

PROGRESS TOWARD THE DESULFURIZATION OF ORGANIC COAL MOLECULES

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Introduction

The broad occurrence of sulfur in coal greatly reduces its economic potential, and it is well recognized that the selective removal of the sulfur that is covalently bonded in organic coal molecules constitutes the key challenge for technology. This brief article concerns the character of the organic sulfur compounds, and strategies for the removal of these substances.

The Organic Sulfur Compounds in Bituminous Coals

There is general agreement (1,2) that sulfur was introduced into coal through secondary reactions of the organic plant materials with inorganic sulfur compounds, and that these substances, which were produced by the microbiological reduction of sulfate ions, reacted with coal precursors in a variety of chemical processes including ionic and free radical substitution and addition reactions. Virtually every model compound experiment that has been performed between a plausible sulfur reagent and an organic substrate has successfully introduced sulfur into the organic matrix. Inasmuch as the natural processes occurred in a variety of different environments, the exact reaction pathways are difficult to define. However, it is evident that the amount of sulfur introduced into the coal precursors and retained in the coal varies significantly.

It has been recognized for a long time that heterocyclic sulfur compounds including thiophenes, benzothiophenes, dibenzothiophenes and other heterocycles and their alkylated derivatives, particularly the methylated compounds, are present in fossil fuels. In addition, many kerogens and the less mature coals have considerable amounts of aliphatic sulfur compounds. Although some workers in this field have been rather slow to accept this view, previous investigations by Attar (3), and Calkins (4) and the recent work of de Leeuw and his coworkers (5,6) on kerogens, and also of Gorbaty (7,8), and Huffman (9,10) and their coworkers on coals has demonstrated that these aliphatic materials are clearly present. Indeed, the aliphatic sulfidic sulfur content of the Argonne Premium Coal Samples increases systematically and the thiophenic sulfur content decreases systematically as the maturity of the coal decreases. The Argonne Premium Sample of lignite contains 30 to 40% aliphatic sulfidic sulfur, but the low volatile, much higher ranking bituminous coal sample contains only 3 to 15% aliphatic sulfidic sulfur (7,8,9,10). Presumably, natural thermal and hydrolytic processes convert the aliphatic sulfur compounds into thiophenic derivatives as the coals mature. The X-ray work and even more recent mass spectroscopic investigations are in good accord with the view that rather high levels of sulfidic sulfur can exist in low rank American coals (7-10,11).

Even more important Winans and White and their associates (11,12,13) have shown that many American coals and high sulfur, low rank coals from Europe such as the Rasa subbituminous coal examined by White and his research group (13) have many molecules with more than one heteroatom. This feature of the chemistry is especially relevant in desulfurization reactions when it is coupled with the concept that these lower ranking coals appear to be dominated by molecules with only one, two, and three rings (14).

In summary, the sulfur rich subbituminous and bituminous coals, of which the coals of the Illinois Basin are often described as representative, are heteroatom rich substances with a broad variety of sulfur compounds bonded to sp^3 as well as to sp^2 carbon atoms and many of the molecules that contain sulfur also contain oxygen atoms. Unfortunately, virtually all of the work on compound speciation has been qualitative, the few quantitative investigations (15) indicate that only a very small fraction of the organic sulfur compounds have actually been defined.

Desulfurization Methods

New methods of the desulfurization of solid coals have been investigated in several laboratories. This work on coal contrasts with the generally well known strategies for the desulfurization of fossil petroleum materials. Molecules that are freely soluble in oils can generally be desulfurized through catalytic hydrogenation reactions involving catalysts that are based upon molybdenum sulfide (16). This chemistry is illustrated by the coprocessing of subbituminous and bituminous coals with petroleum resids. These catalytic reactions enable high coal and asphaltene conversions with the formation of pentane-soluble products in good yield (17). The pentane-soluble oils that are produced in these reactions are virtually free of oxygen, and have rather low concentrations of sulfur and nitrogen. Specifically, the coprocessing of Illinois No. 6 coal and Lloydminster resid provides a product spectrum in which 80% of the sulfur atoms and 40% of the nitrogen atoms have been removed; the oil that is produced contains 1.2% sulfur and 0.4% nitrogen compared to more than 4% sulfur in the resid and coal that were used as the starting fossil materials (17).

An array of other chemical strategies have been studied for the elimination of the organic sulfur from solid coal. Vigorous basic hydrolysis with molten hydroxides has been investigated in some detail (18). The approach requires very severe conditions for effective organic desulfurization, and as a consequence, many workers in the field have sought much lower severity reactions that might accomplish the goal of selective sulfur elimination without comprising the carbon content of the coal or the heat value of the product. One of the key problems that emerged in the early investigations was the fact that of pyritic, organic, and elemental sulfur simultaneously occur in coals that have been exposed to the atmosphere. The elemental sulfur arises from the air oxidation of pyrite and may be reported as organic sulfur as a consequence of the usual analytical scheme. Unfortunately, this complexity can lead to some confusion in the assessment of desulfurization strategies. One solution to this problem is the removal of pyrite and elemental sulfur from samples prior to research on organic desulfurization. Both oxidative and reductive procedures are available. We found that the reaction with lithium aluminum hydride, was convenient, quantitative, and, more important, was essentially free of byproduct formation (19). It is much easier to interpret the results of desulfurization experiments when these pyrite-free coals or other very low pyrite macerals or kerogens are used as the starting materials.

Our research for new approaches for selective organic desulfurization has been successful, and the primary goal has been realized in principal, but the chemistry cannot as yet be practically applied.

It seems pertinent to mention some of the strategies that have been considered. Acid-promoted hydrolysis reactions have received some attention. In one approach, we attempted to intercept and selectively to hydrolyze hemithioacetal intermediates, but the experiments with coals yielded discouraging results (20). We also examined thermal methods and thermal methods coupled with sulfur capture by metals as well as strategies based on organonickel compounds.

However, we placed most of our effort on single electron transfer reactions. Our ideas were based on the concept that the carbon-sulfur bond strengths in anion radicals would be greatly diminished when these substances were reduced to anion radicals, and on the fact, which has been known for many years, that single electron transfer reactions can eliminate sulfur from heterocyclic and aromatic molecules under quite mild reaction conditions. Investigations of these single electron transfer reactions for pure compounds and representative bituminous coal have been very encouraging and some coals can be almost completely desulfurized in such reactions (21,22). For example, the sulfur content of pyrite-free Illinois No. 6 coal could be reduced by SET chemistry to about 1.1% sulfur under quite mild conditions (21,22).

The study revealed that some sulfidic sulfur compounds in the Illinois coals resisted desulfurization by this SET strategy (22). We then considered the use of strong bases which might be more effective for aliphatic desulfurization (23), even though they are not usually effective for the removal of heterocyclic molecules. These basic reactions had to be carried out near 100°C, and the Illinois coals experienced extensive desulfurization. When the SET and base reactions were carried out sequentially, the organic sulfur content was reduced to about 0.7 wt%. Subsequent work has demonstrated that the remaining sulfur compounds have fragile carbon-sulfur bonds that are readily cleaved. Thus, we have demonstrated that chemical reagents can quite selectively remove or alter the properties of the organic sulfur compounds in coal under rather mild conditions and that these reactions can be performed without detrimental losses of material or heat content. The technological challenge remains to implement this chemistry by practical means.

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