DOE/PC/92521--T281

TECHNICAL REPORT
March 1, 1996, through May 31, 1996

Project Title: **DESULFURIZATION OF ILLINOIS COALS WITH HYDROPEROXIDES OF VEGETABLE OILS AND ALKALI**

DOE Cooperative Agreement Number: DE-FC22-92PC92521 (Year 4)
ICCI Project Number: 95-1/1.1D-2P
Principal Investigator: Gerard V. Smith, SIUC
Other Investigators: Ricky D. Gaston, SIUC; Ruozhi Song, SIUC; Jianjun Cheng, SIUC; Feng Shi, SIUC; Yaguang Wang, SIUC
Project Manager: Ken K. Ho, ICCI

ABSTRACT

Organic sulfur is removed from coals by treatment with aqueous base, air, and vegetable oils with minimal loss of BTU. Such results were revealed during exploratory experiments on an ICCI funded project to remove organic sulfur from Illinois coals with hydroperoxides of vegetable oils. In fact, prewashing IBC-108 coal with dilute alkali prior to treating with linseed oil and air results in 26% removal of sulfur. This new method is being investigated by treating coals with alkali, impregnating coals with polyunsaturated oils, converting the oils to their hydroperoxides, and heating. Since these oils are relatively inexpensive and easily applied, this project could lead to a cost effective method for removing organic sulfur from coals. Moreover the oils are environmentally safe; they will produce no noxious products and will improve burning qualities of the solid products. During the first quarter the selection of base for pretreatment and extraction (Task 1) was completed. NaOH is better than NH_4OH for the pretreatment and Na_2CO_3 is better than NaOH for the oil extraction. About 40% of sulfur is removed from IBC-108 coal using 5% NaOH for pretreatment followed by linseed oil oxidation in air and Na_2CO_3 extraction. During the second quarter the effectiveness of linseed oil and NaOH for sulfur removal from IBC-108 coal was further tested by pretreating the coal with two base concentrations (5% and 1% NaOH) at four different times (20hr, 10hr, 5hr, and 1hr) followed by treatment with linseed oil (two different ratios of oil:coal) at 125°C for three different times (20hr, 10hr and 5hr), and finally washing with 5% Na_2CO_3 and methanol. About 17% to 23% of sulfur is removed by prewashing IBC-108 coal with aqueous NaOH alone and about 25% to 43% of sulfur is removed with NaOH prewashing followed by linseed oil treatment under the conditions of investigation. During this third quarter more experimental parameters were systematically varied in order to study the effectiveness of linseed oil and NaOH for sulfur removal from IBC-108 coal. The eight coal samples pretreated with NaOH were further treated with linseed oil at 100°C for three different times (20hr, 10hr, and 5hr) and two oil to coal ratios (1:1 and 1:10). The best result (50% sulfur removal) is obtained by pretreating the coal with 5% NaOH for 20 hr followed by oil treatment at 100°C for 5hr with 1:1 oil to coal ratio.

"U.S. DOE Patent Clearance is **NOT** required prior to the publication of this document."

EXECUTIVE SUMMARY

This project proposes to remove organic sulfur from coal, maintain its BTU, and increase its volatiles, by a new process of pretreating with alkali and impregnating with polyunsaturated vegetable oils. Catalyzed by coal, air converts these oils into their hydroperoxides which are powerful oxidizing agents. A similar agent, peroxyacetic acid, has shown in a previously funded ICCI project to desulfurize coal. But polyunsaturated vegetable oils have advantages which make them attractive for treating coal. First, these compounds are inexpensive, renewable natural products available from Illinois farms; second, they possess chemical properties which can be directed toward oxidizing organic sulfur; third, they furnish carbonaceous residues which will increase BTU's and volatiles; and fourth, they are environmentally safe and produce no noxious products.

Preliminary experiments at SIUC have shown that IBC-108 coal impregnated with linseed oil and heated in air at 50-100°C has its organic sulfur removed. The results show that coal catalyzes formation of hydroperoxides in the oil and these hydroperoxides oxidize the organic sulfur with minimum loss of BTU. Additionally, experiments have shown that pretreating IBC-108 coal with NaOH increases the amount of organic sulfur removed during subsequent treatment with linseed oil. This project proposes to build on this new evidence to aim at a technically feasible and economically viable process step.

Three tasks are proposed: **Task 1** will select the base for pretreating and extraction. Tests will examine NaOH and NH_4OH at two different concentrations followed by treatment with linseed oil at 100°C for 20 hours, then extraction with two different bases, NaOH and Na_2CO_3.. **Task 2** will determine the ability of the above selected base in combination with linseed oil to remove organic sulfur from IBC-108 coal. Tests of base pretreatment will be conducted at 25°C, two different concentrations, and four different times. Tests of oil treatment will be conducted at two different oil:coal ratios, three different reaction times, three different temperatures, and with two different extraction solutions. This task will produce 144 experiments with accompanying plots of sulfur removal as function of temperature and time and will be used to study reaction rates and the mechanism of sulfur removal. **Task 3** will determine the mass balance along with the volatiles and BTU changes from the experiments in Tasks 1 and 2 creating a data base of 152 analyses of mass balances, volatiles, and BTU's along with plots of their dependence on temperature and time. All of these data will be examined for clues to the mechanism of organic sulfur oxidation and removal from Illinois coals.

During the first quarter we completed screening of the bases for pretreating the coal and for extracting the oil after oil treatment. We found that pretreating IBC-108 coal with bases removes 13% to 23% of the sulfur. NaOH is a better treatment than NH_4OH in most experiments and Na_2CO_3 is better than NaOH for the final extraction. Higher temperatures and higher base concentrations remove more sulfur. Thereby, treatments with 5% NH_4OH at 100°C in the presence of bubbling O_2 or with 5% NaOH at 25°C remove more sulfur (21-23%) than any other treatment with alkali alone. However, even more sulfur is removed from the pretreated coal by linseed oil treatment followed by base

DISCLAIMER

extraction. And the best results (about 40% sulfur removal) are obtained with the combinations of 5% NaOH-OIL-5%Na_2CO_3 (B-O-C), 1% NH_4OH-OIL-5%Na_2CO_3 (N1-O-C), and 5% NH_4OH (100°C)-OIL-5% Na_2CO_3 (N_{100}-O-C). This base-oil-base treatment appears to selectively remove organic sulfur and it does this with minimum loss of BTU.

During the second quarter we tested the ability of the selected base (NaOH) in combination with linseed oil to remove organic sulfur from IBC-108 coal. Tests of NaOH pretreatment were performed at 25°C with two base concentrations (5% and 1% NaOH) at five different times (20hr, 15hr,10hr, 5hr, and 1hr). We found that about 17% to 23% of sulfur is removed under these conditions and that the sulfur removal is slightly favored by higher base concentration and longer time. Tests of oil treatment were conducted at 125°C for three different times (20hr, 10hr and 5hr) with two different ratios of oil:coal (1:1 and 1:10). We found that about 25% to 43% of sulfur is removed under these conditions. The best result (43% sulfur removal) is given by pretreating the coal with 1% NaOH for either 1hr or 5hr followed by oil treatment for 5hr with 1:1 oil to coal ratio.

During this third quarter more experimental parameters were systematically varied to determine the effectiveness of linseed oil and NaOH for sulfur removal from IBC-108 coal. The eight coal samples pretreated with NaOH were further treated with linseed oil at 100°C for three different times (20hr, 10hr, and 5hr) and two oil to coal ratios (1:1 and 1:10). The combinations of NaOH pretreatment, then oil treatment followed by Na_2CO_3 extraction remove 23% to 50% sulfur. The best result (50% sulfur removal) is obtained by pretreating the coal with 5% NaOH for 20 hr followed by oil treatment at 100°C for 5hr with 1:1 oil to coal ratio. More sulfur is removed with a 1:1 oil to coal ratio than with a 1:10 ratio under most conditions.

OBJECTIVES

The goal of this project is to develop a cost effective method to remove organic sulfur from pyrite-free and mineral-free coal. The objective is to test the feasibility of using alkali and inexpensive, renewable farm products to desulfurize Illinois coals. The specific objectives of this project are:

1. determine the ability of alkali and oils to remove organic sulfur from Illinois coals,

2. establish the volatile and BTU changes from treating Illinois coals with alkali and oils,

3. establish the mass balance of solids, liquids, and gases resulting from treating Illinois coals with alkali and oils, and

4. study the reaction rate(s) and mechanism(s) of sulfur removal from Illinois coals treated with alkali and oils.

Briefly the tasks scheduled for the current year are:

Task 1. *Selection of base for pretreatment and extraction*

Task 2. *Determination of base and linseed oil ability to remove organic sulfur form IBC-108 coal*

Task 3. *Determination of mass balance, volatiles, and BTU*

INTRODUCTION AND BACKGROUND

Relevance to Illinois Basin Coal Problem and Unique Aspects

This project is relevant to solving the problem of high sulfur content of Illinois coals. Its significance rests on its use of inexpensive farm materials to neutralize organic sulfur in Illinois coals.

The potential importance of this project is its impact on the marketability of Illinois coals. Producing clean products from coal will add to the economic importance of coal. This project has the potential of utilizing cheap, renewable farm products for enhancing coal conversion process, especially for removing sulfur and thereby upgrading solid products.

The unique aspect of this project is its use of inexpensive farm products, such as linseed oil ($0.28/LB) and other vegetable oils, to achieve desulfurization and upgrade char. These farm products are cheap enough that they need not be recycled, rather, they enrich the coal conversion products. On an equivalent weight basis (gram molecular weight per hydroperoxy group), linseed oil with maximum hydroperoxy groups contains about 86% the oxidizing ability of peroxyacetic acid. Yet the cost of each hydroperoxy group in linseed oil is only 23% the cost of each hydroperoxy group in peracetic acid. Therefore this project has the unique aspects not only of being environmentally safe, disrupting the coal matrix, increasing volatiles, oxidizing the sulfur, and adding carbon, oxygen, and hydrogen to the char, but also of being less expensive than peroxyacetic acid.

Background

Each year Illinois farms produce millions of tons of usable and unusable materials which are easily collected, easily transported, and readily available near Illinois coal mining districts. These materials consist mainly of carbohydrates, fats, and oils, which contain hydrogen and oxygen, elements in low concentrations in coals. Therefore, these materials are potentially valuable for coal conversion processes.

There are good reasons for exploring carbohydrates, fats, and oils as participants in coal conversion reactions. First, these compounds are inexpensive and renewable natural products available from Illinois farms; second, they possess chemical properties which can be directed toward oxidizing organic sulfur; third, they furnish carbonaceous residues which will increase BTU's of coal char; and fourth, they are environmentally safe and produce no noxious products.

Hydrogen in some form is frequently added during coal conversion processes. Besides adding hydrogen as H_2 gas or as some readily dehydrogenatable molecule, such as tetralin, hydrogen has been added in the form of other hydrogen-rich organic molecules, such as ethanol and methane[1-3]. Other rich sources of hydrogen are fats and oils from vegetable and animal materials. Carbohydrates likewise contain hydrogen, although not as much on a molar basis as fats and oils. But, carbohydrates contain much more oxygen than fats and oils on a molar basis.

Using carbohydrates as well as fats and oils as sources of oxygen may be beneficial to pyrolysis and desulfurization because small amounts of oxygen seem to increase desulfurization. For example, ICCI funded coal treatments with methane/oxygen[2], ethanol[3], lignin[4], a proprietary oxidant[5], and air[5,6] are all processes in which oxygen, either added or present in the reactants, is beneficial to pyrolysis and desulfurization. Therefore, their oxygen contents make carbohydrates, fats, and oils likely candidates for enhancing coal conversion processes. Moreover, their oxygen may become incorporated into the products and increase their octane ratings. So using carbohydrates, fats, and oils makes chemical sense as sources of oxygen in coal conversion processes.

However, using carbohydrates, fats, and oils merely as sources of hydrogen, carbon, and oxygen is overlooking important coal desulfurization chemistry. For example, fats and oils contain labile allylic hydrogens which react with oxygen in air to form hydroperoxides. These hydroperoxides lead to rancidity, and some oils are so prone to this reaction that radical inhibitors are regularly added to preserve them for the food market. Thus oils can be converted into powerful oxidizing agents by forming hydroperoxides, and these can oxidize organic and inorganic sulfur in coals.

Formation of hydroperoxides in oils occurs from the reaction of singlet oxygen at allylic positions on unsaturated fatty acids. But singlet oxygen is not ordinary oxygen. Singlet oxygen is the excited state of ground-state oxygen (a triplet) and is formed in very low concentrations in air by action of light. Singlet oxygen is not formed in high concentrations because triplet oxygen does not readily absorb energy from light. Thus the rate of formation of hydroperoxides is ordinarily slow in air.

However, the rate of formation can be greatly increased by increasing the concentration of singlet oxygen through photosensitization. Photosensitization methods employ a photosensitizer molecule which absorbs energy from light and transfers that energy to triplet oxygen, raising it into the excited singlet state. Photosensitizers need be present in only low concentrations, so one of the tasks in the 1994-5 project was to test standard photosensitizers and **coal as a sensitizer**.

Results have shown that coal is indeed a sensitizer, perhaps because it contains radicals[7,8,9], which apparently directly convert triplet to singlet oxygen. During the first five months of the current funded project, we have found that coal alone amply catalyzes the formation of hydroperoxides in linseed oil. (We chose linseed oil for tests because it is readily available at the grocery store and relatively rich in polyunsaturated fats, such as glyceryl oleate, and glyceryl linoleate.) In fact, formation of hydroperoxides in the presence of coal equals that in the presence of a known photosensitizer and ultraviolet light. Apparently, coal is a very good singlet oxygen initiator.

We tested the ability of coal to sensitize oxygen in air and produce hydroperoxy groups in linseed oil because these hydroperoxy groups are powerful oxidizing agents. Similar powerful oxidizing agents, such as peroxyacetic acid, had been used in earlier ICCI funded projects to desulfurize coal[10,11]. Moreover, similar methods are well known for oxidizing organic sulfur to sulfate[12-15]. Since hydroperoxides possess about the same oxidizing ability as peracids, it is reasonable to investigate inexpensive hydroperoxides from vegetable oils for desulfurizing coals.

But do linseed oils actually desulfurize coals? To determine whether any coal desulfurization actually occurred we conducted the following experiments: A thin coat of linseed oil was placed on 5g of IBC-108 coal by making a slurry of the coal in a solution of the weighed oil in 30 mL of chloroform and then evaporating the chloroform. The oil-coal mixture was spread uniformly on a petri dish, which was floated on a constant temperature bath at either 100°C or 50°C with or without UV irradiation for 18hrs. The reaction mixture was extracted with 50 mL of tetrahydrofuran and chloroform, the coal was dried, and its sulfur content determined. Clearly, merely treating the coal with linseed oil removes some organic sulfur. Ultraviolet irradiation improves sulfur removal, but increasing the temperature removes more.

In order to remove the oil from the coals so sulfur analyses could be performed, we treated the reacted oil-coal mixture with NaOH. This hydrolyses the oil into the sodium salt of the fatty acids (soap) and glycerol, both of which are water soluble. During experimentation with various procedures, we discovered that pretreatment of the coal with NaOH resulted in subsequently better sulfur oxidation by the impregnated linseed oil. Clearly, pretreatment with NaOH influences the coal matrix such that it is more susceptible to oil impregnation and sulfur oxidation.

Bases, especially NH_4OH, are known to modify coal matrices by chemical comminution[17]. And NH_4OH has been used to pretreat coal before oxidation with NaOCl (sodium hypochlorite) followed by Na_2CO_3 extraction in a procedure for removing organic sulfur from coals[18]. Therefore, this project proposes to test both NaOH and NH_4OH as pretreatments of IBC-108 coal followed by treatment with the hydroperoxides of linseed oil and extracted with NaOH or Na_2CO_3.

Linseed oil has been and will continue to be preferentially used in this project because it is inexpensive, can be easily sprayed on coal, and possesses a high degree of unsaturation. Its main unsaturated groupings are the linolenate group (approximately 58%) which contains three double bonds and the linoleate group (approximately 27%) which contains two double bonds. So approximately 85% of linseed oil is composed of these highly unsaturated groupings.

In summary, adding oils to coals offers:

1. ***in situ* formation of hydroperoxides**, which are powerful oxidizing agents that can oxidize organic sulfur and lead to coal detoxification,

2. **environmental safety of zero discharge**; the oil need not be removed but can remain with the coal, and no noxious products will be formed,

3. **increased volatiles**; the oil will produce volatiles which will enhance the burning qualities of the treated coal,

4. **increased hydrogen content**; the high hydrogen content of the oils will be available to the coal,

5. **increased BTU**; the oils furnish carbon and hydrogen which will increase the heat content of the coal,

6. **decreased costs**; in pure form and truck load quantities these oils can be purchased for $0.28/LB; however, in raw form and tank car quantities the price will be much less. Eliminating purification steps necessary for current markets will reduce the cost of oils, and

7. **ease of use**; vegetable oils should be easily added to coals by simply spraying a thin film on finely divided coal.

EXPERIMENTAL PROCEDURES

Description of Work Proposed

Task 1. *Selection of base for pretreatment and extraction*

Screening of the base to use for pretreating the coal will be conducted in a systematic way: Eight 5 g portions (four pairs) for IBC-108 coal will be immersed for 10 hours at 25°C by pairs in one of the following aqueous solutions: 1% NaOH, 5% NaOH, 1% NH_4OH, or 5% NH_4OH. These eight pretreated portions of coal will each be washed with distilled water until the wash waters are neutral and the dried and treated with linseed oil for 20 hours at 100°C. One member of each pair will them be washed with a solution of 5% NaOH, followed by washings with water and organic solvents, and the other member of the pair will be washed with a solution of 5% Na_2CO_3, followed by washings with water and organic solvents. Sulfur analyses will be obtained on each sample before and after oil treatment, such that comparisons can be made between the samples treated with base only and the same samples receiving the full treatment. Based on which base produces the lowest sulfur content, one base, either NaOH or NH_4OH, will be chosen for pretreating coal and one washing solution, either *aq*NaOH or *aq*Na_2CO_3, will be chosen for washing the oil-treated samples in the next task.

Task 2. *Determination of base and linseed oil ability to remove organic sulfur from IBC-108 coal*

We will test different methods of using linseed oil to remove sulfur and IBC-108 coal. This is the coal from the Illinois Basin Coal Sample Program maintained in Champaign by the Illinois State Geological Survey. Its descriptions are shown in Table 1. Best conditions for the full treatment will be narrowed by a series of 144 experiments in which 5 g portions of IBC-108 coal are treated variously with two concentrations of base at four different temperatures followed by treatment with linseed oil (two different ratios of oil:coal) at three different temperatures for three different times, and finally washed in either NaOH or Na_2CO_3 (depending on which is chosen in Task1) and organic solvents. Mass balances will be obtained on all experiments; sulfur, volatiles, and BTU analyses will be obtained from the Department of Mechanical Engineering at SIUC.

Table 1. Descriptions of IBC-108 Coals

IBC 108. This is a micronized blend of Herrin and Springfield coals (80% and 20%, respectively) cleaned by an advanced froth flotation process (microbubble column flotation) in 1988. It is delivered to requesters as a filter cake (approximately 45% moisture). It is ideal for investigators wishing to use a deep-cleaned Illinois coal with low pyrite content.

Coal analyses (%, moisture free basis except moisture).

	Avg.	SD
Vol. Matter	41.6	0.57
Fixed Carbon	54.7	0.58
H-T Ash	3.7	0.19
Carbon	76.0	0.34
Hydrogen	5.2	0.31
Nitrogen	1.5	0.11
Oxygen	10.9	0.59
Total C	0.0	0.03
Total Sulfur	2.7	0.07
Sulfatic	0.0	0.03
Pyritic	0.4	0.07
Organic	2.3	0.09
BTU/lb	13726	66.33
FSI	3.2	0.78

Task 3. *Determination of mass balance, volatiles, and BTU*

Task 3 will furnish information about how mass balance, volatiles, and BTU vary with the conditions in Task 2. This information will tell how much coal is extracted in the process and furnish a way to correct sulfur, volatiles and BTU analyses for changes in mass of the coal during the process. By comparing the rates of change of mass, sulfur contents, volatiles, and BTU it will be possible to evaluate the feasibility of the process.

RESULTS AND DISCUSSION

IBC-108 coal was pretreated with alkali solutions by suspending 20 g of the coal in 150 mL of 5% or 1% aqueous NaOH solution at 25°C for 1hr, 5hr, 10hr, or 20hr, and the suspension was stirred constantly. Then the coal sample was collected *via* vacuum filtration, thoroughly washed with distilled water until the filtrate is neutral, and then dried at 120°C for 24 hours. A portion of the sample was submitted for sulfur and BTU analyses and the rest of the sample was treated with linseed oil. The sulfur contents for the NaOH treated coal are listed in Table 2 (exps. 1,2, 19-27).

Testing for effectiveness of sulfur removal consisted of the following procedure: a thin layer of linseed oil was placed on the coal in a petri dish first by making a slurry of the base-pretreated coal in a solution of oil in hexane and then by evaporating the hexane.

Table 2. % S Remaining in IBC-108 Coal After Pretreatment with NaOH Followed by Linseed Oil Treatment

	NaOH PRETREATMENT			OIL TREATMENT			RESULTS	
Exp. No	NaOH (%)	Time (hr)	Temp (°C)	Oil:Coal	Time (hr)	Temp (°C)	Sulfur (%)	% Removal
19	5%	20	100				2.06	22.0
20	5%	20	25				2.03	23.1
1	5%	15	25				2.04	22.7
21	5%	10	25				2.05	22.3
22	5%	5	25				2.09	20.8
23	5%	1	25				2.16	18.2
24	1%	20	25				2.09	20.8
2	1%	15	25				2.14	18.9
25	1%	10	25				2.15	18.6
26	1%	5	25				2.16	18.2
27	1%	1	25				2.20	16.7
28	5%	20	100	1:1	20	125	1.69	36.0
29	5%	20	25	1:1	20	125	1.85	29.9
30	5%	10	25	1:1	20	125	1.77	33.0
31	5%	5	25	1:1	20	125	1.77	33.0
32	5%	1	25	1:1	20	125	1.76	33.3
33	1%	20	25	1:1	20	125	1.83	30.7
34	1%	10	25	1:1	20	125	1.75	33.7
35	1%	5	25	1:1	20	125	1.71	35.2
36	1%	1	25	1:1	20	125	1.59	39.8
37	5%	20	25	1:1	10	125	1.90	28.0
38	5%	10	25	1:1	10	125	1.81	31.4
39	5%	5	25	1:1	10	125	1.83	30.7
40	5%	1	25	1:1	10	125	1.85	29.9
41	1%	20	25	1:1	10	125	1.89	28.4
42	1%	10	25	1:1	10	125	1.74	34.1
43	1%	5	25	1:1	10	125	1.73	34.5
44	1%	1	25	1:1	10	125	1.66	37.1
45	5%	20	25	1:1	5	125	1.81	31.4
46	5%	10	25	1:1	5	125	1.72	34.8
47	5%	5	25	1:1	5	125	1.68	36.4
48	5%	1	25	1:1	5	125	1.65	37.5
49	1%	20	25	1:1	5	125	1.80	31.8
50	1%	10	25	1:1	5	125	1.59	39.8
51	1%	5	25	1:1	5	125	1.51	42.8
52	1%	1	25	1:1	5	125	1.52	42.4
53	5%	20	25	1:10	20	125	1.82	31.1
54	5%	10	25	1:10	20	125	1.78	32.6
55	5%	5	25	1:10	20	125	1.78	32.6
56	5%	1	25	1:10	20	125	1.82	31.1
57	1%	20	25	1:10	20	125	1.89	28.4

58	1%	10	25	1:10	20	125	1.97	25.4
59	1%	5	25	1:10	20	125	1.90	28.0
60	1%	1	25	1:10	20	125	1.90	28.0
61	5%	20	25	1:10	10	125	1.87	29.2
62	5%	10	25	1:10	10	125	1.78	32.6
63	5%	5	25	1:10	10	125	1.83	30.7
64	5%	1	25	1:10	10	125	1.85	29.9
65	1%	20	25	1:10	10	125	1.78	32.6
66	1%	10	25	1:10	10	125	1.86	29.5
67	1%	5	25	1:10	10	125	1.81	31.4
68	1%	1	25	1:10	10	125	1.82	31.1
69	5%	20	25	1:10	5	125	1.89	28.4
70	5%	10	25	1:10	5	125	1.85	29.9
71	5%	5	25	1:10	5	125	1.85	29.9
72	5%	1	25	1:10	5	125	1.86	29.5
73	1%	20	25	1:10	5	125	1.67	36.7
74	1%	10	25	1:10	5	125	1.83	30.7
75	1%	5	25	1:10	5	125	1.76	33.3
76	1%	1	25	1:10	5	125	1.79	32.2
77	5%	20	25	1:1	20	100	1.73	34.5
78	5%	10	25	1:1	20	100	1.76	33.3
79	5%	5	25	1:1	20	100	1.46	44.7
80	5%	1	25	1:1	20	100	1.53	42.0
81	1%	20	25	1:1	20	100	1.62	38.6
82	1%	10	25	1:1	20	100	1.55	41.3
83	1%	5	25	1:1	20	100	1.46	44.7
84	1%	1	25	1:1	20	100	1.67	36.7
85	5%	20	25	1:1	10	100	1.53	42.0
86	5%	10	25	1:1	10	100	1.56	40.9
87	5%	5	25	1:1	10	100	1.61	39.0
88	5%	1	25	1:1	10	100	1.57	40.5
89	1%	20	25	1:1	10	100	1.61	39.0
90	1%	10	25	1:1	10	100	1.84	30.3
91	1%	5	25	1:1	10	100	1.48	43.9
92	1%	1	25	1:1	10	100	1.74	34.1
93	5%	20	25	1:1	5	100	1.32	50.0
94	5%	10	25	1:1	5	100	1.47	44.3
95	5%	5	25	1:1	5	100	1.64	37.9
96	5%	1	25	1:1	5	100	1.63	38.3
97	1%	20	25	1:1	5	100	1.49	43.6
98	1%	10	25	1:1	5	100	1.83	30.7
99	1%	5	25	1:1	5	100	1.43	45.8
100	1%	1	25	1:1	5	100	1.41	46.6
101	5%	20	25	1:10	20	100	1.68	36.4
102	5%	10	25	1:10	20	100	1.83	30.7
103	5%	5	25	1:10	20	100	1.65	37.5
104	5%	1	25	1:10	20	100	1.74	34.1
105	1%	20	25	1:10	20	100	1.76	33.3
106	1%	10	25	1:10	20	100	1.98	25.0
107	1%	5	25	1:10	20	100	1.71	35.2

108	1%	1	25	1:10	20	100	1.78	32.6
109	5%	20	25	1:10	10	100	1.79	32.2
110	5%	10	25	1:10	10	100	1.89	28.4
111	5%	5	25	1:10	10	100	1.71	35.2
112	5%	1	25	1:10	10	100	1.68	36.4
113	1%	20	25	1:10	10	100	1.92	27.3
114	1%	10	25	1:10	10	100	2.03	23.1
115	1%	5	25	1:10	10	100	1.70	35.6
116	1%	1	25	1:10	10	100	1.82	31.1
117	5%	20	25	1:10	5	100	1.84	30.3
118	5%	10	25	1:10	5	100	2.01	23.9
119	5%	5	25	1:10	5	100	1.72	34.8
120	5%	1	25	1:10	5	100	1.74	34.1
121	1%	20	25	1:10	5	100	1.70	35.6
122	1%	10	25	1:10	5	100	1.94	26.5
123	1%	5	25	1:10	5	100	1.65	37.5
124	1%	1	25	1:10	5	100	1.74	34.1

oil-coal mixture on the petri dish was heated at the reaction temperature by floating it in a constant temperature bath for certain times as described in Table 2.. After reaction, the oil-coal mixture was treated with 5% Na_2CO_3 at 80°C for 2 hours to saponify the oil and to leach out some sulfur compounds from the coal matrices. After oil extraction, the coal samples were thoroughly washed with water and 50 mL of methanol, then dried and submitted for sulfur and BTU analyses. The results are listed in Table 2.

In all experiments, the chlorinated solvents, such as chloroform and tetrachloroethylene, were completely eliminated because of the possible interference of chlorine with sulfur analyses as suggested by the project monitor.

Figures 1-4 show the percent sulfur remaining in IBC-108 coal after pretreatment with 5% NaOH (Figures 1 and 3) or 1% NaOH (Figures 2 and 4) for four different times (1hr, 5hr, 10hr, and 20hr) followed by linseed oil treatment at 125°C for three different times (5hr, 10hr, and 20hr) with 1:1 oil to coal ratio (Figures 1 and 2) or 1:10 oil to coal ratio (Figures 3 and 4). Figures 5-8 show results from similar treatments but the temperature for the oil treatment is 100°C instead of 125°C. In each figure the percent sulfur remaining is plotted against the times of NaOH pretreatment so that the time effects of NaOH pretreatment on the subsequent sulfur removal can be directly compared. Also results from the same coal sample but treated with oil at different times are grouped together so that the time effects of the oil treatment on sulfur removal can also be compared by examining each individual groups.

<u>Sulfur removal as a function of NaOH concentrations and times of treatment</u>: The bars labeled with 0hr oil (first bar in group of four) in Figures 1 and 2 show the results of pretreating IBC-108 coal with 5%NaOH and 1%NaOH for different times. This shows that some sulfur is removed by treating the coal with NaOH alone. Depending on the time of treatment, sulfur removal varies from 21% to 23% for 5% NaOH and from 17% to 21% for 1%NaOH. Increasing treatment time from 1hr to 20hr results in more sulfur removal under both concentrations. Sulfur removal is slightly favored by higher base concentrations.

Effects of linseed oil treatment on sulfur removal: Figures 1-8 show that linseed oil treatment removes more sulfur from the NaOH treated coal. The combinations of NaOH pretreatment, then oil treatment followed by Na_2CO_3 extraction removes 23% to 50% sulfur depending on the conditions. The best result is achieved by pretreating the coal with 5% NaOH for 20 hr (23% sulfur removal) followed by oil treatment at 100°C for 5 hr with a 1:1 oil to coal ratio (50% sulfur removal in total).

Sulfur removal as a function of time of oil treatment: Comparing the different oil treatments within each group in Figures 1 and 2 reveals that the most sulfur is removed with 5hr oil treatment and the least sulfur is removed with 10hr oil treatment regardless of the time difference in NaOH pretreatment. These results were obtained at 125°C with a 1:1 oil to coal ratio. Similar time effects of oil treatment are also obtained at 100°C with a 1:10 oil to coal ratio (Figure 8). However a different trend occurs with time of oil treatment shown in Figures 3, 6, and 7. More sulfur is removed as the time of oil treatment increases. On the other hand, sometimes more sulfur is removed by decreasing the time of oil treatment (see for example Figure 4, in which oil treatment is conducted on a 1% NaOH pretreated coal sample at 125°C at a 1:10 oil to coal ratio).

Time effects of NaOH pretreatment on the subsequent sulfur removal: As pointed out earlier, Figures 1-8 also show the effects of the duration of NaOH pretreatments on subsequent sulfur removal. In some cases, the time of NaOH pretreatment has significant effect on subsequent sulfur removal, in the other cases it has little effect. For example, under conditions shown in Figures 1 and 2, more sulfur is removed from the pretreated coal by decreasing the time of NaOH treatment. But under conditions in Figure 3, little change in sulfur removal occurs with change in time of NaOH pretreatment.

Sulfur removal as a function of oil to coal ratio: Figures 9-14 show the effects of oil to coal ratio on the sulfur removal under various conditions. The percentages shown in parentheses in the legends represent the NaOH concentrations for the pretreatment. These data show that sulfur removal is favored by a 1:1 oil to coal ratio regardless of the other experimental parameters.

CONCLUSIONS AND RECOMMENDATIONS

Conclusions

- Pretreating IBC-108 coal with 5%NaOH and 1% NaOH removes 17% to 23% of the sulfur under the conditions of this investigation. Higher NaOH concentration and longer impregnation times remove more sulfur.

- More sulfur is removed by the treatment sequence: NaOH pretreatment, then linseed oil treatment, and finally Na_2CO_3 extraction.

- The combinations of NaOH pretreatment, then oil treatment followed by Na_2CO_3 extraction remove 23% to 50% sulfur. The best result is achieved by pretreating with 5% NaOH for 20 hr (23% sulfur removal) followed by oil treatment at 100°C for 5 hr with a 1:1 oil to coal ratio (50% sulfur removal in total, exp. 93). The table below lists the conditions under which 40-50% organic sulfur may be removed from IBC-108 coal. IBC-108 coal has the following sulfur analysis: Percent Total Sulfur, 2.7 ± 0.07% (Sulfatic, 0.0 ± 0.03; Pyritic, 0.4 ± 0.07; Organic, 2.3 ± 0.09).

	NaOH PRETREATMENT			**OIL TREATMENT**			**RESULTS**	
Exp. No	NaOH (%)	Time (hr)	Temp (°C)	oil:coal ratio	Time (hr)	Temp (°C)	Sulfur (%)	S removed (%)
93	5%	20	25	1:1	5	100	1.32	50.0
99	1%	5	25	1:1	5	100	1.43	45.8
79	5%	5	25	1:1	20	100	1.46	44.7
83	1%	5	25	1:1	20	100	1.46	44.7
100	1%	1	25	1:1	5	100	1.41	46.6
94	5%	10	25	1:1	5	100	1.47	44.3
91	1%	5	25	1:1	10	100	1.48	43.9
97	1%	20	25	1:1	5	100	1.49	43.6
51	1%	5	25	1:1	5	125	1.51	42.8
52	1%	1	25	1:1	5	125	1.52	42.4
80	5%	1	25	1:1	20	100	1.53	42.0
85	5%	20	25	1:1	10	100	1.53	42.0
82	1%	10	25	1:1	20	100	1.55	41.3
86	5%	10	25	1:1	10	100	1.56	40.9
88	5%	1	25	1:1	10	100	1.57	40.5

- More sulfur is removed with a 1:1 oil to coal ratio than a 1:10 ratio under most conditions of the investigation.

- The effects of time of oil treatment are complex. Sulfur removal is favored by longer oil treatment in some cases, but disfavored in other cases. This demonstrates that other experimental parameters are important, such as temperature, concentration of base, time of base pretreatment, and oil to coal ratio.

Recommendations

- Continue with the experimental plan specified in the proposal.
- Use lower NaOH concentration (<1%) in the pretreatment

DISCLAIMER STATEMENT

REFERENCES

1. Webster, J. R., R.H. Shiley, R.E. Hughes, P.L. Lapish, D.K. Cowin, G.V. Smith, C.C. Hinckley, T. Nishizawa, N. Yoshida, T. Wiltowski, Y. Wada, and M. Saporoschencko, *Second Annual Pittsburgh Coal Conference, Proceedings,* 1985, p138.

2. Smith, G.V., T. Wiltowski, and J.B. Phillips, *Energy & Fuels*, **3**, 536 (1989)

3. Shiley, R.H., R.E. Hughes, J.R. Webster, C.C. Hinckley, G.V. Smith, and T. Wiltowski, U.S. 4,888,029 19 Dec 1989

4. Akash, B.A., C. B. Muchmore, J.A. Koropchak, J.W. Kim, and S.B. Lalvani, *Energy & Fuels*, **6**, 629 (1992)

5. Chou, M.-I.M., D.H. Buchanan, J.M. Lytle, R.R. Ruch, C. W. Kruse, C. Chaven, K.C. Hackley, R.E. Hughes, R.D. Harvey, J.K. Frost, J.W. Stucki, G.P. Huffman, and F.E. Huggins, *1991-1992 Final Technical Report for the reporting period of September 1, 1991 through August 31, 1992*, Center For Research on Sulfur in Coal, September 1992 pp 16-1 to 16-3.

6. Chou, M.-I.M., J.M. Lytle, R.R. Ruch, C.W. Kruse, C. Chaven, K.C. Hackley, R.E. Hughes, R.D. Harvey, J.K. Frost, D.H. Buchanan, J.W. Stucki, G. P. Huffman, and F.E. Huggins, *Final Technical Report for the period September 1, 1992 through August 31, 1993*, Illinois Clean Coal Institute, September 30, 1993, pp. 12-1 to 12-4.

7. Petrakis, L., D.W. Grandy, *Anal. Chem.*, **50**, 303 (1978)

8. Petrakis, L., D.W. Grandy, *Fuel*, **59**, 227 (1980)

9. Petrakis, L., D.W. Grandy, *Nature*, **289**, (1981)

10. Hippo, E.J. and S.R. Palmer, *1991-1992 Final Technical Report*, Center for Research on Sulfur in Coal, 1992, pp 15-1 to 15-5.

11. Palmer, S.R. E.J. Hippo, M.A. Kruge, and J.C. Crelling, *Coal Preparation*, 1992, **10**, 93-106.

12. *ASTM Standard, D1266-64T, Part 17*, Amer. Soc. for Testing and Materials, Philadelphia, PA, 1966, p. 456

13. Hempel, W., *Z. Angew. Chem.*, **5**, 393 (1892)

14. Parr, S.W., W.F. Wheeler, and R. Berolzheimer, *J. Ind. Engl. Chem.*, **1**, 689 (1909)

15. Ailey-Trent, K.S., C.W. McGowan, W.Lachowicz, and R. Markuszewski, *ACS Division of Fuel, Preprints*, **36**, 1198 (1991)

16. For example, see Buchanan, D.H., M. Amin, R. Cunningham, J. Galyen, and Y.Tong, *First Quarter Technical Report for the period September 1, 1993 through November 30, 1993*, Illinois Clean Coal Institute, pp. 29-1 to 29-4, December 14, 1993.

17. Philip, H. H., and R. S. Datta, *Coal Desulfurization, Chemical and Physical Methods, ACS Symposium Series,* **64**, American Chemical Society, Washington D.C.,(1977) pp58-69

18. Brubaker, I. M., and T. Stoicos, *Coal Science and Technology* ***9***, *Processing and Utilization of High Sulfur Coals,* (Ed. Y.A. Attia) Elsevier, Amsterdam, (1985) pp 311-326

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

Project Title: **DESULFURIZATION OF ILLINOIS COALS WITH HYDROPEROXIDES OF VEGETABLE OILS AND ALKALI**

DOE Cooperative Agreement Number:	DE-FC22-92PC92521 (Year 4)
ICCI Project Number:	95-1/1.1D-2P
Principal Investigator:	Gerard V. Smith, SIUC
Other Investigators:	Ricky D. Gaston, SIUC
	Ruozhi Song, SIUC
	Yaguang Wang, SIUC
	Jianjun Cheng, SIUC
	Feng Shi, SIUC
Project Manager:	Ken Ho, ICCI

COMMENTS

Expenditures are proceeding approximately as projected. No unusual problems have occured.

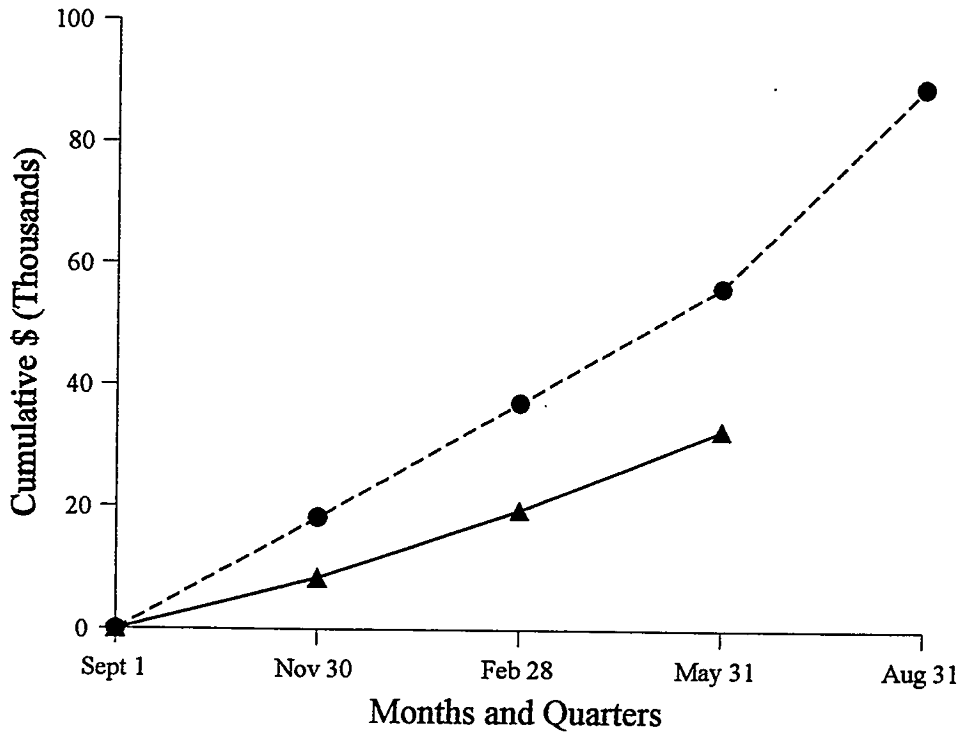
PROJECTED AND ESTIMATED EXPENDITURES BY QUARTER

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	12,717	1,730	750	0	0	1,426	1,662	18,285
	Estimated	6,000	641	568	0	0	384	759	8,352
Sept. 1, 1995 to Feb. 28, 1996	Projected	25,434	3,461	1,500	600	0	2,852	3,385	37,232
	Estimated	12,974	1,648	1,689	0	0	1,394	1,771	19,476
Sept. 1, 1995 to May 31, 1996	Projected	38,151	5,191	2,250	1,200	0	4,279	5,107	56,178
	Estimated	22,410	3,094	2,511	0	0	1,731	2,975	32,721
Sept. 1, 1995 to Aug. 31, 1996	Projected	61,545	8,885	3,000	2,000	0	5,705	8,114	89,249
	Estimated								

*Cumulative by Quarter

CUMULATIVE COSTS BY QUARTER

Desulfurization of Illinois Coals with Hydroperoxides of Vegetable Oils and Alkali

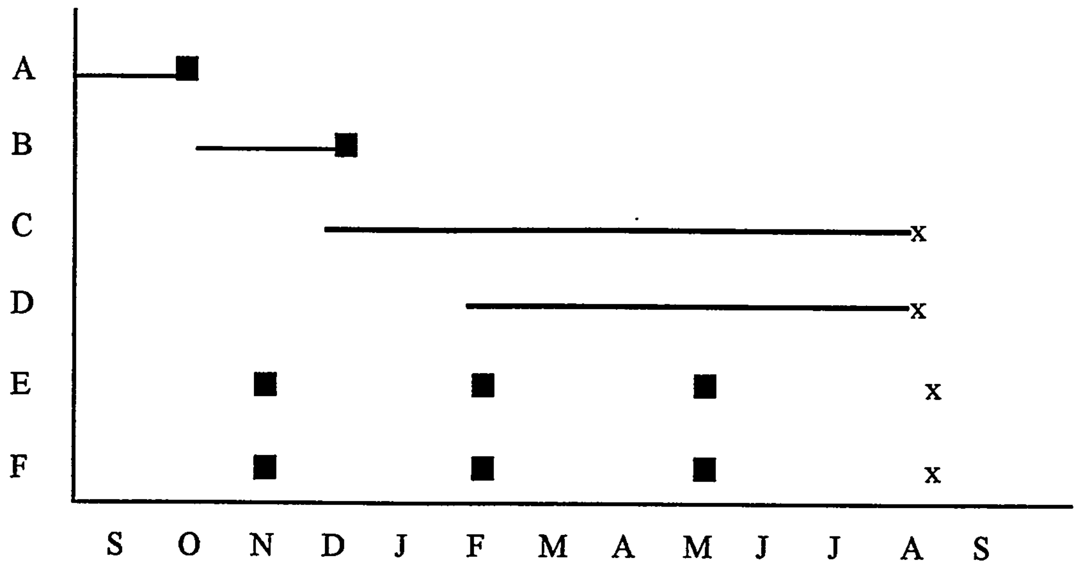


● = Projected Expenditures - - - - - - -

▲ = Actual Expenditures ______________

Total Illinois Clean Coal Instutute Award $89,249

SCHEDULE OF PROJECT MILESTONES



Begin
Sept. 1
1995

Hypothetical Milestones:

- A: Research personnel employed
- B: Task 1, selection of base for pretreatment and extraction
- C: Task 2, determination of base and linseed oil ability to remove organic sulfur from IBC-108 coal
- D: Task 3, determination of mass balance, volatiles, and BTU
- E: Project Technical Reports
- F: Project Management Reports