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Reactions of Coal in a Plasma Jet

R. D. Graves, W. Kawa, and P. S. Lewis

U.S. Bureau of Mines, 4800 Forbes Avenue
Pittsburgh 13, Pennsylvania

INTRODUCTION

The Bureau of Mines has made an exploratory study of the reaction of coal in a plasma jet in which plasma temperatures up to about 15,000° C can be attained. The objective was to obtain new knowledge of coal chemistry which may lead to new methods of producing chemicals from coal. Plasma consists of more or less ionized gases or vapors, and is present in any electrical discharge. Temperatures generated in electrical discharges are high enough for molecular bonds to be broken and for the resultant atoms to dissociate into ions and electrons. The complex mixture of ions, electrons, neutral atoms, and excited molecules produced is called a plasma and is referred to as the fourth state of matter. It conducts electricity, is a good heat conductor, and is luminous. The highly excited species that exist in plasmas can react to produce compounds whose formation is thermodynamically unfavorable at conventional conditions.

A plasma jet is formed when plasma generated from a fluid flowing through an electrical arc confined within a chamber is made to flow out of the chamber through a nozzle or orifice. Various plasma jet devices have been used in recent years to study high-temperature chemical syntheses. Leutner and Stokes[1/], using a consumable graphite anode, produced acetylene by reacting the graphite with hydrogen in an argon-hydrogen plasma. About 34 percent of the carbon consumed was converted to acetylene. Adding graphite in powdered form did not increase the yield of acetylene. These same investigators also reacted methane in argon plasmas and converted 80 percent of the carbon in the methane to acetylene. Acetylene synthesis has also been reported by Freeman and Skrivan[2/], who reacted methane in argon and argon-hydrogen plasmas, and by Baddour and Iwasyk[3/], who reacted hydrogen with carbon vapor obtained from a consumable graphite electrode.

The plasma-jet device used in the present study was a commercial plasma gun designed for spray-coating applications. Experiments were made with high-volatile A bituminous (hvab) coal using argon as the working gas and also as a carrier gas in which coal was entrained and fed into the plasma gun. The effects of coal rate, coal particle size, and plasma temperature on yields and product composition were determined.

EXPERIMENTAL PROCEDURE

Apparatus

The plasma-jet unit consists of a plasma gun, product recovery system, coal feeder, power supply, cooling water facilities, and a control console. Direct current used to operate the plasma gun is supplied by two 3-phase alternating current transformers and selenium rectifiers. This system is rated at 28 kw and is capable of delivering 700 amp at 40 volts or 350 amp at 80 volts. It also contains a high-frequency oscillator used to start an arc. The electrical potential required to sustain an argon plasma was about 20 volts.

The plasma gun, shown schematically in figure 1, has a 3/16-inch thoriated tungsten cathode and a 1/4-inch id cylindrical water-cooled copper anode. The working gas enters the gun radially near the cathode and flows downward into the anode. The gas is converted to a plasma as it flows through the electrical discharge between electrodes. Coal entrained in the carrier gas enters the plasma through an inlet in the side of the anode. The reaction mixture leaves the bottom of the anode as a luminous jet and flows down through the water-jacketed cooler which consists of a 3-inch copper tube about 12 inches long. The residence time of coal in the plasma is less than a millisecond. Reaction products leave the cooler at several hundred degrees C and enter the solids receiver via a dip tube. The receiver is 6 inches in diameter and 12 inches long and contains about 3 inches of water. Most of the solids collect in the bottom of the receiver, while the gases and finer solid particles at near room temperature bubble up through the water and a tubular baffle. Gases flow through a cloth filter, which collects additional fines, and are sampled, metered, and vented.

Operating Procedure

The system is assembled, purged with argon, and pressure tested. Flows of cooling water and working gas are established, and then the electrical discharge between electrodes is started. The flow of carrier gas is established, and the coal feeder is started. Coal is fed into the plasma gun for 10 minutes unless a coal feed stoppage or other system failure causes a premature termination of an experiment. Initially, the system is at a pressure of about 3 to 4 psig but gradually increases several psi as solids accumulate on the filter. Temperatures of cooling water entering and leaving the plasma gun are measured. Product gases are sampled after steady state conditions are reached. At the conclusion of an experiment, solid products are washed from the cooling system, receiver, filter, trap, and interconnecting lines with water. The washings are combined, and then the solids are filtered and dried in air at 70° C for 20 hours.

Calculations

Total power input is determined from electrical current and voltage measurements at the gun, whereas net power input to the plasma is calculated as the difference between total power input and the power loss to the cooling water. The enthalpy of the primary gas and the average plasma temperature are determined from the net power input into the plasma, the working gas flow rates, and a plot of specific enthalpy as a function of temperature. This calculation assumes no energy loss other than that to the cooling water.

Yields of solids are determined from weighings of coal fed and solids recovered. Yields of gaseous products are calculated from analyses of product gas and the known coal and argon feed rates. This calculation assumes constant coal feed rate and steady state conditions at the time the gases were sampled.

RESULTS AND DISCUSSION

Reactions of 70 x 100 Mesh Coal

Experiments with 70 x 100 mesh coal (U.S. sieve) were made using feed rates of about 3.1 and 1.1 pounds per hour. Argon rates were constant at 1.17 scfm as the primary gas and 0.26 scfm as the carrier gas. The power input at each coal rate was varied to give average plasma temperatures ranging from 3,400° to 7,700° C

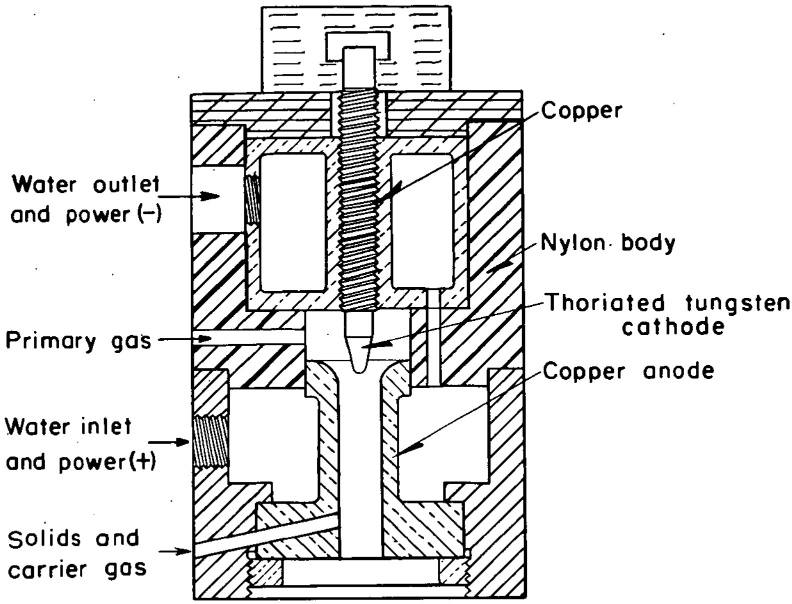

Figure 1.– Schematic diagram of the plasma generator.

at about 3.1 pounds per hour and from 3,900° to 8,600° C at about 1.1 pounds per hour. Reaction products were a solid residue and a gas containing hydrogen, methane, acetylene, diacetylene, and carbon monoxide.

Operating conditions, yield data, and analyses of the coal feed and residues produced are shown in table 1. Yields are expressed as weight-percent of moisture- and ash-free (maf) coal. At a coal rate of 3.1 pounds per hour, increasing the power input (or average plasma temperature) had only a slight effect on the extent of coal decomposition. Yields of solid residue decreased from 92.2 percent at 3,400° C to 89 percent at 7,700° C. Yields of hydrogen and acetylene increased almost linearly from 0.4 to 1.1 percent and from 2.6 to 4.5 percent respectively. The yield of methane was constant at about 0.2 percent, while the yields of diacetylene showed no significant trend. With a coal rate of about 1.1 pounds per hour, the effect of increasing the plasma temperature on yields was similar. Yields of residue decreased while yields of hydrogen increased from 0.4 to 1.7 percent, yields of acetylene increased from 2.2 to 6.0 percent, and yields of diacetylene increased from 0.1 to 0.6 percent with increasing temperature. The amount of methane produced was again constant at about 0.2 percent. At both coal rates, yields of carbon monoxide increased with increasing temperature.

The effect of decreasing the coal feed rate from 3.1 to 1.1 pounds per hour can be seen by comparing the results from experiment 9 with experiment 18 and experiment 10 with experiment 14. Estimated plasma temperatures in each pair of experiments were comparable. At the lower coal rate, higher coal heating rates, higher average coal temperatures, and, hence, more extensive coal decomposition would be expected because there was more heat available per unit weight of coal. However, there was no significant effect of coal rate on yields of gaseous products in these experiments. Although the yields of solid residue were about 5 percent lower at the lower coal rate, this is not necessarily an indication of more coal decomposition. Carbon recoveries were also lower by about the same amount, and it is possible that losses of solid products were higher at the lower coal rate.

Analyses of the solid residues showed that extensive thermal decomposition did not occur in any of the experiments because the coal was not heated sufficiently. Ultimate analyses of the coal and residues did not differ appreciably, and the residues contained only 3 to 6 percent less volatile matter. It is possible that most of the coal particles, because of poor mixing, remained in the periphery of the plasma where temperatures are much lower than along the axis.

The distance between the coal entry port of the anode and the discharge port is 1/4 inch. This may be considered as the coal-plasma mixing zone. To improve the mixing of coal and plasma, an anode was modified to give a threefold increase in the length of the mixing zone. Experiments were then performed at conditions similar to those in experiments 14, 16, and 18 (1.1 pounds of coal per hour). However, as yields and ultimate compositions of the residues produced in the two sets of experiments were similar at comparable conditions, this change was ineffective. Assuming that better mixing was achieved with the extended nozzle, it appeared that heat transfer rate rather than the degree of mixing limited the temperature rise and extent of coal decomposition.

Reaction of -325 Mesh Coal

To reach higher coal temperatures, the particle size of the coal feed was decreased to -325 mesh. Experiments were made with power input as a variable, and average plasma temperatures of 4,800°, 7,300°, and 8,800° C were obtained. Argon rates were constant at 1.17 scfm as working gas and 0.26 scfm as carrier gas. Average coal rates were 1.03, 0.84, and 0.74 pounds per hour although intended to be 1.0 pound per hour. Product distributions and the analyses of the coal feed and

TABLE 1.- Reactions of 70 x 100 mesh hvab coal in argon plasmas
Effects of power input and coal feed
rate on yields and residue compositions
(1.17 scfm argon as primary gas, 0.26 scfm argon as carrier gas)

Experiment number		9	10	4	18	14	16
Average coal rate, lb/hr		3.11	3.06	3.14	1.20	0.99	1.11
Average plasma temp., ° C		3,400	6,300	7,700	3,900	6,600	8,600
Total power input, kw		3.8	7.3	9.4	4.1	7.5	12.6
Net power input, kw		1.7	3.2	3.9	2.0	3.3	4.7
Products, wt pct maf coal							
Solid residue, maf		92.2	89.2	89.0	87.7	84.0	78.3
Hydrogen		0.4	0.8	1.1	0.4	1.0	1.7
Methane		.2	.2	0.3	.2	0.1	0.2
Acetylene		2.6	3.5	4.5	2.2	4.3	6.0
Diacetylene		0.3	0.3	-	0.1	0.4	0.6
Carbon monoxide		4.1	5.3	5.6	3.8	5.6	11.0
Total		99.8	99.3	100.5	94.4	95.4	97.8
Carbon recovery, pct		96.8	96.8	97.1	91.3	92.3	92.8
Hydrogen recovery, pct		96.4	98.0	105.4	94.2	100.3	104.1
Analyses, wt pct							
Material	Coal	--------------Solid residue--------------					
Moisture	0.8	0.8	1.3	0.4	0.1	0.6	0.6
Ash	3.8	4.4	5.4	5.1	4.7	4.2	4.6
Ultimate composition, maf basis							
H	5.6	5.2	5.1	5.0	5.3	5.2	4.6
C	84.3	83.3	87.5	87.0	83.4	87.4	86.0
N	1.7	1.7	1.6	1.5	1.6	1.6	1.5
S	0.9	0.9	0.9	1.0	0.8	0.8	0.9
O (by difference)	7.5	8.9	4.9	5.5	8.9	5.0	7.0
Volatile matter, maf basis	37.6	34.8	31.2	32.6	34.4	33.9	31.1

solid residues produced are shown in table 2. As power input was increased, yields of solid residue decreased from about 74 to 45 percent and yields of hydrogen and acetylene increased. No trends were observed in the yields of methane and carbon monoxide. Trace quantities of diacetylene were formed in each experiment.

There was considerably more decomposition in all experiments with -325 mesh coal than in experiments with 70 x 100 mesh coal. The -325 mesh coal evidently reached higher temperatures. Volatile matter contents of the residues from -325 mesh coal were much lower, and yields of gaseous products were much higher. In experiments with 70 x 100 mesh coal in argon plasmas, the highest yield of acetylene obtained was 6 percent. The solid residue produced from this experiment contained 31 weight-percent volatile matter on a maf basis. As shown in table 2, acetylene yields obtained from -325 mesh coal were about 10, 12, and 15 percent, and the residues contained about 17, 10, and 12 percent volatile matter. These results clearly show that particle size had a pronounced effect on the extent of coal decomposition. However, the -325 mesh coal was still not completely devolatilized although it is estimated that coal temperatures of about 2,900° to 6,300° C would have been reached if thermal equilibrium had been attained. Complete devolatilization would be expected at a temperature somewhat above 1,000° C.

Total yields and carbon and ash recoveries were low in experiments 40 and 41 (table 2), possibly because of losses of extremely fine solid residue that filtered through the recovery system. In all three experiments, the recoveries of hydrogen and oxygen were high, and in experiments 38 and 40, the yields of carbon monoxide obtained would not be possible even if all the oxygen in the coal had been converted to carbon monoxide. It is likely that some leakage of cooling water into the plasma had occurred. The reaction of this water with coal or coal decomposition products would account for the high hydrogen recoveries and the high yields of carbon monoxide.

CONCLUSIONS

Acetylene was the principal hydrocarbon gas produced when hvab coal was injected into argon plasmas and was obtained in yields as high as 15 weight-percent of maf coal. However, the coal was not heated to temperatures high enough for complete devolatilization to occur. To obtain higher coal temperature and yields of gaseous products, changes in plasma generator design and/or operating techniques that will result in more efficient utilization of the heat available in plasmas will be required.

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TABLE 2.- Reactions of -325 mesh hvab coal in argon plasmas
Effect of power input on yields and residue compositions
(1.17 scfm argon as working gas, 0.26 scfm argon as carrier gas)

Experiment number		38	41	40
Average coal rate, lb/hr		1.03	0.84	0.74
Average plasma temp., ° C		4,800	7,300	8,800
Total power input, kw		4.8	7.5	10.2
Net power input, kw		2.4	3.7	4.9
Products, wt pct maf coal				
Solid residue, maf		73.6	62.9	45.3
Hydrogen		2.4	3.0	3.9
Methane		2.7	0.5	0.6
Acetylene		9.5	12.3	15.4
Diacetylene		trace	trace	trace
Carbon monoxide		18.1	11.4	24.3
Carbon dioxide		1.4	0.0	0.0
Total		107.7	90.1	89.5
Carbon recovery, pct		103.2	89.4	80.9
Hydrogen recovery, pct		126.6	115.8	130.5
Analyses, wt pct				
Material	Coal	----Solid	residue----	
Moisture	1.1	0.7	0.5	0.6
Ash	8.3	11.2	11.4	11.9
Ultimate composition, maf basis				
H	4.9	3.2	2.5	2.5
C	81.9	89.2	90.0	90.9
N	1.5	1.5	1.1	1.0
S	1.5	1.1	1.1	1.1
O (by difference)	10.2	5.0	5.3	4.5
Volatile matter, maf basis	37.2	17.4	10.2	12.3