

OXIDATIVE DESULFURIZATION OF COAL

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INTRODUCTION

It is becoming increasingly apparent that the solution to our national energy problems will require a variety of approaches, and that these must be compatible with environmental restrictions. Coal, only recently considered destined for obscurity, has been rescued by a combination of international political events and increasing difficulties in developing a nuclear power industry. Although coal as an energy source presents problems, at least it is available and can be utilized.

The Federal Government, as part of the program administered by the Energy Research and Development Administration, is carrying out research on many phases of coal utilization to overcome the environmental problems involved in the combustion of coal. One such project, which has been in progress at the Pittsburgh Energy Research Center since 1970, is concerned with chemical beneficiation of coal, and most specifically, with removal of sulfur from coal prior to combustion.

EXPERIMENTAL

Batch Experiments. Thirty-five grams of -200 mesh coal and 100 ml of water were placed in a liner (glass or teflon) in a 1-liter, magnetically stirred, stainless steel autoclave. The autoclave was pressurized with air (from a cylinder) to the required gauge pressure, and then heated with stirring until the specified temperature was reached (approximately 1 hour heat-up time). After a specified time at reaction temperature, the autoclave was cooled by means of an internal cooling coil. The contents were removed at room temperature, filtered, washed until the pH of the filtrate was neutral, and then extracted in a Soxhlet thimble with water until sulfate (present as CaSO_4) was no longer present in the fresh extract. The coal was then thoroughly dried in a vacuum oven at 100°C and analyzed by the Coal Analysis Section, U. S. Bureau of Mines.

Semicontinuous Experiments. Using a similar autoclave fitted with pressure regulating valves, the autoclave containing the coal and water was heated to the specified temperature under one atmosphere (initial pressure) of N_2 . At temperature, or shortly before reaching it, air was admitted to the desired pressure. Temperature was kept at the required value by using heating and cooling (cooling coil) while air (approximately $2 \text{ ft}^3/\text{hr}$) flowed through the autoclave. After the required time at temperature, the autoclave was cooled, and the products worked up as in the previous example.

RESULTS AND DISCUSSION

Although the project was initially divided into removal of organic and of inorganic sulfur (1), it was soon evident that, though one could remove pyritic sulfur without removing organic sulfur, the reverse was not true. Any process which removed organic sulfur would also remove pyritic sulfur. So the approach to the problem became one of finding chemistry suitable for removing organic sulfur from coal.

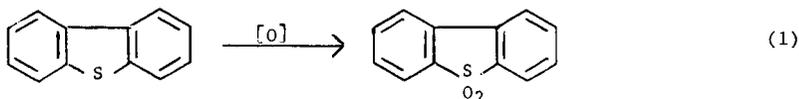
The chemistry which we chose to explore was based on two premises:

1. The major portion of the organic sulfur in coal was of the dibenzothiophene (DBT) type, and,
2. The reagents had to be inexpensive.

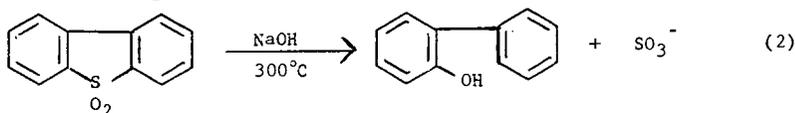
While we now believe that at least a sizable fraction of the organic sulfur in coal is not dibenzothiophenic, we have no reason to doubt that over 50% of it may be.

These premises led us to the following hypothetical two-step removal of organic sulfur from coal.

1. Oxidation of organic (or dibenzothiophenic) sulfur to sulfone.



2. Elimination of the SO_2 from sulfone by base.



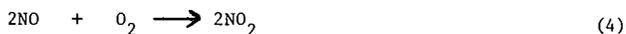
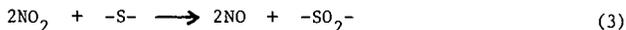
Both of these reactions are in the literature, and so our task became one of modifying and improving them so that they could be applied to desulfurization of coal.

The second step -- the removal of SO_2 from DBT sulfone by base -- was found to be essentially quantitative when the sulfone was heated to 300°C in the presence of aqueous NaOH and nearly as efficient with Na_2CO_3 . This was an improvement on the nonaqueous treatment (2).

The first step in the reaction -- oxidation to sulfone -- though extensively documented in the literature, presented more of a challenge. There are numerous oxidants reported which can effect the conversion of organosulfur compounds to sulfones, including KMnO_4 , HNO_3 , CrO_3 , $\text{H}_2\text{O}_2/\text{HOAc}$, and hydroperoxides (3). These obviously do not fit the second premise -- the reagents must be inexpensive. It was agreed that the only reagent which could be used as an oxidant was the oxygen in air. But DBT, and presumably the organic sulfur in coal, is inert to air at relatively high pressure and temperature. Transfer of oxygen to a carrier to form a hydroperoxide, followed by reaction of the hydroperoxide with DBT, did give sulfone. We found that with a large variety of hydrocarbons, such as tetralin, decalin, and cyclohexane, merely heating DBT with air under pressure in the presence of the hydrocarbon resulted in formation of sulfone (4), presumably as a result of in situ formation of hydroperoxides. Benzene, which does not form a hydroperoxide, affords no sulfone formation under comparable conditions.

Applying our two-step reaction -- air oxidation followed by treatment with aqueous base -- to coal, we were able to achieve up to 50% removal of organic sulfur, as well as almost complete elimination of pyritic sulfur as a bonus. Though this scheme appeared promising, it did require a suitable organic liquid and also NaOH .

We also explored another oxidation system which utilizes air as the ultimate source of oxygen. Nitrogen dioxide -- NO_2 -- is a good reagent for converting sulfides to sulfones, and it can be utilized in an easily regenerable system.



We found that we could, indeed, oxidize DBT to its sulfone in this manner, using NO_2 and air. When the reaction was extended to coal, however, a significant amount of concurrent reaction took place, including nitration of the coal, which consumed the nitrogen oxides and thus would have necessitated a continuous addition of NO_2 rather than the recycling shown in Equations 3 and 4.

In the meantime, our experiments on air oxidations of organosulfur using hydroperoxide precursors led us to the ultimate experiment, the one in which H_2O was used in place of an organic liquid phase. This reaction of coal with steam and compressed air almost quantitatively converted the pyritic sulfur in coal to H_2SO_4 . In addition, we found that we had also removed 25% of the organic sulfur as well. Here was evidence that there was some organosulfur in coal which was not DBT-like, since DBT failed to react with air and water under these conditions.

Initial experiments on the air-steam oxydesulfurization of coal were carried out using a batch, stirred autoclave system. In this apparatus in order to replace oxygen as it was used, it was necessary to cool the autoclave to near room temperature, vent the spent air, repressure, and reheat. Though this gave satisfactory desulfurization, it was an impractical approach for studying reaction parameters. The results cited in Tables 1-3 are from batch studies without repressurization and thus represent less than maximum desulfurization in some cases.

The apparatus was modified to allow air to flow through the stirred reactor while the coal-water slurry remained as a batch reactant. This is our current system. In this way, we can study many of the variables as they will affect the reaction in a continuous system.

Our newest apparatus, now beginning operation, is a fully continuous unit, feeding both air and coal-water slurry into a reactor tube. This system is designed to obtain data on reaction rates, develop information for economic evaluation, and answer those questions which arise concerning engineering aspects of the process.

Heating high-pyrite coals in aqueous slurry with compressed air at total pressure of 1,000 psi and at 150-160°C results in decrease of pyritic sulfur to near the lower limit of detection by standard analytical procedure. Some results of 1-hour batch experiments are shown in Table 1. The sulfur which is removed is converted completely to aqueous sulfuric acid. Experiments in a semicontinuous experiment show as much as 80% of the reaction occurs within the first 5 minutes. At a pressure of 200 psi, the reaction is much slower, requiring several hours to achieve even 60% pyritic sulfur removal. For some coals, at least, the desulfurization is almost as rapid at 500 psi as at 1,000 psi. The oxidation of pyritic sulfur is temperature dependent, but at the conditions of our experiments, reaction is sufficiently fast that above 150°C little improvement is noted. In a few cases, where a coal appears to have some residual pyrite which is not oxidized readily at 150°C, it may be removed at 180°C.

As the temperature at which the oxidation is conducted is increased above 150°C, an increasing amount of organic sulfur is removed from the coal. Although the percentage of organic sulfur removed parallels the temperature rise, so does the amount of coal which is oxidized. To prevent excessive loss of coal a practical limit of 200°C has been chosen for carrying out the reaction on most coals. Removal of organic sulfur from a series of coals, shown in Table 2, varies from 20 to over 40%. Further reduction of organic sulfur content is probably possible with some of these coals without sacrifice of coal recoverability.

An upper limit on organic sulfur removal appears to be between 40 and 50%, and varies from coal to coal. We believe this is due to the functionality of the organic sulfur, and gives some rough measure of oxidation resistant, or DBT type, of sulfur. Obviously, that sulfur which is removed by oxydesulfurization must be in some other structure which is readily oxidized, such as thiol, sulfide, and/or disulfide. These values coincide with removal of sulfur from coal observed when it is heated with aqueous alkali at 300°C, a reagent which does not attack DBT (5,6).

Even at 150-160°C many coals, including some with rather high sulfur contents, can be dramatically desulfurized, as shown in Table 3.

TABLE 1. Pyrite Removal from Representative Coals by Oxydesulfurization

Seam	State	Temp, °C	Pyritic sulfur, wt pct	
			Untreated	Treated
Illinois No. 5	Illinois	150	0.9	0.1
Minshall	Indiana	150	4.2	0.2
Lovilia No. 4	Iowa	150	4.0	0.3
Pittsburgh	Ohio	160	2.8	0.2
Lower Freeport	Pennsylvania	160	2.4	0.1
Brookville	Pennsylvania	180	3.1	0.1

TABLE 2. Organic Sulfur Removal from Representative Coals by Oxydesulfurization

Seam	State	Temp °C	Organic sulfur, wt pct	
			Untreated	Treated
Bevier	Kansas	150	2.0	1.6
Mammoth ^a	Montana	150	0.5	0.4
Wyoming No. 9 ^a	Wyoming	150	1.1	0.8
Pittsburgh	Ohio	180	1.5	0.8
Lower Freeport	Pennsylvania	180	1.0	0.8
Illinois No. 6	Illinois	200	2.3	1.3
Minshall	Indiana	200	1.5	1.2

^a Subbituminous

TABLE 3. Oxydesulfurization of Representative Coals

Seam	State	Temp, °C	Total sulfur, wt pct		Sulfur, lb/10 ⁶ Btu	
			Untreated	Treated	Untreated	Treated
Minshall	Indiana	150	5.7	2.0	4.99	1.81
Illinois No. 5	Illinois	150	3.3	2.0	2.64	1.75
Lovilia No. 4	Iowa	150	5.9	1.4	5.38	1.42
Mammoth ^a	Montana	150	1.1	0.6	0.91	0.52
Pittsburgh	Pennsylvania	150	1.3	0.8	0.92	0.60
Wyoming No. 9 ^a	Wyoming	150	1.8	0.9	1.41	0.78
Pittsburgh	Ohio	160	3.0	1.4	2.34	1.15
Upper Freeport	Pennsylvania	160	2.1	0.9	1.89	0.80

^a Subbituminous

The reaction conditions which we have found to be suitable for oxydesulfurization are:

- Temperature - between 150° and 220° C.
- Pressure - between 220 and 1,500 psi operating pressure.
- Residence time - 1 hour or less.

Most of our experiments have been carried out below 220°C and at approximately 1,000 psi. Recoveries of fuel values are excellent, being generally 90% or better. The only byproduct of the reaction is dilute H_2SO_4 . This can be recycled with no observable effect on desulfurization for at least 5 cycles. When the H_2SO_4 becomes too concentrated for further use, it can be converted to a commercial grade of sulfuric acid if a suitable, economic market exists, or it can be disposed of by limestone neutralization as a readily filterable $CaSO_4$.

The process, outlined in Figure 1, needs no novel technology to produce coal having over 95% of its pyritic sulfur and as much as 40% of its organic sulfur removed. Other than the coal, air, and water, the only other material needed for the process is the limestone used to neutralize the H_2SO_4 . No sludge is formed, much of the water can be recycled, and the only waste product is solid $CaSO_4$ (7).

A preliminary cost estimate for this process indicates a cost of \$3.50 to \$5.00 per ton. Even at twice this cost, the process would still be considerably less expensive than coal conversion to gas or liquid fuel. Assuming removal of 95% pyritic sulfur and 40% organic sulfur, an estimated 40% of the coal mined in the eastern United States could be made environmentally acceptable as boiler fuel, according to EPA standards for new installations. And the sulfur content of the remainder of the eastern coal could be drastically reduced, making it environmentally acceptable for existing boilers.

CONCLUSIONS

Treatment of coal with compressed air and steam at 150°-200°C represents a practical method to desulfurize to acceptable levels a sizable percentage of the available coal in the eastern United States at a cost in money and fuel value less than coal conversion and to an extent greater than can be achieved by physical depyriting methods.

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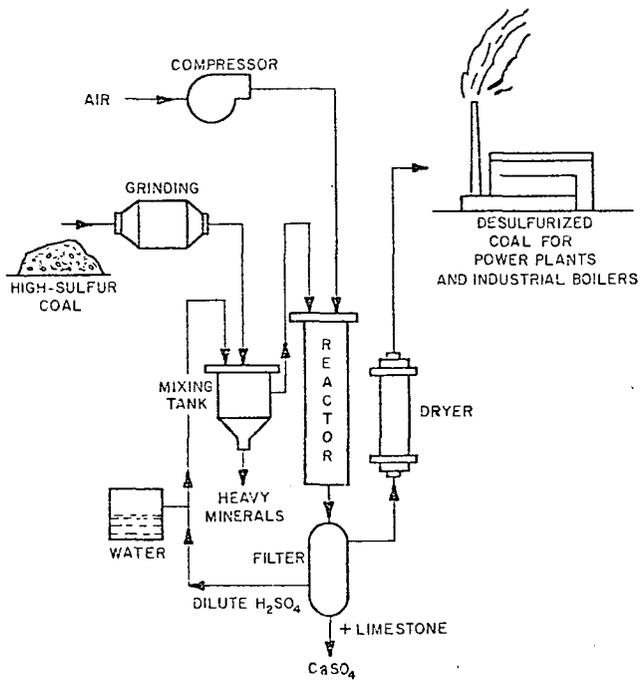


Figure 1 - Air-steam coal desulfurization process.