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Project Title: **DESULFURIZATION OF COAL WITH HYDROPEROXIDES OF VEGETABLE OILS**

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ABSTRACT

This project proposes a new method for removing organic sulfur from Illinois coals using readily available farm products. It proposes to use air and vegetable oils to disrupt the coal matrix, oxidize sulfur forms, increase volatiles, and desulfurize coal. This will be accomplished by 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. Preliminary experiments showed that IBC 104 coal catalyzes the formation of hydroperoxides in safflower oil and that more sulfur is extracted from the treated than untreated coal. During the first quarter the requirement of an added photosensitizer was eliminated, the catalytic effect of coal was confirmed, and the existence of a complex set of reactions was revealed. During this second quarter working with IBC-108 coal (2.3% organic S, 0.4% pyrite S), the effects of different ratios of oil:coal, different extraction solvents, and different temperatures were examined. A new pretreatment which combines alkali with linseed oil was discovered. Best organic sulfur removal is approximately 26% using alkali pretreatment combined with linseed oil at 100°C. BTU loses can be kept to a minimum of 3% with proper use of solvents.

EXECUTIVE SUMMARY

This project proposes to remove organic sulfur from coal, increase its BTU, and increase its volatiles, by a new process of impregnating coal with polyunsaturated vegetable oils. By reaction with air these oils will be converted into their hydroperoxides which are powerful oxidizing agents. A similar agent, peroxyacetic acid, has been 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 enhancing organic sulfur removal; third, they furnish carbonaceous residues which will increase BTU's and volatiles; fourth, they are environmentally safe and produce no noxious products, and fifth, these compounds contain hydrogen and oxygen, elements that aid coal desulfurization.

Preliminary experiments at SIUC showed that IBC-104 coal impregnated with safflower oil and heated in air at 70°C loses sulfur in chloroform extraction. The results show that coal catalyzes formation of hydroperoxides in the oil and these hydroperoxides oxidize sulfur making it more easily removable. This project proposed to build on this evidence to aim at a technically feasible and economically viable process step.

Three tasks were proposed. **Task 1** will test protocols for generating hydroperoxides in linseed oil. Evidence suggests coal alone may be sufficient to generate high concentrations of hydroperoxides in impregnated vegetable oils; however, Task 1 will determine whether addition of a photosensitizer and irradiation are necessary for generating hydroperoxides in the oils. **Task 2** will test sulfur removal from IBC-104 and IBC-108 coals by linseed oil hydroperoxides. Although the main focus will be on IBC-108 coal (2.3% organic S, 0.4% pyritic S, 3.7% ash) and the effects linseed oil hydroperoxides have on its organic sulfur, we will run some tests with IBC-104 (1.8% organic S, 2.4% pyritic S, 38.3% ash) to establish a comparison and to determine whether the presence of mineral matter enhances organic sulfur removal. For example, if mineral matter enhances formation of oil hydroperoxides and their subsequent oxidation of organic sulfur, an effective coal treatment will likely be to remove mineral matter after, rather than before, oil hydroperoxide treatment. This major task will examine the parameters of temperature, time, and the ratio of oil:coal. It will define the effects of these parameters on organic sulfur removal, BTU, and volatiles. **Task 3** will test the effect of the oil-hydroperoxide pretreatment on subsequent removal of organic sulfur from coal by mild pyrolysis. Mass balance data will allow determination of char yields and BTU analyses will reveal whether treatment has enriched the char in heat content. As pointed out by our Project Manager, the heat content of the remaining char is an important point. We will pay careful attention to the effect oil hydroperoxide treatment has on heat content.

Conclusions reached during the first quarter were that the porphine (TPP) is unnecessary for hydroperoxide formation, the coal surfaces catalyze hydroperoxide formation, and a complex set of reactions are occurring between the oxygen, oil, hydroperoxides, and coal. Reactions occurring are hydroperoxide formation, which is catalyzed by the coal surface and by heat, an unknown coal-hydroperoxide reaction, and oil polymerization.

Additionally, diffusion phenomena must be playing a role because oil polymerization occurs, but the importance of diffusion was difficult to assess because less polymerization occurs when coal is present.

During this second quarter we tested for effectiveness of sulfur removal by 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 coal in a solution of oil in chloroform and then by evaporating the chloroform. The oil-coal mixture on the petri dish was heated at the reaction temperature by floating it in a constant temperature bath. After reaction the oil was extracted with 50 mL of tetrachloroethylene (TCE) and two portions of 50 mL of chloroform ($CHCl_3$). It was soon discovered that not all the oil was removed because some of the oil polymerizes, especially for the experiments at 100°C and with a oil:coal ratio of 1:1 (others at 50°C and oil:coal ratios of 1:10 and 1:100 were extractable), so some reaction mixtures were extracted with alkali {or base (B), 5% NaOH} to saponify the oil and these samples were further washed with water and 50 mL of tetrahydrofuran (THF). To determine whether alkali (B) treatment alters the coal structure, coal samples were pretreated with B and found to lose some organic sulfur. So alkali-treated coals were also extracted with TCE and $CHCl_3$ and found to lose even more organic sulfur. This led to a series of experiments in which coals were first pretreated with alkali, then linseed oil (O), and finally extracted with alkali, that is (B-O-B). Various combinations of these treatments were tested on both IBC-108 and IBC-104 coals at different ratios of oil:coal and different temperatures.

Approximately 25% organic sulfur can be removed with minimum loss of BTU by treatment with linseed oil hydroperoxides, providing such treatment is followed by proper extraction procedures which remove the affected sulfur but not other combustible materials. Washing the IBC-108 coal with aqueous alkali (base, B) and with organic solvents (THF and $CHCl_3$) removes organic sulfur, but also removes about 7% of other organics which do not contain sulfur. Therefore, the actual organic sulfur removal is greater than appears because of the loss of other organics. This base-oil-base (B-O-B) treatment removes organic sulfur with minimum loss of BTU, but only slightly removes other organics which do not contain sulfur. However, washing coal with tectrachloroethylene (TCE) extracts nonsulfur containing organics and increases the %S in the remaining coal by about 24%; BTU is lowered only 3%. And irradiating with UV makes some organics susceptible to extraction by THF and/or chloroform.

In contrast to IBC-108, BTU's actually increase when IBC-104 is treated with base and oil. This results because the treatment removes minerals from IBC-104, minerals that are not present in IBC-108. Mineral content of IBC-104 is 38%, and removing these minerals decreases the overall mass of the coal with a corresponding increase in the percentage of combustible matter in the recovered coal. IBC-108 contains practically no mineral matters, so the treatment does not increase the percentage of combustible matter.

OBJECTIVES

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

1. determine the ability of oils to remove organic sulfur from Illinois coals,
2. establish the volatile and BTU changes from treating Illinois coals with oils,
3. establish the mass balance of solids, liquids, and gases resulting from treating Illinois coals with oils, and
4. study the reaction rate(s) and mechanism(s) of sulfur removal from Illinois coals treated with oils.

Briefly the tasks scheduled for the current year are:

Task 1. *Tests of protocols for generating hydroperoxides in linseed oil*

Task 2. *Tests of sulfur removal from IBC-104 and IBC-108 by linseed oil hydroperoxides*

Task 3. *Test of hydroperoxide pretreatment on subsequent removal of sulfur from coal by mild pyrolysis*

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 accomplish coal desulfurization.

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 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 of not only 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 enhancing organic sulfur removal; third, they furnish carbonaceous residues which will increase BTU's of coal char; fourth, they are environmentally safe and produce no noxious products, and fifth, these compounds contain hydrogen and oxygen, elements that aid coal desulfurization.

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 this project will test several protocols, including standard photosensitizers as well as **coal as a sensitizer**.

Coal may be a sensitizer because it contains both radicals[7-9] and complex molecules which absorb light. The radicals will directly convert triplet to singlet oxygen, and some of its complex molecules may be photosensitizers. With this in mind, we tested the ability of coal to sensitize oxygen in air and produce hydroperoxy groups in safflower oil. We chose safflower oil for preliminary tests because it is readily available at the grocery store and is relatively rich in polyunsaturated fats, such as glyceryl oleate, and glyceryl linoleate. Our intent was solely to test the ability of coal to sensitize oxygen and produce hydroperoxides in the unsaturated oils. And the results are encouraging.

Indeed, we found that coal sensitizes oxygen and produces hydroperoxy groups in safflower oil. Coal catalyzes formation of hydroperoxides in safflower oil in amounts depending on time, temperature, and ratio of oil to coal. Not only does the formation of hydroperoxides depend on time and temperature, but also it depends on the thickness of the oil layer on the coal particle. This layer influences how fast oxygen in the air diffuses through the adsorbed oil to the surface of the coal where it is excited to the singlet state and forms hydroperoxides in the oil.

These singlet oxygen molecules react with impregnated oils on the coal surface to produce hydroperoxides, powerful oxidizing agents. Similar powerful oxidizing agents, such as peroxyacetic acid, have been used in 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 vegetable oils actually desulfurize coals? To determine whether any coal desulfurization actually occurred during these preliminary experiments we extracted 0.5 gms of treated coal with 30 mL of boiling pyridine[16] for two hours, filtered, and submitted the pyridine solution for sulfur analysis by Inductively Coupled Plasma (ICP). A pyridine extract of untreated coal was analyzed for comparison. The pyridine extract from the treated coal contained less sulfur than that from the untreated coal. Likely, this resulted from the treated coal having already been extracted with chloroform to recover the impregnated safflower oil for titration with $Na_2S_2O_3$. This chloroform extraction likely removed sulfur as shown by ICCI funded research[5,6]. So the treated coal contained less sulfur available for pyridine extraction. Moreover, as previously mentioned, the absence of continued build up of hydroperoxides suggests reaction of hydroperoxides with the coal. Therefore, these preliminary experiments with safflower oil suggest that coal catalyzes formation of hydroperoxides in vegetable oils and these hydroperoxides oxidize the coal and aid desulfurization. Finally, these results should apply to all unsaturated vegetable oils, so it is reasonable to examine a vegetable oil more suitable for practical use with coal. Such an oil is linseed oil.

Linseed oil is being preferentially used in this project because it is inexpensive, should 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, which means that linseed oil can make more hydroperoxy groups per pound than safflower oil (whose main unsaturated grouping is approximately 75% linoleate) or any other readily available vegetable oil. However, these preliminary results with safflower oil should be directly transferable to linseed oil as well as to other polyunsaturated vegetable oils. Moreover, vegetable oils will be easy to add to coal treatments by processes as simple as spraying a thin coating on finely divided coal.

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 desulfurization,

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. *Tests of protocols for generating hydroperoxides in linseed oil.*

Hydroperoxide preparation will be explored by two general methods. One method will add small amounts of the photosensitizer 5,10,15,20-tetraphenyl-21*H*,23*H*-porphine to linseed oil, saturate the mixture with oxygen, and irradiate the mixtures with appropriate light. The other method will add coal to linseed oil, saturate the mixture with oxygen, and irradiate the mixture with appropriate light. Rates of formation of hydroperoxides will be monitored by $Na_2S_2O_3$ titration and compared for the two methods.

Since we have already determined that coal catalyzes the formation of hydroperoxides in impregnated oil, we will carefully evaluate whether any increased production of hydroperoxides resulting from the photosensitizer will merit its use. For this evaluation we will impregnate one sample of IBC 104 coal with linseed oil and another sample with linseed oil containing the photosensitizer. We will identically irradiate each sample at different temperatures for different times, extract the oils, and determine their hydroperoxide contents.

Task 2. *Tests of organic sulfur removal from IBC-104 and IBC-108 by linseed oil hydroperoxides.*

We will test different methods of using linseed oil to remove sulfur from IBC-104 and IBC-108 coals. These are coals from the Illinois Basin Coal Sample Program maintained in Champaign by the Illinois State Geological Survey. Their descriptions are shown in Table 1. Although the main focus will be on IBC-108 coal and the effects linseed oil hydroperoxides have on its organic sulfur, we will run some tests with IBC-104 to establish a comparison and to determine whether the presence of mineral matter enhances organic sulfur removal. For example, if mineral matter enhances formation of oil hydroperoxides and their subsequent oxidation of organic sulfur, an effective coal treatment will likely be to remove mineral matter after, rather than before, oil hydroperoxide treatment. The specific variables tested will be the temperature, the duration of treatment, and the ratio of oil to coal. Experiments will consist of mixing dried IBC-108 and 104 coals with different quantities of oil (the oil may contain a sensitizer if its need is determined in Task 1) and heating the mixtures in air at different temperatures for different times. Next the coals will be solvent extracted with perchloroethylene (PCE)[5,6], dried and submitted for sulfur and for

Table 1. Descriptions of IBC-108 and IBC-104 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

IBC 104. This is a run of mine Herrin coal obtained in 1984 from southwestern Illinois. It was selected as a feed for physical cleaning tests. About two thirds of its sulfur is pyritic sulfur. The amount remaining in this lot is small and it is reserved for persons who have previously used it.

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

	Avg	SD
Moisture	10.7	0.30
Vol. Matter	28.5	0.49
Fixed Carbon	33.2	0.46
H-T Ash	38.3	0.62
Carbon	46.9	0.48
Hydrogen	3.4	0.28
Nitrogen	0.9	0.14
Oxygen	6.4	0.51
Total C	0.0	0.02
Total Sulfur	4.2	0.15
Sulfatic	0.0	0.03
Pyritic	2.4	0.25
Organic	1.8	0.24
BTU/lb	8533	85.16
FS	2.6	0.88
Eq. Moist	11.93	

BTU analyses. A portion of the same solvent extraction will be used as a standard. A portion of selected coals, described in Task 3, will not be extracted but will be used in Task 3 to evaluate the amount of sulfur removed by mixing oil with the coals, heating in air, and pyrolyzing.

Task 3. *Test of hydroperoxide pretreatment on subsequent removal of sulfur from coal by mild pyrolysis*

Additionally, after oil treatment, a portion of selected coals will be subjected to mild pyrolysis under an inert atmosphere and under a methane/oxygen atmosphere. Not all coal samples from Test 2 will be selected. For each coal we will select one oil:coal ratio (likely 1:100), two temperatures (50°C and 100°C), and two times (5 hr and 15 hr) for a total of 8 samples. Additionally, we will select one sample of unextracted pretreated coal for each coal (to evaluate char in coal treated only with oil/hydroperoxide) increasing the total to 10. The mass balance of the solids, liquids, and gases will be determined, and the chars will be submitted for sulfur and BTU analyses. We will pay particular attention to the effect of oil/hydroperoxide treatment on the BTU of the resulting char. Standards will be prepared from the same mild pyrolyses of untreated-extracted and untreated-unextracted coals. We have extensive experience running such reactions during previous ICCI funded projects; therefore, the necessary equipment is already in place. We will use the optimum parameters determined from these earlier studies.

RESULTS AND DISCUSSION

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 coal in a solution of oil in chloroform and then by evaporating the chloroform. The oil-coal mixture on the petri dish was heated at the reaction temperature by floating it in a constant temperature bath. After reaction the oil was extracted with 50 mL of tetrachloroethylene (TCE) and two portions of 50 mL of chloroform ($CHCl_3$). It was soon discovered that not all the oil was removed because some of the oil polymerizes, especially for the experiments at 100°C and with a oil:coal ratio of 1:1 (others at 50°C and oil:coal ratios of 1:10 and 1:100 were extractable), so some reaction mixtures were extracted with alkali {or base (B),5% NaOH} to saponify the oil and these samples were further washed with water and 50 mL of tetrahydrofuran (THF). To determine whether alkali (B) treatment alters the coal structure, coal samples were pretreated with B and found to lose some organic sulfur. So alkali-treated coals were also extracted with TCE and $CHCl_3$ and found to lose even more organic sulfur. This led to a series of experiments in which coals were first pretreated with alkali, then linseed oil (O), and finally extracted with alkali, that is (B-O-B). Various combinations of these treatments were tested on both IBC-108 and IBC-104 coals at different ratios of oil:coal, different temperatures as described in Table 2 on the next page.

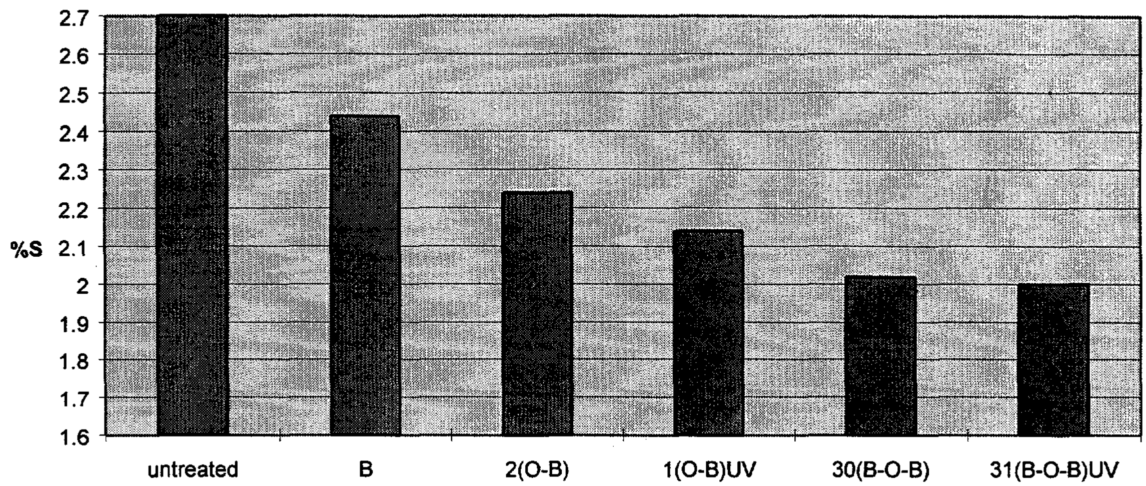
Table 2: Sulfur and BTU Analyses

	Exp.	Coal type/g	Oil (g)	Ratio oil:coal	Temp (°C)	Time (hr)	UV	Sulfur (%)	BTU (/lb.)
1		**104**						4.10[a]	8,853[a]
2								4.17[b]	8,522[b]
3								2.65[c]	7,258[c]
4								3.64[d]	7,019[d]
5		**108**						3.34[a]	12,946[a]
6								2.63[b]	13,700[b]
7								2.44[c]	11,789[c]
8								2.69[d]	13,376[d]
9	1[c]	108/5	5.0	1:1	100	18	yes	2.14	11,624
10	2[c]	108/5	5.0	1:1	100	18	no	2.24	11,062
11	22[c]	108/5	0.5	1:10	100	18	yes	2.83	11,819
12	17	108/5	0.5	1:10	100	18	yes	2.79	12,555
13	5	108/5	0.5	1:10	100	18	no	2.49	12,995
14	15	108/5	0.05	1:100	100	18	no	2.79	12,918
15	16	108/5	0.05	1:100	100	18	yes	3.02	12,198
16	26[c,e]	108/5	5.0	1:1	100	18	no	2.28	10,992
17	27[c,e]	108/5	5.0	1:1	100	18	yes	2.28	10,895
18	30[c,e]	108/5	5.0	1:1	100	18	no	2.02	12,227
19	31[c,e]	108/5	5.0	1:1	100	18	yes	2.00	12,385
20	36[e,f]	108/5	5.0	1:1	100	18	no	2.12	
21	37[f]	108/5	5.0	1:1	100	18	no	2.33	
22	33[g]	108/5	5.0	1:1	100	18	no	2.33	
23	34[g]	108/5	5.0	1:1	100	18	yes	2.44	
24	32[h]	108/5			100	18		2.26	
25	35[i]	108/5	5.0	1:1	100	18		2.28	
26	3[c]	104/5	5.0	1:1	100	18	yes	2.04	8,703
27	4[c]	104/5	5.0	1:1	100	18	no	2.12	9,343
28	18	104/5	0.5	1:10	100	18	yes	3.94	9,149
29	6	104/5	0.5	1:10	100	18	no	3.62	9,007
30	24	104/5	0.05	1:100	100	18	yes	3.64	8,609
31	14	104/5	0.05	1:100	100	18	no	3.94	7,541
32	21[c]	104/5	0.05	1:100	100	18	no	2.95	8,710
33	28[c,e]	104/5	5.0	1:1	100	18	no	2.33	
34	29[c,e]	104/5	5.0	1:1	100	18	yes	2.23	
35	40[f,g]	104/5	5.0	1:1	100	18	no	2.21	
36	41[f,g]	104/5	5.0	1:1	100	18	yes	2.14	
37	38[h]	104/5			100	18		2.33	
38	39[i]	104/5	5.0	1:1	100	18		2.58	
39	23	108/5	5.0	1:1	75	18	no	2.86	13,090
40	25	108/5	0.05	1:100	75	18	no	3.13	13,051
41	19	104/5	5.0	1:1	75	18	no	3.48	9,927
42	20	104/5	0.5	1:10	75	18	no	3.76	9,052
43	7	108/5	5.0	1:1	50	18	yes	2.56	12,841
44	9	108/5	5.0	1:1	50	18	no	2.67	13,039
45	11	108/5	0.5	1:10	50	18	no	2.72	12,460
46	13	108/5	0.05	1:100	50	18	no	2.53	12,739
47	8	104/5	5.0	1:1	50	18	no	3.64	8,777
48	10	104/5	0.5	1:10	50	18	no	3. 0	8,685
49	12	104/5	0.05	1:100	50	18	no	3.69	7,339

[a] Extracted with TCE and $CHCl_3$. [b] from Illinois State Geological Survey. [c] Extracted with 5% NaOH, H_2O, and THF + $CHCl_3$ after oil. [d] Unextracted sample. [e] Extracted with 5% *aq*NaOH before oil. [f] Coal-oil mixture refluxed in 5% *aq*NaOH 1 hr after oil. [g] 2 g NaOH added to oil-coal mixture by dissolving oil in solution of NaOH in 30mL MeOH and 30mL THF. [h] Reflux 18 hours with 100mL 5% *aq*NaOH. [i] Reflux 18 hours in 100mL 5% *aq*NaOH, bubbling O_2.

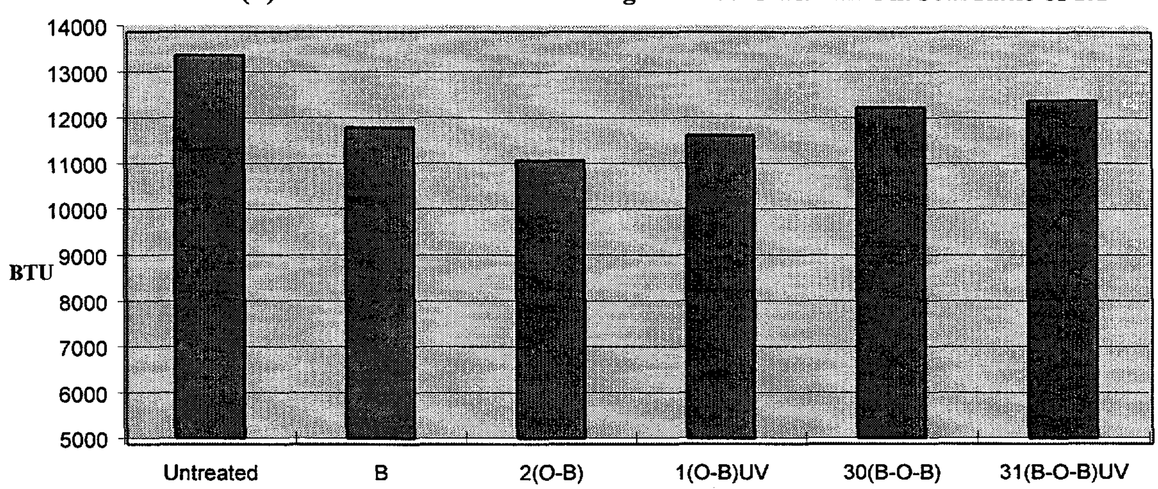
Figure 1 shows results of treating IBC-108 coal with NaOH base (B) and linseed oil (O) with and without ultraviolet light irradiation (UV). Pretreating with base alone (B in Figure 1 and line in Table 2) removes 9% of the organic sulfur, treating with linseed oil and then base {2(O-B) in Figure 1 and Exp. 2 in Table 2)} removes 17% of the organic sulfur, and pretreating with base, then oil with UV irradiation, and finally base {31(B-O-B)UV} in Figure 1 and Exp. 31 in Table 2) removes 26% organic sulfur. Because the large amount of

Figure 1: % S Remaining in IBC-108 Coal After Treatment in Air with Alkali (B) and/or Linseed Oil (O) and UV Light at 100°C with an Oil:Coal Ratio of 1:1



linseed oil in these experiments polymerizes, treatment with base is necessary to remove the oil. The base saponifies the oil and makes it susceptible to extraction with aqueous solutions. Subsequent washings with aqueous base and with organic solvents (THF and $CHCl_3$) removes organic sulfur, but also removes other organics (about 7%, see below and Figure 2) which do not contain sulfur. Therefore, the actual organic sulfur removal is greater than appears because of the loss of other organics. This is also reflected in the BTU changes as shown in Figure 2.

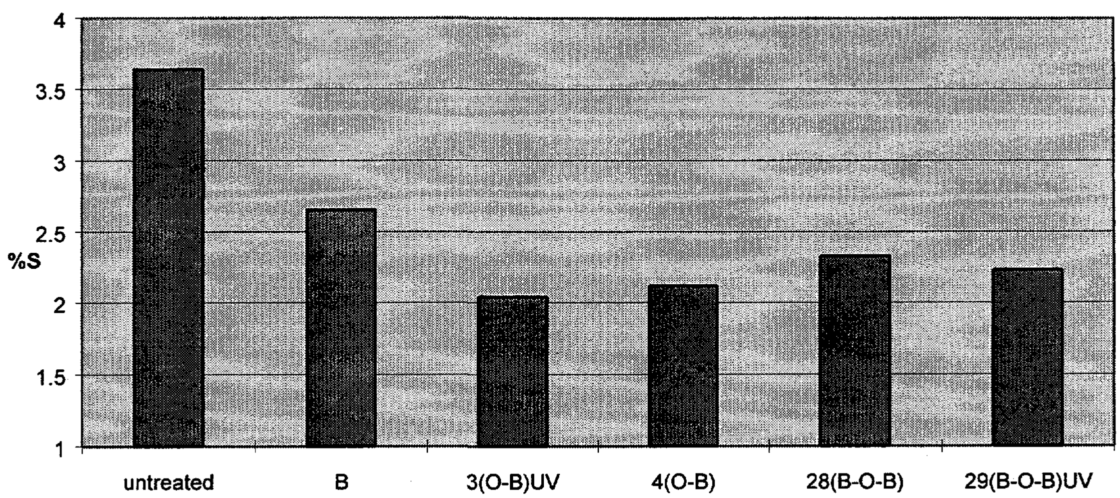
Figure 2: BTU Changes in IBC-108 Coal After treatment in Air with (B) and/or Linseed Oil and UV Light at 100°C with an Oil:Coal Ratio of 1:1



Pretreatment with base alone (B in Figure 2) causes loss of 12% BTU, and treatment with oil and then base {2(OB)} causes loss of 17% BTU. However, pretreatment with base followed by first oil (with UV), then base, and finally organic solvents causes loss of only 7% BTU {31(BOB)UV in Figure 2 and Exp. 31 in Table 2}. Comparing these latter results to those in Figure 1 suggests that the B-O-B treatment removes organic sulfur but only slightly removes other organics which do not contain sulfur. Perhaps oxidation by the linseed oil hydroperoxides converts organic sulfur into an inorganic form which is extracted by aqueous base. Likely, the hydroperoxide oxidation also converts other organics into organic acids which are not readily extractable by organic solvents. Thereby, the treatment selectively removes organic sulfur with minimum loss of BTU. Such is not the case with high mineral content coals, such as IBC-104.

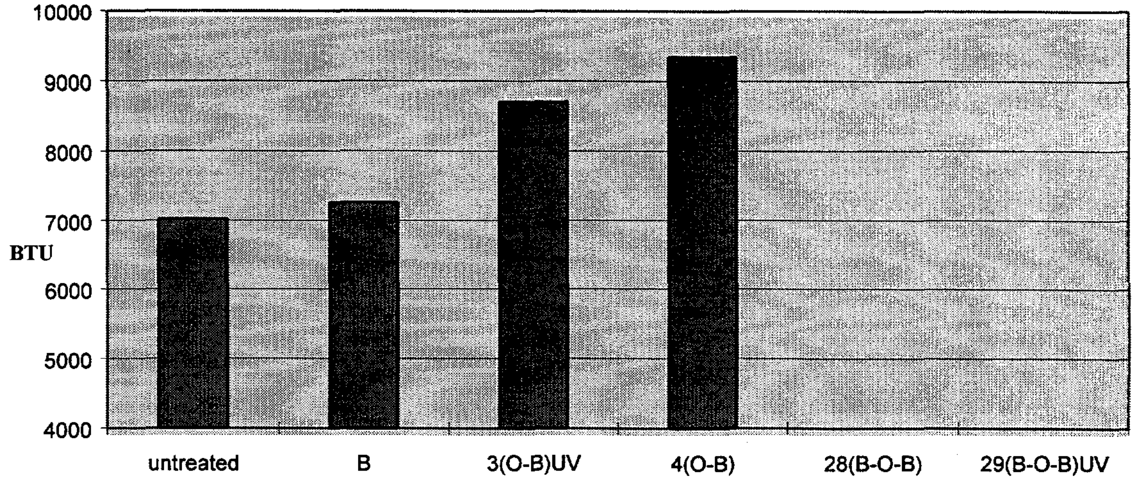
Similar treatments of IBC-104 coal produce some similar and some different results. For example, Figure 3 shows similar decreases in %S for IBC-104 as for IBC-108. The decreases are larger for IBC-104 than for IBC-108 because IBC-104 contains substantial pyrite (2.4%), which is more readily removed by the treatment than the organic sulfur. Although the decrease in % S in the treated IBC-104 (Figure 3) is similar to that for the same treatment of IBC-108, the change in BTU is quite different (Figure 4).

Figure 3: % S Remaining in IBC-104 Coal After Treatment in Air with Alkali (B) and/or Linseed Oil (O) and UV Light at 100°C with an Oil:Coal Ratio of 1:1



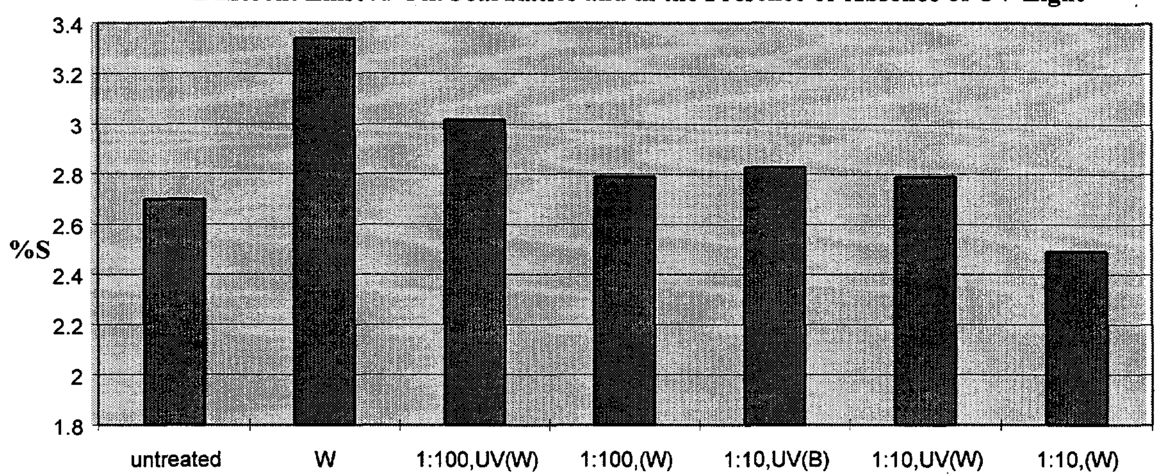
Instead of decreasing, BTU's actually increase when IBC-104 is treated with base and oil. This results from the treatment removing minerals from IBC-104, minerals that are not present in IBC-108. Mineral content of IBC-104 is 38%, and removing these minerals decreases the overall mass of the coal with a corresponding increase in the percentage of combustable matter in the recovered coal. In contrast, IBC-108 contains practically no mineral matters, so the treatment does not increase the percentage of combustable matter.

Figure 4: BTU Changes in IBC-104 Coal After Treatment in Air with Alkali and/or Linseed Oil (O) and UV Light at 100°C with an Oil:Coal Ratio of 1:1



If, on the other hand, the coals are washed with TCE and chloroform before or after treatment with oil and base, the % S increases in the remaining coal (line 5 in Table 2 and W in Figure 5). This increase signals preferential extraction of organics which do not contain sulfur and shows that any successful organic sulfur removal process must not use such a treatment. Apparently, TCE is the solvent that extracts non-sulfur containing organics. For, when extracted with THF and chloroform, no such large increase occurs; rather, small increases occur as noted above when discussing Figures 1 and 2.

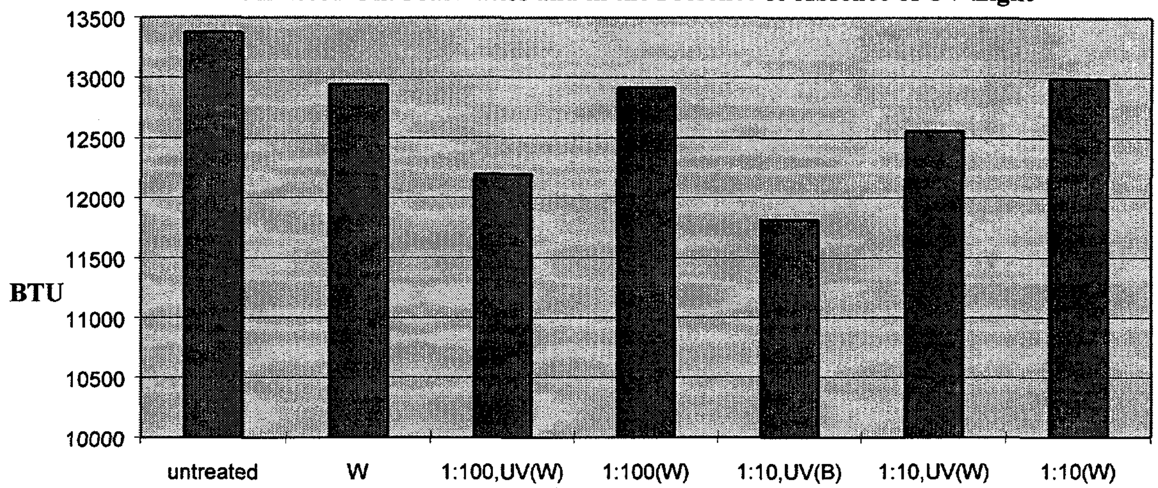
Figure 5: % S Remaining in IBC-108 Coal After Treatment in Air at 100°C with Different Linseed Oil:Coal Ratios and in the Presence or Absence of UV Light



Nevertheless, when the increase in % S is taken into account, treatment with oil removes as much as 25% of the organic sulfur from the IBC-108 coal {compare W and 1:10,(W) in Figure 5}. This decrease is approximately the same as that obtained with the B-O-B treatment shown in Figure 1. So approximately 25% organic sulfur can be removed with minimum loss of BTU by treatment with linseed oil hydroperoxides, providing such treatment is followed by proper extraction procedures which remove the affected sulfur but not other combustible materials. Special circumstances relating to loss of BTU are shown in Figure 6.

Figure 6 shows that BTU loss is minimal except when irradiating with UV. Apparently the UV irradiation makes some additional organics susceptible to extraction by THF and/or chloroform. Treatment with TCE and chloroform lowers BTU only 3% {compare bar labeled "untreated" with bars labeled "W", "1:100(W)", and "1:10(W)" in Figure 6}

Figure 6: BTU Changes in IBC-108 Coal After Treatment in Air at 100°C with Different Linseed Oil:Coal Ratios and in the Presence or Absence of UV Light



Results at 50°C are similar to those at 100°C as shown in Figures 7 and 8.

Figure 7: % S Remaining in IBC-108 Coal After Treatment in Air at 50°C with Different Ratios of Linseed Oil:Coal in the Presence or Absence of UV

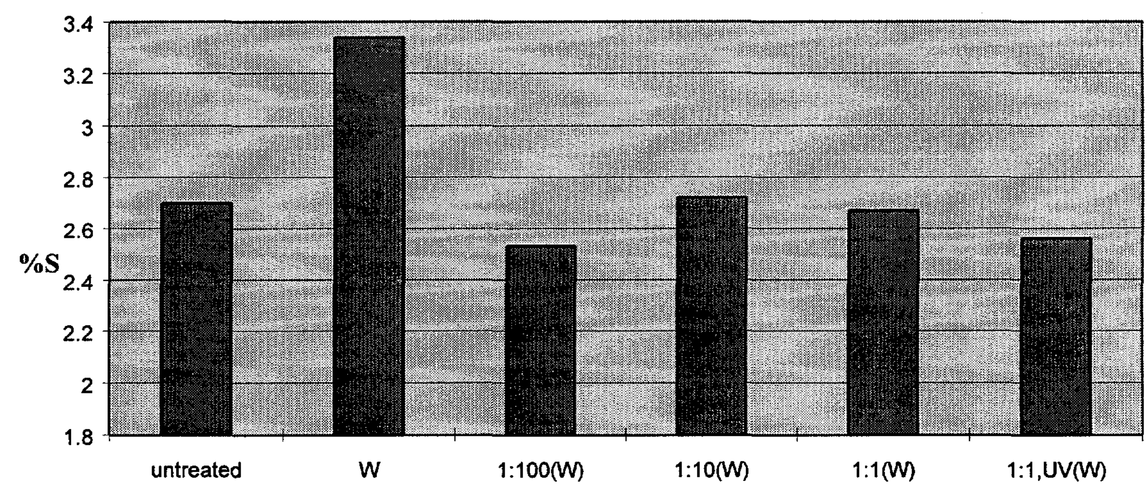
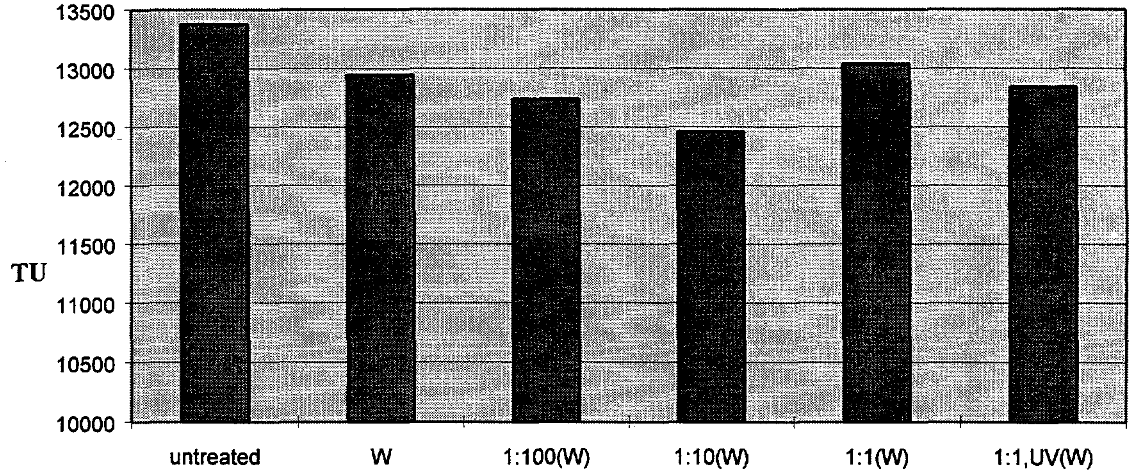


Figure 8: BTU Changes in IBC-108 Coal After Treatment in Air at 50°C with Different Linseed Oil:Coal Ratios and in the Presence or Absence of UV Light



Figures 9 through 12 show results with IBC-104 coal. Because of the large amount of mineral matters, these results are difficult to interpret. As noted earlier in discussing Figures 3 and 4, some trends are similar to those in IBC-108 coal and some are not.

Figure 9: % S Remaining in IBC-104 Coal After Treatment in Air at 100°C with Different Linseed Oil:Coal Ratios and in the Presence or Absence of UV

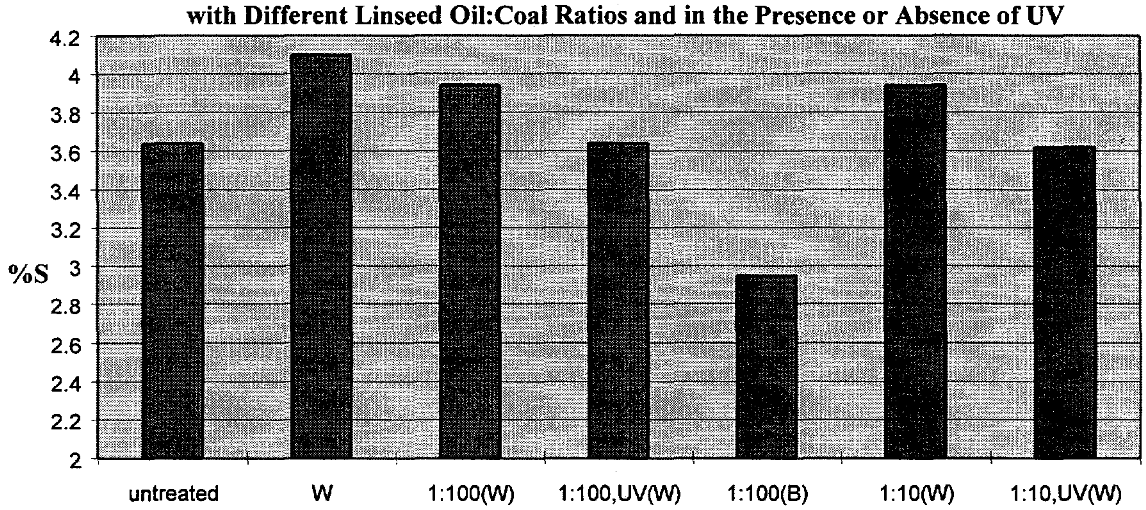


Figure 10: BTU Changes in IBC-104 Coal After Treatment in Air at 100°C with Different Linseed Oil:Coal Ratios and in the Presence or Absence of UV

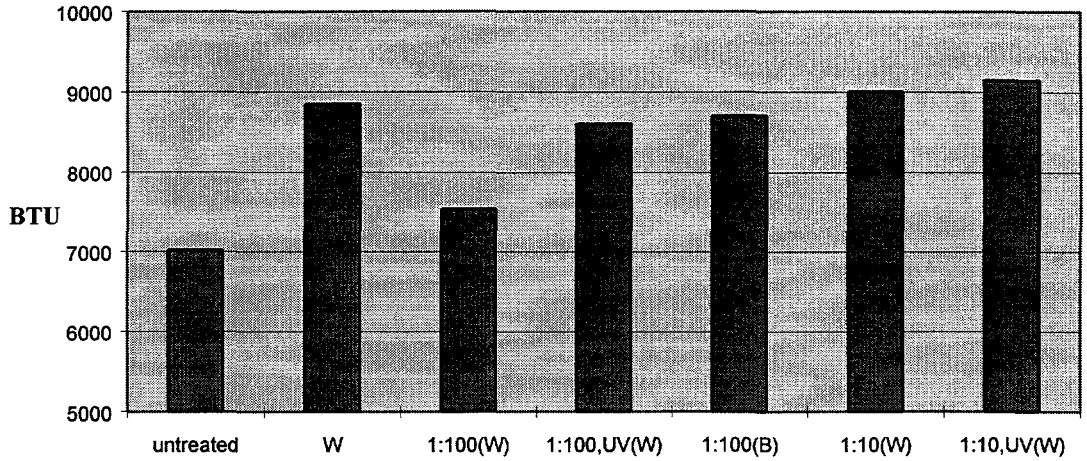


Figure 11: % S Remaining in IBC-104 Coal After Treatment in Air at 50°C with Different Linseed Oil:Coal Ratios

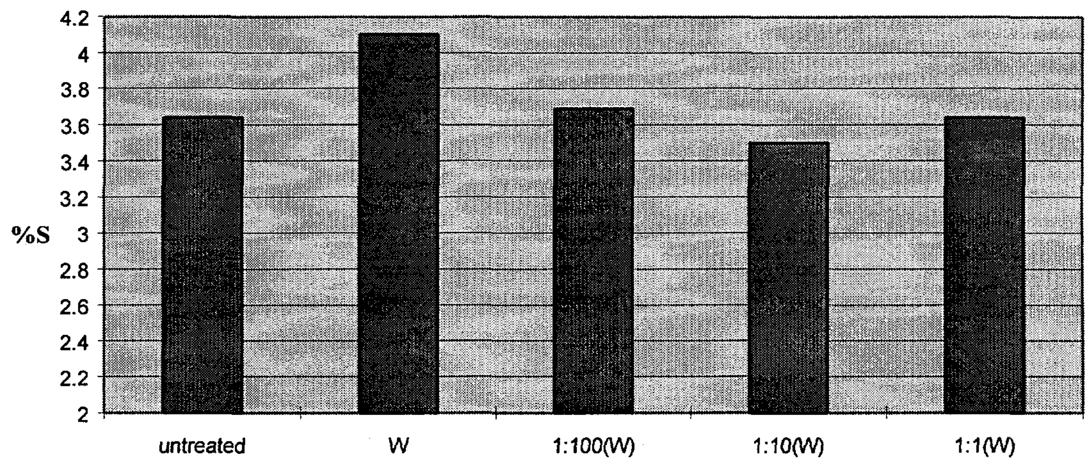
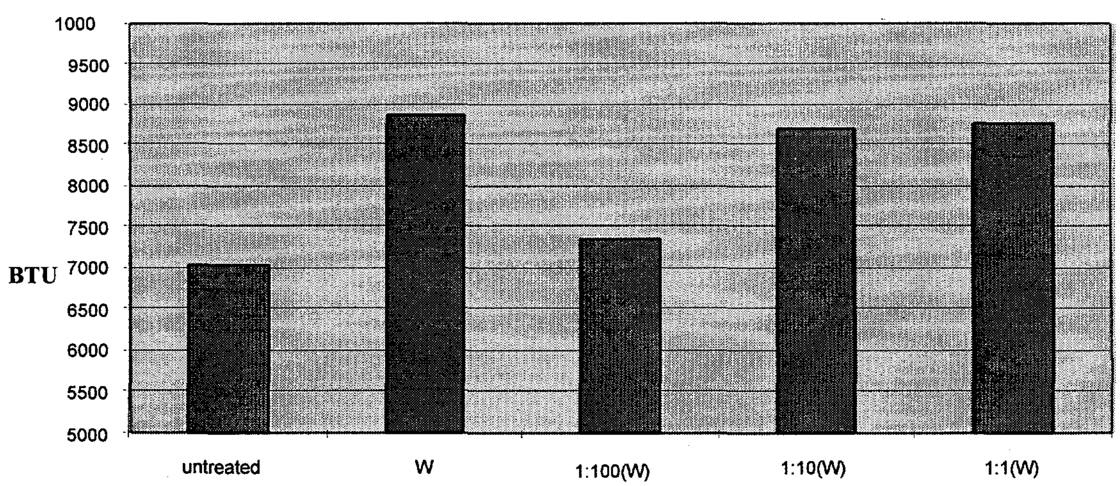


Figure 12: BTU Changes in IBC-104 Coal After Treatment in Air at 50°C with Different Linseed Oil:Coal Ratios



CONCLUSIONS AND RECOMMENDATIONS

Conclusions

- Washing the coals with aqueous base and with organic solvents (THF and $CHCl_3$) removes organic sulfur, but also removes about 7% of other organics which do not contain sulfur. Therefore, the actual organic sulfur removal is greater than appears because of the loss of other organics.

- The B-O-B treatment removes organic sulfur but only slightly removes other organics which do not contain sulfur.

- The B-O-B treatment selectively removes organic sulfur with minimum loss of BTU.

- BTU's actually increase when IBC-104 is treated with base and oil. This results because the treatment removes minerals from IBC-104, minerals that are not present in IBC-108. Mineral content of IBC-104 is 38%, and removing these minerals decreases the overall mass of the coal with a corresponding increase in the percentage of combustible matter in the recovered coal. In contrast, IBC-108 contains practically no mineral matters, so the treatment does not increase the percentage of combustible matter.

- Approximately 25% organic sulfur can be removed with minimum loss of BTU by treatment with linseed oil hydroperoxides, providing such treatment is followed by proper extraction procedures which remove the affected sulfur but not other combustible materials.

- UV irradiation makes some organics susceptible to extraction by THF and/or chloroform.

- Tetrachloroethylene extracts nonsulfur containing organics and thereby increasing the %S in the remaining coal by about 24%; however, BTU is lowered only 3%.

Recommendations

- Obtain material balance data to determine why extracting nonsulfur containing organics increases % S in the remaining coal by 24% but lowers its BTU by only 3%.

- Continue to explore the effect of base and solvents on removal of organic sulfur and change in BTU.

- Continue with the experimental plan specified in the proposal.

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PROJECT MANAGEMENT REPORT
December 1, 1994 to February 28, 1995

Project Title: **DESULFURIZATION OF COAL WITH HYDROPEROXIDES OF VEGETABLE OILS**

DOE Cooperative Agreement Number:	DE-FC22-92PC92521 (Year 3)
ICCI Project Number:	94-1/1.1C-2P
Principal Investigator:	Gerard V. Smith, Southern Illinois University at Carbondale
Other Investigators:	Ricky D. Gaston, Southern Illinois University at Carbondale Ruozhi Song, Southern Illinois University at Carbondale Jianjun Cheng, Southern Illinois University at Carbondale Kristie L. Gholson, Southern Illinois University at Carbondale Feng Shi, Southern Illinois University at Carbondale
Project Manager:	Ken Ho, Illinois Clean Coal Institute

COMMENTS

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

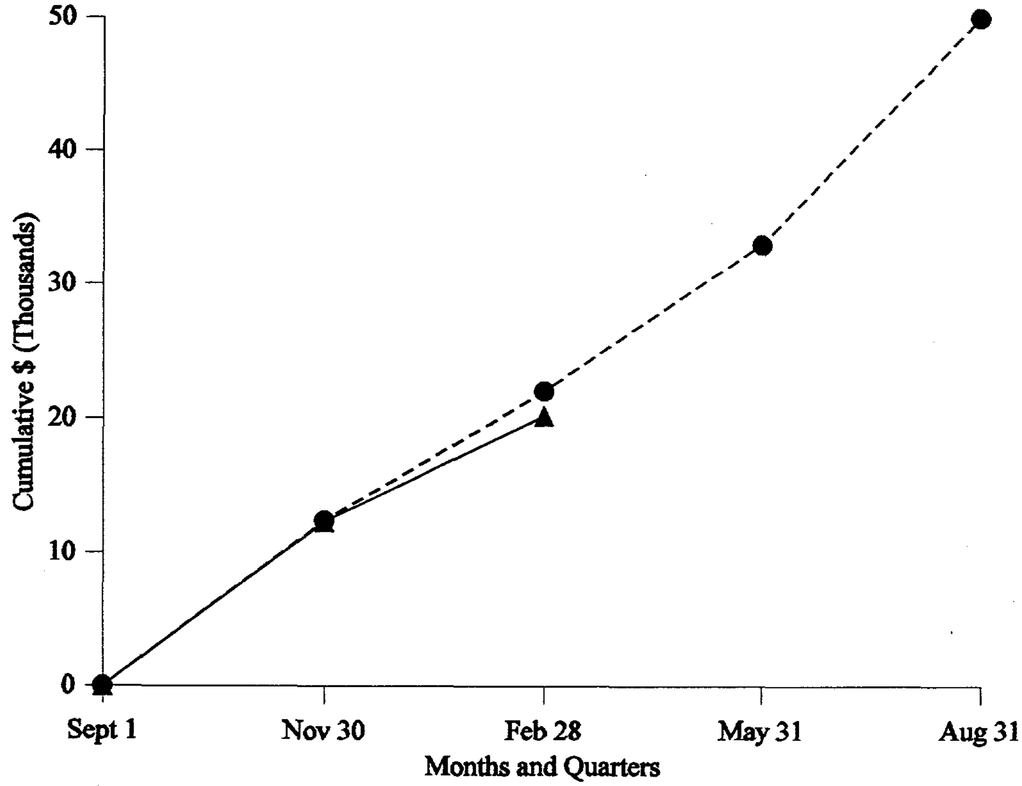
PROJECTED AND ESTIMATED EXPENDITURES BY QUARTER

Quarter*	Types of Cost	Direct Labor	Fringe Benefits	Materials and Supplies	Travel	Major Equipment	Other Direct Costs	Indirect Cost	Total
Sept. 1, 1994 to Nov. 30,1994	Projected	8,323	516	600	0	0	600	1,004	11,043
	Estimated	9,238	1,387	598	0	0	0	1,032	12,255
Sept. 1, 1994 to Feb. 28, 1995	Projected	16,646	1,032	1,200	0	0	1,200	2,008	22,086
	Estimated	15,307	1,585	1,348	0	0	114	1,835	20,189
Sept. 1, 1994 to May 31, 1995	Projected	24,969	1,548	1,800	0	0	1,800	3,012	33,129
	Estimated								
Sept. 1, 1994 to Aug. 31, 1995	Projected	37,188	2,929	2,400	500	0	2,400	4,542	49,959
	Estimated								

*Cumulative by Quarter

CUMULATIVE COSTS BY QUARTER

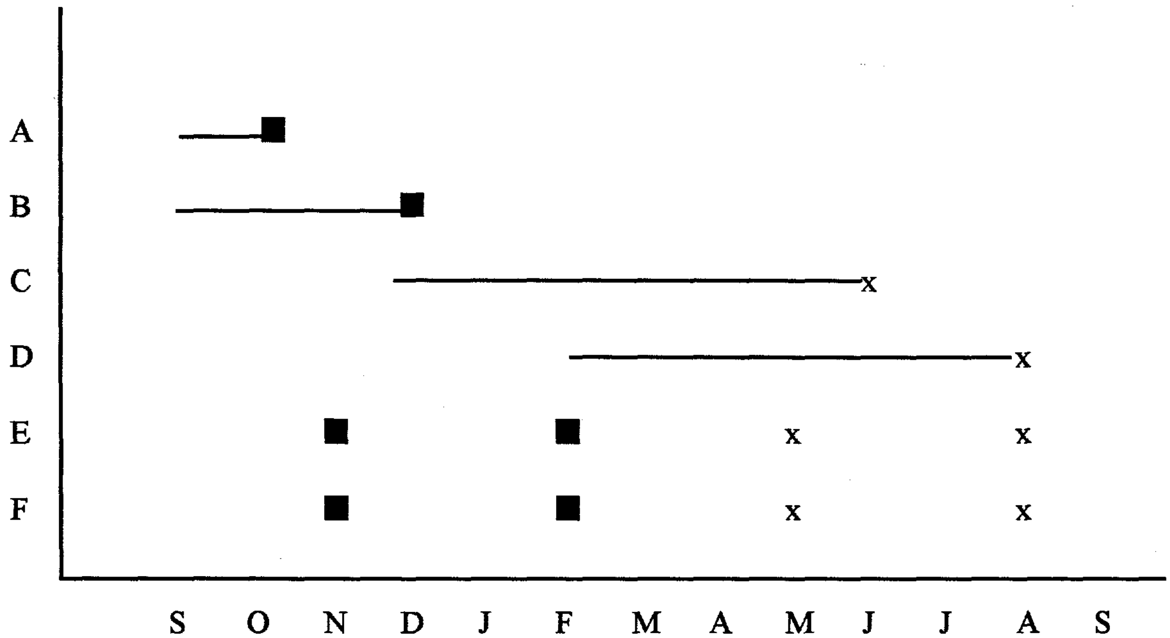
Desulfurization of Coal with Hydroperoxides of Vegetable Oils



● = Projected Expenditures - - - - - - -
▲ = Actual Expenditures _________

Total Illinois Clean Coal Instutute Award $49,959

SCHEDULE OF PROJECT MILESTONES



Begin
Sept. 1
1994

Hypothetical Milestones:

A: Research personnel employed
B: Task 1, tests for need of porphine
C: Task 2, tests of effects of treatment on sulfur, volatile, and BTU of coal
D: Task 3, tests of effects of treatment on mild pyrolysis
E: Project Technical Reports
F: Project Management Reports