PRESSURE EFFECT ON PRODUCT SELECTIVITIES IN THE PYROLYSIS OF METHANE IN AN ARC-PLASMA HEATER

C. Hirayama
M. G. Fey
F. E. Camp

Westinghouse Research Laboratories
Pittsburgh, Pennsylvania 15235

INTRODUCTION

There have been a number of electric arc processes reported for the conversion of hydrocarbons to acetylene and associated products. To date, only two of these processes have been adapted to commercial scale production of acetylene. 1) The original Huels flaming-arc process[1] in Germany pyrolyzed a hydrocarbon feed stock in a direct current arc. The gas was introduced into the heater in a swirling pattern so as to aid in rotating the arc. A heavy hydrocarbon was also injected downstream of the heater nozzle as the initial quench. More recently, the feed stock hydrocarbon has been injected into a hot hydrogen plasma[2] in order to reduce the carbon content in the product. 2) The DuPont process[3] (presently not in use[4]) utilized a direct current arc similar to Huels', but with a magnetic rotation of the arc. In this process, the plenum was maintained below atmospheric pressure. The Huels process, although not so stated in the published literature, presumably cracked the hydrocarbon at atmospheric (or higher) pressure. Unless there is use for the carbon from these pyrolysis processes, it is imperative that the soot content in the product be minimized.

For most practical plant practice, it is desirable that the pressure of the product gas from the heater be as high as possible. This would minimize the compression necessary for efficient absorption of acetylene from the cracked gas in the separation plant. It is known that higher pressure in the cracking chamber tends to yield higher carbon; conversely, lower pressure reduces the carbon yield. For example, the DuPont process, which reportedly operated at 400 torr in the plenum, yielded only about three percent of carbon, whereas the earlier Huels process yielded approximately twenty percent carbon.

We here report the effect on acetylene selectivity of pressures between one and seven atmospheres in the electric-arc heater reaction chamber when methane is pyrolyzed.

EXPERIMENTAL

The electric-arc heater of 3000 kilowatts has been described previously.[5] However, for the present experiments, the heater was operated in the self-stabilizing, high-flow mode on a.c. power, as described by Fey.[6] Suffice it to report here that the chemical data obtained on the present arc heater and that reported by Fey are similar.

Test Conditions

Methane of C.P. grade (98.6% CH_4, 0.2% C_2H_6, 1.1% N_2, 0.1% O_2) was delivered to the heater from a pressurized tube-trailer, and was metered through a critical flow orifice. The gas was introduced to the heater at room temperature. The residence volume of the heater chamber was 0.6 $ft.^3$.

The gas samples at the heater nozzle were collected as previously described[5] with a water cooled copper probe of 1/8 inch i.d. A carbon filter (Purolator part #51383 fiber filter fitted into a glass vessel) was inserted before the sample manifold. The chemical analyses of the product gas were obtained by mass spectrometry.

During a run, the power level was varied over several steps by changing the gas flow rate and/or by changing the arc power. A product gas sample at each step was collected after the desired arc power level became stabilized. The electrical, flow and pressure data were continuously recorded on a Honeywell Model 1612 visicorder.

The pressure in the arc chamber was controlled by an 8" long cylindrical graphite insert fitted into the heater nozzle. Different pressure levels were obtained by inserts of different orifice diameters and by varying the gas flow rate. The orifice diameter varied from 1.06 to 3.00 inches. The heater chamber pressure was measured by inserting a calibrated transducer into the end-plug of the heater.

RESULTS

Table I summarizes typical operational characteristics of the arc heater. The arc power level varied from 1 to 2.5 megawatts, with a thermal efficiency approaching 90%. The methane mass flow rate was as high as 0.78 lbs/sec, and the enthalpy of the gas varied from approximately 1300 to 4000 Btu/lb. The pressure in the heater chamber varied from atmospheric to 87.9 psig.

Table II summarizes the molar composition of the product at conditions corresponding to the operations shown in Table I. The material balance was made on the basis of the C/H ratios of the feed and of the product gas. The results in Table II are slightly in error since a small amount of the product was adsorbed on the trapped carbon in the filter. This was evidenced by an aromatic odor of the carbon sample. However, this error is less than five percent, as shown by a separate test in which the feed gas was doped with 2% argon as a material balance probe.

The concentration of acetylene, C, in the product was fitted to various functions, f(P/H), where P is the heater chamber pressure in atmospheres, and H the enthalpy, in Btu/lb, into the feed stock. The best linear correlation obtained was of the form $\log C = A - B\sqrt{P/H}$, where A and B are constants. Figure 1 shows the plot for all of the data. The scatter in the data was greater at high $\sqrt{P/H}$.

Table III shows the overall conversion (percent reaction) of the methane in the first column. As shown in Figure 2 for all of the collected data at atmospheric and for higher pressures in this experiment, the conversion increases almost linearly with the enthalpy.

Table III also shows the carbon material balance in columns 2 to 10. Note the relatively large amount of methane in the product. The last column in this table shows the specific energy requirement (SER) for acetylene production under the conditions reported herein. At atmospheric pressure, runs 1 to 3, the SER remains approximately constant, around 4.0 kwh/lb C_2H_2, at enthalpies of 2100 to 3650 Btu/lb. At pressures between 4 and 22 psig the SER's are below 5 kwh/lb C_2H_2. The acetylene concentrations in these instances (runs 4 to 8),

Table I. Heater Operating Characteristics

Run No.	Arc Power KW	Mass Flow Rate, lbs/sec	Heater Efficiency %	Enthalpy Btu/lb	Heater Pressure psig
1	1598	0.565	77.5	2100	0
2	1440	0.344	73.1	2900	0
3	1860	0.345	73.2	3650	0
4	1527	0.437	83.4	2760	3.8
5	1411	0.522	83.7	2140	5.7
6	1066	0.623	80.0	1297	13.4
7	1585	0.480	83.8	2620	15.3
8	1670	0.780	85.4	1735	21.6
9	1583	0.441	83.8	2850	22.3
10	2380	0.531	86.1	3660	33.8
11	2290	0.565	85.0	3270	35.0
12	2420	0.627	88.6	3170	44.5
13	1960	0.642	86.4	2500	56.0
14	1612	0.524	86.1	2510	69.5
15	1960	0.608	86.6	2642	87.9

Table II. Molar Composition of Product

Run No.	CH_4	H_2	C_2H_2	C_2H_4	C_2H_6	C_3H_4	C_3H_8	C_4H_2	C_6H_6	C
	Mole %									
1	55.3	33.5	8.2	0.33	0.11	0.26	0.01	0.42	0.04	1.8
2	35.1	48.2	11.2	0.54	0.06	0.31	0.02	0.45	0.10	4.0
3	22.8	56.5	11.8	0.56	0.03	0.23	0.02	0.44	0.08	7.5
4	48.4	38.5	9.2	0.34	0.10	0.34	0.03	0.46	0.05	2.5
5	61.9	28.5	6.8	0.29	0.10	0.27	0.04	0.36	0.04	1.7
6	69.6	22.6	5.3	0.30	0.10	0.18	0.02	0.26	0.04	1.6
7	46.9	38.9	7.8	0.56	0.08	0.24	0.02	0.3	0.08	5.1
8	63.6	26.9	6.0	0.41	0.11	0.23	0.02	0.25	0.05	2.5
9	51.1	35.8	7.2	0.68	0.08	0.25	0.02	0.26	0.10	4.4
10	33.0	48.2	8.0	0.86	0.05	0.23	0.03	0.24	0.12	9.2
11	39.4	43.7	7.1	0.94	0.06	0.23	0.02	0.22	0.14	8.2
12	32.9	48.0	7.5	0.84	0.05	0.21	0.03	0.22	0.11	10.1
13	51.8	34.4	4.8	1.0	0.10	0.19	0.03	0.13	0.14	7.4
14	73.2	19.0	2.2	0.72	0.10	0.11	0.02	0.05	0.11	4.4
15	49.6	35.5	3.4	1.4	0.10	0.16	0.03	0.06	0.17	9.6

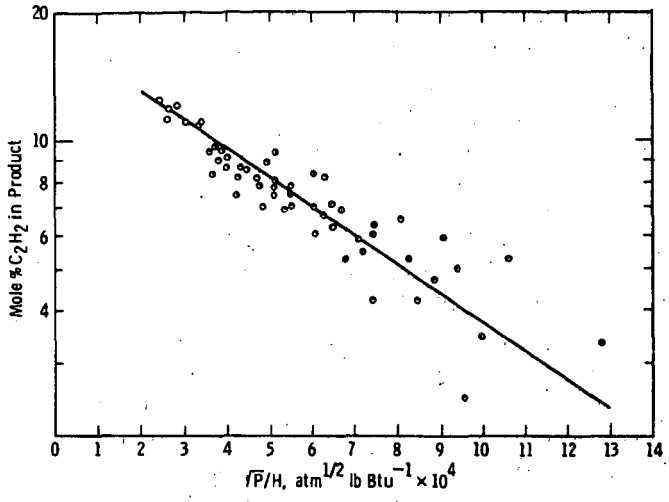

Fig. 1 —Product acetylene concentration as a function of $\sqrt{P}/H$

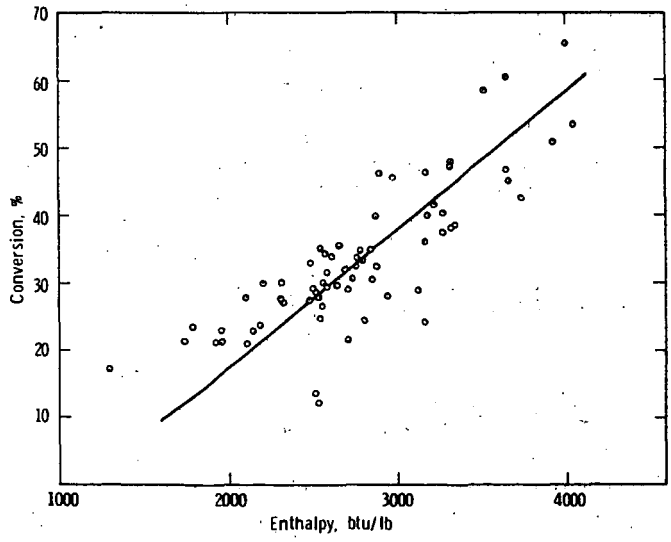

Fig. 2 —Conversion of methane as a function of enthalpy

Table III. Conversion, Carbon Material Balance (Conversion to Carbon Products) and SER

Run No.	Conversion %	Conversion to Carbon Products, Mole %									SER kwh/lb C_2H_2
		CH_4	C_2H_2	C_2H_4	C_2H_6	C_3H_4	C_3H_8	C_4H_2	C_6H_6	C	
1	28.1	71.6	21.4	0.86	0.30	1.0	0.04	2.2	0.30	2.3	4.1
2	46.6	53.2	33.9	1.7	0.17	1.4	0.09	2.7	0.87	6.1	3.8
3	60.5	39.3	40.7	1.9	0.10	1.2	0.10	3.0	0.86	12.8	4.0
4	33.7	65.9	25.1	0.94	0.28	1.4	0.12	2.5	0.41	3.4	4.3
5	22.8	76.8	17.0	0.71	0.25	1.0	0.15	1.8	0.30	2.1	4.9
6	17.2	82.5	12.5	0.70	0.23	0.63	0.07	1.2	0.28	1.9	4.2
7	34.0	65.7	21.9	1.6	0.21	1.0	0.08	1.7	0.72	7.1	4.6
8	21.2	78.4	14.7	1.0	0.26	0.87	0.07	1.2	0.36	3.0	4.5
9	30.5	69.2	19.5	1.8	0.21	1.0	0.08	1.4	0.85	6.0	5.7
10	46.9	52.7	25.7	2.8	0.17	1.1	0.13	1.6	1.1	14.7	5.4
11	40.3	59.5	21.5	2.8	0.20	1.0	0.08	1.3	1.2	12.3	5.8
12	46.6	53.1	24.3	2.7	0.17	1.0	0.13	1.4	1.0	16.2	4.9
13	28.6	71.0	13.0	2.8	0.25	0.80	0.11	0.71	1.1	10.2	7.2
14	13.5	86.1	5.2	1.7	0.25	0.40	0.07	0.22	0.81	5.2	18
15	29.7	69.9	9.7	4.0	0.28	0.70	0.11	0.36	1.5	13.5	10

however, are low because of the low enthalpies. At higher pressures, the SER increases as a result of increasing carbon yield.

Table IV shows typical selectivity (yield) values, arranged in the order of increasing pressure in the heater chamber. (These values are obtained from Table III by dividing the respective quantities in columns 3 to 10 by the quantity in the first column. The selectivities are actually low since the conversions are higher than calculated on the basis of the C/H ratio (see below)). Runs 1 to 3 show the effect of increasing temperature on the selectivities at atmospheric pressure. There is a significant increase in carbon yield as the pyrolysis temperature increases. As the pressure increases, there is a trend toward decreasing acetylene and diacetylene, while the ethylene, benzene and carbon yields tend to increase. The methylacetylene yield remains nearly constant with pressure. Figure 3 shows the correlations between the acetylene and carbon selectivities with pressure. Note that the pressure has been corrected to psia in this figure. The scatter of the data points arises in part from the variation of enthalpy encountered in these runs. The acetylene selectivity is best fitted with a linear correlation, $S = 79 - 0.44\ P$, where S is the selectivity (in mole percent) and P the absolute pressure (psia). The carbon selectivity is a non-linear function of the pressure.

DISCUSSION

In an electric arc process, the acetylene is formed from the hydrocarbon primarily at the high temperature around the arc column. The product is then rapidly quenched as it mixes with more feed gas. At the high flow rates reported here, the acetylene is more or less frozen as it is swept out of the heater. Within the heater chamber, however, the acetylene could polymerize. In the heater, there are regions of very high temperature where local thermodynamic equilibrium exists. Consequently, solid carbon will always be a product. It is well to remember, however, that cracking of a gas in an electric arc heater is considerably more complicated than that in an isothermal system at the same enthalpy. There is considerable local temperature inhomogeneity in an electric arc system.

The conversion of methane to acetylene and to ultimate products is generally believed to follow a path[7]:

$$CH_4 \xrightarrow{k_1} C_2H_6 \xrightarrow{k_2} C_2H_4 \xrightarrow{k_3} C_2H_2 \xrightarrow{k_4} \text{polymers} \rightarrow \text{carbon.}$$

The ratio of $[C_2H_6]$ to $[CH_4]$ is very small, because of the large k_2, so that ethane is often not detected in the pyrolysis product from methane. The ethylene is converted to acetylene by a monomolecular process,[8] whereas the acetylene is polymerized to its product by a bimolecular process.[9] One of the polymerization products of acetylene is diacetylene, which decomposes in a manner very similar to acetylene.[10] The diacetylene further polymerizes to ultimately yield carbon. At temperatures above 1000°C, all of these reactions are very rapid.

It is not surprising that both the acetylene and diacetylene selectivities decrease with increasing pressure since the decompositions of both compounds are similar bimolecular processes whose rates of reaction vary as the square of the pressure.[11] It is apparent from the data in Table IV that the acetylene decomposition is much more sensitive to increasing pressure than is the mono-molecular reaction by which the acetylene is formed from ethylene. The latter reaction rate varies only as the first power of the pressure. The increase in

Table IV. Selectivity of Products in Mole % and Heater Chamber Pressure

Run No.	SELECTIVITY C_2H_2	C_2H_4	C_3H_4	C_4H_2	C_6H_6	C	Pressure, psig
1	76.1	3.1	3.6	7.8	1.1	8.2	0
2	72.5	3.6	3.0	5.8	1.9	13.1	0
3	67.2	3.1	2.0	5.0	1.4	21.1	0
4	74.5	2.8	4.2	7.4	1.2	10.1	3.8
5	74.5	3.1	4.4	7.9	1.3	9.2	5.7
6	72.6	4.1	3.7	7.0	1.6	11.0	13.4
7	64.5	4.7	2.9	5.0	2.1	20.8	15.3
8	69.3	4.7	4.1	5.7	1.7	14.2	21.6
9	64.0	5.9	3.3	4.6	2.8	19.7	22.3
10	54.8	6.0	2.3	3.4	2.3	31.3	33.8
11	53.3	7.0	2.5	3.2	3.0	30.5	35.0
12	52.1	5.8	2.1	3.0	2.1	34.7	44.5
13	45.5	9.8	2.8	2.5	3.8	35.7	56.0
14	38.5	12.6	3.0	1.6	6.0	38.5	69.5
15	32.8	13.5	2.4	1.2	5.0	45.5	87.9

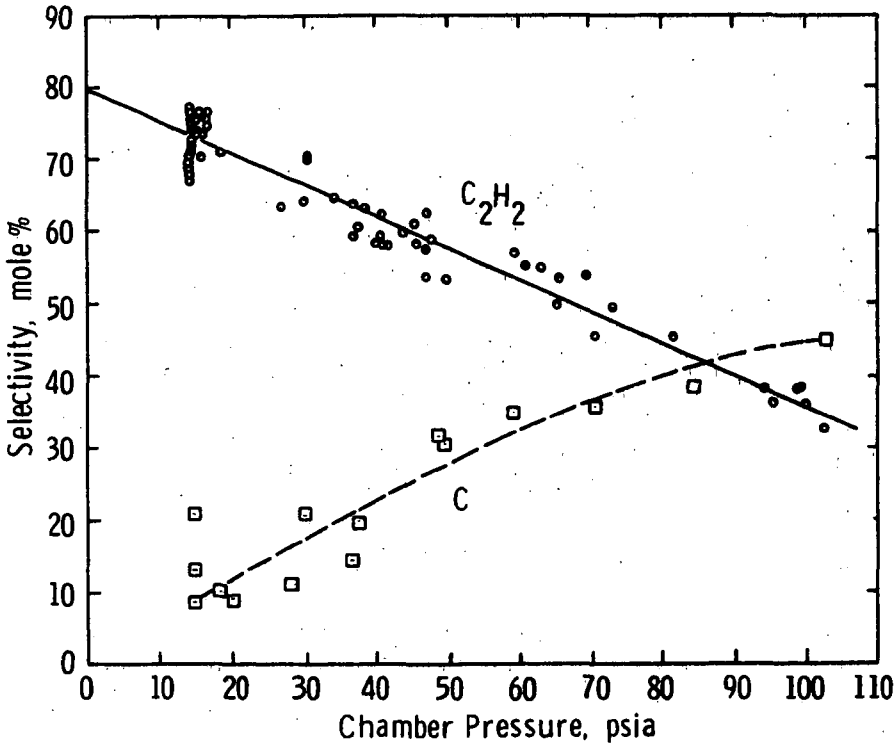

Fig. 3—Acetylene and carbon selectivity as function of chamber pressure

carbon yield with pressure is to be expected since this is the ultimate decomposition product from acetylene, and there is a significant decrease in the C_2H_2 with pressure. The increase in benzene yield with pressure is consistent with the mechanism suggested by Cullis and Franklin[12] for the formation of this species. All of the variations in yield with pressure are in qualitative agreement with the kinetic results reported by the above authors.

The relationship between the acetylene concentration and the enthalpy, as shown in Figure 1, is consistent with the Arrhenius law. However, the exact significance of the correlation between the acetylene concentration and $\sqrt{P}$ is not known. The kinetics of the competing reactions for the formation and decomposition of acetylene at increasing pressures is obviously complex. Nevertheless, the trend of decreasing acetylene with increasing pressure is in qualitative agreement with the kinetics of acetylene decomposition.

Methane is one of the decomposition products of acetylene[10,12] and can become a significant product. Therefore, the actual conversion is higher than that calculated from the C/H ratio. Especially at high pressure and low acetylene selectivity does the contribution of regenerated methane become significant in the overall product concentrations. Unfortunately, the exact amount of regenerated methane is not known, so that the overall conversion cannot be corrected.

For a viable acetylene process it is apparent that the pressure in the reaction zone should be as low as practical in order to increase the C_2H_2 yield and to decrease the soot content. On the other hand, if the carbon content can be economically reduced, for example by downstream injection of steam without seriously affecting the acetylene yield or by absorption in heavy oil, operation around atmospheric pressure would yield acetylene at about 4 kwh/lb C_2H_2. Should the carbon be a desired by-product, this electric arc process would become attractive.

CONCLUSION

The acetylene selectivity from the electric arc pyrolysis of methane decreases linearly with pressure. Consequently, the carbon yield is increased significantly as the pressure increases above one atmosphere.

REFERENCES

1. H. Gladisch, Hydroc. Proc. & Pet. Ref. 41, 159 (1962).
2. H. Gladisch, Chem.-Ing. Tech. 41, 204 (1969).
3. R. A. Schulze, Chem. & Ind. 9, 1539 (1968).
4. Anon., Chem. Engineering, May 20, 1968, p. 71.
5. C. Hirayama and D. A. Maniero, Preprints of papers presented, Div. of Fuel Chemistry, Am. Chem. Soc., Vol. 10, No. 1, pp. 123-132, March 1966.
6. Paper presented, Am. Chem. Soc., Fuel Chem. Div., Chicago, Sept. 1970.
7. e.g., S. A. Miller, "Acetylene, Its Properties, Manufacture and Uses," Vol. 1, Academic Press, New York, p. 373.
8. G. B. Skinner and E. M. Sokolski, J. Phys. Chem. 64, 1028 (1960).
9. H. B. Palmer and F. L. Dormish, J. Phys. Chem. 68, 1553 (1964).
10. K. C. Hou and H. B. Palmer, J. Phys. Chem. 69, 863 (1965).
11. O. A. Hougen and K. M. Watson, "Chemical Process Principles," part 3, John Wiley & Sons, New York, 1947, pp. 832-839.
12. C. F. Cullis and N. H. Franklin, Proc. Roy. Soc. 1964, 139.