

STUDIES OF THE SOLID AND GASEOUS PRODUCTS FROM LASER PYROLYSIS OF COAL

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INTRODUCTION

The Bureau of Mines has made an extensive effort to find new techniques to investigate the structural units in coal for both theoretical and practical purposes. One of the newer research tools is the laser, which can produce high temperatures accompanied by rapid heating and cooling. Although many of the products from laser irradiation have already been produced from coal by other high-temperature devices^{1-3/}, the laser excels in the production of certain pyrolysis products.

EXPERIMENTAL

Two lasers have been used in this study. A pulsed ruby laser with a focused beam gave an energy concentration of 55,000 watts cm^{-2} at a wavelength of 6943 Å.^{4/} A continuous CO_2 laser with a focused beam gave an energy output of 140 watts cm^{-2} at a wavelength of 106,000 Å.^{4/}

The general irradiation procedure was to seal the coal sample in a glass vessel into 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. Samples for the ruby laser were sealed in a pyrex tube under vacuum or under an inert gas at pressures up to 1 atmosphere. Pyrolysis occurred rapidly and both gaseous products and entrained solids escaped from the hot surface at a rate estimated at 11,000 cm sec^{-1} .^{6/} Samples pyrolyzed by the CO_2 laser were irradiated in a tube with a sodium chloride window. Pyrolysis of these samples was a continuous process which could be observed for several minutes, at the end of which the coal sample was usually exhausted. The escape of the gaseous and solid products from the reaction zone of the CO_2 laser was relatively slow, only 28 cm sec^{-1} . Gases were collected in an evacuated bulb for analysis by mass spectrometry. An effort was made to accelerate the solid product out of the pyrolysis zone. Rapid removal of the solid was attempted by increasing the gas evacuation rate, flushing with inert gas, an electric discharge, and use of a refrigerated collection bulb.

RESULTS

Ruby Laser

Coal-pyrolysis products using the ruby laser were 53 percent solid and 47 percent gas. No significant amounts of liquid were recovered, consistent with previous high-energy investigations.^{5/} Gas composition data are summarized in table 1, where ruby-laser data are compared with gases from high-temperature coal carbonization, low-temperature carbonization, and pyrolysis with the CO_2 laser.

The ruby laser produced an increase in acetylene and a decrease in methane and other hydrocarbons relative to gases from pyrolysis at lower temperatures.

Direct observation of pyrolysis with the ruby laser was impossible due to high light intensity and high rate of discharge. Photographic studies were reported previously;^{6/} at 26,000 frames per second the movement of products out

of the reaction zone was observed. Gaseous products cooled quickly and were stable during their introduction into the ionizing chamber of the mass spectrometer. Solids, deposited on the tube walls, were easily removed. The unreacted portion of the sample was weighed for material balance calculations. The solid product was analyzed by infrared. An ultimate analysis of this solid was similar to the original coal (table 2).

The infrared spectrum indicated that most of the bands characteristic of the parent coal are missing.^{4/} The high-resolution mass spectrum of the solid is similar to that of coal. It is probably not significant because some of the original coal was entrained in the rapidly expanding gas stream and mixed with the solid product. This is indicated by high ash in table 2.

Carbon Dioxide Laser

Coal-pyrolysis products using the CO₂ laser were 29 percent gas and 71 percent solid. The only liquids observed were traces of pentane and hexane in the vapor phase. Typical gaseous products are summarized in column 3 of table 1. These gases seem to represent a transition between industrial coal carbonization and the rapid pyrolysis available with the ruby laser. The CO₂ laser produces a series of hydrocarbons, but not acetylene, which apparently requires higher temperatures than available.

Hot gases from the CO₂-laser irradiation were passed through a bed of powdered Raney nickel catalyst.^{7/} The catalyst was not heated directly but only indirectly, by incoming gases and by heats of reaction of the gases. The usual complex mixture of gases was converted into a simple mixture consisting of 91 percent methane, ethane, and propane (table 3). The low yields of hydrogen and carbon oxides indicate a gas synthesis reaction as well as hydrogenation occurred. The fuel value of the gas was increased from 698 Btu/ft³ to 1325 Btu/ft³ by the catalytic treatment.

Solid Product from CO₂ Laser

The solid product from the CO₂-laser pyrolysis evolved as a fine brown powder which was suspended in the reaction tube and slowly deposited on the tube walls. Exposure to the reflected radiation of the laser beam caused melting and condensation reactions which resulted in a tarry mass. Secondary heating could be prevented by intermittent laser operation or by removing the powder in a stream of inert gas.

The solid was removed from the walls of the collection vessel in the form of a powder which softened between 108° and 112° C and volatilized at 250° to 300° C. The apparent density of the freshly prepared solid was 0.033 g cm⁻³, only 2 percent of the density of the coal (table 4). In a closed tube the material remained stable for several months.

This solid was separated into three fractions by extracting with benzene at 80° C, evaporating the solvent, then extracting with hexane.^{8/} The distribution was benzene-insoluble (36 percent), asphaltene or benzene-soluble and hexane-insoluble (26.7 percent), and hexane-soluble (37.3 percent). The average molecular weight of the benzene-soluble material is 396 by the osmotic method. In contrast with the 64 percent solubility of the laser solids Pittsburgh seam coal is less than 1 percent soluble in benzene at 80° C.

Since the solubility of coal is increased by reduction,^{9/} the laser solids were dehydrogenated to determine if their solubility could be attributed to hydroaromatics. The sample was prepared by refluxing the laser solid in phen-

anthridine with a catalyst of palladium on calcium carbonate.^{10/} Thirty percent of the total hydrogen was removed, decreasing the hydrogen to carbon ratio as follows:

	<u>H:C, atomic ratio</u>
Pittsburgh seam coal	0.81
Laser solids	0.90
Dehydrogenated laser solids	0.63

High-Resolution Mass Spectrometry

The mass spectrum of the laser solids was obtained using a Consolidated Electrodynamics Corp. model 21-110B high-resolution mass spectrometer at a source temperature of 300° C. The laser solids are identified as sample 1 in table 5. This spectrum was compared with the spectrum of sample 2, which represents a similar laser product separated by gel permeation chromatography into 52 fractions.^{11/} The fractions were analyzed by the mass spectrometer and their qualitative analyses combined. Spectra for samples 3 and 4 represent the solid products obtained from Pittsburgh seam coal by other processes. Sample 3 is the composite of distillates from a high-temperature coal carbonization^{12/} and sample 4 is a pyridine extract of Pittsburgh coal obtained by mechanical agitation at room temperature.^{13/}

An inspection of table 5 shows that pyrolysis of coal using a CO₂ laser produces a complex product which includes naphthalenes, phenanthrenes, and pyrenes. Many of the methyl substituted homologs are present. The maximum molecular weight of sample 1 (laser solids volatilized into the mass spectrometer) was 440. Since this maximum molecular weight is only slightly higher than the value of 396 found for the average molecular weight by the osmotic method, it indicates that the sample residue (20 percent remained in the sample holder) contains higher molecular weight compounds. Sample 2 has a lower range of molecular weights because only the toluene-soluble portion of the laser sample was introduced.

SUMMARY

Products from the laser pyrolysis of coal are predominantly gases and solids. There is little evidence of tar and pitch which are characteristic of coal carbonization. Gases from the CO₂ laser have high fuel value following catalytic treatment. Solid products are a complex mixture having low-ash, low-density, and high-hydrogen content. Efforts were made to analyze these solids using solvation, dehydrogenation, gel permeation chromatography, and mass spectrometry. Coal pyrolysis using laser irradiation provides a variety of organic compounds.

1. High-energy laser irradiation, available from a pulsed ruby or other solid laser, produces simple gas mixtures which are high in hydrogen, acetylene, and carbon monoxide.

2. A moderate energy irradiation from a 10-watt CO₂ laser produces a more complex mixture of gases with little or no acetylene. The solid product has low density, is highly soluble in benzene, and has an ultimate analysis similar to that of an ash-free coal.

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Table 1.- Gas composition of pyrolysis products, mole percent

Pyrolysis method:	Ruby laser	CO ₂ laser	High-temperature carbonization	Low-temperature carbonization
Estimated temperature, °C ^{a/}	1200	1000	900	500
H ₂	52	47	56	17
CO	22	9	7	3
CO ₂	9	2	0	5
CH ₄	5	21	31	73
C ₂ H ₂	11	0	0	0
Other HC	0	20	5	2

a/ Reference 4.

Table 2.- Elemental analyses of Pittsburgh seam coal and of pyrolysis solids

<u>Weight percent</u>	<u>Pittsburgh seam coal</u>	<u>Solid product</u>	
		<u>Ruby laser</u>	<u>CO₂ laser</u>
C	78.3	79.0	83.0
H	5.3	4.6	6.2
O,N,S	11.6	8.6	9.9
Ash	4.8	7.7	0.9
Atomic ratio, C/H	1.23	1.43	1.11
	C/O	12.3	16.2

Table 3.- Irradiation of Pittsburgh seam coal with CO₂ laser. Gases exposed to Raney nickel

	<u>Direct pyrolysis</u>	<u>Gases over Raney nickel</u>
H ₂ , mole percent	51	3
CO	10	2
CH ₄	23	60
C ₂ H ₆	3	23
C ₃ H ₈	1	8
CO ₂	2	0
Other hydrocarbons	10	4

Table 4.- Data for solid from CO₂-laser irradiation of coal

Apparent density	0.033 g cm ⁻³
Softening point	108° - 112° C
Volatilization temperature	250° - 300° C
Solubility in benzene	64 percent
Molecular weight, benzene-soluble fraction	396

Table 5.- Coal degradation products examined by mass spectrometry

Sample:	1 ^a /	2 ^b /	3 ^c /	4 ^d /
<u>Example of possible compound</u>				
Indene		116	116	
Indan		118	118	
C ₃ alkyl benzene		120	120	
C ₂ alkyl phenol	122	122	122	
Naphthalene		128	128	128
		130	130	130
	132	132	132	132
	134	134	134	134
	136	136	136	136
		138	138	138
		140		
Methylnaphthalene		142	142	
	144	144	144	
	146	146	146	
	148			
Acenaphthylene			152	152
Acenaphthene			154	154
C ₂ alkyl naphthalene	156	156	156	
	160	160	160	
Fluorene			166	
Dibenzo furan			168	168
	170		170	
Anthracene	178	178	178	178
	180	180	180	
	182		182	
	184		184	
	186	186		
Methylphenanthrene	192	192	192	
Phenanthrol	194		194	
	196		196	
	198	198	198	
Pyrene	202		202	

Table 5.- Coal degradation products examined by mass spectrometry
(cont'd)

Sample:	1a/	2b/	3c/	4d/
<u>Example of possible compound</u>				
Dimethylantracene	206	206	206	
	208		208	
	210	210	210	
	212	212	212	
	216	216	216	
	218	218	218	
	220	220	220	
	222		222	
	224		224	
Benzo[ghi]fluoranthene	226		226	226
Chrysene	228	228	228	228
	230	230	230	
	232		232	
	234	234	234	
	236		236	
	238		238	
	244	244	244	
	246		246	
	248	248		
	250		250	
Perylene	252		252	
	*		*	

* Sample has additional mass peaks up to 440.

a/ Solids from CO₂ laser.

b/ Solids from CO₂ laser, dissolved in toluene and separated by gel permeation chromatography.

c/ Composite data from high-temperature coal carbonization, reference 12.

d/ Room-temperature pyridine extract, reference 13.