DOE/PC/92521--T44

[illegible] 21 1993

TECHNICAL REPORT

March 1, 1993 through May 31, 1993

Project Title: **PROTOCOLS FOR THE SELECTIVE CLEAVAGE OF CARBON-SULFUR BONDS IN COAL**

DE-FC22-92PC92521

Principal Investigator: Mark Bausch, Southern Illinois University
Project Manager: Dr. Ken K. Ho, ICCI

ABSTRACT

Chemical reactions that result in carbon-sulfur bond cleavage are an essential aspect of any protocol designed to remove organic sulfur from coal. Planned in the second year of our project "Protocols for the Selective Cleavage of Carbon-Sulfur Bonds in Coal" are investigations of reactions in which organic sulfur-containing coal model compounds are subjected to different conditions of temperature, solvent mixtures and radiation. Other investigations that will result in analyses of the likelihood of C-S bond cleavages resulting from various oxidative processes will also be undertaken. Summarized in this quarterly report are results of our investigations of the following topics: (a) desulfurization of coal model sulfones and sulfides; (b) photolytic desulfurization of coal; (c) differential scanning calorimetric experiments on photooxidized coal; and (d) discussions on C-S bond strengths in radical cations.

MASTER

EXECUTIVE SUMMARY

The following sets of experiments were slated for completion during the two-year funding period for "Protocols for the Selective Cleavage of Carbon-Sulfur Bonds in Coal":

•1. Allow various coal model compounds (species that contain aliphatic and aromatic C-S bonds) to be subjected to various conditions. The variables in these studies include different substrates, solvents, bases, added reagents (catalysts, oxidizing agents, electron acceptors), temperature and pressure. Photochemical reactions of these coal model compounds will also be studied by varying the wavelength of light, using various solvents with or without sensitizers, oxidizing the compounds and subsequently hydrolyzing the products of the reaction.

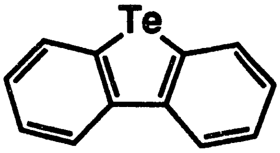
•2. Subject coal and coal model compounds to ultrasonic irradiation for different periods of time. The effects of adding catalysts or oxidizing agents will also be determined. Different substrates, solvents and oxidizing agents, along with ultrasonic irradiation, altogether will form a matrix of results that will allow determination of optimum conditions that will accomplish the desired C-S bond cleavage on coal samples.

•3. Heat the coal model compounds containing both aliphatic and aromatic sulfur, oxygen, carbon, and nitrogen at various temperatures, using a Differential Scanning Calorimeter(DSC). Observe the transitions in the sample brought about by C-S, C-O, C-C and C-N bond cleavages.

•4. Investigate differences in the bond strengths in the radical cations derived from coal model compounds 10-phenylthio-9-methylanthracene and 9-phenylthiomethylanthracene. We will attempt to ascertain the differences in reactivities of different types (i.e. aromatic or aliphatic carbon) of carbon-sulfur bonds, under various reaction conditions, and correlate these differences with their respective bond strengths.

Results presented in this report include the following:

- We have observed C-S bond cleavage when dibenzothiophene sulfone is allowed to react with tellurium powder and sodium borohydride. Products isolated include dibenzothiophene as well as the tellurium analogue of dibenzothiophene (**1**)



1

- We have observed that NaTeH, when allowed to react with dibenzothiophene sulfone at temperatures less than 220°C, does not react. Dibenzothiophene sulfone, when allowed to react with tellurium powder alone, is recovered unchanged.
- We have observed that benzyl phenyl sulfide, when treated with N-chlorosuccinimide followed by ammonium hydroxide, forms benzaldehyde and dibenzyl disulfide, in near quantitative yields.
- We have completed our experiments in the area of photoxidations of organic sulfides. An article summarizing our results in this area is in preparation.
- We have initiated experiments in which IBC-108 is subjected to the same photooxidative protocol that we have developed in our work with the sulfide model compounds. The photooxidation protocol appears to result in a 10% reduction in the organic sulfur content of the coal. Experiments in this area are continuing.
- DSC experiments have been completed using IBC-108 and photooxidized IBC-108 as substrate. Analyses of our initial results indicates that the photooxidation treatment does not substantially overwhelm or degrade the backbone of the coal macromolecule. Experiments in this area are continuing.

OBJECTIVES

Our long range objective in the research funded by ICCI has been to carry out experiments that will aid in solving the problem of coal desulfurization--from the perspective of inventing, understanding, and perfecting new carbon-sulfur bond breaking chemical reactions. Experiments carried out during the past three months included studies of reactions in which base mixtures were allowed to react with sulfur-containing coal model compounds under high temperature (Parr bomb) conditions. Additional experiments carried out during the present reporting period were aimed at cleaving carbon sulfur bonds in α-chlorosulfones,with the aid of various tellurium-based reagents. Other experiments carried out during this reporting period included studies of photochemical and photo-oxidation reactions of sulfur-containing coal model compounds in the presence/absence of sensitizers. It is our objective to develop a set of low-temperature reaction conditions that will enable substantial C-S bond cleavage to be affected in Illinois coal. The described experiments are the first steps in achieving some understanding at the molecular level of a newly-invented process. Details of photooxidative experiments involving IBC-108 are also found in this summary.

Examination of the four tasks listed below reveals details of the experiments planned to aid in the efforts to reach the stated objective:

TASK 1:Carry out experiments that aim to selectively cleave C-S bonds in coal model compounds benzyl phenyl sulfide, phenyl sulfide and dibenzothiophene, as well as physically cleaned Illinois coal. Main thrusts of these investigations include radical- and Lewis acid-initiated, as well as caustic- and photooxidatively-assisted C-S bond cleavages.

TASK 2:Evaluate the effect of ultrasonic radiation on the effectiveness of several C-S bond cleavage protocols.

TASK 3:Utilize differential scanning calorimetry (DSC) techniques in examinations of various methods of cleaving C-S bonds in coal model compounds, as well as gaining understanding of the degree of depolymerization in Illinois coals (coals that contain varying amounts of organic and inorganic sulfur) when these coals are subjected to depolymerization protocols. Also planned are DSC studies of several Illinois coals subjected to a variety of pretreatment conditions.

TASK 4:Carry out experiments that enable determinations of the bond energies for aliphatic and aromatic C-S bonds in the radical ions derived from several coal model compounds. Communicate these results to the coal-desulfurization community through publications in scientific journals.

INTRODUCTION AND BACKGROUND

The organic sulfur found in coal consists primarily of sulfur atoms covalently bonded to aliphatic or aromatic carbon atoms contained in the backbone of the coal macromolecule (there may be a small percentage of S—S and S—H bonds in coal as well). The sulfur present in Illinois coal is problematic because the combustion of high-sulfur coal results in the formation of species implicated in environmental problems related to acid rain. The relevance and significance of the experiments planned for the present funding period is perhaps best described by acknowledgment of the following two statements:

(a) In order to remove the organic sulfur from coal, carbon-sulfur bonds must be broken.
(b) Chemists' knowledge and awareness of reactions that lead to the selective cleavage of carbon-sulfur bonds, and in particular, sulfur atoms bonded to sp^2 (i.e. aryl) carbon atoms, is limited.

The experiments outlined in the four TASKS listed earlier in this quarterly report are aimed, in the short term, at developing an increased understanding of methods that enable cleavage of C-S bonds. The longer term goal of these experiments is the invention of new chemical reactions, or perfection of existing chemical reactions. The attainment of reaction conditions that allow the selective cleavage of carbon-sulfur bonds in coal and coal model compounds is therefore the main goal of "PROTOCOLS FOR THE SELECTIVE CLEAVAGE OF CARBON-SULFUR BONDS IN COAL". An important outcome of these studies is the resulting increase in chemists' knowledge of carbon-sulfur bond cleavage reactions. Successful completion (successful in terms of affecting carbon-sulfur bond cleavages) of the studies described in this proposal thus increases the likelihood of the deployment of a simple and cost-effective protocol designed to remove organic sulfur from Illinois coal.

Much of the coal mined in Illinois suffers from its high sulfur content. Methods have been developed that are quite effective at removing the inorganic sulfur from coal. Unfortunately, the problem of organic sulfur present in Illinois coal remains to be solved. A major reason for the lack of progress in the area of organic sulfur removal is the lack of knowledge concerning carbon-sulfur bond cleavage reactions. Completion of the experiments outlined in TASKS

1-4 will at least partly remedy this situation. It is our desire to convert what we learn from these studies of carbon-sulfur bond breaking reactions into a simple protocol that will offer a reasonable and economically viable solution to the problems of using Illinois coal.

The experiments summarized in this quarterly report are best described as fundamental studies of carbon-sulfur bond cleavage reactions, using both coal and model compounds. At present, none of these experiments describe a process that is cost-effective in terms of removing organic sulfur from coal. It is our desire to develop a practical carbon-sulfur bond-breaking technology from the research described in this proposal, and transition this new technology to the Illinois coal community.

EXPERIMENTAL PROCEDURES

TASKS 1-4 describe experiments that have synthetic, colorimetric, and electrochemical components. The synthetic component of our work is typical of the procedures that practicing organic chemists follow. A uv-visible spectrophotometer is utilized in the collection of appropriate acid-base and kinetic data.

Other experimental techniques and apparatus utilized in our work during the past three months include a Parr high pressure reactor vessel, GC techniques, FT-NMR techniques, DSC techniques, as well as other chromatographic techniques.

RESULTS AND DISCUSSION

TASK 1: Carry out experiments that aim to selectively cleave C-S bonds in coal model compounds benzyl phenyl sulfide, phenyl sulfide and dibenzothiophene, as well as physically cleaned Illinois coal. Main thrusts of these investigations include photo-oxidatively assisted C-S bond cleavage reactions.

RESULTS:

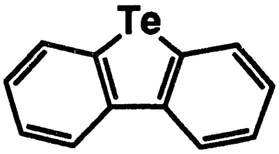
1.1. DESULFURIZATION OF COAL MODEL SULFONES

- Introduction

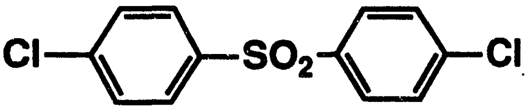
It is likely that sulfides and their oxides exist in coal. We have recently added sulfones to our list of coal desulfurization model compounds. As described in the previous quarterly report, we have investigated tellurium-based reagents in reactions that aim to cleave C-S bonds. In this report, additional results are described for these and related reactions.

- Results

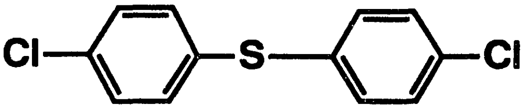
We have investigated the utility of NaTeH as a reagent in C-S bond cleavage reactions. We first allowed $NaBH_4$ to react with dibenzothiophene sulfone. There was no reaction observed. We then allowed the same sulfone to react with a mixture of $NaBH_4$ and tellurium. Below 220°C, we observed no reaction. However, upon heating up to 500°C, we observed that biphenyl formed in 20-30% yields, while dibenzothiophene was formed in yields of about 30%. There are several more (as yet) unidentified products in this reaction. We are currently attempting to identify as many of these products as possible. When allowed to react with NaTeH at 300°C, dibenzothiophene sulfone formed substantial amounts of biphenyl, dibenzothiophene, and the tellurium analogue of dibenzothiophene (**1**). The products of these reactions have been isolated and confirmed by NMR, GC, and MS. In another reaction, we have allowed the sulfone **2** to react with $NaBH_4$ at 240°C. Most of the starting material (**2**) is gone, while thin layer chromatography indicates that at least four products have formed. MS analysis indicates that **3** is one of the products in this reaction. Finally, we have allowed dibenzothiophene sulfone to react with tellurium powder at 300°C. In this reaction, only a trace of dibenzothiophene was formed.



1



2



3

1.2. DESULFURIZATION OF COAL MODEL SULFIDES USING WET METHODS

In the following experiments dibenzothiophene and benzyl phenyl sulfide were used as coal model compounds.

We are continuing our studies of C-S bond cleavage reactions in which chlorination of aliphatic carbon atoms adjacent to sulfidyl sulfur appears to be an essential component. The reaction between benzyl phenyl sulfide and N-chlorosuccinimide (NCS, in carbon tetrachloride), followed by treatment with ammonia in water (30%), results in the formation of benzaldehyde and phenyl disulfide, **in nearly**

quantitative yields. The two products in this reaction have been separated, isolated, and confirmed by NMR and IR.

As described in an earlier report, the reaction between dibenzyl sulfide, NCS, and ammonium hydroxide resulted in the formation of benzaldehyde and dibenzyl disulfide. We are currently evaluating other substrates for study using this protocol.

That the chlorination of the aliphatic carbon is an essential part of this reaction was verified by monitoring similar reactions in which phenyl sulfide was used as a substrate. In this reaction, we now believe, with the aid of TLC analyses, that approximately 20% of the starting material has been transformed into as yet unidentified products.

1.3. DESULFURIZATION BY PHOTOOXIDATION

1.3.1. Photooxidation of Organic Sulfides and IBC-108

- Discussion and Results and Future Plans

Piotr Dobrowolski carried out the majority of the experiments in this area of our ICCI-sponsored research. Piotr spent much of the past three months writing his dissertation (which he successfully defended on May 22, 1993) and verifying many of the results which appeared in it as well as previous quarterly reports. *We have now completed and verified our work on the photooxidation of sulfide model compounds*. Some discussion of the relevance of this work is appropriate here.

Of particular interest to us as coal scientists was to try and understand the sensitivity to photooxidation displayed by dibenzothiophene (DBT). We have now written extensively (in these reports as well as in a paper that is to be submitted to *Energy and Fuels)* about the products observed when DBT is allowed to react with oxygen in the presence of light. The results of these experiments are particularly interesting from the point of view of coal chemistry, since DBT is a notorious bad actor in the desulfurization and conversion of coal.

The previous quarterly report contained details of several sulfide photooxidation experiments in which the role of oxygen, sensitizer, solvent purity, and light were evaluated. Our work shows that dibenzothiophene *alone*, in the present of light and oxygen, when dissolved in acetonitrile, is converted to the corresponding sulfoxide (in 28% isolated yield) and sulfone (in 13% isolated yield).

These results are important from the point of view that coal undergoes changes upon weathering, and that much of the chemistry associated with the weathering of coal may in fact be catalyzed by light. Additional evidence for the importance of light-catalyzed oxidations for substrates of importance to coal scientists is the reaction in which biphenyl, when dissolved in acetonitrile and allowed to react with oxygen in the presence of light and 9.10-dicyanoanthracene, is converted into benzoic acid. This is an extremely important result, and one that has not been recognized by the coal chemistry community. Aryl-aryl C-C bonds are among the most difficult of all chemical bonds to cleave. We estimate that the central C-C bond in biphenyl has a homolytic strength of about 115 kcal/mol. That light and oxygen (in the presence of sensitizer) can in effect destroy or transform such a bond points to the power of these reagents in certain reactions. It therefore seems reasonable to carry out careful experiments in which coal itself is subjected to conditions leading to its controlled photooxidation, particularly in light of published reports claiming that atmospheric weathering leads to desulfurization of coal.[1] This observation was followed by laboratory experiments in which samples of coal were desulfurized in a two stage process (photooxidation and hydrolysis of products)[2]. Up to 35% reduction in sulfur was reported when coal samples (suspensions in ethanol) were irradiated at 254 nm and then hydrolyzed.

In our first attempt to achieve coal desulfurization via a photoxidative process, we have exposed IBC-108 to the standard unsensitized photooxidative conditions followed by hydrolysis by NaOH solution.

The experiments were carried out as described previously. A sample of IBC 108 (250 mg) was suspended in 150 ml of acetonitrile, and irradiated for 72 hours. The coal-acetonitrile suspension was stirred with a magnetic stirrer and agitated by oxygen that was delivered through teflon tubing. A 200 W medium pressure Conrad-Hanovia lamp, modified by a Pyrex 7740 light filter, was used as a light source. After the irradiation was completed the coal was filtered. The filtrate was evaporated leaving 76 mg of brown residue. 205 mg of coal was recovered (this coal is later referred to as UC1). 140 mg of this coal was then suspended in 50 ml of 1 N NaOH and refluxed for 18 hours. The mixture was filtered and coal, after washing with water, was dried in the oven at 120°C for 24 hours. Only 30 mg of coal was obtained (this sample is later referred to as UC2). About 350 mg of a dark brown residue remained after evaporation of the filtrate. In a control run a 140 mg of coal was refluxed in 50 ml of 1N NaOH for 18 hours. The mass of the recovered coal, after filtration and 24 hour drying at 120 °C was about 100 mg (this sample is later referred to as UC3).

We can now report results of the quantitative sulfur analysis for the samples of coal after both stages of photooxidative desulfurization and for the control runs. Four coal samples were submitted for analysis: UC1, UC2, UC3, and UC4 (Table I). Rob Bartelsmeyer of Carterville IL carried out the analyses.

---

[1] Chandra, D.; Chakrabarti, J. N.; Swamy, Y. V. *Fuel* **1982**, *61*, 204.

[2] Mathur,V. K.; Murphy, S. *Am.Chem.Soc.Div.Fuel Chem.* **1988**, *33* (1), 232.

Table I. Sulfur Analyses of IBC-108 Coal. Determination of the Effect of Photooxidation.

sample and description		% sulfur
UC1	IBC-108 photooxidized coal	2.25
UC2	UC1 + hydrolysis	2.01
UC3	hydrolysis alone	2.18
UC4	IBC-108 (untreated)	2.53

Inspection of the data in Table I reveals that our initial experiments indicate that organic sulfur decreases by ca. 10% as a result of photooxidation alone, and that subsequent hydrolysis results in an additional 10% reduction in organic sulfur. It is important to note that no sensitizer was added to coal samples in these experiments. We are now carrying out experiments with added sensitizers and singlet oxygen catalysts in attempts to determine their effect on the photooxidative chemistry. We are also contemplating different stirring protocols as well as the use of additional solvents.

TASK 2:Evaluate the effect of ultrasonic radiation on the effectiveness of several C-S bond cleavage protocols.

RESULTS: No experiments were undertaken for this task for this period.

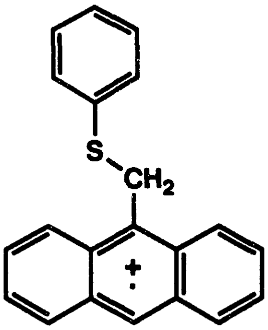
TASK 3: Utilize differential scanning calorimetry (DSC) techniques in examinations of various methods of cleaving C-S bonds in coal model compounds, as well as gaining understanding of the degree of depolymerization in Illinois coals (coals that contain varying amounts of organic and inorganic sulfur) when these coals are subjected to depolymerization protocols. Also planned are DSC studies of several Illinois coals subjected to a variety of pretreatment conditions.

*RESULTS:*Experiments in this area are finally underway. It is often suggested that organic chemists who work in the area of coal research are should focus more on coal and less on coal model compounds. Therefore, we have decided to carry out our initial experiments on IBC-108 itself, as well as photooxidized IBC-108. Our intent in these experiments is to determine what it is that the DSC-based results can tell us about coal, as well as how our photooxidative protocol changes the thermal properties of IBC-108.

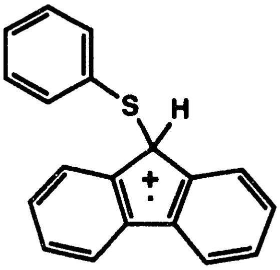
Our initial results have proven to be difficult to analyze and well as somewhat irreproducible. Inspection of a plot of heat vs temperature for UC-1 (i.e. IBC-108 that has been photooxidized) reveals a maximum at ca. 100°C (probably water, an inflection point at about 350°C, and a minimum at about 500°C. After 500°C, the curve continues to rise upward. An identical experiment completed on UC-4 (i.e. untreated IBC-108) is remarkably similar, except for the absence of the inflection point and a somewhat earlier minimum (about 450°C). At this time we interpret the similarity in these data to mean that the photooxidative process does not overwhelmingly change the nature of the coal macromolecule, at least for the samples that we have examined to date. It is likely that the aforementioned inflection point is the result of some moderate depolymerization of the coal macromolecule that results from the photooxidative process. Work in this area is continuing.

TASK 4: Carry out experiments that enable determinations of the bond energies for aliphatic and aromatic C-S bonds in the radical ions derived from several coal model compounds. Communicate these results to the coal-desulfurization community through publications in scientific journals.

RESULTS: Rather involved experiments involving photomodulated voltammetry have been completed in attempts to determine redox potentials for electron transfer reactions involving various organic radicals and cations. The essence of these experiments is that we are trying to perfect a device which will enable us to evaluate redox potentials for transient organic species. Experiments are now underway in which we are determining the oxidation potentials for variously substituted fluorenyl radicals and methylanthracenyl cations. These data, combined with other redox data, will enable us to determine the C-S bond strengths in molecules such as **4** and **5** below. Note that **4** and **5** are radical cations. Radical cations are the first intermediate formed in any strong acid-catalyzed coal desulfurization protocol. It is our goal to evaluate C-S bond strengths in these species and compare



4

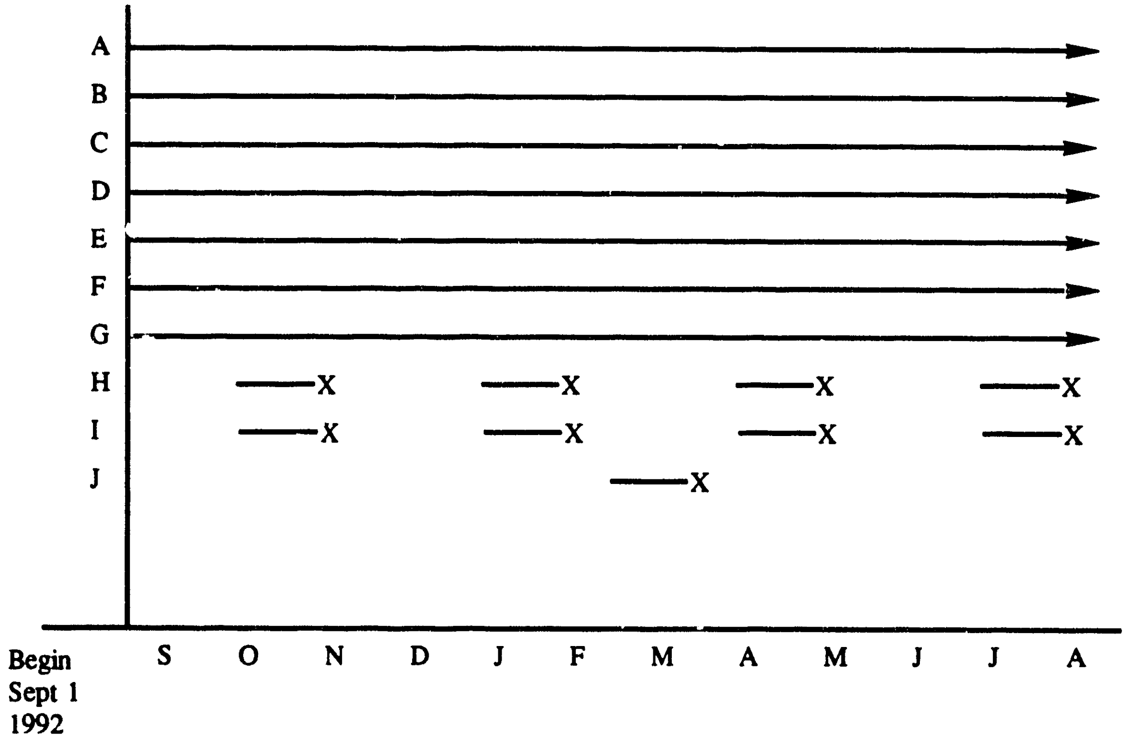


5

these bond strengths to the strengths of various C-O, C-N, and C-C bonds in analogous species, in an attempt to discern if oxidative protocols have any meaningful chance of *selectively* cleaving C-S bonds. These results will be summarized on in our final report.

"PROTOCOLS FOR THE SELECTIVE CLEAVAGE OF CARBON-SULFUR BONDS IN COAL":

SCHEDULE FOR YEAR 2



MILESTONES:"PROTOCOLS FOR THE SELECTIVE CLEAVAGE OF CARBON-SULFUR BONDS IN COAL"

A. Post-doctoral Research Associate Employed
B. Graduate Research Assistant Employed
C. Graduate Research Assistant Employed
D. TASK 1 undertaken; second Bausch group TASK 1 review February 1, 1993
E. TASK 2 undertaken; second Bausch group TASK 2 review March 1, 1993
F. TASK 3 undertaken; second Bausch group TASK 3 review April 1, 1993
G. TASK 4 undertaken; second Bausch group TASK 4 review May 1, 1993
H. Technical reports prepared and submitted
I. Project management reports prepared and submitted
J. Publication prepared and submitted:"Lewis Acid-Promoted C-S Bond Cleavage Chemistry"

PROJECT MANAGEMENT REPORT
March 1 through May 31, 1993

Project Title: **PROTOCOLS FOR THE SELECTIVE CLEAVAGE OF CARBON-SULFUR BONDS IN COAL**

Principal Investigator: M. J. Bausch
Department of Chemistry & Biochemistry
Southern Illinois University at Carbondale
Carbondale, Illinois 62901
618-453-5461
Project Manager: Ken Ho, Illinois Clean Coal Institute

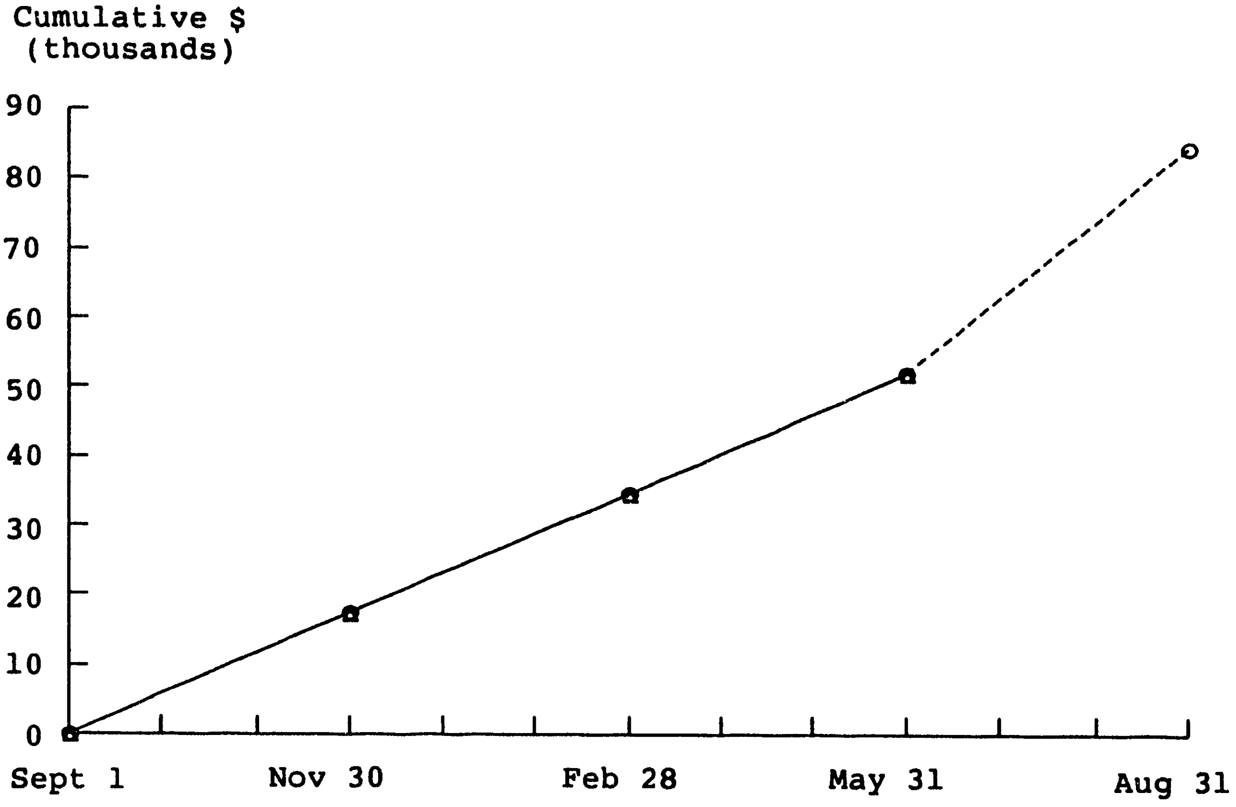
Projected and Estimated Expenditures by Quarter

Quarter*	Types of Cost	Direct Labor	Materials and Supplies	Travel	Major Equipment	Other Direct Costs	Indirect Costs	Total
Sept. 1, 1992	Projected	12,250	1,636	0	500	1,500	1,589	17,475
to Nov. 30, 1992	Estimated Actual	12,250	1,636	0	500	1,500	1,589	17,475
Sept. 1, 1992	Projected	24,500	3,272	0	500	3,000	3,127	34,399
to Feb. 28, 1993	Estimated Actual	24,500	3,272	0	500	3,000	3,127	34,399
Sept. 1, 1992	Projected	36,750	4,908	500	500	4,500	4,716	51,874
to May 31, 1993	Estimated Actual	36,750	4,908	500	500	4,500	4,716	51,874
Sept. 1, 1992	Projected	62,955	6,545	1,000	500	6,000	7,700	84,700
to Aug. 31, 1993	Estimated Actual							

*Cumulative by quarter.

COSTS BY QUARTER

Protocols for the Selective Cleavage of Carbon-Sulfur Bonds in Coal



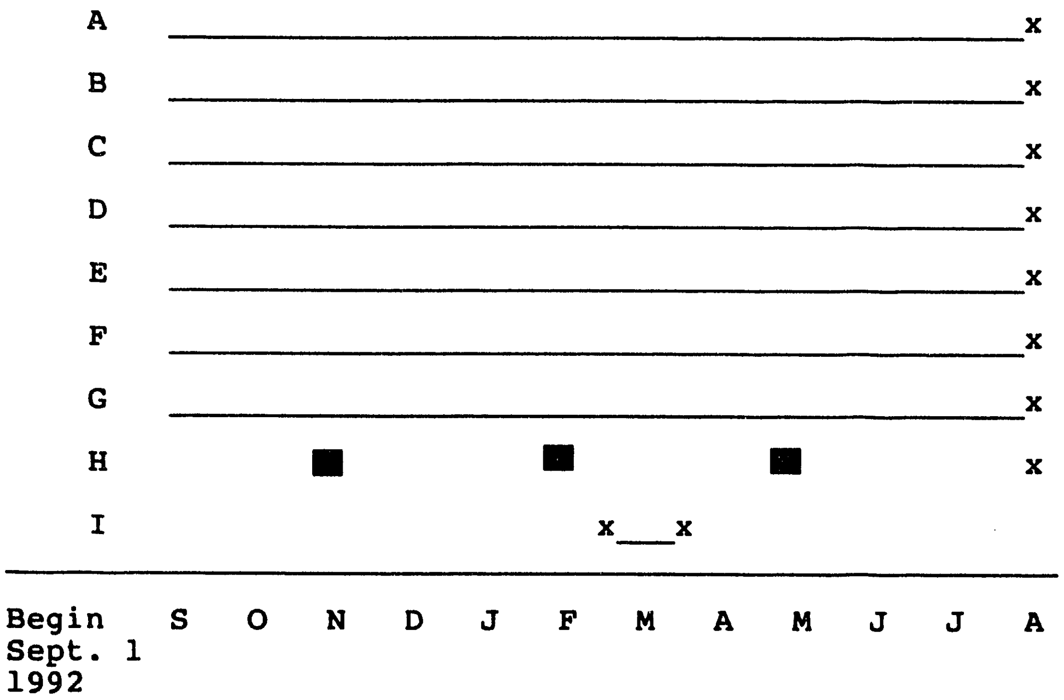
Months and Quarters

O = Projected Expenditures ---------

Δ = Estimated Actual Expenditures ________

Total Illinois Clean Coal Institute Award $84,700

SCHEDULE OF PROJECT MILESTONES



Milestones:

A. Post-doctoral research associate employed
B. Graduate research assistant employed
C. Graduate research assistant employed
D. Task 1 undertaken; second Bausch group Task 1 review 2/1/93
E. Task 2 undertaken; second Bausch group Task 2 review 3/1/93
F. Task 3 undertaken; second Bausch group Task 3 review 4/1/93
G. Task 4 undertaken; second Bausch group Task 4 review 5/1/93
H. Technical reports and project management reports prepared and submitted
I. Publication prepared and submitted: "Lewis Acid-Promoted C-S Bond Cleavage Chemistry"

END

DATE FILMED

9/30/93