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COAL INVESTIGATIONS USING LASER IRRADIATION

By F. S. Karn, A. G. Sharkey, Jr., A. F. Logar,
and R. A. Friedel

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COAL INVESTIGATIONS USING LASER IRRADIATION

by

F. S. Karn,[1] A. G. Sharkey, Jr.,[2] A. F. Logar,[3] and R. A. Friedel[4]

ABSTRACT

Conditions necessary to obtain optimum yield of useful products when coal is rapidly heated to extreme temperatures by laser irradiation were determined by the Bureau of Mines. Product distribution and yield were investigated as functions of several variables. Low-rank coals with high-volatile matter gave highest total gas yields. Medium-rank coals gave the highest yields of H_2 and C_2H_2 and low-rank coals gave highest yields of CO and CO_2. Macerals gave gases of approximately the same composition, but the total gas yield increased in the order fusinite, micrinite, vitrinite, and exinite. Total gas and C_2H_2 yields varied inversely with particle size. The addition of nominally inert gases such as Ar, He, N_2 increased yields of H_2, C_2H_2, and total gas. Metals such as nickel and platinum had little influence on the rate of coal decomposition. Total gas yield increased with total energy of irradiation, and the ratio of C_2H_2-CH_4 increased with concentration of energy. A study was also made of the irradiation temperature, and a material balance was calculated.

INTRODUCTION

The Pittsburgh Coal Research Center of the Bureau of Mines is investigating coal structure by utilizing solid and gas lasers, and preliminary studies of laser irradiation of coal have been reported (10, 19-21).[5] Laser induced coal pyrolysis, compared with conventional coke-oven pyrolysis, provides higher temperatures and faster heating and cooling, resulting in a change in product distribution. The purpose of the present investigation was to use laser induced coal pyrolysis to determine product distribution and yield as a function of several variables: coal rank, maceral, particle size, and atmosphere. There are also variables characteristic of the laser quantity of

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[1] Research chemist.
[2] Supervisory research physicist.
[3] Physical science technician.
[4] Project coordinator, Spectrometry.
All authors are with the Pittsburgh Coal Research Center, Bureau of Mines, Pittsburgh, Pa.
[5] Underlined numbers in parentheses refer to items in the list of references at the end of this report.

energy discharged, rate of discharge, area of target, and wavelength of radiant energy. These material and process variables were examined in the experimental program.

Changes in coal and products from coal resulting from thermal treatment have been the subject of many investigations (2-3, 6, 10, 12, 16, 18-21). (An extensive bibliography is included in reference 2.) Except for 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, 30 pct or more of some coals may be volatilized. At conventional pyrolysis temperatures, the resulting mixture of primary and secondary reactions, particularly polymerization, is difficult to interpret. Temperatures of 1,000° 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, arc-image furnaces, plasmas, flash heating, and lasers (12).

The development of the laser presented a new opportunity for the study of coal pyrolysis. The laser is a device which compresses light energy three ways: (1) In band width--essentially a single frequency is produced; (2) in time--the energy is delivered in about a millisecond; and (3) in area--the beam is approximately the diameter of the laser rod and can be further concentrated by focusing.

High-energy densities and temperatures far exceeding any previously available for the pyrolysis of coals are possible. 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 at 4,000° to 6,000° K (8). 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 in 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 (19). Irradiation of coal with a 6-j (joule) pulse from a ruby laser, compared with conventional high-temperature pyrolysis, caused significant changes in the gas composition. Conventional coal pyrolysis, varying from 450° to about 1,400° C, includes many different processes and coals. A typical high-temperature pyrolysis gas obtained from a Pittsburgh seam hvab coal carbonized at 900° C. Fifteen percent of this coal (40.7-pct volatile matter) was gasified with the product distribution shown in column 1 of table 1. With laser pyrolysis, the coal gasified increased from 15 to 52 pct, and the C_2H_2-CH_4 ratio increased from less than 0.002-1 to 2.1-1.

Flash photolysis was applied to coals of several ranks by Rau and Seglin, and product gases containing up to 16 mole pct of acetylene were reported (16). Bond has reported acetylene values as high as 30 mole pct from the plasma jet heating of coal (2). Graves reported acetylene yields as high as 15 wt pct of the moisture- and ash-free (maf) coal charged to a plasma jet (5). Arc-image techniques have also been applied to the pyrolysis of coal by Rau and Eddinger (15).

TABLE 1. - Product gas analysis, vol pct

Product gases	Pyrolysis	
	900° C	Laser
H_2	55.6	52.2
CO....................	7.4	22.5
CO_2	.4	8.7
CH_4	31.5	5.1
C_2H_2	.05	10.6
C_2H_4	3.4	.0
C_2H_6	1.2	.0
HCN....................	.0	.9
$>C_2$	.5	.0

ACKNOWLEDGMENTS

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EXPERIMENTAL PROCEDURES

A variety of coals and coal macerals have been exposed to laser irradiation. Using a focused beam, energy concentrations as high as 40 megawatts (9.6×10^6 cal per sec) per square centimeter can be attained. Heat input is complete in milliseconds (msec) or microseconds (μsec) compared with seconds in the most rapid conduction and convection methods. Cooling is also rapid due to the explosive expansion of gases and entrained particles.

The general irradiation procedure was to seal the coal sample in a glass vessel through which the laser beam can be fired. Coal samples, usually 8-mm cubes, were heated under vacuum to 100° C for 20 hours before sealing. The glass vessels, 10 mm id and 90 mm long (fig. 1), were evacuated, or evacuated and partially refilled with a specific gas, before irradiation. The usual irradiation was one pulse of a focused beam from a 6-j ruby laser. Gaseous products were analyzed by mass spectrometry in two or more fractions distilled from baths of liquid N_2, solid CO_2, ice water, room-temperature water, and 60° C water. Both total volume and gas distribution were determined for each fraction. Solid products, evaporated and recondensed on the glass walls, were removed for ultimate analysis or for inspection by infrared spectrometry.

Coals were also treated with uniform pulses of light from three different lasers. The ruby laser delivers 6 j of 6943 A light in about 1 msec. The source of the light is a cylindrical ruby 76 mm long by 6.3-mm diameter that is activated by a xenon flash lamp and a capacitor capable of delivering a 2,000-volt pulse. The neodymium (Nd) laser is a glass rod 152 mm long and

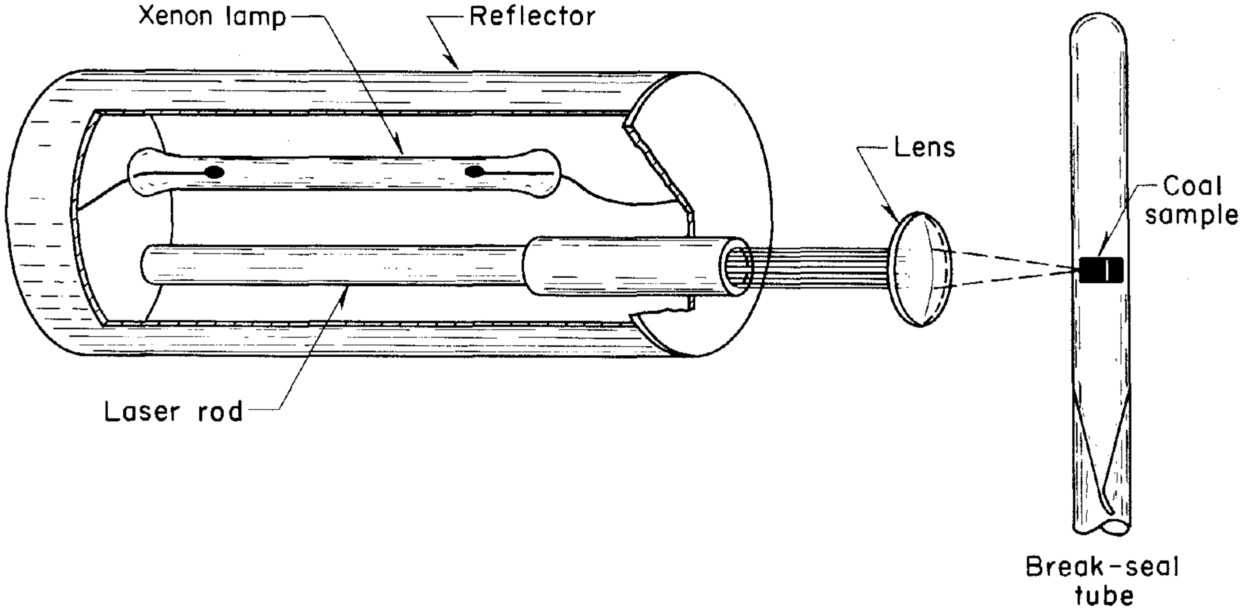


FIGURE 1. - Laser Used for Coal Irradiation.

capable of a 28-j pulsed discharge. A continuous CO_2 laser, the third type, has only a 10-watt power output, but, since it operates continuously, the total energy and the quantity of product gas can be made to equal that of the pulsed lasers. Radiation from the CO_2 laser has a wavelength of 106,000 A. Additional discussion of lasers is given in the "Results" section.

RESULTS

Coal Rank

The coals irradiated with one pulse from a 6-j ruby laser are listed in table 2 from left to right in order of decreasing rank, according to the American Society for Testing and Materials (ASTM) and International Classifications (14); that is, according to volatile matter up to 33 pct and according to calorific value above 33 pct volatile matter.

Analyses of the coals are given in table 2; analyses of the product gases after irradiation are given in table 3. These analyses are averages of from 2 to 8 tests on samples of each coal. Yields of major components (>10 pct), in terms of moles per irradiation, showed deviations of from 4 to 20 pct from the average; minor components (<10 pct) showed variations of up to 50 pct from the average. These variations, resulting from coal heterogeneity and the present state of the experimental technique, do not affect the conclusions.

TABLE 2. - Coal analyses of irradiated samples

Analyses	Dorrance anthracite (Pa.)	Pocahontas lvb (W. Va.)	Sewell mvb (W. Va.)	Pittsburgh hvab (Pa.)	Chilton hvab (W. Va.)	Rock Springs hvcb (Wyo.)	North Dakota lignite	Texas lignite
Proximate, pct maf:								
Volatile..........	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, pct maf:								
Hydrogen..........	2.8	4.7	5.1	5.5	5.7	5.6	5.0	5.4
Carbon............	92.5	89.5	88.4	82.2	79.9	79.2	70.9	72.4
Oxygen............	2.8	3.8	4.4	8.9	11.3	12.4	21.4	18.6
Nitrogen..........	1.0	1.4	1.5	1.7	1.6	1.7	1.1	1.4
Sulfur............	.9	.8	.5	.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

TABLE 3. - Product gases from laser irradiation of coals

Product gas	Dorrance anthracite		Pocahontas lvb		Sewell mvb		Pittsburgh hvab		Chilton hvab		Rock Springs hvcb		N. Dakota lignite		Texas lignite	
	Moles $\times 10^7$	Mole pct	Moles $\times 10^7$	Mole pct	Moles $\times 10^7$	Mole pct	Moles $\times 10^7$	Mole pct	Moles $\times 10^7$	Mole pct	Moles $\times 10^7$	Mole pct	Moles $\times 10^7$	Mole pct	Moles $\times 10^7$	Mole pct
H_2.........	4.3	28.1	22.9	62.9	23.5	62.7	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	4.9	13.0	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	.8	2.3	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	.9	2.5	1.5	4.1	2.9	5.1	2.6	4.4	2.2	3.1	.6	1.0	.8	1.3
C_2H_2.......	.5	3.2	5.8	15.9	5.6	14.8	6.0	10.6	6.8	11.6	5.8	8.2	1.8	3.1	6.0	9.8
HCN........	.2	1.3	.4	1.1	.5	1.3	.5	.9	.4	.7	1.1	1.5	.4	.7	.7	1.1
O_2.........	6.8	-	3.2	-	2.6	-	1.0	-	3.7	-	1.2	-	1.0	-	1.7	-
N_2.........	10.9	-	10.5	-	9.7	-	51.4	-	38.4	-	11.9	-	22.3	-	17.1	-
H_2O........	13.0	-	8.7	-	6.4	-	41.7	-	34.7	-	38.6	-	23.3	-	29.4	-
Total[1]..	15.3	-	36.4	-	36.8	-	56.9	-	58.0	-	71.4	-	57.1	-	61.5	-
$CO-CO_2$.....	1.02	-	3.92	-	6.12	-	2.54	-	9.56	-	2.04	-	4.71	-	2.25	-
$C_2H_2-CH_4$...	.5	-	6.4	-	3.7	-	2.1	-	2.6	-	2.6	-	3.0	-	7.5	-

[1] H_2O, O_2, and N_2 free.

Data have been plotted as functions of volatile matter (moisture- and ash-free basis) of the original coals. Volatile matter generally varies inversely with rank, and it has the advantage over the more conventional expression of rank in that it can be expressed numerically. 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 from 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 (fig. 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.

Gaseous products are given in table 3 as moles of gas per irradiation and as mole pct of total gas. The distributions of H_2, CH_4, C_2H_2, CO, and CO_2 as functions of volatile matter of the coals are shown in figure 3. Results for coals with volatile contents from 50 to approximately 20 pct were similar to the flash-heating results of Rau and Seglin; that is, the younger coals with higher volatile matter show less CH_4 and H_2 (16).

Figure 3 obscures the fact that many lower rank coals yield three or four times as much gas as higher rank coals such as anthracite. To determine the total gas yield it was necessary to reproduce the discharge intensities, the beam focusing, and the sample geometry. Gas yields were plotted against volatile matter in figures 4 to 6. These 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 4. The total gas increased as coal rank decreased, showing about a fourfold increase from anthracite to lignite.

Figure 5 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 H_2 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 C_2H_2 yield is related to the volatile matter (2).

As expected, yields of CO and CO_2 were higher for the lower rank coals having more volatile matter and a higher oxygen content (fig. 6). While the yield of H_2O does not follow a consistent pattern, much higher values were obtained for the lower rank coals, as expected. It is likely that the evacuation of the samples for 20 hours at 100° C in a vacuum oven was only partially successful in removing H_2O, and the values include both water from the surface of the coal and products from thermal reactions. 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 H_2 is obtained from coal of medium rank such as Pittsburgh seam hvab. The distribution of

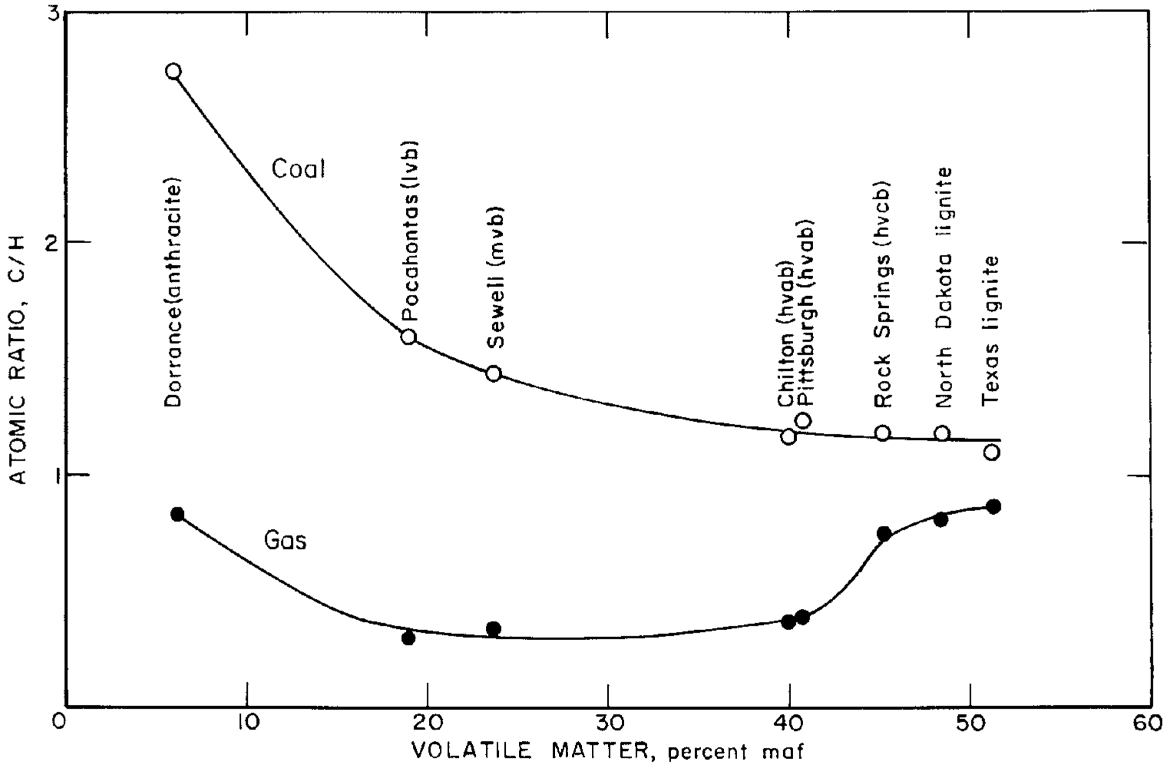


FIGURE 2. - Atomic C-H Ratios of Original Coals and Gases From Laser Irradiation.

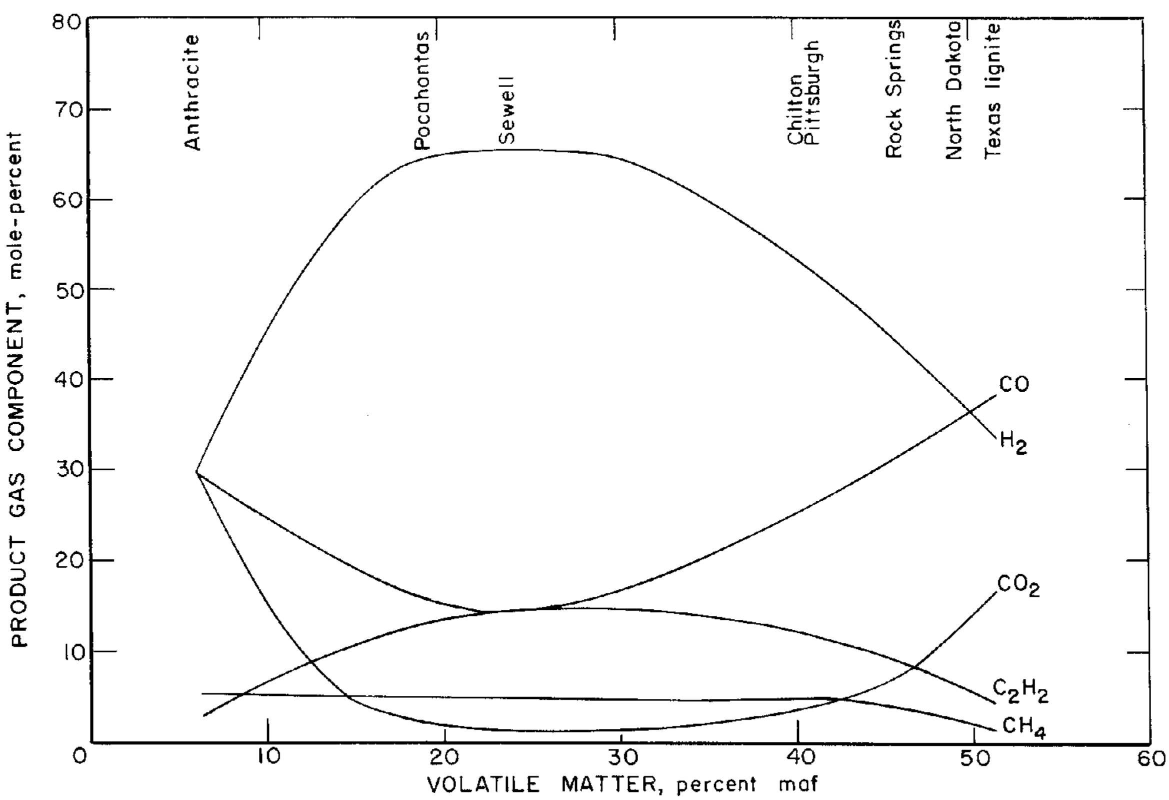


FIGURE 3. - Product Gas as a Function of Volatile Matter in Coal.

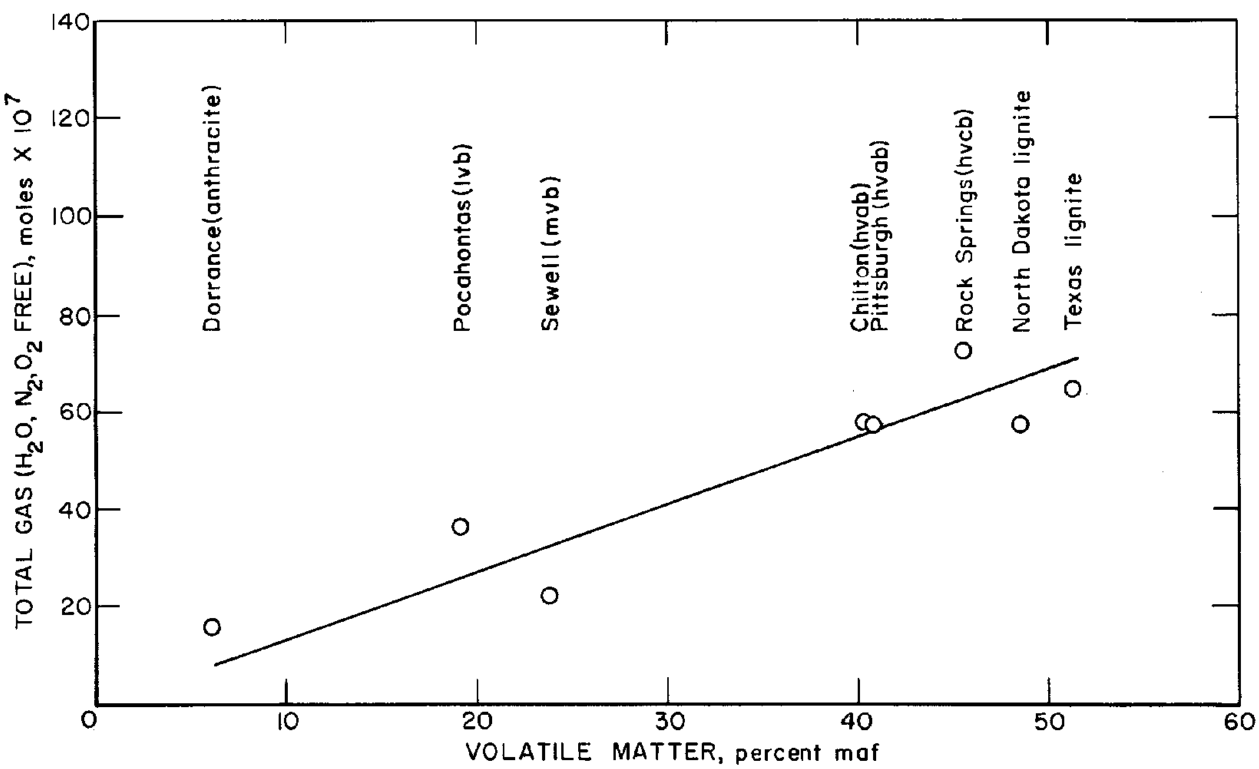


FIGURE 4. - Product Gas as a Function of Volatile Matter in Coal.

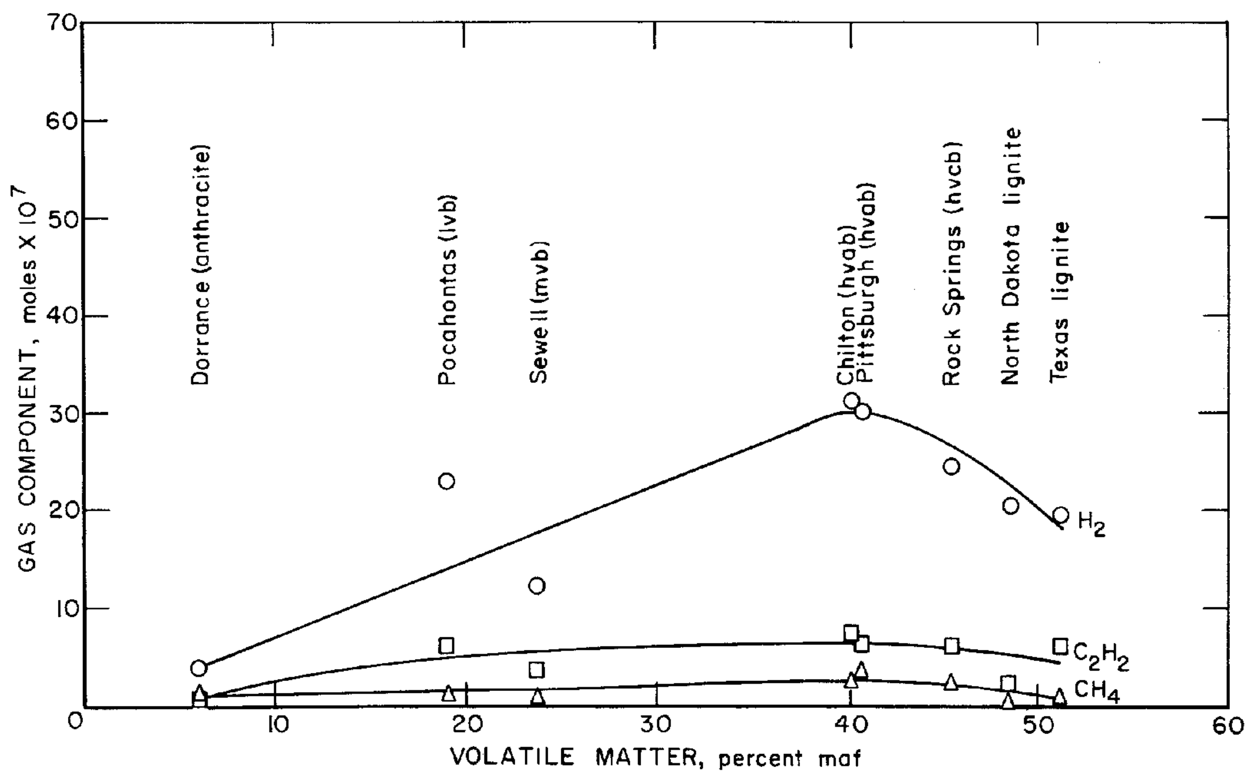


FIGURE 5. - CH_4, C_2H_2, and H_2 in Product Gas as a Function of Volatile Matter in Coal.

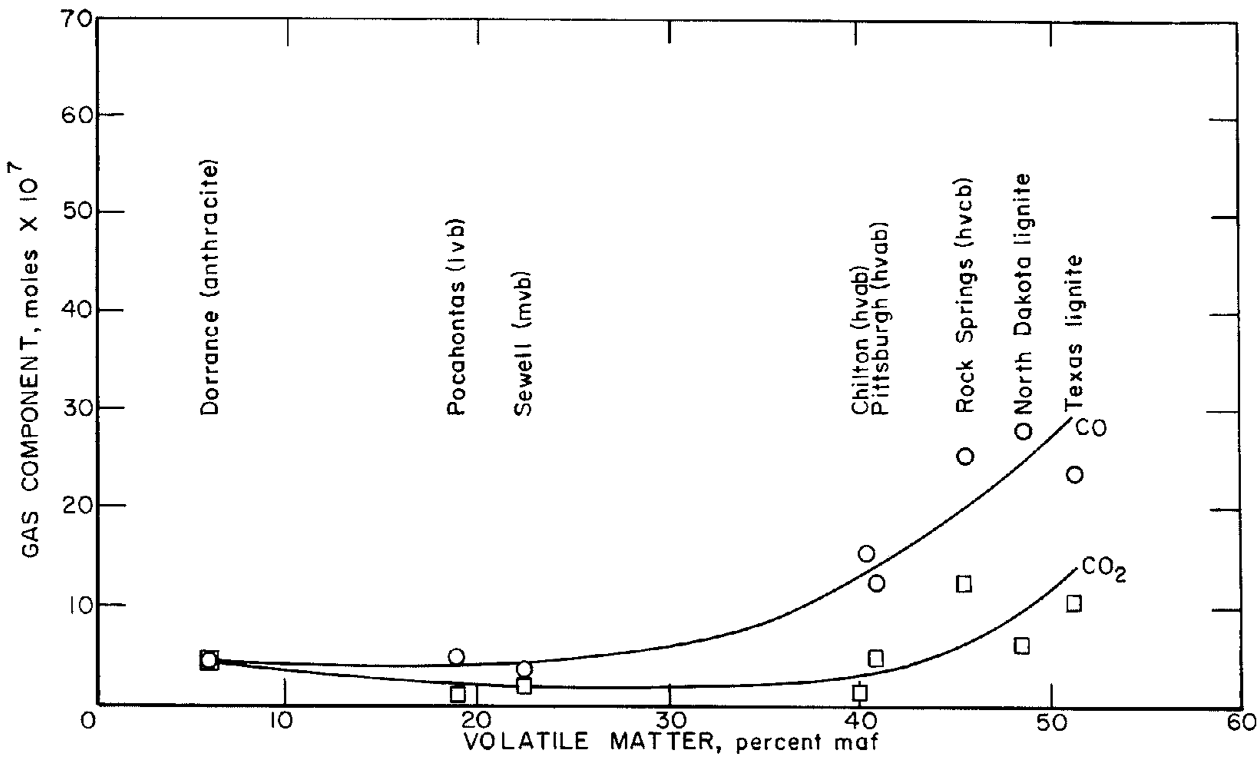


FIGURE 6. - CO and CO_2 in Product Gas as a Function of Volatile Matter in Coal.

products is considerably different from that obtained by the vacuum pyrolysis of coals to 450° C (18) or by 900° C carbonization (19).

In the 450° C, vacuum-pyrolysis studies, H_2 yields were low and independent of rank. Methane yields were a maximum for the medium-rank coals and much higher than the yield of H_2. Carbonization at 900° C produced gas with characteristics of both the high-temperature laser irradiation and gas from low-temperature carbonization, that is, high in H_2 and CH_4 and low in C_2H_2.

As reported previously for the flash irradiation of coal (19), gas from the laser irradiation showed a lower concentration of saturated species such as CH_4 and a higher concentration of unsaturated species, including C_2H_2, than gas from lower temperature processing.

The solid deposited on the walls of the reaction tube during irradiation of Pittsburgh seam hvab coal was removed and an infrared spectrum obtained. As shown in figure 7, most of the bands characteristic of coal were absent in the spectrum of this solid residue.

Craters (fig. 8) produced in coals of different ranks differed greatly. 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 volatile matter. Figure 8 also reveals that there was extensive carbonization in the region surrounding the crater.

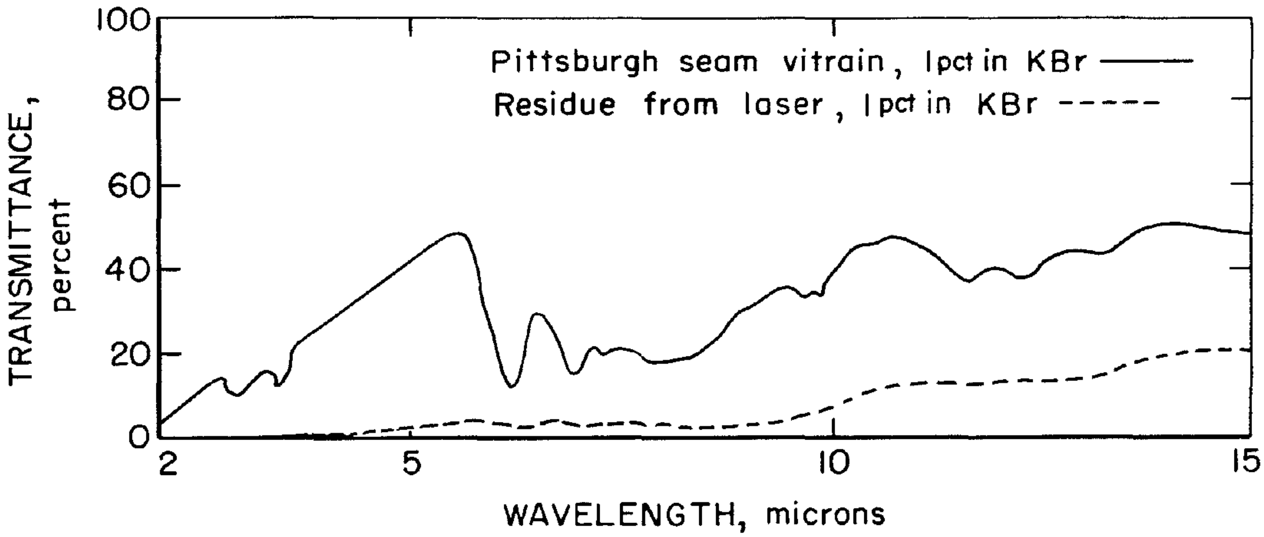


FIGURE 7. - Infrared Spectra of Pittsburgh Seam Vitrain and Residue After Laser Irradiation.

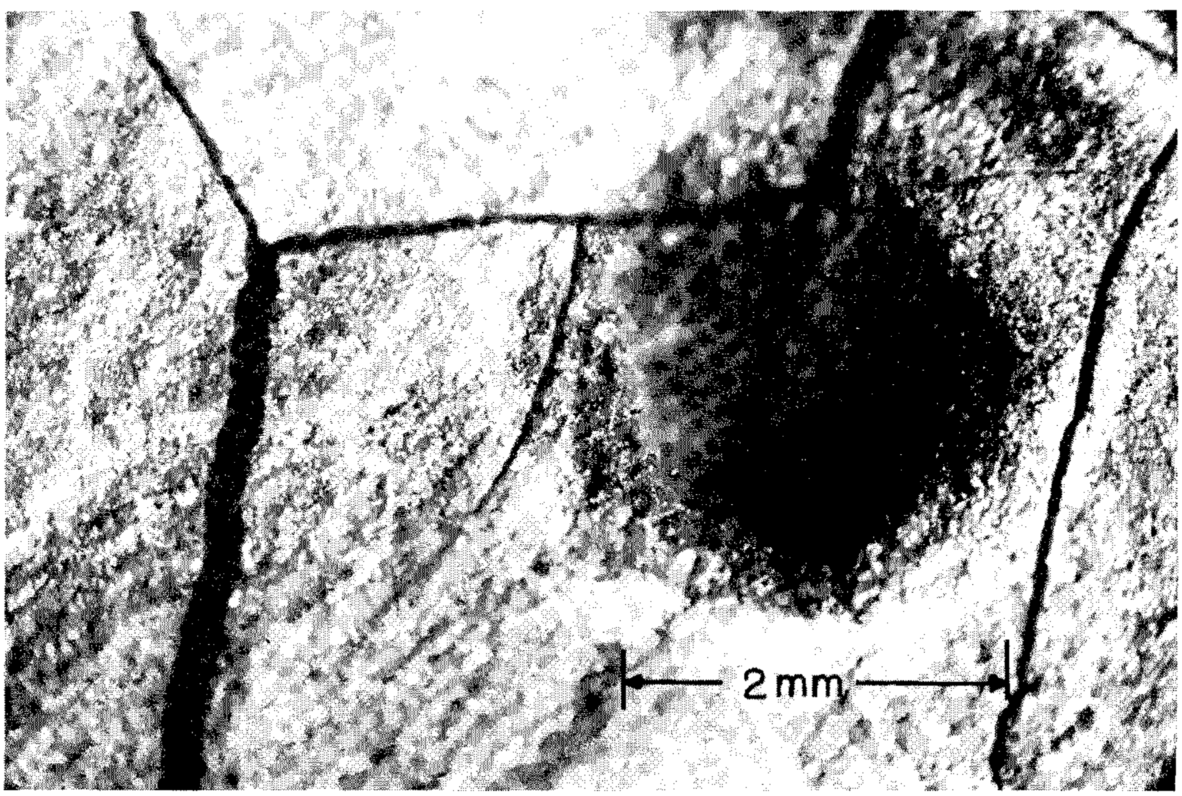


FIGURE 8. - Crater Produced by Laser Irradiation of Coal.

Macerals

In addition to variations between coals of different ranks there are significant differences between the several macerals of a single coal. Since macerals are ultimate identified by microscopic examination, only small samples are available, and this limits most pyrolysis studies. However, laser irradiation studies require only a few milligrams of sample and avoid this limitation. The present work was done on maceral concentrates which were described previously (4, 22). The purpose of this phase of the investigation was to determine the composition and quantity of gas evolved from various macerals pyrolyzed at the high temperatures obtained with laser irradiation.

Concentrates of macerals from Hernshaw bed hvab coal, Boone County, W. Va., were used (4). As reported by Ergun, McCartney, and Mentser, microscopic examination showed the concentrates to contain 86 pct or more of a major component--fusinite, micrinite, vitrinite, or exinite. Samples were pelleted and irradiated with the focused energy from a 6-j ruby laser.

Ultimate analyses of the maceral concentrates and whole coal before irradiation are given in table 4 (4); yields of major and several minor gaseous components are shown in table 5. The total product gas from the concentrates increased in the order fusinite, micrinite, vitrinite, and exinite, the same order shown for increasing volatile-matter content of the macerals. While the total volume of gas evolved during laser pyrolysis varied for the four macerals, the distributions of gaseous components were quite similar. While the concentrations of H_2 and CO in the product gases from the macerals reflect the difference in atomic H-C ratio, the concentrations of C_2H_2 in the product gases are similar.

TABLE 4. - Analyses of macerals, Hernshaw hvab coal

Maceral	Percent, maf				
	Hydrogen	Carbon	Nitrogen	Oxygen	Sulfur
Fusinite...	3.2	91.5	0.6	4.3	0.4
Micrinite..	4.8	85.9	.7	8.0	.6
Vitrinite..	5.4	85.2	1.6	7.2	.6
Exinite....	6.5	86.2	1.1	5.5	.7
Whole coal.	5.5	86.0	1.6	6.0	.9

TABLE 5. - Product gases from laser irradiation of coal macerals, Hernshaw hvab coal

Analyses	Maceral			
	Fusinite	Micrinite	Vitrinite	Exinite
Volatile matter, pct maf	13.4	31.4	33.7	55.4
Atomic ratio, H-C.......	.42	.67	.76	.89
Product gas:[1]				
[2]Moles x 10^7..........	43	52	90	103
H_2....................	46.7	50.0	54.3	52.1
CO....................	25.0	23.1	21.0	18.5
CO_2..................	2.0	1.1	.5	.5
CH_4..................	.4	.7	1.8	2.8
C_2H_2.................	23.8	24.0	21.1	23.2
HCN...................	.2	.3	.8	2.1
C_4H_2.................	1.8	.9	.3	.8

[1]Mole pct; water and air free.
[2]Total gas per irradiation.

Relative quantities of H_2 evolved from the four maceral concentrates are shown in table 6 with the yield from exinite assigned as 100. The relative yields of H_2 correlate quite well with the H_2 content of the macerals ranked in a similar manner. Unpublished results from dehydrogenation studies of these same macerals by Reggel, Wender, and Raymond of the Pittsburgh Coal Research Center show the same order for yields of H_2.

TABLE 6. - Hydrogen evolution from macerals during laser irradiation

Maceral	H_2 evolved, moles x 10^7 per irradiation	Relative quantities of H_2	
		Evolved	In macerals
Exinite.....	53	[1]100	[1]100
Vitrinite...	49	92	83
Micrinite...	27	51	74
Fusinite....	20	38	49

[1]Hydrogen from exinite (and in exinite maceral) assigned value of 100.

In summary, gas yield from the laser irradiation of macerals from hvab coal varies directly with volatile content of the macerals, while the distributions of product gases are very similar for the various macerals. Relative quantities of H_2 evolved with laser irradiation are consistent with the ultimate analyses of the macerals and with the H_2 obtained by dehydrogenation.

Particle Size

A study was made of the variation of gas yield as a function of particle size for Pittsburgh seam hvab coal. All samples were laser irradiated under vacuum with single pulses of 7-j energy. Particle sizes averaged 117, 63, 50, and 10 microns in diameter. Gas composition changed little as the particle size decreased from 117 to 50 microns. A further decrease to 10 microns caused an increase of C_2H_2 from 5 to 7 pct and a decrease of CH_4 from 17 to 12 pct. The total gas yield doubled (fig. 9). In this series of experiments, a defocusing lens was used in the laser beam, producing a lower temperature at the surface of the coal and a low C_2H_2-CH_4 ratio.

In a study of coal heated in an argon plasma, Bond (16) reported a threefold increase in the production of C_2H_2 over the same range of particle sizes. Kroger (11) heated coal rapidly to 1,583° K and reported no change in either gas yield or distribution as the particle size was decreased.

Gas Additives

The above experiments for studying coal decomposition under laser irradiation were made on coal samples that were carefully evacuated. However, it is also necessary to define the effects of various atmospheres on the process. Both inert (Ar, N_2, and He) and reactive (H_2, NH_3, O_2, and CH_4) gases were selected.

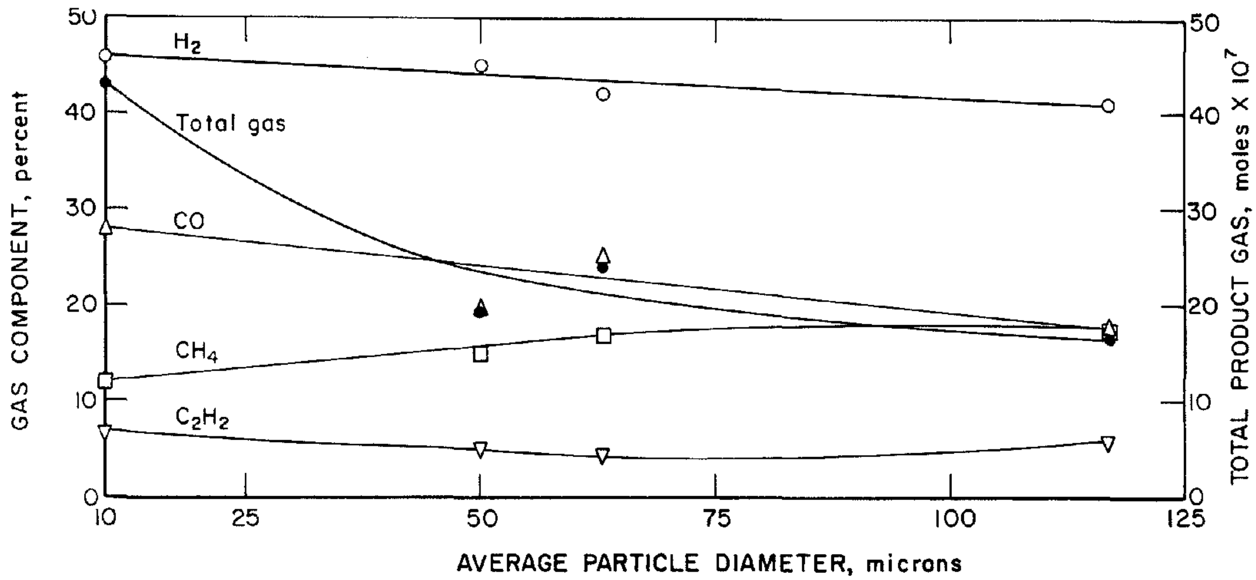


FIGURE 9. - Laser Irradiation of Pittsburgh Coal. Product gas as a function of coal particle diameter.

In each experiment the coal sample was evacuated, then 20, 50, 100, 200, 400, or 600 torr of a selected gas added. The tubes were sealed, irradiated in the usual way with 6 to 7.5 j from the ruby laser, and the product gases analyzed by mass spectrometry.

Inert

Although Ar, N_2, and He are chemically inert, they increased the yields of H_2 and C_2H_2 as well as total product gas (21). Each doubled the yield of C_2H_2 when the inert gas pressure was approximately 200 torr; additional pressure did not produce a significant change in product gas (figs. 10, 11, and 12). The C_2H_2-CH_4 ratio also increased with pressure.

Reducing

A H_2 atmosphere did not increase the yield of either C_2H_2 or CH_4. However, NH_3 caused a large percentage increase in C_2H_2 and HCN. Laser irradiation decomposes much of the NH_3 into H_2 and N_2. Therefore coal irradiation in an NH_3 atmosphere was compared with irradiation in H_2, N_2, and under vacuum (table 7). Much of the NH_3 atmosphere was not recovered in the product gas, either as NH_3 or as decomposition products. This may be due to its high sorptivity on coal, since NH_3 sorption on charcoal is many times greater than H_2 or N_2. As further evidence of the reaction between coal and NH_3, Weinstein and Walker (24) bombarded bituminous coal and NH_3 with neutrons from a nuclear reactor and found N_2-H_2 ratios too low to explain on the basis of NH_3 decomposition. They proposed a mechanism involving the reaction of amine radicals with coal.

TABLE 7. - Gaseous products from laser irradiation of Pittsburgh seam hvab coal in reducing atmospheres

Product gas[1]	Added gas			
	NH_3	H_2	N_2	Vacua
Pressure, torr................	200	100	120	-
H_2	(54.5)	(258.0)	(18.0)	(28.1)
CO........................	19.2	6.9	8.1	11.5
N_2	(135.0)	(30.2)	(296.4)	(8.5)
CH_4	2.5	2.8	2.7	3.0
NH_3	(162.5)	-	-	-
H_2O........................	(39.8)	(3.1)	(.4)	(2.9)
C_2H_2	32.0	7.2	14.5	7.1
HCN........................	3.2	1.1	3.4	1.1
C_3H_8	-	-	.1	.1
C_2H_6	.6	.3	.6	.5
O_2	(27.7)	(3.2)	-	(.4)
Ar........................	(1.5)	-	(.6)	-
C_3H_6	.3	.1	-	.3
CO_2	1.7	1.5	.9	1.4
Total[2]................	59.5	19.9	30.3	25.0
C_2H_2-CH_4	12.8	2.6	5.4	2.4

[1]Moles x 10^7 per 6- to 7.5-j irradiation.
[2]Numbers in parentheses have been excluded from total product.

Oxidizing

In contrast to the reducing effect of H_2 and NH_3, there are several gases which could accelerate the oxidation of coal: O_2, NO_2, NO, H_2O, and CO_2 (table 8).

TABLE 8. - Gaseous products from laser irradiation of Pittsburgh seam hvab coal in oxidizing atmospheres

Product gas[1]	Added gas					
	O_2	NO_2	NO	H_2O	CO_2	Vacua
Pressure, torr................	100	100	100	20	100	-
H_2	6.4	15.8	36.5	35.2	32.0	28.1
CO........................	13.5	52.8	13.0	14.1	12.0	11.5
N_2	(6.6)	(89.4)	(42.0)	(22.5)	(11.0)	(8.5)
CH_4	.6	.7	2.2	6.7	2.2	3.0
H_2O........................	(1.2)	(2.0)	(3.0)	(521.0)	(.9)	(2.9)
C_2H_2	2.7	2.2	6.7	12.1	6.0	7.1
HCN........................	.2	.1	.3	1.5	.2	1.1
C_3H_8	.1	.1	-	-	.5	.1
C_2H_6	.4	-	-	.7	.7	.5
O_2	(202.8)	(.9)	(.8)	(1.2)	(.2)	(.4)
Ar........................	(.8)	(.4)	(.3)	-	-	-
C_3H_6	-	-	-	.2	-	.3
CO_2	89.3	36.7	9.0	4.0	(180.9)	1.4
NO........................	-	(175.6)	(236.5)	-	-	-
NO_2	-	-	-	-	-	-
Total[2]................	113.2	108.4	67.7	74.8	53.6	53.1
C_2H_2-CH_4	7.7	3.1	3.0	1.8	2.7	2.4

[1]Moles x 10^7 per 6- to 7.5-j irradiation.
[2]Numbers in parentheses have been excluded from total product.

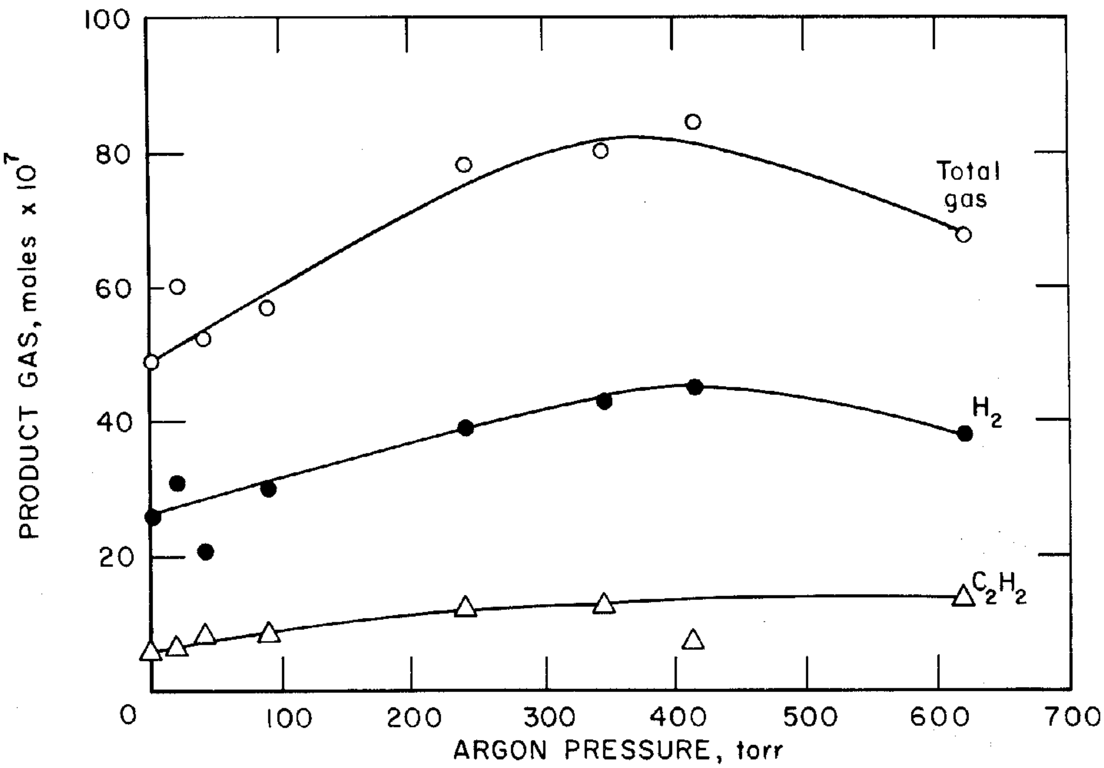


FIGURE 10. - Gaseous Products From Laser Irradiation of Pittsburgh Seam hvab Coal in Argon Atmosphere.

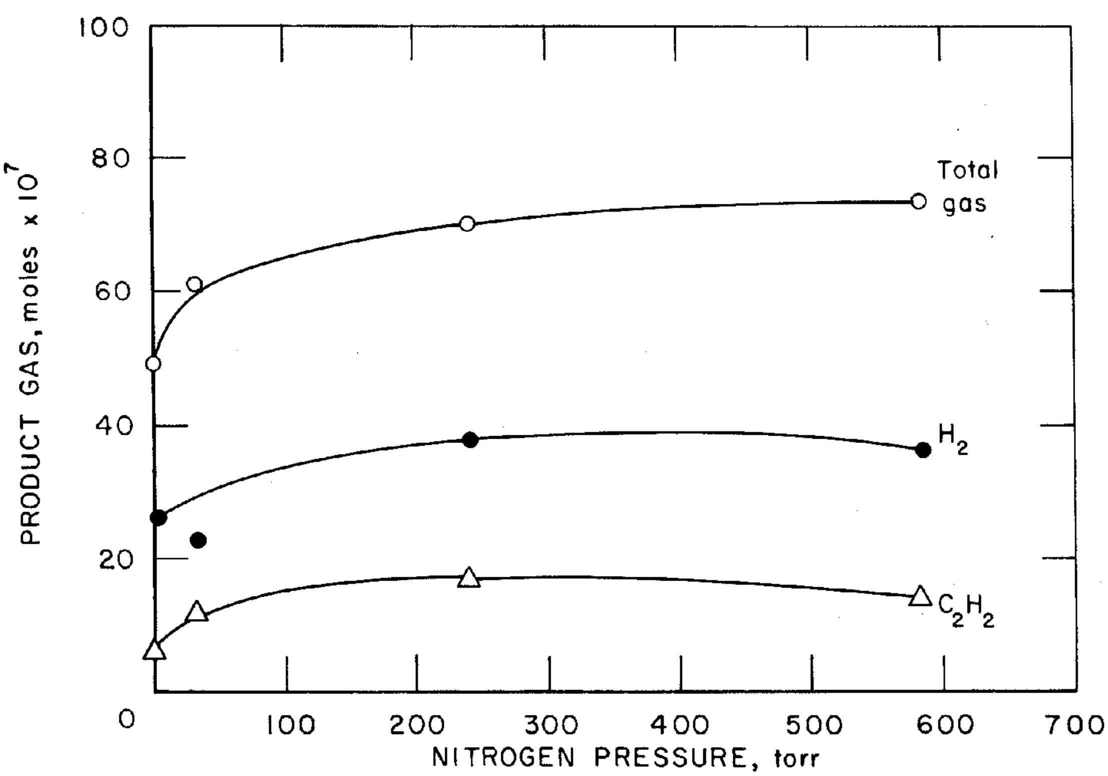


FIGURE 11. - Gaseous Products From Laser Irradiation of Pittsburgh Seam hvab Coal in Nitrogen Atmosphere.

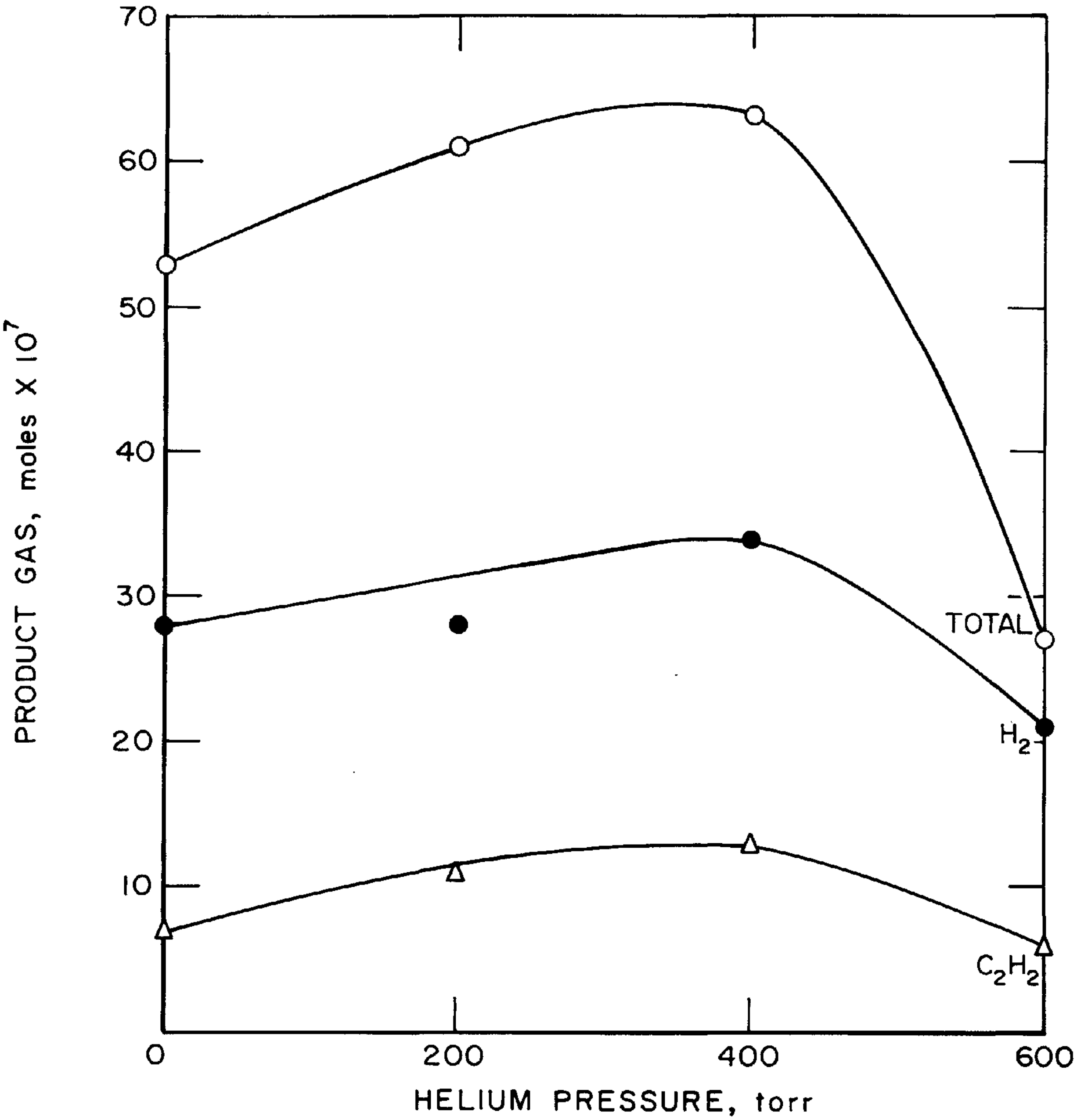


FIGURE 12. - Gaseous Products From Laser Irradiation of Pittsburgh Seam hvab Coal in Helium Atmosphere.

A 100-torr atmosphere of O_2 decreased the C_2H_2 and H_2 yields by 50 to 75 pct, compared with values obtained in vacua. Water yields were negligible, but CO_2 yields were greatly increased with an O_2 atmosphere. This may indicate that in coal the carbon is more susceptible to oxidation than the H_2. The decomposition and oxidation of coal are, of course, complex processes.

A comparison has been made between CO, H_2O, and CO_2 produced in these experiments and the same gases recovered from coal irradiated in vacua:

Product gas	Oxygen in gaseous product, moles x 10^7	
	Coal irradiated in oxygen	Coal irradiated in vacua
CO.....	6.7	5.8
H_2O....	.6	1.4
O_2.....	202.8 (added)	.4
CO_2....	89.3	1.4

CO and H_2O are approximately the same while CO_2 increased. Twenty-five percent of the O_2 introduced was not recovered and could have remained on the coal as adsorbed gas or as an oxidized surface.

The analysis for irradiation in H_2O vapor is the average of six tests. Most H_2O addition was at 20 torr, which is the saturation pressure of H_2O vapor at room temperature. Additional H_2O could be concentrated on the coal surface by only partially evacuating the H_2O sorbed in the coal. The effect of H_2O, either gaseous or absorbed, on irradiation of coal is similar to that of Ar or N_2; that is, yields of H_2 and C_2H_2 increase.

An atmosphere of 100 torr of NO_2 decreased the C_2H_2 yield, similarly to an O_2 atmosphere. The sum of the carbon oxides was approximately the same as with O_2, but CO increased and CO_2 decreased relative to the values with an O_2 atmosphere. Thermal decomposition of NO_2 during irradiation of the coal makes the reactions involved quite complex. Analysis for NO_2 by mass spectrometry is also difficult. The high NO value could result from the anomalous behavior of NO_2 in the mass spectrometer. Since 86 pct of the N_2 charge was recovered, the data appear reliable. Free N_2 exceeds gaseous O_2 (based on the assumption that they both came from NO_2) to again provide indirect evidence for the oxidation of the coal residue. The O_2 deficit is 114 x 10^{-7} moles, which is almost the same as that with the irradiation of coal in an O_2 atmosphere.

Irradiation in a 100-torr atmosphere of NO produced gas similar to that obtained from the irradiation in vacua. The 42 x 10^{-7} moles of N_2 represent decomposition of about 20 pct of the added NO. A similar quantity of O_2 should have been released, which again was not found in the gaseous product.

The addition of CO_2 gave a product similar to that obtained in NO and in vacua. No CO_2 decomposition products were detected. CO_2 recovery was incomplete, but this may be due to its high sorptivity on the coal.

Mixed

Mixtures of $1H_2 + 1CO$ and $1H_2 + 1CO_2$ were investigated at pressures of about 100 torr (table 9). Since these gases are used in the catalytic synthesis of CH_4 and higher hydrocarbons, their influence on reactions of coal during laser irradiation is of interest. The above reactions are exothermic and may supplement the endothermic process of C_2H_2 formation. In several of the tests there was evidence of an increase in C_2H_2 and total gas yields. Data are shown on a starting atmosphere "free" basis.

TABLE 9. - Gaseous products from laser irradiation of Pittsburgh seam hvab coal in gas mixtures

Product gas[1]	Added gas		
	Vacua	H_2 + CO	H_2 + CO_2
Pressure, torr.................	-	50 + 50	43 + 56
H_2............................	(28.1)	(219.9)	(196.2)
CO............................	(11.5)	(179.7)	(12.4)
N_2............................	(8.5)	(12.3)	(7.7)
CH_4............................	3.0	4.8	3.6
H_2O............................	(2.9)	(7.9)	(2.0)
C_2H_2............................	7.1	10.8	10.4
HCN...........................	1.1	2.3	1.4
C_3H_8............................	.1	-	.1
C_2H_6............................	.5	.3	.6
O_2............................	(.4)	(.3)	(.7)
Ar............................	.0	(.2)	(.2)
C_3H_6............................	.3	.2	.3
CO	(1.4)	(1.8)	(135.1)
Total[2].....................	12.5	18.4	16.4

[1]Moles x 10^7 per 6- to 7.5-j irradiation.
[2]Numbers in parentheses have been excluded from total product.

It has been shown that increased yields of C_2H_2 were produced in NH_3, H_2O, N_2, Ar, and He atmospheres. Decreased yields of C_2H_2 resulted from irradiation in O_2 and NO_2. Irradiations in the presence of O_2, NO_2, and NO were accompanied by increases in the total oxides of carbon. NO and CO_2 atmospheres acted primarily as diluents. In the present experiments a relatively large volume of gas (7 mm) and a small target (0.5-mm-diam) were used, producing a strong dilution effect by the added atmosphere. Much of the added gas was physically unavailable to the laser target but was analyzed with the product gas. Variations of laser intensities between 6 and 7.5 j did not produce detectable changes in products.

There are several possible explanations for the influence of gases on the laser irradiation of coal. The product gases may be the result of chemical reactions between the atmosphere and the coal. On the other hand, the added gases may simply represent added pressure during the pyrolysis or alter the "quenching" time. The pressure may prolong the reaction time by slowing gas removal from the "hot zone." The atmosphere may (1) increase the temperature of the reaction by limiting volatility, (2) decrease the temperature by conduction, or (3) increase the reaction rate by concentrating the reactive gases in the pores of the coal.

Metal Promoters

Pittsburgh seam hvab coal (through 200 mesh) was mixed with several nickel and platinum salts. The concentration of nickel was 10 pct and the platinum 2 to 3 wt pct of the coal. The mixtures were irradiated as powders or were pressed into disks 1 cm in diameter by 1 mm thick. Each sample was evacuated at 100° C for 16 hours, sealed, and irradiated with a 6-j laser beam.

Table 10 shows the effect of several nickel promoters on the gaseous products. Yields of total gas and C_2H_2 were generally lower than those from unpromoted coal in disk form. Yields from the unpromoted disk are higher than the standard using a cube of coal. This table indicates that the increased activity is probably due to the form of the coal (pressed disk) and effectively small particle size, rather than the nickel promoter. Tests using $NiCl_2$ on powdered coal are inconsistent due to the high water content and the difficulty of laser irradiating a powdered sample.

TABLE 10. - Gaseous products from laser irradiation of Pittsburgh seam hvab coal using nickel promoters

Product gas[1]	Sample form					
	Cube	Disk	Disk	Disk	Disk	Disk
Promoter......	None	None	$Ni(C_2H_3O_2)_2$	$Ni(NO_3)_2$	NiO	$NiCl_2$
H_2............	30.5	52.3	40.7	44.6	38.1	44.1
CO............	10.3	18.8	16.7	24.1	25.1	10.0
N_2............	-	(2.2)	(4.3)	(4.0)	(1.8)	(3.0)
CH_4...........	3.7	3.3	5.5	3.0	4.3	2.6
H_2O...........	-	(3.8)	(4.5)	(7.2)	(3.0)	(2.3)
C_2H_2..........	7.9	20.2	15.7	13.1	3.2	15.7
HCN...........	1.2	1.0	1.2	.2	.6	.8
C_3H_8..........	-	-	.2	-	-	-
C_2H_6..........	.5	.8	.5	2.9	.3	.1
O_2............	(.5)	(.5)	(.3)	(.5)	(.5)	(.5)
C_3H_6..........	.3	.1	.1	-	-	-
CO_2...........	3.2	.5	4.5	2.6	1.2	.4
C_3H_4..........	-	.3	.3	-	.3	.1
C_4H_2..........	-	.8	.2	.1	.5	.3
Total[2]...	57.6	98.1	85.8	90.6	73.3	74.1
C_2H_2-CH_4......	2.1	6.1	2.8	4.4	.7	6.0

[1]Moles x 10^7 per 6- to 7.5-j irradiation.
[2]Numbers in parentheses have been excluded from total product.

Table 11 shows the effect of platinum on coal irradiation. The platinum-promoted disk appeared to produce less C_2H_2 and total gas.

Metal promoters or catalysts are frequently evaluated according to their surface area or their sorptivity for gases. Since the temperature of the laser irradiated sample can be several thousand degrees, these measures are no longer significant. Perhaps the function of a solid catalyst should be that of a heat reservoir which can further raise the temperature of the coal components.

TABLE 11. - Gaseous products from laser irradiation of Pittsburgh seam hvab coal using platinum promoters

Product gas[1]	Sample form		
	Disk	Disk	Powder
Promoter	None	$PtCl_4$	$PtCl_4$
H_2	52.3	45.8	24.0
CO	18.8	5.7	11.0
N_2	(2.2)	(2.0)	(16.7)
CH_4	3.3	2.0	4.1
H_2O	(3.8)	(4.0)	-
C_2H_2	20.2	15.1	6.4
HCN	1.0	.6	2.7
C_3H_8	-	.0	.6
C_2H_6	.8	.0	1.6
O_2	(.5)	(.5)	1.1
C_3H_6	.1	.0	.5
CO_2	.5	.8	3.3
C_3H_4	.3	.2	.0
C_4H_2	.8	.0	.0
Total[2]	98.1	70.2	54.3

[1]Moles x 10^7 per 6- to 7.5-j irradiation.
[2]Numbers in parentheses have been excluded from total product.

Types of Lasers

Laser activity has been produced in over 100 different materials. This study of coal irradiation has been carried out using only three of the most common types--ruby, neodymium, and carbon dioxide. A typical material for a pulsed laser is a crystal of Al_2O_3 with 0.05 wt pct Cr_2O_3. The chromium ions are excited by a xenon flash lamp and they emit a pulse of 6,943 A laser light in about 1 msec. The intensity of the laser pulse can be varied by changing the input to the xenon lamp, by focusing the laser beam, and by Q-switching to decrease the discharge time. The ruby used in this work was a cylindrical rod 76 mm long by 6 mm in diameter, capable of discharging a 7-j pulse in about 1 msec. Without optical alteration of the beam, the energy concentration at the target was 11 kw cm^{-2}. With a focusing lens this can be increased to over 400 kw cm^{-2} and, using an electro-optical Q-switch, to 40,000 kw cm^{-2}.

The neodymium laser was a glass rod 152 mm long and capable of a 28-j pulsed discharge. The significant contribution of the neodymium laser was the change in wavelength to 10,600 A. With focusing, the light intensity at the target was about 1,800 kw cm^{-2}.

The third type of laser used was a continuous CO_2 laser having a power output of only 10 watts (with focusing 0.03 kw cm^{-2}). However, since operation is continuous, total energy input and the quantity of gaseous product can be made to equal or exceed that of the other lasers. Light from the CO_2 laser has a wavelength of 106,000 A, providing a third wavelength for irradiation.

Irradiations with these three lasers, including several variations in the energy intensities of the ruby, have been compared using approximately the same total energy output to determine if there are differences in the quantity and distribution of product gas. The data are shown in table 12 (gas yields) and table 13 (gas percentages).

TABLE 12. - Pittsburgh seam hvab coal irradiated with ruby, neodymium, and CO_2 lasers, moles

Product gas[1]	Laser type				
		Ruby			
	CO_2	Defocused	Nonfocused	Focused	Nd
H_2	1.7	9.7	20.0	28.5	42.3
CO	.8	2.5	8.7	10.6	14.2
CH_4	2.4	2.4	5.9	3.6	3.3
C_2H_2	-	1.2	6.1	8.8	11.9
HCN	-	1.2	2.8	1.5	.8
C_3H_8	.1	.2	.2	-	-
C_2H_6	.8	.5	.8	.4	.2
CO_2	.5	.1	.4	3.0	.7
Diac	-	-	.3	.9	.1
C_6H_6	-	.1	.2	.2	-
H_2S	.1	.1	.2	-	-
C_3H_4	-	.4	.4	-	-
Total	7.3	18.8	46.9	58.0	73.7
Crater area, mm^2	7.1	134.0	44.0	16.0	1.6

[1]Moles x 10^7 per 6-j pulse.

TABLE 13. - Pittsburgh seam hvab coal irradiated with ruby, neodymium, and CO_2 lasers, vol pct

Product gas	Laser type				
		Ruby			
	CO_2	Defocused	Nonfocused	Focused	Nd
H_2	23.3	48.1	42.8	48.9	57.5
CO	10.9	12.6	18.6	18.3	19.3
CH_4	32.9	12.7	12.6	6.5	4.5
C_2H_2	-	6.6	13.2	14.9	16.1
HCN	-	7.0	6.0	2.7	1.1
C_3H_8	1.4	1.7	.5	-	-
C_2H_6	10.9	2.8	1.5	.6	.3
CO_2	6.8	.9	.9	5.9	.9
Diac	-	-	.5	1.5	.1
C_6H_6	-	.4	.5	.4	-
H_2S	1.4	.3	.3	-	-
C_3H_4	-	1.5	.7	-	-
C_2H_2-CH_4	.0	.5	1.0	2.3	3.6

The CO_2 laser emits the least intense light beam; the ruby pulses can be progressively concentrated with focusing. Variations in energy can be readily measured on the coal targets. Craters in coal irradiated by a defocused ruby laser beam had an average area of 134 mm^2; by a nonfocused beam, 44 mm^2; and by a focused beam, 16 mm^2. The only irradiations with neodymium were focused, and the craters produced with a 6-j pulse were 2 mm^2 in area. The best

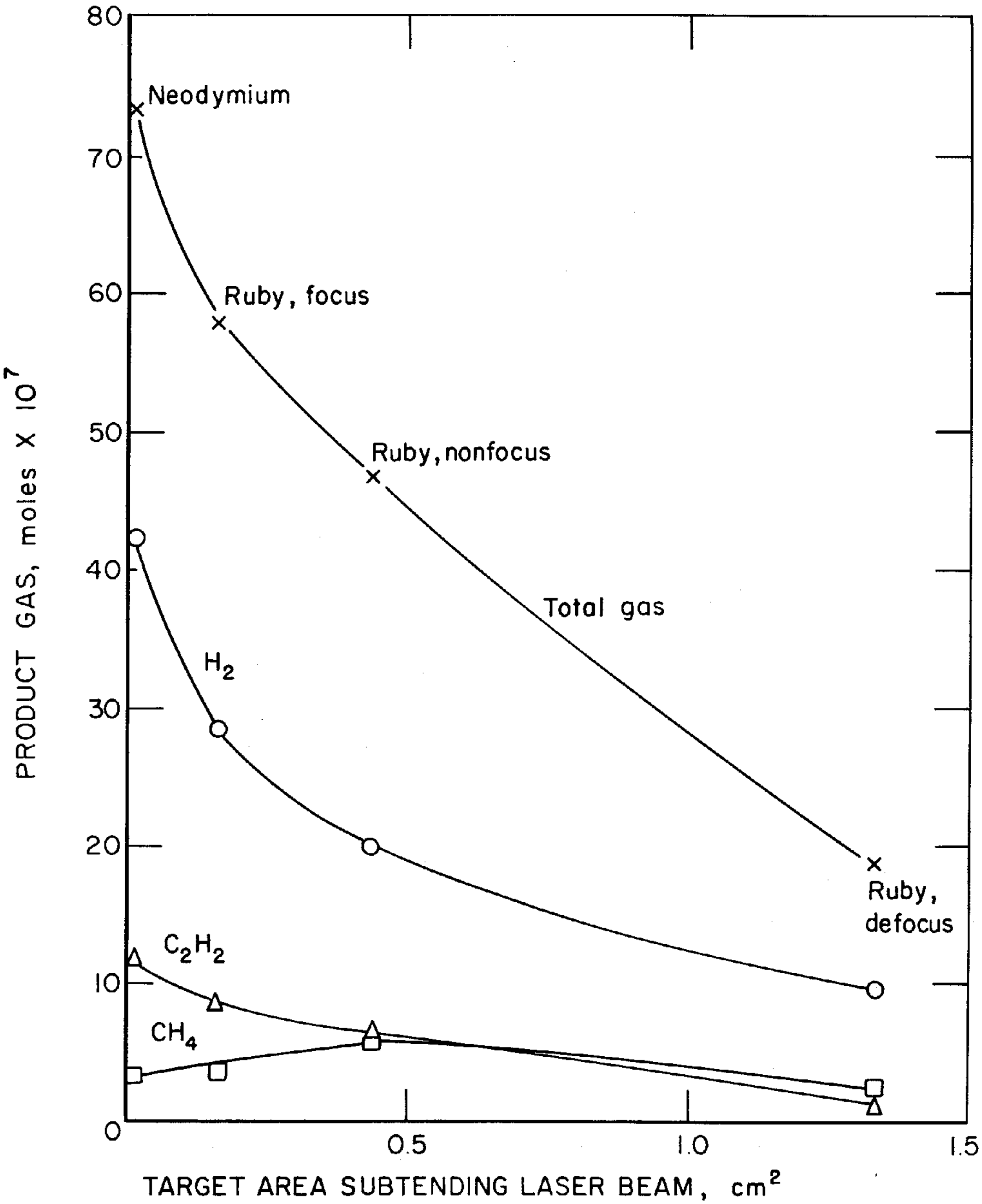


FIGURE 13. - Laser Focusing. Gas yield as a function of laser energy concentration.

focused CO_2-laser beam produced a 7-mm^2 crater. The quantity of product gas increased directly with energy intensity.

	Laser				
	CO_2	Ruby			Neodymium
Focusing lens...........	None	Concave	None	Convex	Convex
Intensity, kw cm^{-2}......	0.032	7.4	18.2	54.6	875
Product gas, moles x 10^7	7	19	47	58	74

The gas yields and analyses are shown graphically as functions of crater area (figs. 13 and 14). Only data from the CO_2 laser were omitted due to its unique heating and cooling rates. The more intense laser beams produced greater quantities of product gas and higher C_2H_2-CH_4 ratios.

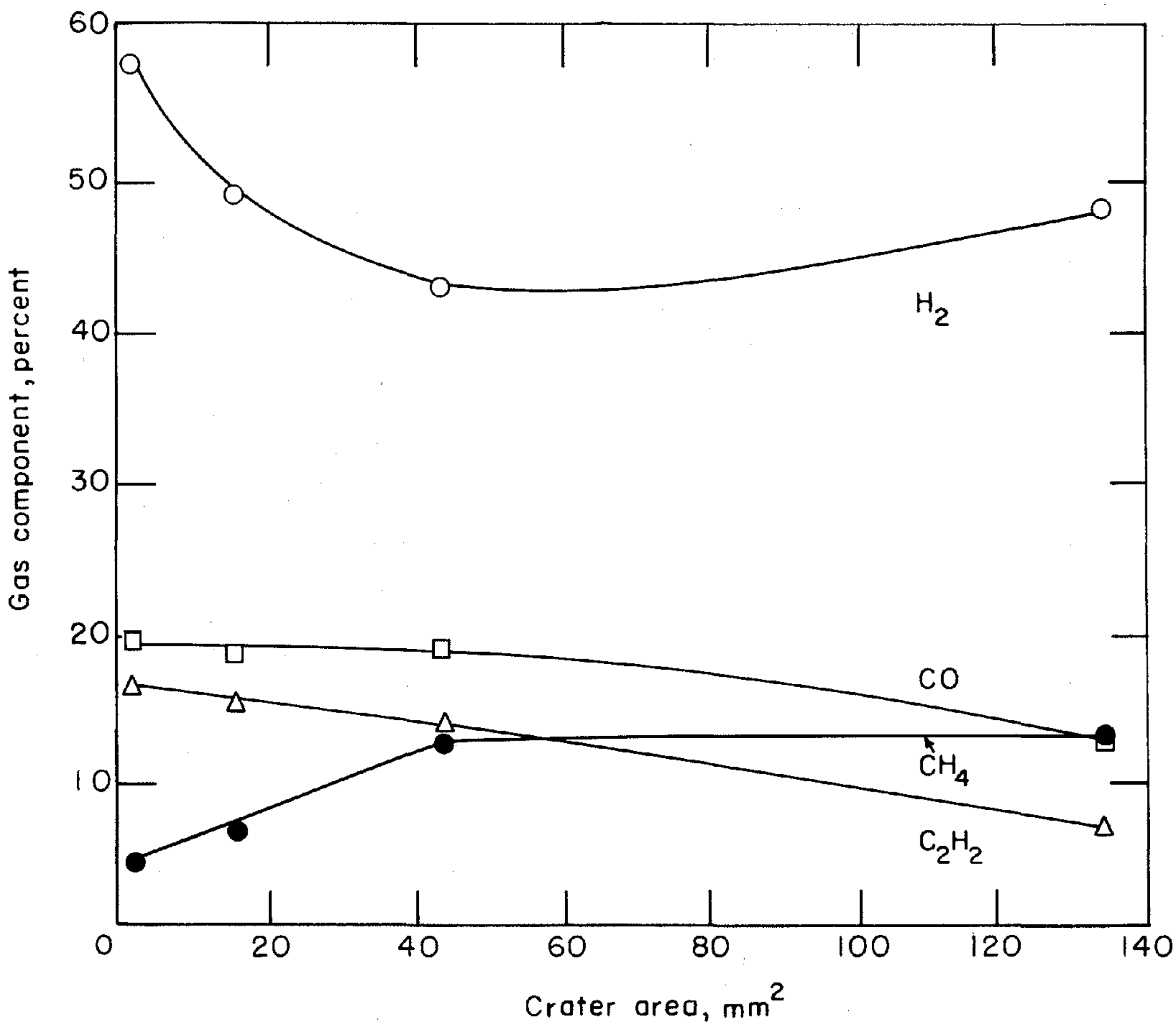


FIGURE 14. - Laser Focusing. Gas distribution as a function of laser energy concentration.

Since the same amount of energy was available in each of these tests the temperatures of the craters (or of the gas generating sites) should be inversely related to crater areas. An attempt was made to estimate temperatures from gas analyses using equilibria data. The analyses were taken from table 13 and the equilibria data from McBride (13). The chief interest is in the relationship between CH_4 and C_2H_2 at temperatures to 4,000° C (fig. 15). Laser data were introduced as shown in the following sample calculation:

$$K = (p_{C_2H_2})(p_{H_2})^3(p_{CH_4})^{-2},$$

$$K = (0.00277)(0.00989)^3(0.000774)^{-2} = 0.00447,$$

$$\log K = -2.350.$$

According to figure 15, this irradiation should have heated the target to 1,270° K if gas equilibrium was established. If the gases do not reach equilibrium during their brief exposure to the laser, the calculation will indicate a minimum temperature.

The various types of laser irradiations are compared in figure 16. The data are consistent, since the temperature increased with increased energy concentration. Since no detectable C_2H_2 was produced by the CO_2 laser, a temperature estimate could not be made. A gas analysis was available for coal carbonized at 900° C. Applied to figure 15, a calculated temperature of 827° C is in good agreement with the measured temperature.

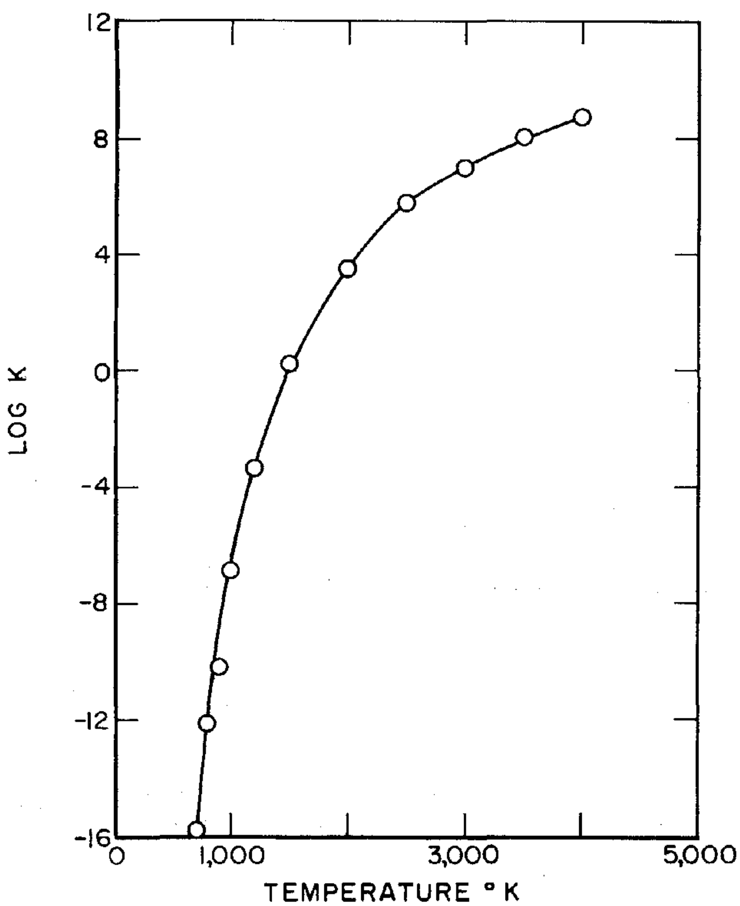


FIGURE 15. - Gas Equilibrium Constants. $2CH_4 \rightleftarrows C_2H_2 + 3H_2$.

Variations in types of irradiations produced large changes in gas yield and selectivity as shown in figures 13 and 14. However, most of these changes can be explained on the basis of energy concentration at the target. A greater energy concentration increased the gas yield, the crater and gas temperature, and the C_2H_2-CH_4 ratio.

A fundamental question in the laser irradiation of coal is the possible importance of the wavelength of the energy. Is the laser simply a thermal

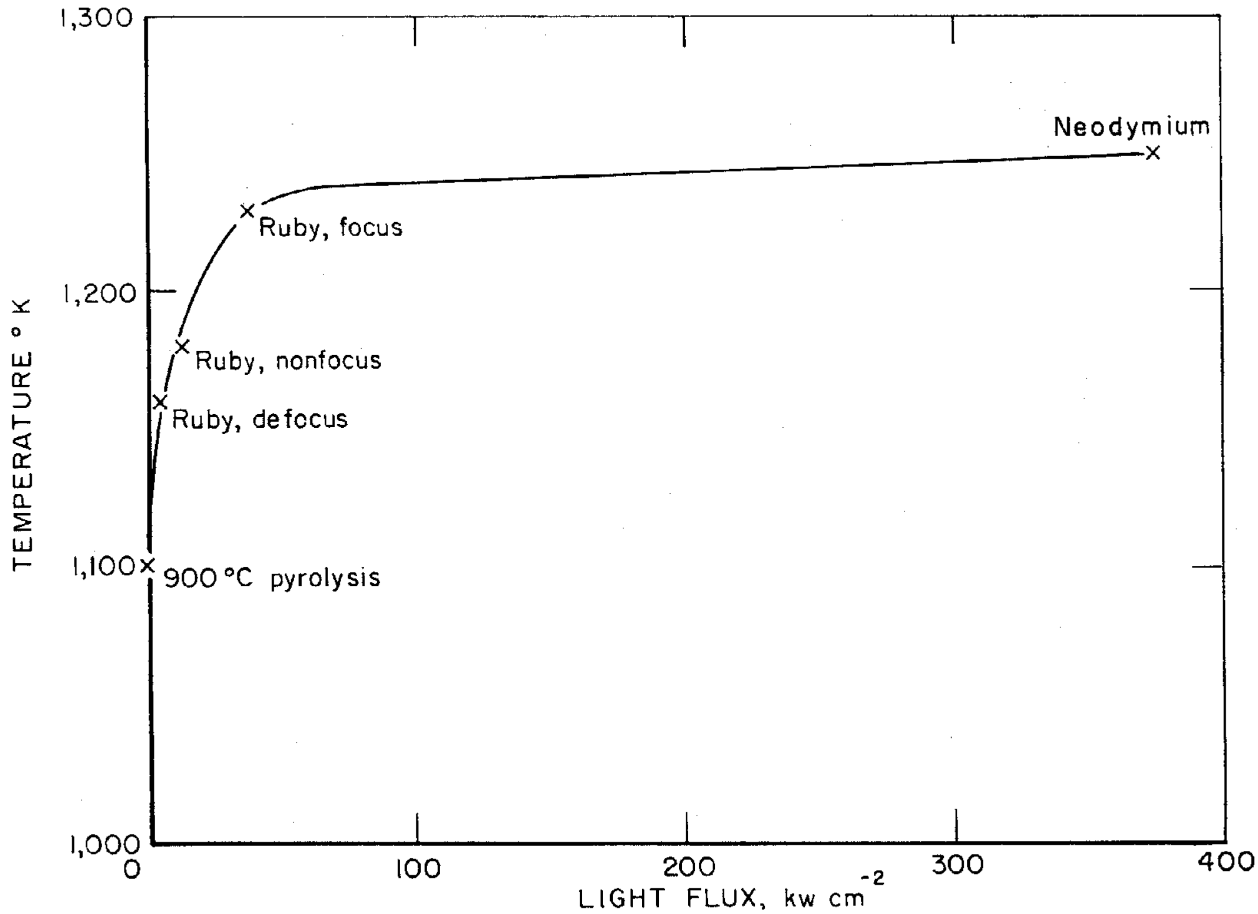


FIGURE 16. - Temperatures of Laser Irradiated Coal as Estimated From Gas Analysis.

energy source capable of raising coal to unusually high temperatures, or can the monochromatic energy stimulate specific chemical reactions in coal? The usual photochemical reactions take place with wavelengths of 2,000 to 4,000 A.

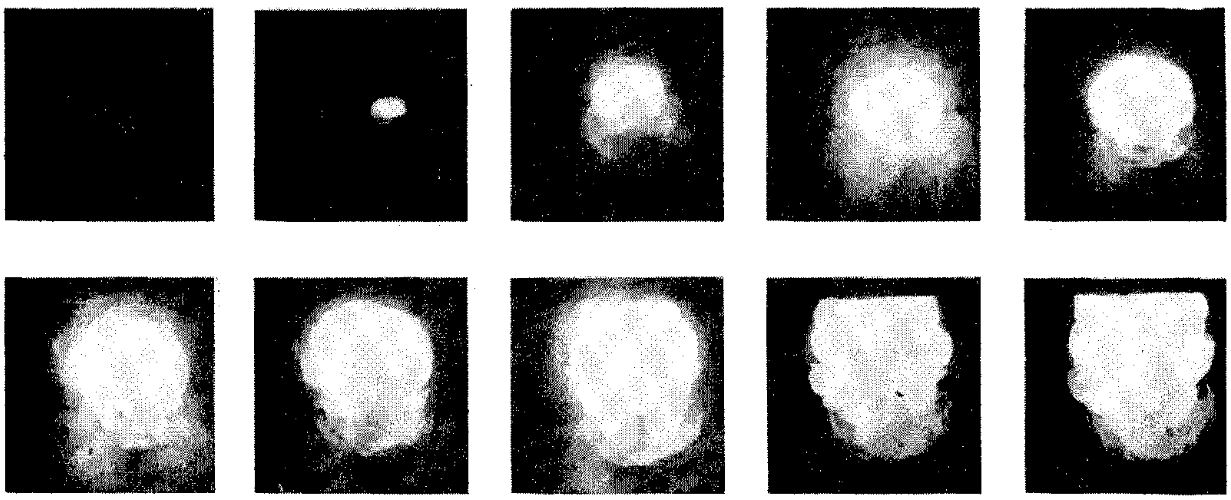
The lasers available for this coal study had the following wavelengths:

Laser	Wavelength
Ruby...............	6,943 A--visible
Neodymium..........	10,600 A--infrared
Carbon dioxide.....	106,000 A--infrared

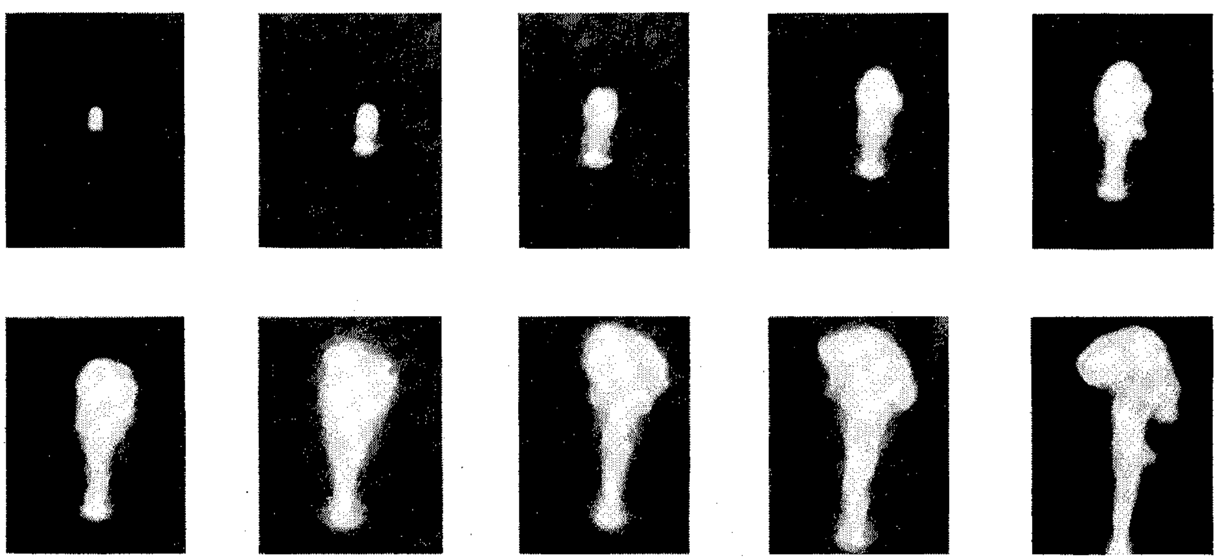
It was impossible to measure the photochemical influence of the laser irradiations because conditions could not be exactly duplicated with the different lasers, and the temperature effect is much greater than the photochemical effect. A first estimate is that the wavelengths used had little if any influence on the products; perhaps differences can be detected by using lower energy pulses.

Photographic Study of Laser Irradiation

Irradiation of coal or graphite produces a luminous plume which has been recorded by high-speed photography. The purpose of this part of the investigation was to study the mechanism of plume formation and to estimate temperature and pressure within the plume. A normal ruby laser pulse was used (of much longer duration than a giant laser pulse). This information supplements data of gaseous products obtained by laser irradiation of coals (10). The laser beam impinged at a 45° angle on a smooth, flat surface of a specimen of



Coal in air



Graphite in air

FIGURE 17. - Luminous Plumes From Laser Irradiation of Coal and Graphite in Air.

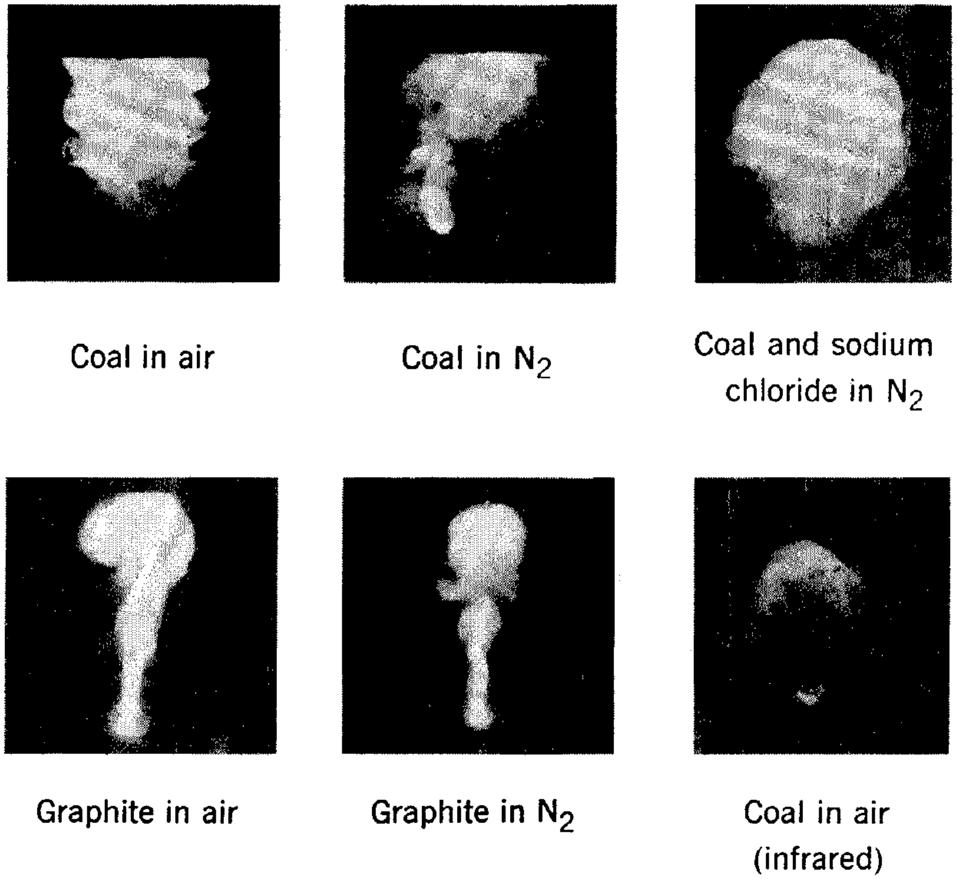


FIGURE 18. - Laser Plumes After 500 Microseconds of Irradiation.

Pittsburgh seam coal or graphite. The experiments were conducted at a pressure of 1 atmosphere. A high-speed framing camera (Dynafax model 326)[6] operating at 21,000 to 26,000 frames per second recorded the luminous surface and plume, following the plume downstream to a distance of at least 10 crater diameters. At these camera speeds the duration of each frame is 2.1 μsec with 39 μsec between frames. Black and white, color, and infrared film were used. Supplementary measurements included sample weight loss, crater dimensions, and mass spectrometric analyses of gases (10). The effect of coating coal surfaces with sodium chloride was briefly explored.

Typical film sequences for coal and for graphite irradiated in air are shown in figure 17. Plumes produced by laser irradiation of coal and graphite in air and in N_2, photographed 500 μsec after the beginning of the laser pulse, are shown in figure 18. Plume growth rate was approximately the same in air and N_2, indicating little secondary reaction in the hot plume.

The laser beam cannot be observed in the atmosphere before the plume forms. The target reflects some light during this period, possibly from the

[6] Reference to trade names is made for identification only and does not imply endorsement by the Bureau of Mines.

xenon pumping light. During irradiation, the crater rim is highly luminous and a few solid luminous particles are ejected.

Table 14 presents discharge times for the 6-j ruby laser which were measured photographically from the duration of luminosity in the plume. The average effective pulse time is about 1.2 msec for coal and 0.6 msec for graphite with a weak luminosity persisting for a somewhat longer period. Plume formation begins within a few μsec of the beam impact or as soon as the sublimation temperature of the surface is reached. The coal surface is probably not significantly superheated, although the subsequent vapor plume may be. The vapor expands owing to a simultaneous heating of the surface and of the vaporized material. Weichel and Avizonis (23), who investigated graphite irradiation by a giant laser pulse (700 j cm^{-2} discharged in 1 μsec), report that superheating occurred in the vapor but not in the solid target.

TABLE 14. - Discharge time for 6-joule laser pulse (based on plume luminosity)

Target	Time per frame, millisecond	Number of frames		Total time, millisecond	
		Plume	Afterglow	Plume	Afterglow
Coal.......	0.038	33	51	1.2	1.9
	.047	25	51	1.2	2.4
	.040	30	45	1.2	1.8
Graphite...	.038	16	10	.6	.4

The photographs showed that the plume grew during the first 300 μsec at a rate of 1.1×10^4 cm per sec for coal and 0.9×10^4 cm per sec for graphite. Using a similar laser and a probe method, Howe and Molloy (9) found a plume velocity of 1.0×10^4 cm per sec from irradiated graphite. Plume growth due to irradiation of carbon by the giant pulse laser (1,000 times the discharge rate of the present work) has been reported as 7×10^6 cm per sec, Weichel and Avizonis (23); 2×10^6 cm per sec, Ready (17); and 7×10^6 cm per sec, Afanasyev (1). Vaporization rates of irradiated coal and graphite were computed from weight losses, crater measurements, and total laser discharge times (table 15). Vaporization for graphite was 14 g cm^{-2} sec^{-1}. This can be compared with a vaporization rate of 9 g cm^{-2} sec^{-1} obtained by extrapolation of Honig's data (7) to vaporization at 1 atmosphere. Therefore the pressure and temperature of the impact area cannot be much above normal vaporization conditions for graphite (3,900° C at 1 atm).

TABLE 15. - Six-joule laser irradiation of coal and graphite

Target	Specific gravity	Crater area, cm^2	Crater volume, cm^3	Crater weight, g	Evaporation rate, g cm^{-2} sec^{-1}
Pittsburgh coal...	1.3	0.018	0.00031	0.00041	19.0
Graphite..........	2.3	.008	.00003	.00007	14.1

If average temperatures of 1,000° C are assigned to the plumes, the volumes of the coal plumes estimated from the photographs equal the gas volumes calculated from the experimental weight loss of coal. Mass spectrometric analyses of gas products collected after laser irradiation of coal also indicate satisfactory material balances (100 ± 10 pct of the weight loss recovered). Plumes produced by irradiation of graphite cannot be analyzed in this manner because of condensation and fallout. The smaller size of graphite plumes may be due to condensation as well as to a lower evaporation rate. Seventy-two percent of the input energy was accounted for as sensible heat and heat of evaporation of graphite.

Material Balance

To evaluate the effect of laser irradiation on coal a complete material balance is necessary. After several attempts, Pittsburgh hvab coal and Pocahontas lvb coal, irradiated in evacuated glass vessels, gave high recoveries. Fifty-two percent of the vaporized Pittsburgh coal was recovered as gaseous products and 59 pct as a carbonaceous deposit on the vessel wall. Twenty-one percent of the vaporized Pocahontas coal was recovered as gaseous products and 71 pct as a carbonaceous deposit. Elemental analyses of the Pittsburgh coal showed that 72 pct of the carbon was recovered, 105 pct of the H_2, and 83 pct of the O_2. The gaseous product distribution is given in table 16. Of most interest is the fact that for 1 gram of coal consumed, 0.22 gram of C_2H_2 was produced.

TABLE 16. - Gaseous product recovery from Pittsburgh seam coal irradiated with a 6-joule pulse from a ruby laser

Product gas	Moles x 10^7	Grams x 10^7	Grams per g coal converted
H_2	29.84	59.68	0.02
CO	14.23	398.44	.11
CH_4	2.53	40.48	.01
H_2O	18.91	340.38	.09
C_2H_2	30.80	800.80	.22
HCN	2.22	59.94	.02
C_2H_4	.31	9.30	.00
C_3H_6	.19	7.98	.00
CO_2	.82	36.08	.01
Diac	1.18	59.00	.02
C_6H_6	1.16	90.48	.02

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 product gases obtained in this investigation were similar to those reported previously from flash- and argon-plasma irradiations. The unsaturated species (primarily C_2H_2) were much higher and the CH_4 lower than the concentrations found from 900° C carbonization of coal. The lower rank coals not only produced approximately four times as much gas as the higher rank coals, such as anthracite, but also showed much higher concentrations of C_2H_2. 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. While coal rank had a significant influence on the composition of the product gas, different macerals and particle sizes changed the total gas yield but had little effect on gas composition. Addition of gases such as Ar, N_2, Ne, H_2O, and NH_3 increased the yield of C_2H_2. O_2, NO_2, and NO atmospheres decreased the yield. Metal promoters such as platinum and nickel were ineffective. The most significant factor in increasing the C_2H_2 yield was the intensity of irradiation.

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