

## COAL DESULFURIZATION BY PHOTOOXIDATION

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### ABSTRACT

Oxidative desulfurization of coal has been studied by several workers. These methods primarily involve selective oxidation of organic sulfur to sulfoxide and sulfones, followed by thermal decomposition of the oxidation product.

In this investigation, photooxidation of sulfur functionalities in coal is studied. Finely divided coal, suspended in a solvent, is exposed to radiations of wavelength 300-600 nm using a xenon mercury lamp. The coal sample, is next subjected to hydrolysis to remove the oxidized sulfur from the coal matrix. It is observed that coal desulfurization increased by 7.4%, 3.4%, and 23.7% when coal was photooxidized prior to hydrolysis by water, hydrochloric acid and sodium hydroxide, respectively. Sulfur removed by this technique as sulfonic, sulfurous or sulfuric acid or their salts would be mostly organic in nature.

### Introduction

Coal is unquestionably the fuel of the future for the generation of electrical energy but its use gives rise to a number of ecological problems, such as acid mine drainage and air pollution from particulate, sulfur dioxide, and  $\text{NO}_x$  emissions. Man-made sulfur dioxide and nitrogen oxides emissions in the U.S. are estimated to be over 40 million ton/year. Coal-fired utility power plants account for 55% and 27% of all the man-made sulfur dioxide and nitrogen oxides emissions, respectively in the United States. Sulfur dioxide emissions appear to acidify fresh-water lakes located in acidic soil areas whereas nitrogen oxides emissions appear to kill trees. As U.S. environmental groups become more aware of the tree losses in the Appalachian Mountains, reduction of nitrogen oxides emissions in existing coal-fired utility boilers is expected to be a critical issue.

There are many acid rain control technology options for existing large coal-fired electric utility boilers, namely

- (i) switch to low sulfur coal or natural gas,
- (ii) coal cleaning,
- (iii) flue gas treating,
- (iv) limestone injection multistaged burning,
- (v) fluidized bed combustion, and
- (vi) coal gasification.

The first three options are commercially proven techniques. Coal cleaning reduces only small percent of sulfur as it removes only pyritic sulfur. Coal cleaning and nitrogen reduction potentials using the flue gas treatment technique are high but the capital and operating retrofit costs are exorbitant. Consequently, there is still a need for an efficient and inexpensive coal desulfurization technique which utility companies could readily use.

In this paper, desulfurization of coal using a photooxidation technique is discussed. Coal samples exposed to radiation of wavelength 300-600 nm using a xenon mercury lamp are subsequently analyzed for sulfur content.

## Scientific Rationale for Photo Desulfurization of Coal

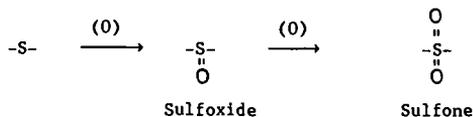
Coal is a highly heterogeneous solid originating from plant remains. It contains, in varying amounts, essentially all elements of the periodic table combined into nearly all of the minerals normally present in the earth's crust. In other words, coal is a complex mixture of organic and inorganic compounds in which the organic matrix comprises most of the coal weight. Organic coal matrix can be viewed as a complex macromolecular structure containing the classical organic functional groups such as carbonyl and hydroxyl, aromatic and heterocyclic ring units, and aliphatic bridges.

Coal structure and processing have been the subject of intense research for several years. The exact chemical structure of organic coal matrix varies and is not completely understood. However, enough information is available on the nature of sulfur containing functional groups in organic coal matrix. The organic sulfur in coal can be categorized into one of the functionalities such as thiol, sulfide, disulfide, thiophene, benzothiophene, and dibenzothiophene.

Desulfurization of coal has been investigated by several workers (1,2). They have used techniques such as oxidation (3-6), chlorinolysis (7-8), electrolysis (9), etc. All these methods essentially oxidize sulfur in coal. There are other methods reported in the literature involving hydrogenolysis, hydrolysis, etc. It is observed that among the organic sulfur functionalities, removal becomes increasingly difficult in the order thiolic < sulfide < disulfide < thiophenic < benzothiophenic < dibenzothiophenic. As the complexity of the sulfur containing functionality increases the selectivity of desulfurization, without affecting the rest of the coal matrix, becomes difficult. For example, the selectivity of hydrodesulfurization is reduced whenever the n-electrons of sulfur are in resonance with  $\pi$ -electrons as in the cases of thiophene, benzothiophene, etc. This leads to competing hydrogenolysis of the carbon-carbon bonds since the energies of carbon-sulfur and carbon-carbon bonds become practically identical due to resonance (10). It has been reported that atmospheric weathering leads to desulfurization of coal which can be due to the combined effect of air oxidation and photo-oxidation. However, the authors have not presented any mechanism or photonic role for this process (6).

It has been suggested that accompanying the oxidation of the sulfur to sulfone, the bond energy between the carbon and the sulfur is reduced on the average by 5.2 kcal/mole for aliphatic sulfides and by 11.8 kcal/mole for aromatic sulfides and thiophenes. Thus, the selectivity of decomposition at the sulfur-carbon bond is increased (3).

Oxidative desulfurization of coal has been studied by several workers (1-8). These methods primarily involve two steps: (1) selective oxidation of organic sulfur to sulfoxide and sulfones as shown below and (2) thermal decomposition of the oxidation product expelling sulfur dioxide.



### Photo-oxidation of Sulfur in Coal

No work is reported on the photochemical oxidation of coal. It is important to understand how the coal molecule would react in the presence of light and air. Coal due to its strong absorption of the entire visible spectrum has black color. It is also well known that coal has a complex aromatic structure with polyaromatic nuclei capable of absorbing light in the visible region. Attached to these are the sulfur atoms. The  $n$ -electrons on sulfur can resonate with the aromatic  $\pi$ -cloud. Hence, in the presence of light the  $n, \pi^*$  transition is also feasible which would affect the bonding properties of sulfur. This might lead to either electron deficient sulfur linkage or formation of diradical or free radicals. Due to the complexity of coal structure it is difficult to theoretically predict the exact course of reaction from the excited state.

There is enough literature evidence that oxygen in air attacks the organic sulfur compounds photochemically (11). Extending the mechanism of photo-oxidation of sulfur compounds to coal, two courses of reaction can be predicted. One of them could be the formation of free radical/diradical center at sulfur from the excited coal molecule and subsequent oxidation and hydrogen abstraction leading to oxidized sulfur functionalities such as sulfonic acid. The second one would be the attack of sulfur center by excited molecular oxygen, namely, singlet oxygen, if the reaction conditions are conducive to the production of singlet oxygen. Either of these mechanisms would cause the formation of sulfoxides, sulfones or sulfonic acids depending upon the reaction conditions. Hence, it is safe to predict that the organic sulfur functionalities in coal could be oxidized in the presence of oxygen and visible light.

By this photo-oxidation treatment the sulfur in coal would remain in an oxidized form. The next step would then be to eliminate the oxidized sulfur from the coal matrix. This can be achieved by subjecting the photo-oxidized coal to hydrolysis. This procedure is reported to be used in other chemical desulfurization techniques also. It is envisaged that most sulfur removed by this technique as sulfonic, sulfurous or sulfuric acid or their derivatives would be organic in nature.

### Experimental Set-up and Procedure

Finely crushed coal was suspended in 95% ethanol and kept agitated by bubbling oxygen at such a rate that the coal particles were not allowed to settle down. Also, oxygen bubbling would facilitate the removal of sulfur by oxidation. The coal slurry was subjected to photolysis in an internally lighted reaction vessel. Methylene blue was used as a sensitizer for the production of singlet oxygen. The photo-oxidized coal was washed thoroughly with ethanol to remove the dye and the ethanol was separated by centrifugation. Next, the coal was dried at 110°C for 8 hours. A portion of the photo-oxidized coal was subjected to hydrolysis either in boiling water or by refluxing with solutions of HCl or NaOH. Reference coal was also hydrolyzed with water, acid or base under the same conditions employed for photolysed coal in order to study the effect of photolysis. The samples were analyzed for their sulfur contents. The experimental conditions are summarized in the following Table 1.

Table 1: Experimental Conditions

Coal Illinois No. 6, Bituminous  
 Slurry Concentration 2% in coal and 0.1% in methylene blue  
 Hydrolysis Conditions 2% in coal; reflux; 6 h.

Parameters	Set I	Set II	Set III
Particle Size	74 micron	44 micron	44 micron
Solvent	95% Ethanol	95% Ethanol	95% Ethanol
Reactor	Internal	Internal	Internal
Sensitizer	Methylene Blue	Methylene Blue	Methylene Blue
Radiation	350-550 nm	300-600 nm	300-660 nm
Light Intensity	45 Watts	450 Watts	450 Watts
Reaction Time	10 h.	16 h.	16 h.
Hydrolysis Medium	Water	1 N HCl	1 N NaOH

### Results and Discussion

The sulfur contents of the coal samples are presented in Table 2.

Table 2: Sulfur Contents of Coal Samples

Sample	Set I			Set II			Set III		
	Run 1	Run 2	Mean	Run 3	Run 4	Mean	Run 5	Run 6	Mean
Reference	3.92	3.86	3.89	4.56	4.51	4.54	4.56	4.51	4.54
Light Unhydrolysed	3.83	3.80	3.82	4.65	4.45	4.55	4.65	4.45	4.55
Dark Hydrolysed	3.66	3.77	3.72	3.88	3.94	3.91	4.18	4.50	4.34
Light Hydrolysed	3.45	3.42	3.44	3.88	3.60	3.74	3.32	3.22	3.27

Table 3: Percent Sulfur Reduction

Reaction	Set I	Set II	Set III
Dark Hydrolysis	4.5	14.9	4.2
Light Hydrolysis	12.0	17.4	27.8
<u>Photonic Advantage</u>	<u>7.4</u>	<u>3.4</u>	<u>23.7</u>

The desulfurization based on total sulfur is on the average higher by 7.4% (Set I, Table 3) when hydrolysis is conducted by refluxing with water if coal is subjected to photolysis prior to hydrolysis. In other words, the desulfurization increased by about 7.4% as a consequence of photooxidation. It is also seen from Table 3 that photonic advantage increased on the average by 23.7% (Set II) if hydrolysis is conducted in boiling sodium hydroxide solution. However, with acid hydrolysis the photonic advantage is very low (3.4%; Set II, Table 3).

The probable mechanism of desulfurization is the oxidation of some of the organic sulfur functionalities such as sulfide and thiol to sulfoxides, sulfones and sulfonic acids and subsequent hydrolysis of these functional groups. A strong base such as sodium hydroxide would eliminate sulfonic acid from the sulfones and with some difficulty from the sulfoxides while hydrochloric acid would convert the sulfoxide to the original sulfide. It is to be noted that pyritic sulfur would also be affected by hydrolysis though the photolysis might not have significant influence on the removal of pyritic sulfur.

### Conclusions

These results show a definite photonic advantage in desulfurization of coal. However, the understanding of the mechanism of desulfurization, nature of functional groups that are affected by photolysis, role of pyrite in modifying the excited state reactivities, influence of reaction medium and optimization of desulfurization conditions need further study.

### Acknowledgment

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