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DISTRIBUTION OF GASEOUS PRODUCTS FROM LASTER PYROLYSIS OF COALS OF VARIOUS RANKS

By

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Changes in coal and products from coal resulting from thermal treatment have been the subject of many investigations. (1, 6) An extensive bibliography has been included in reference 6. With the exception of the evolution of water and small quantities of light hydrocarbons, coals are but little affected by temperatures up to about 300°C. However, at 500°C as much as 50 percent of some coals can be volatilized. Temperatures of 1,000°C to 5,000°C are of special interest because it is in this range that equilibrium concentrations of acetylene and hydrogen cyanide become significant. Such temperatures can be attained by induction furnaces, plasmas, flash heating, and lasers. (4)

The development of the laser has presented a new opportunity for the study of coal pyrolysis. The laser is a device which compresses light energy three ways: (a) in band width--essentially a single frequency is produced; (b) in time--the energy is delivered in about a millisecond; (c) in area--the beam is approximately the diameter of the laser rod and can be focused. High energy densities and temperatures far exceeding any previously available for the pyrolysis of coals are produced. Temperatures of several thousand degrees centigrade can be attained quickly without sample or product contamination. Laser techniques have been used for the rapid vaporization of metals and graphite at temperatures estimated as 7,000° K to 8,000° K. (7) Light energy from the laser source passes readily through the walls of a glass reaction vessel and can be quickly converted into heat and chemical energy by a dark absorbing medium such as coal. Thus, the laser is a particularly good source of energy for converting coal into gases rich in acetylene and HCN.

Previous attempts at this laboratory to pyrolyze coal at high temperatures using flash and laser techniques have produced more acetylene and less methane than conventional coke oven pyrolysis. (1) Flash photolysis was applied to coals of several ranks by Rau and Seglin and product gases containing up to 16 mole percent of acetylene were reported. (5) Bond has reported acetylene analyses as high as 30 mole percent from the plasma jet irradiation of coal. (6) Arc image techniques have also been applied to the pyrolysis of coal by Rau and Eddinger. (8)

EXPERIMENTAL PROCEDURE

The following coals were used in this investigation:

Rank	Coal	Source
Anthracite	Dorrance	Pennsylvania
Low Volatile Bituminous	Pocahontas No 3	West Virginia
Medium Volatile Bituminous	Sewell	West Virginia
High Volatile A Bituminous	Pittsburgh	Pennsylvania
High Volatile A Bituminous	Chilton	West Virginia
High Volatile C Bituminous	Rock Springs	Wyoming
Lignite	McLean	North Dakota
Lignite	Sandow	Texas

The coals are listed above in order of decreasing rank according to the American Society for Testing and Materials (ASTM) and International Classifications; that is, according to volatile matter up to 33 percent and according to calorific parameter above 33 percent volatile matter.

Samples (3/8-inch cubes) were sealed in pyrex tubes 10 mm ID and 90 mm long as shown in Figure 1. All samples were heated to 100°C for 20 hours in a vacuum oven, then sealed and irradiated. Five pulses of 1.5 joules of focused energy were impinged on each coal sample. Gaseous products were admitted to the mass spectrometer in five fractions distilling from liquid nitrogen, dry ice, ice water, room temperature, and 60°C baths. The total volume of each fraction was determined and each fraction was analyzed by mass spectrometry. A carbonaceous residue deposited on the wall of the glass tube during irradiation of Pittsburgh seam coal was examined by infrared.

RESULTS AND DISCUSSION OF RESULTS

Gaseous products from coals of several ranks were compared. Analyses of the coals are given in Table 1 and analyses of gaseous products are shown in Table 2. Gas analyses are averages of from two to eight tests on different samples of the same coal. Yields of major components (above 10 percent) in terms of moles/irradiation showed deviations of from 4 to 20 percent from the average; minor components (under 10 percent) showed variations of up to 50 percent from the average. These variations, resulting at least partly from the present state of the experimental technique, do not affect the conclusions.

Atomic C/H Ratios

Figure 2 gives the atomic C/H ratios for the original coals as well as for the gaseous products. For the coals, this ratio decreases rapidly between anthracite and Pittsburgh seam (hvab); little change is shown in the C/H ratio for the hvab coals to the lignites. The gaseous products are richer in hydrogen than their parent coals although this difference is small for the lignites. Since rapid heating occurs in and around the region of irradiation, volatile matter will comprise a large portion of the gas from a high volatile coal (Figure 3). In coals with a low volatile content the laser energy will again release the more volatile components but these gases, comprising less of the coal, will be less characteristic of the whole coal.

Distribution of Gaseous Product

Gaseous products are given in Table 2 as mole percent of total gas and also as moles of gas per irradiation. The distributions of hydrogen, methane, acetylene, carbon monoxide, and carbon dioxide as functions of volatile matter of the coals are shown in Figure 4. Results for coals with volatile contents from 50 to approximately 20 percent were similar to the flash heating results of Rau and Seglin, that is, the younger coals with higher volatile matter show less methane and hydrogen. (5)

This type of plot, however, obscures the fact that many lower rank coals yield three or four times as much gas as higher rank coals such as anthracite. An investigation of the absolute gas yield is now underway. Weight balances obtained in this investigation have not been considered reliable. However, as the same irradiation procedure was used for all samples, an attempt was made to correlate the gas yield with volatile matter, as shown in Figures 5, 6 and 7. The data, while not as reproducible as desired, do give a truer indication of changes in gaseous product with volatile content and coal rank.

The total volume of gas per irradiation on a H_2O, N_2, and O_2 free basis, is shown in Figure 5. The total gas increased as coal rank decreased, showing about a four-fold increase from anthracite to lignite.

Figure 6 shows the moles of H_2, CH_4, and C_2H_2 produced per irradiation as a function of volatile matter. Methane yields were quite low and showed little change with volatile matter. Acetylene from the low rank, high volatile coals exceeded that from anthracite by approximately 15 times while hydrogen increased by a factor of 10 over the same range of volatile matter. These data are similar to those of Aust for the plasma jet heating of coal to extreme temperatures, namely, that acetylene yield is related to the volatile matter. (6)

As expected, yields of CO and CO_2 were higher for the lower rank coals having more volatile matter and a higher concentration of oxygen (Figure 7). The ratio of CO to CO_2 shown in Figure 8 indicates little variation in the ratio for coals from Texas lignite to Sewell (mvb). The oxygen content for these coals ranges from 4.4 percent (Sewell) to 18.6 percent (Texas lignite).

While the yield of water does not follow a consistent pattern, much higher values were obtained for the lower rank coals as would be expected. It is likely that the evacuation method (100°C for 20 hours in a vacuum oven) was only partially successful and that the values include both water from the surface of the coal and product from the reaction. The yield of HCN was low, but did show a trend toward higher values for the lower rank coals. These data indicate that with laser irradiation the maximum yield of hydrogen is obtained from coal of medium rank, that is,

Table 1.- Coal analyses

Coal Rank	Dorrance anthracite	Pocahontas lvb	Sewell mvb	Pittsburgh hvab	Chilton hvab	Rock Springs hvcb	North Dakota lignite	Texas lignite
Proximate, percent maf								
Volatile matter	5.9	18.9	23.7	40.7	40.2	45.4	48.5	51.2
Fixed carbon	94.0	81.0	76.3	59.2	59.7	54.6	51.5	48.8
Ultimate, percent maf								
H	2.8	4.7	5.1	5.5	5.7	5.6	5.0	5.4
C	92.5	89.5	88.4	82.2	79.9	79.2	70.9	72.4
O	2.8	3.8	4.4	8.9	11.3	12.4	21.4	18.6
N	1.0	1.4	1.5	1.7	1.6	1.7	1.1	1.4
S	0.9	0.8	0.5	0.8	1.4	1.1	1.6	2.1
Atomic ratio, C/H	2.75	1.59	1.44	1.24	1.17	1.18	1.18	1.12

coal such as Pittsburgh seam (hvab). The distribution of products is considerably different from that obtained by the vacuum pyrolysis of coals to 450°C. (3) In the 450°C vacuum pyrolysis studies, the hydrogen yields were low and independent of rank. Methane yields were a maximum for the medium rank coals and much higher than the yield of hydrogen. Carbonization at 900°C produces gas with characteristics of both the high-temperature laser irradiation and gas from low-temperature carbonization, that is, high concentrations of hydrogen and methane and a low concentration of acetylene. As reported previously for the flash irradiation of coal, gas from the laser irradiation showed a lower concentration of saturate species such as methane and a higher concentration of unsaturate species, including acetylene, than gas from lower temperature processing.

Infrared Spectrum of Solid Residue

An infrared spectrum was obtained of the solid residue deposited on the walls of the reaction tube during irradiation of Pittsburgh seam (hvab) coal. As shown in Figure 9, most of the bands characteristic of the coal spectrum were absent in the spectrum of the solid residue, indicating that the product was primarily carbon.

Craters Produced by Laser Irradiation

Craters (Figure 3) produced in coals of different ranks differed greatly. A preliminary examination indicated that craters produced in low rank coals such as lignite were much deeper than those produced in high rank coals such as anthracite. It therefore appeared that the energy penetrated deeper in the low rank coals having more volative matter. Figure 3 also reveals that there was extensive carbonization in the region surrounding the crater.

CONCLUSIONS

Laser irradiation has several advantages over other techniques for studies of the high-temperature reactions of coal: (1) The energy can be focused and directed on specific areas, (2) heating is done by an external source negating contamination, (3) rapid heating of the sample and cooling of the gases occurs. The products obtained in this investigation were similar to those reported previously from flash and argon plasma irradiations. The unsaturated species (primarily acetylene) were much higher and the methane lower than the concentrations found from 900°C carbonization of coal. The lower rank coals not only produced approximately 4 times as much gas as the higher rank coals, such as anthracite, but showed, also, much higher concentrations of acetylene, indicating that further studies of lower rank coals might be fruitful. Infrared studies of the carbonaceous residue indicated that the high temperatures attained with Laser irradiation volatilize a major portion of the components that produce infrared spectra of medium rank coals.

ACKNOWLEDGMENT

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Table 2.- Product gases from laser irradiation of coals

Coal Rank	Dorrance Anthracite		Pocahontas lvb		Sewell mvb		Pittsburgh hvab		Chilton hvab		Rock Springs hvcb		North Dakota lignite		Texas lignite	
	Moles x 10^7	Mol. %	Moles x 10^7	Mol. %	Moles x 10^7	Mol. %	Moles x 10^7	Mol. %	Moles x 10^7	Mol. %	Moles x 10^7	Mol. %	Moles x 10^7	Mol. %	Moles x 10^7	Mol. %
Product gas																
H_2	4.3	28.1	22.9	62.9	12.5	57.6	29.8	52.2	31.3	54.1	24.3	34.0	20.6	36.1	19.5	31.7
CO	4.7	30.8	5.1	14.0	3.7	17.1	12.7	22.5	15.3	26.4	25.5	35.7	27.8	48.7	23.9	38.9
CO_2	4.6	30.1	1.3	3.6	1.9	8.8	5.0	8.7	1.6	2.8	12.5	17.5	5.9	10.4	10.6	17.2
CH_4	1.0	6.5	0.9	2.5	0.8	3.6	2.9	5.1	2.6	4.4	2.2	3.1	0.6	1.0	0.8	1.3
C_2H_2	0.5	3.2	5.8	15.9	2.6	12.0	6.0	10.6	6.8	11.6	5.8	8.2	1.8	3.1	6.0	9.8
HCN	0.2	1.3	0.4	1.1	0.2	0.9	0.5	0.9	0.4	0.7	1.1	1.5	0.4	0.7	0.7	1.1
O_2	6.8		3.2		14.4		1.0		3.7		1.2		1.0		1.7	
N_2	10.9		10.5		42.1		51.4		38.4		11.9		22.3		17.1	
H_2O	91.8		33.4		16.3		41.7		34.7		38.6		23.3		29.4	
Total gas, moles x 10^7 1/	15.3		36.4		21.7		56.9		58.0		71.4		57.1		61.5	
CO/CO_2	1.02		3.92		1.95		2.54		9.56		2.04		4.71		2.25	

1/ H_2O, O_2 and N_2 free.

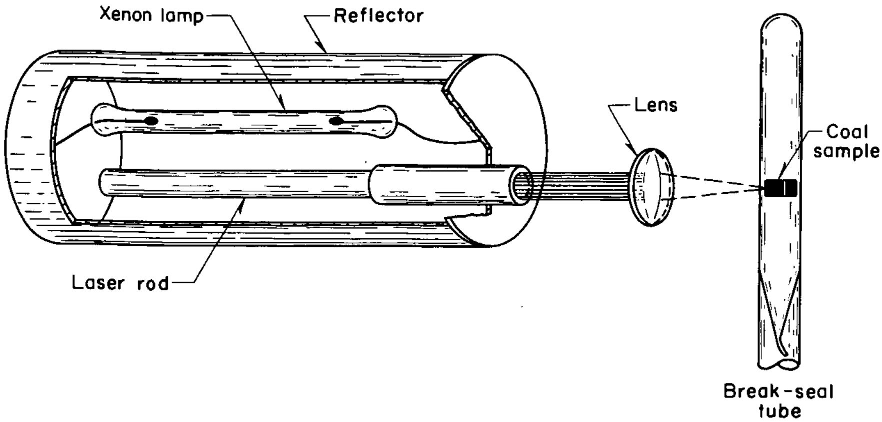

Figure 1.- Laser used for coal irradiation.

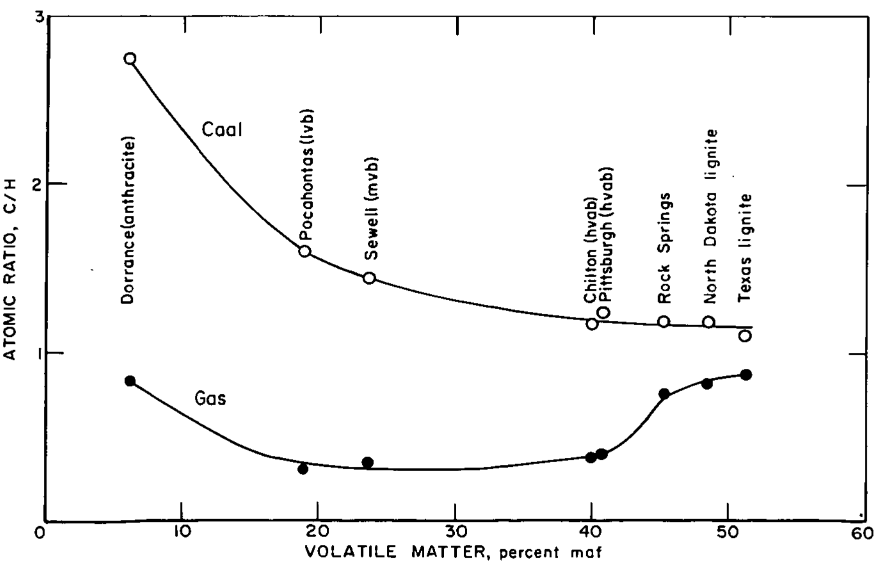

Figure 2.—Atomic C/H ratios of original coals and gases from laser irradiation.

Figure 3.- Coal crater produced by laser irradiation.

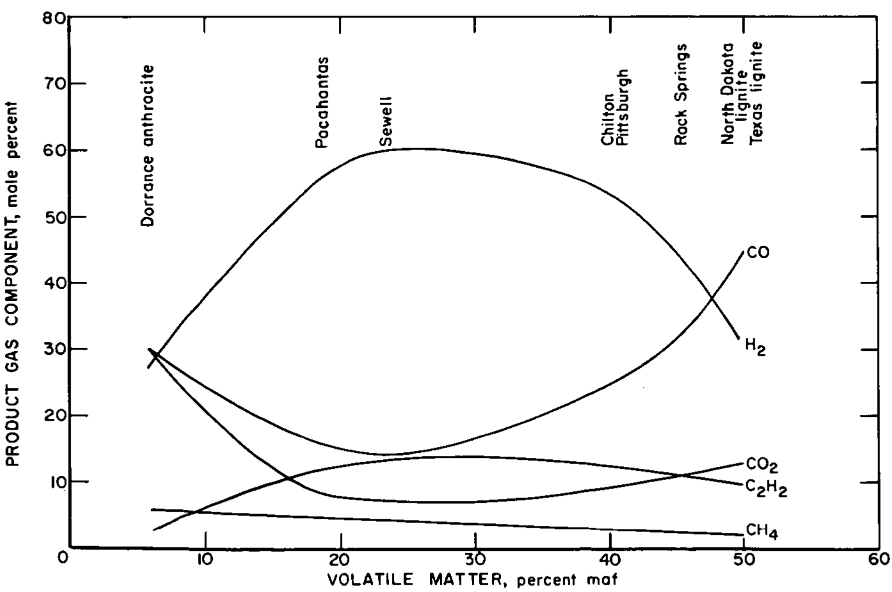

Figure 4.—Product gas as a function of volatile matter in coal

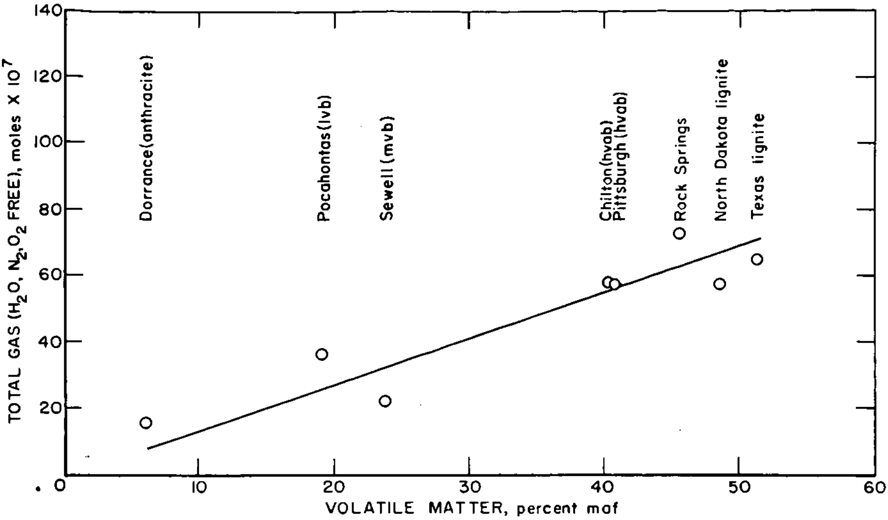

Figure 5.—Product gas as a function of volatile matter in coal.

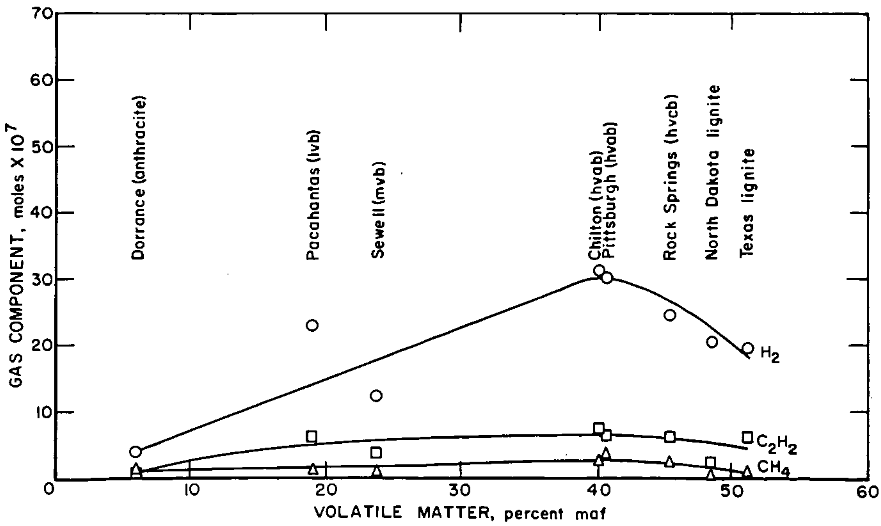

Figure 6.—CH_4, C_2H_2 and H_2 in product gas as a function of volatile matter in coal.

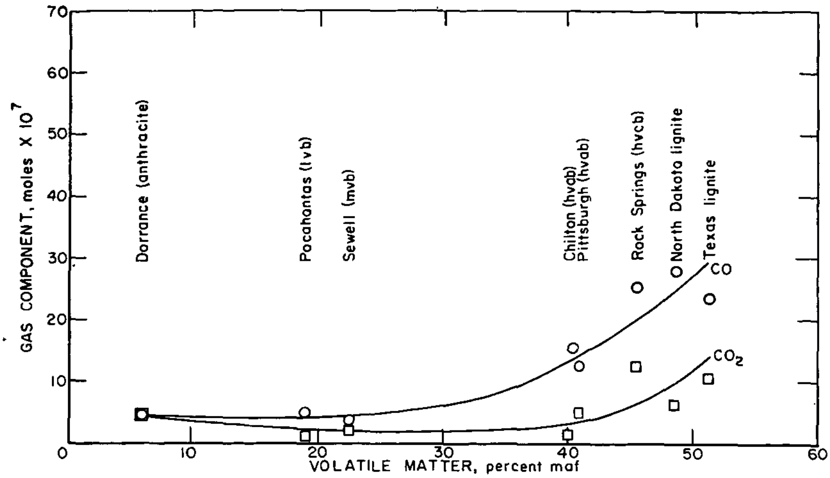

Figure 7 — CO and CO_2 in product gas as a function of volatile matter in coal.

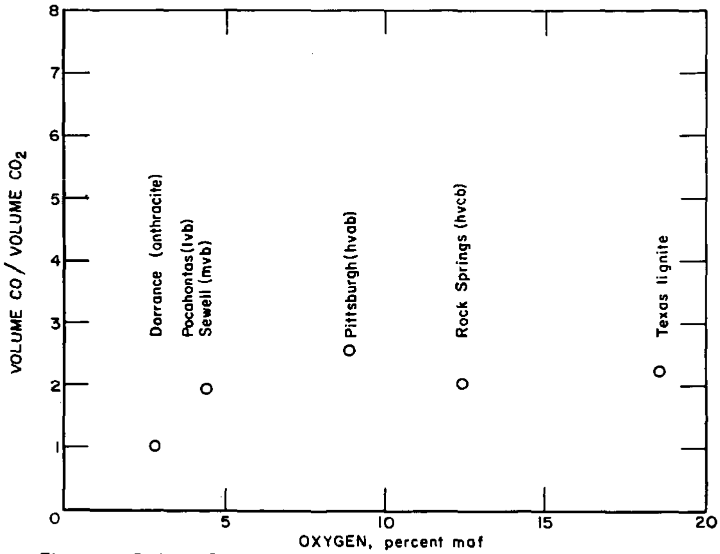

Figure 8. — Ratio of CO to CO_2 in product gas as a function of oxygen in coal.

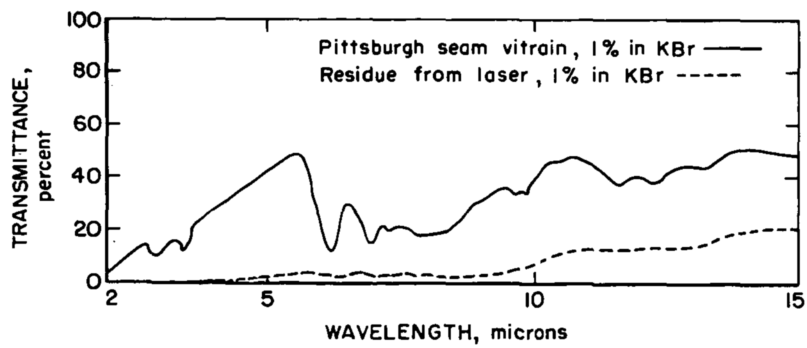

Figure 9.- Infrared spectra of Pittsburgh seam vitrain and residue after laser irradiation.