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Project Title: Extraction, Separation, and Analysis of High Sulfur Coal

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Technical Progress Report: 14

Reporting Period: Oct 16, 1990 to January 15, 1991

Technical Progress Report:

Work advanced this quarter in both the two major areas of coal desulfurization that we are considering. The reactive oxidation chemistry will be discussed first. As described in the previous report the reaction of cupric chloride with coal under aqueous conditions did not produce high desulfurization yields until the reaction conditions were quite strenuous. Then while the coal was further desulfurized the remaining coal solid was also chlorinated.

I. Oxidative Desulfurization Process

As mentioned in the previous report, an alternate plan of attack was to try to oxidize the sulfur in coal in a nonaqueous solvent, such as DMF. Copper oxidation reactions are known to have much greater reaction rates in apolar solvents such as DMF.

In this experiment the reaction solvent was 50% v/v H₂O-DMF with 14% CuCl₂ dissolved in it. The coal sample used was Illinois #6. The reaction temperature used was 95 °C and the reaction time was 17 hrs. The remaining coal solid was then sent to Blackrock Test Labs, Morgantown, WV for analysis of sulfur in the extracted coal sample.

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The original sample of Illinois #6 has 4.83% total sulfur content, of which, 2.81% was pyrite, 0.01% was sulfate and 2.01% was organosulfur species with 14.25 % ash. The results obtained from Blackrock show that total sulfur content after reaction was 1.75% of which 0.54% was pyrite, 0.20% was sulfate and 1.01 % was organic sulfur with an ash content of 25%. This reaction shows considerable promise in that approximately 50% of the organosulfur type compounds were eliminated along with similar proportions of pyrite. The resulting ash content is still too high. The major contribution to the ash content is not destroyed coal but inorganic copper salts. We have yet to determine the specific nature of these salts but for this to be a viable technique these inorganic species must stay in solution rather than precipitating out onto the coal.

-11% ash
if not destroyed

What is
R+N
analysis

The required stoichiometry of the oxidation reaction also has not been determined yet. The quantity of copper salt in solution was kept high to force the reaction to completion.

Plans For Next Quarter's Activities on This Project.

Now that there is clear evidence that in an aprotic solvent the desulfurization reaction does work. We will optimize the reaction conditions to minimize the quantity of ash produced and also minimize the quantity of reagents used in the reaction. The above type of reaction chemistry will be repeated. The extract solutions will be separated by SFC/MS and also analyzed for extracted sulfur species using the Siever's Sulfur Chemiluminescence Detector. This type of reaction chemistry also shows great promise as being extendable to supercritical fluid solvents. However, we will need the next quarter to nail down more of the appropriate reaction conditions.

or not

II. Desulfurization Process Using Selective Solvation

The SFC/MS was not functioning well during this quarter. Therefore large scale extractions of coal under conditions thought to be optimum from the model coal compound studies were done. These extractions used (7 grams) of coal in a 300 ml extraction cell using the 400 °C and 3500 psi extraction condition. The percent of solid coal remaining was 65.2%. The resultant coal sample was then sent to Black Rock testing Laboratory for analysis. The following results were obtained.

35% coal loss

Coal Composition Before	Coal Composition After
Reaction	Reaction
4.83% Total Sulfur	3.46% Total Sulfur $\times 35\% = 4.6\%$ (close)
2.81% Pyrite	0.51% Pyrite
0.01% Sulfate	0.01% Sulfate
2.01% Organic Sulfur	2.94% Organic Sulfur (PYRRHOTITE FORMED?) OR ORG S CONCENT.
14.25% Ash	20.88% Ash (ASH CONCENTRATED?)

As we discussed over the phone the "measured" increase in the organic coal may be formation of a different form of pyrite rather than an actual increase in the amount of organosulfur species in the coal. However, the presence of pyrite in the coal before this reaction may also be causing a serious problem with respect to desulfurization chemistry. Therefore the next step in this study is to first remove the pyrite and then repeat analysis. Also one other interesting piece of

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information should be reported. In the ethanol extracts a monolayer oil film formed on the solvent surface. This film had incredible "easily observable" structure with repeating units of hexagons that were macroscopic in dimension with the entire film have a spans of 2-3 inches.

Plans For Next Quarter's Activities on This Project.

In the next quarter the collected extracts will be analyzed using the chemiluminescence detector and the SFC/MS. New extractions will be done with the pyrite being remove with dilute HNO_3 first. Also the compound that formed the film on the top of the ethanol extract will be identified.

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