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CATALYTIC EFFECTS IN COAL GASIFICATION

Quarterly Report for April - June 1980

T. D. Padrick

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ABSTRACT

This quarterly report, for the period April through June 1980, summarizes the activities of Sandia National Laboratories' program on mineral matter effects in coal gasification. The objective is to determine the effects of mineral matter on the devolatilization of coal and on the subsequent char gasification. We have selected a basis set of Eastern bituminous coals whose mineral matter content, as determined by x-ray analysis of low-temperature ash, ranged from less than 5% to more than 20%. Chemical and physical characterization revealed that these coals had similar rank and petrographic content. Baseline thermal gravimetric experiments, in which the coals were heated from ambient to 1000°C at 5°C/min under nitrogen or hydrogen, have been completed. Work has been initiated to measure the composition of the gas evolved during both the devolatilization regime and the subsequent period of slower char gasification.

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Introduction and Summary

This quarterly report, for the period April through June 1980, summarizes the activities of Sandia's program on mineral matter effects in coal gasification.¹ The objective of this program is to determine the role of inherent mineral matter in the devolatilization and subsequent gasification of coal. The work will be directed towards a fundamental understanding of the mechanisms of catalytic gasification and will attempt to correlate the properties of several coals with their behavior under various gasification conditions. The ultimate objective will be to develop an understanding of both mineral matter effects and other catalytic effects in coal gasification, and to use this knowledge as the impetus for future process improvements.

Our approach is to work with a carefully selected, and well-characterized basis set of coals. We will investigate both the rapid devolatilization regime and the subsequent char gasification. We will measure the gasification rates and the product composition. After obtaining baseline data in both inert and reactive atmospheres, we will carry out experiments with demineralized coals and by adding mineral matter to raw coals. We will correlate these results to the chemical and physical properties of the coals to identify specific mineral matter effects and to elucidate the mechanism of such effects.

Accomplishments during this reporting period include:

- Each of the five high volatile bituminous coals (IL No. 6, Elkhorn No. 3, KY No. 11, and Pittsburgh Seam coals from West Virginia and Pennsylvania) selected for this study has been chemically and physically characterized by contract analysis laboratories.
- A Dupont 1090 Thermal Analysis System was received and installed. Thermal gravimetric analysis (TGA) runs, in which the coals were heated from ambient to 1000°C at 5°C/min, have been obtained for each coal under both nitrogen and hydrogen atmospheres.
- A second TGA instrument in a different Sandia organization (Division 2516) has been fitted with a gas trapping system which will sample the product gas stream at selected time

intervals. The product gas composition will be determined by gas chromatographic (GC) analysis.

- A Chemical Data Systems rapid pyrolysis unit, which will allow heating rates up to 10^4 °C/sec was received. The unit was defective and has been returned to the supplier for repair. A collaborative effort on a similar unit is providing product gas identification through mass spectrometric analysis of the GC column effluent, to which the rapid pyrolysis unit is attached.

A Milestone Schedule is shown in Figure 1.

Figure 1. Milestone Schedule

Results and Discussion

Chemical and Physical Characterization

Each coal sample selected for this study was pulverized until the entire sample passed through a 200 mesh screen. This size was chosen to reduce particle size effects which have been shown to exist in hydrogasification.² The entire sample was crushed to this size rather than using a screened portion of the sample to insure that certain mineral matter or macerals were not indiscriminately removed. After preparation, the coals were carefully sampled and sent out for analysis.

Table 1 lists the results of the proximate, ultimate, and sulfur forms analyses. Also listed is the coal rank determined from the calorific heating value and the free swelling index, which is a measure of the agglomerating property of the coal. Inspection of Table 1 reveals many differences and similarities among these coal samples. For example, the coals vary by a factor of ~ 5 in ash content and total sulfur content. The carbon to hydrogen ratio is similar for all but the Bruceton coal, which is only $\sim 10\%$ higher. These are a few examples of similarities and/or differences which will be correlated with the measured gasification rates and product gas yields.

The petrographic analysis of the coal samples is shown in Table 2. These coals were selected not only because of varying mineral matter content but because in earlier work, they were found to be of similar petrographic content.³ The analysis presented here indicates that the Bruceton Mine coal and Guaranty Mine coal are higher in inertinite than the other coals. Additional analyses are being performed to confirm these results.

Table 3 lists the values of the low temperature ash (LTA) for each coal sample. Also listed are the mineralogical analyses of those ashes performed by x-ray diffraction and infrared spectrometry. Comparison of Tables 1 and 3 shows that, for the Bruceton Mine coal, the LTA and the ash value from the proximate analysis are the same. However, for the Ireland Mine coal and the Fies Mine coal, the LTA value is about 30% higher than the ash value from the proximate analysis. Table 4 is a tabulation of the metal oxides present in a high temperature ash of each coal. Calcium has been shown to have a catalytic effect in coal gasification.⁴ Table 4 indicates a factor of 10 difference in the calcium concentration (wt % of coal) between the

Table 1. Analysis of coals used in this study*

	Pittsburgh Seam Bruceton Mine, PA	Pittsburgh Seam Ireland Mine, WV	Elkhorn #3 Seam Guaranty Mine, KY	IL #6 Seam River King Mine, IL	KY #11 Seam Fies Mine, KY
<u>Proximate Analysis Wt %</u>					
Moisture:	1.47	1.40	1.57	2.07	2.14
Ash:	3.80	9.80	14.42	13.27	17.56
Volatile:	34.66	38.61	34.86	38.46	35.93
Fixed Carbon:	60.07	50.19	49.15	46.20	44.37
<u>Ultimate Analysis Wt %</u>					
Moisture:	1.47	1.40	1.57	2.07	2.14
Carbon:	79.43	70.35	68.46	65.53	60.76
Hydrogen:	5.13	4.96	4.83	4.61	4.36
Nitrogen:	1.67	1.28	1.29	1.27	1.25
Chlorine:	0.01	0.02	0.02	0.01	0.02
Sulfur:	1.02	4.33	2.03	3.83	5.41
Ash:	3.80	9.80	14.42	13.27	17.56
Oxygen (diff):	7.47	7.86	7.40	9.41	8.50
<u>Sulfur Forms Wt %</u>					
Pyritic:	0.31	1.20	1.00	1.32	2.94
Sulfate:	0.06	0.63	0.03	0.19	0.79
Organic (diff):	0.65	2.50	1.00	2.32	1.68
<u>Rank</u>					
	hvAb	hvAb	hvAb	hvBb	hvBb
<u>Free Swelling Index</u>	7	6-1/2	4-1/2	1/2	2

* Analysis performed by Commercial Testing & Engineering Co.

Table 2. Petrographic analysis of coal samples*

	<u>Maceral Group</u>		
	<u>Vitrinite</u>	<u>Exinite</u>	<u>Inertinite</u>
	(Volume % mmfb)		
Pittsburgh Seam Bruceton Mine, PA	72.1	7.2	20.7
Pittsburgh Seam Ireland Mine, WV	81.2	4.4	14.4
IL #6 Seam River King Mine, IL	83.4	4.0	12.6
KY #11 Seam Fies Mine, KY	79.8	8.0	12.2
Elkhorn #3 Seam Guaranty Mine, KY	69.7	10.5	19.8

* Analysis performed by Commercial Testing & Engineering Co.

Table 3. Mineralogical Analysis of the low temperature ash of coal samples*

	Pittsburgh Seam Bruceton Mine, PA	Pittsburgh Seam Ireland Mine, WV	Elkhorn #3 Seam Guaranty Mine, KY	IL #6 Seam River King Mine, IL	KY #11 Seam Fies Mine, KY
<u>Low Temperature Ash</u>					
(Wt % of coal)	3.84	12.8	15.9	15.4	22.4
<u>Minerals</u>					
(Wt % of LTA)					
Quartz:	10-15	15-20	30-35	20-25	15-20
Kaolinite:	40-50	15-20	20-25	15-20	15-20
Pyrite:	10-15	30 [†]	15 [†]	20-25 [†]	35 [†]
Illite:	10-20	10-20	10-20	10-20	5-10
M.L.C.:	N.D.	N.D.	5-10	N.D.	5-10
Feldspar:	N.D.	5-10	5-10	5-10	5-10
Calcite:	1-5	N.D.	1-5	5-10	5

* Analysis performed by the Mineral Constitution Laboratories, The Pennsylvania State University.

[†] Marcasite also observed.

N.D. - Not Detected.

Table 4. Quantitative spectrometric analysis of 750°C coal ashes*

	Pittsburgh Seam Bruceton Mine, PA	Pittsburgh Seam Ireland Mine, WV	Elkhorn #3 Seam Guaranty Mine, KY	IL #6 Seam River King Mine, IL	KY #11 Seam Fies Mine, KY
<u>Constituent Oxides</u>					
(Wt % of Ash)					
SiO ₂	48.1	42.0	55.7	48.8	42.4
Al ₂ O ₃	28.3	20.7	22.6	17.5	18.4
TiO ₂	1.14	0.93	1.42	0.87	0.94
FeO ₂	17.5	28.8	12.5	17.6	29.6
MgO	0.54	0.71	0.99	1.12	1.03
CaO	2.20	2.47	1.56	6.07	2.97
MnO	0.02	0.03	0.03	0.07	0.04
Na ₂ O	0.42	0.30	0.28	0.30	0.35
K ₂ O	0.84	1.63	2.17	1.84	1.88
P ₂ O ₅	0.24	0.18	0.21	0.25	0.35
SO ₃	1.5	2.5	1.8	6.3	2.7

* Analysis performed by the Mineral Constitution Laboratories, The Pennsylvania State University.

Bruceton Mine coal and the River King Mine coal. Again, these properties will be correlated with the experimental results.

TGA Results

Initial experiments with the DuPont 1090 Thermal Analysis System involved determination of the effect of purge gas flow rate and heating rate. Following this parameter optimization, we made TGA runs in which each coal sample was heated from 50°C to 1000°C at 5°C/min in either a hydrogen or a nitrogen purge of 150 cc/min. Figure 2 is a typical thermogram showing the weight loss versus temperature, the derivative of the weight loss curve and a plot of time versus temperature. The basic shape of each weight loss curve was comparable for each coal with small differences in final weight % and small weight loss changes following the major devolatilization region. The most interesting feature of these runs was the different effect hydrogen had on the various coals. For example, with the Pittsburgh Seam coal from the Ireland Mine, the presence of hydrogen began to enhance the weight loss at temperatures greater than 450°C or during the period of rapid devolatilization. However, for the Illinois No. 6 coal from the River King Mine, enhanced weight loss in hydrogen did not begin until > 575°C or after the rapid devolatilization. Figure 3 is a plot of the weight loss curves for the Bruceton Mine coal in nitrogen and hydrogen. It can be seen that the presence of hydrogen vs. nitrogen actually inhibited the weight loss in the temperature range of 425°C-750°C. These results are summarized in Table 5. While no conclusions can be drawn at this time from such observations, they are important as we accumulate baseline data for later comparison to runs with minerals added and/or removed and for comparison to the chemical and physical properties of the coals.

TGA Product Gas Composition

A gas sampling device has been constructed to trap the product gas contained in the purge stream of a TGA unit. The device consists of a switching valve to collect gas at selected times on small U-tubes packed with Pora-Pack-Q. Gas is collected while the U-tube is at liquid nitrogen temperature. Later the tube is heated to drive the sample onto the head of the GC column. This device is currently being tested in a different Sandia organization (Division 2516) which has a GC that is slaved to their TGA unit. Continuous use of this device on our TGA system will begin when our new GC is operational.

Sample: IL 8 - RIVER KING MINE
Size: 24.81 mg
Rate: 5 DEG C/MIN-150 CC/MIN
Program: Advanced Playback V1.0

TGA

Date: 20-Jun-80 Time: 8:26:26
File: RIVERKING.01
Operator: TDP NITROGEN

Figure 2. Representative Thermalgram.

Figure 3. Comparison of weight loss curves for the Bruceton Mine coal run in nitrogen and hydrogen purge gas flows.

Table 5. Results of TGA Runs in N₂ and H₂*

	<u>Purge Gas</u>	<u>Temperature at Peak Rate of Wt. Loss</u>	<u>Peak Rate of Wt. Loss</u>	<u>Wt. % at 1000°C</u>	<u>Noticeable Differences</u>
Pittsburgh Seam Bruceton Mine, PA	N ₂	445°C	1.31%/min	53%	425-750°C - Wt. loss greater in N ₂ . >750°C - Wt. loss greater in H ₂ .
	H ₂	445°C	1.06%/min	54%	
Pittsburgh Seam Ireland Mind, WV	N ₂	430°C	1.53%/min	57%	>450°C - Wt. loss greater in H ₂ .
	H ₂	430°C	1.60%/min	50%	
IL #6 Seam River King Mine, IL	N ₂	425°C	1.30%/min	58%	>575°C - Wt. loss greater in H ₂ .
	H ₂	425°C	1.25%/min	51%	
KY #11 Seam Fies Mine, KY	N ₂	430°C	1.26%/min	58%	525-575°C - Wt. loss greater in N ₂ . >575°C - Wt. loss greater in H ₂ .
	H ₂	430°C	1.22%/min	51%	
Elkhorn #3 Seam Guaranty Mine, KY	N ₂	435°C	1.50%/min	62%	400-600°C - Wt. loss greater in N ₂ . >600°C - Wt. loss greater in H ₂ .
	H ₂	435°C	1.35%/min	57%	

* Heating rates of 5°C/min and gas flow rate of 150 cc/min were used.

Rapid Pyrolysis Results

In order to investigate the role of mineral matter during the devolatilization that occurs upon the initial heating of coal, we purchased a rapid pyrolysis unit with heating rates up to 10^4 °C/sec (the range for process conditions). While some previous data suggest that there is no effect of the heating rate above 250°C/sec,⁵ this unit was required to reach that regime since the maximum linear heating rate of the TGA system is ~ 1 °C/sec. The unit connects directly to a GC, providing analysis of the product gas generated during the rapid heat-up of the coal.

The rapid pyrolysis unit, as received, was defective and was returned for repair. In the meantime, some work is being done on a similar unit within Sandia which is connected to a GC/MS system. Experiments on the apparatus are providing us with the correct operating parameters and GC peak identification through the mass spectrometry system.

Future Work

The following activities are planned for the next quarter:

1. Measure the surface area and pore volume distribution of each coal sample.
2. Measure the gasification rates at 600°C, 800°C and 1000°C in H_2 with the TGA system.
3. Measure the gasification rates in H_2 with mineral matter added to raw coals and demineralized coals.
4. Measure gasification rates in H_2 of the higher ash coals which have been demineralized by gravitational separation.
5. Perform product gas analysis on the TGA experiments to ascertain if the mineral matter is altering product gas composition.
6. Begin rapid pyrolysis experiments to investigate effect of mineral matter on the devolatilization of the coal under process heating rates.

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