

Sulfur Analysis of Bolu-Mengen Lignite before and after Microbiological Treatment Using Reductive Pyrolysis and Gas Chromatography/Mass Spectrometry

S. Mullens,[†] J. Yperman,* and R. Carleer

Laboratory of Applied Chemistry, CMK, Limburgs Universitair Centrum,
B-3590 Diepenbeek, Belgium

T. Bozdemir and T. Durusoy

Department of Chemical Engineering, Hacettepe University,
Beytepe, TR-06532 Ankara, Turkey

Y. Yürüm

Faculty of Engineering and Natural Sciences, Sabanci University,
Tuzla, TR-34956 Istanbul, Turkey

Received July 12, 2004. Revised Manuscript Received February 17, 2005

Atmospheric pressure–temperature programmed reduction coupled with on-line mass spectrometry (AP–TPR/MS) is used for the first time on microbiologically treated coal samples as a technique to monitor the degree of desulfurization of the various sulfur functionalities. The experimental procedure enables the identification of both organic and inorganic sulfur species present in the coal matrix. A better insight in the degradation of the coal matrix and the accompanying processes during the AP–TPR experiment is obtained by a quantitative differentiation of the sulfur. The determination of the sulfur balance for the reductive pyrolysis gives an overview of the side reactions and their relative contribution in the total process. The volatile sulfur species are unambiguously identified using AP–TPR off-line coupled with gas chromatography/mass spectrometry (GC/MS). In this way, fundamental mechanisms and reactions that occur during the reductive pyrolysis could be quantified, explaining the differences in AP–TPR recoveries. Therefore, this study gives a clearer view on the possibilities and limitations of AP–TPR as a technique to monitor sulfur functionalities in coal.

Introduction

To minimize the emission of sulfur compounds during the combustion of fossil fuels, desulfurization has become an important issue in environmental care.^{1,2} In the area of precombustion desulfurization, the distinction is made between physical,³ chemical^{4–6} (both reductive as oxidative), and microbiological methods.^{7–9} The advantages of the latter method, like low costs, easy

experimental conditions, and little or no energy loss after treatment, have drawn great attention.

A variety of bacteria has been applied in removing sulfur from model compounds (mostly dibenzothiophene) and from coals.^{10,11} Bacterial activity depends on the kind and the concentration of the microorganism, the kind of coal, the surface area, the temperature, and the pH value.

The evaluation and comparison of different biotreatments and desulfurization procedures in general necessitate an adequate and unambiguous determination of the sulfur distribution in the sample. But despite numerous reports, the identification of sulfur functional groups and, more particularly, the organic sulfur present in the coal still causes many problems.⁷

In this report, biodesulfurized lignite samples are investigated with AP–TPR, AP–TPR/MS (atmospheric pressure–temperature programmed reduction/mass spec-

* Corresponding author. E-mail jan.yperman@luc.ac.be.

[†] Present address: Vlaamse Instelling voor Technologisch Onderzoek (VITO), Materials Technology, Boeretang 200, B-2400 Mol, Belgium.

(1) Vernon, J. L.; Jones, T. *IEACR/57*; IEA Coal Research: London, March 1993.

(2) Record, F. A.; Bubenick, D. V.; Kindy R. J. *Acid Rain Information Book*; Noyes Data Corp.: Park Ridge, NJ, 1982.

(3) Jagtoyen, M.; Groppo, J.; Derbyshire, F. *Fuel Proc. Technol.* **1993**, *34*, 85.

(4) Maes, I. I.; Mitchell, S.; Yperman, J.; Franco, D. V.; Marinov, S.; Mullens, J.; Van Poucke, L. C. *Fuel* **1996**, *75* (11), 1286.

(5) Álvarez, R.; Clemente, C.; Gómez-Limón, D. *Environ. Sci. Technol.* **1997**, *31* (11), 3148.

(6) Van Aelst, J.; Yperman, J.; Franco, D. V.; Mullens, J.; Van Poucke, L. C.; Palmer, S. R. *Fuel* **1997**, *76* (14/15), 1377.

(7) Olson, G. J. *Fuel Process. Technol.* **1994**, *40*, 103.

(8) Klein, J.; van Afferden, M.; Pfeifer, F.; Schacht, S. *Fuel Proc. Technol.* **1994**, *40*, 297.

(9) Juszcak, A.; Domka, F.; Kozłowski, M.; Wachowska, H. *Fuel*, **1995**, *74*(5), 725.

(10) Karavaiko, G. I.; Lobyreva, L. B. *Fuel Proc. Technol.* **1994**, *40*, 167.

(11) Olsson, G.; Pott, B. M.; Larsson, L.; Holst, O.; Karlsson, H. T. *Fuel Proc. Technol.* **1994**, *40*, 277.

trometry) and AP-TPR off-line coupled with GC/MS. By combining the quantitative information of the potentiometric detection and qualitative information of the mass spectroscopic data, the degradation process of these coal samples can be described in more detail. The AP-TPR profiles are assigned by comparison with AP-TPR/(MS) profiles of model sulfur compounds.¹² The temperature region in which certain sulfur species are reduced or hydrogenated can be confirmed by following the accompanying evolution of other volatile organic aliphatic and aromatic compounds.

The reliability of the AP-TPR assignments and sulfur distributions greatly depends on the amount of H₂S released during the pyrolysis. AP-TPR experiments on a wide variety of coal samples (and other solid materials) show that the reduction efficiency of the sulfur functionalities scatters broadly as a function of coal type, the mineral content, or the pretreatment.¹³ Especially sulfates (apart from iron sulfate) and oxidized coal samples are characterized by a low AP-TPR sulfur recovery, making its sulfur analysis by AP-TPR, using only the potentiometric detection system, doubtful.

This problem is however not reserved for samples with high level of oxidized sulfur functionalities. A recent report by Rutkowski et al.¹⁴ also showed low sulfur recoveries for pyridine extracts, caused by the release of small amounts of volatile sulfur species in the lower temperature range not hydrogenated in to H₂S (alkane thiols, thiophene, and its C₁-C₂ alkylated derivatives) and the entrapment of sulfur species in the tar and char fraction. These mechanisms and side reactions have also been observed in thiophene-based model compounds.¹²

The on-line coupling of the AP-TPR setup with a mass spectrometer together with a more elaborate experimental scheme for each sample offers a more detailed and semiquantitative view of these mechanisms. The oxidation of the residue after the AP-TPR experiment (AP-TPO) provides information on the organic and inorganic sulfur species that are incorporated in the tar and char fraction. On the other hand, the atmospheric pressure-temperature programmed pyrolysis (AP-TPP) of the sample in an inert atmosphere can be useful for the determination of oxidized sulfur species.

However, as the unambiguous identification of sulfur-containing compounds using MS is greatly hindered by the simultaneous degradation of the coal matrix, fractions of the evolved gases at different temperature intervals are also investigated using an off-line GC/MS detection system coupled with the AP-TPR setup.

As the signals of the mass spectrometer are difficult to interpret in a quantitative manner, the total sulfur content of the char fraction and the tar fraction are measured by oxygen bomb combustion. Combining all this with the potentiometric analysis of the amount of H₂S fraction, the sulfur balance for the reductive pyrolysis of a sample can be determined in a more

quantitative manner. This procedure gives insight in the relative contribution of each side reaction in the total pyrolysis process.

Experimental Section

AP-TPR, AP-TPR/MS, and AP-TPO/MS. The detailed description of the AP-TPR/(MS) procedure and experimental setup can be found elsewhere.¹² The sample is mixed with fumed silica and placed in the AP-TPR reactor. The sulfur-containing sample is heated at a steady heating rate (5 °C min⁻¹) in an atmosphere of pure hydrogen gas (100 mL min⁻¹), which will reduce or hydrogenate the different sulfur functionalities in discrete temperature regions. This results in a maximum H₂S evolution in a temperature region that is characteristic for each sulfur group. To measure the H₂S using the potentiometric detection system, the pyrolysis gases are bubbled through an aqueous solution of sulfide antioxidant buffer and converted into HS⁻ and S²⁻. Ion-selective electrodes are used to continuously measure the latter. The obtained AP-TPR profile is presented as the differentiation of the S²⁻ signal (in mg of sulfur/g of sample) as a function of the temperature of the reactor.

The shown AP-TPR profiles and H₂S recoveries are an average of at least two experiments. All AP-TPR profiles are normalized, meaning that the raw AP-TPR data are divided by the experimental AP-TPR sulfur recovery and multiplied by the total sulfur content. This procedure enables a more quantitative comparison between samples of AP-TPR profiles, using the potentiometric detection system, with different yields.

Apart from the potentiometric detection of the S²⁻, all evolved gases can also continuously be measured by a mass spectrometer, as a function of the temperature of the furnace. The mass spectrometer (Fisons-VG Thermolab MS) is on-line connected after the water cooler of the AP-TPR reactor by a heated capillary (170 °C). This experimental setup enables a deeper insight on the competing and successive reactions that are occurring during the pyrolysis.

Apart from the reducing pyrolysis, the sample can also be studied under an inert atmosphere (100 mL/min He) (i.e. AP-TPP coupled on-line with MS). Certainly when oxidized sulfur functionalities are present, the inert pyrolysis gives useful information by measuring the SO₂ evolution.

The characterization of the tar and char fraction after an AP-TPR experiment is done by atmospheric pressure-temperature programmed oxidation (AP-TPO/MS). Therefore, the tar and char fractions that remain in the reactor after the reductive pyrolysis are collected and subsequently heated (to 1200 °C at 20 °C/min) in a continuous flow of pure oxygen (100 mL/min). During the combustion of this residue, sulfur species will be oxidized and decomposed, leading principally to the release of SO₂. The evolution of SO₂ as a function of temperature during this oxidative pyrolysis gives insight into the nature of the sulfur functionalities remaining in the tar/char fraction and completes the analysis of the sulfur distribution. Experiments with model sulfur compounds have shown that a differentiation between residual organic and inorganic sulfur species in the tar and char fraction is possible by this procedure.¹²

A schematic view of the full experimental procedure is given in Figure 1.

Samples. Bolu-Mengen lignite from the Western Black Sea area (Turkey) was chosen for the biodesulfurization procedure for its high total sulfur content. It was ground in a ball mill, sized to <63 μm, and dried at 106 °C before subjecting the sample to the biodesulfurization procedure. The proximate analysis of the untreated sample (sample 1) showed a moisture content of 3.6 wt %. The volatile matter, the ash content, and the fixed carbon content of this sample constituted 46.5, 12.6, and 37.3 wt %, respectively.

(12) Mullens, S.; Yperman, J.; Reggers, G.; Carleer, R.; Buchanan, A. C., III; Britt, P. F.; Rutkowski, P.; Gryglewicz, G. *J. Anal. Appl. Pyrolysis* **2003**, *70*, 469.

(13) Yperman, J.; Maes, I. I.; Van den Rul, H.; Mullens, S.; Van Aelst, J.; Franco, D. V.; Mullens, J.; Van Poucke, L. C. *Anal. Chim. Acta* **1999**, *395*, 143.

(14) Rutkowski, P.; Gryglewicz, G.; Mullens, S.; Yperman, J. *Energy Fuels* **2003**, *17*, 1416.

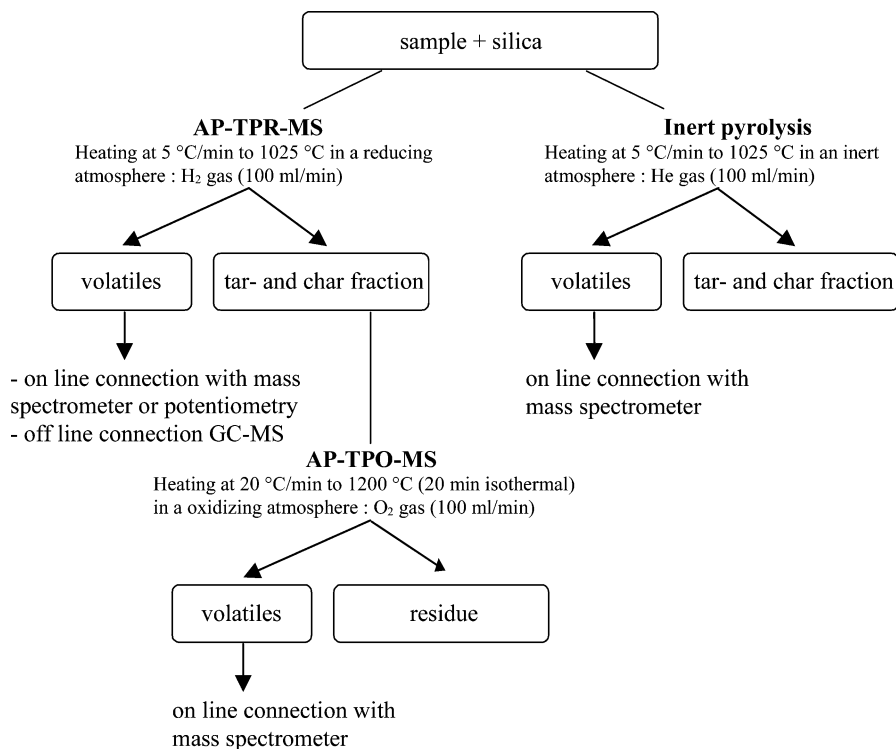


Figure 1. Scheme of the experimental procedure.

Biodesulfurization. Although the details of this procedure are already described elsewhere,¹⁵ some important aspects will be given here.

Previous studies revealed that *Rhodococcus rhodochrous*, a dibenzothiophene degrading microorganism, can remove organic sulfur from coal (unlike *Thiobacillus ferrooxidans* or *Thiobacillus thiooxidans*) and is already used for the desulfurization of petroleum.^{7,16} Furthermore, its optimum growth temperature of 28 °C could be of economic interest.

The coal sample was not washed before the treatment with *R. rhodochrous*. A pure culture of this bacterium was obtained from ATCC (American Type Culture Collection) with strain no. 53968. To ensure sterile conditions in the biodesulfurization procedure, the medium was autoclaved at 121 °C for 20 min.

The lignite was added to the culture 24 h after the inoculation of the medium (20 mM sodium acetate) with the bacterium. Periodic sampling from the culture media was done at $t = 50$ h (sample 2) and $t = 96$ h (sample 3).

After the treatment, the samples were filtered from the medium, washed with distilled water, and dried at 106 °C. Taking into account the dry weight of the microorganism at the optimum growth conditions (0.05 g L⁻¹) and the amount of sample used for the experiment (20 g L⁻¹), biomass contamination in this procedure is unlikely. The desulfurization experiments were performed together with control experiments. These blank experiments that contained no culture did not show a significant change in sulfur content of the coal samples.¹⁷

The total sulfur content (as determined by the Eschka method¹⁸) together with the sulfur distribution (according to ASTM method D2492) and the AP-TPR sulfur recoveries are presented in Table 1.

Table 1. Total Sulfur Content, Sulfur Distribution (according to ASTM D2492), and the AP-TPR Recoveries of the Investigated Samples

| | $t_{\text{desulfurization}}$ (h) | S_{total} (wt %, db ^a) | S_{organic} (wt %, db) | S_{pyritic} (wt %, db) | S_{sulfate} (wt %, db) | sulfur yield (%) |
|----------|-------------------------------------|--|------------------------------------|------------------------------------|------------------------------------|------------------------|
| sample 1 | 0 | 12.9 | 8.5 | 1.5 | 2.9 | 64 |
| sample 2 | 50 | 9.3 | 8.0 | 1.2 | 0.1 | 88 |
| sample 3 | 96 | 8.6 | 7.5 | 1.1 | 0.0 | 90 |

^a db stands for dry basis.

Determination of the Sulfur Balance. As the determination of the sulfur balance for the reductive pyrolysis involves the measurement of the sulfur content of both tar and char fraction, several duplicate AP-TPR experiments were performed. After each experiment, the tar fraction which was deposited in the region of the reactor just above the furnace was separated from the AP-TPR reactor by washing with chloroform.

The total sulfur content in the tar and char fraction was determined using oxygen bomb combustion. Enough tar and char was collected to run the analysis in triple. All shown values, with error bar, are averages of these three measurements. The sulfate content in the absorption liquid (2.5% Na₂CO₃ solution) is measured by ion chromatography (model Dionex Series 2000i/SP; separation column AS4A; eluent Na₂CO₃ (2.4 mM)/NaHCO₃ (1.9 mM)).

Gas Chromatography/Mass Spectrometry. The identification of the volatile sulfur species that are released during the reductive pyrolysis of sample 1 is performed by adsorption/desorption experiments. The outlet of the AP-TPR reactor is connected to a dry-ice-cooled tube containing tenax, a porous polymer of 2,6-diphenyl-*p*-phenylene oxide. The adsorption is performed in three temperature ranges during an AP-TPR experiment: between 290 and 305 °C, between 390 and 405 °C, and between 490 and 505 °C. Each collection period lasts 3 min. After thermal desorption at 240 °C, the adsorbed gases are transferred to the GC/MS. The gas chromatograph (type Trace 2000, Thermoquest) is equipped with a CP-SIL-5CB column ($L = 25$ m, thickness = 5 μm, $\Phi = 0.32$ mm). The temperature program is as follows: isothermal for 1 min at

(15) Bozdemir, T. Ö.; Durusoy, T.; Erincin, E.; Yürüm, Y. *Fuel* **1996**, *75*(13), 1596.

(16) Kilbane, J. J.; Bielaga, B. A. *DOE/PC/88891-T8 1991*; US Department of Energy, Office of Science and Technical Information: Oak Ridge, TN, 1991.

(17) Durusoy, T.; Özbaz, T.; Tanyolac, A.; Yürüm, Y. *Energy Fuels* **1992**, *6*, 804.

(18) Durusoy, T.; Bozdemir, T. Ö.; Erincin, E.; Yürüm, Y. *Fuel* **1997**, *76* (4), 341.

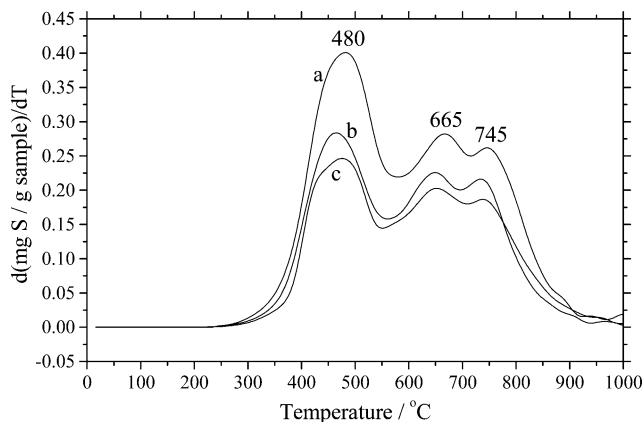


Figure 2. AP-TPR kinetograms of (a) untreated sample and the samples biodesulfurized for (b) 50 h and (c) 96 h (potentiometric detection system).

35 °C, heating to 260 °C at 10 °C/min, followed by an isothermal period for 5 min. The temperature of the transfer line to the quadripole MS (type Voyager, Thermoquest) is 280 °C.

Results and Discussion

AP-TPR On-Line Coupled with the Potentiometric Detection System. The AP-TPR profile of the untreated sample (sample 1) is shown in Figure 2a. It consists of a major peak at 480 °C and two smaller maxima at 665 and 745 °C. The peak at 480 °C can be assigned to the presence of dialkyl and alkyl aryl sulfides. From AP-TPR experiments performed on coals with high pyrite content, it could be concluded that the hydrogenation of pyrite occurs also between 500 and 600 °C.¹⁹ For all the samples in this study, the pyrite content is not high enough to observe the hydrogenation of pyrite as a resolved maximum in the AP-TPR profile. As a consequence, the degree of desulfurization of pyrite cannot be followed in this case. The broad maximum at 665 °C indicates the presence of diaryl sulfides. The peak at 745 °C is caused by the reduction of complex thiophenes. As the coal samples were not acid-washed before biodesulfurization, sulfates are likely to be present in the coal (Table 1). This results in an increase in the AP-TPR signal above 900 °C for sample 1. Due to the low sulfur recoveries for inorganic sulfates, the AP-TPR intensities in this region are not a good measure for the amount of oxidized inorganic sulfur groups that are actually present in the sample.²⁰

The AP-TPR profiles of the biodesulfurized samples are given in Figure 2b,c. Periodic sampling from the biodesulfurization reactor occurred at 50 h (Figure 2b) and 96 h (Figure 2c). Both profiles consist of the same maxima as those for the untreated sample. The assignment is therefore analogous. But the intensity of all peaks has diminished, indicating a continuous biodesulfurization of all sulfur groups present in the coal.

The lowering of the intensity of the peak at 480 °C for sample 2 is slightly more expressed compared to the lowering of the other maxima. A possible explanation is that, in the early stages of the biodesulfurization,

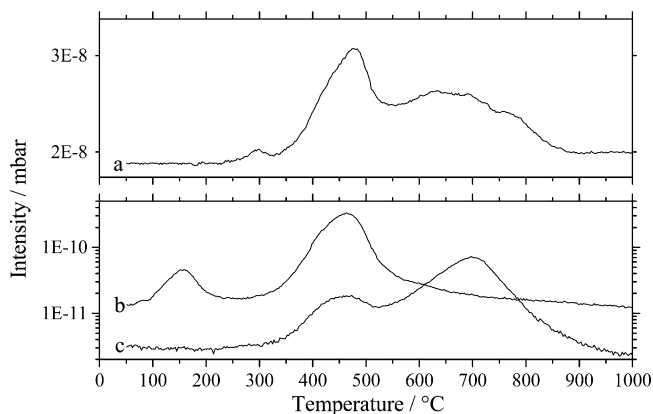


Figure 3. The evolution of (a) the total pressure and (b) alkanes ($C_3H_7^+$, $m/z = 41$) and (c) aromates ($C_6H_6^+$, $m/z = 78$) during the reductive pyrolysis of sample 1.

dialkyl and alkyl aryl sulfides are preferably attacked. A longer reaction time (sample 3) will cause further biodesulfurization of all sulfur groups present in the coal.

These trends are confirmed by the gradual lowering of the total sulfur content (Table 1) and the evolution of the sulfur distribution determined by ASTM D2492 (Table 1), showing a desulfurization of all sulfur groups in the early stages of the reaction.

Table 1 lists the AP-TPR sulfur yields as H_2S using the potentiometric detection system for all samples. The major part of the sulfur present in the treated samples—88 and 90%—is converted to H_2S in an AP-TPR experiment. For sample 1, this is only 64%. This difference in the AP-TPR H_2S recovery is in part a result of the relatively high content of sulfate sulfur (22.5% of the total amount of sulfur present, which is almost not reduced to H_2S under these AP-TPR conditions²⁰) and the high ash content (12.5%, acting as a H_2S catcher²¹) and will be further investigated using AP-TPR/MS and the determination of the total sulfur balance.

AP-TPR/MS. Degradation of the Coal Matrix. Figure 3a presents the evolution of the total pressure (i.e. the sum of all partial pressures measured by the mass spectrometer) during the degradation of sample 1. Clearly, the pyrolysis of the coal matrix is a two-steps process with a maximum at 480 °C and a broad maximum between 550 and 850 °C. There is a small maximum found around 300 °C that can be attributed to adsorbed small, but easy to evaporate, molecules in the coal matrix.

The second maximum (Figure 3a) at 480 °C coincides with that for H_2S (Figure 2a) and is attended with the liberation of predominantly alkanes. As exemplified in Figure 3b by the liberation of $C_3H_7^+$ ($m/z = 43$), all signals that can be assigned to alkanes give—apart from the small maximum at 160 °C—a maximum only at 480 °C. The simultaneous release of both species, H_2S and alkanes, at this temperature confirms the attribution of the first maximum in the AP-TPR profile (Figure 2a) not only to the hydrogenation of dialkyl but also to mixed alkyl aryl sulfides. Indeed, for aromatics, as shown by Figure 3c, a first evolution peak of a typical compound at around 480 °C can be observed.

(19) Gryglewicz, G.; Wilk, P.; Yperman, J.; Franco, D. V.; Maes, I. I.; Mullens, J.; Van Poucke, L. C. *Fuel* **1996**, *75*, 13.

(20) Van Aelst, J.; Yperman, J.; Franco, D. V.; Van Poucke, L. C.; Buchanan, A. C., III; Britt, P. F. *Energy Fuels* **2000**, *14*, 1002.

(21) Maes, I. I.; Gryglewicz, G.; Yperman, J.; Franco, D. V.; Mullens, J.; Van Poucke, L. C. *Fuel* **1997**, *76* (2), 143.

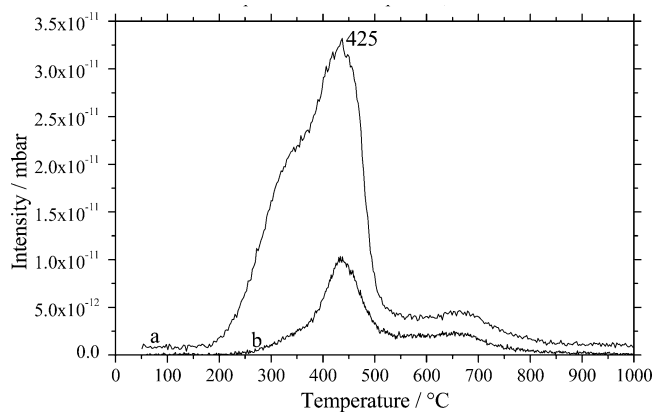


Figure 4. The release of SO_2 ($m/z = 48 + m/z = 64$) for (a) sample 1 and (b) sample 3 during the reductive pyrolysis.

Table 2. Overview of the Sulfur Species Evolved during the Reductive Pyrolysis of Sample 1 in Three Temperature Regions as Detected by GC/MS

| | t_R (min) | 290–305 °C | 390–405 °C | 490–505 °C |
|---------------------------|----------------|---------------|---------------|---------------|
| sulfur dioxide | 0.8 | ¥ | ¥ | |
| methanethiol | 1.2 | ¥ | | |
| thiophene | 4.0 | ¥ | ¥ | |
| methylthiophene | 6.1/6.2 | ¥ | ¥ | |
| dimethylthiophene | 8.1 | ¥ | ¥ | |
| trimethylthiophene | 8.8/10.1 | | ¥ | |
| toluenethiol | 8.9 | | ¥ | |
| ethylthiophene | 9.7 | ¥ | | |
| methylethylthiophene | 9.7 | ¥ | | |
| diethylthiophene | 10.9 | | ¥ | |
| (methylthio)methylbenzene | 11.7 | | ¥ | |
| butylthiophene | 12.2 | ¥ | | |
| ethylpropylthiophene | 13.0 | | ¥ | |
| benzothiophene | 13.5/13.8 | | | ¥ |
| benzothiazole | 14.2 | ¥ | | |
| methylbenzothiophene | 15.3 | | | ¥ |

The broad maximum, in Figure 3a, between 550 and 800 °C is only caused by the increase of signals typically related to aromatics (Figure 3c), as indicated by the evolution of benzene (C_6H_6^+ , $m/z = 78$). The liberation of toluene (C_7H_7^+ , $m/z = 91$) is completely similar to that of benzene and therefore not shown in this figure. No alkanes could be observed in this temperature region. The maxima of H_2S (Figure 2a) in this temperature region were therefore attributed to the hydrogenation of diaryl sulfides and complex thiophenes, respectively. The degradation of both is known to involve the formation of aromatics.²²

AP–TPR/MS. Release of Other Sulfur Species.

Figure 4 presents the evolution of SO_2 for samples 1 and 3, as calculated by the sum of $m/z = 64$ (SO_2^+) and $m/z = 48$ (SO^+) (both profiles exhibit the same trend). For sample 1 (Figure 4a), the release of SO_2 starts earlier than that of H_2S (Figure 2a), namely at 200 °C, and gives a maximum around 425 °C. Above 480 °C, the signal for SO_2 decreases rapidly, due to the larger hydrogenating capacity of hydrogen gas at higher temperatures under these AP–TPR circumstances. This means that from this temperature SO_2 is maximally reduced to H_2S .

The intensity of the SO_2 profile for sample 3 (Figure 4b) has decreased substantially compared with that of sample 1. The release of SO_2 also starts at higher

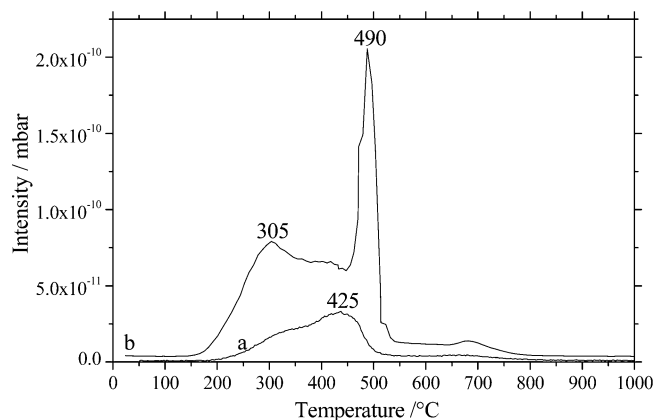


Figure 5. The evolution of SO_2 ($m/z = 48 + m/z = 64$) for sample 1 in H_2 (a) and in He (b).

temperatures (around 250 °C), although less steep and intense, and the low-temperature shoulder (Figure 4a) in the SO_2 profile has almost completely disappeared. Therefore, the release of SO_2 for sample 1 must be attributed to the degradation of organic sulfonic acids¹² for the lower temperature range (shoulder around 350 °C), and the peak maximum around 425 °C refers to the degradation of sulfones.²⁰ The small peak found at the higher temperature zone of around 675 °C for sample 1 and 3 can be attributed to some small amounts of sulfoxides.²⁰ Although one has to keep in mind that, in this temperature range, the H_2 gas reduction capacity is much more pronounced. This may not mislead us into concluding that its amounts are much smaller than the one found for sulfonic acids and sulfones, as could be suggested by their intensities in Figure 4a,b. For sample 3, one must conclude that most of the organic sulfates are biodesulfurized [the absence of a shoulder in the lower temperature range in the SO_2 profile (Figure 3b)] and that only sulfones and sulfoxides are still present, although to a lesser extent [peak maxima are found around the same temperature values but with lower intensities (again precaution is needed since comparison of MS intensities signals of different samples is quantitatively not really possible)]. However, the release of SO_2 cannot completely account for the differences in AP–TPR sulfur yield using the potentiometric detection system (Table 2) between samples 1 and 3.

The detection of other sulfur-containing species apart from H_2S and SO_2 with a mass spectrometer is also greatly hindered by the decomposition of the coal matrix. This degradation leads to complicated MS spectra because of the lack of a preceding separation of the evolving volatiles. This makes the unambiguous identification of other sulfur groups such as thiols, sulfides, or thiophene derivatives unlikely in the current experimental setup. Therefore, a further modification of the experimental setup was established. The AP–TPR system was coupled off-line with a GC/MS. The evolved gases, as already mentioned, are first adsorbed on tenax tubes (cooled in dry ice) at different preset temperatures ranges and afterward desorbed and analyzed by GC/MS.

AP–TPP/MS. Pyrolysis in Inert Atmosphere.

Pyrolyzing of the samples in an inert atmosphere can give additional information on the nature of oxidized sulfur species. Figure 5 compares the SO_2 evolution (a)

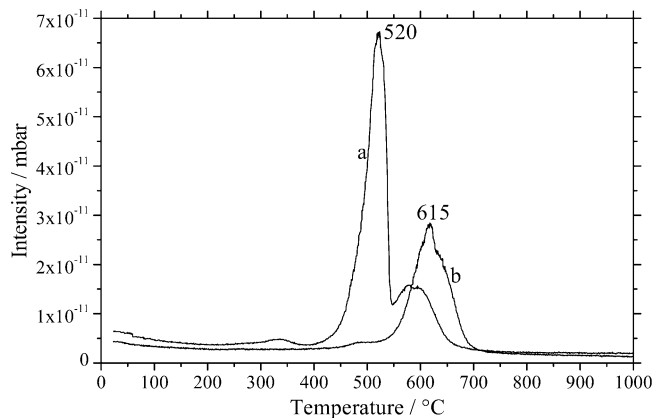
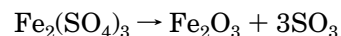
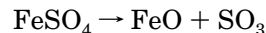


Figure 6. The evolution of SO_2 ($m/z = 48 + m/z = 64$) for (a) 10 mg of FeSO_4 and (b) 5 mg of $\text{Fe}_2(\text{SO}_4)_3$ both in He.

in H_2 and (b) in He for sample 1. Obviously, the atmosphere influences both the intensity and the profile itself. The more substantial release of SO_2 in He (Figure 5b) starts earlier (at 150 °C) and shows a first maximum at 305 °C and a very steep peak at 490 °C. In this case, the broad SO_2 signal can be assigned to oxidized organic as well as to inorganic sulfur forms. Therefore, in Figure 5b, at the lower temperature range the SO_2 signal can be assigned to organic sulfonic acids and at higher temperature to sulfones (maximum around 400 °C) and to sulfoxides (higher temperature range, last maximum around 700 °C). More noticeable is the sharp signal at 490 °C referring to the reduction of iron sulfate. In a reducing atmosphere this maximum completely disappears (Figure 5a); additionally, the intensity of the whole SO_2 signal in H_2 is also significantly lower below 450 °C, meaning that SO_2 is nevertheless also partly reduced to H_2S (the catalytic effect of iron sulfate combined with the extra presence of H_2 and the reducing ability of the coal matrix). Since the hydrogen gas reduces SO_2 maximal at temperatures above 450 °C, the maximum at 490 °C in the evolution of SO_2 in He (Figure 5b) will thus not be found in the experiment in H_2 (Figure 5a). The sharp shape of this peak (Figure 5b) points to a fast release of SO_2 , which might indicate that a very specific sulfur-containing compound degrades at this temperature, resulting in the liberation of SO_2 . This compound has, as already mentioned, been identified as iron sulfate.

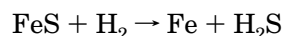
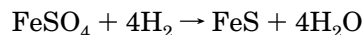
In Figure 6 the release of SO_2 during the pyrolysis of (a) iron(II) sulfate and (b) iron(III) sulfate in an inert atmosphere is shown.

In the kinetogram of iron(II) sulfate, a sharp maximum indeed occurs around 520 °C, similar to the release of SO_2 in the pyrolysis of sample 1 (Figure 5b). The small shift of the reduction temperature toward a higher value is the result of some matrix effects.¹³ The second maximum at 590 °C in Figure 6a is probably caused by the presence of small amounts of iron(III) sulfate (a shift to lower reduction temperature must again be attributed to some matrix and occurrence aspects). This iron(III) compound, when using an almost pure state, gives a less intense but clear degradation signal for SO_2 at around 615 °C (Figure 6b). The degradation reactions of these compounds can be written as follows:



These reactions thus release SO_2 during the pyrolysis in an inert atmosphere for sample 1 (Figure 5b).

In an reducing atmosphere, iron(II) sulfate will, to some extent, be converted into troilite, which is hydrogenated to H_2S at higher temperatures, according to^{19,23}



As the hydrogenation of dialkyl and alkyl aryl sulfides occurs in the same temperature region, the last two reactions will interfere with a qualitative analysis of the sulfur functionalities, resulting in an overestimation of these organic sulfides by the AP-TPR analysis.

As sample 3 does not contain any iron sulfates, no SO_2 peak at 490 °C could be detected (profile thus not shown).

AP-TPO/MS. Combustion of Tar and Char Fraction. Apart from the liberation of SO_2 during an AP-TPR experiment, a second side reaction has to be considered. From experiments with model compounds, it is known that some part of the sulfur remains in the residue after an AP-TPR experiment in H_2 .²⁴ Combustion of tar and char fractions of sulfur model compounds have shown that organic sulfur species that remain in the residue after reductive pyrolysis are oxidized during the AP-TPO experiment in the temperature range up to 600 °C. Inorganic sulfur model compounds showed a release of SO_2 during the AP-TPO experiment in the temperature range between 600 and 1200 °C.

Figure 7 shows the evolution of some m/z values during the combustion of the combined tar and char fraction of sample 1. In the first temperature range, between 200 and 600 °C, CO_2 (Figure 7a), SO_2 (Figure 7b), acetic acid (Figure 7c), and a small amount of benzene (Figure 7d) are released. The evolved SO_2 in this temperature range originates from the oxidation and subsequent decomposition of organic sulfur compounds that are incorporated in the tar and char fraction during the AP-TPR experiment. Cross-linking and/or aromatization reactions can form complex thiophenes that are to some extent resistant to hydrogenation under the experimental conditions of an AP-TPR experiment. In the second temperature range of the AP-TPO profile, between 900 and 1200 °C (Figure 7b), only SO_2 can be detected, caused by the oxidation of metal sulfides and/or the degradation of inorganic sulfates.

Determination of the Sulfur Balance. The sulfur yield in an AP-TPR experiment reflects the balance between complete hydrogenation and side reactions: (1) the formation and volatilization of sulfur species that are not reduced or hydrogenated to H_2S (leading to a sulfur enrichment of the tar fraction or the release of

(23) Maes, I. I.; Yperman, J.; Van den Rul, H.; Franco, D. V.; Mullens, J.; Van Poucke, L. C.; Gryglewicz, G.; Wilk, P. *Energy Fuels* **1995**, *9*, 950.

(24) Brown, S. D.; Sirkecioglu, O.; Snape, C. E.; Eglinton, T. I.; *Energy Fuels* **1997**, *11*, 532.

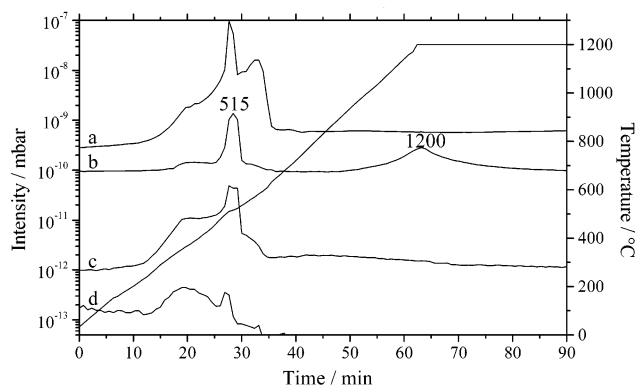


Figure 7. Release of (a) CO_2^+ ($m/z = 44$), (b) SO_2 ($m/z = 48 + m/z = 64$), (c) CH_3COOH^+ ($m/z = 60$), and (d) C_6H_6^+ ($m/z = 78$) during the combustion of the tar and char fraction of sample 1.

volatile sulfur species) and (2) the incorporation of sulfur species in the char fraction during the aromatization.

By analyzing the total sulfur content in the tar fraction and in the char fraction collected after an AP-TPR experiment, the relative contribution of each side reaction can be determined. The differentiation of the total sulfur enables a quantitative sulfur balance of the reductive pyrolysis:

$$S_{\text{tot}} = S_{\text{H}_2\text{S}} + S_{\text{tar}} + S_{\text{char}} + S_{\text{res}}$$

Each fraction corresponds with a certain type of reaction: (1) sulfur released as H_2S ($S_{\text{H}_2\text{S}}$, i.e., sulfur completely reduced or hydrogenated to H_2S), (2) sulfur incorporated in the tar fraction (S_{tar} , i.e., semivolatile sulfur species condensing at cold spots in the reactor), (3) sulfur incorporated in the char fraction (S_{char} , i.e., nonvolatile sulfur species either present or formed during the AP-TPR experiment and resistant to the hydrogenating conditions of an AP-TPR experiment, e.g. complex thiophenic structures, some metal sulfides or sulfates), and (4) the rest fraction (S_{res}) corresponds to noncondensable volatile sulfur species (apart from H_2S).

The rest fraction can be calculated by difference from the original total sulfur content of the sample and the sulfur yield as H_2S using the potentiometric detection system and the sulfur content in the tar and char fraction collected after an AP-TPR experiment, all measured by oxygen bomb combustion.

Figure 8 shows the sulfur content (in mg of sulfur/g) for each term in the sulfur balance for samples 1 and 3. The relative contribution with regard to the total sulfur content in the sample is presented above each bar.

For the untreated sample (sample 1), 10% of the total sulfur content remains in the char fraction after an AP-TPR experiment. The tar fraction consists of 5% of the original sulfur. From the AP-TPO/MS experiment (Figure 7), it is clear that these sulfur species are a combination of both organic and inorganic species, either present or formed during the reductive pyrolysis itself. The rest fraction, about 21% (by difference), consists of volatile sulfur species (other than H_2S) that are not (completely) reduced during the reductive pyrolysis. Most probably, these sulfur species are released in the lower temperature region, as the reduction efficiency of H_2 and the coal matrix are low. A full

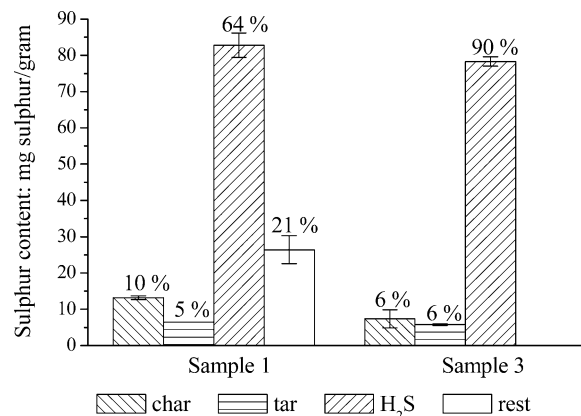


Figure 8. Sulfur content (in mg of S/g of sample) in the char fraction, the tar fraction, released as H_2S , and the rest fraction for the reductive pyrolysis of samples 1 and 3.

identification of these kinds of species is performed using GC/MS (see further).

For the microbiologically treated sample (sample 3), 90% of the remaining sulfur is converted to H_2S during the AP-TPR experiment. About 6% of the original sulfur remains in the char fraction, while about the same fraction is condensed in the tar fraction. As the sum of these three contributions exceeds already the total sulfur content in the sample, it is assumed that no rest fraction is liberated during the reductive pyrolysis (as could be confirmed by an AP-TPR/GC/MS experiment).

From these results, it can be concluded that the microbiological treatment predominantly affects the evolution of volatile sulfur species. The substantial differences in AP-TPR sulfur yield using the potentiometric detection system (Table 1) between samples 1 and 3 are mainly caused by the evolution of volatile sulfur species (inorganic as organic).

AP-TPR/GC/MS. Identification of volatile sulfur species. As the fraction of volatile, noncondensable sulfur species is substantial in the sulfur balance for sample 1, identification of these sulfur species is performed by AP-TPR/GC/MS. Gases evolving from the AP-TPR reactor are first adsorbed on tenax and analyzed off-line by GC/MS after been desorbed. Figure 9 shows the chromatograms of the evolved gases during such an AP-TPR experiment of sample 1 in three temperature regions: (a) between 290 and 305 °C, (b) between 390 and 405 °C, and (c) between 490 and 505 °C.

The retention time and the identification of the sulfur species are summarized in Table 2. From this table, it can be concluded that at the start of the pyrolysis, i.e., from 300 °C, several sulfur species are released. Apart from mainly H_2S and SO_2 , also methanethiol and thiophene and its methyl and ethyl derivatives are detected. These findings are consistent with early work²⁵ using GC/MS on-line coupled with the AP-TPR setup.

At higher temperature, somewhat more complex thiophene derivatives are released (like trimethyl-, diethyl-, ethylpropyl-substituted species), together with toluenethiol and (methylthio)methylbenzene. At 500 °C,

(25) Stefanova, M.; Marinov, S.; Carleer, R.; Yperman, J. *Ecol. Future* 2003, II (3-4), 83.

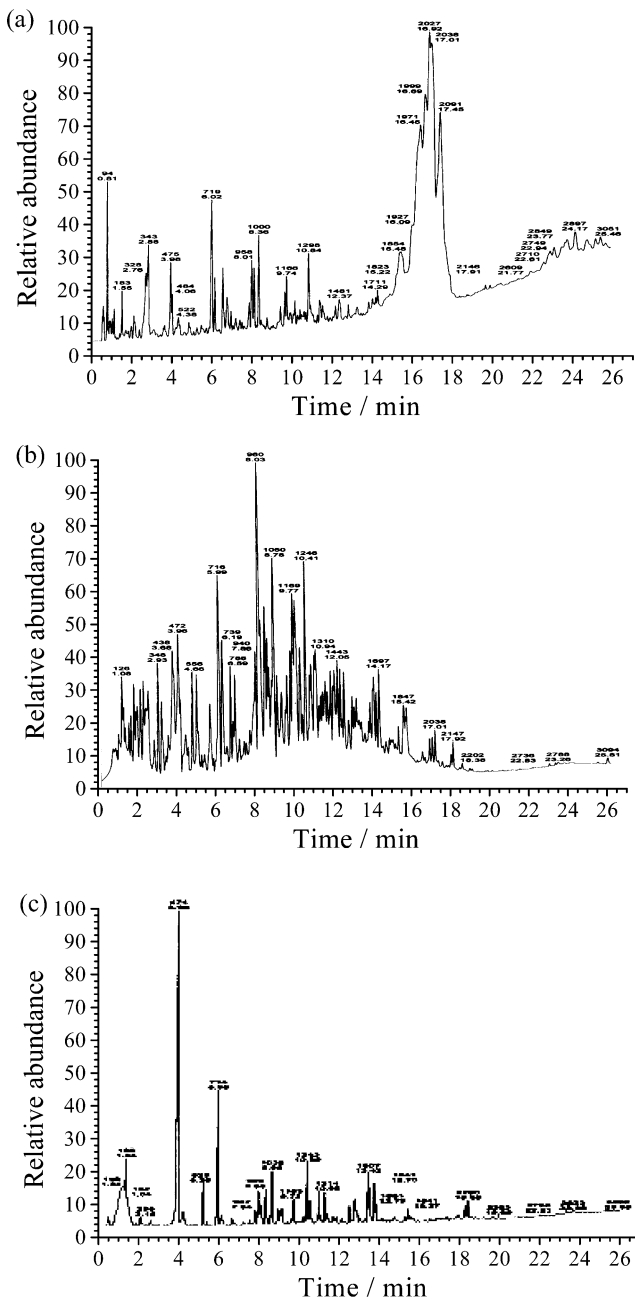


Figure 9. GC/MS chromatogram of the evolved gases adsorbed on tenax in the temperature region between (a) 290 and 305 °C, (b) 390 and 405 °C, and (c) 490 and 505 °C during the reductive pyrolysis of sample 1.

only high-boiling thiophene derivatives are detected. It is likely that these species also contribute to the incorporation of sulfur in the tar fraction by partly condensing above the oven.

Conclusions

Concerning the biodesulfurization of Bolu-Mengen lignite, the AP-TPR experiments clearly show that the bacterium *R. rhodochrous* is able to remove partially all kind of sulfur groups that are present in this type of coal. The removal of the total sulfur content up to 33% makes the biodesulfurization an interesting alternative for other, mostly chemical, methods.

A more fundamental insight in the reductive pyrolysis and the accompanying reactions, apart from the hydrogenation to H_2S , is gained by coupling the AP-TPR reactor to a mass spectrometer. However, the unambiguous identification of volatile sulfur species using AP-TPR/MS, apart from the small quantities of SO_2 , is hindered by the simultaneous degradation of the coal matrix.

Using off-line GC/MS, other sulfur volatiles, such as methanethiol and thiophene and its derivatives are identified. These species are not hydrogenated to H_2S due to the insufficient reduction efficiency of the H_2 gas, especially in the lower temperature regions.

The combustion of the tar and char residues after the reductive pyrolysis shows the presence of both organic and inorganic sulfur species, either formed in situ or present in the coal as reduction resistant in the temperature range of an AP-TPR experiment.

The fundamental reactions that occur during the reductive pyrolysis can be quantified by constructing a total sulfur balance. For this type of coal, about 10% of the total sulfur in the sample is incorporated in the char fraction. Semivolatile sulfur species account for up to 6% of the total sulfur. The differences in sulfur yields can be mainly attributed to the evolution of noncondensable sulfur volatiles for sample 1 (21% of the total sulfur), to a large extent evolving at the start of the degradation. Especially in case of low sulfur yield, a complete quantitative sulfur balance is a valuable tool in obtaining a more fundamental insight in the competing and successive reactions that are occurring during the reductive pyrolysis.

By pyrolyzing in an inert atmosphere, iron sulfate could be identified as part of the oxidized sulfur present in the untreated sample.

Acknowledgment. The authors wish to thank Mr. J. Kaelen and Mr. K. Van Vinckenroye for their technical help in building the experimental AP-TPR/MS set up and also Mrs. M. Ruysen and Mrs. L. Boelenders for their technical assistance with the GC/MS analysis.

EF0498364