reducing mixture.[14] According to the results of our earlier work[12] for model compounds, the presence of the reducing mixture during AP-TPR determinations was rather disadvantageous in the past, which was manifested as an increased contribution of

Table 4. Total Content of Sulfur in Coals and CH_2Cl_2 Residues (wt %, Dry Coal) and Sulfur Recovery by AP-TPR Method (%)

sample	total sulfur	sulfur recovery	sulfur recovery (with reducing mixture)
Mequinenza Coal			
raw coal	9.67	73	84
reduced 1×	9.15	85	93
reduced 2×	8.08	91	98
CH_2Cl_2 Residue of Mequinenza Coal			
raw	9.71	76	
reduced 1×	9.74	87	
reduced 2×	9.27	69	
Illinois No. 6 Coal			
raw coal	3.91	93	98
reduced 1×	2.89	82	95
reduced 2×	2.46	76	81
CH_2Cl_2 Residue of Illinois No. 6 Coal			
raw	3.64	79	
reduced 1×	2.91	81	
reduced 2×	2.36	74	

side reactions and a decreased sulfur recovery. However, on the other hand, addition of the reducing mixture decreases the hydrogenation temperature of the thiol groups,[12] and that is why we decided to use it as a complementary analysis. Interestingly, the data from Table 4 prove that addition of the reducing mixture to the samples studied leads to an increased sulfur recovery (compare the third and fourth columns of Table 4), which is opposite to the effect observed for model compounds and well-known for both Mequinenza and Illinois No. 6 coals. This fact proves that the results obtained for simple model compounds may not hold for a more complex structure of coal. A comparison of the results obtained on raw, 1 time reduced, and 2 times reduced coal leads to the conclusion that reduction of the Mequinenza coal in the potassium/liquid ammonia system causes a successive increase of sulfur recovery by the AP-TPR analysis, irrespective of whether the reducing mixture is used in the AP-TPR experiment. The opposite dependence is observed for the Illinois No. 6 coal, for which the sulfur recovery gradually decreases after reduction in the potassium/liquid ammonia system for both AP-TPR conditions. This different behavior is a consequence of the higher content of calcium compounds in the Mequinenza than in Illinois No. 6 coal, which will be explained further on in this paper.

AP-TPR kinetograms of all samples studied reveal two main broad peaks (Figures 1−6). One of them, with a maximum in the range 390−460 °C, can be interpreted on the basis of the data in Table 3 as a result of a superposition of the signals due to groups of nonthiophene sulfur. The other one, with a maximum in the range 580−700 °C, can be interpreted as corresponding to different groups of thiophene sulfur. Of course, inorganic sulfur also brings a certain contribution to these peaks, however, regarding its low content (especially in the reduced samples, Table 2), this contribution is small.

As follows from the kinetograms shown in Figure 1 that the proceeding potassium/liquid ammonia reduction causes a shift of the maximum of the peak initially localized at 420 °C toward lower temperatures, which is a consequence of cleavage of the C−S bonds in sulfide and disulfide groups with simultaneous formation of thiol groups. Since the hydrogenation temperature for

Table 5. Results of Determination of the Elements in Coals and Coal Ashes (Expressed as Element Oxides, wt %)

oxide	Mequinenza coal		Illinois coal	
	ash	raw coal	ash	raw coal
SiO_2	66.1	14.48	48.3	5.31
Al_2O_3	11.5	2.52	16.9	1.86
CaO	13.2	2.89	4.7	0.52
Fe_2O_3	6.7	1.47	17.6	1.94
MgO	2.3	0.50	1.0	0.11
K_2O	2.0	0.44	2.2	0.24
Na_2O	0.8	0.18	1.5	0.17

the AP-TPR experiment of the thiol groups is lower than that of the sulfide and disulfide groups they have originated from (Table 3), the maximum of the peak which is a superposition of signals from all these groups shifts toward lower temperatures. The opposite phenomenon is observed for the peak whose maximum originally is at about 580 °C. As follows from earlier work,[15] the calcium compounds present in coal can react with the hydrogen sulfide forming during AP-TPR measurements to give CaS. This effect is responsible for the deformation of the AP-TPR kinetograms, in particular at higher temperatures. Thus, the phenomenon observed in this work should be related to the changes in the content of calcium in the Mequinenza coal. As the reduction of coals in the potassium/liquid ammonia system ends with acid treatment, which removes calcium compounds, after each stage of reduction, the peak was observed to shift toward higher temperatures. For the same reason, the sulfur recovery successively increases (Table 4). To verify the high calcium content in the Mequinenza coal, the ash analysis was performed, and these results are displayed in Table 5 (13.2% CaO in the ash and 2.89% CaO in coal).

Figure 2 presents kinetograms of the same samples as in Figure 1 but now with the addition of the reducing mixture in the AP-TPR experiment. Similarly, as for the samples without the reducing mixture, the reduction of these samples in the potassium/liquid ammonia system results in a shift of the maximum of the peak ascribed to nonthiophene sulfur groups toward lower temperatures (transformation of sulfides and disulfides into thiols). Also, the maximum of the peak due to thiophene sulfur is shifted toward higher temperatures (removal of calcium compounds). Moreover, kinetograms of the reduced samples reveal a new signal at about 200 °C, attributed to thiol sulfur, which appeared as a consequence of addition of the reducing mixture and a decrease in the thiol hydrogenation temperature.[12] Despite the appearance of this peak, for the reduced samples, the maximum of the peak due to nonthiophene sulfur is still shifted. This fact may indicate that as a result of coal reduction in the potassium/liquid ammonia system, different kinds of thiols are obtained. The signal at 200 °C should probably be attributed to aliphatic thiols, whereas the one that is a component of the broad peak at about 400 °C should be due to more thermally stable aromatic thiols. This indicates the presence of different kinds of sulfides and disulfides (aryl–aryl, aryl–alkyl, and alkyl–alkyl) in the raw coal. As the signal at 200 °C is similar for the sample after the first and the second stage of reduction in the potassium/liquid ammonia system, it can be concluded that a single reduction is

practically sufficient for breaking up all C–S bonds in sulfides and disulfides from which the aliphatic thiols are formed. A similar conclusion was drawn on the basis of the Siersza coal studies reported in our earlier paper.[22]

Figure 3 presents the AP-TPR kinetograms of Illinois No. 6 coal without the reducing mixture. Similar to Mequinenza coal, the potassium/liquid ammonia reduction causes a successive shift of the maximum of the peak ascribed to the nonthiophene sulfur toward lower temperatures, which suggests thiol formation and simultaneous disappearance of sulfides and disulfides. However, in the kinetograms of this coal, the position of the maximum of the peak corresponding to thiophene sulfur does not change, which can be explained by very small amounts of calcium compounds. This explanation is sustained by the results presented in Table 5, which show that Illinois No. 6 contains 6 times less calcium than Mequinenza coal.

Analysis of the same kinetograms (Figure 3) also indicates that potassium/liquid ammonia reduction leads to a successive decrease of the intensity of all signals, which is interpreted as a consequence of the decreasing content of sulfur and the value of sulfur recovery (Table 4). However, the content of thiophene sulfur (the peak at 680 °C) decreases faster than that of nonthiophene sulfur (the peak at 470 °C), which suggests that during the reduction in the potassium/liquid ammonia system certain C–S bonds in thiophene groups can also be broken. Results of earlier works[19,21] were interpreted as excluding such a possibility, however, the results of the studies performed on certain model compounds prove that some thiophenes can indeed be broken.[33] Such a reaction probably occurs for Mequinenza coal also, but it is difficult to observe because of the disturbing effect of calcium compounds. This problem will be discussed in more detail in our future paper devoted to investigations on demineralized coals.

Analysis of AP-TPR kinetograms obtained for the samples with the reducing mixture (Figure 4) revealed that the raw Illinois No. 6 coal originally contained a certain amount of aliphatic thiols (peak at about 200 °C). Reduction in the potassium/liquid ammonia system causes an increase in the intensity of the corresponding peak, but as a result of the second stage of the reduction, practically no new aliphatic thiols are formed (similar to the case of the Mequinenza coal). However, aromatic thiols are formed all the time, which is shown by a shift of the maximum of the peak at 450 °C toward lower temperatures. The AP-TPR experiments performed with addition of the reducing mixture confirm the low content of calcium compounds in Illinois No. 6 as there is no shift of the peak at about 700 °C. The change in the relative intensity of the peaks ascribed to thiophene and nonthiophene sulfur, indicating breaking of thiophene groups, is more visible in the kinetograms taken for the samples with the reducing mixture added. This is most probably related to the higher value of sulfur recovery when the reducing mixture is used (Table 4).

Reduction of coals in the potassium/liquid ammonia system leads to an increase in their solubility in organic solvents.[24] A detailed analysis of the soluble compo-

(33) Hückel, W.; Nabich, I. *Chem. Ber.* **1956**, *89*, 2115.

nents gives important information on the coal structure. The next step of our study was to determine the effect of extraction with dichloromethane on the sulfur compounds contained in coal. The extraction yield of the coals studied with dichloromethane is low and is 1.28% for raw Mequinenza and 5.03% and 6.52% after the first and second stage of potassium/liquid ammonia reduction, respectively, and 1.03% for raw Illinois No. 6 and 6.04% and 8.60% after the reductions.[32] For this reason, AP-TPR studies were performed for the extraction residues. A comprehensive listing of the coal extracts and the residues is given in earlier work.[32] The AP-TPR kinetograms of the Mequinenza and Illinois No. 6 residues are shown in Figures 5 and 6, respectively. Comparison with the kinetograms of the coals, Figures 1 and 3, allows one to conclude that extraction of the coals with dichloromethane has little effect on the sulfur compounds. This means that sulfur in these coals is preferably bound to their macromolecular structure and, thus, gets extracted only to a small degree. An independent confirmation of this conclusion is results from the total sulfur determination, indicating that the content of sulfur in the coals and in the residues is comparable (Table 4).

Conclusions

AP-TPR kinetograms of raw coals reveal the presence of two main broad peaks, appearing as a superposition of signals due to sulfur groups that undergo hydrogenation during an AP-TPR experiment, in a partially overlapping temperature range. This makes the interpretation of these kinetograms difficult. More information can be elicited from the kinetograms of coals modified in the potassium/liquid ammonia system. It has been shown that reduction of coals in such a system leads to conversion of sulfide and disulfide groups into thiol groups. The AP-TPR studies for the samples with addition of the reducing mixture verified the formation of different kinds of thiols during potassium/liquid ammonia reduction, indicated by the presence of different kinds of sulfides and disulfides in the raw coals studied (e.g. alkyl−alkyl, aryl−aryl, and aryl−alkyl). The results of the studies indicated a possibility of breaking the C−S bonds in the thiophene groups in the potassium/liquid ammonia system, which has been considered highly unlikely by other authors. Addition of the reducing mixture on the sulfur recovery values had a favorable influence, which was clearly demonstrated. This result is contradictory to the results obtained earlier for model compounds, which means that the conclusions drawn for simple compounds may not always hold for more complex substances such as coal. The data presented in this work fully confirmed our earlier observation of the unfavorable effect of calcium compounds on the results of AP-TPR analysis. The results of AP-TPR analysis of coals devoid of the fraction soluble in organic solvent were interpreted as indicating that sulfur was mainly bound to the macromolecular part of coals.