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TECHNICAL REPORT

September 1 through November 30, 1993

Project Title: **ANALYZING ORGANIC SULFUR IN COAL/CHAR:
INTEGRATED MILD DEGRADATION/XANES METHODS**

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ABSTRACT

To address the problem of acid rain considerable effort has been expended on finding methods for the removal of sulfur from coal. Despite these efforts organic sulfur has proven very difficult to remove. Perhaps the single most important reason for this is the fact that the organic sulfur in coal remains very poorly characterized. Thus, the overall objective of this study is to combine advanced non-destructive and advanced destructive methods of sulfur analysis so as to provide complete characterization of the organic sulfur in Illinois Basin coals and mild gasification chars derived from them. Thus, the current study combines selective oxidation strategies, analytical pyrolysis, and sulfur X-ray Absorption Near Edge Structure Spectroscopy (XANES) analysis. In addition identical samples are to be provided for W-Band EPR spectroscopy.

During the previous quarter ten coal derived samples have been prepared. The sulfur content of these samples varies from 0.77% to 4.4%. Each sample has been submitted for XANES analysis, W-Band EPR analysis, and analytical pyrolysis. Although the sulfur characterization data from these analyses is not yet available it is anticipated that the variety of samples provided will establish a detailed record of sulfur forms and their transformations during gasification, oxidation and desulfurization. In addition, a mild gasification reactor has been designed and is undergoing final assembly.

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EXECUTIVE SUMMARY

The release of sulfur oxides into the environment via the combustion of high sulfur coals is the primary cause of acid rain. To address this problem considerable effort has been expended on finding methods for the removal of sulfur from coal prior to combustion. Although some success has been achieved with the removal of inorganic sulfur forms (primarily pyrite), no technique is currently available for the cost-effective removal of organic sulfur.

Perhaps the single most important reason why organic sulfur removal is so difficult is the fact that the organic sulfur in coal remains very poorly characterized. Since different organic sulfur species are easier to desulfurize than others it is essential that a knowledge of the different types of organic sulfur and their distribution in coal be obtained. Only then will it be possible to design the required technologies for their effective removal.

Recently, two approaches have received considerable attention for the characterization of organic sulfur in coal. The first is the use of so-called 'destructive' techniques which degrade the coal into small, more readily analyzable fragments. The second is the so-called 'non-destructive' techniques which observe the sulfur in the whole coal without degradation. Each technique has advantages and disadvantages. For instance the destructive techniques such as chemical and thermal degradation can provide very detailed molecular structure information but they suffer from the inability to observe all of the sulfur at one time, and from the possibility that degradation induced rearrangement reactions may corrupt the structural information. On the other hand non-destructive techniques can observe all of the organic sulfur species simultaneously in situ and hence can provide the best overall picture of the organic sulfur distribution. However, non-destructive techniques often fail to provide the very detailed structural information such as substitution patterns, the nature of substituents and the nature of bonding between the different units that may be provided by the degradative methods. All information is needed if the organic sulfur in coal is to be adequately characterized.

The overall objective of this study is to combine advanced non-destructive and advanced destructive methods of sulfur analysis so as to provide complete characterization of the organic sulfur in Illinois Basin coals and mild gasification chars derived from them. To achieve this overall objective a number of specific goals and objectives can be identified. These are:

1. Obtain and analyze, by standard ASTM coal analysis methods, a series of Illinois Basin coals and mild gasification chars derived from them.

2. Use analytical pyrolysis techniques, dichromate and peroxyacetic acid oxidation and sulfur K-edge XANES analysis to compare and contrast the organic sulfur distribution of the coals and their mild gasification chars.
3. Use the organic sulfur distribution obtained to investigate any transformation of organic sulfur species that occur as a result of mild gasification.
4. Explore relationships between the organic sulfur species identified by the destructive techniques with those identified by the XANES analysis, thereby evaluating the combination of these techniques for organic sulfur characterization purposes.
5. To combine the information from all techniques to provide a detailed quantitative analysis of organic sulfur.
6. Screen the oxidation and analytical pyrolysis products for organic nitrogen compounds.

During the previous quarter ten samples have been prepared for analysis. Aliquots of these samples have been delivered to Dr. G.P. Huffman at the Consortium for Fossil Fuel Liquefaction Science, University of Kentucky, for sulfur K-edge XANES analysis and to Dr. R. Clarkson, University of Illinois, for W-Band EPR analysis. In addition, aliquots of these samples are currently under investigation in laboratories at SIUC using the analytical pyrolysis and selective oxidation techniques. The available ultimate and proximate data for the ten samples prepared so far are listed in table 1. (The data is reported on a dry basis)

The samples with a M suffix have been micronized only. Samples with a FE suffix are aliquots of the micronized coals that have been floated at 1.6 g/mL and then extracted with the methanol/chloroform azeotrope. Samples with the SO suffix are aliquots of the micronized coals that have been selectively oxidized with peroxyacetic acid for 6 hours at room temperature. The suffix MG1 denotes a micronized sample that has been mildly gasified with steam at 450°C for 1 hour. The DES1 suffix denotes a micronized sample that has been desulfurized using a combination of selective oxidation and subsequent alcohol/base treatment at 350°C for 1 hour.

As can be seen from the data in table 1 samples have been prepared which have a wide variety of sulfur contents. (0.77% to 4.40%) In addition, since the methods of preparation vary, it is likely that the sulfur compound distributions in each sample will vary also. This sample set should therefore provide a good test for the various sulfur characterization techniques.

Table 1. Ultimate and proximate composition data.

Sample	Elemental Composition				Ash
	%C	%H	%N	%S	wt%
101M	72.41	4.51	1.30	4.40	10.82
102M	73.71	4.33	1.44	3.27	10.73
106M	79.41	4.94	1.79	3.90	9.06
109M	74.90	3.78	1.70	1.10	8.30
101FE	65.49	4.68	1.25	3.22	2.63
106FE	70.43	4.88	1.64	2.68	
101SO	63.07	4.64	1.21	2.84	7.84
106SO	66.07	4.46	1.47	1.95	6.55
101MG1				3.16	
101DES1				0.77	

It is clear that the demineralization procedures (acid treatment and sink/float) reduce the sulfur content of the samples considerably. This is due to the removal of mineral forms of sulfur, especially pyrite. However, the sulfur contents for the floated coals is not as low as predicted from the sulfur forms data provided by the IBCSP and it is suspected that some pyrite remains in these samples. This situation is probably due to the incomplete liberation of the pyrite during the micronization of the coals. This is a particular problem with the Illinois Basin coals because of the highly dispersed nature of the pyrite in these coals.

The oxidation treatment with peroxyacetic acid lowers the sulfur content of the coals further, primarily by the dissolution of any remaining pyrite but also by reaction with the organic sulfur. Previous investigations showed that between 10 and 20% of the organic sulfur in these coals was removed by peroxyacetic acid oxidation. It is anticipated that many of the remaining organic sulfur species in the oxidized coals are in the sulfoxide, sulfone or sulfonic acid form. If XANES analysis shows otherwise it will have been demonstrated that the oxidation reagents failed to react with some of the organic sulfur structures. This in turn may reflect a specificity in the reaction or perhaps a failure of the reagents to penetrate the coal particles. It is anticipated that the distribution of the sulfur species in the oxidation product as compared with that for the original coal will help determine which possibility is correct.

OBJECTIVES

The overall objective of this study is to combine advanced non-destructive and advanced destructive methods of sulfur analysis so as to provide complete characterization of the organic sulfur in Illinois Basin coals and mild gasification chars derived from them.

Specific Objectives

The specific goals and objectives of this study are:

1. Obtain and analyze, by standard ASTM coal analysis methods, a series of Illinois Basin coals and mild gasification chars derived from them.
2. Use analytical pyrolysis techniques, dichromate and peroxyacetic acid oxidation and sulfur K-edge XANES analysis to compare and contrast the organic sulfur distribution of the coals and their mild gasification chars.
3. Use the organic sulfur distribution obtained to investigate any transformation of organic sulfur species that occur as a result of mild gasification.
4. Explore relationships between the organic sulfur species identified by the destructive techniques with those identified by the XANES analysis, thereby evaluating the combination of these techniques for organic sulfur characterization purposes.
5. To combine the information from all techniques to provide a detailed quantitative analysis of organic sulfur.
6. Screen the oxidation and analytical pyrolysis products for organic nitrogen compounds.

To achieve these goals a series of tasks were scheduled for completion within the contract period. These tasks include:

Task 1. Sample selection and preparation.

Four coals, IBC-101, IBC-102, IBC-106 and IBC-109 are to be obtained from the Illinois Basin Coal Sample Program. Aliquots of each are to be micronized, sink/floated and solvent extracted. Aliquots of these samples are then to be selectively oxidized, mildly gasified and chemically desulfurized.

In addition, a mild gasification reactor is to be designed and constructed and used for the preparation of mild gasification chars. The object of task 1 is to provide a

variety of samples with different sulfur contents and distributions.

Task 2. Analytical pyrolysis.

The first sulfur characterization technique to be applied to the samples prepared in task 1 is analytical pyrolysis. Both py-GC-FPD and py-GCMS is to be used to characterized organic sulfur species present in the pyrolysis products.

Task 3. Coal/char oxidation with sodium dichromate.

The samples prepared in task 1 are to be characterized by selective oxidation with sodium dichromate also. Soluble oxidation products will be methylated and then analyzed for organic sulfur compounds using GC-FPD and GC-MS. Insoluble oxidation products will be examined by XANES and W-Band EPR as described in task 5.

Task 4. Coal/char oxidation with peroxyacetic acid.

The samples prepared in task 1 are to be characterized by selective oxidation with peroxyacetic acid also. Soluble oxidation products will be methylated and then analyzed for organic sulfur compounds using GC-FPD and GC-MS. Insoluble oxidation products will be examined by XANES and W-Band EPR as described in task 5.

Task 5. Sulfur XANES and W-Band EPR analysis.

Samples prepared in task 1 and selected samples produced in tasks 3 and 4 are to be examined by sulfur K-edge XANES and W-Band EPR. By analyzing the samples before and after selective oxidation, mild gasification and desulfurization, it will be possible to determine which sulfur forms are released from the coal, those which remain and transformations between sulfur forms resulting from the various treatments.

Task 6. ASTM methods of coal/char analysis.

Selected samples from tasks 1-5 are to be analyzed by standard ASTM methods of analysis such as proximate, ultimate, sulfur forms and BTU analysis.

INTRODUCTION AND BACKGROUND

The release of sulfur oxides into the environment via the combustion of high sulfur coals is the primary cause of acid rain.(1) To address this problem considerable effort has been expended on finding methods for the removal of sulfur from coal prior to combustion. Although some success has been achieved with the removal of inorganic sulfur forms (primarily pyrite) (2,3), no technique is currently available for the cost-effective removal of organic sulfur.

Perhaps the single most important reason why organic sulfur removal is so difficult is the fact that the organic sulfur in coal remains very poorly characterized. Since different organic sulfur species are easier to desulfurize than others it is essential that a knowledge of the different types of organic sulfur and their distribution in coal be obtained. Only then will it be possible to design the required technologies for their effective removal.

There have been many attempts to characterize the organic sulfur in coal and some important progress has been made.(4) However, a universally excepted method for organic sulfur characterization has yet to be provided. The problem is due to the extreme complexity of the chemistry of coal, a fact that prevents any single characterization technique from providing all of the necessary information. The solution to this problem would therefore appear to be the use of a combination of several techniques such that the combined information would be sufficient for complete sulfur characterization. This idea serves as the basis for this current research program.

Recently, two approaches have received considerable attention for the characterization of organic sulfur in coal. The first is the use of so-called 'destructive' techniques which degrade the coal into small, more readily analyzable fragments. The second is the so-called 'non-destructive' techniques which observe the sulfur in the whole coal without degradation. Each technique has advantages and disadvantages. For instance the destructive techniques such as chemical and thermal degradation can provide very detailed molecular structure information but they suffer from the inability to observe all of the sulfur at one time, and from the possibility that degradation induced rearrangement reactions may corrupt the structural information. On the other hand non-destructive techniques can observe all of the organic sulfur species simultaneously in situ and hence can provide the best overall picture of the organic sulfur distribution. However, non-destructive techniques often fail to provide the very detailed structural information such as substitution patterns, the nature of substituents and the nature of bonding between the different units that may be provided by the degradative methods. All information is needed if the organic sulfur in coal is to be adequately characterized.

The current study combines selective oxidation strategies, analytical pyrolysis with subsequent GC-FPD and GC-MS analysis, and Sulfur X-ray Absorption Near Edge Structure Spectroscopy (XANES) analysis of Illinois Basin coals and mild gasification chars derived from them for the complete characterization of organic sulfur.

It is anticipated that this characterization approach will provide both the detailed molecular structure, and the overall quantitative distribution, of organic sulfur thereby leading to a more complete analysis of organic sulfur structures in coals and chars.

EXPERIMENTAL PROCEDURES

Sample Preparation

Typical coal preparation includes coal micronization, coal demineralization, coal flotation and solvent extraction. Micronization is achieved using a nitrogen powered fluid energy mill and is necessary to liberate the mineral component of coal from the organic component. Approximately 200 grams of each coal were micronized. To remove minerals from the coal acid treatments with HCl and HF, and a subsequent sink/float procedure are required. The acid treatment is performed by dispersing 100 grams of the micronized coal in a 500mL mixture of HF and HCl (3:1). After the mixture has been stirred for 3 hours the coal is recovered by filtration and the residual acid washed away with hot distilled water until the filtrate is neutral.

To remove minerals such as pyrite that are insoluble in the HF/HCl mixture the sink/float procedure was employed. This involves dispersing the acid treated coal in a cesium chloride solution of specific density 1.6g/mL. This coal slurry is then centrifuged so that the mineral sinks and the organic coal floats. The mineral free coal (approximately 1-1.5% ash) is collected by filtration, washed sequentially with dil. HCl and hot distilled water and finally dried.

Solvent extraction was performed on aliquots of the demineralized coal using an azeotropic mixture of methanol and chloroform. Soxhlet apparatus was used.

Coal Oxidation

Two selective oxidation procedures have been used. The first is a relatively mild oxidation which results in little coal dissolution. This is used to provide samples for subsequent XANES, W-Band EPR and analytical pyrolysis analysis. The second procedure is more extensive and results in almost complete dissolution of the coal. This procedure is used for sulfur characterization by GC-FPD and GCMS.

Typical mild selective oxidation with peroxyacetic acid involves dispersing 2g of the solvent extracted coal sample in a mixture of 50 mLs glacial acetic acid and 50mLs 30% (wt/v) hydrogen peroxide. The mixture is then stirred at room temperature for six hours. After this time the oxidation product is recovered at the filter largely as undissolved coal solids. This material is washed with dist. water and dried.

The procedure used for subsequent GC-FPD and GCMS analysis used the same quantities of coal and reagents but this time the reaction is carried out under reflux for 24 hours. After this time the coal is almost completely in solution. The solubilized oxidation products are recovered by first removing any residual undissolved material by filtration. Any excess peroxides in the oxidation products solution are then destroyed by the addition of 10mg of platinum on carbon (1% wt Pt). The peroxide free solution is then rotary evaporated to recover the soluble coal products. For GC-FPD and GCMS analysis these oxidation products are first methylated with diazomethane.

Coal Gasification

A preliminary mild gasification experiment was performed by sealing 2g of the IBC-101 micronized sample in a 10mL stainless steel micro-reactor with 2 mL of water. After purging the reaction with nitrogen it was sealed and heated to 450°C in a fluidized sand bath for 1 hour. After this time the reactor was cooled and the product recovered at the filter where it was washed with distilled water and dried.

Coal Desulfurization

The method of coal desulfurization used incorporates a oxidative pretreatment step followed by an alcohol/base desulfurization reaction. The pretreatment step involved dispersing coal (50g) in glacial acetic acid (200mL) and adding 50mL of 30% (wt/v) hydrogen peroxide solution. After stirring this mixture for 6 hours at room temperature the oxidized coal product is recovered by filtration, washed with distilled water and finally dried in a vacuum oven. The oxidized coal (2g) is then dispersed in a suspension of 0.2g NaOH in 5ml methanol. This mixture is placed in a 10 mL stainless steel micro-reactor, purged with nitrogen, sealed and then heated to 350°C for 1 hour. The resulting desulfurized coal is then collected at the filter, washed with distilled water and finally dried.

XANES Analysis

The sulfur XANES spectra are measured at beam-line X-19A at the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory, NY. This beam line is well suited for soft X-ray measurements because the X-rays are in vacuum right up to the sample and are therefore minimally absorbed before interacting with the sample. Spectra are collected in fluorescence geometry and stored in a MicroVAX II computer at NSLS before being transferred to a similar computer at the University of Kentucky. Standard computerized methods are used to separate the XANES region from the XAFS spectrum. A least-squares fitting program (EDGFIT) is then applied to the XANES spectrum to determine the contribution of different

sulfur forms to the spectrum. The areas under the peaks in the fitted spectrum are then converted to wt% sulfur in the various forms.

RESULTS AND DISCUSSION

Sample Preparation

During the previous quarter ten samples have been prepared for analysis. Aliquots of these samples have been delivered to Dr. G.P. Huffman at the Consortium for Fossil Fuel Liquefaction Science, University of Kentucky, for sulfur K-edge XANES analysis and to Dr. R. Clarkson, University of Illinois, for W-Band EPR analysis. In addition, aliquots of these same are currently under investigation in laboratories at SIUC using the analytical pyrolysis and selective oxidation techniques. The available ultimate and proximate data for the ten samples prepared so far are listed in Table 1. (The data is reported on a dry basis)

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The oxidation treatment with peroxyacetic acid lowers the sulfur content of the coals further, primarily by the dissolution of any remaining pyrite but also by reaction with the organic sulfur. Previous investigations showed that between 10 and 20% of the organic sulfur in these coals was removed by peroxyacetic acid oxidation. (5) It is anticipated that many of the remaining organic sulfur species in the oxidized coals are in the sulfoxide, sulfone or sulfonic acid form. If XANES analysis shows otherwise it will have been demonstrated that the oxidation reagents failed to react with some of the organic sulfur structures. This in turn may reflect a specificity in the reaction or perhaps a failure of the reagents to penetrate the coal particles. It is anticipated that the distribution of the sulfur species in the oxidation product as compared with that for the original coal will help determine which possibility is correct.

Design and construction of mild gasification reactor

To provide samples of mild gasification char it was necessary to design and construct a suitable reactor. This has been completed with the exception of the final assembly of the liquid collecting condenser. The apparatus consists of a 20mL stainless steel reactor fitted with porous plugs at both ends. The gas inlet side of the reactor is equipped with a fine metering valve to control the flow rate of the incoming gas, and a preheat coil to allow the gas to achieve reaction temperature prior to entering the reactor. The outlet side of the reactor is connected to a condenser which will allow any liquids to be collected directly into a glass vial. The

reactor will be immersed in a fluidized sand bath maintained at the desired temperature.

CONCLUSIONS AND RECOMMENDATIONS

Ten coal derived samples have been prepared. The sulfur content of these samples varies from 0.77% to 4.4%. Each sample has been submitted for XANES analysis, W-Band EPR analysis, and analytical pyrolysis. Although the sulfur characterization data from these analyses is not yet available it is anticipated that the variety of samples provided will establish a detailed record of sulfur forms and their transformations during gasification, oxidation and desulfurization.

A mild gasification reactor has been designed and is undergoing final assembly. This apparatus will provide both chars and liquids for sulfur characterization studies.

It is recommended that the co-pyrolysis of a sulfur free carbonaceous solid and sulfur containing inorganic minerals be studied. For example a mixture a polyethylene and pyrite could be co-pyrolyzed. The identification of organic sulfur species in the pyrolyzate would demonstrate the possibility that organic sulfur species form via reactions of pyrite with the coal during thermal treatments.

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