

## HYDROCARBONS AND CARBON FROM A ROTATING ARC HEATER

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INTRODUCTION

A brief description of the rotating arc heater utilized in this work, and some preliminary hydrocarbon processing data, were described a year ago.<sup>1</sup> A more detailed description of the heater, and some of the operating characteristics have also been presented within the past year.<sup>2</sup> The arc heater consists essentially of water-cooled, toroidal electrodes, in which the arc is rapidly rotated as a result of interaction of the arc current with a magnetic field. The heater is a high current, low voltage device with a rating of 3 megawatts into the arc. Both alternating and direct current power operation are possible with this device. In contrast, most arc devices previously reported<sup>3</sup> are of the long arc, high voltage type which are operated on d.c. only.

We wish to report, herewith, some of the results obtained more recently in the pyrolysis of methane at atmospheric and at slightly elevated pressures.

EXPERIMENTAL

The feed gas was commercial grade methane of 96 per cent purity which was injected into the heater at ambient temperature. The flow rate was controlled by regulating the pressure drop across a sonic orifice.

The arc heater was operated only on a.c. power at electrode separations of 0.38, 0.75 and 1.0 inch. The arc power with methane ranged from 550 to 2200 kilowatts, with thermal efficiencies between 25 and 76 per cent, depending on operating conditions. For operation at elevated chamber pressure, the nozzle was choked with a graphite plate which had an orifice of 0.5 or 0.75 inch diameter in the center of the plate. The chamber pressure was as high as 100 psig.

The heater was operated at two different field coil currents to determine arc rotation velocity on the degree of reaction.

The products of the reaction were quenched and collected through a water-cooled copper probe, 1/8 or 1/4 inch I.D., inserted about an inch inside of the nozzle. The product from the probe was first passed through a fiber filter (Purolater Co.) to separate the carbon, then collected at appropriate intervals in gas sampling tubes on a manifold, as previously described.<sup>1</sup>

The gas analyses were made mass spectrometrically. A typical composition of a sample is shown in Table I; Table II shows the approximate material balance based on the  $H_2/C$  ratios of the feed and product gases. The only variation with operating conditions is in the relative concentration of the different species.

TABLE I. COMPOSITION OF GASEOUS PRODUCT, MOLE PERCENT

$H_2$	CO	CO <sub>2</sub>	CH <sub>4</sub>	C <sub>2</sub> H <sub>2</sub>	C <sub>2</sub> H <sub>4</sub>	C <sub>3</sub> H <sub>4</sub>	C <sub>4</sub> H <sub>2</sub>	C <sub>6</sub> H <sub>6</sub>
77.68	1.27	0.09	5.81	13.58	1.01	0.12	0.32	0.14

TABLE II. MATERIAL BALANCE OF PRODUCTS IN MOLE PERCENT

$H_2$	CO	CO <sub>2</sub>	CH <sub>4</sub>	C <sub>2</sub> H <sub>2</sub>	C <sub>2</sub> H <sub>4</sub>	C <sub>3</sub> H <sub>4</sub>	C <sub>4</sub> H <sub>2</sub>	C <sub>6</sub> H <sub>6</sub>	C
73.06	1.19	0.08	5.46	12.77	0.95	0.11	0.30	0.13	15.00

Electron micrographs were obtained on a number of the carbon samples by replicating an amyl acetate suspension on a carbon film. X-ray spectra were obtained by packing the soot into a disc-sample holder and irradiating with Cu K- $\alpha$  radiation. The sample packing and irradiation were kept as nearly identical as possible for all of the samples. The d-spacing and line intensity were compared against AUC graphite measured under identical conditions.

### RESULTS AND DISCUSSION

As shown in Table II, the product consists of species which are expected from the high temperature pyrolysis of methane. The primary products are  $H_2$ ,  $C_2H_2$ , and carbon, with varying concentration of  $CH_4$ , depending on the degree of reaction. The diacetylene and benzene are formed from the polymerization of the acetylene; the methyl acetylene, although not an intermediate in the conversion of  $CH_4$  to  $C_2H_2$ , is known to be a minor product found in the pyrolysis of diacetylene.<sup>4</sup> The  $C_2H_4$  is an intermediate in the  $CH_4 \rightarrow C_2H_2$  reaction. There is a slight error in the material balance since the hydrogen content of the soot was not taken into account because of sampling difficulty. The soot usually contains about one percent of hydrogen, and the presence of aromatic constituents is evident from the odor.

Considering the difficulty of obtaining exact experimental parameters during an experiment, quite good correlation was obtained between the degree of reaction and arc enthalpy, whereas the correlation was poor with respect to the net enthalpy increase of the gas. Figure 1 shows the relative degree of methane pyrolysis as a function of the arc enthalpy. The curves show the comparison between runs made at 2500 and 1500 amperes field coil current. The former effects an arc rotation velocity approximately 66 percent greater than that at the 1500 amps field coil current. There is a significantly steeper slope at higher arc rotation velocity, this result probably arising from the greater degree of mixing. Note that the curves saturate at high enthalpies, where the system is at equilibrium, or near equilibrium condition. A minimum just above the critical enthalpy (or initiation temperature).

The electron micrographs of the soot, quenched at the heater nozzle, at 25,500X magnification, Figure 2, shows spherical particles of less than 100 Å to approximately 5000 Å diameter. The nature of the background is not known at present, but blow-ups of the photomicrographs to approximately 153,000X suggests that the cloud consists of extremely fine, smokey carbon dust.

The d-spacings obtained from the x-ray diffraction of the soot varies between 3.45 and 3.49 Å, compared to 3.35 Å for pure, crystalline graphite. The lower value of 3.45 Å was obtained on the carbon collected from the high pressure runs, where the residence times were up to seven times longer than the runs at atmospheric pressure. The degree of crystallinity of the soot, based on the x-ray intensity, varied from two to ten percent of AUC graphite. The x-ray crystallinity, as suspected, is a function of the residence time.

It was of interest to plot the major product compositions on a semi-log plot, as a function of reciprocal arc enthalpy since the latter is proportional to the temperature in the gas. Figure 3 shows that the slopes for acetylene and hydrogen are approximately the same, whereas the slope for carbon is much steeper. The difference in slopes for carbon, as compared to  $C_2H_2$  and  $H_2$ , clearly shows the different mechanisms for the formation of these species.

REFERENCES

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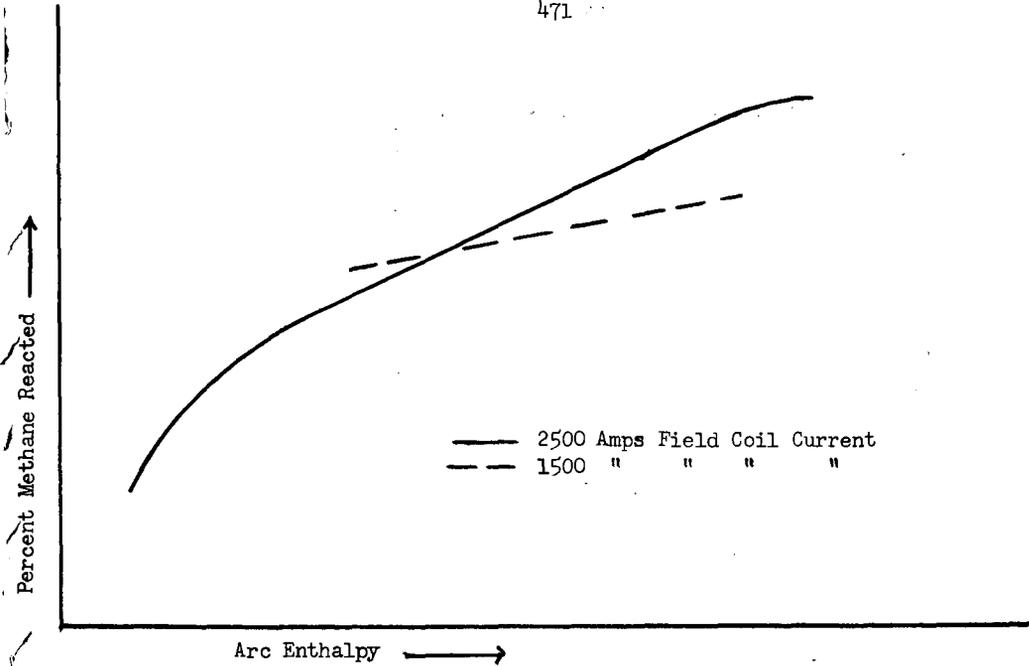


Fig. 1. Methane conversion as functions of arc enthalpy and arc rotation



Fig. 2. Electron micrographs of carbon at 25,500X

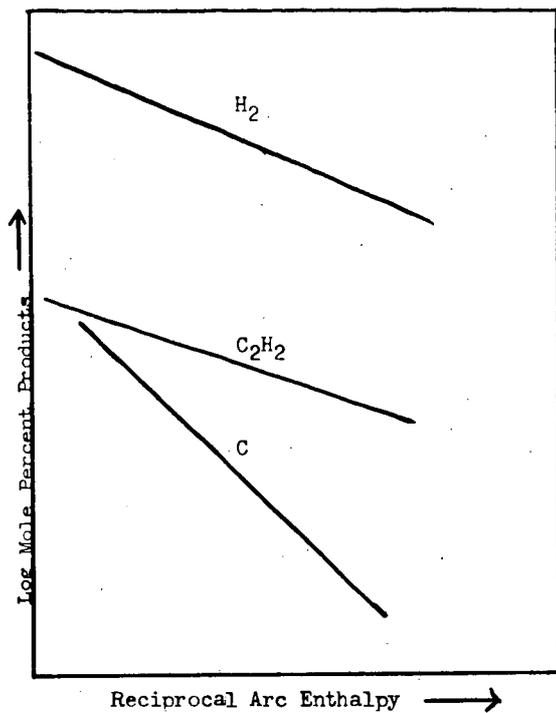


Fig. 3. Product composition as a function of reciprocal arc enthalpy