

REACTIVITY OF OXIDIZED ORGANIC SULFUR FORMS IN COAL

S. R. Kelemen, M. L. Gorbaty, G. N. George and P. J. Kwiatek

Exxon Research and Engineering Company
Route 22 East; Clinton Township
Annandale, N.J. 08801-0998, USA.

1. INTRODUCTION

Recent work has shown that it is possible to distinguish and quantify the different organic sulfur types in coal using X-Ray Photoelectron Spectroscopy (XPS) [1-3] and X-Ray Absorption Near Edge Structure Spectroscopy XANES [3-6]. These methods have been employed in the study of fresh coals of different rank and to follow the transformation of organic sulfur under mild pyrolysis conditions ($T = 400^{\circ}\text{C}$) [7]. The characterization of oxidized organic sulfur forms resulting from mild coal oxidation [2, 8-11] and the subsequent thermal reactivity of these oxidized sulfur forms have not been as extensively explored. The nature of oxidized organic sulfur forms can yield insight into the forms initially present [12]. Initial work with Rasa coal showed that sulfide sulfur forms are converted to oxidized forms while thiophenic forms were mostly unreacted [2]. This paper extends that work to other coals and explores the subsequent thermal reactivity of the oxidized organic sulfur forms.

2. EXPERIMENTAL

The procedures for obtaining XPS and XANES spectra have been discussed elsewhere [1,3]. Pyrolysis with GC gas product analysis were done in a quartz reactor contained within a furnace. The details of these experimental arrangements have been previously described [7,13]. Heating rates were on the order of $0.5^{\circ}\text{C}/\text{min}$ up to 400°C . The temperature and heating conditions were chosen because little of the ultimate amount of hydrocarbons in the volatile matter is released, while much of the H_2S and SO_2 evolve from low rank coals. Spanish lignite (Mequinenza), New Zealand (Charming Creek) and Rasa coal were chosen for study because of the unusually high amounts of organically bound sulfur and unusually low levels of pyritic sulfur [14-16] present. Oxidation was done in the dark, in air (ambient relative humidity 60%) and in an oven kept at 125°C for 5 days.

3. RESULTS and DISCUSSION

The oxidation conditions were chosen because it was found in other coal oxidation studies that the relative rate of total organic oxidation corresponded closely with that of oxidized organic sulfur during the first 5 days at 125°C [10]. Also, the oxidation rates at 125°C can be related kinetically to those that occur near ambient conditions [10,11]. There is roughly two orders of magnitude acceleration of time at 125°C relative to room temperature. Table I shows the XPS quantitative speciation of sulfur forms in the fresh and oxidized coals. Note that sulfides, mercaptans and disulfides are included as "sulfide" in Table I. These results show that a large fraction of the sulfides initially present in the fresh coals is converted to oxidized forms, while thiophenic forms are relatively stable under these mild conditions. For Rasa coal, the dominant oxidation product was identified to be sulfonic acid. For the other

coals, sulfones and sulfoxides are the major oxidation products. Pure compound work has shown that sulfonic acids can arise from the oxidation of disulfides or mercaptans, while sulfoxides and sulfones result from oxidation of sulfides [17,18]. It is apparent from the data above for the Spanish and New Zealand coals that sulfides are converted to sulfoxides and sulfones. For Rasa coal, the evidence supports the speculation that disulfides are the precursors of sulfonic acids. In support of this, the "sulfidic" value for the fresh Spanish coal contains a 15% contribution from an XPS feature associated with mercaptans [7]. This feature does not decrease upon oxidation, nor is sulfonic acid a major product of oxidation. Mercaptans were not identified in fresh Rasa and New Zealand coals. Thus disulfides appear to be the most likely precursors of sulfonic acids in oxidized Rasa coal.

It has been shown that aliphatic sulfur forms decompose to H_2S with some conversion to aromatic forms upon mild pyrolysis [7]. Table II shows the amount of H_2S and SO_2 generated upon pyrolysis for 5 minutes at $400^\circ C$, expressed on an atomic S/C basis. Data in Table II show that for fresh Rasa coal sulfide sulfur preferentially decomposes to H_2S , while H_2S formation and conversion to aromatic forms takes place with New Zealand and Spanish coal. The thermal reactivity of the oxidized coal samples shows considerably less H_2S product than the fresh coals. The relative loss in H_2S production roughly tracks the relative loss of sulfide forms in each coal. This supports the view that sulfide sulfur forms are preferentially converted upon oxidation. Data in Table II show that the oxidized organic sulfur forms are lost as SO_2 upon mild pyrolysis. Rasa coal is the most reactive with the appearance of 43% of the oxidized forms as SO_2 . For the New Zealand and Spanish coals 7% and 18% respectively of bound oxidized sulfur appeared as SO_2 by this analysis.

These results together with XPS and XANES analysis of the low temperature chars indicate that most of the sulfur present as sulfoxides and sulfones formed during low temperature oxidation is retained in the coal after low temperature pyrolysis. As found for these initial coals [7,14] little sulfide sulfur remains after pyrolysis. While previous work demonstrated that the relative level of aliphatic or "sulfide" sulfur decreases with increasing coal rank [3,7] the present work shows that there can be significant differences in the nature of the components that comprise "sulfide" sulfur. Distinctions can be made on the basis of products following mild oxidation and subsequent thermal reactivity of the oxidized coals.

4. CONCLUSIONS

Sulfide sulfur forms are converted to oxidized forms during mild coal oxidation. Thiophenic forms are largely unreactive. The oxidation products of Spanish lignite and New Zealand coal were mostly sulfones and sulfoxides while Rasa coal gave sulfonic acids. TPD and reactor studies show that the conversion of organic sulfides to oxidized products causes a large decrease in H_2S production upon pyrolysis. A portion of the oxidized organic sulfur forms are lost during low temperature pyrolysis as SO_2 . Rasa coal is the most reactive and the amount of SO_2 produced corresponds to 43% of the oxidized species originally present. XPS analysis of oxidized Rasa coal after pyrolysis shows sulfonic acids represent most of the loss. A much smaller fraction of the oxidized sulfur forms initially present in the other coals yield SO_2 upon low temperature pyrolysis. TPD, XPS and XANES results indicate that most of the sulfur initially present as sulfoxides and sulfones is retained in the coal after low temperature pyrolysis.

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Table I XPS analysis of sulphur before and after oxidation at 125°C

Sample	Mole per cent				
	Sulfide	Thiophene	Sulfoxide	Sulfone	Sulfonic Acid
Rasa Initial	26	70	1	1	2
Rasa Oxidized	7	69	4	8	12
Spanish Initial	66	34	0	0	0
Spanish Oxidized	38	42	5	8	4
N.Z. Initial	38	62	0	0	0
N.Z. Oxidized	13	67	8	8	4

Table II Amount of oxide and sulfidic components and the subsequent amount of H₂S and SO₂ produced upon pyrolysis

Sample	Atom Ratio S/C (x100)			
	XPS Sulfide	H ₂ S Pyrolysis	XPS Oxides	SO ₂ Pyrolysis
Rasa Initial	1.83	1.53	0.24	0
Rasa Oxidized	0.42	0.18	1.43	0.61
Spanish Initial	4.25	1.49	0	0
Spanish Oxidized	2.64	0.89	1.18	0.21
N.Z. Initial	1.06	0.17	0	0
N.Z. Oxidized	0.35	0.08	0.56	0.04