DOE/PC/91334-T75

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DE93 000524

TECHNICAL REPORT

March 1, 1992 Through May 30, 1992

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. Microorganisms are capable of specifically cleaving carbon-sulfur bonds and removing substantial amounts of organic sulfur from coal; however, the removal of organic sulfur from 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.

During this quarter tests were performed involving prolonged (7 day) exposure to chemical comminution agents followed by explosive comminution. Combined chemical plus physical comminution yielded only minor differences between the chemical treatments tested (0.1N NaOH, methanol plus 0.1N NaOH, isopropanol plus 0.1N NaOH, and ammonia vapor) as regards particle size distribution. The densities of treated products varied somewhat with 0.1N NaOH and ammonia yielding the lowest and highest densities respectively. Biodesulfurization tests indicate that pre-grown IGTS8 biocatalysts can be used to desulfurized chemically treated IBC-107 coal.

This project is funded by the U. S. Department of Energy (PETC) and by the Illinois Department of Energy and Natural Resources as part of their cost-shared programs.

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 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 comminution 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 of sodium hydroxide with and without explosive comminution was investigated previously. Ammonia vapor was found to be the most effetive chemical comminution agent, and the greatest swelling of coal occurred upon exposure to 0.1N NaOH. During the current quarter it was found that combined chemical and physical treatment of coal yields only minor differences in particle size distribution. Chemical treatments were of seven days duration and included 0.1N NaOH, methanol plus 0.1N NaOH, isopropanol plus NaOH, and ammonia vapor. Explosive comminution waste at 240°F and 1200 psi. Chemical treatment with ammonia vapor without explosive comminution was able to achieve particle size reductions comparable to chemical plus explosive comminution treatments. Coal swelling/density varied among coal samples receiving combined chemical ard physical treatments with 0.1N NaOH and ammonia yielding the least and most dense samples respectively.

Biodesulfurization of chemically treated coal samples using pre-grown IGST8 biocatalysts achieved about 11% sulfur reduction. This is highly significant if it can be confirmed as it is the first successful use of biocatalysts to desulfurize solid coal. Additional biodesulfurization experiments with chemically/physically treated coal samples are currently in progress.

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

The explosive comminution reactor consists of an upper chamber having a volume of 308 mls connected to a lower chamber having a volume of 3900 mls. During operation, IBC-107 coal samples (usually 10 grams) are added to the upper chamber through a quarter inch opening. To insure that coal can be readily added to the upper chamber of the reactor and so that coal can pass from the upper to the lower chamber, which are connected by a quarter inch valve, all coal is sieved either to -12+20 mesh prior to use. A liquid, 25 mls per 10 g sample of coal, is also added to the upper chamber along with the coal. The liquids used are water, an aqueous solution of 0.1N NaOH, methanol containing 0.1N NaOH, or isopropanol containing 0.1N NaOH. (It is necessary to add small amounts of water to methanol or isopropanol in order to prepare 0.1N NaOH solutions). The upper chamber is then pressurized either to 800 or 1200 psi, using nitrogen, and is either operated at ambient temperature or at 240°F. The lower chamber is evacuated to a pressure of 5 millimeters Hg by means of a vacuum pump. Both the upper and lower chambers are equipped with pressure gauges to allow the accurate establishment of appropriate pressure/ vacuum for each run. Each chamber is also fitted with valves that allows the reactor to be a closed system (unconnected to pressure and vacuum lines after appropriate conditions have been achieved) during each explosive comminution run. The upper chamber is equipped with electric heating tape connected to a rheostat, insulation, and a thermocouple to allow temperature to be controlled and monitored. The upper and lower chambers are connected by an electronic valve that has a one quarter inch opening. This valve allows uniform/ reproducible conditions to be used in the release of pressure in each explosive comminution run.

Coal characterization includes weight, and particle size distribution measurements (performed on dry coal samples). Coal weights (dried to a constant weight at 90°C) are obtained so that product recoveries can be calculated. All of the coal used in chemical/explosive comminution runs is sized to -12+20 mesh, and after each comminution run the recovered coal is dried and sieved. Particle size reduction alone does not permit rapid biodesulfurization as prior experiments employing -200 mesh coal have shown. Accordingly, in this study chemically treated and physically/chemically treated coal samples with particle sizes greater than 80 mesh will be used in biodesulfurization experiments. In this way the effects of altering/softening the organic matrix of the coal upon subsequent biodesulfurization efficiency can be examined directly with minimal interference due to the mere reduction of the particle size of coal.

Chemical treatments alone were performed by exposing 10 g samples of -12+20 mesh IBC-107 coal samples to 25 mls of water containing 0.1N NaOH, isopropanol containing 0.1N NaOH, or methanol containing 0.1N NaOH. Coal was also exposed to ammonia vapor in a sealed container Chemical treatments were performed at ambient temperatures and pressures and were of one week duration without shaking/agitation. After chemical exposure, the coal samples were dried to constant weights at 90°C and sieved for some experiments and were subsequently subjected to explosive comminution in other experiments.

Biodesulfurization experiments were performed in two ways: concentrated pre-grown IGTS8 cells were used as biocatalysts to desulfurize coal with coal/water ratios of 1 g/50 ml, or growing cell experiments were performed in which 1 g of coal served as the sole sulfur source for the growth of 6 liters of IGTS8 cells.

RESULTS AND DISCUSSION

Previous experiments utilized IBC-107 coal sized to -10+12 mesh or -12+80 mesh and the characterization of treated coals was similarly limited to determining +10, -10+12, -12+80, and -80 mesh fractions of coal. This was sufficient for preliminary experiments but during this quarter more precisely sized coal was utilized and treated coals were more thoroughly characterized. Figure 1 illustrates the size classification of untreated/as received IBC-107 coal. About 33% of the coal is in the -12+20 mesh fraction and it was this fraction that was used exclusively in chemical/explosive comminution experiments this quarter. Sized IBC-107 coal was riffled into 10 gram samples before experimental treatments. Previous preliminary experiments indicated that the preferred conditions for explosive comminution are 240°F and 1200 psi. Those experiments indicated that chemical treatment with aqueous 0.1N NaOH followed by explosive comminution yielded greater particle size reduction than chemical treatments with either isopropanol plus 0.1N NaOH or methanol plus 0.1N NaOH followed by explosive comminution. Those results could have been observed either because aqueous 0.1N NaOH is a better comminution agent than the other chemical solutions or because the other chemical solutions caused greater coal swelling. More information is required to evaluate these alternative possibilities. Those preliminary chemical/explosive comminution experiments involved only 5 to 10 minutes exposure of the chemical solution to the coal prior to explosive treatment (only that time needed to heat and pressurize the reactor). To more fully examine combined chemical/explosive comminution experiments were performed this quarter in which ten gram samples of -12+20 mesh coal were exposed for seven days at ambient temperature and pressure to various chemical solutions: 0.1N NaOH, isopropanol plus 0.1N NaOH, methanol plus 0.1N NaOH, and ammonia vapors. After this prolonged exposure to the chemical solutions the coal was explosively comminuted at 240°F and 1200 psi. The particle size distribution of treated coal samples (after drying) was determined and density readings were obtained on -20+40 mesh coal samples. The size classification data and density data for treated coal samples are shown in Figures 2 and 3 respectively. Figure 2 illustrates that rather similar results were obtained for aqueous 0.1N NaOH, ammonia, and isopropanol plus 0.1N NaOH in as much as about 55% of these coal samples was greater than 80 mesh and 45% was smaller than 80 mesh. The sample treated with methanol plus 0.1N NaOH yielded 65%A greater than 80 mesh suggesting that either this solution was less effective as a coal swelling agent. Coal swelling should be reflected by decreased density so the -20+40 mesh fraction of the treated coal samples shown in Figure 2 were used in density determinations reported in Figure 3. The densities of these coal

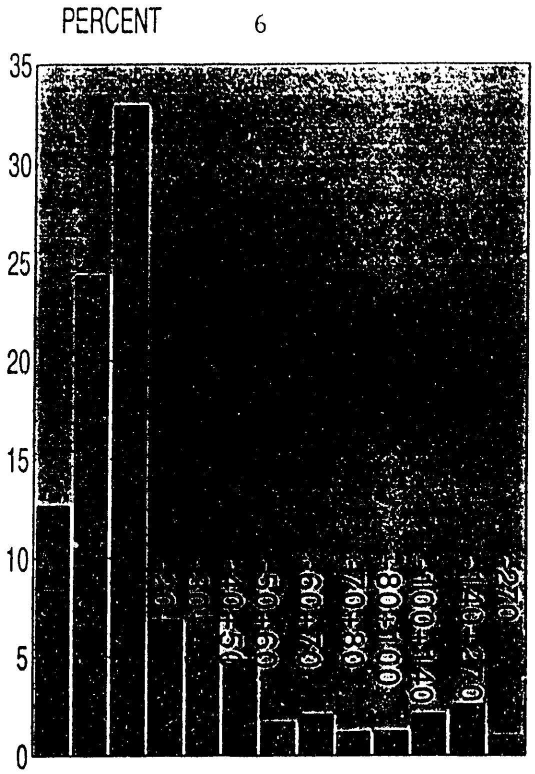

Figure 1. SIZE FRACTIONATION OF UNTREATED IBC-107 COAL

samples varied from about 0.62 to 0.69 g/ml with aqueous 0.1N NaOH having the lowest density and methanol plus 0.N NaOH having the next lowest density. Decreased density should be beneficial for the subsequent biodesulfurization of coal due to increased porosity and hence greater accessibility of treated coal samples to microorganisms. These coal samples that have received combined chemical/explosive comminution treatments are currently being evaluated in biodesulfurization experiments.

Results of biodesulfurization experiments employing previously treated coal samples are available and reported in Table 1. Coal samples that received chemical treatment with methanol plus 0.1N NaOH (5 to 10 minute exposure) plus explosive comminution as well as untreated coal samples were included in biodesulfurization experiments of three weeks duration in which IGTS8 was challenged to grow with these coal samples serving as the sole sulfur source. The IGTS8 culture did not grow well in these experiments and the amount of desulfurization observed was only 1.5% for the untreated IBC-107 coal sample and a modest improvement to 5.3% for the chemically/explosive treated coal sample. These data suggest that treated coal samples may respond better to biodesulfurization than untreated coal samples but that most be confirmed through further testing. Table 1 also contains the results of biodesulfurization experiments involving chemically treated (7 days at ambient temperature and pressure) coal and pre-grown biocatalysts. These experiments were of 24 hours duration and utilized one gram of coal in a total reaction volume of 50 mls. Each of these experiments contained 31 enzyme units of biodesulfurization activity as measured by the Gibbs assay. (One enzyme unit is the activity required to convert one micromole of DBT-sulfone to 2-HBP in

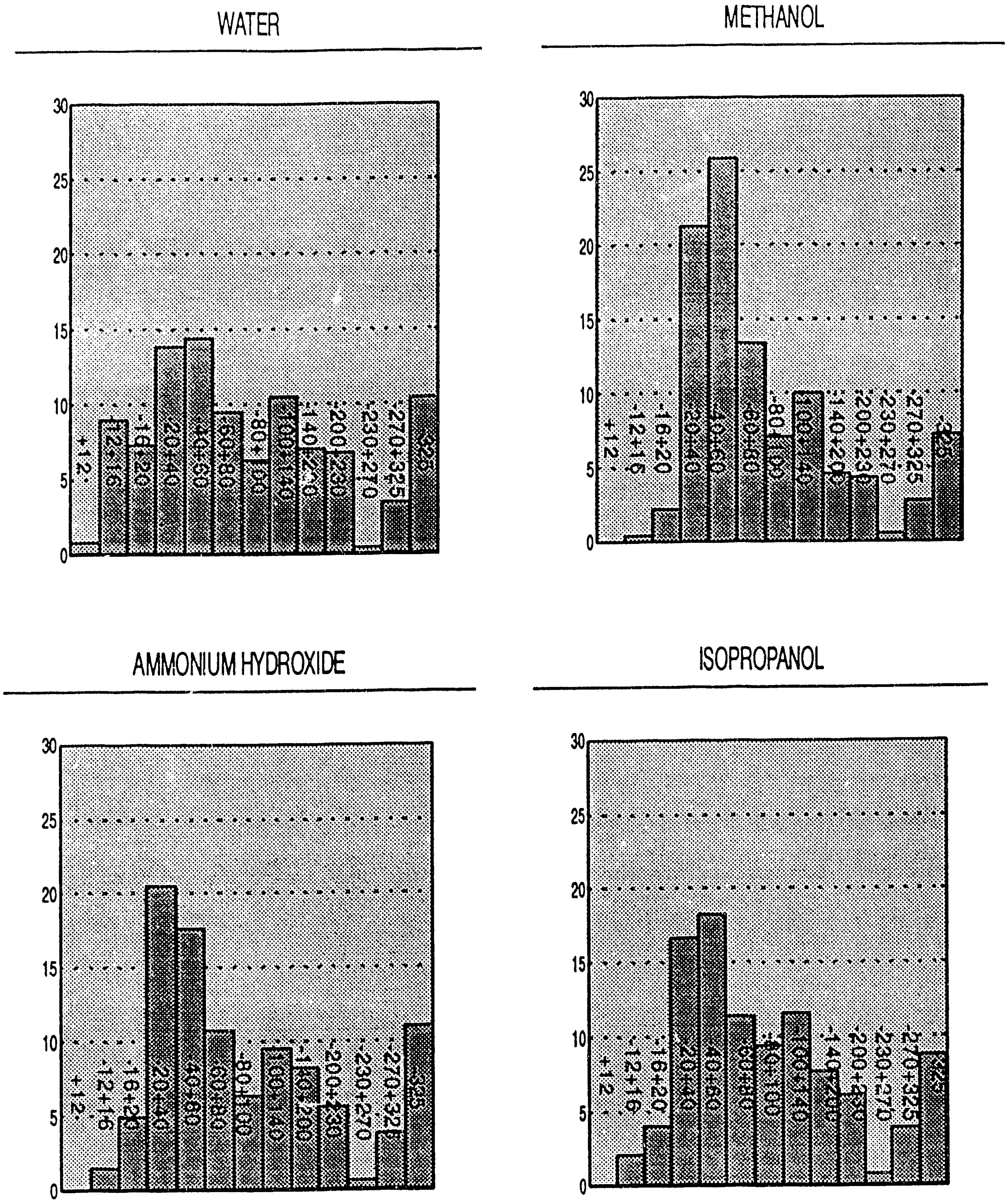

Figure 2. SIZE FRACTIONATION OF CHEMICALLY TREATED AND EXPLOSIVELY COMMINUTED IBC-107 COAL
(All Chemical Solutions Contained 0.1N NaOH Except Ammonia Vapor)

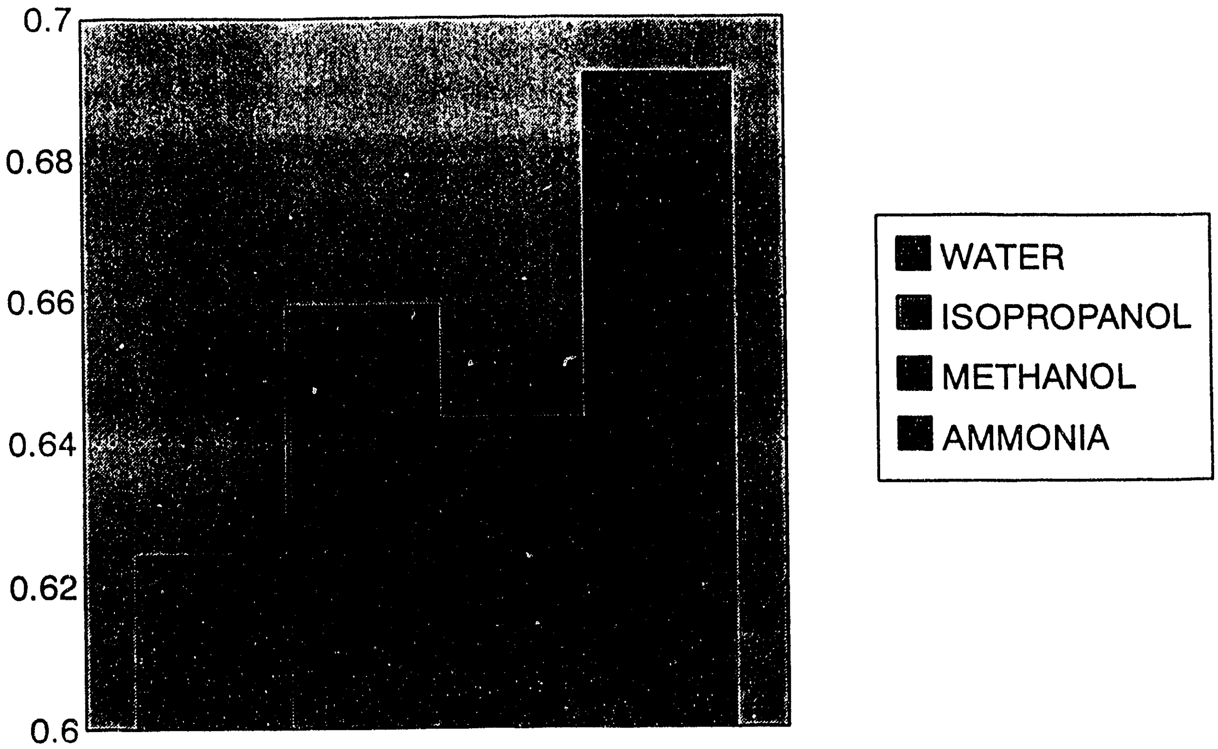

Figure 3. DENSITY OF CHEMICALLY TREATED AND EXPLOSIVELY COMMINUTED IBC-107 COAL

Table 1. BIODESULFURIZATION OF IBC-107 COAL

Treatment: Chemical	Treatment: Exploded	Biotreatment	% Carbon	% Sulfur	% Desulfurization
None	No	None	67.44	3.65	
Methanol + 0.1N NaOH	Yes	None	66.81	3.68	
None	No	Growing cells	67.17	3.61	1.5
Methanol + 0.1N NaOH	Yes	Growing cells	67.74	3.47	5.3
0.1N NaOH	No	Biocatalysts	66.81	3.27	10.8
Isopropanol + 0.1N NaOH	No	Biocatalysts	67.47	3.40	7.2
Methanol + 0.1N NaOH	No	Biocatalysts	68.49	3.45	5.9

one hour). The results of these experiments are highly encouraging as from 6 to 11% total sulfur reduction was observed, and these are the first data that indicate that biocatalysts can be successfully used to desulfurize solid coal. In a multitude of experiments performed prior to this project it was shown that biocatalysts could successfully desulfurize water-soluble coal-derived material or model compounds but could not desulfurize untreated solid coal samples. The data in Table 1 indicates that the basic objective of the project has been achieved by demonstrating that treated/modified solid coal samples can be successfully biodesulfurized using biocatalysts. The use of biocatalysts allows much briefer reactions times and smaller reactor volumes than using growing cultures to desulfurize coal. This important observation must be verified with further testing.

CONCLUSIONS AND RECOMMENDATIONS

Biocatalysts appear to be capable of desulfurizing chemically treated solid coal samples in only 24 hours and using smaller reactors. This important observation will be investigated further during the next quarter with additional biodesulfurization tests.

PROJECT MANAGEMENT REPORT

March 1, 1992 Through May 31, 1992

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Principal Investigator(s):	Vipul J. Srivastava/John J. Kilbane II Institute of Gas Technology
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COMMENTS

The project is proceeding as scheduled.

This project is funded by the U. S. Department of Energy (PETC) and by the Illinois Department of Energy and Natural Resources as part of their cost-shared programs.

SCHEDULE OF PROJECT MILESTONES

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1 |--Δ
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2 |----------------Δ
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3 |-------------------------------Δ
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4 |        ----------------------------------------------X
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5 |            ---Δ            ---Δ            ---Δ         --------X
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1. Coal samples are received from CRSC.
2. Lab-scale device for explosive comminution of coal is constructed.
3. Characterization of chemically treated coal is completed.
4. Characterization of biotreated coal is completed.
5. Preparation of technical and project management reports.

CRSC2/jp

END

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12/2/92