

ENZYMATIC REMOVAL OF ORGANIC SULFUR FROM COAL

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ABSTRACT

A process is described for the enzymatic (not microbiological) removal of organic sulfur from coal. The process evaluated utilizes ultra ground coal (<50 microns) and froth flotation to first remove pyritic sulfur. In this design conceptual mild alkali oxidation followed by enzymatic treatment is then used to reduce the organic sulfur. A preliminary economic analysis for processing 20,000 metric tons of coal/day is being carried out for reducing 4.5% sulfur content bituminous coal (containing an assumed 50:50 W/W pyritic/organic) to under 1% sulfur in order to meet clean air standards. The background work leading to this conceptual process is encouraging. Experimental work is now proceeding and preliminary results are encouraging.

INTRODUCTION

Background to the Problem of Sulfur in Coal

The use of fossil fuels for power generation is expected to increase, despite diminishing world reserves of high quality crude oil and coal. The demand for low-sulfur and low-nitrogen fossil fuels has been intensified by increasingly stringent regulatory standards for reduced levels of sulfur- and nitrogen-oxides in released atmospheric emissions. Amendments to the 1964 Clean Air Act require not only compliance with emission standards but also a percentage reduction in emissions that otherwise would occur from the burning of untreated fuel, requiring that low-quality fuels be subjected to either pre- or post-combustion desulfurization.

Post-combustion processes, e.g., flue-gas desulfurization, are generally inconvenient, expensive, and definitely limited with respect to the scope of their remedial action. These processes usually ignore other aspects of (sulfur) contamination which are certainly as economically important as emissions control, e.g., corrosion of mills and conveyors due to pyritic sulfur. Pre-combustion cleaning processes, on the other hand, can offer significant advantages over post-combustion processes, such as flue gas desulfurization, because these pre-combustion schemes can eliminate problems associated with both environmental pollution and equipment corrosion.

Traditional pre-combustion processes exploit either physical or chemical methods. Physical methods include flotation or magnetic separation of the pyrite from coal. As compared to chemical methods, these are generally more economical. The drawbacks to these physical methods, however, lie in the limited removal of the overall sulfur and the notable energy losses. Chemical pre-combustion cleaning methods usually employ some sort of oxidizing agent, e.g., ferric salts, chlorine, or ozone, or reducing agent, e.g., solvent-hydrogen mixtures. In contrast to physical methods, chemical methods can be reasonably effective in removal of some of the organic sulfur along with the pyrite. Some of the disadvantages which have an impact on the efficiencies associated with chemical

cleaning operations include corrosion problems resulting from the use of high concentrations of the chemical agents, the energy intensiveness of the high temperature/high pressure operations, and the costliness of reagent recovery.

Thus, there is a need for methods of coal desulfurization which improve upon these traditional processes. Of particular need is a method for removal of organic sulfur, a contaminant which often is only secondarily removed. This paper focuses on a processing concept for the resolution of that need. Drawing upon the experiences derived from the aforementioned types of cleaning operations, the technical feasibility of a novel concept is considered within the context of process efficiency. Reagent costs, recovery operations, waste products, and operating conditions are also under consideration in this new plan for coal beneficiation while the technical concepts are researched. Development goals and research goals are of coincident interest, as is necessary for programs addressing new cleaning processes.

Background to Biodesulfurization

An obvious means to the circumvention of some of the cost problems found in traditional coal cleaning processes lies in the use of biological methods because of the inherently lower capital and operating costs. Indeed, microbial coal desulfurization already has a history. Early interests in this field focused upon microorganisms for pyritic sulfur removal; these microorganisms were "naturally" suited to this task having themselves adapted to sulfur utilization in mine waters (e.g., as with Thiobacillus) or sulfur springs (e.g., as with Sulfolobus). However, while interesting from the standpoint of process-type manipulations, these microorganisms do nothing for organic sulfur removal. Thus, if substantial sulfur removal is of interest, biological methods must do more than remove only the inorganic sulfur.

Several more recent efforts have focused upon the adaptation and use of various strains of microorganisms to act upon and remove the organic sulfur (e.g., those projects at the Atlantic Research Corporation(1,2), The Institute of Gas Technology(3), and the University of Georgia(4)). These "coal bugs" are becoming well-known and have been shown to have "appetites" for organic sulfur. Oxidation of sulfur for removal as organic sulfate has been the most commonly demonstrated mechanism for microbial removal of organic sulfur; as a result, some of the organic, i.e., the energy, content is often lost as part of the sulfate. While encouraging demonstrations of the feasibility of organic sulfur removal via biological means have been shown, these projects by no means represent optimized solutions. Microbial efficiencies and process operations await improvements. These works continue, for the most part, in that vein while additional lessons in coal cleaning are made available for further conceptual developments of the sort being exploited, as described herein.

A consideration in these microbially-based cleaning operations lies in the potential for some degree of process sensitivity. That is, because these operations exploit live organisms, there is concern as to their maintenance as both viable and selective populations. While ample precedent exists for microbially-based treatment systems, e.g., wastewater treatment, there are recognized sensitivities implicit in the use of live systems, such as mutational problems, reactor upsets, substrate variations, etc. A possible solution may lie in the use of an enzyme-based cleaning process, that is, a process which solely uses the "active extract" of the microbial process to effect desulfurization(5). The concept of enzymatic removal of sulfur from coal is discussed in the following.

Enzymes for Removal of Organic Sulfur From Coal

An enzymatic (not microbiological) process for organic sulfur removal from coal would first require the identification, characterization and production of an enzyme known to cleave sulfur from a representative polymer. These enzymes would then be immobilized or "tethered" on a standard packing material such as is used to support conventional catalytic materials in the bioprocess industries (the enzymes may be in solution, as discussed later, but immobilized enzymes are used in this explanation.) Upon passing the coal/water slurry through the packing material, the immobilized enzymes tethered on the packing would cleave the organic sulfur, acting as a type of biocatalyst. Coal particles, free of organic sulfur, would then be recovered; sulfur could also be readily recovered.

With this introduction, some of the pertinent technical background is given in the following section.

TECHNICAL BACKGROUND

Overview

The subject of sulfur removal from fossil fuels by biologically based means has been receiving increasing attention in recent years(6). This is due, in part, to the enhanced ability of controlling the genetic make-up of various organisms, but also to the possibility of selectively removing the objectionable sulfur compounds at the front-end of a power generation process and without affecting the hydrocarbon structure (hence, the thermal value) of fuel. Other advantages include mild operating conditions, possible use of natural earth formations as reactor systems, and possible longer biocatalyst life under concentrated sulfur and heavy metal conditions observed in refining and cracking operations.

Pyrite Removal

Sulfur content of coal has been reported to be at least 4.5%, approximately equally distributed between organic and inorganic compounds. The latter, predominantly in the form of pyrite, have been investigated recently, with regards to their dissolution potential through the mediation of soil acidophilic bacterial. A large number of such organisms have been isolated to date, the most important among them being members of the genera of Thiobacillus and Sulfolobus. Extensive studies with such organisms, in pure as well as in mixed cultures, demonstrated the feasibility of oxidative dissolution of the pyrite sulfur from coal(7,8,9). Dissolution kinetics were found to be first order with respect to the specific surface area of the coal, and, based on these preliminary kinetic data, a feasibility assessment of a coal water slurry pipeline was carried out for the simultaneous transport and pyritic sulfur removal from the coal.

Organic Sulfur Removal

The removal of organic sulfur from coal is a significantly more demanding task than pyritic sulfur removal mainly because of two reasons. Foremost, organic sulfur is deeply embedded in the coal matrix requiring a very fine pulverization of coal in order to expose the sulfur compounds to the action of chemicals or catalysts. Second, the primary sulfur compounds are far more resistant to degradation or assimilation by organic or biological catalysts and often poisonous or toxic to their activity.

The possibility of using microorganisms for organic sulfur removal from coal

has been examined in the past forty years. The patent literature is rather imaginary and inconclusive. The majority of these studies were carried out with model compounds representative of the three types of organic compounds that the approximately 195 sulfur substances in coal can be classified into, namely, A) sulfides, B) thioles, and C) thiophenes(10). In particular, due to the relative ease of removing aliphatic sulfides and other sulfur compounds of low boiling point by simple chemical means, most of the attention has been focused on aromatic sulfur compounds such as thiophenes, especially benzothiophene (BT) and dibenzothiophene (DBT)(10). Attempts to isolate microorganisms capable of degrading simple thiophene aerobically have been unsuccessful(11). However, microbial degradation of the nucleus of substituted thiophenes has been demonstrated(12). Other studies have addressed the possibility of degrading BT and DBT. For example, a mixed culture of *Arthrobacter sp.* and *Pseudomonas sp.* was shown to be able to grow on DBT and residue oil with products being cellular mass and inorganic sulfate(13). DBT could also be converted to water soluble oxygenated derivatives which accumulated during metabolism, but the sulfur in the thiophene nucleus remained untouched by this action(14). Several other studies have confirmed these findings showing that BT, DBT, and related organic sulfur compounds can be converted into soluble sulfur compounds through the use of pure cultures or microbial consortia(15-17).

There are, however, some serious problems associated with the use of living organisms in considering large scale organic sulfur removal from coal. First, the conditions which are optimal for the growth and activity of such organisms are usually incompatible with the concept of the envisioned large-scale process or require expensive additives so that they can be maintained for extended periods of time. Second, objectionable amounts of growth factors and carbon sources are needed which could cause insurmountable economic difficulties. Third, toxic by-products or other compounds in a realistic process environment could be the source of severe poisoning problems that render the microorganisms incapable of performing the tasks for which they were isolated. Finally, culture stability is always a serious concern especially in open, continuous flow ecosystems. For this reason, the concept considered here is a combination of chemical pretreatment with an enzymatic process which could be a viable alternative to the above mentioned possibilities.

Enzymatic Desulfurization Process

It is assumed that it is feasible and economical to pulverize coal down to 10 to 50 micron fine particles so that most of the organic sulfur compounds become either exposed to or reachable by the chemical reagents involved in the pretreatment and the subsequent enzymatic process. If this is not so, significant carbon oxidation may take place before the sulfur compounds can be acted upon by the oxidizing agents.

The coal particles are mixed with water for the preparation of a coal/water slurry (available technology) which is subsequently subjected to a chemical oxidation pretreatment with a hot alkaline reagent. The objective is to partially oxidize the maximum possible amount of the organic sulfur compounds to sulfate. Full oxidation to SO_4 is obviously undesirable and so are many destructive effects of the oxidizing agent on the carbon of the coal matrix. There is clearly an optimum for the degree of oxidation, and this can be achieved by varying the temperature, strength of alkali, and duration of pretreatment, followed by titration for the fraction of overall sulfur converted to sulfate for each combination of operating conditions.

The next step is to remove the sulfates from the coal particles. One way to selectively accomplish this is by contacting the coal/water slurry with a sulfatase enzyme solution. Enzymes are commercially available that have the property of catalyzing the dissolution of sulfur compounds by cleaving the sulfate anions from the aliphatic aromatic backbone. The resulting sulfate solution can be further treated with lime to finally contain sulfur in the form of calcium sulfate solids.

Concept Presented

The present work addresses the feasibility of organic sulfur removal from coal via select enzymatic methods. These methods focus upon the stepwise biochemical transformation of the coal matrix for extraction of the organic sulfur as sulfur oxides such as sulfate. These transformations proceed via enzymatic pretreatment of the coal to both (bio)chemically oxidize the available organic sulfur and (bio)physically "loosen" the matrix followed by enzymatic cleavage about the pretreated sulfur moieties.

Thus, this concept followed from the basic demonstrations of microbial desulfurization in that technical sense which supports oxidative methods for removal of organic sulfur. However, this concept focused on a unique approach to circumvention of the process inefficiencies associated with microbial desulfurization methods by testing the use of only the "active" fractions of microbial populations, i.e., the enzymes, to effect the necessary coal chemistry for sulfur transformations and removal. This evaluation was conducted within the context of considering a feasible process template for an enzymatic coal cleaning operation. A brief discussion of the enzymatic removal of organic sulfur from coal, the concept on which our concept is based, is as follows.

ENZYMATIC COAL BIODESULFURIZATION

Rationale For Processing Concept

The intricacies of coal structures and their chemistries are the subject of continuing study. However, some of the basic elements of coalification and depolymerization chemistries can be considered. Coal is formed via dehydration processes and coal is broken down via combinations of hydrolytic, oxidation, and other displacement chemistries. The understanding of these types of chemical transformations in coals forms the basis for various processes addressing coal upgrading or beneficiation via traditional methods, e.g., liquefaction or chemical desulfurization.

Microorganisms which have been shown capable of interacting with coal also take advantage of these coal chemistries. Basically, microbes establish an interaction with the coal because the coal has something which the microbe can use or, at least, tolerate. The microorganism requires its "balanced diet" for growth and survival. If given coal as the mainstay of that "diet", then it has to acclimate its biological machinery in such a way so as to be able to utilize the coal. This means that the microorganism's consortia of available reagents (e.g., water) and catalysts (i.e., enzymes) must go to work to selectively extract and/or cleave the nutrients it needs, and, in doing so, this microorganism uses established chemistries. There is no reason to suggest that, in these instances, coal is extracted or cleaved in a manner any different than those demonstrated via conventional chemical processing. Indeed, some of the early work which has been done on the mechanisms of microbially-mediated coal

processing shows (through product analysis) that this is certainly so. Studies of microbial liquefaction, for example, demonstrate oxidation and hydrolysis of the coal matrix.

Current knowledge of microbial desulfurization processes lends further support to the cited mechanism for coal breakdown. Those microbial processes specifically intended for organic sulfur removal from coal implicate oxidation of the carbon-sulfur linkages to yield sulfur oxides (in most cases, sulfates) which then are susceptible to a hydrolysis to liberate the sulfur oxides from the remainder of the coal matrix. There have been, however, some serious problems associated with the use of these living organisms in large-scale organic sulfur removal from coal. First, the conditions which are optimal for the growth and activity of such organisms are usually incompatible with the concept of the envisioned large-scale process or required expensive additives so that they can be maintained for extended periods of time. Second, objectionable amounts of the growth factors and carbon sources are needed which could eventually cause insurmountable economic difficulty. Third, toxic by-products or other compounds found in a realistic process environment could be the source of severe poisoning problems that render the microorganisms incapable of performing the desulfurization task for which they were isolated. Finally, culture stability is always a serious concern particularly in an open, continuous-flow ecosystem.

Given microbial ability to effect the coal chemistries necessary for desulfurization, but also given the concerns of a "living" processing system, our team early considered an alternative biologically-based desulfurization scheme. In this alternative concept was seen the advantages of bioprocessing in perhaps an eventually more efficient manner. Specifically, the concept investigated has focused on the sole use of the "active extracts" of the microbes with the consideration that the problems associated with reactor upset can be minimized. The concept subject to the investigation is an enzymatic desulfurization process.

While enzymatic processes have been proven in large-scale industrial applications, it is important to note that their use in coal cleaning is not merely a transfer of technology to a new process substrate. Specific enzymatic action about the organic linkages of interest, as well as the efficiencies of any demonstrated action, must be investigated. The issues of enzymatic accessibility must also be addressed. In addition, the constraints imposed by a solid substrate must be incorporated into design consideration, particularly if the use of raw coal is the major interest. Thus, both scientific and engineering feasibilities are important components to process development.

Processing Concept

Overall, the present concept is a desulfurization system that derives its processing reagents from biological sources. In contrast to chemical operations, processing catalysts (i.e., enzymes) are of natural origin thus, potentially, processing may be more benign. In contrast to microbial operations, the active agents are molecularly discrete; thus, potentially, processing may be less sensitive to the reactor upsets associated with "living" microbial systems.

In this concept enzymes are being used as processing tools in an effort to affect the removal of the organic sulfur from coal. The coal chemistries are those of oxidation and hydrolysis. "Oxidases" are being used to catalyze the oxidation about the sulfur bond; "hydrolases" are being used to catalyze the hydrolysis about the prepared sulfur. In other words, biochemicals are being

investigated for their potential to direct the chemistry of desulfurization thus leading to a potentially more efficient cleaning process. The overall objective is to investigate the feasibility of a practical, bioreactor-based enzymatic desulfurization process specifically intended for organic sulfur removal from coal.

Technical Considerations

The basic premise of our concept for enzymatic desulfurization of coal is that the use of specific hydrolases will reduce the organic sulfur content. For example, the reaction to remove organic sulfur may use one type of hydrolase, namely an "arylsulfatase". That is, in the presence of the arylsulfatase enzyme, the hydrolysis of organic sulfate compounds to organic phenols is catalyzed. The sulfur is effectively isolated from the organic starting components and is retrievable as water-soluble sulfate. Aside from the issues of biocatalyst selectivity and operating efficiency, the use of an arylsulfatase for organic sulfate removal is fairly straightforward.

The complexity which arises from the actual exploitation of arylsulfatases or sulfur removal lies in the consideration of the forms of sulfur in coal. The three major forms of organic sulfur in coal are: (1) thiophenes (approximately 65% of the total organic sulfur), (2) sulfides (approximately 25%), and (3) thiols (approximately 10%). Very little of the accountable sulfur is presumed to be in the form of organic sulfur oxides, such as sulfate. However, it is possible to survey these available sulfur forms and propose their conversion to oxides for removal via hydrolase, e.g., sulfatase, enzymes. Specifically, it is our concept to oxidatively pretreat coal for conversion of as much of the organic sulfur to oxides, such as sulfate, then effect the actual desulfurization via enzymatic hydrolysis of the sulfur oxide.

Thus, our concept for enzymatic desulfurization of coal presently organizes the processing effort into two areas: (1) oxidative pretreatment, and (2) actual desulfurization. The former has as its goal the oxidation about the sulfur moiety and includes investigation of both chemical and enzymatic methods. The latter has as its goal the actual removal of the prepared sulfur from the organic matrix and focuses on enzymatic methods only. The results in each area are intended for use in a reasonable process model, the template of which has been prepared.

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