Microwave Pyrolysis of Coal and Related Hydrocarbons

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INTRODUCTION

The pyrolysis of coal at high temperatures and short reaction times has been investigated by a number of laboratories using a variety of experimental techniques. These techniques include reactions with plasmas[1-7], flash heating[7-9], arc-image furnaces[10], laser irradiation[11-14] and microwave discharges[15-20]. Temperatures of thousands of degrees Kelvin are achieved in a fraction of a second. Gases are evolved and char and tar are produced from the coal. The yields of gaseous products vary with experimental conditions, rank of coal, and reactor design. Major gaseous products from high-temperature pyrolysis are H_2, CO, C_2H_2, CH_4 and HCN. The gaseous products contain higher mole percentages of C_2H_2 and CO and lower percentages of CH_4 than the gaseous products of coal carbonization at 900°C. Temperatures in the reactor vessels are not uniform and differences of thousands of degrees may exist between the center and the walls of the vessel. The composition of the product gas is controlled by kinetics and may vary significantly from thermodynamic equilibrium.

Microwave discharges have been extensively used to study chemical reactions. Blaustein and Fu[21] have reviewed the reactions of organic molecules in electric discharges. Studies of coal and other carbonaceous materials include direct pyrolysis in a microwave field and reaction with reactive species produced by a discharge. Pyrolysis products include H_2, CO, CO_2, H_2O and hydrocarbons[19]. Acetylene is the major hydrocarbon, while CH_4 and C_2H_6 are present in lesser amounts. Quenching of primary reaction products enhances the yield of C_2H_2. Hydrogen and H_2O vapor in the discharge increased the yield of hydrocarbons and of total gas[16].

In this work, coal was subjected to rapid heating in a microwave discharge of argon. Naphthalene, anthracene, methane, ethane and acetylene were also studied.

EXPERIMENTAL

The experimental equipment is shown in Figure 1. The microwave field was generated by Raytheon Model PGM-100 Microwave Power Generator. The frequency of the field was 2450 MHz and the power level was about 200 watts. The microwaves traveled down a wave guide containing a monitor and tuner and were focused by a tapered section. The reaction vessel was constructed of Vycor and quartz. The sample could be suspended in the microwave field or below the field in a discharge generated plasma. The volume of the reaction vessel was 160 ml. Pressures of 20 torr was used for argon discharges.

After irradiation the gases were collected in the trap and analyzed by gas chromatography. A Packard 7401 dual column chromatograph with flame ionization and thermal conductivity detectors was used for analysis. A 1/4 inch by 10 feet column of activated alumina was used for separation of gases. The column temperature was increased at 5°C/min to 250°C. In some cases, chromatographic results were checked by mass spectrometry using a Hewlitt-Packard mass spectrometer. The residue from naphthalene pyrolysis was extracted with tetrahydrofuran and analyzed by gas chromatography using 10 foot column of 10% carbowax 20 M supported on chromosorb W.

The coal sample is from the Hiawatha, Utah mine and is a high volatile bituminous coal (47% VM, daf basis). A -60 + 100 mesh sample was used. Mallinckrodt purified naphthalene and Baker grade anthracene were used in these experiments. Matheson ultra purity grade methane and CP grade ethane and acetylene were used. A dry ice-acetone trap was used to remove impurities from the gases.

RESULTS AND DISCUSSION

The gaseous pyrolysis products from coal, naphthalene and anthracene are shown in Table. I. The samples were placed in the focus of the microwave field and the bottom of the vessel was immersed in a dry-ice acetone bath. H_2, CO, and CO_2 were not measured in these experiments. Hydrogen yields have been determined for naphthalene pyrolysis, in which case hydrogen is a major product. Coal and anthracene do not react when the sample is placed outside the microwave field, but within the argon discharge. Naphthalene was found to react in the discharge, but the product yield is different.

The results for coal pyrolysis are in agreement with the observations of other investigators[15-20]. The yield of C_2H_4 is higher than others have reported.

Naphthalene and anthracene both give high yields of C_2H_2. Wiley and Veeravagu[22] observed over 80 percent yield of C_2H_2 from these compounds in laser pyrolysis. Fu and Blaustein[16] obtained C_2H_2 as the major hydrocarbon product in the reaction of crysene in an argon plasma.

Table I
Gaseous Products From Pyrolysis of Solids

	Coal	Naphthalene	Anthracene
Sample weight, gm	0.196	0.140	0.140
Argon pressure, torr	20	20	20
Reaction time, sec.	15	20	30
Gaseous products mole % of hydrocarbons			
CH_4	25.70	6.85	32.75
C_2H_6	1.62	0.40	2.02
C_2H_4	19.91	2.48	8.13
C_2H_2	46.70	83.57	50.28
C_3H_8	0.23	0.06	-
C_3H_6	2.54	0.34	1.14
C_4H_{10}	Trace	0.01	-
C_4H_8	1.60	-	0.32
Butadiene	-	0.12	0.32
Benzene	1.70	5.96	4.58
Toluene	-	0.21	0.46
Liquid Products	-	Naphthalene α-methyl naphthalene	Anthracene α-methyl naphthalene

Sanada and Berkowitz[20] attributed the formation of C_2 to C_4 saturated hydrocarbon in the microwave pyrolysis of coal to the non-aromatic structures in the coal. These results indicate that saturated hydrocarbons are produced from totally aromatic molecules.

The yield of hydrocarbon gases from pyrolysis of organic gases is shown in Table II. Methane pyrolysis yielded C_2H_6, C_2H_4 and C_6H_6 as hydrocarbon products. Acetylene was not detected as a major product from CH_4 or C_2H_6 pyrolysis. Other investigators report[20,21,23,24] acetylene as a major product and benzene as a minor product. The presence of benzene was verified by mass spectrometry. Acetylene shows a high yield of aromatic products. Naphthalene also yields little C_2H_2 when reacted with the argon plasma. Acetylene seems to be produced only at the very high temperatures at the focus of the field.

Table II
Products from Pyrolysis of Organic Gases

	CH_4	C_2H_6	C_2H_2
Sample pressure, torr	10	10	10
Argon pressure, torr	20	20	20
Reaction time, sec.	30	30	60
Mole % of hydrocarbons			
CH_4	94.74	0.61	0.18
C_2H_6	2.73	97.63	0.17
C_2H_4	0.14	1.23	0.07
C_2H_2	-	-	96.56
C_3H_8	0.02	0.18	0.08
C_3H_6	-	0.04	0.01
C_4H_{10}	-	0.09	Trace
Benzene	2.33	0.20	0.55
Toluene	-	-	2.38
Unidentified	0.04	0.02	

The yield of products varies significantly with reaction time as shown in figures 2 and 3. Figure 2 is for naphthalene placed at the focus point and figure 3 is for naphthalene placed 5 cm below the focus point.

Griffiths and Standing[25] have reviewed the thermodynamics of hydrocarbon gases. Above 900°K the free energy of formation of CH_4 is positive. The free energy of formation of C_2H_2 decreases with temperature and becomes negative at about 4000°K. Acetylene is thermodynamically favored over methane above 1200°K. Although the pyrolysis system is not at thermodynamic equilibrium, thermodynamics influences the formation of H_2 and C_2H_2 at the high temperatures of the discharges.

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This research is sponsored by the Office of Coal Research on contract no. 14-32-0001-1200.

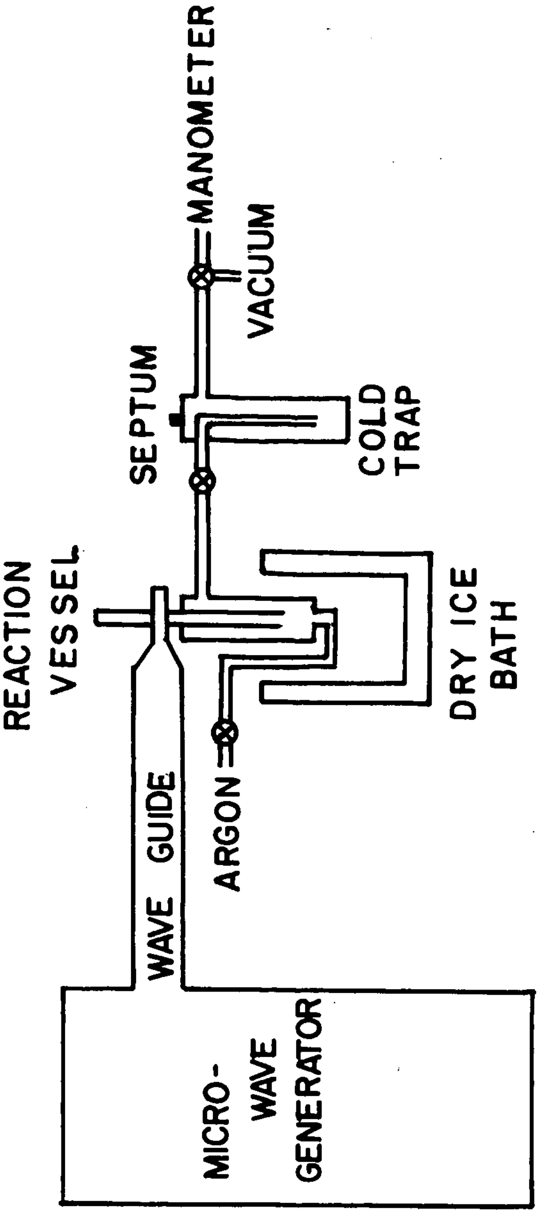

FIGURE I
MICROWAVE EQUIPMENT

FIGURE 2

HYDROCARBON GASES FROM NAPHTHALENE PYROLYSIS

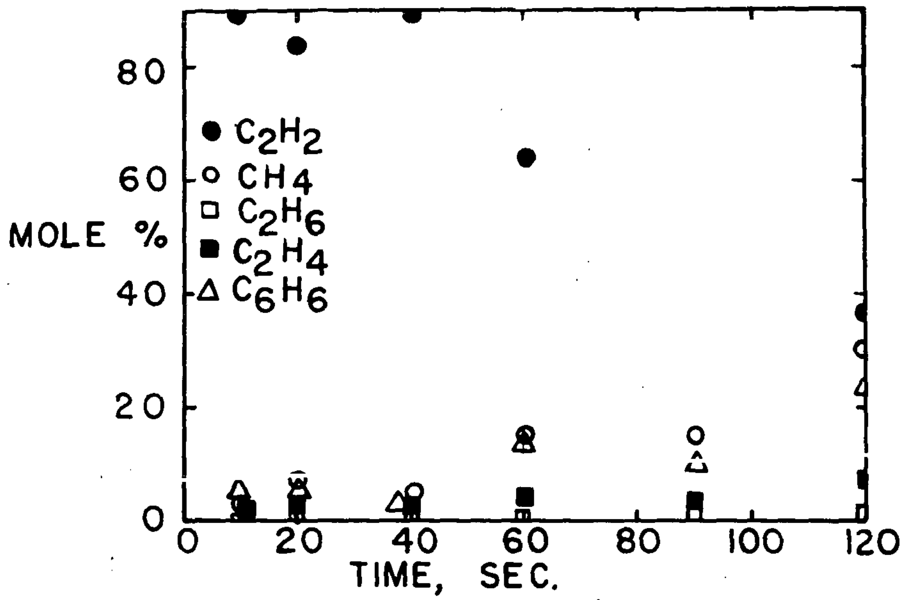

FIGURE 3

HYDROCARBON GASES FROM REACTION OF NAPHTHALENE IN ARGON PLASMA