DESULFURIZATION OF COAL BY CHLORINOLYSIS

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INTRODUCTION

Since most of the coals, particularly the eastern coals, in this country have high sulfur content, there is a need for an economical process of converting high sulfur coals to clean fuel (<0.7% sulfur by EPA standard) to utilize coal as a source of energy without causing serious air pollution.

Most of the earlier studies[1,2,3,4,5] on chlorinolysis of coal were conducted to understand the chemistry of the process, to produce a non-caking fuel suitable for burning, and to the possibility of producing chlorohydrocarbons from coal. However, there was a limited amount of work[6,7] on desulfurization by chlorination of coal in the gas phase and at high temperature (400°C) and elevated pressure. These studies showed that both organic and inorganic sulfurs could be removed to a certain extent but the loss of coal was more than 20%, and because of high temperature chlorination, satisfactory dechlorination was not achieved. A few studies[8] on the chlorination of coal in the aqueous media at 25°C resulted in poor removal of sulfur.

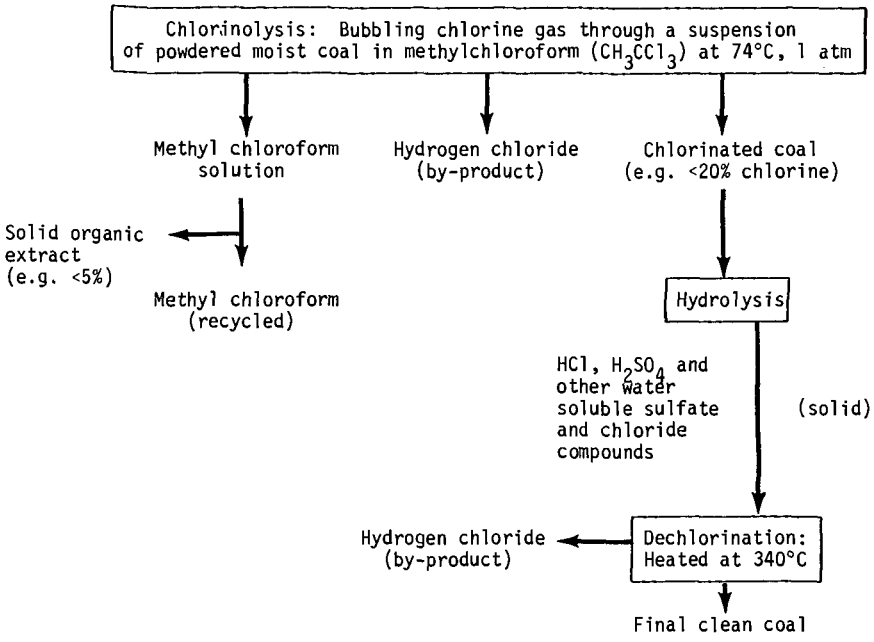
This paper describes some of the experimental results showing the feasibility of removing sulfur particularly organic sulfur from high sulfur coals by a simple method of low temperature chlorinolysis followed by hydrolysis and dechlorination. At first the process concept of this chlorination method will be described. Experiments, results and discussion of this method of desulfurization will be described for two bituminous coals.

PROCESS CONCEPT OF COAL DESULFURIZATION BY CHLORINOLYSIS

Based on the results of earlier studies on chlorination of coal, the experimental conditions were selected in such a way that there should be high degree of organic and inorganic sulfur removal at a low degree of chlorination, and dechlorination of the product would be carried out easily. In the presence of water and at a temperature much higher than room temperature, the S_2Cl_2 formed from FeS_2 chlorination[9] is readily converted to HCl and H_2SO_4. However, at room temperature this reaction is slow and S_2Cl_2 reacts with organic compounds to form organo-sulfur compounds. Due to the reactive nature of carbon-sulfur and sulfur-sulfur bonds, chlorinolysis[10] may bring about the scission of these bonds in organic compounds. These reactions are catalyzed by acids or Friedel Crafts catalysts such as $FeCl_3$ and $AlCl_3$. The resulting chlorinated organo-sulfur compounds can be hydrolyzed and oxidized at a relatively high temperature to produce sulfate compounds. Chlorination at a relatively high temperature in an organic solvent is slower than in aqueous media at room temperature, but gives a greater degree of structural loosening of coal and thereby may remove more organic sulfur at a lesser degree of chlorination. Chlorination of coal is mainly a substitution reaction and hydrogen chloride is evolved as a product. Chlorine in coal chlorinated under mild conditions, can be completely removed as hydrogen chloride by heating at 340°C[2].

EXPERIMENTAL

Based on the concepts and facts described above, a simple method of coal desulfurization by chlorinolysis was selected as described in the following flow diagram.



In this method chlorine gas is bubbled through a suspension of powdered moist high sulfur coal in methyl chloroform at 74°C and atmospheric pressure for 1 to 4 hours. Methyl chloroform was chosen because it is an economical non-hazardous industrial solvent which cannot be further chlorinated and has a suitable normal boiling point of 74°C. The slurry is filtered and the filtrate is distilled for solvent recovery. The chlorinated coal is hydrolyzed with water at 25°C, and the slurry is filtered. The hydrolyzed chlorinated coal is dechlorinated by heating at 300-350°C and atmospheric pressure.

Several experiments were conducted with a high sulfur bituminous coal from Hillsboro, Illinois. The moisture content in the powdered coal (-100 to +150 mesh) was varied from 0 to 50% with respect to coal. Samples were collected at 1/2 hr., 1 hr., 2 hrs., 3 hrs., and 4 hrs. period. The chlorinated coal was then hydrolyzed and dechlorinated. The results of a typical experiment are presented in Table I. The treated coal samples were analyzed mainly for sulfur forms and chlorine. To find the effect of $AlCl_3$ as catalyst on organic sulfur removal, a similar experiment was conducted by adding 0.5% $AlCl_3$ with respect to coal. Chlorinolysis experiment was carried out with a powdered (-200 mesh) moist (30% moisture) bituminous coal with high organic sulfur. The desulfurization results are presented in Table II.

RESULTS AND DISCUSSION

Results of a desulfurization experiment with a high sulfur bituminous coal from Hillsboro, Illinois are presented in Table I. It shows that chlorinolysis of the coal for an hour in the presence of moisture can remove 77% of pyritic sulfur, 70% of organic sulfur, 30% of sulfate sulfur, and 69% of total sulfur. Since sulfate compounds are soluble in hot water, all the sulfate compounds would be removed by improving the hydrolysis step. Chlorinated coal had 22% chlorine before and 11% after the hydrolysis step. After hydrolysis and dechlorination at 300°C for an hour, the residual chlorine in the final treated coal was 2.6%. According to the results of earlier chlorination experiments[2], all the chlorine in coal could be removed as hydrogen chloride by heating at 350°C for 2 hours. Results of all the experiments with this coal indicate that removals of up to 60% organic sulfur, 90% pyritic sulfur, 30% sulfate sulfur, and 70% total sulfur have been achieved by current chlorinolysis procedures. Further work is underway to improve the process and to achieve better understanding of the chemistry.

Results of a chlorinolysis experiment with 0.5% $AlCl_3$ as catalyst indicate that $AlCl_3$ does not have any noticeable effect on the removal of organic sulfur from coal. Coal contains iron compounds in the mineral matter sufficient to form about 1 to 2 percent of $FeCl_3$. This quantity would be sufficient to catalyze ionic chlorination reactions.

Results of a chlorinolysis experiment with dried coal and 0.5% $AlCl_3$ shows that only 18.5% of organic sulfur can be removed. So the presence of moisture has a significant effect on the removal of organic sulfur from coal. An optional solvent extraction step with tetrahydrofuran at room temperature of chlorinated coal shows that it can extract a considerable amount (>20%) of organic matters from coal composition which in turn would be a desirable feed stock for liquid fuel synthesis.

The kinetic data of chlorination and coal desulfurization are presented in Figure 1. The initial rate of chlorination is very fast and the chlorine content in coal is 23% in half an hour and then slowly increases to 26% within the next one and a half hours. Within half an hour period most of the pyritic sulfur and a portion of organic sulfur are converted to sulfate sulfur. In the next one and a half hour period pyritic and organic sulfurs are slowly converted to sulfate sulfur. According to sulfur balance from data, the gain in sulfate sulfur is equal to the combined losses in pyritic and organic sulfurs. This result supports the possible reaction mechanisms for the conversion of pyritic and organic sulfurs to sulfate sulfur as described below.

$$FeS_2 + 2Cl_2 \rightarrow FeCl_2 + S_2Cl_2$$

$$2FeS_2 + 7Cl_2 \rightarrow 2FeCl_3 + 4SCl_2$$

$$2FeS_2 + 10SCl_2 \rightarrow 2FeCl_3 + 7S_2Cl_2.$$

$$S_2Cl_2 + 8H_2O + 5Cl_2 \rightarrow 2H_2SO_4 + 12HCl. \quad \text{(FAST)}$$

$RH + S_2Cl_2 \rightarrow RS_2Cl + HCl$, where R represents a hydrocarbon group. (SLOW)

Due to high steric accessibility of bicovalent S and electron releasing and electron demanding nature of S atom, the carbon-sulfur (sulfide) and sulfur-sulfur (disulfide) bonds in coal will be highly reactive. Chlorinolysis[10] can bring about the scission of these bonds in organic compounds as follows.

$$R\text{-}S\text{-}R' + Cl^+\text{-}Cl^- \xrightleftharpoons{H^+} RSCl + R'^+ + Cl^- \rightleftharpoons RSCl + R'Cl$$

$$R\text{-}S\text{-}S\text{-}R' + Cl^+ - Cl^- \xrightleftharpoons{H^+} RSCl + R'S^+ + Cl^- \rightleftharpoons RSCl + R'SCl$$

where R and R' represent hydrocarbon groups. The resulting chlorinated organo-sulfur compounds can be hydrolyzed and oxidized in the presence of chlorine at a moderately high temperature to produce sulfate compounds.

$$RSCl \xrightarrow{H_2O} RSO_2Cl \xrightarrow{\Delta, H_2O, Cl_2} RCl + SO_4^{=}.$$

Results identify that these sulfate compounds produced are removed from coal in the hydrolysis step.

Heating value of the original coal and that of the final treated coal were 11052 Btu/lb and 10900 Btu/lb, respectively, on an as received and chlorine free basis.

Results presented in Table II show that 57% of organic sulfur can be removed by chlorinolysis of a bituminous coal with high organic sulfur.

CONCLUSION

A simple method of coal desulfurization by chlorinolysis of powdered moist coal in methyl chloroform at 74°C and 1 atmosphere can remove up to 70% organic sulfur, 90% pyritic sulfur, 30% sulfate sulfur and 70% total sulfur from a high sulfur bituminous coal. After hydrolysis, the chlorinated coal is dechlorinated by heating at 300-350°C for two hours.

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Table I. Results* From Preliminary Chlorinolysis Experiments (A Bituminous Coal from Hillsboro, Illinois)

Reaction Conditions	Composition	Raw Coal	Percent Sulfur Removal (Chlorine free basis)	Finely Treated Coal
Chlorination:				
74°C 1 atm, 1 hr	Pyritic sulfur	1.89%	77	0.43%
Powdered (-100 to 150 mesh)				
	Organic sulfur	2.38%	70	0.72%
Moist (50% moisture)				
Coal in methyl chloroform	Sulfate sulfur	0.50%	30	--**
	Total sulfur	4.77%	69	1.15%
Before dechlorination	Chlorine			11%
Dechlorination:				2.6%
At 300°C for 1 hr.	Chlorine			

* All the chemical analyses were conducted by the Galbraith Laboratories, Inc. at Knoxville, Tennessee.
** The 0.35% sulfate sulfur left is expected to be removed by further water washing.

Table II. Results From Preliminary Chlorinolysis Experiments for a Bituminous Coal (Hamilton, Kentucky)

Chlorination Conditions	Composition	Raw Coal	Finely Treated Coal	Percent Sulfur Removal
74°C, 1 atm, 4 hrs	Pyritic sulfur	0.08%	0.03%	62.5%
Powdered (-200 mesh)	Organic sulfur	2.67%*	1.16%	56.5%
Moist (30% moisture)	Sulfate sulfur	0.15%	0.29%	--**
Coal in methyl chloroform	Total sulfur	2.90%	1.48%	59.0%

* Sulfur in this coal is mostly organic sulfur.
** Sulfate sulfur can be removed in the hydrolysis step.

FIGURE 1. **SULFUR AND CHLORINE IN COAL DURING CHLORINOLYSIS**