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Co-firing High Sulfur Coal with Refuse Derived Fuels

Technical Progress Report #9

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1. Abstract

The objectives of this quarter of study on the co-firing of high sulfur coal with refuse derived fuels project were two-fold. First, the effect of SO_2 on the formation of chlorine during combustion processes was examined. To simulate the conditions used in the AFBC system, experiments were conducted in a quartz tube in an electrically heated furnace. The principle analytical technique used for identification of the products from this study was GC/MS. The evolved gas was trapped by an absorbent and analyzed with a GC/MS system. The preliminary results indicate an inhibiting effect of SO_2 on the Deacon Reaction. Secondly, information on the evolution of chlorine, sulfur and organic compounds from coals 95031 and 95011 were studied with the AFBC system.

2. Introduction

Incineration is an important waste-to-energy technology used for the disposal of municipal solid waste (MSW). However, it is necessary to reduce the possibility of the formation of volatile organic compounds (VOCS) during combustion before the incineration can reach its full potential. In previous work, the proposed mechanism for the formation of chlorinated organics and possibly PCDDs and PCDFs has been demonstrated as follows:¹

In this mechanism, molecular chlorine is thought to be the key starting material. Therefore, the formation of VOCS can be suppressed by preventing the formation of Cl_2 during the incineration of MSW. According to some recent reports, co-firing MSW with high-sulfur coal can drastically reduce the emissions of chlorinated organic compounds. The mechanism assumed to be responsible for the inhibition is as follows:

This report presents results from a series of experiments designed to test the effect of SO_2 on the formation of molecular chlorine during combustion processes. Our AFBC system has

been designed to simulate the system at the TVA Shawnee Steam Plant near Paducah, KY. The emission of chlorine, sulfur and organic compounds for two coals were studied during this reporting period. The results will serve as our baseline and will be compared to those from the addition of RDF (MSW) during combustion processes.

3. Experimental

3.1 Studies with the Tube Furnace

To closely simulate conditions in an AFBC combustor, our experiments were conducted in a quartz tube (length 30 inches, internal diameter 1 inch), mounted horizontally in an electrically heated twelve-inch Lindberg Furnace. The flow rates of HCl (1% hydrogen chloride in nitrogen), SO₂ (4.86% sulfur dioxide in nitrogen), and air were adjusted to give the desired concentrations of reactants and then introduced into the reactor. The list of different amounts of gases used is given in Table 1. The reaction was run for 4 hours at 800°C. The evolved gases were trapped by a carefully chosen absorbent, which was prepared by dissolving 50 mg phenol (reagent grade) in 25 mL methylene chloride (reagent grade). The absorbent solutions were concentrated to 1 mL, then injected into the GC/MS system for analysis. A Shimadzu QP 5000 system with a NIST/EPA/NIH 62,000 compound database was used for GC/MS analysis.

3.2 Fluidized Bed Combustion Studies

Two 1000-hour test runs have been completed in this quarter. Two coals (WKU 95011 and WKU 95031) were studied. The first coal (Kentucky #9) is a high sulfur (2.8%) and low chlorine (0.012%) coal, whereas the second coal (Illinois #6) is a high sulfur (2.1%) and high chlorine (0.28%) material. The principal operating parameters were as follows:

Excess air level:	approximately 1.3
Ca/S ratio:	near 3
Bed temperature:	near 1500°F
Oxygen in the flue gas:	4 - 6%
Unburned carbon in the fly ash:	6 - 15%

The results will serve as our baseline and will be compared to those after the addition of RDF in future combustion runs.

4. Results and Discussion

As given in the last quarterly report, it was shown that the Deacon Reaction is more favored at higher temperatures. In our experiments, we chose 800°C as the first test temperature, at which a substantial amount of molecular chlorine can be produced from the oxidation of HCl, even without a catalyst. Also, the temperature is close to the operating temperature of the AFBC system. In case any molecular chlorine is released, it can be absorbed easily by phenol to produce chlorophenol. Therefore, the formation of Cl_2 is monitored by analyzing the concentration of chlorophenol in the absorbent solution.

Table 1 lists the results from the experiments. As one can see from these data, as soon as SO_2 is introduced the production of chlorophenol decreases. These preliminary results indicate the inhibiting effect of SO_2 on the formation of Cl_2 during combustion. In a future study, we will hold the concentration of HCl and O_2 constant and change the flow rate of SO_2 to find the optimum ratio of SO_2 in the mixture.

Figures 1 and 2 show the effect of different coals on the emission of sulfate and chloride in the AFBC system. The rate of sulfation is the rate determining step for complete desulfurization. If the sulfation step is limited, the conversion efficiency is drastically reduced. This concept is a balance between the rate of sulfation and the amount of available surface area of from calcium oxide. The results indicate the temperature ranges for maximum desulfurization in our AFBC experimental conditions are between 1120K and 1170K. The poor desulfurization was observed above 1170K. The higher concentration of HCl was identified in the high-chlorine content coal. The reaction between HCl and CaO is generally not favored at the higher temperature (1073K) except with higher concentrations (400 ppm) of HCl. Also, no chlorine was identified in the absorbent solution. Naphthalene was the only organic compound identified in the flue gases from the combustion of both coals.

5. Further Study

The focus of future research work will be to:

- study quantitatively the effect of SO_2 on the Deacon reaction
- establish the gas emission data for coal WKU 95010.
- prepare fuel pellets containing PVC, newspaper and plastics.

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Table 1. Comparison of the Products from the Deacon Reaction as a Function of the SO₂ Concentration in the Reaction Mixture

<u>Run</u>	<u>Reaction Ratio (%)</u>			<u>Product Ratio (%)</u>		
	<u>SO₂</u>	<u>HCl</u>	<u>O₂</u>	<u>Chlorophenol</u>	<u>Phenol</u>	<u>Chlorophenol/ Phenol</u>
1	0	0.5	10.5	4.11	29.51	13.9
2	0.69	0.56	6.0	1.56	39.15	3.98
3	0.81	0.50	7.0	0.63	36.54	1.72
4	1.62	0.33	7.0	1.44	45.30	3.18
5	1.62	0.33	7.0	1.62	32.11	2.90
6	2.08	0.28	6.0	0.61	28.45	2.14
7	2.43	0.25	5.25	0.64	28.45	3.16
8	2.43	0.25	5.25	0.53	26.52	2.00

Figure 1. The effect of different coals on the emission of SO₂ during combustion in an AFBC system

Figure 2. The effect of different coals on the emission of HCl during combustion in an AFBC system