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COMBUSTION OF CALCIUM-EXCHANGED COAL

1st Quarterly Report

By
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February 10, 1984

Work Performed Under Contract No. FG22-83PC60801

California Institute of Technology
Pasadena, California

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Principal Co-Investigators

G. R. Gavalas and R. C. Flagan

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SUMMARY

This is the first quarterly report for DOE grant DE-FG-22-83PC60801, "Combustion of Calcium Exchanged Coal." The work performed during this first period includes equipment modification, development of analytical methods, oxidative pretreatment runs and combustion runs. The coal feeding section of an existing furnace was modified for uninterrupted feeding and better control of residence time. Analytical methods for sulfur and calcium in the coal and ash and for gaseous SO_2 were standardized. Oxidative pretreatment experiments were conducted in a fluidized bed at temperatures about 200°C to evaluate the potential of this method for increasing the ion exchange capacity of coals and determine the accompanying loss of heating value. Combustion experiments were carried out at very high particle temperatures (2000°K) at which a large fraction of the calcium additive was vaporized while 50-80% of the sulfur evolved as sulfur oxide. Continuing combustion experiments will be conducted at lower particle temperatures.

INTRODUCTION

This project is a fundamental study of combustion of calcium exchanged coal with the objective of determining the retention of sulfur in the ash as a function of coal pretreatment and conditions of combustion. The project includes experimental investigations in three areas.

- (i) oxidative pretreatment at low temperatures ($\sim 200^\circ\text{C}$) to increase the ion exchange capacity of coal to a sufficient level,
- (ii) rate and total capacity of exchange by calcium cations

- (iii) combustion of the calcium exchanged coal with emphasis on determining how sulfur retention in the ash depends on operating conditions and how the calcium additive affects the combustion rate and the size distribution and chemical composition of flyash particles.

The bulk of the experimental research is represented by item (iii), the combustion of calcium exchanged coal. Theoretical analysis and kinetic modeling will be undertaken to interpret the experimental results.

TECHNICAL PROGRESS REPORT

1. Oxidative Pretreatment

While lignites usually have considerable ion exchange capacity (carboxylic and phenolic groups), bituminous coals require preoxidation to develop adequate capacity for calcium loading commensurate with their sulfur content. Low temperature ($\sim 200^{\circ}\text{C}$) oxidation of coal has been known to increase the concentration of acidic groups, carboxylic and phenolic; however, quantitative information concerning the associated rates, ultimate level of acidity and relation to loss of carbon and heating value have not been available. The following experiments were carried out to determine the necessary information.

a. Experimental procedure

Oxidation experiments were carried out in an $3/8$ " fluid bed reactor with bed temperature controlled by a heating tape and a proportional controller. At the start of an experimental run, air is flowing through an empty bed. After the temperature has reached the desired level, a few grams of coal are added through a tube feeder. After an initial decrease, the temperature quickly stabilizes a few degrees above the initial level. Samples are withdrawn through a side tube at several times during the reaction that typically lasts for a few hours. During the same period carbon monoxide and carbon dioxide are analyzed by continuous infrared analyzers. The samples withdrawn from the bed as well as the final oxidized coal are analyzed by the following methods:

- (i) total acidity (carboxylic plus phenolic groups) is measured by barium cation exchange at pH of 12.5

- (ii) carboxylic acid groups are measured by barium cation exchange at pH of 8.3.
- (iii) phenolic groups are determined by difference; this determination by difference entails considerable uncertainty and a direct method would be more desirable.
- (iv) elemental analysis is used for C, H
- (v) heat content is measured by bomb calorimetry

b. Results

Experiments have been performed mostly with a high volatile bituminous coal, PSOC 704. Figure 1 shows the rates of oxide formation for a typical oxidation run. Table 1 provides data on the cation exchange capacity, carboxylic and phenolic, as a function of temperature and time of oxidation. The sulfur content of this coal is 3.45% (ash-free basis) corresponding to 1.08 milligram equivalent of sulfur per gram of coal. It is seen that the cation exchange capacity produced by oxidation is adequate to easily provide Ca:S in the range 2-5. Figure 2 shows the decline of the heating value of PSOC 704 coal with time of oxidation at 200°C. Comparing the results of Table 1 and Figure 2 it is seen that four hours of oxidation has produced ion exchange capacity corresponding to Ca:S = 3, while reducing the heating value by 13.5%.

2. Cation Exchange

A series of calcium-exchange experiments had been conducted before the initiation of this project. The results indicate that as long as the coal contains adequate ion-exchange capacity (which can be added if necessary by low temperature oxidation as shown in the previous section), sufficient calcium can be added to provide Ca/S ratios in the range 2-5. Results from a typical experimental run with a high volatile bituminous coal are shown in Figure 3.

3. Combustion of Calcium Exchanged Coal

a. Equipment - Procedure

The combustion experiments are carried out in a laminar flow furnace 2" diameter and 2' length. The furnace consists of two insulated sections of approximately one foot each. The temperature of the walls of the upper heated section is controlled in the range 1200-1700°K. The lower section is not directly heated. The temperature through this section drops gradually to room level.

A water-cooled injector tube located at the top of the heated section serves for feeding the coal as a dilute stream of particles in a stream of nitrogen. A oxygen-nitrogen mixture is introduced concentrically in the annulus around the injector tube. The fully or partially burned coal collected on a filter at the base of the furnace is removed upon the completion of each run for analysis.

The variables that have been investigated so far are flow rate (determining the residence time), oxygen concentration and wall temperature, the latter two variables determining the temperature of the burning particles.

During the first quarterly period of this project three major modifications were made to improve the operation of the furnace. The coal injector was redesigned to prevent accumulation of coal deposits near the injector tube that caused periodic tube plugging. The other two modifications were made to allow higher particle residence times. A new flow straightener was designed to prevent buoyancy effects from causing upward flow of particles at low gas flowrates through the furnace. Air-driven vibrators were mounted on the coal injector to improve coal-feed system. The furnace has shown much improved behavior after the modifications were implemented.

b. Analytical

(i) Sulfur

Sulfur analyses were performed on coal samples before combustion and on ash samples after combustion using a modified ASTM procedure. A known amount of the sample is first slowly combusted in a tube furnace at 1350°C with a stream of oxygen for 15 minutes. Then a stream of helium is passed through the furnace for 10 minutes to decompose sulfates into sulfur dioxide. The exit gas from the furnace is scrubbed with a solution of 1% hydrogen peroxide to convert sulfur dioxide into sulfuric acid. The hydrogen peroxide solution is then titrated with sodium hydroxide to determine the amount of sulfuric acid formed, which in turn gives the sulfur content of the sample analyzed.

The amounts of sulfur dioxide formed during the combustion experiments were determined by scrubbing the combustion gases in a solution of hydrogen peroxide gases in a solution of hydrogen peroxide as previously described.

(ii) Calcium

Calcium analyses were performed on coal and ash samples by atomic absorption. The samples are first digested with H_2SO_4 and HNO_3 . The calcium contents of the samples are then determined from the atomic absorbancies.

c. Results and Discussion

A series of preliminary combustion runs was conducted with a calcium-exchanged lignite PSOC 623 with the furnace wall temperature maintained at 1600°K and at different residence times and oxygen concentrations. The

results are presented in Table 2.

The results listed in Table 2 show that a large fraction of the calcium in coal cannot be accounted for in the ash collected on the filter. This loss of calcium may be attributed to vaporization at high particle temperatures. In view of the high concentration of oxygen used, the particle temperatures would be several hundred degrees above the furnace wall temperature, i.e. around or above 2000°K. The high particle temperatures that cause vaporization of the calcium also adversely affect the equilibrium of the $\text{SO}_2 + \frac{1}{2} \text{O}_2 + \text{CaO} = \text{CaSO}_4$ reaction. The result of both these factors is low sulfur retention in the ash. Future combustion runs will utilize lower oxygen concentration and longer residence times to ensure complete burn-off while maintaining particle temperatures at a lower level.

Table 1. Cation exchange capacity of a hvA bituminous coal (PSOC 704) as a function of temperature and time of oxidation.

Oxidation Temperature (°C)	Time (Hours)	Cation Exchange Capacity (mgeg/g coal)		
		Total (pH = 12.5)	Carboxylic (pH = 8.3)	Phenolic (Total Minus Carboxylic)
-	0	0.64	0.2	0.44
200	4	3.39	0.98	2.41
	12	5.27	2.12	3.15
	24	6.95	2.88	4.07
230	2	2.80	0.98	1.82
	6	4.25	1.38	2.87
	12	6.45	3.09	3.36
250	12	7.72	3.73	3.99

Table 2. Sulfur distribution in the combustion products from a calcium-exchanged lignite (PSOC 623) containing 8.1% calcium, 0.81% sulfur.

<u>O₂ (%)</u>	<u>Residence Time (S)</u>	<u>Ash</u>		<u>Gas</u>
		<u>%Ca</u>	<u>%S</u>	<u>SO₂ as % of Sulfur in Coal</u>
100	0.8	trace	0.47	79
100	1.5	3.5	0.89	70
100	3.0	50.4	1.31	54
60	1.5	2.0	0.75	77
40	1.5	26.8	0.46	76

Figure 1. Rate of Carbon Oxides Production from Fluidized Oxidation of a hvA Bituminous Coal (PSOC 740) in Air at 200°C. Coal Particle Size 125-149 μm .

Figure 2. Heating Value of hvA Bituminous Coal Oxidized at 200°C.

Figure 3. Extent of Calcium Exchange of a hvB Bituminous Coal, PSOC 680, 120 x 200 mesh with 0.1 N Solution of $\text{Ca}(\text{Ac})_2$ at pH = 8.3 at 22°C. Coal Preoxidized in Air at 195°C, 8 hrs ■; 260°C, 2 hrs ●