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TECHNICAL REPORT

September 1 Through November 30, 1991

Project Title: The Effects of Moderate Coal Cleaning on the Microbial Removal of Organic Sulfur

DE-FG22-91PC91334

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ABSTRACT

The purpose of this project is to investigate the possibilities of developing an integrated physical/chemical/microbial process for the pre-combustion removal of sulfur from coal. An effective pre-combustion coal desulfurization process should ideally be capable of removing both organic and inorganic sulfur. A variety of techniques exist for the removal of inorganic sulfur from coal, but there is currently no cost-effective method for the pre-combustion removal of organic sulfur. Recent developments have demonstrated that microorganisms are capable of specifically cleaving carbon-sulfur bonds and removing substantial amounts of organic sulfur from coal. However, lengthy treatment times are required. Moreover, the removal of organic sulfur form coal by microorganisms is hampered by the fact that, as a solid substrate, it is difficult to bring microorganisms in contact with the entirety of a coal sample. This study will examine the suitability of physically/chemically treated coal samples for subsequent biodesulfurization. Physical/chemical processes primarily designed for the removal of pyritic sulfur may also cause substantial increases in the porosity and surface area of the coal which may facilitate the subsequent removal of organic sulfur by microorganisms. During the current quarter, coal samples that have been chemically pretreated with methanol, ammonia, and isopropanol were examined for the removal of organic sulfur by the microbial culture IGTS8, an assay for the presence of protein in coal samples was developed, and a laboratory-scale device for the explosive comminution of coal was designed and constructed.

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EXECUTIVE SUMMARY

The pre-combustion removal of organic sulfur from coal is a formidable technical challenge. A variety of physical, chemical, and microbiological coal desulfurization processes have been investigated during the past several decades. Efficient and effective methods for the pre-combustion removal of inorganic sulfur, from at least some coals, have been developed; however, no cost-effective method for the pre-combustion removal of organic sulfur from coal currently exists. Biodesulfurization; the removal of organic sulfur from coal using microorganisms such as Rhodococcus rhodochrous IGTS8, is a promising new technology. While the microbial removal of organic sulfur from coal appears to be technically feasible, it is currently too slow to be practical. One of the chief limitations is the relative inaccessibility of solid coal particles to bacteria. It can be readily appreciated that the surface area of a coal sample (particle size and porosity) can greatly influence the effectiveness of a microbial desulfurization treatment. Accordingly, the goal of this project is to examine the suitability of coal samples with increased surface area/porosity due to physical and/or chemical treatments for the subsequent removal of organic sulfur by microorganisms.

Some coal treatment processes designed for the removal of inorganic sulfur from coal exhibit substantial increases in the surface area/porosity of the product coal. Such coal samples may well be preferred substrates for a microbial process for the removal of organic sulfur from coal as compared with untreated coal. Therefore, the possibility exists that an integrated physical/chemical/microbial process can be developed for the pre-combustion removal of both organic and inorganic sulfur from coal.

Chemicals that are capable of comminuting coal, which by definition requires a softening/cleaving of the organic matrix of coal, are of particular interest. The exposure of coal to chemical comminuition agents may well result in coal products that have increased porosity and surface area and; therefore, are better substrates for biodesulfurization. Exposure of coal to ammonia, isopropanol, and methanol in the presence and absence of sodium hydroxide was investigated during this quarter. Changes in the density of coal samples exposed to these chemicals at room temperature and after autoclaving (120°C, 25 psi, 20 min.) were measured. The greatest decrease in coal density (and presummably increased porosity and surface area), from 1.50 g/ml to 1.69 g/ml, was seen upon exposure to isopropanol plus 0.1 N NaOH and this effect persisted upon the drying of the coal. Chemically-treated and untreated coal samples were included in coal biodesulfurization tests but no enhancement in sulfur removal was observed.

In related work performed during this quarter an assay was developed that allows protein/biomass content of coal samples to be assayed directly. The accurate measurement of the organic sulfur content of coal samples is challenging: a prerequisite is pure/clean samples. Biodesulfurization experiments entail an admixture of microorganisms with coal during treatment followed by the separation of microorganisms from coal after treatment. Protein measurements are often used in microbiological research to quantify the amount of biomass in samples of various types;

however, coal itself reacts in conventional protein assays to such a degree that these assays can not be used to measure the amount of protein/biomass present in coal samples. A modified protein assay was developed here and shown to be capable of accurately measuring protein in coal samples. This assay will help insure that clean coal samples are obtained from biodesulfurization experiments.

A laboratory-scale device for the treatment of coal by explosive comminution of coal was designed and constructed. Sample sizes of about 25 grams of coal can be treated at a time in this batch reactor. During the coming quarter this device will be used to treat coal in the presence of various chemicals to obtain products with enhanced surface area and porosity. These treated coal samples will subsequently be included in biodesulfurization experiments.

OBJECTIVES

The objective of this research is to provide data relevant to the development of an integrated physical, chemical, and microbiological process for the desulfurization of coal, utilizing existing technologies insofar as is possible. Specifically, the effect of increased surface area and porosity achieved by physical and/or chemical treatments of coal on the subsequent microbiological removal of organic sulfur will be evaluated. Specific tasks scheduled for this reporting period include obtaining and characterizing treated coal samples and initiating biodesulfurization experiments for the microbial removal of organic sulfur.

INTRODUCTION AND BACKGROUND

There are numerous physical, chemical, and microbiological techniques that can effectively remove inorganic sulfur from coal prior to combustion. Moreover, there are physical and chemical techniques for pyrite/ash removal that have been successfully commercialized and are routinely employed in the coal industry. However, while there are technologies capable of removing organic sulfur from coal prior to combustion no commercially viable technology currently exists. The removal of organically bound sulfur from coal by physical/chemical techniques requires harsh conditions as compared with microbiological techniques; therefore, the microbiological approach to the removal of organic sulfur might result in the development of a coal treatment process with more favorable economics than currently available technologies.

IGT has succeeded in developing a bacterial culture, Rhodococcus rhodochrous IGTS8, that specifically cleaves carbon-sulfur bonds in a range of organic substrates and coal. The removal of organic sulfur from coal could be a component of an overall coal preparation process that also involves chemical and physical technologies and will be capable of removing inorganic as well as organic sulfur. One of the chief hurdles or rate-limiting factors in the microbiological removal of organic sulfur from coal is the accessibility of the organosulfur compounds in the coal matrix. In other words, even though a microorganism is capable of cleaving carbon-sulfur bonds, the ability of the microorganism to contact and react with organosulfur compounds will be influenced by the physical structure of the coal (i.e., particle size, pore size distribution, and rigidity/plasticity). These physical characteristics of coal can be altered dramatically depending upon which physical/chemical/microbial treatment technologies are used. This research project will attempt to identify those physical/chemical coal treatment technologies that might be particularly beneficial when used in conjunction with the microbiological removal of organic sulfur in an integrated coal treatment process.

Nearly all Illinois coals contain finely dispersed pyritic granules and classical physical methods for coal cleaning and achieve relatively limited sulfur removal. Therefore, physical coal cleaning alone will not produce a coal with a sulfur content that complies with the New Source Performance Standard for SO_2, and additional techniques such as

microbiological treatments to remove organic sulfur are needed. This project will seek to identify those physical/chemical coal treatment technologies that simultaneously render the coal amenable to the removal of organic sulfur by microbial techniques, as well as allow for the efficient separation/removal of pyritic sulfur. This research, then, will contribute to the development of a combined physical/chemical/microbiological coal treatment process for the removal of both organic and inorganic sulfur, thereby allowing extended utilization of Illinois coals.

EXPERIMENTAL PROCEDURES

MEDIA AND CULTURE CONDITIONS

Media for the growth of microorganisms under sulfur-deficient conditions (BSM medium) consisted of 2.44 g of KH_2PO_4, 5.57 g of Na_2HPO_4, 2 g of NH_4Cl, 0.2 g of $MgCl_2 \cdot 6H_2O$, 0.001 g of $CaCl_2 \cdot 2H_2O$, and 0.001 g of $FeCl_3 \cdot 6H_2O$ per liter of distilled, deionized water. The carbon source, glycerol, was used at a concentration of 20 mM. The pH of BSM is 7.0 and the pH drops to 6.0 to 6.5 as a consequence of microbial growth.

Biodesulfurization experiments were performed by placing from 1 to 2 grams of coal in from 7 to 20 liters of sulfur-deficient bacterial growth medium, inoculating with IGTS8, and incubating at 30°C for 2 to 3 weeks to allow bacterial growth to occur at the expense of the sulfur in coal.

After incubation, the coal was recovered by centrifugation, washed free of bacteria by differential centrifugation, dried at 105°C, and was submitted for analysis. Final stages of obtaining coal sample free from biomass involved placing aqueous coal slurries in a boiling bath for 15 minutes followed by differential centrifugation, then placing coal suspended in 0.1 N NaOH into a boiling water bath for 15 minutes, followed by differential centrifugation. The bacterial biomass recovered from coal biodesulfurization experiments was also dried at 105°C and analyzed for total sulfur content by the LECO technique. Aqueous supernatants derived from coal biodesulfurization experiments were analyzed by inductively coupled plasma spectroscopy to determine total sulfur. Coal samples were analyzed for sulfur forms according to ASTM methods. The mercury intrusion and nitrogen desorption methods were used to determine the porosity and surface area of coal samples.

RESULTS OF DISCUSSION

A variety of chemical agents are known to swell coal an some chemicals have also been used to comminute coal. A major goal of this project is to determine physical and/or chemical means of pretreating coal such that it is an improved substrate for the subsequent removal of organic sulfur using microorganisms. Chemical treatments that were investigated during this quarter include methanol, isopropanol, and ammonia (10% aqueous solution) with or without the presence of 0.1 N sodium hydroxide. Treatment with distilled water was included as a control. IBC-107 coal was used because it contains predominantly organic sulfur. Two pounds of IBC-107 coal were riffled (as received) into 10 gram portions to provide

uniform coal samples. Then 10 gram samples were exposed to 25 mls of the various chemical agents at room temperature for 24 hours to allow complete saturation to occur. Volume measurements were made on each sample before and after chemical exposure. The coal/chemical slurries were then autoclaved at 120°C, 25 psi for 15 minutes. Volume measurements were again obtained. The coal samples were washed free from the chemical treatment agents using distilled water and vacuum filtration. The washed coal samples were dried at 105°C then volume and weight measurements on these tried samples were obtained. All of the volume data of the chemical treatment of coal samples described above are shown in Table 1.

Table 1. THE EFFECT OF CHEMICAL TREATMENT ON THE VOLUME/DENSITY OF IBC-107 COAL*

Treatment	Volume Before Autoclaving, mls	Volume After Autoclaving, mls	Volume of Dry Samples, mls
H_2O	15.2	15.2	15.0
H_2O + NaOH	18.8	17.5	16.3
Ammonia	16.5	16.5	16.7
Ammonia + NaOH	17.7	16.5	16.6
Isopropanol	19.0	19.0	16.1
Isopropanol + NaOH	19.2	17.1	16.9
Methanol	17.7	17.5	15.0
Methanol + NaOH	19.0	17.5	15.5

* The volume of dry untreated IBC-107 coal was 15.0 ml.

The most relevant data are the volume measurements on the dry samples because chemically treated samples must be washed and dried prior to biodesulfurization experiments. The data in Table 1 show that isopropanol causes the greatest swelling of coal but the magnitude of the effect is not fully preserved in the dry coal samples. Autoclaving the coal in the presence of the chemical treatment solutions shows no benefit; whereas, the presence of 0.1 N NaOH uniformly increases coal swelling. The dry sample with the greatest increase in volume (decreased density) was obtained using isopropanol plus 0.1 N NaOH.

Some of these chemically treated coal samples were included in biodesulfurization experiments and the results are shown in Table 2. It was hoped that more rapid and complete desulfurization might be possible with these chemically pre-treated coal samples; however, no significant sulfur reductions were observed in any of these samples. These results are unexpected and should be repeated. Neverthless, no stimulation in biodesulfurization is apparent as a consequence of chemical pre-treatment with the data obtained thus far but further research is needed.

Table 2. BIODESULFURIZATION OF CHEMICALLY TREATED IBC-107 COAL SAMPLES

Sample	% Carbon	% Sulfur
Control	67.58	3.63
Control	66.63	3.40
Control	66.70	3.66
Control	67.33	3.54
H_2O + NaOH	66.98	4.00
Ammonia + NaOH	67.51	3.58
Isopropanol + NaOH	67.16	3.83
Methanol + NaOH	67.49	3.82
No Chemical or Biotreatment	63.23	4.15
No Chemical or Biotreatment	67.51	3.86

The accurate determination of organic sulfur levels in coal can be challenging and using pure samples is a pre-requisite. Verifying that coal samples obtained from biodesulfurization experiments are pure has been frustrated by the lack of appropriate assays.

Coal samples chemically react with reagents in protein assays and interfere to such a degree that the accurate/meaningful measurement of biomass present in coal samples is not possible with conventional protein assays. A modified protein assay was developed here and shown to be capable of reproducibly measuring the amount of biomass in mixtures of IBC-107 and biomass. The direct measurement of biomass/protein content of the biotreated IBC-107 samples listed in Table 2 was uniformly less than 10%.

A modified version of a standard protein assay (reagents provided by the Pierce Chemical Co.) was employed for spectrophotometric determination of residual biomass concentration in recovered biotreated IBC-107 samples. This reagent system combined the reaction of protein with Cu^{2+} in an alkaline medium (yielding Cu^{1+}) with a highly sensitive and selective detection reagent for Cu^{1+}, namely bicinchoninic acid.

Known mixtures of 0-100% biomass and untreated coal totaling 5 mg were prepared to construct a standard curve relating protein concentration and % biomass. Samples of biotreated IBC-107 with sterile controls weighing 5 mg each, were tested simultaneously to determine the amount of associated biomass as compared to the standard curve. Blank-corrected IBC-107 sterile controls and untreated samples show minimal interference with assay reagents using the modified protein assay method.

Samples to be assayed were tested at a total weight of 5 mg, dissolved in 2 ml BSM, 50 µl 0.1 N NaOH and placed in a boiling water bath for 30 minutes. Upon cooling, a 25 µl addition of 1 N HCl was made to

precipitate soluble material and the samples were centrifuged at 10,000 x g for 15 minutes. Immediately following centrifugation 0.1 ml of supernatant was transferred to a clean test tube containing 2 ml of Pierce working reagent. The solution was mixed and incubated for 30 minutes at 60°C, cooled to room temperature and the absorbance was measured on a spectrophotometer (Beckman DU-65) at 562 nm versus a water reference. This assay will be useful in ensuring the purity of biotreated coal samples throughout the course of this project.

A laboratory-scale device for the explosive comminution of coal was designed and constructed. The device is illustrated in Figure 1, and consists of two chambers separated by a valve. When the device is operated, the coal sample is added to the upper, smaller chamber along with a chemical solution. The upper chamber is then heated and pressurized to temperatures and pressures approaching the supercritical conditions for the chemical used. This treatment allows the chemical to thoroughly permeate the coal. The lower, larger chamber is evacuated and a valve is instantaneously opened allowing the coal-chemical solution to exit the upper chamber and to explosively enter the lower chamber assisted by gravity and pressure. Chemical molecules that have permeated into the coal will expand explosively due to the sudden change in pressure. That plus some possible softening of the structure of the coal due to the chemical treatment will result in the shattering of the coal yielding a product that should have a greatly enhanced porosity as compared with the original coal. Coal thus treated by chemical/physical explosive comminution will then be thoroughly characterized as regards density, surface area, porosity, sulfur content, and most importantly, it's treatability in terms of the removal of organic sulfur using IGTS8. The device pictured in Figure 1 has now been completely assembled and the results of its use should be available for inclusion in the next report.

CONCLUSIONS AND RECOMMENDATIONS

The exposure of IBC-107 coal to chemical comminution agents under autoclaving conditions did result in modest decreases in the density of some of the samples; however, no stimulation of organic sulfur removal was seen in biodesulfurization tests. Further research including the treatment of coal by explosive comminution followed by biodesulfurization is recommended.

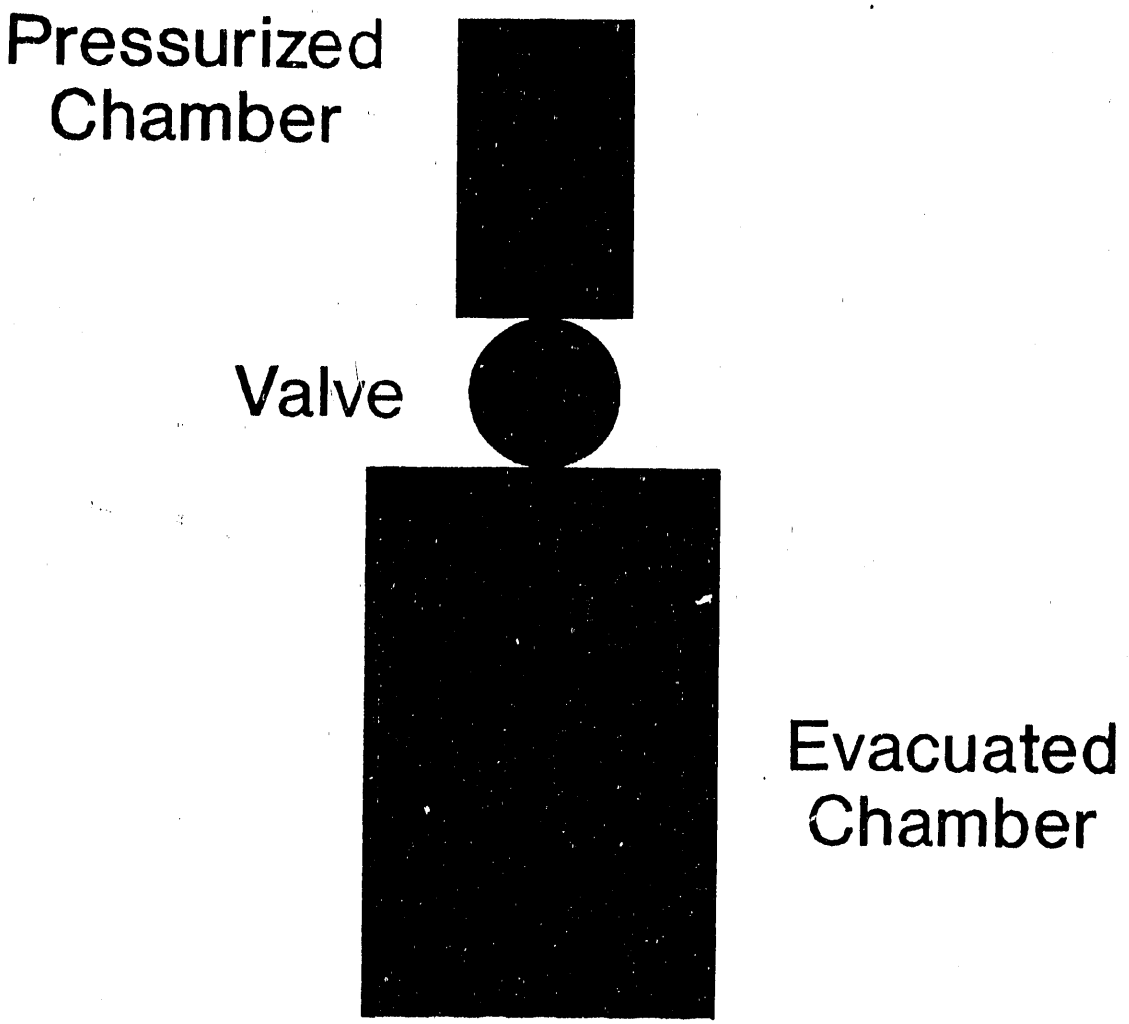

Figure 1. LABORATORY-SCALE REACTOR FOR THE EXPLOSIVE COMMINUTION OF COAL

PROJECT MANAGEMENT REPORT

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COMMENTS

The project is proceeding as schedule.

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