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HIGH SULFUR COAL RESEARCH AT THE SIUC COAL TECHNOLOGY
LABORATORY

Quarterly Progress Report

Work Performed Under Contract No. FC22-83FE60339

Southern Illinois University at Carbondale
Carbondale, Illinois

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HIGH SULFUR COAL RESEARCH AT THE SIUC COAL
TECHNOLOGY LABORATORY
Quarterly Progress Report

Under Contract No. DE-FC01-83FE60339

Southern Illinois University at Carbondale
Coal Extraction and Utilization Research Center
Carbondale, Illinois

EXECUTIVE SUMMARY

The overall objective of the research effort addressed in this cooperative agreement includes the conduct of a high-sulfur coal research program and the establishment of a research facility, the Coal Technology Laboratory (CTL) at the site of the former Carbondale Mining Technology Center (CMTC). The associated research program is broadly based and directed toward high-sulfur coal, the goal being expand the technology to allow for the increased use of high-sulfur coal in an environmentally acceptable manner.

Remodeling in the former Ground Control Building is essentially complete and modification of space in the Administration Building to accommodate laboratories will be completed in the next thirty days. Delivery of the mass spectrometer which was ordered last quarter is scheduled for delivery in April 1984. Another major piece of equipment important to the research, a fluidized bed combustion system, has been ordered and delivery is expected June 1, 1984. Further modification to the CTL facility is required to accommodate the combustor. It is expected that activity on most of the research projects will be located at CTL by the end of next quarter.

Progress continues to be made on the research in the four areas of coal science, coal preparation, coal conversion, and coal utilization. In the Coal Science area, the maceral separation laboratory is about 90% operational. Preconcentration of maceral lithotypes has begun, and an innovative method of forced filtration through selective membranes has been developed. A sample of ultrasonically comminuted coal has been examined using scanning electron microscope/automated image analysis techniques. A sample preparation method was developed for distributing

coal particles evenly on polished copper sample holders. In the carbonyl dienes and unsaturated enolates have been examined, and preliminary characterizations of representative carbonyl sulfide adducts have been described. In addition, computer modeling of the interaction of carbonyl sulfide and transition metal complexes was undertaken.

In the area of coal preparation, a mechanical auger feeder device for introducing material into an experimental hydrocyclone along its axis was constructed and incorporated. A froth flotation pilot plant has been acquired and renovated. Prior to becoming operational, six channel samples from selected southern Illinois coal mines have been collected, and a bench scale froth flotation cell is being used for initial tests. Electrolysis experiments have begun to examine the electrochemical desulfurization of coal slurries.

Coal conversion studies included experiments to examine the effects of chemical pretreatment on supercritical extraction and desulfurization of coal. It was found that with pretreatment a high-sulfur coal containing predominantly organic sulfur experienced a 57% reduction in sulfur on a concentration basis. Without pretreatment, the sulfur reduction was only 40%. In the work examining the mechanism of hydrogen sulfide formation from iron sulfides, it was found that hydrogen sulfide is formed from hydrogen and iron sulfides by a Langmuir-Hinselwood mechanism. Mixtures of H_2 and D_2 produce $(H,D)H_2S$ with random distributions of H and D.

In the area of coal utilization, preliminary studies have been conducted in a 10 cm diameter laboratory scale AFBC unit preparatory to the tests to be conducted on waste fuels, in addition to the specification and placement of an order for a twelve-inch bed fluidized bed combustion

system. In the modeling analysis, several scale coal models were examined, and the Argonne National Coal Model obtained. The model has now been put into operation. Research into slurry pipeline options has been concluded, and equations estimating the response to various factors have been developed. Existing regulations and literature on sulfur removal and control as well as coal residuals were reviewed. Site visits to collect data on costs of sulfur emission control were undertaken, and data on solid waste and waste water disposal and handling costs were also collected. In addition, preliminary design has been completed on questionnaires for use in interviews of coal users.

The brief reports that follow describe in more detail the technical progress made on projects during the second reporting period.

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1. Coal Science

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SEPARATION AND FLUORESCENCE CHARACTERIZATION OF COAL MACERALS

John C. Crelling
Department of Geology

and

Donald M. Miller
Department of Physiology

Reporting Period: October-December, 1983

ABSTRACT

One of the major problems in coal science is characterizing the individual maceral components of coal. While the most successful characterization has been done with petrographic methods, further characterization requires the availability of pure maceral concentrates. In the past, concentrates have usually been obtained by hand picking and have not been of the desired purity. The recent application of the cell separation techniques of physiology to the problem of concentrating macerals shows great promise. The overall objective of this proposal is to establish a facility to produce and characterize maceral concentrates at the Coal Technology Laboratory in Carterville, Illinois.

The primary purpose of this proposal is to set up an independent laboratory at the Cartersville facility to separate and characterize coal macerals. However, extensive modification of the Cartersville facility, of necessity, required a time delay. To allow some progress in the research objectives, it was decided to first set up the entire project on the Carbondale campus and to later transfer the facility to Cartersville. We succeeded in identifying space and facilities in the Coal Characterization Laboratory. Plans were drawn up and the proper power and other logistics installed. Our progress is described in the two areas: Acquisition and setup of equipment, and Progress in our objectives.

Acquisition and Setup of Equipment (By Functional Area):

<u>Equipment</u>	<u>Status</u>
1. <u>Grind to 6 Mesh.</u> Ball Mill	Ordered
2. <u>Mill to micron size.</u> Nitrogen Mill	Ordered
Nitrogen Gas (tanks)	Available
3. <u>Demineralization.</u> Heater	Operational
Stirrer	Operational
Distilled Water	Available
Sink w/tap	Available
Hydrofluoric Acid	Available
Hood (Fume)	Available
4. <u>Solubilization.</u> Brij Detergent	Available
Sonicator	Operational
5. <u>Gradient preparation.</u> Density Gradient Former	Operational
Rotary Pump	Operational
Tubing	Available
Fittings	Available
CsCl ₂	Available
6a. <u>Centrifugation-Large Samples.</u> Rotor	Ordered: Delivery expected 30 January 84
Rotor Lid	Available
Rotary pump	Operational
Centrifuge	Delivered; not operational

6b. Centrifugation-Small Samples.

Balance	Operational
Rotor, Swinging Bucket	Available
*Centrifuge (Same as above)	

7a. Separation-Large Samples.

Fractionator,	Operational
Rotary Pump	Ordered: Del Exp 30 Jan 84
Spectrophotometer	Operational
Recorder	Not Ordered Yet

7b. Separation-Small Samples.

*Fractionator, Micro	Operational
*Rotary Pump (Same as Above)	
Detector-Monitor	Operational

*Recorder (Same as Above)

8. Filtration of Samples.

Millipore Heads	Operational
Millipore Filters	Operational
Vacuum Pump (Rotary)	Operational

9. Drying of Samples.

Vacuum Oven	Under Consideration
Vacuum Pump	Under Consideration

10. Processing of Samples.

Microbalance	Operational
Glove Box	Available
Argon Gas (Tank)	Available

11. Storage of Samples.

Dessicators	Available
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12. Embedding of Samples.

Epon	Available
Agar	Available

As can be seen by the above approximately 90% of the equipment has been received and is functional. As of this date the only functional areas which are not 100% operational are: (1 & 2) Grinding, (6 & 7) Centrifugation, and (9) Drying of Samples. The centrifuge complete with rotors is expected to be operational by 14 February 1984. However, once the centrifuge is installed and checked out by the manufacturer we will be committed to a one year tenure in the present laboratory if we wish to take advantage of the full warantee on the instrument. Therefore, any move of the present facility in the Coal Characterization Laboratory should be projected after March 1985.

RESEARCH PROGRESS(By Functional Area):

1. Grind to 6 Mesh. & 2. Mill to micron size.

Examination of this particular process in maceral separation is being scrutinized very carefully. In the Nitrogen mill process, very large amounts

of the material are lost in the process and perhaps the separation technique itself discriminates in the selection of particles. The grinding of the material in a controlled atmosphere chamber would be a reasonable alternative. Initially the construction of the chamber would cost more but be able to make all future runs cheaper and provide a greater percentage of sample recovery. Consideration is being given to temporarily locating these mills with a similar facility in the Coal Characterization Laboratory because of the large amount of space and the high-frequency noise generated. Recognizing that this would perhaps be one area which may impede our progress, we arranged for coal samples to be ground at Argonne National Laboratories for our use. We have utilized these samples as starting material in our initial studies.

We have also started experiments with the pre-concentration of maceral groups by float-sink methods and with hand-picking of selected lithotypes.

3. Demineralization. & 4. Solubilization.

Utilizing the preground samples we have carried through the demineralization and solubilization processes.

5. Gradient preparation.

The gradient maker has been setup and gradients have been made routinely using a cheaper medium sucrose. Further work with gradients will require a functioning centrifuge.

6. Centrifugation-Large & Small Samples.

The centrifuge was ordered and has been delivered. A power outlet (208 V) has been installed. The swinging bucket rotor has been delivered. We now only await the delivery of the gradient rotor.

8. Filtration of Samples.

This is one area of the separation process that has come under scrutiny, primarily because of the time that the coal samples are in contact with air. While the traditional method of filtration is by gravity filtration, we have experimented with and are using an alternate method of forced pressure filtration thru selective membranes. Our results have shown this to be a far superior method and we believe this will be a significant innovation in the entire process.

9. Drying of Samples. & 10. Processing of Samples.

Inasmuch as we do not desire to heat the maceral sample in order to dry it for storage and use, we are alternately putting it into a reduced atmosphere in the presence of phosphorus pentoxide.

11. Storage of Samples.

Samples are stored in sealed vials in a vacuum dessicator.

12. Embedding of Samples.

Because this area is vital to the entire project and the processing of the final sample we are giving it a great deal of attention. We have been experimenting with different films and methods of preparing the samples for fluorscent microscopy.

PROJECTED DATES:

14 February 1984	Centrifuge Operational
21 February 1984	First Maceral Separation
14 March 1984 (or later)	Public Demonstration of Maceral Laboratory
14 April 1984	Fluorscent results on initial sample

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MICROCHEMISTRY OF ILLINOIS COAL--
IMPACT FOR SULFUR REMOVAL

Monte R. Hall

Department of Engineering Mechanics and Materials

Reporting Period: October-December, 1983

ABSTRACT

Sample preparation procedures have been established and the electron microprobe system has been set up to examine coal. Data collection is currently underway.

During the second quarter the sample preparation procedures were brought to a satisfactory state, the necessary fixtures and equipment were produced or acquired and a student assistant was fully trained to mount samples and to polish them. The four GRI reference samples (CTL 65AR, 85AR, 86AR, and 159AR) and several samples to serve as sulfur standards were mixed with epoxy resins, pressed and cured, and polished for maceral analysis and microanalysis. Aliquots of the same samples were stored under argon gas and reserved for thermal reaction, solvent reaction and dielectric heating. Work continued using other coal samples to work out satisfactory procedures for the thermal and solvent tests.

Much of the second quarter has been devoted to making the electron microprobe system ready for the work on coal. The system is fourteen years old and has required considerable reworking in order bring it to a state of sensitivity and reliability sufficient for the microanalysis of coal. The beam stability has been improved and x-ray spectrometers have been realigned and tested for stability, accuracy and sensitivity. Tests were performed to determine the uniformity and thickness of the carbon coating which was applied by vacuum evaporation and the interaction with beam stability and x-ray sensitivity was measured. Sample holders for heating and cooling samples in the microanalyzer have been designed but have not been tested.

The hiring and training of new project personnel are expected to aid in achieving project goals. In response to various electronic failures requiring a number of instrument shutdowns, an employee has been hired specifically for electronics maintenance and repair. Several graduate students assigned to the project for the Spring 1984 Semester are being trained to operate the microanalyzer and the thermal analysis equipment.

Analytical procedures for sulfur analysis are working well but procedures for light element analysis need further refinement. Some problems may be related to equipment malfunction and are expected to clear up when the instrument is fully upgraded. More analytically accurate standards for testing C, N, and O are being applied to the coal samples. Data collection is well underway and is expected to proceed rapidly.

ULTRASONIC VS MECHANICAL COMMINUTION OF COAL: SIZE, SHAPE AND
FRACTURE CHARACTERISTICS OF RESULTANT PARTICULATES

Paul D. Robinson
Department of Geology

October 1983 through December 1983

ABSTRACT

The objectives of this study are to investigate the size, shape and fracturing characteristics of ultrasonically comminuted coal and to compare and contrast the results with measurements and observations taken from mechanically ground coal from the same feedstock. The techniques being utilized are scanning electron microscope based automated image analysis (SEM/AIA) and high resolution scanning electron microscopy. If significant differences are found during this study, the next phase will be designed to collect specific details on the three particulate types within each comminuted sample, i.e., coal, composite, and mineral particles, in order to pinpoint the unique characteristics of ultrasonically comminuted coal which can be exploited by the beneficiation technologist.

During this reporting period a sample preparation method was developed which produces evenly distributed coal particulates on polished copper sample holders. The particulates are held in place by a thin (100 Angstrom) plastic overlayer made of Formvar. Samples of an ultrasonically comminuted Herrin No. 6 coal were prepared, SEM/AIA analysis was initiated and size and shape data was collected on over 2700 particulates. Parameters measured are width, length, area and perimeter. Statistical analysis of this data has produced parameter extremes, means, medians, RMS deviations, and frequency distribution histograms for each measured parameter.

PROGRESS DURING SECOND QUARTER

Sample Acquisition

During this reporting period the first sample of ultrasonically comminuted coal was obtained from PETC subcontractor Dr. Scott Taylor of Energy and Minerals Research Company. The sample, from the Herrin No. 6 coal seam, was split into representative portions using a microsplitter and stored in an argon atmosphere.

Sample Preparation

In order to perform scanning electron microscope based automated image analysis it is necessary to have good backscattered electron image contrast between the particulates and the binder or substrate. Epoxy binders are generally not acceptable because their atomic number is much too close to that of coal, although doping of epoxy with heavy metals such as barium or iodine has proved successful in some applications. Other problems with epoxy binders include bubbles (holes) and a tendency toward particle segregation according to size and/or density. After considerable experimentation with epoxy it was decided that a simple dispersion of particles on a polished, high atomic number substrate would prove superior. Thus, a draft free chamber (2' x 2' x 4') was built and a dry aerosol sprayer which sprays its charge of dry coal particulates into the open (top) end of the 4 foot chamber was devised. In order to insure representative sampling, a series of five samples were taken at intervals across the bottom of the chamber.

A major difficulty was insuring that the particles were affixed to the copper substrate. Numerous adhesives were tried and rejected because their

thickness masked the backscattered electron signal from the copper substrate. Eventually, a satisfactory procedure utilizing Formvar, a plastic used primarily by TEM researchers, was developed. Formvar, which is normally dissolved in ethylene dichloride, can be formed into extremely thin films (100-200 Angstroms) and is essentially transparent to the electron beam. Our original intent was to use Formvar as an adhesive; however, this attempt failed because of the extremely quick drying rate of the Formvar solution. Our successful procedure uses Formvar films formed by dipping a standard microscope slide into the solution, allowing it to dry, and floating the ultra-thin Formvar sheet off the slide and onto the surface of water in an appropriate container. The procedure is:

- 1) Cast several thin films onto water
- 2) Place films (still on water) in bottom of draft free chamber
- 3) Aspirate particles onto floating films
- 4) Apply copper sample holders to floating films

The result is a copper substrate covered in particles which are held in place by a transparent cover of Formvar.

SEM/AIA Analysis of Ultrasonically Comminuted Coal

After a preliminary survey of the particulates, the SEM/AIA equipment was carefully calibrated at 50X and the image analyzer was programmed so that the picture point density was less than one micron. Selecting the correct magnification and point density is critical when dealing with a wide range of sizes such as are present in our sample. It is desirable to minimize the magnification so that the images of the largest particles do

not become excessively large and to use the smallest possible picture point density so as not to lose information from the smaller particles. Unfortunately, this procedure produces very slow analysis speeds when the larger particles are encountered. Seventy-one frames (3.24 sq mm. each) were analyzed on the five samples yielding measurements on more than 2700 particles. Statistical analysis of the data produced the following results:

	LARGEST	SMALLEST	MEAN	RMS DEV.	MEDIAN
AREA (SQ.UM.)	7.45E 04	1.93E-01	6.45E 02	2.63E 03	3.10E 01
WIDTH (UM)	1.37E 02	1.68E-01	8.206	14.153	2.916
LENGTH (UM)	5.61E 02	1.10E 00	25.917	42.817	11.426
W/L RATIO	9.12E-01	4.50E-02	0.340	0.167	0.305
PERIMETER (UM)	1.36E 03	2.64E 00	6.46E 01	1.05E 02	-----

In addition, frequency distribution histograms for each measured parameter were produced and will be included in a future report.

Computer Modeling

Preliminary computer modeling of the data seems to indicate that the very fine portions of the sample make up only a small fraction of a percent of the total sample volume. If this does prove to be the case, future analyses will discriminate against the smallest sizes so that sample acquisition speed can be increased and more particulates analyzed.

High Resolution Scanning Electron Microscopy

Considerable time has been spent on visual examinations of the coal and mineral particulates in a preliminary attempt to get a feeling for the breakage characteristics of ultrasonically comminuted coal. At this time

we can provide no insights into breakage characteristics which are unique to the ultrasonic comminution method itself since we do not as yet have samples of mechanically comminuted coal from the same feedstock.

PLANS FOR NEXT REPORTING PERIOD

We have established the necessary methodology to obtain the experimental data required to carry out the primary mission of this investigation. During the next reporting period we will focus our efforts toward obtaining of additional samples, to collect SEM/AIA data on each sample and to begin the statistical comparison of ultrasonically vs mechanically comminuted coals. We will also continue our visual SEM investigations into breakage characteristics and will document this portion of the study with appropriate SEM photographs.

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CHEMISTRY OF CARBONYL SULFIDE

C. C. Hinckley (a)

L. V. Dunkerton (b)

J. Tyrrell (c)

Department of Chemistry and Biochemistry

A B S T R A C T

The objectives of this project are (a) to prepare and characterize lanthanide monothiocarbamate complexes and investigate their potential as precursors of disulfide ions, (b) to develop efficient and regioselective oxidative addition of OCS using metal complexes of OCS, and (c) to examine stabilities and potential reaction pathways of OCS complexes by ab initio calculations of OCS and model complexes of OCS.

(a) Lanthanide complexes of monothiocarbamates can be formed in solution. They are, as expected, sensitive to temperature and decompose to yield carbamic acids and other materials which have not yet been identified. IR indicates the presence of disulfide ions in the products.

(b) The objective of this part is to develop efficient oxidative addition reactions of OCS, including preparation and characterization of OCS metal complexes. The choice of metal and of addition reactants will be varied in an effort to achieve selectivity in the cleavage of the CS or CO bond. In this reporting period, the reaction of OCS with dienes and unsaturated enolates has been initiated, and preliminary characterization of representative OCS adducts is described. These adducts will be compared to those formed in the reaction of the same diene and unsaturated enolates with OCS metal complexes, and the selectivity compared.

(c) The objective of this work is to model the interaction between carbonyl sulfide (OCS) and transition metal complexes with a view to determining the structure of the reaction intermediates and to further the understanding of the reaction mechanism. In the current reporting period, the geometry of the Fe-OCS complex is in the process of being optimized.

II. Body of Report: (a, Hinckley)

a) Full account of progress.

Lanthanide monthiocarbamates complexes are prepared by combining methanol solutions of monothiocarbamate (mtc) and a lanthanide salt. The mtc is prepared by bubbling OCS through a methanol solution of an amine.

The lanthanide is added in one to three ratio with the mtc.

The product $La(mtc)_3$ is one of several possible, including ions of the form $La(mtc)_4^-$. Work-up procedures for separating the various components are in development.

The reaction which we have proposed to study combines a base with the lanthanide-mtc complex to yield a disulfide, as:

Bases to be studied include alkoxides and water.

Experiments have shown that the first reaction (Eq. 1) occurs smoothly without complication. The formation of lanthanide complexes (Eq. 2) is also direct, but complicated by the sensitivity of the following reaction (Eq. 3) to temperature, the presence of water, and the identity of the lanthanide salt anion.

Dicyclohexyl amine has been used in most experiments. The bulky organic groups on this amine are expected to yield greater organic solvent solubility for the lanthanide products, and simplify purification. Two groups of preparations with this amine have been performed, using $La(NO_3)_3 \cdot 5H_2O$ and $LaCl_3 \cdot 6H_2O$.

When $\text{La}(\text{NO}_3)_3$ was used, the La-mtc complex was stable in methanol solution up to 30°C . At this temperature, the compound decomposes producing a white precipitate. NMR and IR indicate that carbamic acid has formed. In this case, the base (Eq. 3) was water. It is important to note that monothiocarbamates are stable at these conditions with small amounts of water. The lanthanide ion is needed for the rapid decompositions observed.

When $\text{LaCl}_3 \cdot 6\text{H}_2\text{O}$ is used to prepare La-mtc complexes, the complexes decompose at 10°C . This increased sensitivity to temperature may involve Cl^- . The product of this decomposition is also the carbamic acid.

We have investigated the use of ethanol amine in this reaction series, and will pursue that line of research further. The goal in this case is to achieve a cyclization using the lanthanide ion as the reaction site, as:

We have found that the monothiocarbamate of ethanol amine forms smoothly and that the lanthanide complex forms and decomposes on warming. The reaction proposed in Eq. 4 has not been demonstrated as yet. The reaction products are complex, and oxygen sensitive. The product is blue in DMSO, and the solution is reversibly decolorized in air.

b) Technical problems to be addressed.

1) Purification methods for lanthanide-mtc complexes are still in development and are complicated by the temperature sensitivity of the compounds.

2) Anhydrous preparation methods will be developed.

c) Technical plans.

The principle processes which form the basis of the research proposal have been verified. That is, lanthanide-mtc complexes can be formed and they are precursors to disulfide ions. In the next period, La-mtc complexes will be

prepared, purified, and their decompositions characterized. The cyclization of ethanol amine will be pursued.

II. Body of Report (b, Dunkerton)

a) Full account of progress this period.

For the initial period, we reported that literature searching was underway, and during that time, a significant number of references were found regarding so-called hetero Diels Alder reactions. Also, an occasional reference or two showed that a hetero Diels Alder reaction could be a stepwise process, with formation of the C-C bond preceding formation of the C-X bond where X is O, N, or S. Within the variety of hetero Diels Alder reactions, those which occur stepwise were most usually initiated by Lewis acids, such as boron trifluoride etherate. For example, siloxydienes react with aldehydes regioselectively, and it was anticipated that OCS or an OCS metal complex would also react in a regioselective manner. In order to compare the metal complex OCS reaction with the reaction of OCS with a particular diene, it was necessary to carry out a control reaction of the siloxydiene with OCS. Thus, instead of a Lewis acid or a metal to activate the reaction, we chose to run this control reaction by "activating" the diene by converting it to its unsaturated enolate using a desilating reagent such as fluoride. Thus, trans-1-methoxy-3-trimethylsiloxy-1,3-butadiene was prepared by the procedure of Danishefsky (Org. Syn. 1983, 61, 147). A solution of this diene in tetrahydrofuran was desilated by addition of a solution of tetra-n-butylammonium fluoride in tetrahydrofuran. To the resulting unsaturated enolate in tetrahydrofuran was added OCS, until the solution was saturated at one atmosphere with OCS. Stirring in the dark was continued for 24 hours, after which the reaction was quenched with anhydrous methanol. The resulting solution was evaporated, and the residue filtered through silica gel, washing with 30% ethyl acetate in hexanes. The eluant, free

of tetra-*n*-butylammoniumtrimethylsilyl fluoride, was evaporated and the product mixture analyzed by thin layer chromatography, proton NMR, and infrared spectroscopy. Two major products were formed in good yield, and they were separated by flash column chromatography on silica gel, eluting with 10% ethyl acetate-hexane to 30% ethylacetate-hexane in a gradient fashion. The less polar product with infrared absorptions at 3595, 3009, 2932, 2867, 1720, 1365, 1257, 1217, 1197, 1323, 909, and 875 cm^{-1} shows a proton NMR with peaks at δ 5.5-4.8 (m, 1H), 3.2-2.8 (m, 1H), 2.2 (m, 2H). The mass spectrum and ^{13}C NMR data, obtained at outside facilities, are needed for complete confidence in the structure assignment, but tentatively, this compound is suggested to be the OCS "Diels Alder" adduct followed by elimination of methanol. This compound 1 shown below has other tautomers, so it is representative of the suggested regioisomer formed by sequential acylation- Michael addition followed by methanol elimination.

The more polar product with infrared absorptions at 3595, 3025, 2387, 1720, 1365, 1220, and 1197 shows a proton NMR with peaks at δ 3.2-2.9 (m, 2-3H), 2.9 (s, 3H, OCH_3), 2.2 (m, 2 or 3H). While awaiting ^{13}C NMR and mass spectral data, this compound is tentatively assigned as the adduct 2 which contains the methoxy group. Providing that the mass spectrum verifies the incorporation of OCS, we will rerun the NMR spectra at lower temperatures, trying to slow down the keto-enol tautomerization, so as to more distinctly assign the complex proton NMR spectra.

With this control reaction in hand, now we will move on to the characterization of OCS metal complexes and their reactions with this and other dienes. Since Lewis acids and transition metals both catalyze desilation, it is expected that reaction of an OCS complex of Pd(II), or Ti(IV), for instance, with this diene will simultaneously desilate and set up an intra-complex reaction of OCS with the resulting unsaturated metal enolate. This acylation adduct can then undergo the Michael reaction, and the net result will be a facile metal-OCS complex catalyzed Diel Alder reaction, which hopefully is very regioselective, a mild reaction, and capable of being applied to a wider range of dienes.

b) Technical problems discussion.

The following technical problems will be addressed regarding this work:

1. Characterization of tautomers by low temperature NMR, both ^1H and ^{13}C .
2. Optimizing addition reactions with no elimination.
3. Monitoring intra-complex reactions by infrared spectroscopy or NMR.
4. Optimization of procedures.
5. Extension of selective reactions to more complex molecules, including enamides, furans, and conjugated polyenes.
6. X-ray crystal structures of metal OCS complexes.

c) Technical plans for next reporting period.

The following experiments are representative of work to be carried out for the next period.

1. Characterization of OCS metal complexes of SnCl_4 , TiCl_4 , $\text{Ni}(\text{cod})_2\text{Ph}_2\text{P}(\text{CH}_2)_4\text{PPh}_2$, $\text{Pd}(\text{Ph}_2\text{P}(\text{CH}_2)_4\text{PPh}_2)\text{Cl}_2$
2. Reaction of the above complexes with dienes, ene substrates, and 1,3 dipoles; product characterization.

3. Generation of OCS aluminum and mercury complexes in situ and their reactions with substrates mentioned in #2 above; product characterization.

4. Generalizing the above results with respect to regioselectivity, reaction efficiency, and metal-OCS bonding geometry.

II. Body of Report (c, Tyrrell)

a. Full account of progress this period.

After completing a series of calculations revealing the general nature of the potential energy surface for the approach of titanium to a fixed linear geometry carbonyl sulfide as discussed in the previous report, calculations were begun to optimize the geometry of the $\text{Ti}(\text{OCS})$ complex with the titanium located either end-on to the oxygen, above the mid-point of the O-C bond or attached to the carbon. All calculations show a substantial lengthening of the C-S, indicating a weakening of that bond, and the formation of a complex which may be a precursor to sulfur elimination. The most complete set of results were obtained for the complex in which the titanium is bonded end-on to the oxygen (Table 1). These results show a slight lengthening of the C-O bond but a substantially longer C-S bond and a non-linear structure with the sulfur out of the linear by about 13° . The complex in which titanium lies about the mid-point of the O-C bond appears to have a similar structure but it was impossible to complete the optimization due to convergence problems. Table 1 shows the lowest energy structure obtained. Similar calculations on the complex in which titanium is bonded to the carbon are underway and Table 1 shows the results so far obtained.

Table 1
Titanium-Carbonyl Sulfide (Optimized Geometries)

1)	$ \begin{array}{c} \text{Ti} \text{---} \text{O} \text{---} \text{C} \text{---} \text{S} \\ \qquad \\ 1.570 \quad 1.210 \\ \text{Ti} \\ \\ 1.840 \\ \text{O} \text{---} \text{C} \text{---} \text{S} \\ \qquad \\ 1.210 \quad 2.091 \end{array} $	$E_{\text{TOT}} = -31.467127 \text{ hartrees}$
2)	$ \begin{array}{c} \text{Ti} \\ \\ 1.840 \\ \text{O} \text{---} \text{C} \text{---} \text{S} \\ \qquad \\ 1.210 \quad 2.091 \end{array} $	$E_{\text{TOT}} = -31.428036 \text{ hartrees}$
3)	$ \begin{array}{c} \text{Ti} \\ \\ 2.178 \\ \text{O} \text{---} \text{C} \text{---} \text{S} \\ \qquad \\ 1.154 \quad 1.963 \end{array} $	$E_{\text{TOT}} = -31.391533 \text{ hartrees}$

Calculations on additional segments of the potential energy surface for approach of iron to a fixed linear carbonyl sulfide have been completed. The results obtained for direct bonding of iron to the oxygen are shown in Table 2. The geometry for the iron end-on to the oxygen side of OCS is being optimized and lowest energy structure so far obtained is given in Table 2.

Table 2
Iron-Carbonyl Sulfide

$ \begin{array}{c} \text{Fe} \\ \\ \text{O} \text{---} \text{C} \text{---} \text{S} \\ \qquad \\ 1.154 \quad 1.563 \end{array} $	<p>No optimum O-Fe distance Repulsive</p>
$ \begin{array}{c} \text{Fe} \text{---} \text{O} \text{---} \text{C} \text{---} \text{S} \\ \qquad \qquad \\ 1.921 \quad 1.154 \quad 1.563 \end{array} $	$E_{\text{TOT}} = -49.241784 \text{ hartrees}$
$ \begin{array}{c} \text{Fe} \text{---} \text{O} \text{---} \text{C} \text{---} \text{S} \\ \qquad \qquad \\ 1.921 \quad 1.158 \quad 2.083 \end{array} $	$E_{\text{TOT}} = -49.432399 \text{ hartrees}$

b) Technical problems discussion.

c. Technical plans for next period.

We are currently preparing input data files for the next phase of the project, which is twofold in nature. One step is to study the $\text{Ti}(\text{OCS})$ system using a somewhat larger basis set including 4p functions in the titanium basis set and 3d functions in the sulfur basis set. The other step is to coordinatively saturate the titanium and determine the effect of this on the structure of the $\text{Ti}(\text{OCS})$ complex. This will be accomplished initially using hydrogen atoms as ligands to reduce the computational complexity. Two possible geometrical arrangements are possible (Fig. 1) and will be studied.

Figure 1

Possible Structures of $\text{TiH}_4(\text{OCS})$

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2. Coal Preparation

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CHARACTERISTICS OF A HYDROCYCLONE WITH RAW MATERIAL INPUT ALONG
THE CENTRAL AXIS - A NEW DESIGN FOR THE SEPARATION OF COAL
FROM HEAVIER MATERIALS SUCH AS PYRITIC SULFUR

Second Quarterly Report for the Period
October 1, 1983-December 31, 1983

Philip K. Davis, Principal Investigator
Contract No. DE-FC01-83FE60339
January 13, 1983

ABSTRACT

A. Statement of Objectives

The objective of this project is to determine if a hydrocyclone with the raw solid material input along the central axis gives preferable performance compared to a conventional hydrocyclone. The application of specific interest is in an economically feasible method of recovery of coal fines from the thousands of acres of gob piles and settling ponds that are available. It has been demonstrated, by means of a previous project supported by the U.S. Department of Energy (Grant #DE-FG22-81-PC40807 entitled "Flow and Design Characteristics of the Hydrocyclone for the Recovery of Coal Fines"), that good separation can be achieved on a batch basis by using conventional hydrocyclones provided they are adjusted to the right configurations. The next logical step is to demonstrate by means of a laboratory size pilot system that hydrocyclones can also efficiently separate the coal fines from gob on a continuous basis.

The main question in the present research is whether a new hydrocyclone designed for central feeding of the solid raw material do the job with less energy and less water than conventional hydrocyclones. Very briefly, the procedure is as follows:

1. Identify the design and flow variables and do a dimensional analysis to guide the experimental work.

2. Modify an existing experimental hydrocyclone (constructed under the previous project mentioned above) for central feed of the solid raw material.
3. Spheres of appropriate densities simulating particles of coal, shale, ash, pyrite and sandstone, for example, will be color coded and used to model the solid raw materials.
4. Using the sphere data as a guide for a hydrocyclone configuration, samples of gob will then be used.
5. The data will be compared to data taken on a conventional hydrocyclone to determine whether or not a new design employing a central feed arrangement is preferable.

B. Summary of Progress

During the previous reporting period (see first progress report dated October 1983) the design and flow variables were identified and a dimensional analysis to guide the experimental work was performed. Also, a previously constructed experimental hydrocyclone was modified to input the raw material hydraulically along the central axis. This method of inputting the spheres did not work as well as had been expected. Consequently, a better design was sought.

During this reporting period a mechanical auger type feeder device was constructed and incorporated into the existing experimental hydrocyclone. After several modifications of the drive assembly and pick-up device, the auger inputting arrangement is now working and data are being taken. It is not clear at this time whether the auger assembly is the best arrangement for inputting the spheres. Also, insufficient data have been taken to make a determination about whether or not the new design using a central feed is preferable to a conventional hydrocyclone design.

REPORT

A. Progress This Reporting Period

During the first quarter of this project a hydraulic device to feed the solid raw materials into the hydrocyclone along the central axis was designed, constructed and incorporated into an existing experimental hydrocyclone system. It was found that this design did not work as well as had been expected. Since then, a mechanical auger type feeder device, shown schematically in Figure 1, has been designed and constructed. An auger of the size needed ($\approx 1\frac{1}{2}$ inches) was not available commercially. Therefore, it was necessary to machine the auger in the University's Fine Instrument Shop. Machining the auger and fabricating the drive assembly, feed arrangement, housing, etc., took a period of several weeks. After several modifications of the drive and feeder assemblies, the experimental hydrocyclone with the auger feeder assembly installed is now functional and data are being taken. However, insufficient data have been taken to make a judgment as to whether or not this design is preferable to a conventional hydrocyclone. Examples of plots showing some of the data that have been taken are shown in Figures 2 and 3.

B. Discussion

The auger feeder is driven by a $\frac{1}{8}$ horsepower Servo-Tek variable speed drive. In order for the spheres to be drawn into the auger at the bottom (starting place) it has been found that it works better wet, i.e., with a small amount of water flowing into the feed device along with the spheres. The main reason for this difficulty is that the auger is being used in the vertical position. If it were at an angle to the vertical, this difficulty would probably not exist. The outside diameter of the tube containing the auger is $1\frac{5}{8}$ inches. It has been found that the auger works best at a rotational speed of 1600 rpm for feeding the spheres into this hydrocyclone.

Figure 1. Diagram Showing Auger for Raw Material Input Along the Central Axis.

Figure 2. Percent of Solids to Overflow Versus Specific Gravity for 1/4 Inch Spheres.

Figure 3. Percent of Solids to Overflow Versus Specific Gravity for 1/4 Inch Spheres.

The plots in Figures 2 and 3 show a sharper cut-point by feeding the spheres into the hydrocyclone tangentially. However, these preliminary data also indicate the possibility that the specific gravity cut-point can be increased by feeding the spheres into the hydrocyclone along the axis using the same flow rate.

C. Plans for Next Reporting Period

The idea of a hydraulic system for inputting the raw material has not been completely discarded. For a continuous operation such as in a processing plant, wear may be a significant problem to deal with with an auger arrangement. The plans are to consider other possible designs of a hydraulic inputting system than the first one that was tried. This will take place concurrently while continuing to take data using the auger feed arrangement.

PROJECT QUARTERLY REPORT

DEVELOPMENT OF SYSTEM OPERATING PARAMETERS FOR
ASH AND SULFUR REDUCTION IN ILLINOIS BASIN COALS
BY FROTH FLOTATION

Coal Technology Laboratory
(USDOE Contract No. DE-FC01-83FE60339)

A. K. Sinha
Department of Mining Engineering
Southern Illinois University

Jan. 1, 1984

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Second Quarterly Report

Performance Period: October 1 to December 31, 1983

Contract Objectives: The objectives for this period were:

- a) Sample Preparation
- b) Bench Scale Testing
- c) Pilot Scale Froth Flotation Facilities Development

Achievements:

The second quarter of the contract period was very productive.

Sampling:

Six channel samples have been obtained from selected coal mines operating in Southern Illinois. Three of the samples have been ground to minus 35 mesh in size for bench scale testing. A representative sample from each group is carefully obtained and analyzed before being packaged in plastic bags for further testing. The data obtained to date indicate that each of the three channel samples contain over 4 percent total sulfur which is very representative of the high sulfur coals in Illinois Basin. Further preparation of the other samples is now in progress.

Bench Scale Testing:

A Denver D type bench scale froth flotation cell with a capacity of up to 2000 grams is being used for the bench scale tests. A series of initial tests were conducted to select the froth flotation reagents and cell operating parameters for the bench scale tests. Thus, the following reagent and cell operating parameters were selected for further testing:

Collector for Coal	-	Kerosene
Depressant for pyrite	-	Cyanide
Frother	-	Dow froth 1263
PH	-	7
Agitation	-	900 rpm
Conditioning time	-	12 minutes
Aeration	-	2 minutes

In order to optimize the reagent concentrations and the cell operating parameters, a series of 27 experiments is conducted on each sample and the data thus obtained are analyzed using a nonlinear computer model. Two series of such tests have already been completed and the data obtained are presently being analyzed. The confirmatory tests on these samples will be completed soon. The data obtained are too premature at this stage to be reported.

Pilot-Scale Froth Flotation Facilities

A Denver, 8 cell - No. 8 Sub-Aeration, cell to cell, pilot plant froth flotation machine has been acquired which is suitable for de-sulfuring and cleaning coal. It has a continuous capacity of 500 lbs per hour. Each cell has a pulp volume of 2.75 cu. ft. The 8 cells are arranged in 2 groups with four cells each. A feed splitter box is provided at the beginning of each group of cells. Four 1 h.p. - 3 phase induction motors drive the agitator in the eight cells.

The flotation machine was completely disassembled, thoroughly cleaned, and painted with epoxy paint to prevent contamination of the samples during testing. The cells have now been assembled together at the DOE's Coal Technology Laboratory in Cartersville. Facilities for handling, conditioning and feeding the samples are now being developed. The system parametric monitoring instruments have already been ordered.

It is planned to conduct a series of tests on each sample in a single cell before conducting the pilot scale tests on a continuous flow basis.

ELECTROCHEMICAL DESULFURIZATION OF COAL SLURRIES

Principal Investigator: Shashi B. Lalvani
Department of Thermal and
Environmental Engineering

ABSTRACT

The objectives of this investigation are to: i) electrochemically desulfurize the coal slurries and ii) simultaneously produce valuable H_2 gas at electrode potentials lower than that required for ordinary water electrolysis. Experiments were performed at an electrode potential of 1.2 V, SCE on Illinois No. 6 coal (63-75 μm) suspended in aqueous electrolytes of HCl and H_2SO_4 . A pyrex reactor provided with Pt mesh electrodes was used for the electrolysis purpose. Up to 42% of the total sulfur removal was accomplished when electrolysis was performed for a period of 23 hours. In other experiments various concentrations of Ce(IV) were added to the electrolytes to improve the process efficiency and selectivity. Faraday current efficiencies for H_2 production were observed to be as high as 87 - 98%. Anodic current versus time behavior of coal slurries is also discussed.

ELECTROCHEMICAL DESULFURIZATION OF COAL SLURRIES

Second Quarterly Report

The coal is first contacted with an acid (usually HCl and H₂SO₄) and brought to the desired temperature of reaction in the reactor described in our previous report (refer to Figure 1 of September 1983 Progress Report). Contact between the acid and Illinois No. 6 coal produced CO₂, presumably released by mineral matter (such as CaCO₃, MgCO₃) of the coal. Reacting 15 g of Illinois No. 6 coal (63 - 75 μ m) with 300 - 325 ml of acid at a temperature of 65°C released up to 23 ml of CO₂ in 6 hours. After the production of CO₂ ceased, a constant potential was applied to the electrochemical reactor.

Figure 1 shows a typical current versus time behavior of 15 g of Illinois No. 6 coal (63 - 75 μ m) electrolyzed at 65°C in 300 ml of a solution containing 5% HCl and 15% H₂SO₄ by weight at an applied electrode potential of 1.2 V, SCE. In some experiments electrocatalysts (Ce (IV)) were added to the electrolyte to enhance the reactivity and selectivity of the process. It can be gleaned from Figure 1 that the reactivity of coal electrolysis is high initially and the anodic current reaches a constant limiting value after about 2 - 4 hours of electrolysis.

During the course of electrolysis, hydrogen gas was found to evolve at the cathode compartment which was carefully measured in water-filled inverted graduated cylinders. Faraday current efficiencies were calculated and a plot of this current efficiency versus time of electrolysis shown in Figure 2. The Faraday efficiencies were found to be quite high (between 86 - 99%). Although the current efficiencies were initially relatively low when the catalyst (cerium cation) was added to the electrolyte, the efficiencies increased significantly with the time of electrolysis.

Fig. 1. Oxidation current as a function of electrolysis time.
Potential + 1.2V SCE; temperature 65 C; 15 gms of coal in 300 ml acid.

Fig. 2. Faraday current efficiencies for H_2 production as a function of electrolysis time. Potential + 1.2V SCE, temperature 65 C, 15 gms of coal in 300 ml acid.

Sulfur assays were performed on coals electrolyzed under different operating conditions as indicated in Table 1. Sulfur removal was computed in two ways:

(1) reduction in sulfur content:

$$\frac{\% \text{ S in initial coal} - \% \text{ S in reacted coal}}{\% \text{ S in initial coal}} * 100$$

(2) the fraction of sulfur removed:

$$\frac{(\text{coal mass} * \text{sulfur fraction}) \text{ feed} - (\text{coal mass} * \text{sulfur fraction}) \text{ product}}{(\text{coal mass} * \text{sulfur fraction}) \text{ feed}} * 100$$

The latter value is more reliable as a measure of sulfur removal because it is not affected by any possible increase of mass of the coal, e.g., by addition of oxygen which is usually the case in most oxydesulfurization processes.

Sulfur removals as high as 41.5% have been achieved in 23 hours by electrolyzing Illinois No. 6 coal in 300 ml of an electrolyte containing 5% HCl + 15% H₂SO₄ by weight. It can also be observed that mild electrolysis for 6 hours in a mixture of HCl and H₂SO₄ results in 38% sulfur removal. From our point of view, the mixture of HCl and H₂SO₄ results in the most suitable electrolyte for sulfur removal.

Table 1

Sulfur removal from coal. 15 g of Illinois No. 6 (63 - 75 μ m) were electrolyzed in 300 ml of electrolyte at 1.2 V, SCE, the reaction temperature being 65°C.

FXPT NO	Electrolyte	Time of Electrolysis, Hours	Reduction in S Content, %	Sulfur Removal, %
*2	1 M H_2SO_4	6	23.5	32.6
*3	1 M H_2SO_4	6	31.7	37.1
**4	5% HCl + 15% H_2SO_4	23	40.6	41.5
**5	5% HCl + 15% H_2SO_4	6	33.9	38.1

*Raw (unelectrolyzed) coal was found to contain 4% sulfur by weight.
Sulfur removals have been based on 4% sulfur in the feed.

**Raw (unelectrolyzed) coal was found to contain 3.06% sulfur by weight.
Sulfur removals have been based on 3.06% sulfur in the feed.

3. Coal Conversion

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EXTRACTION AND DESULFURIZATION OF CHEMICALLY DEGRADED COAL WITH SUPERCRITICAL FLUIDS

Principal Investigators:

Juh W. Chen, (Project Director), Charles B. Muchmore
Albert C. Kent and H. Peter Hombach

Department of Thermal and Environmental Engineering

ABSTRACT

The research project is to conduct a systematic study of extraction and desulfurization of coal with supercritical fluids. The objectives are: (1) to determine the effect of process variables on yield and selectivity of the extraction and desulfurization of coal; (2) to determine the effect of chemical treatment of coal on supercritical extractability; (3) to develop an interrelationship between selective supercritical extraction and coal characteristics; (4) to evaluate the product streams and solid char; and (5) to design and build a continuous flow reactor system (Process Development Unit) for the process development study.

The experimental study has been very productive during the first six month period. The data indicated that a significant progress has been made to understand the extraction and desulfurization of coal with supercritical fluids and to evaluate the process potential for removing organic materials including sulfur compounds from coal matrix.

From the experimental findings, it was found that the supercritical extraction and desulfurization of coal with ethanol can be described by the semi-empirical equation with first-order kinetics between 250°C to 350°C at 1750 psi. Furthermore, the general relationship between coal solubilities and the density of the supercritical fluids is valid under different temperatures and pressures. The selectivity of desulfurization over coal extraction was found to be between 3.0 to 4.4 for four coal samples tested.

Methanol and ethanol are both excellent supercritical fluids for desulfurization. The liquid product from ethanol contained more aromatics and polars, and less asphaltenes than those of methanol. The constituents in liquid product were also affected with temperature, pressure and chemical treatment.

In the experiments to study the effect of chemical treatment on supercritical extraction and desulfurization of coal with methanol, it was found that a high sulfur coal (73% organic sulfur) was reduced from 4.43% sulfur to 1.9% at 350°C and 4100 psi with 5% KOH/methanol solution. It was 57% sulfur reduction on concentration basis. Without KOH treatment, only 40% reduction was observed.

The construction of the continuous flow reactor system (PDU unit) is nearly completed. It is anticipated that preliminary testing of the reactor will be conducted in the next reporting period.

INTRODUCTION

The research project is to embark on a systematic study of coal-derived feed-stock with supercritical fluids. The research objectives during the first year of the funding period are: (1) to determine the effect of process variables such as temperature, pressure, retention time on the supercritical extractability of coal. This will allow us to develop semi-empirical mathematical equations for describing the supercritical extraction process; (2) to develop an interrelationship between selectivity, defined as the ratio of percent of sulfur removed to percent of coal extracted for various coal samples; (3) to determine the effect of supercritical extractability with chemical treatment; (4) to evaluate both liquid products and the coal char; and (5) to design and to construct a Continuous Flow Reactor (PDU) for process development study. It is anticipated that the information obtained from the experimental investigation will enable us to establish a data base for the supercritical extractability of coal with ethanol.

SCIENTIFIC SIGNIFICANCES

Although the principles underlying the characteristics of supercritical extraction have been known for a long time, it has only generated an active interest in the research community during recent years. Fluids under supercritical conditions exhibit enhanced dissolution power which can increase the solubilities of various involatile organic compounds hundred or thousand folds. The dissolution power of supercritical fluids is dependent on temperature and pressure of the system and the characteristics of the fluids.

A semi-empirical equation has been used to describe the relationship

$$\ln C = m \ln \rho + n \quad (1)$$

where C is solubility of organic compound

ρ is density of supercritical fluid

m and n are empirical constants for each fluid

When the coal is degraded by chemical treatment, cross-linkings of coal matrix may be decreased due to chemical reaction(s). It is one of the most important steps to break down coal structure and to extract organic compounds from coal particles.

EXPERIMENTAL

Reactor System

A Bertly gradientless 300 cc reactor equipped with a Magne-drive impeller and internal recirculation was used for the experiments. The continuous flow of supercritical fluid through the reactor was maintained by using a high-pressure variable flow metering pump. For each run, a sample of pre-dried coal was placed in a stainless steel container inside the reactor, the supercritical fluid was pumped at a constant flow rate under constant temperature and pressure conditions. Throughout the entire experiment, the supercritical product stream was continuously released from the reactor through a cooling loop and a two-stage pressure letdown vessel to recover the liquid products and to separate the non-condensable gases. The liquid and gaseous samples were collected for analyses at different extraction times. The coal char after extraction was dried. Sulfur, ash and calorific value of the original coal as well as each coal char sample were determined. The percent of weight loss of coal and the percent of sulfur removed were calculated on a dry coal basis.

Liquid Product Analysis

A 4-ml of liquid sample was first evaporated under vacuum to remove the solvent. The coal liquid was then redissolved in a 4-ml n-Hexane. The part of coal liquid which is insoluble in n-Hexane is called asphaltenes. The remainder which is soluble in n-Hexane, is called oils. A High Pressure Liquid Chromatograph (HPLC) technique has been developed to identify organic fractions of saturates, aromatics and polars in the oils by using a μ -Bondapak-Amino Column with UV and Refractive Index detectors.

RESULTS AND DISCUSSIONS

The data of supercritical extractability of Coal A (Illinois No. 6) at a temperature range between 250°C to 350°C, a pressure of 1750 psi and an extraction time up to 8 hours were correlated with semi-empirical equations listed in the following

$$W = W_{\infty} - (W_{\infty} - W_0) e^{-kt} \quad (2)$$

$$S = S_{\infty} - (S_{\infty} - S_0) e^{-k_s t} \quad (3)$$

where W , W_{∞} and W_0 are instantaneous, ultimate and zero-time weight loss of coal respectively; S , S_{∞} and S_0 are instantaneous, ultimate and zero-time sulfur content of the coal respectively; k and k_s are empirical rate constants of supercritical extraction and desulfurization respectively.

The data fitted in equations (2) and (3) reasonably well. A plot of k and k_s versus $1/T$ are presented in Figure 1. The activation energy for coal extraction and for desulfurization are 30.3 K cal and 21.0 K cal respectively. It can be seen that sulfur removal is much easier than coal extraction under these supercritical conditions. Therefore, the selectivity of sulfur removal, defined as the ratio of percent of sulfur removed to percent of coal extracted should be much greater than one.

A semi-log plot of percent weight loss of coal versus density of supercritical ethanol at different temperatures and pressures is delineated in Figure 2. It is obvious that the semi-empirical relationship described in equation (1) fits the data very well.

Figures 3 and 4 show the data of sulfur removal and coal extraction for four different coal samples at 325°C and 1750 psi. The coal samples include the three standard reference coals [C-22440 (Coal B), C-22443 (Coal C) and C-22441 (Coal D)] supplied by the Illinois State Geological Survey. The selectivity with supercritical ethanol is found to be between 3.0 to 4.4 for these four coal samples. This

Figure 1

Figure 2

Figure 3

Figure 4

may mean when the supercritical ethanol attacks the cross-linkings of coal matrix, it not only breaks the bonds of coal structure, but also preferably reacts with sulfur groups to form sulfur compounds which are easily removed by the supercritical fluid.

As we reported previously, the desulfurization potential of supercritical ethanol is similar to that of supercritical methanol. Recent data at 350°C and 3500 to 4100 psi have indicated that a high sulfur coal (73% organic sulfur) was reduced from 4.43% to 1.9 with a 5% KOH/methanol treatment for one hour reaction time. It was a 57% reduction in sulfur content. Under similar experimental conditions without KOH treatment, only 40% and 38% reduction in sulfur content were observed for supercritical methanol and supercritical ethanol respectively. An increase of 42 percent of sulfur removal efficiency can be attributed to chemical degradation.

In the product evaluation, it was found that the calorific value of the solid char was similar to that of the original coal with a slight increase of ash content. Only a small amount of non-condensable gas was produced in the semi-continuous reactor experiments. The gas mainly consisted of methane, ethane and carbon dioxide. There were no detectable sulfur compounds in the gas phase. The liquid product distribution of a supercritical extraction with ethanol at 275°C and 1750 psia was found to be asphaltenes 80%, saturates 9.1%, aromatics 5.8% and polars 4.9%. However, when the reaction conditions were at 400°C and 3000 psi with 5% KOH treatment, the distribution was asphaltenes 48.4%, saturates 0.3%, aromatics 35.7% and polars 15.6%. It is important to note that the content of the liquid product was varied considerably under different operating conditions and with chemical treatment.

PROCESS DEVELOPMENT UNIT (PDU)

A continuous flow, stirred tank reactor system has been designed and is being constructed. The major system components include a coal/solvent slurry

preparation tank with recycle pump, a variable flow high pressure pump, a two liter stirred tank reactor, and a product collection system. To avoid the high cost and operational problems inherent to small scale pressure let-down devices, dual product collection chambers are being utilized that will operate at system pressure. A three-way valve in the product transfer line from the reactor will permit alternate collection of product in those vessels; system pressure will be maintained by a gas control valve on the gas product lines leading from the collectors. After initial pressure testing of the system, the PDU will be moved to the Coal Technology Laboratory at Cartersville and supercritical reaction runs will commence.

CONCLUSIONS

1. The supercritical extraction and desulfurization of coal with ethanol can be described by semi-empirical equations with first-order kinetics. The activation energy for coal extraction as well as for desulfurization obtained can be used as a measurement to evaluate the relative difficulty of the process. For supercritical ethanol, the selectivity of desulfurization is ranged between 3.0 to 4.4 for four coal samples tested. It means that sulfur compounds are easier to be remove.
2. The general relationship between coal solubilities and the density of supercritical fluids is valid under different temperatures and pressures with various solvents. Even though the solubilities of coal in supercritical ethanol and methanol are low, the selectivity of desulfurization is much greater than those solvents with high solubility.
3. The selectivity of desulfurization for supercritical ethanol and for supercritical methanol are similar.
4. The desulfurization potential is enhanced by KOH treatment, especially for high organic sulfur coals.

5. The content of liquid product consists of asphaltenes, saturates, aromatics and polars. The relative distribution is varied with different operating conditions. At a higher temperature (400°C), more aromatic and polar compounds were extracted than those at a lower temperature (275°C). In the latter case, the liquid has a higher content of asphaltenes.

PLAN FOR NEXT REPORTING PERIOD

1. To continue to supercritical extractability study with methanol.
2. To concentrate the chemical treatment study with KOH and other chemicals.
3. To operate the continuous flow reactor, and to test mechanical systems including feed, pressure release, product collection subsystems.
4. To identify and to isolate organic materials including sulfur compounds in the liquid products.

STRUCTURE-SENSITIVE CATALYTIC DEHYDROGENATION OF HYDROGEN
DONORS OVER IRON-SULFIDES: NEW METHODS FOR INCREASING
COAL DEPOLYMERIZATION UNDER MILD CONDITIONS

Gerard Smith and John Phillips

Department of Chemistry and Biochemistry

Reporting Period: October-December, 1983

ABSTRACT

The objectives of this project are to examine the mechanism of hydrogen sulfide formation from iron sulfides, to explore the conditions for enhancement of in situ hydrogen sulfide production in coal, and to study the conditions for stabilizing iron sulfide structures under reaction conditions.

Progress on the first objective has revealed that hydrogen sulfide is formed from hydrogen and iron sulfides by a Langmuir-Hinselwood mechanism. Mixtures of H_2 and D_2 produce $(H,D)_2S$ with random distributions of H and D. Moreover HD is desorbed from the iron sulfides.

EXPERIMENTAL: The mechanism of H_2S formation from iron sulfides was established as the Langmuir-Hinshelwood type by passing a 50-50 mixture of H_2 and D_2 over 0.5g Colorado pyrite at 673 K in a plug flow reactor and observing the $(\text{H,D})_2\text{S}$ formed. After deconvolution of the mass spectra due to H_2S , HDS , D_2S , and their fragments it is clear that the hydrogen and deuterium are randomly mixed in the $(\text{H,D})_2\text{S}$ formed. This can best be explained if the hydrogen and deuterium are dissociating and scrambling on the pyrite surface.

To further test this mechanism we studied the exchange of H_2 and D_2 over iron sulfides. We prepared a sulfur poor iron sulfide (troilite) by passing H_2 over Colorado pyrite at 673K for 48 hrs. Then the reactor temperature was decreased to 300K and a 50-50 mixture of H_2 and D_2 was passed over the iron sulfide for one hour. Finally, with the H_2 - D_2 mixture flowing at 30 ml/min., the temperature was increased to 373K and held 30 min. followed by 50K steps at 30 min. intervals to 673K after which the temperature was decreased in 50K (30 min. intervals) steps. Mass spectra (scans run every 47 sec.) of the $(\text{H,D})_2$ mixture revealed the presence of HD.

DISCUSSION: From the random distribution of hydrogen and deuterium in the $(\text{H,D})_2\text{S}$ and from the appearance of HD in the H_2 - D_2 exchange it is clear that hydrogen is dissociated by iron sulfides. This contradicts previous conclusions (see reference 3 in proposal) which were based upon the inability of pyrite to catalyze the hydrogenation of naphthalene to tetralin.

Although this latter is true, it is also true that iron sulfides catalyze the hydrogenation of other molecules. For example, we have

observed the hydrogenation of acetone to isopropanol, butadiene to butene, and butene to butane (very slow). Furthermore, a recent paper reports the hydrogenation of quinoline to tetrahydroquinoline (J.A. Guin, C.W. Curtis, and K.C. Kwan, FUEL, 62 1412 (1983)).

Therefore, it appears that iron sulfides can dissociate hydrogen and the resulting hydrogen atoms (ions) are adsorbed into the iron sulfide matrix and can be used to form H_2S . Additionally, these hydrogen atoms (or ions) can be used to hydrogenate certain bonds. The most susceptible bonds are those which are polarized, for example, carbon-oxygen, carbon-nitrogen, and nitrogen-oxygen double bonds, or carbon-carbon double bonds which are readily polarizable, such as butadiene. Hydrogenation is resisted by isolated carbon-carbon double bonds (very slow) and aromatic carbon-carbon double bonds which are not in a heterocycle.

TECHNICAL PLANS:

We plan to continue to study the mechanism of H_2S formation using ethanol as the hydrogen source as outlined in the proposal. The Perkin-Elmer laboratory computer has arrived and will be interfaced with the microbalance (also recently arrived) to form a special catalytic reaction system.

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4. Coal Utilization

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USE OF FLUIDIZED BED COAL COMBUSTION TECHNIQUES
TO STUDY EFFICIENCY, EMISSION REDUCTION,
BOILER EFFECTS AND WASTE UTILIZATION

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Report Dates: October 15, 1983 to January 16, 1984

ABSTRACT

To provide flexibility of data acquisition, the research efforts utilize two fluidized bed combustor systems. The laboratory scale AFBC will provide fundamental data on the combustion characteristics of waste fuels, and indicate the variables needing pilot scale testing. These data will then be studied using the 1 foot diameter pilot scale system.

Preliminary studies have been conducted on the combustion of regular coals in the 10 cm diameter laboratory scale AFBC unit preparatory to the tests to be conducted on waste fuels. The results indicate the importance of the various sulfur forms in the coal on the efficiency of sulfur oxides retention in the bed.

The pilot scale system drawings are being revised to best suit test needs and building resources. Construction permits have been filed and the system should be delivered about June 1. Analytical equipment specifications are now being prepared for both systems and working areas are being prepared for operation/construction.

PROGRESS ACCOMPLISHED

Overall Project

Discussion with DOE and Coal Technology Laboratory personnel resulted in the project being divided into two distinct areas of study. One part consists of the bench scale work using the existing Department of Thermal and Environmental Engineering 10 cm (approximately 3 inch) diameter AFBC and as time and funds permit constructing and operating a companion 6 inch diameter bench scale AFBC. The other portion of the study consists of installing and operating the pilot scale 1 foot diameter AFBC at the Cartersville laboratory. Direction will be obtained using the bench scale facilities and verification will be made on the pilot scale system.

Laboratory Scale Studies

Preparatory to investigation of the basic combustion characteristics of waste fuels, tests were conducted on normal bituminous and subbituminous coals to evaluate system performance. The object of the study was to determine the role of sulfur forms -- pyrite, organic and sulphate sulfur -- on the efficiency of SO₂ retention in a limestone fluidized bed. The total sulfur content and the breakup of the various sulfur forms of selected coals was first determined. The analytical techniques employed followed standard procedures for determining this data. The selected coals were then burnt in the laboratory scale 10 cm AFBC unit under identical conditions. The Ca/S ratio for all the tests was fixed at a value of 3:1. The superficial velocity was held constant and the coal feed rate was adjusted for each coal such that the bed temperature was also constant. Sulfur dioxide emissions and other relevant data was measured.

The role of coal sulfur forms during in-situ desulfurization in fluidized beds is shown in Figure 1. Although there is a large concentration of calcium in the bed material, the data of Figure 1 show that the influence of the pyritic sulfur content is significant, with the observed SO₂ emissions being highest when the ratio of

pyritic to total sulfur is about 0.4. The study shows that the manner in which the various sulfur forms are bound to the organic structure strongly influences their release rates and subsequent oxidation characteristics.

Figure 1. Relationship between SO₂ emissions and the ratio pyritic sulfur/total sulfur

Similar information along with other data will be gathered for the test fuels.

Pilot Scale Work

Three bids were made to supply the pilot plant AFBC - York Shipley, Johnston Boiler and G. A. Technologies. The York Shipley 1.2×10^6 Btu/hr system met our specifications and was awarded the contract to construct for \$82,500. This single stage system will be able to operate in either circulating or conventional fluidized bed modes. A meeting was held with DOE personnel at MERC to review the preliminary system drawings. They indicated agreement with the basic facility and suggested refinements which have been incorporated. One meeting has been held with York Shipley at their offices to review their drawings and it is expected that final drawing approval should be made late in January. Delivery is to be 120 days after that time. Detailed building dimension sketches have been made and submitted to York Shipley to incorporate the best possible use of the building arrangement. The required Illinois EPA Construction Permit forms were completed and submitted for this system in December.

Work is now in progress to prepare test equipment specifications for the analytical needs of the facility. In addition, work is underway to prepare the building for the system. This includes among other items planning locations, preparing pads, and obtaining LPG start-up fuel and lines.

FUTURE PLANS

Our immediate plans are to proceed to obtain fundamental data on the laboratory scale fluidized bed combustor relevant to the use of waste fuels. Tests to be conducted will investigate the influence of sulfur forms, C/H ratio, precombustion process variables, etc. on the combustion and emission characteristics. This will serve as a data base and indicate the direction for the pilot scale tests.

Also, preparations for installing the pilot scale unit will continue to be made.

Critical Points in the Coal Fuel Cycle: A Modeling Analysis

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Abstract

a. Statement of Objectives:

The research proposal for the modeling project contained six general research goals. Each of these was broken down into specific tasks in the project work plan.

The tasks associated with the general goal of determining the feasibility of using coal models were to explore the existing coal models and select one for use by the CTL. Other general goals in the first half of the project were basically in the areas of literature review, and the identification and gathering of data pertinent to the coal model. These data are in the areas of coal supply and demand, transportation technology and costs, pollution control regulation and the options available to comply with regulations, the costs of these options, and the range of evaluations of sulfur reduction strategies by commercial users and developers.

b. Summary of Progress

Modeling. Several coal models were examined in the early stages of the project, and the Argonne National Coal Model (ACM) was obtained. During this reporting period the model was placed in an operational status. Because there were significant problems associated with ACM, the modeling team turned to the recently developed Coal Supply and Transportation Model (CSTM). This model has been reviewed and will soon be operational at the CTL. The data on which runs of CSTM will be based are being generated by the other elements of the project team.

Transportation. Team members concluded research into slurry pipeline options, created an equation for estimating the response of rail rates to monopoly conditions, and developed econometric methods of rate estimation as opposed to engineering cost methods.

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Air pollution abatement. Researchers completed review of existing regulations and literature pertaining to technical options for sulfur removal and control. They also completed first round site visits to collect data on costs of sulfur emission control.

Water and solid waste problems. Other team members completed review of issues and regulations affecting coal residuals, collected data on solid waste and waste water disposal and handling costs, and completed preliminary design of questionnaires for use in interviews of coal users to establish the likelihood of adoption of new technologies.

II. Report

a. Progress and Technical Problems

Modeling. Early in the quarter, problems with the SIU-C computer system in compiling a linear programming pre-processor called NULEMKE were resolved and the Argonne National Coal Model (ACM) was successfully run. Also, since the ACM scrubbing equations were outdated and based on old regulations, new equations including the mandatory scrubbing regulations were developed.

The demand and supply data for the ACM was out-of-date, so a methodology was explored for updating based on the DOE National Coal Model (NCM). Also the ACM transportation equations based on engineering methods for estimating the railroad coal delivery rates, as developed by Reiber and Soo,¹ were investigated. It became clear that a considerable effort would be required in these areas to update the ACM.

In October 1983, the DOE released information on the Coal Supply and Transportation Model (CSTM), and this model was thoroughly examined by the modeling team. The program was studied line-by-line and the data requirements were analyzed. Based on this review, it was concluded that the CSTM would be appropriate to establish the feasibility of using an on-board model at the Coal Technology Laboratory (CTL). The model itself was obtained on January 12, 1984.

While the CSTM was being studied, work continued on developing equations relating coal sulfur content to pre-combustion treatment and combustion oriented techniques for reducing sulfur content. Also, background information on transportation was generated.

Transportation. Two objectives relating to coal transportation identified in this grant are: 1) examination of alternative coal hauling methods, i.e. coal slurry pipelines; and 2) evaluation of current and historical rail rates and capacity to project impacts on future distribution patterns. Relevant to these issues are eminent domain legislation for coal slurry pipelines and the Staggers Act deregulating the railroads. The defeat of eminent domain legislation in September by the House of Representatives has tabled the construction of most slurry pipelines now under consideration. Therefore, the primary focus of this study will be on rail rate-setting after deregulation has made the (legal)

connection between rates and cost less direct. Therefore, engineering cost studies of railroads may not accurately reflect the rates that carriers will charge their customers. The transportation component of the CSTM is based on the origin-destination link rate equation. The equation yields predicted rates, given route indices of congestion, competition, capacity, and distance. It is econometrically based, utilizing recent rate data on unit trains. The econometric approach is felt to be an improvement over the engineering approach in capturing rate setting in the deregulated market.

In order to better model the impact of railroad monopoly power (or lack of competition) along specific links a new rate equation has been specified based on the original CSTM rate equation. Data used for estimation of the original equation has been obtained from the Department of Energy. These data are being combined with data compiled from the "Cost and Quality of Fuels for Electric Utility Plants - 1982 Annual." In particular, a measure of available rent has been compiled.

Air Pollution Abatement. Progress was made toward review of the issues and regulations affecting coal residuals and obtaining estimates of abatement costs. Much of the literature has been combed and collation of the estimates has begun. Different reports give costs in different units (¢/quad mils/kwh etc.) and most include capital and operating expense while some do not. Also, there is variation in the handling of financial estimations such as return on investment and capital costs. Special attention has been paid to questions of estimating the time frame for possible application of abatement technologies. This work has been accomplished in two ways: literature search through published data (including telephone contact to obtain recently released but as yet unpublished data), and visits with operators and researchers concerned with coal combustion and air quality. The sites visited thus far have been:

1. Tennessee Valley Authority - Knoxville, TN
2. EPA's Industrial Environmental Research Laboratory - Research Triangle Park, NC
3. Oak Ridge Associated Universities - Oak Ridge, TN
4. Institute for Mining and Minerals Research at Univ. of Kentucky - Lexington, KY
5. Argonne National Laboratory - Argonne, IL

6. Conference on Acid Rain, sponsored by the Illinois Department of Energy and Natural Resources - Chicago, IL

There is a range of technologies available for present and future pollution abatement. Table 1 identifies the leading technologies and classifies them according to their availability, costs, and applicability.

TABLE 1
AIR POLLUTION ABATEMENT TECHNOLOGIES

TECHNOLOGY	AVAILABILITY	COSTS	APPLICABILITY
Physical Coal Preparation	present	known	Old I/U*, New I/U
Chemical Coal Preparation	future	projected	unknown - presumably new units
FBC - Fluidized Bed Combustion	future	unknown	New I/U
LIMB	near future	projected	Old I/U**
FGD wet	present	known	New I/U
FGD dry	present	known	Old I, New I

*I = industrial application, U = Electric utility applications.

**With limitations dependent on boiler design.

The site visits have allowed us to draw the following tentative conclusions:

1. Physical Coal Preparation or coal cleaning is in use at several locations, the most advanced operation in utility service is at the TVA Paradise Plant.
2. Chemical Coal Preparation is a developing technology with several methods proven to significantly reduce organic sulfur content of coal prior to combustion. No commercial application has been attempted, however.

3. Fluidized Bed Combustion is being developed by the TVA and the Illinois Department of Energy and Natural Resources. Pilot projects are in existence at several sites. Problems with scale-up limit the potential to project meaningful cost estimates, and bring into question the application of this technology for utilities.
4. Limestone Injection in Multistage Boilers is a technology favored by the EPA as having a significant potential for retrofit in existing utilities. This is a leading strategy to deal with short-term sulfur reduction in answer to acid rain legislation.
5. Flue Gas Desulfurization - Wet is a proven technology in widespread use. Attention here will be directed toward estimating the possibility of changing costs of application and use downward as time goes on.
6. Flue Gas Desulfurization - Dry is in use at the Argonne National Laboratory at the industrial scale of operations. Cost data from the ANL project have been obtained and can be integrated into the model.
7. Other technologies and combinations of coal preparation and combustion alternatives remain to be explored.

In the area of water and solid waste water treatment, two of the three tasks of environmental assessment of post-extraction coal utilization schemes are nearly completed. These include 1) the review of the issues and regulations that affect coal residuals; and 2) an assessment of the reported abatement costs. The third task, the evaluation of the attitudes and opinions held by commercial coal users toward various coal preparation and utilization schemes, is only partially completed. Two survey techniques, personal interview and mail survey questionnaire, have been selected as best suited to the objectives of this task. Preliminary designs of both instruments are completed except for questions pertaining to the impacts of the proposed environmental legislation.

The first area is the widely publicized problem of acid rain and the anticipated enactment of acid rain control legislation. The existing information on this legislation is not well integrated in the literature. Nevertheless, an attempt was made to formulate the most likely outcome in the form of changes to the existing regulations. The second issue pertains to the impact of the Resource Conservation and Recovery Act and the Clean Water Act on handling coal residuals. Of these the most important is the

decision to classify these residuals as either hazardous or nonhazardous which remains an unresolved issue. It is anticipated that both the acid rain legislation and the enforcement of the RCRA and Clean Water Acts will be resolved during the upcoming months.

Finally, the review of the literature aimed at the selection of the existing and proposed coal utilization schemes has been completed. Costs of residuals management for these technologies have been compiled from the literature; however, additional information must be obtained in order to ensure comparability of costs from different sources.

B. Plans for next reporting period.

The next quarter will see continued development in all of the objectives of the project. The CSTM should be completely operational and a start will be made at integrating the abatement information being developed with the analysis component of the modeling capacity. That is, we will begin to ask "what-if" type questions to evaluate the model's capacity to indicate market sensitivities to technological and regulatory changes. Also, since the objective of determining the feasibility of using coal models is not limited to in-house models, contacts will be made to ascertain whether the CTL could link to outside coal models at a reasonable cost.

In order to model the impact of railroad monopoly power along specific links, the rate equation in CSTM will be examined. The data from DOE would be combined with data compiled from the "Cost and Quality of Fuels for Electric Utility Plants - 1982 Annual" to obtain estimates of the rates along the special links.

Air pollution abatement and water and solid waste technology options will be further explored. Specifically, site visits are planned to: Inland Steel Corporation, Mt. Vernon, IL; EPRI, Palo Alto, CA; Homer City, PA (EPRI and EPA installations); and TVA, Chattanooga.

Initial survey of the user population will be undertaken with site visits to several Illinois utilities and mail survey developed and sent out.

¹"Comparative Cost transportation Costs," Center for Advanced Computation, University of Illinois, Vol 1-7. August, 1977.