

## PYROLYSIS OF COAL IN A MICROWAVE DISCHARGE\*

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## INTRODUCTION

The nature of the thermal decomposition of coal differs greatly depending on the reaction temperature and the rate of heating. Recent investigations using various energy sources, e.g., plasma jets,<sup>1-3</sup> laser beam,<sup>4,5</sup> flash heating,<sup>6</sup> arc-image reactors,<sup>7</sup> etc., have shown that extremely rapid pyrolysis of coal produces high yields of acetylene. It has also been shown that high-volatile bituminous coal, when reacted in a microwave discharge in argon,<sup>8</sup> is readily gasified to produce a significant yield of acetylene.

The present study deals with the pyrolyses of coals of various ranks under the influence of a microwave discharge. The readiness of coal to give up a small part of its volatiles under the microwave irradiation permits the discharge to be sustained even when starting initially under a high vacuum. The relationship between the pressure increase during the discharge pyrolysis of coal and time shows that the principal reaction is a rapid gasification, which is induced by the active bombardment of the coal by energetic species present in the discharge. Studies of the gas composition at various stages of the discharge pyrolysis; of the effect of initial presence of Ar; and of the effect of cooling the gaseous products (as they are being formed); have all given further insight into the nature of the decomposition of coal which takes place in the microwave discharge.

## EXPERIMENTAL

Experiments were carried out in a Vycor tube reactor attached to a vacuum system provided with a Pace Engineering pressure transducer. The transducer was connected to a Fisher recorder, so that the pressure increase due to the devolatilization of coal in a known volume could be recorded during its discharge pyrolysis. The discharge was produced by a Raytheon microwave generator (2450 MHz) coupled to an air-cooled Opthos coaxial cavity. The discharge was initiated by a Tesla coil either in a vacuum ( $\sim 10^{-4}$  mm Hg) or in the initial presence of argon (5-10 mm Hg), and the power level was maintained at 50 watts. The coal was located in the discharge zone.

All pressure-time data were obtained from experiments using 10 mg of vitrain of coal in a 163 ml reactor. Chemical analyses and origins of the vitrains of different coals used are given in Table 1. All the vitrains were -200 mesh, and were degassed in a high vacuum at 100° C prior to the experiment. The gaseous products were analyzed by mass spectrometry.

Tars and chars were pressed into KBr pellets for infrared analysis. Tars were also dissolved in benzene or ethanol for ultraviolet analysis.

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\* Vitrains of coals were used throughout this paper.

Table 1. Analyses of vitrains (moisture free basis, percent)

	C	H	N	S	O (by diff.)	Ash	Volatile matter
Anthracite <sup>1/</sup>	91.06	2.49	0.96	0.83	2.98	1.77	6.1
Low volatile bituminous <sup>2/</sup>	89.57	4.67	1.25	.81	2.17	1.53	20.2
High-volatile bituminous <sup>3/</sup>	81.77	5.56	1.71	.97	7.93	2.06	39.2
Lignite <sup>4/</sup>	66.45	5.40	.31	1.40	22.84	3.60	44.0

<sup>1/</sup> Dorrance Mine, Lehigh Valley Coal Co., Luzerne County, Pennsylvania.

<sup>2/</sup> Pocahontas No. 3 Bed, Buckeye No. 3 Mine, Page Coal and Coke Co.,  
Stephenson, Wyoming County, West Virginia.

<sup>3/</sup> Bruceton, Pennsylvania Bed, Allegheny County, Pennsylvania.

<sup>4/</sup> Beulah-Zap Bed, North Unit, Beulah Mine, Knife River Coal Mining Co.,  
Beulah, Mercer County, North Dakota.

#### RESULTS AND DISCUSSION.

##### Gas Evolution During the Discharge Pyrolysis

Coal, on being subjected to microwave radiation and excitation by a Tesla coil, readily gives up enough of its volatiles to sustain the discharge initially. Figure 1 shows the pressure-time relationships during the discharge pyrolyses for a lignite, a high-volatile bituminous coal, a low-volatile bituminous coal, and an anthracite. The zero time is the time the plasma appeared, and there is usually some sort of "induction period" before an extensive build-up of the pressure takes place, except for the lignite where the pressure rise is spontaneous. For each vitrain, the pressure reaches a plateau after some time. Substantial amounts of tars were produced from the hvab and the lvb coals, and it was noticed that the tars deposited on the reactor wall immediately after the discharge was initiated.

The results and the pressure-time relationships show that the discharge pyrolysis of coal (except for lignite) may be divided into three stages:

(1) Partial carbonization to produce tar. This proceeds at a relatively low rate without significant gas evolution -- an "induction period" for gas evolution.

(2) The principal reaction -- pyrolysis with accompanying gasification. This proceeds at a relatively high rate.

(3) Degassing of residual char. This rate is very slow.

The high evolution of gases in the second stage takes place only after the pressure in the system has gradually built up to a point (0.5 to 1 mm), where there are sufficient concentrations of electrons, atoms, and ions present in the discharge so that these energetic species can actively bombard the coal to accelerate the decomposition of the coal. For the lignite the rapid gas evolution takes place spontaneously, presumably owing to its readiness to release sufficient amounts of volatile matter which is converted to the energetic species. As shown in Figure 1, the rate of gas evolution at this stage increases with volatile matter content of the coal.

In the third stage, the gas evolution reaches a limit. Table 2 shows the typical product analyses obtained at the end of the reaction time indicated in Figure 1. The extent of devolatilization or gasification increases with volatile matter content of the coal. In general, the amounts of gases evolved are comparable to those evolved from thermal decompositions of the coals at about 1000° C, but the products are richer in H<sub>2</sub> and C<sub>2</sub>H<sub>2</sub>.

Table 2. Discharge pyrolysis of coal

	<u>Lignite</u>	<u>hvb</u>	<u>lvb</u>	<u>Anthracite</u>
Volatile matter, percent	44.0	39.2	20.2	6.1
Reaction time, min	10	20	20	20
<u>Product, 10<sup>-1</sup> mmoles/g. coal</u>				
H <sub>2</sub>	86.5	103	120	60.2
CH <sub>4</sub>	2.7	3.5	1.4	5.0
C <sub>2</sub> H <sub>2</sub>	7.8	15.0	7.9	1.8
C <sub>2</sub> H <sub>4</sub>	0.7	0.9	0.2	trace
CO	83.5	35.7	11.3	3.9
CO <sub>2</sub>	8.7	0.8	0.1	trace
H <sub>2</sub> O	5.5	2.0	3.5	1.9
Total gases, wt pct	32.6	17.5	8.6	3.3
C gasified, percent	20.6	11.1	4.2	1.2
C converted to gaseous hydrocarbons, percent	3.9	5.7	2.7	0.6

#### Effect of Initial Presence of Argon

The pressure-time relationship during the discharge pyrolysis in the presence of added argon (Figure 2) shows that the rapid gas evolution takes place as soon as the discharge is initiated and proceeds at a higher rate. Here, the gas evolution also quickly reaches a limit, but the initial "induction period" for the gas evolution does not exist. Evidently, the added argon immediately forms sufficient concentrations of energetic species upon initiation of the discharge, thus allowing stages 1 and 2 to proceed concurrently. The gas evolution reaches a limit sooner, but the extent of devolatilization of the coal and the gaseous product type do not differ significantly. The results are shown in Table 3.

#### Gas Composition at Various Stages of Discharge Pyrolysis

In order to investigate the composition of the gases evolved at various stages of the devolatilization, the pyrolysis was interrupted at several stages by discontinuing the discharge. At each stage, the evolved gases were measured and collected for mass spectrometric analysis. The discharge -- and the pyrolysis -- were then continued for the remaining coal until no more noticeable devolatilization could be observed.

Figures 3 and 4 show the results obtained for the lignite and the hvb coal, respectively. The gas composition at various stages of the thermal pyrolysis (the gases were collected at 200° C interval) of the hvb coal is also shown in Figure 5 for comparison. Acetylene in addition to methane are the major constituents of the hydrocarbons produced from the discharge pyrolysis, and their concentrations are nearly constant at each stage, except that they decrease at the later stages, possibly because of less evolution of hydrogenated carbon-species from the coal.

Table 3. Discharge pyrolysis of coal in the presence of Ar

	<u>Lignite</u>	<u>hvab</u>	<u>lvb</u>	<u>Anthracite</u>
Volatile matter, percent	44.0	39.2	20.2	6.1
Initial pressure of Ar, mm	5.1	5.1	5.1	5.1
Reaction time, min	5	20	20	20
<u>Product, 10<sup>-1</sup> mmoles/g. coal</u>				
H <sub>2</sub>	86.8	98.5	113	64.5
CH <sub>4</sub>	2.1	2.5	4.0	0.4
C <sub>2</sub> H <sub>2</sub>	10.4	15.8	8.8	2.0
C <sub>2</sub> H <sub>4</sub>	0.6	0.7	0.8	trace
CO	79.5	31.9	10.8	4.2
CO <sub>2</sub>	8.6	0.7	0.2	trace
H <sub>2</sub> O	7.5	3.4	4.9	1.6
Total gases, wt pct	33.5	16.5	9.4	3.4
C gasified, percent	19.4	11.4	4.9	1.2
C converted to gaseous hydrocarbons, percent	4.5	6.6	3.5	0.7

**Tar** -- Substantial amounts of tars were obtained from the hvab and the lvb coals in the discharge pyrolyses. The tars were compared by IR and UV analyses with the tar obtained from the thermal pyrolysis (at 700° C) of the hvab coal. All the IR spectra showed the presence of usual aliphatic C-H bands (2860-2940 cm<sup>-1</sup>) and aromatic bands (740-860 cm<sup>-1</sup>) which are typical of pitch and coal. The tars obtained from the discharge pyrolyses, however, exhibited weaker aromatic bands and a stronger carbonyl band (1710 cm<sup>-1</sup>) than the tar obtained from thermal pyrolysis. The UV spectra (of the tars extracted by benzene or ethanol) exhibited no distinct absorption band for the tar obtained from the thermal pyrolysis, but exhibited bands at 3140, 3300, and 3470 Å (which could be attributed to derivatives of pyrene) for those obtained from the discharge pyrolyses.

All the residual chars exhibited no distinct band over the entire IR spectrum.

#### Effect of Cooling by Liquid Nitrogen

A. Hvab Coal -- When one end of an h-shaped reactor (vol. = 41 ml) was cooled with liquid N<sub>2</sub> while the other leg containing the hvab coal was subjected to the discharge pyrolysis, it was observed that the pressure reading of the reactor never exceeded 0.5 mm during the course of the decomposition. The end products consisted mainly of hydrocarbons and water, without significant amounts of H<sub>2</sub> and CO. Acetylene was the main hydrocarbon, but substantial amounts of other C<sub>2</sub>, C<sub>3</sub>, C<sub>4</sub>, C<sub>5</sub> and C<sub>6</sub> hydrocarbons were also formed. Without liquid N<sub>2</sub> cooling, the other C<sub>2</sub> and C<sub>3</sub> hydrocarbons were insignificant and the C<sub>4</sub>, C<sub>5</sub> and C<sub>6</sub> hydrocarbons were not measurable. The product analyses, except that for C<sub>4</sub>, C<sub>5</sub> and C<sub>6</sub> hydrocarbons which constitute less than 2 percent of the gases, are shown in Table 4. The extent of devolatilization and the hydrocarbon yield are significantly increased.

Table 4. Effect of liquid nitrogen cooling on discharge pyrolysis of coal

P Ar mm	Time, min.	Product, 10 <sup>-1</sup> mmole/g. coal										Total gases, wt percent	Percentage of C present as		
		H <sub>2</sub>	CH <sub>4</sub>	C <sub>2</sub> H <sub>2</sub>	C <sub>2</sub> H <sub>4</sub>	C <sub>2</sub> H <sub>6</sub>	C <sub>3</sub> H <sub>4</sub>	C <sub>3</sub> H <sub>6</sub>	C <sub>3</sub> H <sub>8</sub>	CO	CO <sub>2</sub>		H <sub>2</sub> O <sup>2/</sup>	Gaseous products	Gaseous hydro- carbons
hvab $\frac{1}{1}$	-	15	1.2	0.4	40.4	3.4	5.6	2.9	1.7	2.7	0.8	23	20.4	17.2	16.7
$\frac{1}{1}$	-	30	3.2	0.5	48.4	3.6	9.4	3.8	2.7	3.6	0.7	30	26.2	21.7	21.1
$\frac{1}{1}$	-	45	1.1	0.4	48.8	2.6	7.5	4.5	3.0	4.5	0.7	26	25.3	21.6	20.8
	10	30	17.6	0.4	85.2	6.1	5.4	0.9	0.7	6.7	1.3	14	31.7	30.4	29.3
Lignite	-	7	0.6	0.5	47.0	1.9	3.7	0.7	0.9	0.8	13.8	74	34.3	22.7	20.1
	-	10	0.9	0.3	50.2	1.0	3.2	0.6	1.0	0.6	11.9	75	34.0	22.8	20.6
	10	20	12.9	0.2	38.2	0.8	1.3	0.3	0.3	9.8	14.2	43	27.8	19.3	14.9

<sup>1/</sup> C<sub>4</sub>, C<sub>6</sub>, and C<sub>8</sub> hydrocarbons were also formed.

<sup>2/</sup> H<sub>2</sub>O content as obtained from mass spectrometric analyses are only approximate, and data are reported only to show trends.

With Ar initially present and with cooling, however, the pressure reading increased rather rapidly to a maximum within a few minutes, and then decreased gradually. Presumably, large amounts of H<sub>2</sub>, CO (noncondensable at -196° C) and hydrocarbons were rapidly formed due to the high rate of gasification of the coal in the Ar discharge. The pressure decrease in the later stage is attributed to the continuous reaction of H<sub>2</sub> and CO to form condensable hydrocarbons. As seen in Table 4, however, appreciable H<sub>2</sub> and CO still remained after 30 minutes of reaction. The yield of acetylene is very high, but that of other C<sub>2</sub> and C<sub>3</sub> hydrocarbons is low. No measurable amounts of C<sub>4</sub>, C<sub>5</sub> and C<sub>6</sub> hydrocarbons were found

These results may be interpreted as follows. In the absence of added Ar, small reactive species (H, O, C, CH, etc.) and perhaps some larger fragments (radicals) are slowly detached from coal molecules, but are rapidly converted to stable products such as acetylene, higher hydrocarbons, and water, which are finally condensed at the liquid N<sub>2</sub> temperature. In the presence of Ar, however, the detachment of these fragments proceeds at such a high rate that all the products formed cannot be immediately condensed by the liquid N<sub>2</sub>. As a result, the larger molecules further decompose or react with O-species to form large amounts of H<sub>2</sub> and CO. It is also quite possible that different types of species (or smaller fragments) are released in the presence of Ar, resulting in rapid formation of noncondensable H<sub>2</sub> and CO. With prolonged reaction time, the H<sub>2</sub> and the CO would then continue to react to form relatively lower hydrocarbons and water.

Increases in the extent of devolatilization and in the hydrocarbon yield under these conditions are due primarily to the removal of hydrocarbons (therefore no further decomposition or polymerization), and of water<sup>9</sup> (therefore no reaction of water with hydrocarbons to form H<sub>2</sub> and CO).

B. Lignite -- As seen in Figure 1, lignite releases gases spontaneously at a higher rate than the hvab coal. Thus, when the discharge pyrolysis of the lignite was subjected to liquid N<sub>2</sub> cooling, it was observed that the pressure reading increased rapidly to a maximum within 1 to 2 minutes, and then decreased gradually to practically zero after several minutes. At this point, the major part of the pyrolysis of the coal seemed to be completed and the discharge could not be maintained.

The reasons for this different behavior (from that of the hvab coal) may be (i) the spontaneous gas evolution at a higher rate and (ii) the release of more numerous smaller fragments from lignite, resulting in rapid formation of noncondensable H<sub>2</sub> and CO. All the H<sub>2</sub> and the CO are eventually converted to hydrocarbons and water in the later stage. The results in Table 4 also show that the hydrocarbon yield is very significantly increased under these conditions.

Similar behavior was observed with added Ar except that some part of the H<sub>2</sub> and CO remain unreacted, owing perhaps to the slowness with which the product species diffusing into the cold trap in the presence of high concentration of Ar.

It was also noticed that the lignite yielded a significant amount of CO<sub>2</sub>, while the hvab coal yielded very small amounts of CO<sub>2</sub> under all conditions. This suggests that CO<sub>2</sub> molecules are released from the lignite structure rather than formed from interactions of CO and active O-species in the discharge.

### CONCLUSIONS

The principal reaction in the discharge pyrolysis of coal is rupture of the bonds in the coal structure by bombardment of energetic species (whether released from the coal or formed from argon in the discharge) on the coal surface. Numerous species such as H-species, O-species, gaseous C, and hydrogenated carbon fragments (CH, C<sub>2</sub>H or C<sub>x</sub>H<sub>y</sub>) are produced from coal in the discharge, these in turn decompose or combine with each other to form hydrogen, water, carbon oxides, and hydrocarbons. After extensive decomposition of the coal structure, all the species present in the discharge reach a steady state, where the formation of hydrocarbons is limited by back reactions with water to form H<sub>2</sub> + CO and gasification of solid is somewhat compensated by polymerization of hydrocarbons.

Thus, if the decomposition products are rapidly removed by a liquid nitrogen trap as they are formed, high yield of hydrocarbons consisting mainly of acetylene can be obtained. The process for the discharge pyrolysis of high-volatile bituminous coal under these conditions is unique in that it converts more than 21 percent of carbon in coal to higher hydrocarbons (up to C<sub>6</sub>) without the accompanying formation of H<sub>2</sub> and CO. With argon initially present under similar conditions, however, the pyrolysis products are lower hydrocarbons (below C<sub>4</sub>) and substantial amounts of H<sub>2</sub> and CO, owing to the increased rate of gasification. Hence, the product type and distribution can be influenced by the rate of formation or removal of the products.

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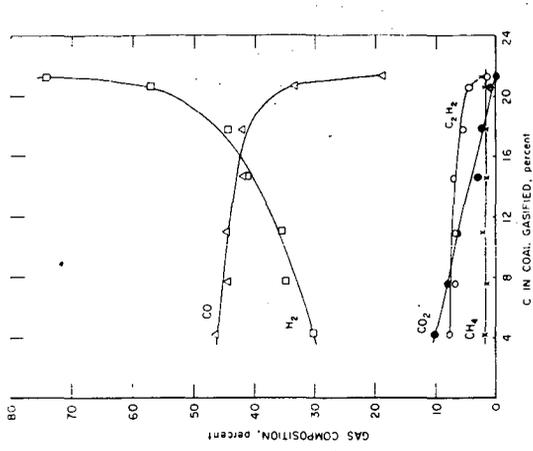


Figure 3 - Gas composition at various stages of discharge pyrolysis of lignite.

12-5-67 L-10289

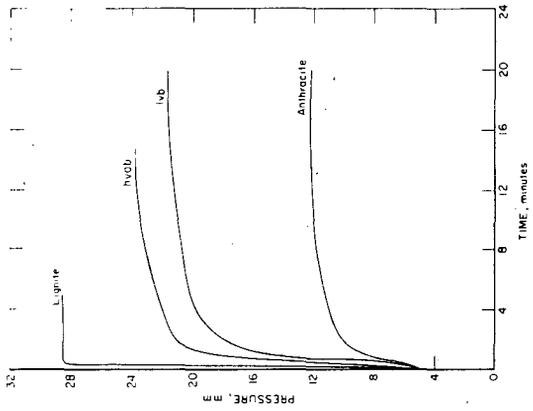


Figure 2 - Pressure as a function of time during the discharge pyrolysis of lignite in the presence of air (1/20 S.T.M., 10mg coal in 100ml reactor)

12-5-67 L-10288

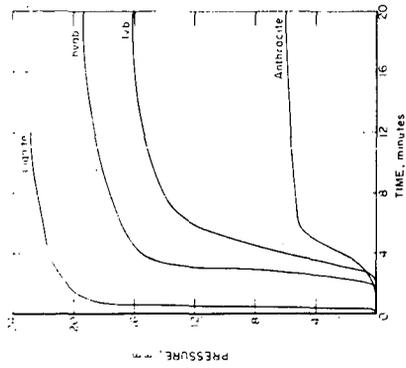


Figure 1 - Pressure as a function of time during the discharge pyrolysis of coal (10 mg coal in 100 ml reactor)

12-12-67 L-10305

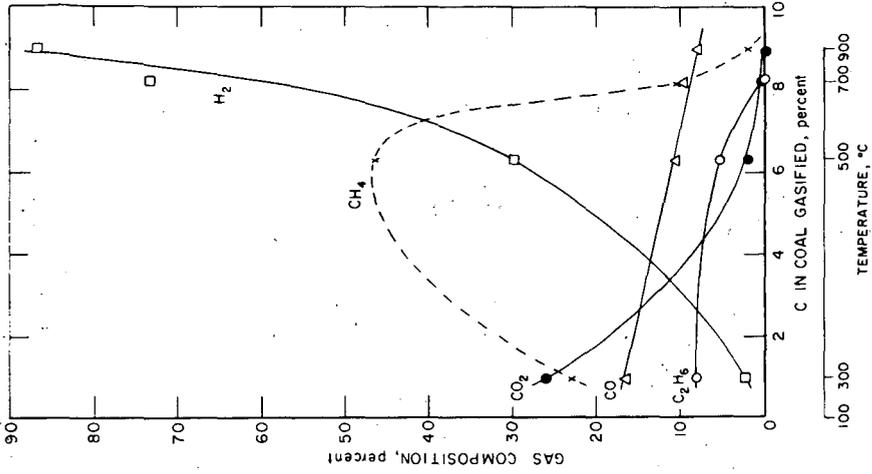


Figure 5. - Gas composition at various stages of thermal pyrolysis of hvab coal.

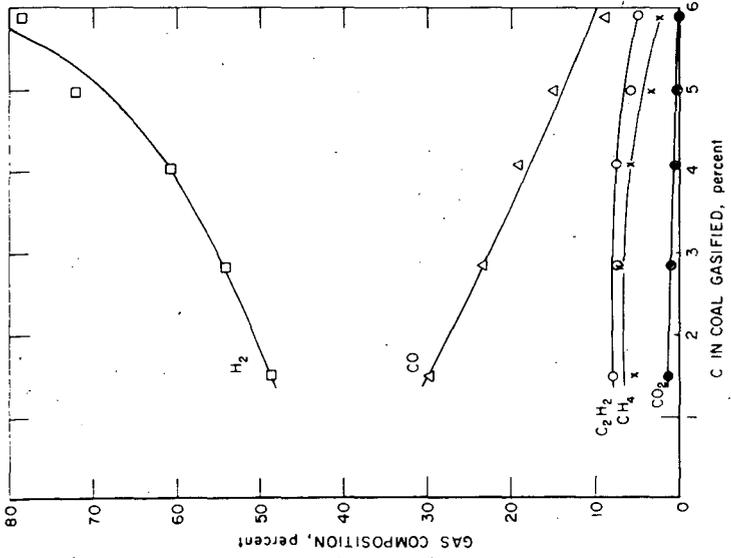


Figure 4. - Gas composition at various stages of discharge pyrolysis of hvab coal.

12-5-67 L-10290

12-5-67 L-10291