

THE DIRECT PRODUCTION OF ACETYLENE BY THE PYROLYSIS OF
COAL IN PLASMA JETS

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ABSTRACT

Rapid heating of coal to temperatures in excess of 1500 K yields lower hydrocarbons which, if conditions are correct, will consist mainly of acetylene. Such conditions involve reaction times of 0.1 to 10 ms, together with rapid rates of quenching. Appropriate conditions have been achieved on a laboratory scale using a d.c.-arc plasma jet.

1. INTRODUCTION

During the past two decades there has been a number of investigations into the high-temperature reactions of coal (1-8). Although the temperatures and residence times to which the coal was subjected differ widely, there is a similarity in the nature of the products formed. Little or no tar is produced and at the high temperatures employed acetylene formation is thermodynamically favoured and appreciable quantities are found in the pyrolysis products.

2. INVESTIGATIONS AT SHEFFIELD

Work at Sheffield on the high-temperature decomposition of coal began in 1962. Preliminary experiments by James (9) were directed at comparing the yield of volatiles from the high-temperature devolatilization of coal with that obtained during the B.S. volatile matter test (10). The most convenient device available at that time for attaining temperatures above 1500 K was a small arc-image furnace. Deyasi (11) later carried out a more thorough investigation. They both found that the yield of volatiles was very much greater than that of the standard test and that about 8% by weight of the coal carbon had been converted to acetylene.

In an effort to improve the acetylene yield by increasing the heating rate and shortening the residence time, James (12)

subsequently pyrolyzed coal in an argon plasma jet. Complete devolatilization of the coal was not achieved, but a maximum of 24% by weight of coal carbon was converted to acetylene. Based on the results of a complementary cold-model study, James concluded that penetration of the coal-carrier gas stream, which was injected radially into the argon plasma stream, was a critical factor in the devolatilization process.

To ensure that the coal was introduced into the hottest part of the plasma, Nicholson (13), in a subsequent investigation, fed the coal axially into the argon plasma through holes drilled in a hollow cathode holder. He noted that the yield of acetylene was determined principally by the operating conditions. The maximum conversion of coal carbon to acetylene was 36% by weight. Nicholson concluded that, because of the unfavourably low H/C atomic ratio of coal, this was the upper limit of conversion when pyrolyzing coal in an inert atmosphere. Consequently, on the basis of equilibrium considerations, he predicted that addition of hydrogen to the arc-gas stream should enhance the acetylene yield. Subsequently, Nicholson used argon-hydrogen mixtures as arc gas. He observed that stable operation was possible only over a narrow range of experimental conditions and, in general, plasmas containing more than 10% by volume of hydrogen could not be operated satisfactorily because of the unfavourable geometry of his plasma head. However, one run was carried out successfully using a 10% hydrogen plasma and this realized an acetylene yield of 74% by weight of coal carbon. The investigations up to this stage have been fully described by Littlewood (14) and Nicholson and Littlewood (15).

The objective of the latest investigation was to pyrolyze coal in plasmas employing argon-hydrogen mixtures and hydrogen alone as arc gas in order to ascertain the upper limit of conversion of coal to acetylene. For this purpose, a plasma jet capable of operating on such gases was designed and built by Garratt (16, 17).

3. PLASMA JET APPARATUS

The final design of the plasma head was the result of many trials with an experimental plasma jet. This experimental jet was built such that its geometry could be altered to achieve optimum conditions when using argon-hydrogen mixtures and hydrogen alone as arc gas. Anode inserts, which enabled the nozzle diameter and throat length to be varied, and an adjustable cathode were the important features. When using argon, stable operation was possible over a wide range of experimental conditions. However, plasmas containing more than 10% by volume of hydrogen were unstable and caused severe erosion of the anode nozzle. Generally, plasmas containing hydrogen were found to be stable when using smaller diameter anode inserts and longer throat lengths. A more efficient anode water-cooling system

and a magnetic coil to spin the arc overcame the problem of erosion. The final design of the plasma head shown in Fig. 1 incorporated all these features.

The cathode was machined from a 2% thoriated tungsten rod and was housed in a copper block which was attached to the base of three concentric brass tubes. The inner tube conveyed the coal-carrier gas stream to the copper block in which were drilled three holes to allow the coal to pass axially into the plasma stream. The two outer tubes formed the system for directly water cooling the cathode.

The anode was fabricated from high-conductivity copper and was held in a casing fitted with a baffle system to facilitate efficient water cooling by directing the flow of water around the inside of the anode nozzle. The outside of the anode block was wound with a thin copper wire coil through which d.c. current was passed to create the magnetic field for spinning the arc.

With argon as arc gas, the plasma jet proved to be stable over a wide range of operating conditions with electrothermal efficiencies between 42 and 62%, attaining high temperatures (up to 11 000 K) at relatively low specific enthalpies.

Hydrogen plasmas were stable only at total gas flow rates above 140 l/min. Efficiencies were in the range 75-87% and, although these plasmas operated at higher specific enthalpies, they attained much lower temperatures (up to 4 000 K).

Plasmas operating on argon-hydrogen mixtures were stable over a wide range of mixture compositions and operating conditions. The properties of these plasmas were intermediate between those of the other two.

The power supply was a transformer-rectifier unit capable of providing 185 or 320 V on open circuit and a maximum current of 350 A. Typical ranges of operating conditions for the various types of arc are given in Table 1.

4. EXPERIMENTAL

Coal, crushed to -200 mesh in a hammer mill, was fed into the carrier-gas stream by a screw feeder which was supplied from a continuously stirred hopper. The coal feed rate was monitored by a photo-electric cell, the output from which was displayed on a chart recorder. On emerging from the plasma head, the coal-plasma stream passed to a reaction chamber and the resulting pyrolysis products were then quenched in a water-cooled chamber. Gas samples were withdrawn by means of a water-cooled probe, filtered and collected in sample bottles prior to analysis by gas chromatography. Residual gas exited via an exhaust duct.

5. RESULTS AND DISCUSSION

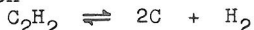
Four coals were used in the investigation; their analyses are presented in Table 2.

Consistent with previous findings, pyrolysis of coal in the plasma jet gave rise to yields of volatiles in excess of those obtained by the standard test. No liquid products or carbon dioxide were detected. When operating on argon, the major products were acetylene, hydrogen and carbon monoxide, with traces of methane and ethylene. With argon-hydrogen and hydrogen plasmas, the principal products were acetylene, methane, ethylene and carbon monoxide, with traces of ethane and hydrogen cyanide.

Preliminary experiments with total gas flow rates in the range 90-140 l/min revealed that maximum acetylene yields were obtained when employing an arc-gas composition of about 50:50 argon-hydrogen. At hydrogen concentrations greater than this, the yield of acetylene decreased markedly. However, the yields of methane and ethylene increased with increasing hydrogen content of the arc gas.

The pyrolyses were repeated at a lower total gas flow rate of 4.5 l/min using arc gases containing up to a maximum of 58% by volume of hydrogen. The highest acetylene yields were obtained with a 54:46 argon-hydrogen mixture at an optimum power input of about 15 kW. Again, the yields of methane and ethylene increased with increasing hydrogen content over the range of arc-gas compositions investigated (see Table 3).

The initial increase in acetylene yield with increasing hydrogen content of the arc gas can be attributed to several contributory factors. Firstly, the presence of hydrogen will inhibit the decomposition of the product acetylene by causing the equilibrium reaction



to move to the left. Secondly, any hydrogen present in the plasma as atoms or in an excited state can act as a chemical intermediate to enhance the acetylene yield by combining with any carbon-bearing radicals formed at the higher temperatures. Finally, confirmation that hydrogen from the arc gas had taken part in the plasma reactions was afforded by hydrogen balances which revealed that the product hydrocarbons contained more hydrogen than was present in the parent coal.

Decreases in the acetylene yield accompanying increases in the hydrogen content above a 50:50 mixture can be attributed to the fall in the mean bulk plasma temperature that is associated with increased hydrogen concentrations in the arc gas. Furthermore, lower temperatures favour methane formation and this is consistent with the higher methane yields that were obtained with plasmas operating on higher hydrogen contents. For instance, the methane yield was 3% for a 75:25

argon-hydrogen plasma compared with 65% by weight of coal carbon for a 100% hydrogen plasma. The total carbon converted to hydrocarbons also increased with increasing hydrogen content of the arc gas. Using argon, only 15.7% by weight of coal carbon appeared as hydrocarbons, whereas with a 100% hydrogen plasma conversions up to 87% were achieved.

Since the greatest yields of acetylene occurred at an arc-gas composition of 54:46 argon-hydrogen, this composition was employed in all subsequent experimental runs.

The total gas flow rate and mode of entry of the arc gas also affected the acetylene yield. With tangential entry of the arc gas, the acetylene yield decreased from 73% at 25 l/min to 60% by weight of coal carbon at 55 l/min. Although the highest acetylene yields were obtained at a total gas flow rate of 25 l/min, continued operation at this flow rate gave rise to noticeable electrode damage. Consequently, gas flow rates in all subsequent experiments were maintained between 40 and 45 l/min. Acetylene yields also increased with increasing ratio of tangential/axial arc gas.

The coal feed rate was varied over the range 0.045 to 0.270 g/min. Above 0.270 g/min, the plasma became unstable and led to marked non-reproducibility in the experimental measurements. At coal feed rates less than 0.045 g/min, the coal feeder malfunctioned, probably because at the low speeds of revolution involved the motor driving the screw could not develop sufficient torque. The results of these runs are presented in Fig. 2. It can be seen that coal feed rates in the range 0.045-0.270 g/min gave rise to acetylene yields between 55.5 and 67% by weight of coal carbon. The methane yields were between 22 and 9%.

To increase the residence time of the coal particles in the hot zone, extension sections, fabricated from alumina cement, were fitted below the anode nozzle. However, maximum yields of acetylene were obtained when the pyrolysis products were quenched immediately, i.e. when the quenching chamber was attached directly below the anode. A water-cooled sampling probe, capable of initial quenching rates of 1.4 MK/s, was used to aspirate the pyrolysis products from the quench chamber. The optimum probe position, equivalent to a residence time of about 1 ms, coincided with the maximum acetylene yield of 70.5% by weight of coal carbon. With longer residence times the acetylene yield was correspondingly lower. The effect of residence time on the yields of methane, ethylene and acetylene is depicted in Fig. 3.

Pyrolysis of the four coals listed in Table 2 under identical conditions revealed that there was no correlation between acetylene yield and volatile matter content. Highest yields of acetylene were obtained with the Barnborough coal, even though its volatile matter content differed little from those

of the Calverton and Peckfield coals. Moreover, the Ferrymoor coal, containing the highest volatile matter of 39.8% by weight (d.a.f.), produced an acetylene yield of only 59.9% by weight of coal carbon. Thus it would appear that the aromatic components of coal also play an important role in the formation of acetylene during coal pyrolysis in hydrogen-enriched atmospheres. This is in direct contrast to coal pyrolysis in inert atmospheres when it is presumed that the aliphatic components of coal provide the necessary hydrogen and, consequently, the yield of acetylene is proportional to the coal volatile matter content (13).

The solid char remaining after pyrolysis was collected and examined under a Stereoscan electron microscope. Extensive size reduction had occurred and pores had developed which were attributed to diffusion to the particle surface of the volatiles released during pyrolysis. Further size analysis using a Coulter counter indicated that the residual char was about half the size of the parent coal. Examination of the soot that was deposited in the quench chamber showed that 94% by weight of it was less than 7 microns in size.

The results of the pyrolysis experiments revealed that when the acetylene yield was maximized, that of the methane was minimized. The converse was also true. Methane is considered to be an important precursor to acetylene (18). To obtain information on the possible mechanism of acetylene formation from coal, methane was pyrolyzed in a 54:46 argon-hydrogen plasma under conditions similar to those used for coal. Gas samples aspirated from the quench chamber showed that conversion of methane to acetylene attained a maximum of 53% by volume; the conversion decreased with increasing residence time. The effect is shown in Fig. 4. A methane route to acetylene does not satisfactorily explain the much higher yields obtained from coal, but the similarity between Figs. 3 and 4 would seem to suggest that methane is important in the formation of acetylene from coal.

The decomposition of acetylene was investigated by injecting metered quantities into the plasma. Approximately 60% by volume of the acetylene was decomposed in the argon plasma compared with only 25% in the 54:46 argon-hydrogen plasma. In the former case, a hydrogen balance revealed that the acetylene had decomposed mainly into carbon and hydrogen. In the latter, the acetylene was converted principally to methane, ethane and ethylene. As anticipated, it would appear that hydrogen in the plasma retards the decomposition of the product acetylene.

In conclusion, it may be said that acetylene and/or methane can be produced directly in considerable quantities by pyrolyzing coal in hydrogen-enriched plasmas. Unfortunately, the specific energy requirement (kWh/kg product) is at least two orders of magnitude too high for the process to be

commercially viable. This is because the coal throughput is too low. Thus work in hand at Sheffield is concerned with increasing the coal throughput whilst maintaining the same degree of conversion.

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Plasma Gas	Gas Flow (l/min)	Voltage (V)	Power Input (kW)	Mean Bulk Temperature (K)
Argon	40-100	20-25	3-10	1000-11 000
Argon-hydrogen Mixtures	40-100	80-105	15-30	3600-5800
Hydrogen	140-200	160-175	30-50	3200-4000

TABLE 1. OPERATING CONDITIONS FOR THE PLASMA JETS.

Sample No.	NCB Code No.	Colliery and Seam	Ultimate Analysis (d.a.f. basis) % by weight					V.M. (d.a.f.) % by weight
			C	H	S	N	O	
1.	901	Calverton High Main Seam	79.1	5.83	1.14	1.38	12.60	36.5
2.	702	Barnborough Newhill Seam	81.2	5.85	1.81	1.43	9.71	37.7
3.	902	Ferrymoor Shafton Seam	82.7	6.20	2.11	1.74	7.25	39.8
4.	801	Peckfield Beeston Seam	81.5	5.40	2.89	1.34	8.89	35.6

TABLE 2. ANALYSES OF THE COAL SAMPLES.

A/H ₂ Ratio in Arc Gas (v/v)	Coal No.	Power Input (kW)	Coal Feed Rate (g/min)	Coal Carbon Converted to Products (% by weight)					Hydrogen Recovery (vol. %)
				CH ₄	C ₂ H ₆	C ₂ H ₄	C ₂ H ₂	CO	
100:0	2	4.35	0.22	0.42	-	0.20	17.5	10.9	78.7
	2	5.10	0.28	0.17	-	0.06	24.1	6.4	80.9
	2	6.75	0.31	0.07	-	0.04	27.4	5.5	87.4
	2	8.10	0.31	0.07	-	0.04	25.6	5.3	85.7
90:10	2	7.80	0.24	2.2	-	3.7	48.5		
	2	9.80	0.23	2.3	-	4.2	52.2		
	2	11.90	0.24	2.2	Nil*	3.6	43.6		
	2	14.10	0.20	2.8	"	4.6	37.2		
	2	15.60	0.20	2.6	"	2.9	32.0		
82:18	2	8.40	0.23	4.6	0.14	7.8	64.7		
	2	11.00	0.24	4.7	0.13	7.0	60.0		
	2	12.80	0.23	4.9	0.18	6.5	50.4		
	2	15.00	0.23	4.6	0.18	5.4	35.0		
	2	16.30	0.23	4.5	0.14	5.1	32.9		
70:30	2	9.75	0.22	7.4	0.39	10.7	62.0		
	2	12.00	0.22	7.1	0.37	11.0	62.6		
	2	14.30	0.21	7.4	0.35	10.0	59.1		
	2	16.50	0.20	7.8	0.30	9.6	51.3		
	2	17.10	0.22	7.7	0.48	9.4	49.0		
62:38	2	9.60	0.24	7.8	0.31	11.9	64.6		
	2	11.60	0.24	8.6	0.49	12.1	68.0		
	2	13.50	0.24	8.8	0.57	13.1	65.9		
	2	15.60	0.24	9.1	0.52	11.9	56.8		
54:46	2	11.00	0.24	11.0	0.85	12.9	64.6		
	2	12.80	0.23	11.5	0.86	14.8	64.7		
	2	14.90	0.25	10.0	0.84	11.2	68.8		
	2	15.30	0.24	10.8	0.67	11.6	56.9		
	2	16.90	0.24	11.3	0.75	11.8	60.8		
42:58	2	11.90	0.24	13.2	0.96	12.8	59.5		
	2	14.80	0.24	12.2	0.85	11.1	60.0		
	2	17.50	0.24	13.5	0.96	12.4	59.6		
	2	19.50	0.22	14.2	0.85	10.6	56.4		
	2	20.50	0.22	13.6	0.81	9.9	57.8		

Nil* < 0.1% by weight of coal carbon.

TABLE 3. EFFECT OF ATMOSPHERE ON THE COMPOSITION OF THE PYROLYSIS PRODUCTS.

KEY:

1. Coal-carrier gas
2. Cathode connection
3. Cooling water inlet
4. Cooling water outlet
5. Cooling water system
6. Perspex cathode holder
7. Cathode
8. Axial arc gas
9. Tangential arc gas
10. Magnetic coil
11. Anode section
12. Anode body
13. Water baffle
14. Tufnol spacer
15. Syndanyo shield

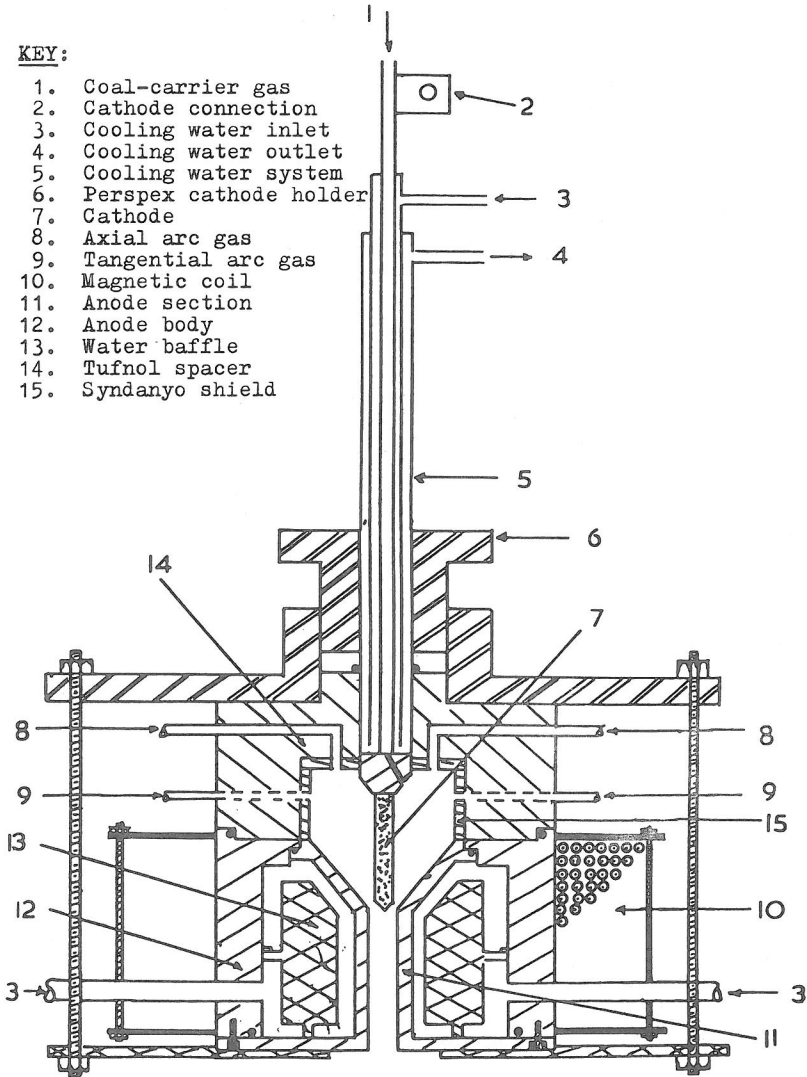


FIGURE 1. THE PLASMA JET

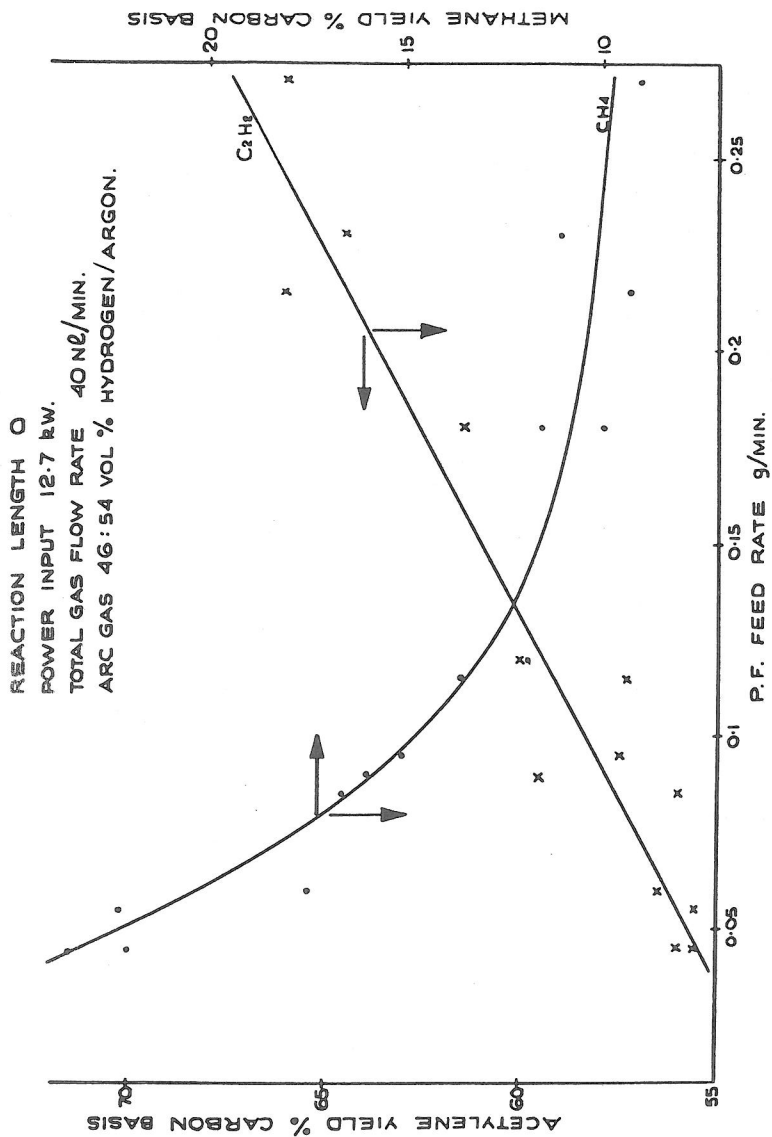


FIGURE 2. EFFECT OF COAL FEED RATE

TOTAL GAS FLOW RATE 40 NL/min
 COAL FEED RATE 0.15 g/min
 REACTION ZONE LENGTH 0
 POWER INPUT 15.2 kW
 ARC GAS 54:46 ARGON:HYDROGEN (v/v)

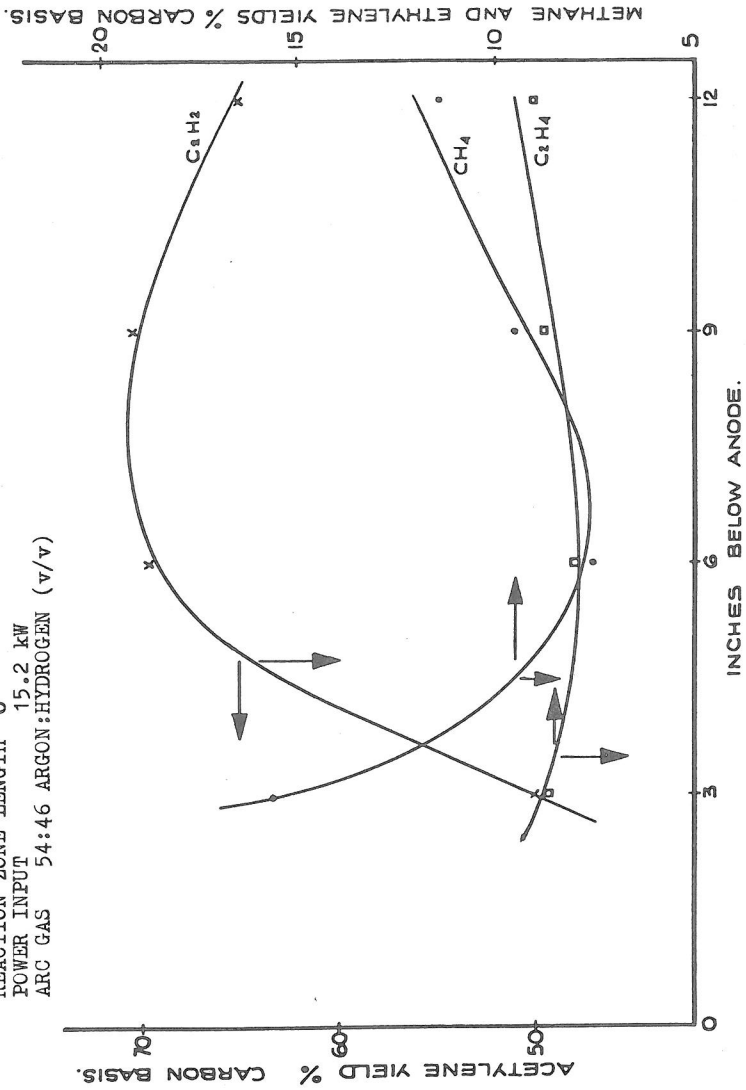


FIGURE 3. EFFECT OF PROBE POSITION ON YIELDS OF HYDROCARBONS

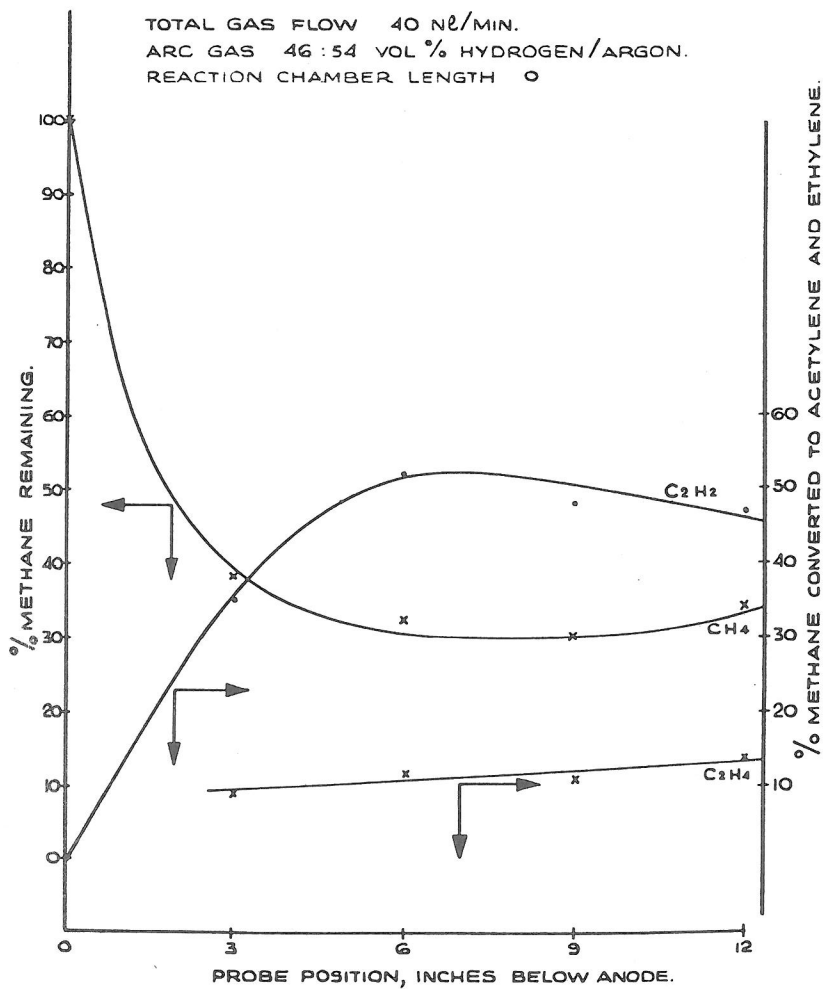


FIGURE 4. METHANE PYROLYSIS IN THE ARGON-HYDROGEN PLASMA JET