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

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*Please note the last progress report actually covered the work through July 15, 1991. This report therefore covers the work since then.

TECHNICAL PROGRESS REPORT

I. STUDY OF OXIDATIVE DESULFURIZATION PROCESS

Earlier research indicated that the use of copper-promoted oxidation of the organic and inorganic sulfur species in coal showed considerable promise. Initial studies utilizing CuCl_2 demonstrated that the desulfurization yields were much lower than previously quoted. However, the experiments suggested that the reactant pathway showed promise and further investigations were conducted varying the solvent and replacing the Cl^- anion with the OH^- species. Ultimate analyses of these reactions are reported in addition to the experimental conditions used.

Experimental

The Illinois #6 coal samples used were all from the Argonne Premium Coal Program. They were high volatile bituminous, ground to a size of 100 mesh at Argonne.

The experimental procedure is described in the following text. Runs 2, 5-14, and 17-

20 used coal samples which were pretreated by washing with a 1:7 (concentrated nitric:distilled water) solution of nitric acid for 24 hours. All samples were then washed with 200 mLs of distilled water, followed by an acetone wash. Although the principle goal was to remove only the pyritic, elemental, and sulfate sulfur, reactions of the coal with nitric acid produce soluble carboxylic acids which were also removed by the acetone wash. This did not account for a detectable amount of the coal sample. A 6 gram coal sample was then placed in a reaction vessel with 200 mLs of reaction solution. The vessel was stirred and heated to the appropriate reaction temperature for a set reaction time. After the reaction, the vessel was cooled, the coal sample filtered and then washed with a nitric acid solution again. This second wash was to remove any copper-based mineral matter introduced by the reaction (note previous results which reported an ash content of 50%). The sample was then again washed with water and acetone for the purpose of removing sulfate and elemental sulfur. A few samples were reacted with a copper salt, copper cyclohexane butyrate, in hexane to determine if this species would cause any further desulfurization. The weighed samples were then sent to Black Rock Test Labs (Morgantown, WV) for sulfur and ash analyses. A summary of the specific conditions for the experiments is listed in Table 1.

Results and Discussion

The results of the desulfurization experiments are shown in table 2. A tentative examination of this data reveals the following:

Cu(OH)₂ Reactions

Initial experiments of model coal compounds, specifically those with disulfide

**Table 1: Summary of Reaction Conditions for
Coal Desulfurization Experiments**

RUN #	REACTION		REACTANT	SOLVENT	NOTES:
	TIME (hours)	TEMPERATURE (°C)			
1	10	90	10% Cu(OH) ₂	Water	No nitric pretreat
2	10	90	10% Cu(OH) ₂	Water	
3	10	170	10% Cu(OH) ₂	Water	No nitric pretreat
4	10	250	10% Cu(OH) ₂	Water	No nitric pretreat
5	10	90	10% CuCl ₂	Water	No nitric pretreat
6	10	90	10% CuCl ₂	Water/DMF	
7	10	90	10% CuCl ₂	DMF	No nitric pretreat
8	10	50	10% CuCl ₂	Water	
9	10	50	10% CuCl ₂	Water/DMF	No nitric pretreat
10	10	50	10% CuCl ₂	DMF	
11	10	90	10% Cu(OH) ₂	Water	No nitric pretreatment
12	10	90	10% Cu(OH) ₂	Water/DMF	
13	10	90	10% Cu(OH) ₂	DMF	No nitric pretreatment
14	10	50	10% Cu(OH) ₂	Water	
15	10	50	10% CuCl ₂	Water	No nitric pretreatment
16	10	50	10% Cu(OH) ₂	Water	
17	1	90	Organo-Cu Compound	Hexane	4.5 g/900 mLs
18	4	90	Organo-Cu Compound	Hexane	"
19	10	90	Organo-Cu Compound	Hexane	"
20	10	50	Organo-Cu Compound	Hexane	"

Table 2: Coal Desulfurization Results Utilizing Copper-Based Reactants
(Experimental Conditions Listed in Table 1)

RUN #	BTU	ASH	TOTAL	SULFUR (Dry, Ash-Free)			CHLORINE
				PYRITIC	SULFATE	ORGANIC	
Unreact.	10999	15.48	5.71	3.32	0.01	2.38	0.06
1	-	15.98	5.10	2.48	0.02	2.61	-
2	-	13.03	3.06	0.87	0.08	2.10	-
3	-	41.30	7.15	0.90	0.05	6.20	-
4	-	29.48	5.70	0.89	0.03	4.78	-
5	11061	11.35	2.32	0.43	0.05	1.85	0.55
6	11533	10.69	2.36	0.37	0.02	1.97	0.87
7	10434	11.13	2.25	0.44	0.02	1.79	3.86
8	11220	9.51	2.00	0.02	0.01	1.97	0.33
9	10556	9.58	1.96	0.02	0.03	1.90	0.55
10	10643	9.74	1.81	0.01	0.07	1.73	1.12
11	11121	11.38	2.45	0.42	0.05	1.99	0.20
12	11328	10.82	2.37	0.52	0.06	1.79	0.10
13	11366	11.36	2.40	0.38	0.06	1.96	0.10
14	11000	13.84	2.38	0.35	0.12	1.90	0.15
15	11353	9.85	2.23	0.29	0.03	1.91	0.29
16	12481	14.28	5.41	3.70	0.09	1.17	0.10
17	10845	9.60	1.97	0.02	0.01	1.94	-
18	9405	9.64	2.06	0.01	0.01	2.04	-
19	11227	9.26	1.82	0.01	0.04	1.76	-
20	11345	9.40	1.93	0.04	0.04	1.85	-

linkages, with $\text{Cu}(\text{OH})_2$ appeared to produce elemental sulfur. This may provide a possible explanation for the results obtained in the first series of experiments (runs 1 - 4). As the temperature is increased (from run 1 to run 3 to run 4), the pyritic sulfur may have been converted to elemental sulfur. Because the organic sulfur is determined by difference in the Ultimate Analysis, this would increase the apparent amount of organic sulfur in the coal. This is exactly what was observed in runs 1, 3, and 4. This is further supported by comparing run 1 with run 2 (same experimental conditions except that pyritic sulfur was removed by nitric acid pretreatment in run 2) in that the organic sulfur did not increase.

Based on this work, the next series of experiments was conducted using a nitric pretreatment step. A lower temperature was used for these experiments based on the early results from the first batch of experiments showing that a greater degree of desulfurization occurred at the lower temperatures. The results from this second series of experiments is interesting in that the sample run without a nitric acid pretreatment step (run 16) actually had a greater degree of organic sulfur removal than the corresponding experiment using nitric acid pretreatment (run 14). A second result of these experiments was that the solvent did not appear to have much of an effect on the desulfurization results (comparing runs 11-13), although there did appear to be a slightly greater degree of desulfurization for the 50:50 mix of water:dimethyl formamide.

CuCl_2 Reactions

A series of experiments were conducted utilizing copper chloride as the reactant to further study the effect of solvent on the reaction. Under both the 50°C and 90°C conditions, the use of pure dimethyl formamide appears to favor the desulfurization of

organic sulfur although it does not appear to affect the desulfurization of pyritic sulfur at all. Pyritic sulfur removal is greatly facilitated at the lower temperature. Organic sulfur desulfurization is slightly better at the lower temperature. This shows, as suggested before, that the predominant desulfurization reaction is that of chlorinolysis. Chlorinolysis has been shown to be enhanced at lower temperatures. This is also supported by the increase in chlorine content as the solvent is varied from water to 50:50 to pure dimethyl formamide. It can be concluded that either chlorinolysis is favored in the dimethyl formamide solvent or chlorine gas formation is favored in this solvent.

Copper Cyclohexane Butyrate

The reaction of a organocopper compound, copper cyclohexane butyrate, with coal was also examined. The purpose of this was to investigate possible interaction of the organic anion with the organic coal matrix to facilitate closer interaction between the copper cation and the sulfur moiety. The results of these experiments are shown in runs 17-20. This salt appear to be exceeding effective in removing the pyritic sulfur from the coal matrix. It also shows moderate effectiveness in removing organic sulfur. A beneficial side effect of this reaction is that it removes a large fraction of the ash, thereby improving the heat content of the coal, as listed in table 2.

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II. DESULFURIZATION PROCESS USING SELECTIVE SOLVATION

The following results were described in a previous progress report showing the extent of desulfurization that occurred for reaction conditions of 400°C and 3500 psi with supercritical ethanol. These results showed that the total amount of sulfur could be lowered by the reaction of supercritical ethanol with coal but most of this sulfur loss was from pyrite.

We therefore decided to see if the organic sulfur content of the coal could be further lower if the reaction of the supercritical ethanol occur after the pyrite was removed from the coal first. The following results were obtained when the pyrite was removed first by washing the coal with HNO_3 and then the coal was reacted with supercritical ethanol at 400°C and 3500 psi. The coal studied was again Illinois #6. Forty One Percent of the organic sulfur was removed in the extraction process relative to the quantities relative to that remaining after the nitric acid wash. Also after the extraction with supercritical ethanol, 61% of the coal solid remained.

Table 3 Results of Selective Solvolysis Experiment

Reaction	%	%	%	%	%
Conditions	Ash	Total	Pyrite	Sulfate	Organic
		Sulfur	Sulfur	Sulfur	Sulfur
Untreated	15.48	4.83	2.81	0.01	2.01
Nitric Acid					
Washed Coal	8.22	1.88	0.01	0.06	1.81
Extraction					
After Nitric					
Acid Wash	11.57	1.09	0.01	0.02	1.06

WORK PLANNED FOR NEXT QUARTER

The preliminary results on the reactions of copper salts with coal samples will be further substantiated by replicate studies and these reactions will also be attempted in reverse micelles. To finish the work with the selective solvolysis reactions, the organosulfur reaction products that are in the ethanol extract will be identified by GC/MS, SFC/MS and GC/FPD.

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