

# DEVELOPMENT OF AN EFFICIENT COAL DESULFURIZATION PROCESS: "OXY-ALKALINOLYSIS"

Tetsuo Aida, Clifford G. Venier

Ames Laboratory\*, Iowa State University, Ames, IA 50011

Thomas G. Squires  
Advanced Fuel Research, Inc, 87 Church Street  
East Hartford, CT 06108

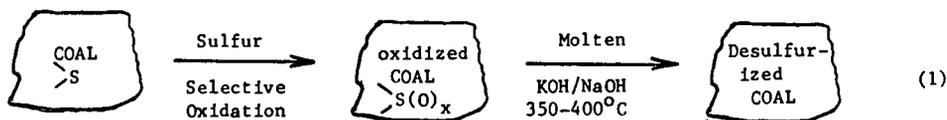
## INTRODUCTION

While it is clear that utilization of coal as an energy source will increase substantially during the next decades, it is equally clear that our present technology will not be able to cope with the environmental threat posed by the potential increase in the emission of sulfur oxides. Specifically, existing precombustion beneficiation procedures are not capable of reducing sulfur concentrations to the necessary levels, and the reliability of postcombustion flue gas desulfurization has yet to be established.

Many physical and chemical desulfurization processes have been developed which effectively remove inorganic sulfur from coal prior to combustion (1); but these techniques have not been effective in removing organic sulfur (1d,2). This is not surprising in view of the well established chemical stability of divalent organic sulfur species (3), such as thiophenols, aryl sulfides, and thiophenes, which are believed to comprise the organic sulfur component of coal.

Although a number of groups have proposed and investigated oxydesulfurization processes (1), their selection of chemical reagents and process conditions for the preferential oxidation of sulfur and for displacement of the oxidatively activated  $\text{SO}_x$  has quite often had little or no basis in the documented chemistry of organic sulfur compounds (3). Not surprisingly, attempts to validate these processes through the use of model compounds and coal extracts have not been successful (2,4).

However, the concept of first oxidizing the sulfur and then exploiting the enhanced chemical reactivity of functionalities such as sulfoxides, sulfones, and sulfonic and sulfinic acids is valid. Here we report our initial attempts to utilize this concept to design a coal desulfurization process. Our approach is based on the facile oxidation of organic sulfur by electrophilic reagents and the long established cleavage of  $\text{C}-\text{S}(\text{O})_x$  bonds by molten alkali. The process is best described as "Oxy-Alkalinolysis" as<sup>x</sup> shown in the following reaction sequence.



\*Operated for the U.S. Department of Energy by Iowa State University under Contract No. W-7405-Eng-82. This research was supported by the Assistant Secretary for Fossil Energy, Office of Coal Mining, WPAS-AA-75-05-05.

## EXPERIMENTAL

### General

The solvents and reagents were obtained from commercial sources and were purified as required by appropriate procedures. Potassium hydroxide, Fischer Certified ACS pellets, was used as received. The Western Kentucky No. 9 coal was from the Ames Coal Library and had been rigorously protected from oxygen during grinding, sizing, riffing, and storing. The samples used had been sized between 60 and 100 US mesh. Elemental analyses were performed by Galbraith Laboratory, Knoxville, TN or by Ames Laboratory Analytical Services.

### Oxidation of Dibenzothiophene with Chlorine in $\text{CH}_2\text{Cl}_2\text{-H}_2\text{O}$

A mixture of 100 mg. of dibenzothiophene, 2.0 ml of water, and 4.0 ml of  $\text{CH}_2\text{Cl}_2$  was stirred in a small flask; and  $\text{Cl}_2$  was bubbled into the mixture for 10 minutes. The residual  $\text{Cl}_2$  and the  $\text{CH}_2\text{Cl}_2$  were then removed under aspiration, and approximately 1.0 ml of saturated  $\text{Na}_2\text{SO}_3$  solution was added. The resulting mixture was then extracted thrice with 7.0 ml of  $\text{CH}_2\text{Cl}_2$ , and the  $\text{CH}_2\text{Cl}_2$  solution was washed with  $\text{NaHCO}_3$  solution. After drying the solution over  $\text{Na}_2\text{SO}_4$ , it was analyzed by gas chromatography using phenyl sulfide as an internal standard.

### Reaction of W. Kentucky No. 9 Coal with Chlorine

A mixture of 3.0 g of W. Kentucky No. 9 coal, 10.0 ml of water, and 20.0 ml of methylene chloride was stirred vigorously at room temperature for one hour while  $\text{Cl}_2$  was bubbled through the mixture. The residual  $\text{Cl}_2$  and the  $\text{CH}_2\text{Cl}_2$  was then removed by aspiration before adding 150 ml of water to the reaction mixture. The resulting slurry was heated to 60°C and maintained at that temperature for 2 hours with occasional shaking. After filtering and washing with fresh water, the coal was dried under vacuum (0.01 mm Hg, 70°C, 2 hours). The coal was analyzed for sulfur and chlorine content.

### Reaction of Model Organic Sulfur Compounds with Molten Potassium Hydroxide

In a typical experiment, 200 mg of KOH and 0.15 mmoles of the organic sulfur compound were sealed in a glass ampoule. The sealed ampoule was then immersed for 10 minutes in a  $\text{KNO}_3$  salt bath at the appropriate temperature (200-350°C). After retrieving the ampoule, it was cooled to room temperature, opened, and the contents were extracted with 5.0 ml of  $\text{CH}_2\text{Cl}_2$ . The residual solid was dissolved in 5.0 ml of water and combined with the  $\text{CH}_2\text{Cl}_2$  solution. Acidification with 6 N  $\text{H}_2\text{SO}_4$  and separation of the layers was followed by extraction of the aqueous layer with two additional portions of  $\text{CH}_2\text{Cl}_2$ . The combined  $\text{CH}_2\text{Cl}_2$  solution was dried over  $\text{Na}_2\text{SO}_4$  and analyzed by gas chromatography, IR, and NMR.

### Reaction of Coals with Molten Potassium Hydroxide

Both the untreated W. Kentucky coal and the coal which had been treated with  $\text{Cl}_2$  were reacted with KOH as follows. A mixture of 500 mg of coal and 15.0 g of KOH were placed in a stainless steel mini-reactor equipped with a  $\text{N}_2$  purge and mechanical stirrer. After purging the apparatus for 15 minutes, the reactor was immersed into a  $\text{KNO}_3$  salt bath at 400°C, and the reaction mixture was stirred for 20 minutes. The molten mixture was removed from the salt bath and quickly poured into a 500 ml Erlenmeyer flask. After cooling, the reactor was rinsed with 100 ml of water which

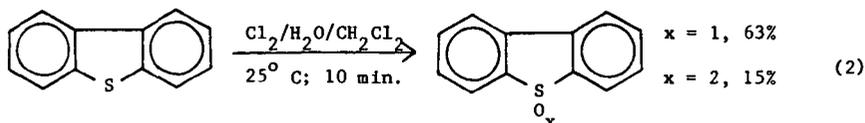
was added to the cooled KOH reaction mixture. The resulting mixture was rendered slightly acidic with concentrated HCl, diluted with 150 ml of water, and warmed to 60°C. This mixture was maintained at 60°C for one hour with occasional shaking. Then the coal was filtered, washed thoroughly with water, and dried under vacuum (0.01 mm Hg, 100°C, overnight). The resulting coaly material was analyzed for sulfur and chlorine.

## RESULTS AND DISCUSSION

### Oxidation of Organic Sulfur

Recently, we established that, using molecular oxygen as the oxidant, the rate of oxidation of organic sulfur in a coal extract is less than the rate of oxidation of the hydrocarbon matrix (5). On the other hand, the reactivity of organic sulfur toward electrophilic oxidants is well known (6) and was the basis for our selection of peroxytrifluoroacetic acid as a reagent for the selective oxidation of organic sulfur in coal (7).

Of the organic sulfur functionalities which have been detected in coal, dibenzothiophene is one of the least reactive toward electrophilic oxidants. However, using chlorine at room temperature, this heteroaromatic sulfur compound was converted rapidly to its oxidized analogs as shown by the following equation.

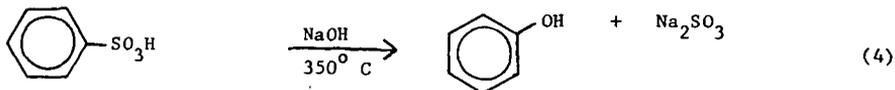
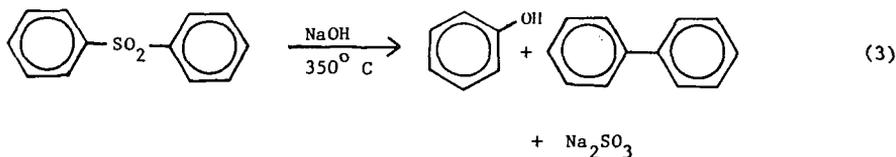


On the basis of this facile reaction, W. Kentucky No. 9 coal in  $\text{CH}_2\text{Cl}_2$ - $\text{H}_2\text{O}$  was treated with chlorine at room temperature for 60 minutes. The sulfur and chlorine analyses before and after treatment are shown in Table I. Even under these mild conditions, substantial amounts of chlorine were incorporated into the coal, probably via electrophilic aromatic substitution. Chlorine incorporation has been reported previously under the more rigorous conditions of the JPL "Chlorinolysis Process" (8) and certainly poses a problem if not removed prior to combustion. It is also, however, a clear indication that chlorine has reacted with the organic matrix; and thus there is presumptive evidence that the organic sulfur has also reacted with the chlorine.

The sulfur reduction in the treated coal accounts for 53% sulfur removal if a correction is made for the increased sample weight due to chlorine incorporation. Within experimental error, this reduction corresponds to complete removal of the pyritic sulfur.

### Reaction of Organic Sulfur Functionalities with Molten Potassium Hydroxide

The enhanced reactivity of oxidized sulfur functionalities such as sulfones and sulfonic and sulfinic acids toward molten alkali has been known for over a century (9,10,11). As shown in equations (3) and (4), these reactions



are ideal for the chemical desulfurization of coal because carbon-sulfur bond breaking occurs rapidly under reasonably mild conditions to generate a water soluble sulfur product, and the alkali reagent is cheap.

The initial model compound experiments which are reported here were designed to gain a qualitative measure of the relative reactivity of selected organic sulfur functional groups; these results are reported in Table II. From these results, it is clear that, in general, oxidized sulfur functions are substantially more reactive toward molten KOH than the reduced, divalent sulfur species. Benzyl phenyl sulfide is an obvious exception to this observation. However, the carbon-sulfur bond in this system is exceptionally susceptible to cleavage by several mechanisms, and, in fact, has been demonstrated to be quite reactive under the much milder conditions of the Ames Process (5).

On the basis of the enhanced reactivity of the oxidized organic sulfur forms and on the assumption that the organic sulfur in W. Kentucky No. 9 coal was oxidized by treatment with  $\text{Cl}_2$ , the raw coal and the  $\text{Cl}_2$ -treated coal were stirred under  $\text{N}_2$  with KOH at  $400^\circ\text{C}$  for 20 minutes. A comparison of the sulfur and chlorine contents of the starting materials and products from these experiments is presented in Table I. The substantially lower sulfur content of the  $\text{Cl}_2$ -treated coal is entirely consistent with the chemical concepts which were developed as a basis for this new desulfurization method.

Treatment of raw coal with  $\text{Cl}_2$  is the basis of the JPL "Chlorinolysis Process" (8), and treatment of coal with molten caustic is the basis of the TRW "Gravimelt Process" (12). In Figure 1 the efficiency of these processes is contrasted with that of the "Oxy-Alkalinolysis Process". Clearly, the latter process (88% total sulfur removal) represents a very significant improvement over both the JPL process (53% sulfur removal) and the TRW process (62% sulfur removal). Furthermore, at this time, we have investigated only the chemistry of the "Oxy-Alkalinolysis Process"; no effort has been directed toward optimization of the process.

Finally, it is noteworthy (though not surprising) that the chlorine content of the "Oxy-Alkalinolysis" product is the same as that of the original coal. Treatment of chlorinated coal with molten KOH is a very effective method for removing chlorine from aromatic systems and is, in fact, analogous to the industrial preparation of phenol from chlorobenzene.

### CONCLUSIONS

Our conclusions from this investigation are the following:

1. This desulfurization method was developed on the basis of the demonstrated chemistry of organic sulfur functionalities.
2. Organic sulfur in coal can be activated with  $\text{Cl}_2$  for removal by molten KOH, probably through electrophilic oxidation.
3. "Oxy-Alkalinolysis" is a method for "deep cleaning" of coal, i.e. efficient removal of organic sulfur, under mild conditions.
4. Residual chlorine can be removed from coal with molten KOH.

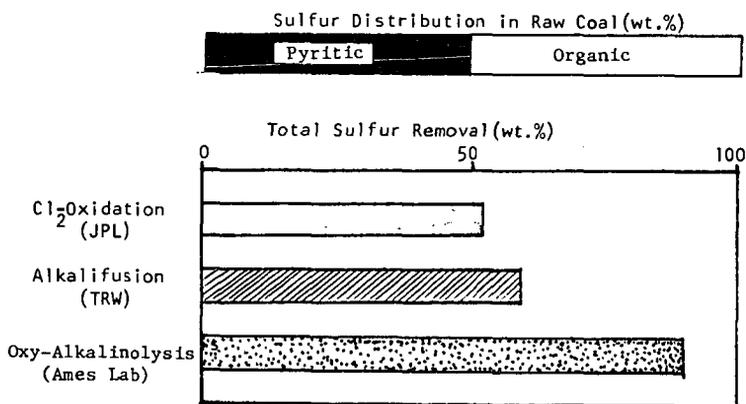


Figure 1. Comparison of Desulfurization Processes for W. Kentucky No. 9 Coal.

## REFERENCES

1. For general references on coal desulfurization prior to combustion see:
  - a) Wheelock, T.D., ed., Coal Desulfurization, A.C.S. Symposium Series, 1977, 64.
  - b) Meyers, R.A., Coal Desulfurization, Marcel Dekker, Inc., New York, 1977.
  - c) Eliot, R.C. ed., Coal Desulfurization Prior to Combustion, Noyes Data Corporation, Park Ridge, N.J., 1978.
  - d) Morrison, G.F., Chemical Desulphurization of Coal, IEA Coal Research Report No. ICTIS/TR15, London, 1981.
2. a) Squires, T.G., et al., An Evaluation of the Chemistry of Coal Desulfurization, Proceedings of the International Conference on Coal Science, Dusseldorf, W. Germany, 1981, 169.  
b) Warzinski, R.P., et al., Air/Water Oxydesulfurization of Coal-Laboratory Investigation, Pittsburgh Energy Technology Center Report, Pittsburgh, August 1978, 120 pp.
3. Oae, S., ed., Organic Chemistry of Sulfur, Plenum Press, New York, 1977.
4. Warzinski, R.P., LaCount, R.B., Friedman, S., Ruether, J.A., Oxydesulfurization of Coal and Sulfur-Containing Compounds, Paper presented at AIChE Meeting Chicago, November, 1980.
5. Squires, T.G., et al., ACS Fuel Div. Preprints, 1981, 26 (1), 50.
6. Plesnicar, B. in Trahanovsky, W.S., Oxidation in Organic Chemistry, Part C, Academic Press, New York, 1978, Chapter 3, especially pp 280 ff.
7. Venier, C.G., et al., ACS Fuel Div. Preprints, 1981, 26 (1), 20.
8. Kalvinskas, J. et al., Coal Desulfurization by Low Temperature Chlorinolysis, JPL Final Report, January 15, 1980.
9. a) Otto, R., Chem. Ber., 1886, 19, 2425.  
b) Otto, R., Ann., 1868, 145, 322.
10. Wurtz, C., Ann., 1867, 144, 121.
11. Kekule, A., Compt. rend., 1866, 64, 753.
12. Meyers, R.A., Laboratory Study for Remodel of Organic Sulfur from Coal TRW Final Report, July 1, 1981.

TABLE I

EFFECT OF TREATMENTS ON SULFUR AND CHLORINE CONTENT OF W. KENTUCKY NO. 9 COAL

Sample Description	Total S (WT %)	Pyritic S (WT %)	Organic S (WT %)	Chlorine (WT %)
Raw Coal	3.47	1.68	1.77	0.03
Coal/Cl <sub>2</sub>	2.33	-	-	25.65
Coal/KOH	1.30	-	-	-
Coal/Cl <sub>2</sub> /KOH	0.42	-	-	0.03

TABLE II

REACTIVITY OF ORGANIC SULFUR COMPOUNDS WITH POTASSIUM HYDROXIDE

Compound	Recovered Starting Material at Indicated Condition (%)		
	200°C, 10 min.	250°C, 10min	350°C, 10 min
Dibenzothiophene	100	100	100
Phenyl Sulfide	-	-	100
Phenyl benzyl sulfide	-	-	0
Dibenzothiophene-5-oxide	-	24	0
Dibenzothiophene-5, 5-dioxide	88	22	0
Thiophenol	-	-	100
2-Phenylbenzenesulfonic Acid	-	98 <sup>a</sup>	12 <sup>a</sup>

a. Maximum value based on quantitative analysis of 2-phenylphenol product.