

## DESULFURIZATION OF COAL BY PHOTO-OXIDATION

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### Abstract

Desulfurization of coal by oxidative methods has been investigated by several workers. These techniques primarily involve selective oxidation of organic sulfur to sulfoxide and sulfones, followed by thermal decomposition of the oxidation product.

In this study, photo-oxidation of sulfur in coal is investigated. Finely divided coal samples, suspended in solvent(s), are exposed to radiation using ultraviolet and xenon lamps. The coal samples are next subjected to hydrolysis to remove the oxidized sulfur from the coal matrix. The effect of wave length, light intensity, slurry concentration, and duration of exposure is studied. The maximum desulfurization achieved is about 42%.

### Introduction

The U.S. has about one-third of the world's known coal reserves. But coal is difficult to mine, expensive to transport and heavily polluting. The pollution is mainly due to the presence of mineral matter (ash) and sulfur which gives rise to the formation of fly ash and sulfur dioxide. Fossil energy research, development, and demonstration strategy is to develop a wide variety of coal utilization techniques that are clean, efficient and conserve resources. Industry can then choose promising processes which will eventually be commercialized. However, there is one serious limitation to increased consumption of coal namely, sulfur dioxide pollution caused by its direct combustion. 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 photo-oxidation technique is discussed.

### Scientific Rationale for Photo-Desulfurization of Coal

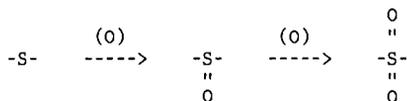
Coal is a complex mixture of organic and inorganic compounds in which the organic matrix comprises most of the coal weight. Organic coal matrix can be viewed as a complex macromolecular structure containing the classical organic functional groups such as carbonyl and hydroxyl, aromatic and heterocyclic ring units, and aliphatic bridges. 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 (12).

#### Experimental Set-up and Procedure

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

In a second set of experiments, coal samples suspended in solvent(s), are exposed to high intensity light using an apparatus as shown in Figure 1. The other details remain the same as for experiments conducted in an internally lighted reaction vessel.

#### Results and Discussions

Details of the experimental conditions and results are presented in Table I through Table III. Effect of wave length on sulfur reduction is presented in Table I, showing a photonic advantage of about 35% when coal samples are exposed to radiation of wavelength 254nm as compared to 23% for 300-600nm. In both cases coal samples are subjected to hydrolysis in 1N NaOH medium. It is to be noted that same % sulfur reduction is obtained for water hydrolysis at 254nm. On the other hand, a photonic advantage of only 5% is achieved when coal samples are exposed to wave length 300-600nm and subjected to water hydrolysis.

Effect of methylene blue, as a sensitizer, on sulfur reduction when added to coal samples suspended in 95% alcohol and exposed to wave length 300-600nm is presented in Table II. No change in sulfur reduction is observed.

Effect of light intensity on sulfur reduction in coal is presented in Table III. The coal samples are suspended in water, 1N NaOH, and 95% alcohol and exposed to xenon light (800 watts) for 4 hours duration. Coal slurry is maintained at 8.3%. In spite of this high slurry concentration the photonic advantage is observed to be 16.5%, 22.5%, and 20.5% for water, 1N NaOH, and 95% alcohol, respectively. It may also be noted that coal samples are exposed for 4

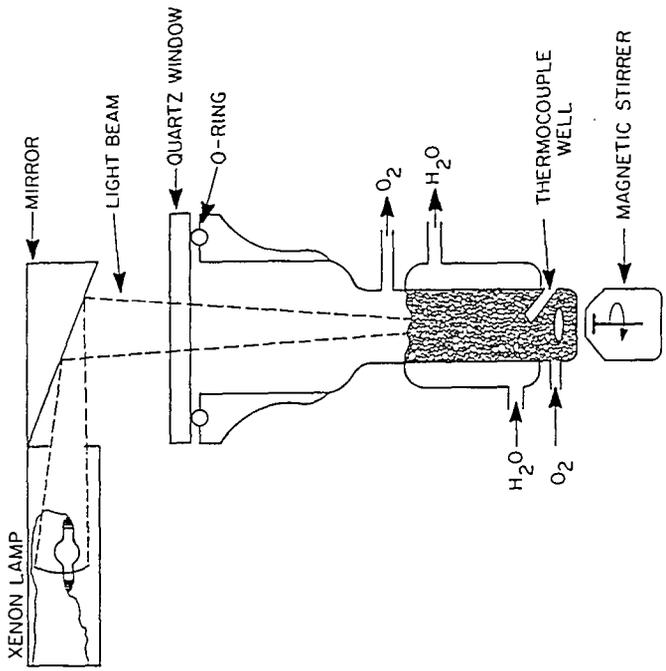


FIG. 1 HIGH INTENSITY PHOTOREACTOR ASSEMBLY

Table I  
Effect of Wavelength on Sulfur Reduction

Parameters	S.N. 1	S.N. 2	S.N. 3	S.N. 4
Coal	Ill#6 Bituminous	Ill#6 Bituminous	Ill#6 Bituminous	Ill#6 Bituminous
Slurry Concentration	2%	2%	2%	2%
Particle Size	44 micron	44 micron	44 micron	44 micron
Solvent	95% ethanol	95% ethanol	95% ethanol	95% ethanol
Reactor	internal	internal	internal	internal
Sensitizer	none	none	none	none
Radiation	300-600nm	254nm	300-600nm	254nm
Light Intensity	450 watts	100 watts	450 watts	100 watts
Reaction Time	16 hr	16 hr	16 hr	16 hr
Hydrolysis Duration	reflux 8 hr	reflux 8 hr	reflux 8 hr	reflux 8 hr
Hydrolysis Medium	water	water	1N NaOH	1N NaOH

% Sulfur Reduction

Dark Hydrolysis	6.1%	6.1%	6.5%	6.5%
Light Hydrolysis	11.5%	41.9%	30.0%	41.8%
Photonic Advantage	5.4%	35.8%	23.5%	35.3%

hours only. An experiment is also conducted with light intensity of 450 watts using the internal photo-reactor (S.N.4) for coal slurry of 8.3% exposed for 4 hours duration. A photonic advantage of only 10% is obtained. An advantage of using high intensity light is clearly observed.

### Conclusions

The results of this study show that there is a reduction in sulfur of about 24% when coal particles are subjected to 300-600nm radiation. It is also observed that coal slurry concentration can be increased and time of photolysis reduced at high intensity light exposure. The use of ultraviolet light (254nm) shows higher sulfur reductions compared to when coal samples are exposed to radiation of wavelength 300-600nm.

### Acknowledgment

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Table III  
Effect of Light Intensity on Sulfur Reduction

Parameters	S.N. 1	S.N. 2	S.N. 3	S.N. 4
Coal	Ill#6 Bituminous	Ill#6 Bituminous	Ill#6 Bituminous	Ill#6 Bituminous
Slurry Concentration	8.3%	8.3%	8.3%	8.3%
Particle Size	44 micron	44 micron	44 micron	44 micron
Solvent	water	1N NaOH	95% ethanol	95% ethanol
Reactor	High Intensity	High Intensity	High Intensity	internal
Sensitizer	none	none	none	none
Radiation	Xenon	Xenon	Xenon	300-600nm
Light Intensity	800 watts	800 watts	800 watts	450 watts
Reaction Time	4 hr	4 hr	4 hr	4 hr
Hydrolysis Conditions	reflux 8 hr	reflux 8 hr	reflux 8 hr	reflux 8 hr
Hydrolysis Medium	1N NaOH	1N NaOH	1N NaOH	1N NaOH

% Sulfur Reduction

Dark Hydrolysis	6.5%	6.5%	6.5%	6.5%
Light Hydrolysis	23.0%	29.0%	27.0%	16.2%
Photonic Advantage	16.5%	22.5%	20.5%	9.7%

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