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Enzymatic coal desulfurization.

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Coal is desulfurized by treatment with a hydrolase to convert organic sulfur moieties in the coal matrix to sulfates, and by treatment with a sulfatase to cleave the sulfates.

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ENZYMATIC COAL DESULFURIZATION

FIELD OF THE INVENTION

This invention relates to fossil fuel desulfurization, and particularly to coal desulfurization with enzymes such as oxidases and hydrolases.

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BACKGROUND OF THE INVENTION

Due largely to environmental concerns, there is an increasing need for low-sulfur emissions from fossil fuels such as coal which contain sulfur. Heretofore, both post-combustion and pre-combustion desulfurization techniques have been available. For example, flue gas desulfurization is a well know post-combustion process. However, it is generally inconvenient, expensive and limited with respect to the amount and types of sulfur combustion products which can be removed. Flue gas treatment also ignores other economic impacts from the handling and processing of fuels containing sulfur, such as corrosion caused by the sulfur in coal to the equipment used to handle the coal. Pre-combustion processes, on the other hand, which result in low-sulfur fuels, can reduce both sulfur emissions and equipment corrosion.

Conventional coal desulfurization processes include physical methods such as pyrite flotation or magnetic separation. While these physical methods are convenient and economical, they are capable of removing only inorganic sulfur and generally result in notable energy losses. On the other hand, chemical coal desulfurization processes, such as oxidation with ferric salts, chlorine or ozone, or reduction with solvent-hydrogen mixture, are somewhat more effective in removing organic sulfur, but generally have numerous disadvantages, such as, corrosion problems from reagents, high energy requirements, and costly reagent recovery.

Attempts have also been made to remove sulfur from coal by microbiological methods. Early interest in this field focused on microorganisms which were naturally suited for sulfur digestion, such as Thiobacillus found in mine waters and Sulfolobus found in sulfur springs, as reported in Detz et al, American Mining Congress Journal, vol. 65, p. 75 (1979); Kargi et al, Biotechnology and Bioengineering, vol. 24, pp. 2115-2121 (1982). However, such bacteria utilize only inorganic sulfur and have no propensity for organic sulfur removal. More recently, efforts have focused on the adaptation of microorganisms for organic sulfur removal. Such attempts are reported, for example, in Isbister et al, "Microbial Desulfurization of Coal", in Attia (ed), Processing and Utilization of High Sulfur Coal, p. 627 (1985); and Robinson and Finnerty, "Microbial Desulfurization of Fossil Fuels" (University of Georgia). There are, however, numerous obstacles which must be overcome before such techniques become practical. For example, optimal growth conditions in a large scale process are difficult and expensive to maintain, typically requiring expensive growth factors and excessive nutrients or additives. Such additives themselves can be a potential environmental concern and possibly as difficult to remove economically as the sulfur. The growth of the microorganisms can also produce toxic by-products or compounds which may result in mortality or render the microorganisms incapable of catabolizing sulfur. In addition, such fermentation processes are usually plagued with problems such as culture stability, mutation or contamination, reactor upsets, substrate variation, and the like. Thus, there remains an unfilled need for an economical and efficient method for desulfurizing coal and other fossil fuels.

SUMMARY OF THE INVENTION

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The present invention involves the biochemical treatment of coal and other fossil fuels to remove sulfur or to desulfurize the fossil fuel. The biochemical treatment comprises contacting the sulfur-containing fossil fuel with an enzyme or enzymes in an amount generally effective to reduce the amount of sulfur in the fuel. The enzymes are added directly to the fossil fuel and need not be produced by microorganisms growing on the fossil fuel as a substrate or growth medium. Thus, the process need not be controlled to maintain the viability of any enzyme-producing microorganisms, but can be optimized to favor enzymatically mediated conversion of the sulfur into a form that can be separated from the fossil fuel.

In a broad aspect, the present invention provides a method for desulfurizing a fossil fuel. The process comprises optionally at least selectively oxidizing organic sulfur in a fossil fuel, and thereafter contacting the oxidized fossil fuel with a sulfur-removing enzyme, and recovering the fossil fuel with a reduced sulfur

content.

BRIEF DESCRIPTION OF THE DRAWINGS

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Fig. 1 is a schematic illustration of an embodiment of the process according to the present invention;

Fig. 2 is a schematic illustration of an alternate embodiment of the process according to the present invention;

Fig. 3 is a graphical illustration of spectral data of filtrates of dibenzothiophene (DBT) treated with a peroxidase and a sulfatase as described in Example 1 hereinbelow;

Fig. 4 is a graphical illustration of spectral data of filtrates of Wyodak coal at various periods of time following treatment with a peroxidase and a sulfatase, as described in Example 2 hereinbelow; and

Fig. 5 is a graphical illustration of spectral data of filtrates of Illinois No. 6 coal at various periods of time following treatment with a peroxidase and a sulfatase as described in Example 3 hereinbelow.

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DESCRIPTION OF PREFERRED EMBODIMENTS

The present invention includes a process for treating fossil fuels, and especially fossil fuels containing organic sulfur. Contemplated fossil fuels include petroleum and coal; products of fossil fuel conversion processes, e.g., coal-derived liquids, are also considered. As used herein, coal includes any coalified organic material such as peat, lignite, sub-bituminous coal, bituminous coal and anthracitic coal. The fossil fuel should contain organic sulfur to obtain the most benefit from treatment according to the present invention, although inorganic sulfur could also be removed by this process. By organic sulfur is generally meant organic thiophenes, sulfides and thiols, whereas inorganic sulfur generally refers to sulfates and metallic sulfides such as pyrite.

According to the present process, a two-step reaction pathway is generally employed. Initially, the organic sulfur is converted into a sulfur oxide, e.g., sulfate, by oxidation. However, in some rare instances oxidation may not be necessary, because the organic sulfur may be predominantly in the sulfate form or substantially only the naturally occurring sulfate is to be removed. In this sense, the oxidation can be considered to be an optional reaction. However, for optimal sulfur removal, oxidation is preferred. The oxidation substantially converts the organic sulfur into sulfate. The sulfate is enzymatically removed, for example, by hydrolysis induced by a sulfur hydrolase, e.g., a sulfatase.

The fossil fuel may be prepared for treatment according to the present method by generally known methods; e.g., solid fossil fuels, such as coal, can be ground and slurried in water. The slurry can be prepared by grinding the solid fossil fuel to an appropriate particle size, typically 10-50 μm , and mixing it with water. For the purpose of illustration only, the invention is described hereinbelow with reference to a ground coal slurry with the understanding that other fossil fuels and media may be analogously employed. For example, in the case of oil, it may be sufficient to prepare an emulsion if an aqueous enzymatic treatment is employed, or to treat the oil neat, with a solvent, or in mixture with another immiscible fluid.

The oxidation of the coal slurry may be effected by treatment with an oxidation enzyme, such as, a peroxidase, a laccase, or a like oxidase. As used herein, a peroxidase is any enzyme having the E.C. number 1.11.1.7, e.g., horseradish peroxidase, and a laccase is any enzyme having E.C. number 1.10.3.2, e.g., *Pyricularis oxyzae* laccase.

Alternatively, partial oxidation may be effected by mild alkaline or acidic treatment of the coal particles. For the former case, generally the coal is contacted with 5-10 parts by weight of caustic per 100 parts by weight coal. The contact is for a brief period at an elevated temperature of 125-200 $^{\circ}\text{C}$, preferably 150-180 $^{\circ}\text{C}$. The exposure to the elevated temperature is preferably effected by rapid heating to the treatment temperature, e.g., in less than about three minutes, preferably in less than about one minute, and most preferably in about thirty seconds. The duration of the coal alkali contact at the treatment temperature is preferred about 1-10 minutes and especially preferred about 3-5 minutes. Following the exposure to the elevated temperature, the coal/alkali mixture is rapidly cooled or quenched to below 100 $^{\circ}\text{C}$, preferably in less than about three minutes, and most preferably in less than about one minute, i.e., about 30 seconds.

It should also be understood, however, that acidic oxidation at ambient temperature may be performed instead. This would be done in the conventional oxidative manner of pretreatment of coal prior to desulfurization as an alternative chemical oxidation technique.

The oxidation serves to convert the organic sulfur moieties into sulfur oxide or moieties, such as sulfate. It is desirable to convert the maximum possible amount of organic sulfur to sulfur oxides. On the other hand, full oxidation to sulfur dioxide is generally undesirable, as also is excessive oxidation of the carbon in

the coal matrix. Usually the desired degree of oxidation can be achieved by varying the type of alkali, oxidase or other oxidant, the oxidant concentration, duration of contact between the coal and the oxidant, and other conditions of treatment, e.g., pH, temperature, oxygen availability.

The hydrolysis of the oxidized sulfur moieties is then effected, as mentioned above, by sulfatase treatment. As used herein, sulfatase includes any enzyme capable of hydrolyzing the sulfur moieties to yield a water-soluble sulfur compound. Specific examples include enzymes having the E.C. number 3.1.6.1, such as limpet sulfatase, Aerobacter aerogenes sulfatase, abalone entrail sulfatase, Helix pomatia sulfatase, and the like.

The coal particles may be treated with the sulfatase and/or oxidation enzymes, with or without additional chemical oxidation. One contemplated process scheme is a fluidized bed reactor as illustrated in Fig. 1. Generally, uniform concentration and temperature are maintained throughout the fluid bed reactor 100, and the enzyme is immobilized on support particles E which are relatively larger in size than the coal particles in the slurry typically fed into the lower portion of the reactor 100. This size difference permits retention of the enzyme support particles E by catalyst retention screen S and gravity separation in the upper portion of the reactor 100 near the effluent port C in the conventional manner of fluid bed operation. Air or other suitable gas is typically supplied to the bottom of the reactor 100 to promote back mixing and CSTR conditions.

An alternative processing scheme for a moving bed reactor, which generally follows the format of the Examples set forth below, is illustrated in Fig. 2. The coal slurry is introduced from hold-up/preparation tank 200 generally to the upper end of inclined moving bed 202 and discharged from the lower end thereof. As the coal descends through the reactor 202, it is continuously contacted with enzyme solution in a countercurrent fashion to release the sulfur as sulfate which is soluble in the enzyme solution. The enzyme/sulfate solution effluent from the reactor is recovered by adsorption on a sorbent in enzyme adsorption unit 204. The sulfate solution is readily separated from the sorbent and collected in tank 206 in which, for example, lime or other basic material may be used to precipitate the sulfate prior to disposal. The adsorbed enzyme from unit 204 is then desorbed in unit 208. The desorbed enzyme is then recycled to the reactor 202 along with any makeup enzyme, while the sorbent may be recycled through the enzyme adsorption/desorption cycle.

The invention is illustrated by way of the examples which follow.

Example 1

A suspension was prepared of 100 mg dibenzothiophene ("DBT") in 3 ml of 0.1 M Tris buffer, pH 7.0. To this suspension at room temperature was added 0.5 ml of horseradish peroxidase (Sigma P 8000) at 2 mg/ml in buffer, and 0.5 ml of Aerobacter aerogenes sulfatase (Sigma S 1629) at 2 mg/ml in buffer. The mixture was maintained at room temperature in an air atmosphere, and reaction samples were periodically removed and filtered. Solids were analyzed for elemental composition and such analyses are presented in Table 1.

TABLE 1

Sample	Elemental Analysis (weight percent)				
	C	H	N	O	S
DBT	78.26	4.35	0	0	17.39
DBT/Peroxidase	77.80	4.38	0.01	1.16	16.65
DBT/Peroxidase/Sulfatase	76.62	4.12	0.19	3.88	15.19

Filtrates from the peroxidase/sulfatase treated DBT were analyzed for spectral changes and such spectral data are presented in Fig. 3. The spectral data demonstrate a spectral shift in the direction of longer wavelengths indicative of increased polarity which would be expected from conversion of DBT by the peroxidase/sulfatase enzymes. The elemental analysis demonstrates an increase in oxygen content and a decrease in sulfur content. Moreover, it was also observed that starting reaction mixtures were distinctly two-phase liquid-solid mixtures whereas later reaction mixtures were strongly wetted and appeared as milky suspensions.

Example 2

The procedure of Example 1 was repeated using 100 mg ball-milled Wyodak coal instead of DBT. The results are presented in Table 2 and Fig. 4.

TABLE 2

Sample	Hours	Elemental Analysis (weight percent)			
		C	H	N	S
Wyodak Coal	--	65.96	4.57	0.95	1.70
Wyodak Coal/Peroxidase/Sulfatase	1	59.47	4.99	0.98	0.90
Wyodak Coal/Peroxidase/Sulfatase	2	60.42	5.12	1.15	0.79
Wyodak Coal/Peroxidase/Sulfatase	4	58.84	5.04	1.08	0.95
Wyodak Coal/Peroxidase/Sulfatase	24	60.35	5.30	1.22	0.30

The spectral changes demonstrated in Fig. 4 for Wyodak coal are similar to, although more pronounced than those observed with DBT, indicating more extensive reacting of the Wyodak coal than the DBT, in the presence of the peroxidase and sulfatase.

The large drop in sulfur percentage by elemental analysis seen in the data in Table 2 indicates that about 80% of the sulfur was removed. It is believed that the results with the Wyodak coal are better than with DBT because only a fraction of the organic sulfur in coal is aromatic, thiophene-type sulfur which is generally more recalcitrant to chemical conversion than other types of organic sulfur found in coal. The increase in nitrogen percentage is probably due to adherence of the enzymes to the coal particles.

Example 3

The procedure of Example 2 was repeated using Illinois No. 6 coal instead of Wyodak coal. The results are presented in Table 3 and Fig. 5.

TABLE 3

Sample	Hours	Elemental Analysis (weight percent)			
		C	H	N	S
Illinois No. 6 Coal	0	70.39	4.48	1.44	3.60
Illinois No. 6 Coal/Peroxidase/Sulfatase	1	58.72	5.01	0.94	0.91
Illinois No. 6 Coal/Peroxidase/Sulfatase	2	58.56	5.00	1.14	0.98
Illinois No. 6 Coal/Peroxidase/Sulfatase	4	58.36	5.07	1.22	1.72
Illinois No. 6 Coal/Peroxidase/Sulfatase	24	58.27	5.14	1.21	0.84

As seen from Table 3 and Fig. 5, the enzyme-mediated treatment of Illinois No. 6 coal desulfurizes the coal in a manner similar to the Wyodak coal.

The foregoing disclosure and description of the invention are illustrative and explanatory thereof, and various changes in the size, shape and materials, as well as in the details of the illustrated construction may be made without departing from the spirit of the invention.

Claims

1. A method for desulfurizing fossil fuel from a fossil fuel substrate containing organic sulfur, comprising

the steps of:

contacting the substrate with a sulfur-removing enzyme; and
recovering a fossil fuel having a reduced sulfur content from the substrate.

- 5 2. The method of claim 1, wherein the substrate includes coal or petroleum, or process-derived products thereof.
3. The method of claim 1, wherein the organic sulfur is thiophene, sulfide, thiol or a combination thereof.
4. The method of claim 1, further including the step of:
oxidizing the fossil fuel substrate prior to said step of contacting the substrate.
- 10 5. The method of claim 4, wherein step of oxidizing includes contacting the substrate with alkali.
6. The method of claim 4, wherein step of oxidizing includes contacting the substrate with acid.
7. The method of claim 4, wherein said step of oxidizing includes contacting the substrate with an oxidation enzyme.
8. The method of claim 7, wherein the contact with oxidation and sulfur-removing enzymes is consecutive.
- 15 9. The method of claim 7, wherein the contact with the oxidation and sulfur-removing enzymes is concurrent.
10. The method of claim 7, wherein the enzymes are immobilized on packing during said step of contacting with the oxidation and sulfur-removing enzymes.
11. The method of claim 7, wherein the oxidation enzyme is peroxidase or laccase.
- 20 12. The method of claim 7, wherein the oxidation enzyme is horseradish peroxidase.
13. The method of claim 12, wherein the horseradish peroxidase contact in the presence of excess oxygen at a temperature from 0 to 80 °C and a pH of from 5 to 9, and with an amount of the peroxidase ranging from about 0.01 to 10 parts by weight per 100 parts by weight of substrate.
14. The method of claim 1, wherein the sulfur-removing enzyme is sulfatase.
- 25 15. The method of claim 14, wherein the sulfatase is selected from the group consisting of: Aerobacter species sulfatase, limpet sulfatase, abalone entrail sulfatase, and Helix species sulfatase.
16. The method of claim 15, wherein the hydrolase is Aerobacter aerogenes arylsulfatase.
17. The method of claim 16, wherein the sulfur-removing enzyme contact is in the presence of excess water at a temperature from 0 to 80 °C and a pH of from 5 to 9, and with an amount of the arylsulfatase
30 ranging from about 0.01 to about 10 parts by weight per 100 parts by weight of substrate.
18. The method of claim 17, wherein the sulfur-removing enzyme contact is in the presence of from about .1 to about one parts by weight of water per 100 parts of weight of the substrate.
19. The method of claim 1, further comprising the step of:
separating soluble sulfate from the reduced sulfur content substrate by filtration, centrifugation or ion
35 exchange adsorption.

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DIBENZOTHIOPHENE/PEROXIDASE, SULFATASE SPECTRAL DATA

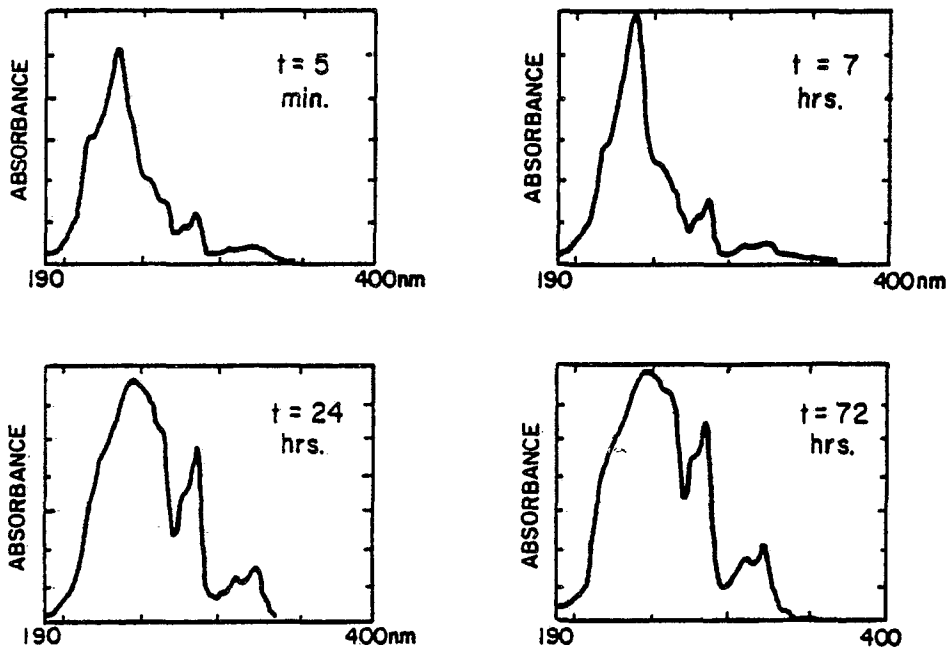


FIG. 3

WYODAK COAL/PEROXIDASE, SULFATASE SPECTRAL DATA

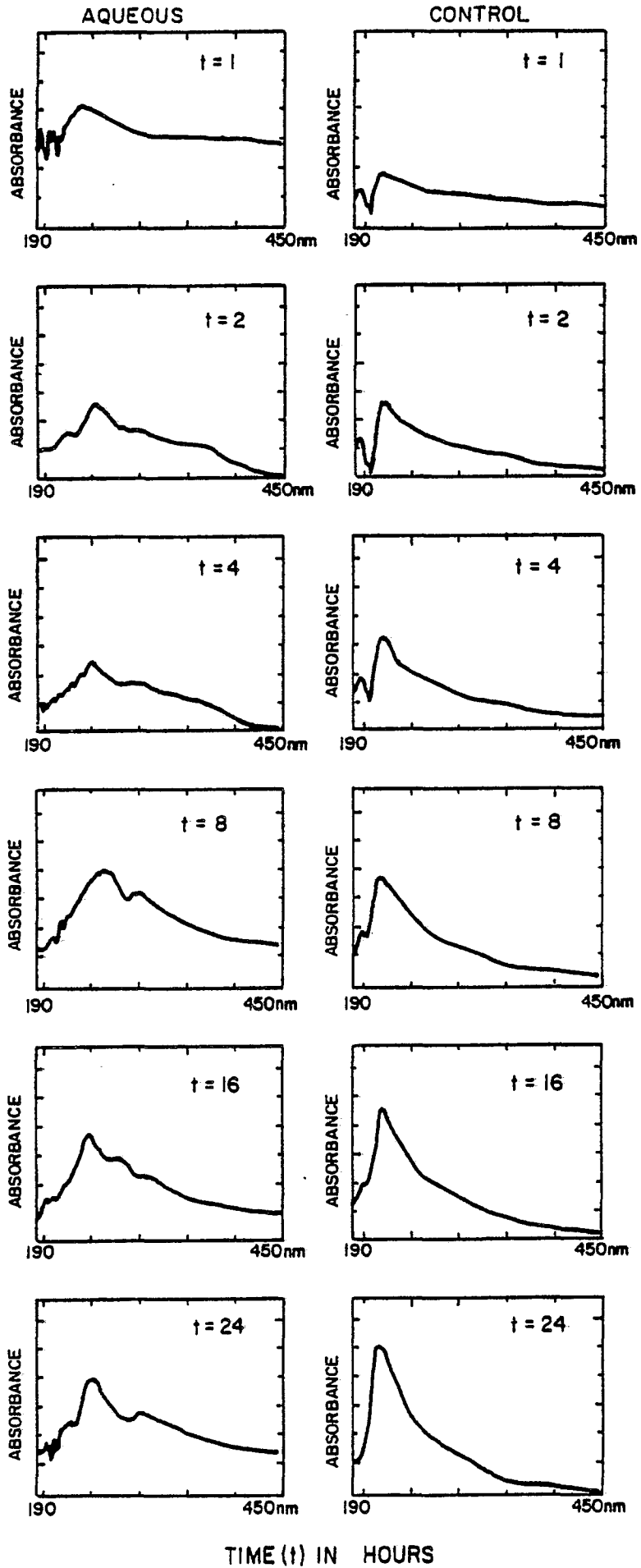


FIG. 4-1

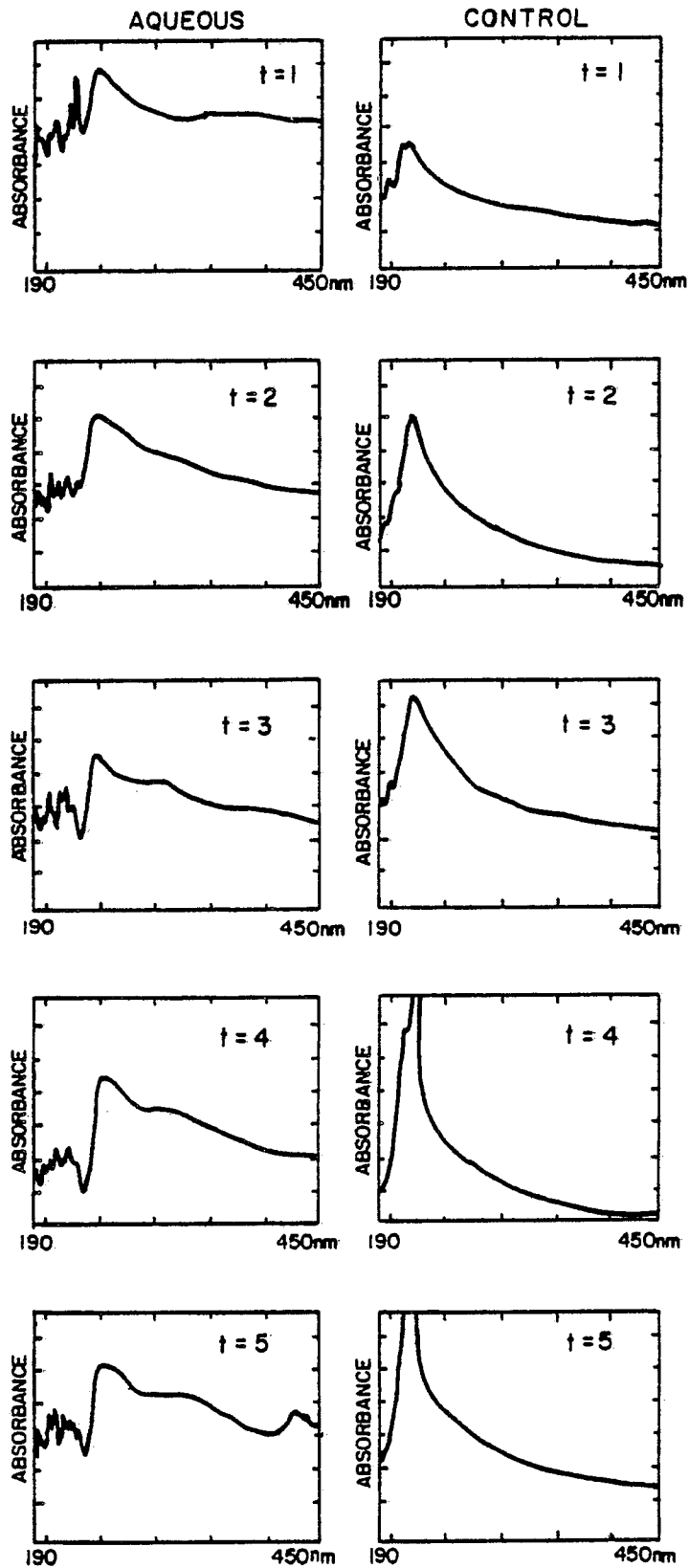
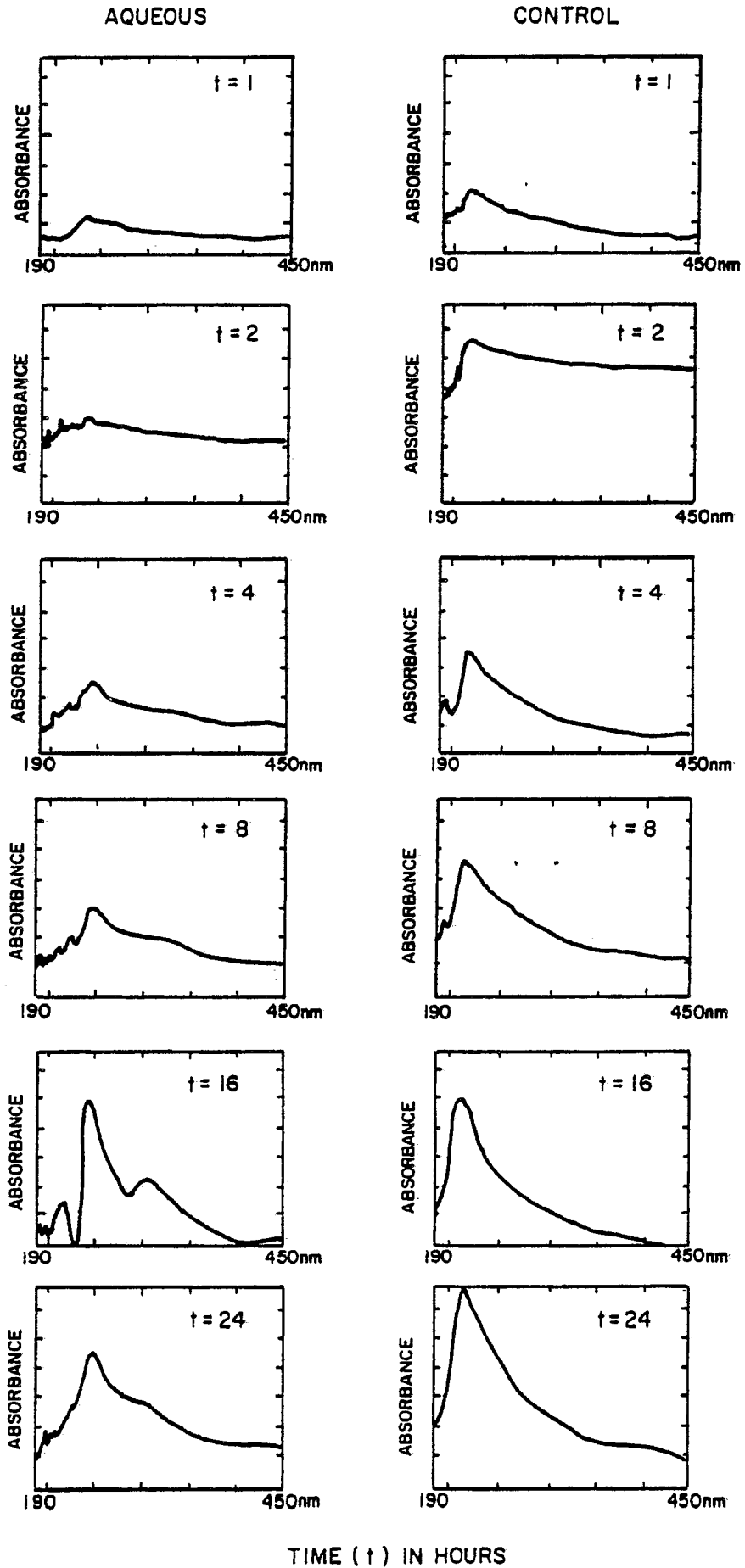


FIG. 4-2

TIME (t) IN DAYS

ILLINOIS COAL/PEROXIDASE, SULFATASE SPECTRAL DATA

FIG. 5



TIME (t) IN HOURS



DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
X	CHEMICAL ABSTRACTS, vol. 109, 1988, pages 170-171, abstract no. 233905h, Columbus, Ohio, US; O.G. NGAIZA et al.: "Enzymic removal of organic sulfur from coal", & PREPR. PAP. - AM. CHEM. SOC., DIV. FUEL CHEM. 1988, 33(4), 623-30 * Abstract *	1-5,14	C 10 L 9/00 C 12 S 1/02
A	IDEM ---	6-13,14 -19	
A	CHEMICAL ABSTRACTS, vol. 95, 1981, pages 190-191, abstract no. 172382d, Columbus, Ohio, US; & DD-A-147 365 (VEB PETROLCHEMISCHES KOMBINAT SCHWEDT) 01-04-1981 ---	1-19	
A	US-A-2 641 564 (ZOBELL) * Claims 5,6 *	1-19	
A	US-A-4 808 535 (ISBISTER) * Claims 1-5 *	1-19	
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			C 10 L C 10 G C 12 P C 12 S B 01 J
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 18-12-1989	Examiner MEERTENS J.
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	

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