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TECHNICAL REPORT
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Project Title: **DESULFURIZATION OF COAL: ENHANCED SELECTIVITY USING PHASE TRANSFER CATALYSTS**

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ABSTRACT

Due to environmental problems related to the combustion of high sulfur Illinois coal, there continues to be interest in the development of viable pre-combustion desulfurization processes. Recent studies by the authors have obtained very good sulfur removals but the reagents that are used are too expensive. Use of cheaper reagents leads to a loss of desired coal properties.

This study investigates the application of phase transfer catalysts to the selective oxidation of sulfur in coal using air and oxygen as oxidants. The phase transfer catalyst is expected to function as a selectivity moderator by permitting the use of milder reaction conditions than otherwise necessary. This would enhance the sulfur selectivity and help retain the heating value of the coal.

The use of certain coal combustion wastes for desulfurization, and the application of cerium (IV) catalyzed air oxidations for selective sulfur oxidation are also being studied. If successful this project could lead to the rapid development of a commercially viable desulfurization process. This would significantly improve the marketability of Illinois coal.

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EXECUTIVE SUMMARY

Due to environmental problems related to the combustion of high sulfur Illinois coal, there continues to be interest in the development of commercially viable pre-combustion desulfurization processes. These processes would allow the continued use of high sulfur Illinois coal for electricity generation, without the need for post combustion scrubbers.

Recent studies by the authors use a combination of a selective oxidation pretreatment reaction with a subsequent base desulfurization reaction to obtain very good sulfur removals (up to 95%). Unfortunately the cost of the chemical reagents used in the oxidative pretreatment is too high for commercial development and the use of cheaper oxidants results in too much carbon oxidation and hence Btu loss.

Although these studies failed to provide a cost effective desulfurization process, they do point us towards the types of chemical reactions needed for successful desulfurization. It is believed that the key to the success of the two-step process lies in the ability of the oxidant to selectively oxidize the organic sulfur species to their sulfoxides, sulfones or sulfonic acids in the pretreatment step. This selectively weakens the C-S bonds and therefore makes the subsequent removal of sulfur much easier.

The challenge that we face at this time is finding an inexpensive oxidant system that retains the desired sulfur selectivity and preserves the desired properties of the coal such as Btu value. Identifying this inexpensive oxidant system is the primary goal of this study. Specifically the application of phase transfer catalysts to the selective oxidation of sulfur over that of carbon, using air and oxygen as oxidants, is being investigated.

Phase transfer catalysts are substances that have the ability to transport chemical reagents across phase boundaries. This ability promotes chemical reactions in heterogeneous systems that would not otherwise take place or which would take place only very slowly. In this sense they are true catalysts and as such permit the formation of desired products under much milder, and therefore more selective, reaction conditions. It is these features that make phase transfer catalysts so attractive for reactions involving coal. It is anticipated that phase transfer catalysts would act as selectivity moderators in the oxidation of sulfur in coal.

Although the moderation of oxidative selectivity using phase transfer catalysts is the primary area for research in this project, a number of related features are also being examined. These include the potential use of coal combustion residues for the desulfurization step and the application of cerium (IV) catalyzed air oxidation to the selective oxidation of sulfur in coal.

Specific objectives have been identified for the completion of this project. These are:

1. Use physically cleaned coals from the Illinois Basin, to prepare a variety of selectively oxidized coals using air and oxygen under phase transfer catalysis conditions.

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2. Test these selectively oxidized coals for enhanced desulfurization under standard desulfurization conditions.
3. Compare these desulfurization results with those obtained for oxidized coals prepared without the phase transfer catalyst.
4. Investigate the applicability of cerium (IV) catalyzed air oxidation for selective oxidation of sulfur in coal, both with and without phase transfer catalysts.
5. Examine the ability of alkaline coal combustion wastes (scrubber wastes and fly ash) to desulfurize selectively oxidized and unoxidized coals.
6. Investigate the kinetics and mechanism of desulfurization under these various conditions by varying the time and temperature of the treatments on coals and model compounds.
7. Measure Btu contents after both oxidation and desulfurization reactions to quantify Btu recoveries after each process.
8. Test selected products for trace element content to determine if these elements can also be removed by the process.
9. Investigate the influence of the amount of phase transfer catalyst on the level of selective oxidation and subsequent desulfurization.
10. Examine the recovery of phase transfer catalysts from the reaction media to see if recycling of the catalyst would be possible.

As far as the authors have been able to determine the application of phase transfer catalysts to the selective oxidation of sulfur in coal has not been investigated before. Similarly, the authors could not find reference to the application of the cerium (IV) catalyzed selective air oxidation of organic sulfur to the study of coal desulfurization. In addition, the use of coal combustion wastes for the precombustion desulfurization of coals appears to be another unique feature of this project.

The achievements made in the third quarter are listed below:

- Over eighty oxidation experiments have been performed using a variety of conditions including the presence of phase transfer catalysts in the reaction mixture.
- All of the oxidized samples prepared so far have been subsequently desulfurized using our standard sodium hydroxide/methanol desulfurization reaction.
- 90% of all oxidation and base desulfurization products have been analyzed for ash and moisture by TGA, and analyzed for sulfur using a Leco total sulfur analyzer.

From the data received so far we can see that recovery of the coal oxidation product is high with yields approaching 95-97% in many cases. Unfortunately, if we compare the sulfur contents of the oxidation products we see that there is very little difference between them and the sulfur content of the blank sample (ie. No oxidant, no catalyst). This indicates that no or very little sulfur has been removed during the oxidation process.

The sulfur reductions obtained for all of the oxidized samples after base desulfurization are around 60 to 65%. Thus the use of the phase transfer catalysts and the cerium catalyst, under the oxidation conditions employed, does not appear to have significantly impacted the level of desulfurization obtained. However, it should be noted that the introduction of the cerium catalyst, by itself and in combination with TBAC, did improve the level of desulfurization by around 5%. This may be an indication of better results in the future.

Attempts to optimize the level of desulfurization by employing other variables such as increased reaction time (1hr to 24hrs), increased catalyst loading (5% to 20%), introduction a catalyst soak time (1hr to 24hrs), changing the solvent to include methanol and THF, increased oxidant flow rates (200ml/min to 600ml/min), and the introduction of ultrasonic reaction conditions, have not been successful at this time. Further experiments are planned to investigate this further.

OBJECTIVES

The overall objective of this study is to develop a cost-effective process for the removal of organic sulfur from high sulfur Illinois coals. This project focuses on the use of phase transfer catalysts to moderate the selective oxidation of organic sulfur in coal using air and oxygen. The desulfurization of coal treated this way would be significantly enhanced. In addition, the use of coal combustion wastes to aid the desulfurization of these selectively oxidized coals is being explored.

A number of specific goals and objectives can be identified for the successful completion of this project. These are:

1. Use physically cleaned coals from the Illinois Basin to prepare a variety of selectively oxidized coals using air and oxygen under phase transfer catalysis conditions.
2. Test these selectively oxidized coals for enhanced desulfurization under standard desulfurization conditions.
3. Compare these desulfurization results with those obtained for oxidized coals prepared without the phase transfer catalyst.
4. Investigate the applicability of cerium (IV) catalyzed air oxidation for selective oxidation of sulfur in coal, both with and without phase transfer catalysts.
5. Examine the ability of alkaline coal combustion wastes (scrubber wastes and fly ash) to desulfurize selectively oxidized and unoxidized coals.
6. Investigate the kinetics and mechanism of desulfurization under these various conditions by varying the time and temperature of the treatments on coals and model compounds.
7. Measure Btu contents after both oxidation and desulfurization reactions to quantify Btu recoveries after each process.
8. Test selected products for trace element content to determine if these elements can also be removed by the process.
9. Investigate the influence of the amount of phase transfer catalyst on the level of selective oxidation and subsequent desulfurization.
10. Examine the recovery of phase transfer catalysts from the reaction media to see if recycling of the catalyst would be possible.

INTRODUCTION AND BACKGROUND

To reduce coal derived sulfur oxide emissions the electricity generating industry has been forced to switch to low sulfur coal and to use flue gas scrubbers. This has led to high unemployment in areas where high sulfur coal is mined and to the generation of significant quantities of scrubber wastes.(1)

Due to these considerations there continues to be interest in the development of pre-combustion desulfurization processes which would allow the continued use of high sulfur coal for electricity generation without the need for post combustion scrubbers.

Although some success has been achieved with the development of processes that can remove inorganic sulfur species from coal, an acceptable process for the removal of organic sulfur has yet to be found.

Laboratory studies have shown that very high levels of organic sulfur removal are technically possible. The problem has been that all of these processes have proven too expensive to become commercially viable.

Recent studies by the researchers used a combination of a selective oxidation pretreatment reaction with a subsequent base desulfurization reaction. Very good sulfur removals (up to 95%) were obtained but as with previous processes the cost of the reagents, especially those used in the selective oxidation step, inhibits the development of a commercial process (2-7). Use of cheaper oxidants were found to give similar levels of desulfurization but there are concerns regarding the selectivity of the oxidants and the possibility that too much carbon oxidation and therefore Btu loss occurs. The success of bases to desulfurize the oxidized coals raises the possibility that certain alkaline coal combustion wastes might be useful for desulfurization. If coal combustion wastes could be used for the desulfurization of coal, not only would process economics be influenced favorably, but a use for these problem wastes would be found. The possibility of using these waste materials for the desulfurization of coal is being investigated in this project.

Using XANES analysis it was found that oxidation with peroxyacetic acid converts most of the pyrite to sulfate and most of the sulfides and thiophenes to sulfoxides, sulfones and sulfonic acids.(8) This is the expected result. In addition the desulfurization treatment effectively removed the sulfoxides, sulfones and sulfonic acids that were formed by the oxidative pretreatment. Indeed, the only significant sulfur form still present after the combined treatment is thiophenic sulfur, and this has been reduced by some 70%. Both pyrite and organic sulfides were completely removed.

Although these studies failed to provide a cost effective desulfurization process, they do at least point us towards the kinds of processes that might become viable. It is believed that the key to the success of this process lies in the ability to selectively oxidize the organic sulfur

species to their sulfoxides, sulfones or sulfonic acids in the pretreatment step. This selectively weakens the C-S bonds and therefore makes the subsequent removal of sulfur much easier.

The problem that we face at this time is finding an inexpensive oxidant system that retains the desired sulfur selectivity. Unfortunately the inexpensive oxidants such as air, oxygen, nitric acid, etc. are not known for their oxidative selectivity and excessive oxidation of carbon is often observed.

For reasons that will be explained later it is believed that the selective oxidation of sulfur over carbon can be performed using inexpensive oxidants by employing substances called phase transfer catalysts (PTC). It is anticipated that the PTC would act as a selectivity moderator in the oxidation of sulfur in coal.

Phase transfer catalysts are substances that have the ability to transport chemical reagents across phase boundaries. This ability promotes chemical reactions in heterogeneous systems that would not otherwise take place or which would take place only very slowly. In this sense they are true catalysts and as such permit the formation of desired products under much milder, and therefore more selective, reaction conditions. It is these features that make phase transfer catalysts so attractive for reactions involving coal.

Phase transfer catalysts such as tetrabutyl ammonium hydroxide (TBAH) have been found to aid the swelling of the coal structure thereby allowing the penetration of other reactants. Indeed, the rate of O-methylation was not limited by the mass transport of the chemical reagents into the coal structure. This result supports the proposed mechanism whereby the PTC promotes the penetration of reagents into the coal matrix.

It is believed that phase transfer catalysts could be used to enhance the accessibility of oxidants in coal thereby permitting the use of mild oxidation conditions which would only oxidize sulfur. A highly selective reaction should be the result because, in most situations, the divalent sulfur atom is inherently more reactive towards oxidants than the carbon atom.(9,10) This is because the divalent sulfur atom can easily accommodate oxygen atoms becoming tetravalent or hexavalent without having to break any bonds. Carbon on the other hand is usually unable to form bonds with the oxygen without first breaking a C-C or C-H bond. This is why the oxidation of sulfur containing model compounds usually results in the formation of the sulfoxides, sulfones or sulfonic acids in high yield with no or very little oxidation of the carbon in the molecules.

The ability of PTCs to promote oxidations with air and oxygen from the gas phase has been demonstrated with the development of a number of synthetic pathways for organic chemicals. (11-14) For instance, fluorenone can be formed from fluorene using air as the oxidant and tricaprylammonium chloride as a PTC. (11) Similarly 9,10 dihydroanthracene can be oxidized to anthraquinone by air with dicytyldiethylammonium chloride as the PTC. (12) In both these

reactions the molar ratio of PTC to substrate was only 0.03 and the air pressure was 1 atm.

In addition, a new selective oxidation process has recently been developed for the conversion of sulfides into sulfoxides using air as the oxidant. This process uses a cerium catalyst $[(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6]$ to promote a single electron transfer from the sulfur species to molecular oxygen forming the radical cation and the superoxide anion, followed by triplet oxygen trapping of the radical cation. This catalytic air oxidation is also being investigated for the selective oxidation of sulfur in coal under PTC conditions.

EXPERIMENTAL PROCEDURES

The work that has been and will be undertaken during this project is outlined in the following text as a number of tasks.

Task 1. Sample selection and preparation

IBCSP coal samples Nos. 101 and 106 were selected for use in this study. These coals will be used because they have relatively high, but different, organic sulfur contents, and therefore provide the best challenge to the desulfurization process.

Each coal was riffled into suitable aliquot sizes and excessive deterioration prevented by storage under nitrogen. To provide beneficiated coal fines samples, aliquots of each coal was micronized using a nitrogen gas powered micronizer in order to liberate the very fine minerals found in these coals. Since previous results imply that pyrite removal prior to oxidation and desulfurization is essential, extra effort is being applied towards pyrite removal. To this end aliquots of coal have been passed through the micronizer up to three times while other aliquots have been treated with liquid nitrogen prior to micronization. The micronized coals are in the process of being centrifuged in a 1.6 g/cm^3 cesium chloride solution to establish the extent of pyrite liberation. After centrifugation the mineral-attenuated float material are washed with 1N HCl and distilled water, and finally dried under vacuum below 40°C . Coals treated in this way typically have less than 1% ash and very little residual pyrite. Analysis of these various products will determine the extent of physical pretreatment necessary to obtain optimum pyrite liberation. This level of coal preparation is required to provide a physically clean coal of very high quality. This will enable the desulfurization study to focus on organic sulfur removal, without worrying about any complications resulting from pyrite reactions or interactions.

Aliquots of each coal, both before and after physical cleaning, have been submitted for analysis including proximate, ultimate, Btu and particle size determination.

All solvents, reagents and catalysts have been obtained from chemical supply houses. Coal combustion wastes have been obtained from the Coal Combustion Residues Management (CCRM) Program Sample Bank maintained by the mining engineering department at SIUC.

Task 2. Selective oxidation using phase transfer catalysts.

Two phase transfer catalysts are being examined in this study. These are tetrabutylammonium hydroxide (TBAH) and tetrabutylammonium chloride (TBAC). These PTC's were chosen because they have been used in coal related studies before and because one is a base while the other is a neutral salt. Comparison of the two will therefore help to establish the role of pH in these oxidations.

Three oxidant systems are to be evaluated under PTC conditions. These are air oxidation, oxygen oxidation and cerium (IV) catalyzed air oxidation. Each will be studied in the presence of each PTC and also in the absence of any PTC. Four temperatures with a standard reaction time of 1 hour will be investigated for each PTC/oxidant combination. This will give the reaction matrix shown in Table 2.

Table 2. Reaction matrix for PTC assisted oxidations

PTC/Oxidant Combination	0°C	20°C	50°C	100°C
no oxidant	X	X	X	X
air	X	X	X	X
oxygen	X	X	X	X
cerium/air	X	X	X	X
air/TBAH	X	X	X	X
air/TBAC	X	X	X	X
oxygen/TBAH	X	X	X	X
oxygen/TBAC	X	X	X	X
cerium/air/TBAH	X	X	X	X
cerium/air/TBAC	X	X	X	X

For these initial investigations the oxidant flow rate would be held constant at 20 ml/min and the PTC concentration maintained at 5% (wt% based on coal). Each experiment will be conducted on 5 grams of coal. This will provide sufficient sample for the subsequent desulfurization reaction, and for the Btu and proximate analysis of products both after oxidation and again after desulfurization.

Task 3. Optimization of pretreatment reaction

At this point the most promising oxidative pretreatment process will be selected for further detailed study. This study will investigate variations in PTC concentration, other oxidant flow rates and different reaction times and temperatures. Many of these variables would be determined from an analysis of the results obtained in Task 2. This new data will be used to help identify the oxidation conditions that lead to optimized levels of sulfur removal with subsequent desulfurization reactions. In addition, the recovery of the phase transfer catalysts from the reaction medium would be examined under this task.

Task 4. Standard desulfurization reaction

Each selectively oxidized coal and unoxidized control coal would be desulfurized under standard desulfurization conditions. A typical desulfurization experiment involves dispersing 2 grams of coal (oxidized or unoxidized) in 4 mL of methanol with 1 gram of sodium hydroxide. This slurry is placed in a 10 mL stainless steel microreactor. The microreactor is purged with argon, sealed and then placed in a fluidized sand bath maintained at a temperature of 350°C for 60 minutes. After this time the reactor is cooled to room temperature and the contents collected at the filter. The product is washed with dil. HCl then distilled water and finally dried overnight in a vacuum oven. Products are then be submitted for analysis as described in Task 7.

Task 5. Desulfurization with coal combustion residues

To test the ability of scrubber sludge and fly ash for the desulfurization of coal, up to five selectively oxidized samples and the unoxidized sample from each coal would be selected. The desulfurization reaction would use the same conditions as used for the standard desulfurization procedure but the sodium hydroxide would be replaced with an equal quantity of the combustion waste. Products would be tested as described in Task 7.

Task 6. Studies involving sulfur model compounds

A set of sulfur-containing model compounds comprising a thiol, an aliphatic sulfide, an alkyl aryl sulfide, an aryl aryl sulfide, an aliphatic disulfide, an aromatic disulfide, a thiophene, benzothiophene and dibenzothiophene will be oxidized using the conditions identified in Task 2. The oxidation products (probably sulfonic acids and sulfones) will be characterized and then treated using the standard desulfurization conditions. Desulfurization of this model compound mixture would also be attempted using the coal combustion waste identified in Task 5. GCMS and GC-FID/FPD analysis of the products will be used to identify any desulfurized model compound products. Compounds identified in this way will be used in attempts to elucidate the mechanism of desulfurization and as a characterization tool for the organic sulfur in coal.

Task 7. Product analysis and evaluation

The analysis of all products obtained during this work will be performed. Initially, this will involve recording the product yield, the sulfur content and the ash/moisture content. Other tests such as proximate analysis, Btu analysis, elemental analysis and sulfur forms analysis will be performed throughout the project on selected samples. In addition selected products will be examined by digestion and then ICP-ES analysis to monitor trace element concentrations. The information provided will be used to evaluate the processes under investigation and to indicate the direction of future experiments.

RESULTS AND DISCUSSION

The achievements made in the third quarter are listed below:

- Over eighty oxidation experiments have been performed using a variety of conditions including the presence of phase transfer catalysts in the reaction mixture.
- All of the oxidized samples prepared so far have been subsequently desulfurized using our standard sodium hydroxide/methanol desulfurization reaction.
- 90% of all oxidation and base desulfurization products have been analyzed for ash and moisture by TGA, and analyzed for sulfur using a Leco total sulfur analyzer.

Sample Preparation (Task 1)

Results for the physical cleaning of the coals and the preparation of the pyrite free coal can be found in previous quarterly reports. To summarize the combined HF/HCl followed by LAH treatment generated a pyrite free sample with only 0.3% ash.

Fly ash and Scrubber Sludge Desulfurizations (Task 5)

The results for the desulfurizations using fly ash and scrubber sludge can be found in previous quarterly reports. To summarize no beneficial effect upon desulfurization was obtained through the use of these coal combustion wastes.

Oxidation experiments using phase transfer catalysts (Task 2)

A list of the oxidation experiments conducted in the previous quarter, together with the available yield and ultimate data for the products, is given in Table 2.

From the data received so far we can see that recovery of the coal product is high with yields approaching 95-97% in many cases. This indicates that the oxidation conditions are mild and

If we compare the sulfur contents of the oxidation products we see that there is very little difference between them and the sulfur content of the blank sample (ie. No oxidant, no catalyst). This indicates that no or very little sulfur has been removed during the oxidation process. This does not necessarily mean that the sulfur was not oxidized, just that it was not removed by the oxidative process. If the sulfur has been selectively oxidized but not removed then we should see enhanced desulfurization when these products are reacted under the base/methanol desulfurization conditions. This will be discussed in the following section.

Base desulfurization of oxidation products. (Task 4)

Available yield and ultimate data for the subsequently desulfurized oxidation products generated in task 2 is reported in Table 3.

The sulfur reductions obtained for all of the samples analyzed so far are around 60 to 65%. Thus the use of the phase transfer catalysts and the cerium catalyst, under the oxidation conditions employed, does not appear to have significantly impacted the level of desulfurization obtained. However, it should be noted that the introduction of the cerium catalyst, by itself and in combination with TBAC, did improve the level of desulfurization by around 5%. This may be an indication of better results in the future.

Optimization of PTC oxidation reaction (Task 3)

To investigate the PTC assisted oxidation of coal further a number of additional reaction variables were investigated under this task. These include increasing the reaction time (1hr to 24hrs), increasing the catalyst loading (5% to 20%), introducing a catalyst soak time (1hr to 24hrs), changing the solvent to include methanol and THF, increased oxidant flow rates (200ml/min to 600ml/min), and the introduction of ultrasonic reaction conditions.

The results of the oxidation experiments are presented in table 4, while the results of the subsequent desulfurization of these products is presented in table 5. At this time we have seen very little improvement in the levels of desulfurization obtained in task 2.

Table 2. Oxidation conditions and results obtained in Task 2

run	coal	temp (deg C)	time (hr)	flowrate (ml/min)	oxidant	catalyst	moisture %	dry ash	dry yield	dry S	dry S ash free
BPX1	101 3P	100	1		none	none	5.3	11.3	95.8	3.77	4.25
BPX2	101 3P	100	1	200	oxygen	none	4.2	11.3	94.4	3.73	4.20
BPX3	101 3P	100	1	200	oxygen	TBAC	2.6	13.2	92.4	3.70	4.26
BPX4	101 3P	100	1	200	oxygen	TBAH	3.2	11.7	81.5	3.58	4.06
BPX5	101 3P	100	1	200	oxygen	Ce	3.9	11.3	95.4	3.91	4.41
BPX6	101 3P	100	1	200	oxygen	TBAC/Ce	1	11.4	98.7	3.57	4.03
BPX7	101 3P	100	1	200	oxygen	TBAH/Ce	0.6	11.9	100.9	3.75	4.26
BPX8	101 3P	NA	NA	NA	NA	NA	3.3	12.6	NA	4.39	5.02
BPX9	101 3P	50	1	200	oxygen	none	3.8	11.0	93.6	3.92	4.40
BPX10	101 3P	50	1	200	oxygen	TBAC	3.8	11.7	91.2	3.93	4.45
BPX11	101 3P	50	1	200	oxygen	TBAH	4.8	11.2	93.7	3.96	4.46
BPX12	101 3P	50	1	200	oxygen	Ce	4.4	11.4	94.3	3.87	4.37
BPX13	101 3P	50	1	200	oxygen	TBAC/Ce	5	10.9	83.1	4.02	4.52
BPX14	101 3P	50	1	200	oxygen	TBAH/Ce	4.8	10.9	93.3	3.94	4.42
BPX15	101 3P	20	1	200	oxygen	none	3.3	11.4	95.3	3.91	4.41
BPX16	101 3P	20	1	200	oxygen	TBAC	5.3	10.9	95.0	4.02	4.51
BPX17	101 3P	20	1	200	oxygen	TBAH	4.1	11.2	93.4	3.94	4.44
BPX18	101 3P	20	1	200	oxygen	Ce	5.2	11.3	93.1	3.98	4.48
BPX19	101 3P	20	1	200	oxygen	TBAC/Ce	3.8	11.0	94.2	3.95	4.44
BPX20	101 3P	20	1	200	oxygen	TBAH/Ce	3.9	11.0	93.3	3.89	4.37
BPX21	101 3P	100	1	200	air	none	4.4	11.1	95.5	3.93	4.42
BPX22	101 3P	100	1	200	air	TBAC	6.7	11.4	93.9	3.89	4.39
BPX23	101 3P	100	1	200	air	TBAH	4.8	11.6	94.9	3.88	4.38
BPX24	101 3P	100	1	200	air	Ce	9.8	11.2	96.4	4.01	4.52
BPX25	101 3P	100	1	200	air	TBAC/Ce	7.8	10.8	96.7	3.61	4.05
BPX26	101 3P	100	1	200	air	TBAH/Ce	9.2	11.7	99.7	3.74	4.24
BPX27	101 3P	50	1	200	air	none	2.7	12.9	93.5	4.02	4.62
BPX28	101 3P	50	1	200	air	TBAC	2.8	11.4	85.3	3.61	4.08
BPX29	101 3P	50	1	200	air	TBAH	3.1	10.9	77.0	3.91	4.39
BPX30	101 3P	50	1	200	air	Ce	3.1	11.8	92.7	3.92	4.44
BPX31	101 3P	50	1	200	air	TBAC/Ce	3	11.2	85.9	3.89	4.38
BPX32	101 3P	50	1	200	air	TBAH/Ce	2.6	11.7	89.3	3.55	4.02
BPX33	101 3P	20	1	200	air	none	9.3	10.9	90.8	4.00	4.49
BPX34	101 3P	20	1	200	air	TBAC	7.6	11.0	93.3	4.13	4.65
BPX35	101 3P	20	1	200	air	TBAH	7.5	11.0	90.4	3.94	4.42
BPX36	101 3P	20	1	200	air	Ce	7.6	12.6	87.6	4.05	4.63
BPX37	101 3P	20	1	200	air	TBAC/Ce	2.4	11.7	87.5	3.85	4.36
BPX38	101 3P	20	1	200	air	TBAH/Ce	10.2	12.0	93.9	3.98	4.52

Table 3. Base desulfurization results for oxidation products formed in Task 2

run	temp (°C)	time (hr)	NaOH (g)	MeOH (ml)	moisture %	dry ash	dry yield	dry S	dry S ash free
BPD1R	350	1	1	7.5	1.9	10.1	84.6	2.08	2.31
BPD2	350	1	0.5	7.5	2.1	10.0	71.9	2.08	2.32
BPD3	350	1	1	7.5	3.9	7.4	69.7	2.09	2.26
BPD4R	350	1	1	7.5	2.9	8.1	74.3	2.06	2.24
BPD5	350	1	1	7.5	2.3	5.6	76.2	1.92	2.04
BPD6	350	1	1	7.5	5.2	9.0	73.9	1.91	2.10
BPD7	350	1	1	7.5	4.8	9.1	66.3	2.11	2.32
BPD8	350	1	0.15	7.5	2.1	8.9	73.9	2.02	2.22
BPD9	350	1	1	7.5					
BPD10	350	1	1	7.5	4.2	7.6	70.7	1.95	2.11
BPD11	350	1	0.15	7.5	2.5	9.7	86.3	1.88	2.08
BPD12	350	1	0.15	7.5	3.7	14.5	84.7	2.19	2.56
BPD13	350	1	0.15	7.5	3.3	8.9	84.3	1.88	2.07
BPD14	350	1	0.15	7.5	2.6	9.7	84.2	1.87	2.07
BPD15	350	1	0.15	7.5	1.8	10.4	82.3	1.80	2.01
BPD16	350	1	0.15	7.5	3.6	14.7	89.0	2.23	2.62
BPD17	350	1	0.15	7.5	1.7	16.2	82.4	1.81	2.16
BPD18	350	1	0.15	7.5	2.2	10.0	82.9	1.77	1.97
BPD19	350	1	0.15	7.5	3.2	9.3	87.4	1.89	2.08
BPD20	350	1	0.15	7.5	2.3	8.7	83.7	1.86	2.04
BPD21	350	1	0.15	7.5	0.8	10.5	89.1	1.90	2.12
BPD22	350	1	0.15	7.5	0.1	10.9	89.9	1.84	2.07
BPD23	350	1	0.15	7.5	2.6	10.2	84.8	1.89	2.10
BPD24	350	1	0.15	7.5	3.5	8.3	83.6	1.85	2.02
BPD25	350	1	0.15	7.5	3.3	7.8	85.5	1.89	2.05
BPD26	350	1	0.15	7.5	3.1	10.6	85.6	1.82	2.03
BPD27	350	1	0.15	7.5					
BPD28	350	1	0.15	7.5					
BPD29	350	1	0.15	7.5					
BPD30	350	1	0.15	7.5					
BPD31	350	1	0.15	7.5					
BPD32	350	1	0.15	7.5					
BPD33	350	1	0.15	7.5					
BPD34	350	1	0.15	7.5					
BPD35	350	1	0.15	7.5					
BPD36	350	1	0.15	7.5					
BPD37	350	1	0.15	7.5					
BPD38	350	1	0.15	7.5					

Table 4. Oxidation conditions and results obtained in Task 3

run	coal	temp (deg C)	time (hr)	flowrate (ml/min)	oxidant	catalyst	catalyst loading	soak time (hr)	soak temp (deg C)	media	moisture %	dry ash	dry yield	dry S	dry S ash free
APX1	101 3P	b.p.	1	200	oxygen	TBAC	0.05	24	20	water	3.3	11.8	93.8	3.98	4.51
APX2	101 3P	b.p.	1	200	oxygen	TBAC	0.2	none	NA	water	2.4	11.7	95.7	4.02	4.55
APX3	101 3P	b.p.	1	600	oxygen	TBAC	0.05	none	NA	water	3.5	11.5	94.6	4.11	4.85
APX4	101 3P	b.p.	6	200	oxygen	TBAC	0.05	none	NA	water	3.6	11.6	94.3	3.85	4.35
APX5	101 3P	b.p.	1	200	oxygen	TBAH	0.05	24	20	water	2.9	11.8	95.2	3.91	4.44
APX6	101 3P	b.p.	1	200	oxygen	TBAH	0.2	none	NA	water	2.4	11.0	98.1	3.61	4.05
APX7	101 3P	b.p.	1	600	oxygen	TBAH	0.05	none	NA	water	4.4	12.7	93.4	4.06	4.65
APX8	101 3P	b.p.	6	200	oxygen	TBAH	0.05	none	NA	water	1.7	11.6	94.2	3.83	4.33
APX9	101 3P	b.p.	1	200	oxygen	Ce	0.05	24	20	water	3.8	11.6	93.1	4.07	4.61
APX10	101 3P	b.p.	1	200	oxygen	Ce	0.2	none	NA	water	4.6	11.3	94.2	3.90	4.40
APX11	101 3P	b.p.	1	600	oxygen	Ce	0.05	none	NA	water	4.6	10.9	95.8	3.86	4.45
APX12	101 3P	b.p.	6	200	oxygen	Ce	0.05	none	NA	water	1.4	13.0	92.5	3.42	3.93
APX13	101 3P	b.p.	6	200	oxygen	none	NA	none	NA	water	0.8	11.9	93.5	3.73	4.23
APX14	101 3P	b.p.	24	600	oxygen	TBAC	0.2	24	20	water	5.2	11.9	93.0	3.59	4.07
APX15	101 3P	b.p.	24	600	oxygen	TBAH	0.2	24	20	water	4.1	11.3	99.8	3.41	3.84
APX16	101 3P	b.p.	24	600	oxygen	Ce	0.2	24	20	water	6.1	10.8	92.1	3.57	4.00
APX17	101 3P	b.p.	24	600	oxygen	none	NA	24	20	water	4.9	11.3	92.7	3.52	3.97
APX18	101 3P	b.p.	1	600	oxygen	none	NA	none	NA	water	4.2	11.5	92.5	3.87	4.38
APX19	101 3P	b.p.	24	600	oxygen	TBAH	0.2	24	100	water	5.2	10.7	98.2	3.43	3.84
APX20	101 LAH	b.p.	24	600	oxygen	TBAH	0.2	24	100	water	5.8	0.3	99.7	3.41	3.42
APX21	101 3P	b.p.	24	600	oxygen	TBAH	0.2	24	b.p.	MeOH	4.7	10.6	95.9	3.49	3.91
APX22	101 LAH	b.p.	24	600	oxygen	TBAH	0.2	24	b.p.	MeOH	6.2	0.5	99.9	3.50	3.52
APX23	101 LAH	b.p.	24	600	oxygen	TBAC	0.2	24	b.p.	MeOH	10.7	0.7	93.4	3.57	3.60
APX24	101 LAH	b.p.	24	600	oxygen	Ce	0.2	24	b.p.	MeOH	11.3	0.7	95.1	3.63	3.65
APX25	101 LAH	b.p.	1	600	oxygen	TBAH	0.2	none	NA	MeOH	6.6	0.7	98.4	3.50	3.53
APX26	101 LAH	b.p.	1	600	oxygen	none	NA	none	NA	MeOH	7.3	0.8	92.7	3.76	3.79
APX27	101 LAH	b.p.	24	600	oxygen	TBAH	0.2	none	NA	MeOH	4.9	0.6	99.9	3.72	3.75
APX28	101 LAH	b.p.	24	600	oxygen	none	NA	24	b.p.	MeOH	7.3	0.5	91.2	4.10	4.12
APX30	101 LAH	b.p.	NA	NA	NA	TBAH	0.2	24	b.p.	MeOH	6.2	0.5	99.9	3.70	3.72
APX31	101 LAH	b.p.	24	200	oxygen	TBAH	0.2	none	NA	THF	6.6	0.6	99.4	3.47	3.49

Table 5. Base desulfurization results for oxidation products formed in Task 3

run	temp deg(C)	time (hr)	NaOH (g)	MeOH (ml)	moisture %	dry ash	dry yield	dry S	dry S ash free
APD1	350	1	0.15	7.5	2.1	7.4	78.6	2.15	2.32
APD2	350	1	0.15	7.5	1.8	9.6	82.9	2.07	2.29
APD3	350	1	0.15	7.5	2.1	8.5	82.9	2.08	2.28
APD4	350	1	0.15	7.5	1.6	9.0	81.4	2.15	2.37
APD5	350	1	0.15	7.5	1.5	10.4	79.6	2.05	2.29
APD6	350	1	0.15	7.5	2.3	10.2	79.7	2.14	2.38
APD7	350	1	0.15	7.5	1.5	10.8	81.5	2.07	2.32
APD8	350	1	0.15	7.5	2.3	8.5	80.5	2.09	2.28
APD9	350	1	0.15	7.5	2.7	9.4	77.1	2.11	2.32
APD10	350	1	0.15	7.5	2.6	8.5	79.9	2.16	2.36
APD11	350	1	0.15	7.5	2.4	10.1	76.0	2.11	2.35
APD12	350	1	0.15	7.5	2.3	9.5	80.9	2.09	2.31
APD13	350	1	0.15	7.5	2.5	9.2	82.2	2.10	2.32
APD14	350	1	0.15	7.5	1.6	8.5	78.6	1.99	2.18
APD15	350	1	0.15	7.5	2.1	8.6	79.3	2.05	2.25
APD16	350	1	0.15	7.5	1.6	8.9	82.2	2.11	2.32
APD17	350	1	0.15	7.5	2.2	10.0	75.1	2.07	2.30
APD18	350	1	0.15	7.5	1.7	10.6	81.8	2.07	2.31
APD19	350	1	0.15	7.5	4.7	8.0	66.3	2.10	2.28
APD20	350	1	0.15	7.5	3.8	1.0	76.3	2.20	2.23
APD21	350	1	0.15	7.5	4	8.8	75.2	2.10	2.31
APD22	350	1	0.15	7.5	3.4	1.7	76.3	2.12	2.16
APD23	350	1	0.15	7.5	3.2	3.0	82.6	2.40	2.47
APD24	350	1	0.15	7.5	2.5	1.4	78.0	2.42	2.46
APD25	350	1	0.15	7.5	3.6	5.4	69.7	2.21	2.34
APD26	350	1	0.15	7.5	3.8	5.0	79.0	2.41	2.54
APD27	350	1	0.15	7.5	2.7	1.2	78.1	2.28	2.31
APD28	350	1	0.15	7.5	2.6	2.6	70.4	2.34	2.40
APD30	350	1	0.15	7.5					
APD31	350	1	0.15	7.5					

CONCLUSIONS AND RECOMMENDATIONS

Analysis of the six samples of IBC-101 coal that had undergone various physical pretreatments in order to liberate minerals revealed that the cryogenic pretreatment and the additional passes through the micronizer did not give superior liberation. Indeed, despite improved particle size reduction with increasing micronizer passes, the ash content of the subsequently floated material, was not reduced beyond the 4.5 to 4.9% level.

Preparation of a pyrite free coal sample was achieved using HF/HCl and then LAH treatment. This sample had an ash content of only 0.3%.

At this time we have not been able to identify oxidation and desulfurization condition using PTC's which aid the desulfurization of coal. At best the levels of desulfurization achieved through the application of PTC's are only marginally better than those obtained without the addition of PTC.

DISCLAIMER STATEMENT

This report was prepared by Dr. Stephen R. Palmer, SIUC with support, in part by grants made possible by the U.S. Department of Energy Cooperative Agreement Number DE-FC22-92PC92521 (Year 4) and the Illinois Department of Commerce and Community Affairs through the Illinois Coal Development Board and the Illinois Clean Coal Institute. Neither Dr. Stephen R. Palmer, SIUC nor any of its subcontractors nor the U.S. Department of Energy, the Illinois Department of Commerce and Community Affairs, Illinois Coal Development Board, Illinois Clean Coal Institute, nor any person acting on behalf of either:

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Notice to Journalists and Publishers: If you borrow information from any part of this report, you must include a statement about the DOE and Illinois cost-sharing support of the project.

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PROJECT MANAGEMENT REPORT
March 1, 1996, through May 31, 1996

Project Title: **DESULFURIZATION OF COAL: ENHANCED SELECTIVITY
USING PHASE TRANSFER CATALYSTS**

DOE Cooperative Agreement Number: DE-FC22-92PC92521 (Year 4)
ICCI Project Number: 95-1/1.1D-3P
Principal Investigator: Dr. Stephen R. Palmer, SIUC
Other Investigators: Dr. Edwin J. Hippo, SIUC
Project Manager: Dr. Ken Ho, ICCI

COMMENTS

Dr. Stephen Palmer has resigned from his position at Southern Illinois University and has taken a position at Biosystems Engineering in Houston, Texas. Dr. Edwin Hippo will be resuming fiscal officer authority on the project, which will include completion of experimental work and participation in the Contractor's Conference.

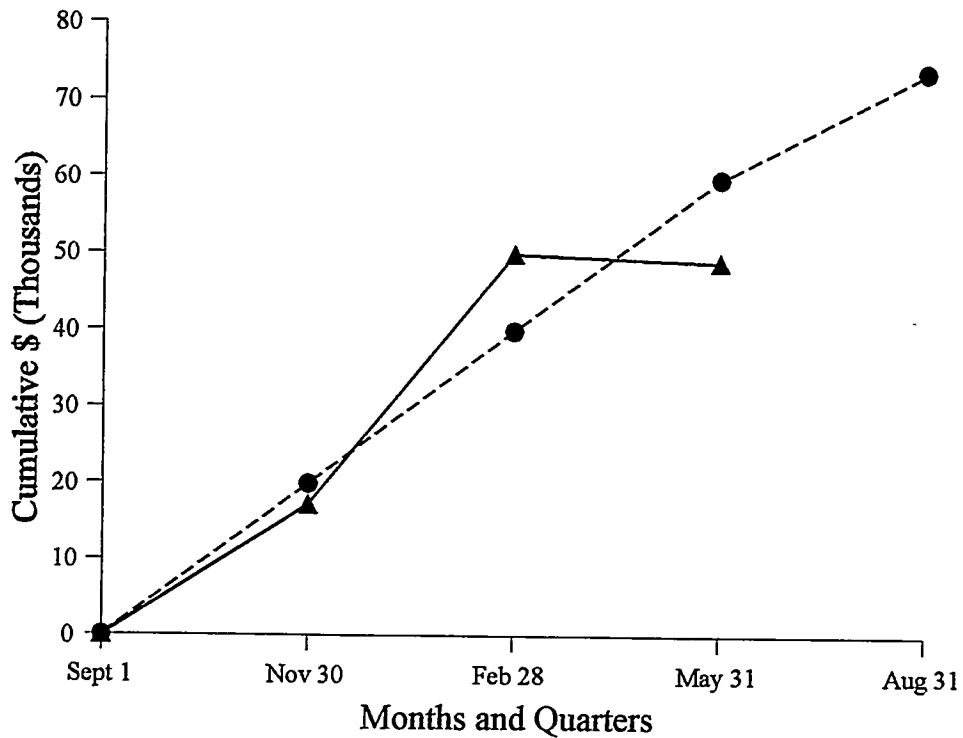
PROJECTED AND ESTIMATED EXPENDITURES BY QUARTER

Quarter*	Types of Cost	Direct Labor	Fringe Benefits	Materials and Supplies	Travel	Major Equipment	Other Direct Costs	Indirect Cost	Total
Sept. 1, 1995 to Nov. 30, 1995	Projected	10,855	3,010	1,875	0	0	2,375	1,812	19,927
	Estimated	12,760	1,833	394	0	0	619	1,561	17,167
Sept. 1, 1995 to Feb. 28, 1996	Projected	21,710	6,020	3,750	0	0	4,750	3,623	39,853
	Estimated	34,298	6,832	2,021	0	0	2,300	4,545	49,996
Sept. 1, 1995 to May 31, 1996	Projected	32,565	9,030	5,625	0	0	7,125	5,435	59,780
	Estimated	32,785	4,971	2,059	0	0	4,800	4,462	49,077
Sept. 1, 1995 to Aug. 31, 1996	Projected	39,879	11,218	7,500	500	0	8,000	6,710	73,807
	Estimated								

*Cumulative by Quarter

CUMULATIVE COSTS BY QUARTER

Desulfurization of Coal: Enhanced Selectivity Using Phase Transfer Catalysts

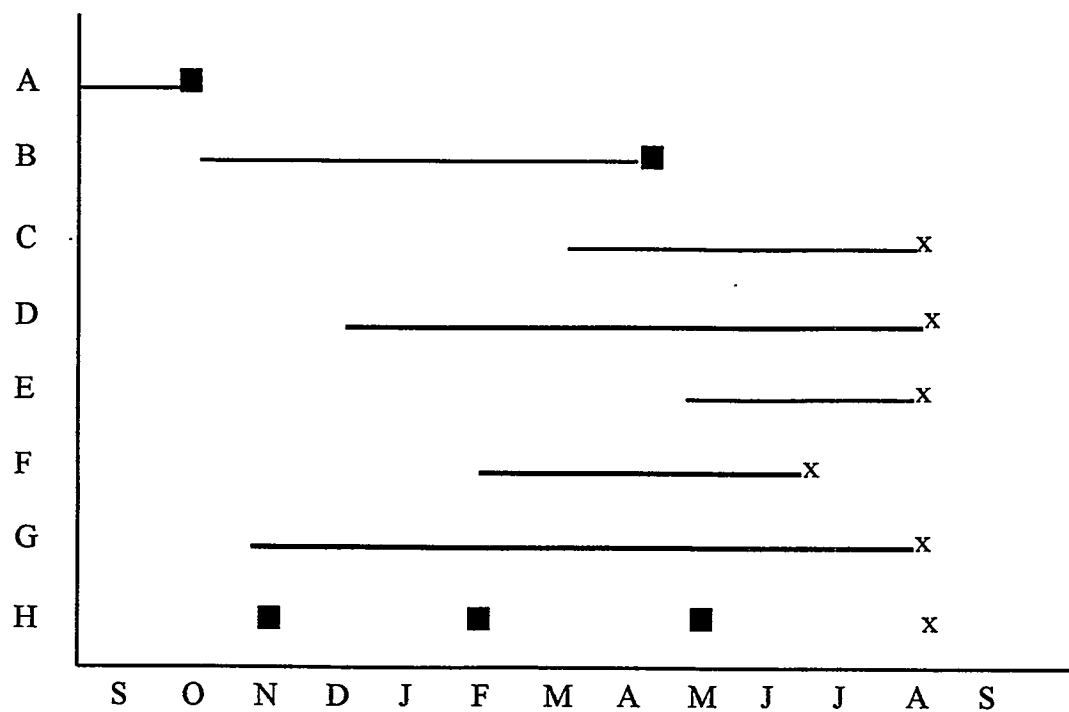


● = Projected Expenditures - - - - -

▲ = Actual Expenditures _____

Total Illinois Clean Coal Institute Award \$73,807

SCHEDULE OF PROJECT MILESTONES



Begin
Sept. 1
1995

Hypothetical Milestones:

- A: Sample preparation
- B: Selective oxidation with PTC
- C: Optimization
- D: Standard desulfurization reaction
- E: Desulfurization with coal wastes
- F: Model compounds
- G: Product evaluation
- H: Reporting

Comments:

None.