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Technical Progress Report:

The work completed this past quarter has centered around the further study and characterization of the selective desulfurization of coal through the oxidative interaction of aqueous copper chloride. A comprehensive study of this reaction has been completed this past quarter as well as a preliminary reaction with an Illinois #6 coal sample.

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SUMMARY: REACTION OF CUPRIC CHLORIDE WITH MODEL COAL COMPOUNDS

Experimental

The last quarterly report described the initial quantitative analysis of the aqueous cupric chloride reaction with the model coal compounds. This report concludes that work. The model compounds examined and their structures are listed on page 8 of this report. The Illinois #6 coal was obtained from Argonne National Labs. A brief review of the experimental design is described below.

Model Coal Compound Study: A 1 mL solution of 50 % (wt/wt) CuCl_2 is combined with approximately 0.02 grams of the model coal compound in a pyrex reaction vessel. The reaction of the CuCl_2 with the particular model compounds is conducted at a series of reaction times and reaction temperatures. The reaction times studied were 1, 3, 6, 12, and 24 hours. The reaction temperatures studied were 50, 130, 210, and 295°C. After the reaction, the organic compounds were extracted with a 3 mL aliquot of methylene chloride (CH_2Cl_2). These products were then analyzed via GC/IRD/MS and SFC/SCD (sulfur chemiluminescence detector). The aqueous fraction collected was analyzed using ion chromatography to determine the presence of sulfate ions. In addition, there were several samples which produced an insoluble product. This product will be characterized via FT-IR analysis.

Coal Reaction Study: Approximately 5.5 grams of Illinois #6 coal was reacted with 250 mLs of a 50% (wt/wt) solution of CuCl_2 and water. The reaction vessel was a 300 mL stainless steel autoclave. The vessel was resistively heated and the temperature monitored with a thermocouple. Stirring was achieved through the use of an air-driven magnetic stirrer. Reaction

time was 6 hours held at a reaction temperature of 210°C. The organic products of the reaction were extracted with methylene chloride and analyzed via GC/IRD/MS. The aqueous layer was analyzed via ion chromatography to determine amount of sulfate produced. The resulting coal was sent to Black Rock Test Labs (Morgantown, WV) for analysis of; Ash, Sulfur (and all its forms), and chlorine.

Results and Discussion

Model Coal Compounds: The results of the work on the model coal compounds is shown on pages 9-20. In addition to the graphical results shown, there are several results that are not presented in graphical form. First, at 50°C, only four (4) compounds reacted at all. The results from two of these, tetrahydrothiophene (cmpd #1) and methyl p-tolyl sulfide (cmpd #4), are shown. The other two compounds that reacted were cyclohexyl mercaptan (cmpd #2) and thiophenol (cmpd #3). These species immediately reacted with the CuCl_2 to form the disulfide. That is, the thiophenol immediately reacted to form phenyl disulfide (cmpd #8) and cyclohexyl mercaptan reacted to form its disulfide. At 130°C, in addition to these compounds reacting, reactions were also detected for phenyl sulfide (cmpd #6) and benzo[b]thiophene (cmpd #5). The results of these reactions are shown on pages 9-12. Evaluating these results, several points can be made.

- 1) The sulfur-hydrogen bond was easily broken and converted to a disulfide linkage in the presence of CuCl_2 .
- 2) The sulfur-carbon bond is relatively reactive when part of a small, non-aromatic ring structure. However, when the sulfur is part of an aromatic ring structure, the additional stabilization provided by the aromaticity, prevents oxidative reaction. This explains why the dibenzothiophene (cmpd #7) does not react at the lower temperatures. It also explains why the reaction of benzo[b]thiophene (cmpd #5) is not an oxidative reaction with the sulfur, but rather is a chlorinolysis reaction where chlorine is substituted on the aromatic ring.
- 3) The sulfur-carbon bond, when the carbon is part of an aromatic ring structure, but the sulfur is not, is less reactive than the aliphatic sulfur-carbon bond. This may be due to two possibilities. First, the additional stabilization provided by the aromatic ring increases the bond strength enough so that the reaction is no longer favored. Second, the presence of large aromatic ring structures near the sulfur atom could pose a steric hinderance problem in that the reactant does not get to the sulfur-carbon bond. Both of these points may help to provide an explanation as to why methyl p-tolyl sulfide (cmpd #4) is more reactive than phenyl sulfide (cmpd #6).
- 4) The results at lower temperatures indicated that the extent of desulfurization is

much too low.

The reactions were then run at higher temperatures (210°C and 295°C) to see if the extent of desulfurization could be increased for the compounds that reacted at the lower temperatures and could be achieved for the compounds that hadn't reacted at all. A representative sampling of the graphical results obtained at 210°C is presented on pages 13-19. These plots show the amount of organosulfur compound, the amount of chlorinated organic compound, and the amount of pure organic (hydrocarbon) compound present as products in the methylene chloride extract. Although these results demonstrate a high percentage of organic desulfurization of the model compounds, they unfortunately demonstrate a large amount of chlorinolysis occurring. In addition, further work, both by our group and others, has demonstrated that a large fraction of the desulfurization is occurring through the chlorinolysis pathway rather than the oxidative reaction with the copper ion. At even higher temperatures (295°C), the parent compounds are completely degraded and the only organic products detected are chlorinated benzene rings. A summary of this work is shown on page 20 which lists the model compound number on the horizontal rows and the number of chlorine atoms on the benzene ring on the vertical columns. The table itself lists the percentage of species present for each compound. Evaluating these high temperature results, a couple conclusions can be made.

- 1) At the higher temperatures, the chlorinolysis reaction is favored and a high fraction of the desulfurization is occurring along this pathway.
- 2) In addition to desulfurizing the model compounds, structural degradation occurs

to a large extent, most presumably due to the presence of the chlorine. (Thermal degradation has been ruled out as blanks were run and little to no degradation products were observed.

Coal Reaction Study: The results of the reaction of aqueous cupric chloride with Illinois #6 coal are listed on page 21. These results indicate that the oxidative desulfurization of coal with cupric chloride is more complex and less effective than previously reported. Although almost all the pyritic and sulfate sulfur are removed from the coal, the organic sulfur is actually reported to have increased. This may be due to an actual increase in the organic sulfur through a side reaction of the pyrite, or it may be caused by inaccuracy of the ASTM method when large proportions of chloro substituents are present. The amount of chlorine added to the coal (from 0 to 3.18%) is quite large and counterproductive. Most importantly, the amount of non-combustible ash has increased from 15.48 to 51.21%, most likely in the form of copper. This will dramatically decrease both the efficiency of combustion in terms of altering the heat capacity of the coal as well as decrease the amount of energy produced per ton of coal. As a result, it is quite evident that this method of desulfurization needs some modification prior to further exploitation.

Conclusions

Our data show that the mechanism that was originally proposed in the literature for the desulfurization of coal with cupric chloride is incorrect. The resulting desulfurization is clearly caused by the reaction of evolved Cl_2 with the organosulfur compounds. We are not interested

in studying the chlorinolysis reaction and will therefore change to a reagent that will not be capable of such side reactions.

PLANS FOR NEXT QUARTER

The oxidation of sulfur in coals with other copper salts will be considered. In addition, other solvents will be tried (such as DMF) to determine the effect on the reaction that the solvent is having. Copper oxidation reactions are known to have much greater reaction rates in apolar solvents such as DMF. If the aprotic solvent dramatically increases the reaction rate and yield, we will immediately move to performing the reaction in supercritical fluids for the purpose of achieving the advantage of increased diffusion, selective solvation, and (possibly) milder reaction conditions. The effects of doing these reactions in reverse micelles will also be considered.

Final Comment:

These results were presented at the recent International Conference on Coal Structure and Reactivity and were well received. While we openly admitted that this reaction has less than positive results, many of the coal scientists seemed interested in the possibility of finding favorable reactions in supercritical fluids.

Structure of Model Sulfur Compounds

COMPOUND

STRUCTURE

1. TETRAHYDROTHIOPHENE

2. CYCLOHEXYL MERCAPTAN

3. THIOPHENOL

4. METHYL p-TOLYL SULFIDE

5. BENZO[b]THIOPHENE

6. PHENYL SULFIDE

7. DIBENZOTHIOPHENE

8. PHENYL DISULFIDE

Tetrahydrothiophene

Methyl p-Tolyl Sulfide CC1=CC=C(S)C=C1

Phenyl Sulfide

130 °C

Benzo[b]thiophene

130 °C

Cyclohexyl Mercaptan

210 °C

Thiophenol

210°C

Methyl p-Tolyl Sulfide

210°C

Benzo[b]thiophene

210 °C

Phenyl Sulfide

210 °C

Dibenzothiophene

210 °C

Phenyl Disulfide

210 °C

Wt % of Organic Species Produced

Model #	# of Cl on benzene ring					
	1	2	3	4	5	6
1	0	0	0	0	0	0
2	0	0	0	0	0	0
3	6	14	19	30	25	6
4	40 (plus 60% benzene)					
5	9	25	46	18	1	0
6	5	17	41	32	0	0
7	0	0	0	4	24	75
8	0	5	11	18	29	38

Reaction conditions: 295° C, 12 hrs.

Illinois #6 Coal

	<i>Before Oxidation (wt %)</i>	<i>After Oxidation (wt %)</i>
<i>Total Sulfur</i>	<i>4.83</i>	<i>2.83</i>
<i>Pyritic</i>	<i>2.81</i>	<i>0.06</i>
<i>Organic</i>	<i>2.01</i>	<i>2.77</i>
<i>Sulfate</i>	<i>0.01</i>	<i>0.00</i>
<i>Chlorine</i>	<i>0.00</i>	<i>3.18</i>

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