

DETERMINATION OF ORGANIC SULFUR FORMS IN SOME COALS AND KEROGENS BY ATMOSPHERIC PRESSURE TEMPERATURE PROGRAMMED REDUCTION (AP-TPR).

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ABSTRACT

The following samples have been investigated as examples for the applicability of the atmospheric pressure temperature programmed reduction (AP-TPR) technique: Indiana #5, Herrin #6, and Upper-Freepot (Argonne Premium coal, USA), Kimmeridge Dorset-Cuddle (Type II kerogen, UK) and Mequinenza (lignite, Spain). The Mequinenza lignite has been treated with diluted nitric acid in order to remove pyrite while for the Upper Freepot and the Kimmeridge the pyrite was removed by a LiAlH_4 treatment. The Indiana #5 and Herrin #6 were treated with a peroxy-acetic acid solution at room temperature in order to remove beside pyrite also other sulfur groups. The AP-TPR profiles of the treated and untreated samples are discussed and compared with each other. It is demonstrated that LiAlH_4 as the peroxide treatment not only removes pyrite, but also changes and removes other sulfur functionalities. The AP-TPR technique proved that the pyrite signal is clearly resolved and that possible retrogressive reactions might be hidden under other sulfur functionalities, which has no important influence on the interpretation of the AP-TPR profile after pyrite reduction.

INTRODUCTION

As often discussed, the presence of sulfur is undesirable in metallurgical coke, as well as in the production of smokeless and formed fuels. Therefore a prior desulfurization is recommended. While inorganic sulfur can mostly be removed by simple physical methods, the removal of organic-bound sulfur always needs a chemical treatment. Therefore, it is necessary to know which sulfur forms occur in the coal in order to choose a suitable method of desulfurization and to estimate the extent of desulfurization as well as the kind of sulfur functionalities that have been removed. At the moment a number of chemical and instrumentation methods are used for the determination of these different sulfur functionalities in coal¹. AP-TPR²⁻⁵ proved to be a powerful technique to gain more insight into the sulfur form distribution in the raw as well as in the treated coal.

EXPERIMENTAL

Samples: the treatments and the analyses of the coals and kerogens have been described previously⁶⁻⁷ and are listed in table I and II.

Apparatus: the atmospheric pressure TPR setup has been described previously³⁻⁵.

Samples were heated from 20° to 1000°C, at a rate of 5°C/min. Experiments were always recorded in a pure H_2 -atmosphere.

RESULTS AND DISCUSSION

a) Mequinenza Lignite

In figure 1 the AP-TPR-results are shown for the Mequinenza lignite as received (a) and treated (b) with diluted nitric acid. Based on model compound work⁵, it is possible to assign the regions in the AP-TPR profiles to specific organic sulfur groups. For the raw Mequinenza lignite figure 1 curve (a), the first peak at 395°C must be attributed to alifatic sulfide as well as to mixed aryl-alkyl sulfides. The quite pronounced shoulder around 500°C can be attributed to pyritic sulfur. The second peak at 605°C represents the di-aryl sulfides. Above 700°C, simple thiophenes are visible. Above 800°C, even more complex thiophenic structures can be observed. The total amount of sulfur detected by the AP-TPR-technique is 6.0%, or an overall 76% sulfur recovery.

Looking at the HNO_3 -treated Mequinenza lignite AP-TPR profile [figure 1 curve (b)] and comparing it with curve (a) of the native coal, pyrite as well as alifatic sulfides have been mostly removed. This results in a less pronounced first signal still demonstrating the presence of aryl-alkyl sulfides. But also aryl sulfides are present as shown by the peak at 645°C. A well pronounced signal at 730°C refers to the presence of simple thiophenes. It is believed that due to the effect of the HNO_3 treatment also a better accessibility of the coal towards the reduction process is established. The sulfur yield of this AP-TPR-experiment is 4.6%, i.e. a 53% sulfur recovery of the total amount of sulfur present in the coal sample.

b) Kimmeridge Kerogen

In figure 2 the Kimmeridge Dorset-Cuddle AP-TPR-profiles are shown. The sulfur recovery is quite high for the native kerogen (a) as for the LiAlH_4 -treated (b). The changes in the AP-TPR-profiles [see curve (a) vs. (b)] are spectacular. This was also the case for the HP-TPR plots⁶. The pyrite peak is not visible in the raw material kinetogram. The first main peak for the kerogen can be attributed to aryl-alkyl sulfur forms (T_{max} at 410°C). The second corresponds with di-aryl sulfur functionalities. The onset of the first peak starts later suggesting the absence of pure alifatic sulfur forms in Kimmeridge Kerogen. The AP-TPR results show some differences with the HP-TPR findings, probably due to the disturbing role

of pyrite.

Looking at figure 2 curve (b), the LiAlH_4 treatment not only removes pyrite, but obviously has also a drastic influence on the other sulfur groups. Beside pyrite aliphatic sulfur forms as well as certain amounts of aryl-alkyl sulfides are also removed. The signal starting at 175°C, indicates that beside some desulfurization also some new, easy to reduce, sulfur compounds are formed, in this case thiols. The main peak (T_{max} at 630°C) in figure 2 curve (b) is much more narrow than the corresponding one in figure 2 curve (a) with a maximum at 600°C. This indicates that the LiAlH_4 treatment also partly removes or changes di-aryl sulfides. It is quite clear that the LiAlH_4 treatment disturbs the other sulfur forms in the kerogen as well during the desulfurization by breaking certain sulfur bonds and creating others.

c) Bituminous coal

Figure 3 gives the AP-TPR-spectra of the raw and LiAlH_4 -treated Upper Freeport samples (both with almost a 100% sulfur recovery). The peak at 530°C is believed to be the pyrite signal. The shoulders at lower and higher temperatures must be assigned to alifatic sulfides and aryl-alkyl sulfides, and pure aryl sulfides (T_{max} at 585°C), respectively.

Because of the high amount of pyrite, the LiAlH_4 treatment is quite effective. This is shown by the AP-TPR-profile in figure 3 curve (b). Only simple thiophenic structures are detected, but only in very small amounts. These findings are in agreement with the one of the HP-TPR experiment. It is clear that according to the coal type, the LiAlH_4 -treatment can cause different effects during the desulfurization process.

d) Argonne Premium coals

In figure 4 the AP-TPR profiles of Indiana #5 as received [curve (a)] and after treatment with peroxy-acetic acid for 6 hours [curve (b)] and 24 hours [curve (c)] are shown. The sulfur amount in wt % detected by the set-up is 2.9%, 1.1% and 0.73%, respectively. Using the model compound work⁵, the signal at 460°C can be attributed to alifatic sulfides and aryl-alkyl sulfides. The shoulder around 540°C is attributed to pyrite and the peak at 595°C refers to di-aryl sulfur compounds. The feature at higher temperature is caused by simple thiophenes.

Comparing figure 4 curve (a) with curves (b) and (c), it is clear that beside the removal of pyrite [minimum in both profiles (b) and (c) at 540°C] the other non-thiophenic compounds are also partly removed by the peroxy-acetic acid treatment. The longer the treatment is performed, the less non-thiophenic sulfur is found. One can conclude that the peroxide method is an overall desulfurization method as many sulfur forms are affected by this oxidation. In how far condensed or complex thiophenic sulfur is attacked by this treatment is not clear at the moment. At the moment AP-TPR is not capable to reduce these sulfur functionalities effectively.

In figure 5 the AP-TPR results are shown for the Herrin #6. The profile for the raw material is given by figure 6 curve (a). The peak at 425°C corresponds with alifatic sulfides. The one at 485°C refers to aryl-alkyl sulfur functionalities. In this case the pyrite peak is not visible because of its low presence. The 485°C signal and the huge signal with a maximum at 605°C refer to aryl sulfur compounds and even some simple thiophenic structures. For the oxidised samples, the AP-TPR profiles in figure 5 curves (b) and (c) show the same trends as for the Indiana #5, i.e. all sulfur forms present in the raw coal are attacked by the peroxide treatment. The longer the experiment is performed the more sulfur forms of all kind are removed. The sulfur recoveries in wt% for the AP-TPR experiments in figure 5 are again quite high: 3.4%, 2.0% and 1.3%, for curves (a), (b) and (c) respectively.

CONCLUSIONS

It is demonstrated that AP-TPR provides differentiated profiles which can be explained in terms of different organic sulfur functionalities. The pyrite signal can be distinguished very easily from the organic sulfur peaks. It is shown by the AP-TPR technique that different desulfurization treatments not only removed the specific sulfur group, but also affect other sulfur forms present in the coal as well. This is also found by other treated coal samples using the same or other methods.

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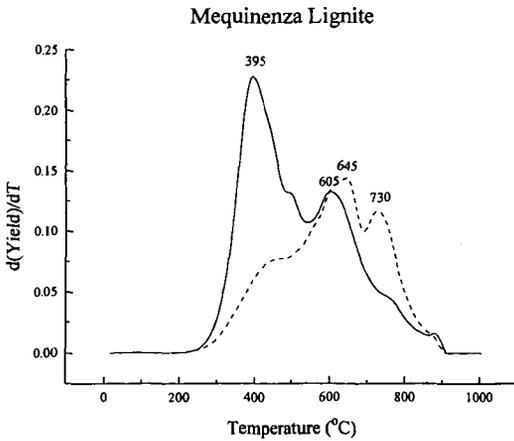


Figure 1: TPR-profiles of a Mequinenza Lignite as received (a) and after HNO_3 treatment (b).

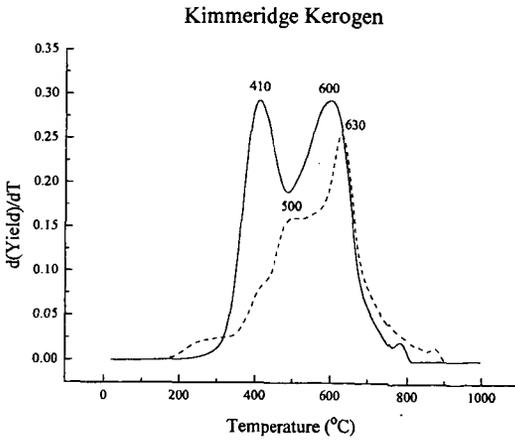


Figure 2 : TPR-profiles of Kimmeridge Kerogen as received (a) and after LiAlH_4 -treatment (b).

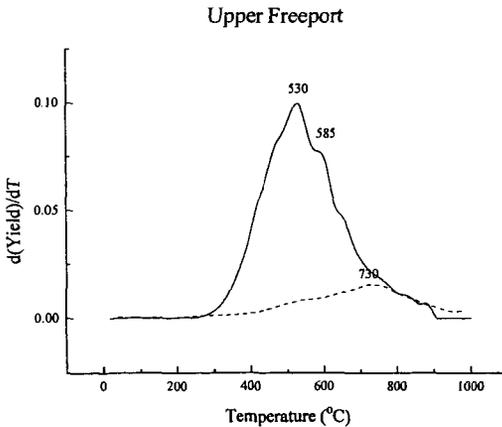


Figure 3 : TPR-profiles of Upper Freeport as received (a) and after LiAlH_4 -treatment (b).

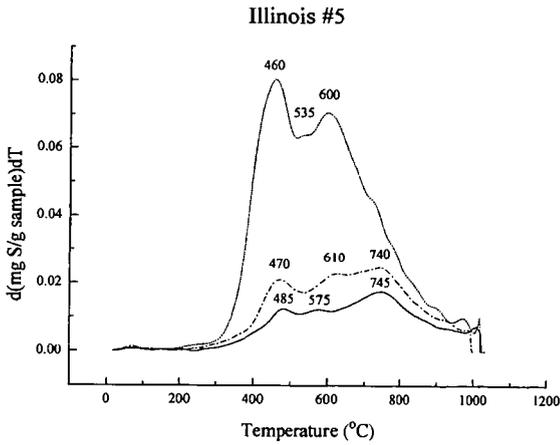


Figure 4 : TPR-profiles of Indiana #5 as received (a) and after 6 hours (b) and 24 hours (c) oxidation.

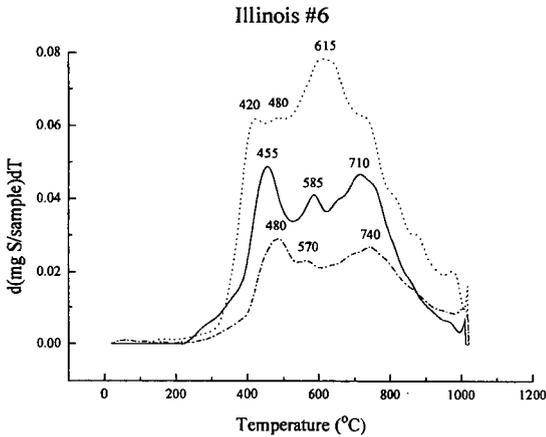


Figure 5 : TPR-profiles of Herrin #6 as received (a) and after 6 hours (b) and 24 hours (c) oxidation.

sample (wt % dmmf)		Mequenza	Kimberidge	Upper Freeport
Sulfur (wt % db)	C	66.4	55.5	88.0
	H	5.8	6.2	4.8
	N	1.6	2.1	1.6
Sulfur (wt % db)	Total	9.0	8.3	2.32
	pyritic	0.5	n.d.	1.77
	sulfatic organic	0.5	n.d.	0.01
after treatment				
Sulfur (wt % db)	Total	8.6	5.8	0.48

sample (wt % db)		Herrin #6	Indiana #5
Sulfur (wt % db)	C	69.1	72.1
	H	5.1	5.1
	N	4.4	1.5
	O	9.5	8.4
Sulfur (wt % db)	Total	4.4	3.8
	pyritic	1.2	1.8
	sulfatic organic	0.1	0.0
		3.1	2.0

After 6 hours ox.
total sulfur (wt % db)

3.1

2.2

After 24 hours ox.
total sulfur (wt % db)

1.9

2.0