DEUTERIUM LABELING OF PRODUCTS FORMED DURING PLASMA PYROLYSIS OF COAL

R. E. Gannon and V. J. Krukonis

AVCO Corporation S/D
Lowell Industrial Park
Lowell, Massachusetts 01851

INTRODUCTION

Studies have shown that rapid high temperature pyrolysis of coal produces gaseous products with acetylene as the predominant hydrocarbon species. (1-12) This is consistent with thermodynamic data (13,14) which indicate that at reaction temperatures of 1500 to 2000°C acetylene is the most stable of hydrocarbon species. The thermodynamic data also show that the stability of acetylene decreases below 1200°C; consequently, in a pyrolytic process for the production of acetylene two distinct steps must be considered, viz., a high temperature generation step and a quench step to inhibit acetylene decomposition.

During the Avco Arc Coal Program, sponsored by the Office of Coal Research, a program whose goal is the development of a commercially feasible plasma process for the conversion of coal to acetylene, it was observed that acetylene yields are greater when plasma pyrolysis is carried out in a hydrogen atmosphere rather than in other environments, e.g., helium, argon, or nitrogen. A comparison of acetylene yields for coal pyrolysis carried out in hydrogen and in argon is shown in Figure 1. The data show that yields in hydrogen are about twice those obtained in argon. Other experiments showed that helium and nitrogen were no more effective than argon.

The improved acetylene yields in hydrogen can undoubtedly be related to the two reaction paths by which acetylene is generated from coal. The first involves the reaction of hydrogen contained in the coal and the second utilizes an external source of hydrogen. The reactions are illustrated by the following equations:

$$\text{Coal } (CH)_n \longrightarrow C_2H_2 \qquad (1)$$

$$C + H_2 \longrightarrow C_2H_2 \qquad (2)$$

The reaction described by equation (1) has been reported by several authors (5-9) and is illustrated by the data given in Figure 1 for the formation of acetylene in argon which shows the carbon and hydrogen in coal can react to form acetylene. The second reaction has been verified by injecting hydrogen-free char into a hydrogen plasma to form acetylene, (9), and also by reacting carbon and hydrogen at high temperature (16). The pyrolysis of coal in a hydrogen plasma, therefore, allows both reactions to contribute to the formation of acetylene, whereas, pyrolysis in an argon or helium plasma allows only reaction (1) to occur.

During the investigation of the quench step of the process, it became evident that hydrogen is also a more effective quench medium than is argon or helium. The quench reaction is complicated by the uncertainties in the acetylene generation reaction but uncertainties can be avoided, however, by separating the acetylene generation from acetylene quenching. For the investigation of the quenching reactions, known amounts of acetylene were used to model the generation step and reaction and decomposition during quenching were studied separately. The experiments were performed at a reduced pressure of 0.5 atmosphere, typical of the operating conditions of the AVCO Arc-Coal Process. Acetylene was metered into the arc plasma and inlet and exit gases were sampled and analyzed in order to measure the decomposition of the acetylene that occurred during

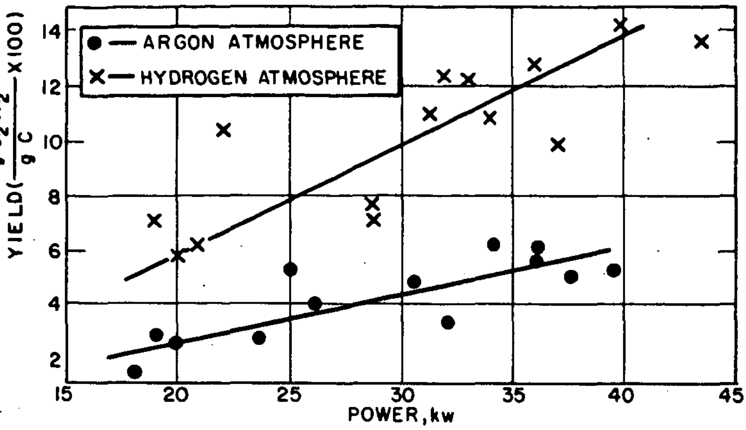

Figure 1 EFFECT OF ATMOSPHERE ON ACETYLENE YIELD

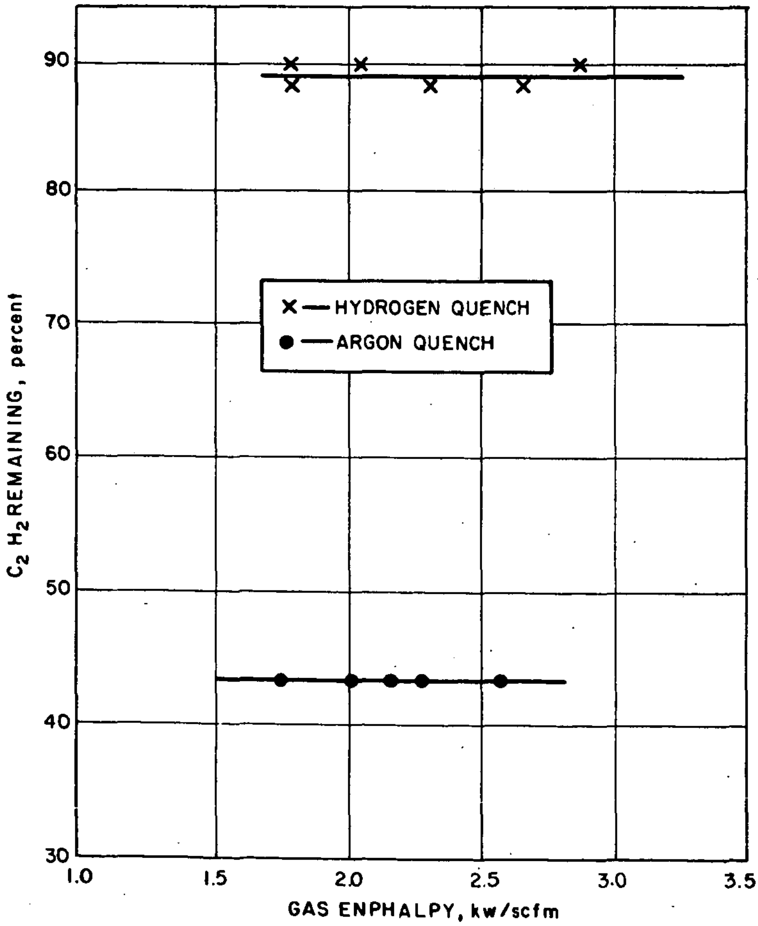

Figure 2 DECOMPOSITION OF ACETYLENE IN PLASMA PIPE REACTOR

the quenching process. The results, given in Figure 2, show that in hydrogen only about 12% of the acetylene is lost, whereas, in argon, decomposition was about 57%. Thus, at similar plasma enthalpy levels, the gross results show that hydrogen is a more effective quench medium.

Two reasons for the improved results with the hydrogen quench can be postulated, viz.,

a. Hydrogen is a more effective coolant and rapidly lowers the temperature of the reaction mixture preventing excessive decomposition of acetylene.

b. Hydrogen acts as a primary chemical reactant.

Using deuterium as "tagged" hydrogen atoms, a series of experiments was performed to elucidate the mechanism and to obtain a better understanding of the role of the hydrogen quench. For example, even though the data in Figure 2 showed that only 12% C_2H_2 decomposed in H_2, it could not be determined whether the molecules analyzed in the effluent were the same molecules that were injected into the plasma. Deuterium was injected into the plasma with acetylene and the exit gases were analyzed mass spectrometrically to determine if any exchange occurred between acetylene and deuterium. If the role of the quench medium were strictly to prevent decomposition of C_2H_2 molecules (as inferred by postulate a) there should be no exchange of the deuterium with acetylene and the product stream should be mainly C_2H_2, H_2, D_2 (and perhaps HD). If, on the other hand, postulate b, involving a chemical reaction, represents the role of the quench hydrogen (deuterium), then significant amounts of C_2HD and/or C_2D_2 should be identifiable in the product stream.

RESULTS AND DISCUSSION

Initial deuterium plasma reactions were designed to study the acetylene decomposition mechanism. A reactor, consisting of a 30 Kw, high temperature plasma generator, as shown in Figure 3, was used for the study. The generator could be operated on either hydrogen or deuterium and acetylene was injected directly into the plasma using either a hydrogen or deuterium carrier gas.

For the initial tests of the series, the plasma generator was operated at a reduced pressure of 0.5 atmosphere using deuterium as both the arc gas and as the carrier gas to convey given amounts of acetylene into the plasma. Gas flows were selected to give a mixture with an acetylene concentration typical of the product stream of the acetylene-coal reaction. Chromatographic analysis of the streams showed that the original mixture contained 7.1% acetylene which is representative of the 7 - 10% concentrations obtained during coal pyrolysis tests. Analysis of the effluent showed that 6.2% C_2H_2 was present. The 13% loss of acetylene due to the decomposition in the deuterium plasma is consistent with previous data given in Figure 2 which shows about 12% decomposition for acetylene in the hydrogen plasma.

Mass spectrometric analysis of the product stream showed that only 1.0% of the acetylene present in the effluent (0.05% of the gas mixture) was not deuterated. Acetylene composition data are given in Table I and show that the acetylene does not remain molecular in the plasma, thus eliminating from further consideration Postulate a which states that the hydrogen quench acts to "preserve" C_2H_2 molecules formed from coal by rapidly cooling the product stream. The data in Table I are also consistent with the data in Figure 2 which show for the range of power levels investigated that decomposition is relatively insensitive to gas enthalpy.

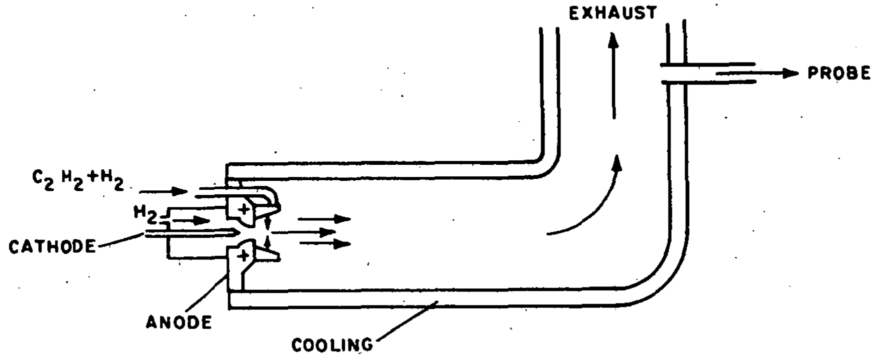

Figure 3 TUBE REACTOR

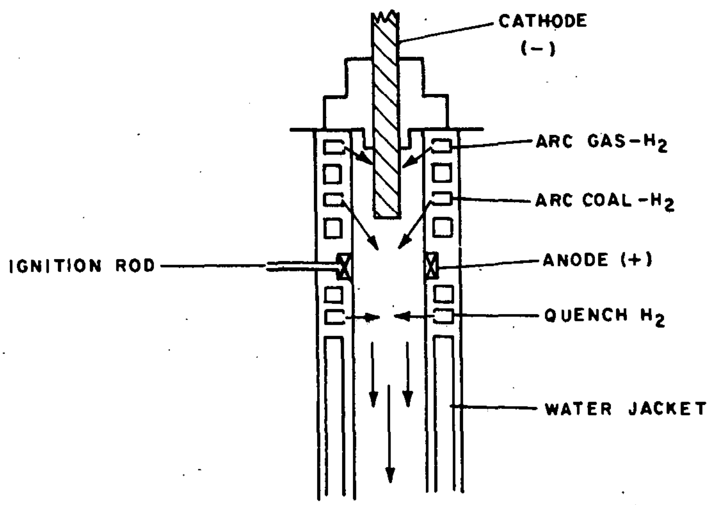

Figure 4 ROTATING ARC REACTOR

TABLE I

Measured Isotopic Composition of C_2H_2 in Deuterium Plasma

(D_2 - Arc Gas, D_2 - Quench Gas)

Isotopic Species	Measured Composition 11.4 Kw	19.8 Kw
C_2H_2	1.1%	1.0%
C_2HD	15.1%	15.7%
C_2D_2	83.5%	83.2%

Based on the observed results of the initial experiments, that is, 1) that essentially all the original C_2H_2 exchanges with the deuterium and, 2) that about 87% of the deuterated product is identified as acetylene, it is evident that the description of the reactions of acetylene with hydrogen in the plasma (Postulate b) must allow for the high temperature decomposition of acetylene followed by its interconversion during the rapid cooling. A more complete description of the mechanism requires a better definition of the species present in the plasma.

Previous workers, Steacie (15), Plooster and Reed (16), and Borisova and Ermin (17), have considered the formation and decomposition of acetylene and its intermediate species under different test conditions but all came to a similar conclusion, viz., the most likely intermediate species at high temperature or other energetic conditions would be the C_2H radical. Their conclusions were generally based on considerations of minimum energy requirements. In the decomposition of acetylene, five simple carbonaceous species are possible: C, CH, CH_2, C_2 , and C_2H. In order to form C, CH or CH_2, the rupture of the triple acetylenic bond, requiring approximately 240 kcal, is necessary. The formation of C_2 requires the rupture of two C-H bonds, 150 kcal, whereas the formation of C_2H requires the rupture of a single C-H bond, about 100 kcal. Other workers, Baddour and Iwasyk (18) and Baddour and Blanchet (19), studying the carbon-hydrogen reactions at plasma temperatures have also shown by calculation that C_2H should be the prevalent species at temperatures between 2000 and 3000° K. Although the decomposition of acetylene via a C_2H intermediate followed by re-combination with an H atom to re-form acetylene appears to be most likely from least energy considerations, the C_2H radical has not been isolated or experimentally identified by any of the previous workers. On the other hand, traces of the C_2 radical which requires an additional 50 kcal for its formation has been identified by Steacie (15) and by Borisova and Ermin (17),

The C_2H route has achieved among workers in plasma pyrolysis of hydrocarbons a foremost position to describe and explain yields of acetylene greater than those predicted by equilibrium calculations. The following reaction can be written to describe the C_2H route in the deuterium plasma experiments.

$$C_2H_2 + xsD_2 \xrightarrow{\text{plasma}} C_2H + H + xsD \xrightarrow{\text{cooling}} C_2HD + HD + xsD_2 \qquad (3)$$

If equation (3) were a valid description of the reaction of acetylene in an arc plasma, then C_2HD should be the predominant acetylenic species present in the product stream.

The experiments were carried out using 4.95 SCFM of D_2 and 0.38 SCFM or C_2H_2. Based upon statistical probability, the acetylene in the product stream should consist of 3.7% C_2H_2 and 96.1% C_2HD. The measured composition of 1.0% C_2H_2, 15.7% C_2HD, and

83.2% C_2D_2 shown in Table I was not consistent with equation (3) probability and it must be concluded that the mechanisms as written for postulate b, is not valid. It is also evident, because of the large amount of fully deuterated acetylene 83%, that any mechanism that postulates a C_2H radical as an incontravertable entity throughout the lifetime of species in the plasma is not substantiate.

Because the C_2 radical has been identified in some of the high temperature mixtures (15, 17), the contribution of this species should be considered as an intermediate. The following reaction describes such a mechanism:

$$C_2H_2 + xsD_2 \xrightarrow[\text{plasma}]{} C_2 + 2H + xsD_2 \xrightarrow[\text{cooling}]{} C_2D_2 + C_2DH + C_2H_2 + D_2 + HD + H_2 \qquad (4)$$

Again, using the laws of statistical probability, it can be shown that for an original mixture of 4.95 SCFM D_2 and 0.38 SCFM C_2H_2 a product stream of 86% C_2D_2, 13.2% C_2DH, and 0.5% C_2H_2 can be predicted, based on the reaction (4). The predicted composition is in excellent agreement with the measured composition given in Table I, and consequently indicates that the postulated C_2 mechanism is an adequate model for predicting the product mix for the decomposition and reformation of acetylene in a plasma. In reconciling these results with the C_2H mechanism suggested by the previous authors (15, 16, 17), it must be recognized that, although the data precludes the existence of a C_2H entity that retains its identity throughout the decomposition and re-formation of acetylene, it does not preclude the existance of a C_2H radical that is able to experience multiple exchanges as indicated by Reaction (5), viz.,

$$C_2H + D_2 \longrightarrow C_2DH \xrightarrow{+D_2} C_2D_2 \qquad (5)$$

Table II summarizes the experimental results given in Table I and compares the data to those calculated on the basis of a mechanism that assumes: 1) a stable C_2H_2 molecule, i.e., the C_2H_2 mechanism, 2) a C_2H intermediate, and 3) a C_2 intermediate species. The excellent agreement between the experimental results and those predicted by the C_2 mechanism are obvious.

TABLE II

Isotopic Composition of Acetylene in Deuterium Plasma

(D_2 - Arc Gas, D_2 - Quench Gas)

Species	Measured Composition		Predicted Composition		
	14.4 kw	20.6 kw	C_2H_2 mech.	C_2H mech.	C_2 mech.
C_2H_2	1.1	1.0	100%	3.7%	0.5
C_2HD	15.1	15.7	---	96.3%	13.2
C_2D_2	83.5	83.2	---	----	86.0

The C_2 mechanism and the associated statistics were applied to subsequent tests in an effort to understand the roles of the various gas streams and their interactions with the coal feed. To distinguish between the roles of the arc gas and the quench stream, deuterium was used as the arc gas and hydrogen was used as the quench gas. The results of these tests are shown in Table III. An additional column, (the measured value minus the predicted value) has been added to indicate discrepancies from the predictions based on purely random selectivity (and equal reactivity) of the separate streams.

TABLE III

Isotopic Composition of Acetylene

(D_2 - Arc Gas, H_2 - Quench Gas)

Species	Measured Composition		Predicted Composition	Measured -Predicted	
	14.1 kw	20.5 kw		14.1 kw	20.5 kw
C_2H_2	21.4%	18.5%	29.2%	-7.8%	-10.7
C_2HD	47.5	46.5	49.6	-2.1	-3.1
C_2D_2	31.0	35.0	21.2	+9.8	+13.8

The data indicate that the exchange is not purely statistical but instead that the acetylene exchanges with the higher enthalpy deuterium which has passed through the arc. The preference is obvious since the arc gas is hotter and more ionized than is the quench. If the explanation is valid, it should be possible to verify the preference of acetylene to exchange with gas which has passed through the arc by reversing the gas streams and using hydrogen as the arc gas and deuterium as the quench. Results of such tests are given in Table IV.

TABLE IV

Isotopic Composition of Acetylene

(H_2 - Arc Gas, D_2 - Quench Gas)

Species	Measured Composition		Predicted Composition	Measured -Predicted	
	15.7 kw	21 kw		15.7 kw	21 kw
C_2H_2	38.0	40.7	30.2	+7.8	+10.5
C_2HD	45.7	45.6	49.6	-3.9	-4.0
C_2D_2	16.0	13.7	20.2	-4.2	-6.5

Again, consistent with the previous tests, it is seen that the arc gas is more reactive than the carrier gas, and it is also consistent that in each test the arc gas appears to be more reactive at higher power levels.

In order to investigate the combined or simultaneous reactions of acetylene generation and quench reactions during coal pyrolysis, deuterium was used as a carrier gas to conduct coal into a deuterium plasma. Although deuterium was the only gas introduced into the reactor, it was necessary to consider the amount of hydrogen which was liberated from the coal in applying the statistical analysis. With a Pittsburgh Seam Coal with a 5% hydrogen content and 160 g/min feed, a maximum of 3.24 SCFM of H_2 was introduced into the arc reactor. The measured distribution of the deuterated acetylenic species at several power levels is given in Table V and the data are compared with the predicted distribution based on C_2 statistics.

TABLE V

Isotopic Composition of Acetylene Generated During Coal Pyrolysis

(D_2 - Arc Gas, D_2 - Quench Gas, 0.5 Atm)

Species	Measured Composition 10.8 kw	13.6 kw	16.0 kw	Predicted Composition (100% Utilization of H_2 in Coal
C_2H_2	3.6%	3.8%	5.1%	10.8%
C_2HD	25.0	27.5	31.6	44.2
C_2D_2	71.3	68.8	63.2	45.0

The discrepancy between the measured and predicted values is probably caused by the assumption in the calculations that 100% of the hydrogen in the coal is liberated for acetylene generation. Chemical analyses have shown that appreciable amounts of hydrogen still remain in the char. Recalculating the predicted distribution based on a fractional availability of hydrogen from the coal results in more quantitative agreement with the measured values as shown in Table VI.

TABLE VI

Comparison of Measured and Predicted Isotopic Distribution of Acetylene Generated During Coal Pyrolysis

(D_2 - Arc Gas, D_2 - Quench Gas, 0.5 Atm.)

Species	Measured Composition			Calculated Dist. Based on Available H_2				
	10.8 kw	13.6 kw	16.kw	30% H_2	35%	40%	45%	50%
C_2H_2	3.6	3.8	5.1	1.6	2.2	2.7	3.4	4.0
C_2HD	25.0	27.5	31.6	22.6	25.4	27.6	30.0	32.0
C_2D_2	71.3	68.8	63.2	75.6	72.8	69.7	66.5	64.0

By comparing the measured distribution with the calculated values, it appears that at 10.8 kw about 35% of the hydrogen in the coal is available for acetylene formation, at 13.6 kw the value increases to about 40%, and at 16 kw it increases to 50% level.

The role of the quench medium in the prototype reactor for the AVCO Arc-Coal Process was then investigated. The prototype reactor, shown in Figure 4, basically consists of a solid cylindrical graphite cathode, 5/8" in diameter and an annular graphite anode with a $1\frac{1}{2}$" I.D. Pulverized coal is injected directly into the plasma as shown in the figure and quenching is accomplished by injecting hydrogen about $\frac{1}{2}$" below the anode. The arc operates at power levels between 80 and 120 kw. Magnetic field coils around the anode induce a high speed rotation to the arc which increases the effectiveness of contact between the pulverized coal and the high temperature environment, and also serves to stabilize the arc.

In these tests the arc gas and coal-carrier gas was hydrogen but deuterium was used as the quench gas so that the role of the quench could be studied. The resulting distribution of the acetylenic species is given in Table VII as well as a calculated distribution based on test parameters, viz., 11.5 SCFM arc gas, 5.8 SCFM coal carrier gas, 3.24 SCFM of H_2 contained in the coal and 10.6 SCFM deuterium quench gas. The 3.24 SCFM of H_2 from the coal is based on 100% availability of the H_2 in the coal. This estimate is undoubtedly high and 60 to 70% is probably more realistic, but in this test in which 17.3 SCFM and H_2 were passed through the arc any small error in the amount of the H_2 liberated from the coal would have a negligible effect on the calculation.

TABLE VII

Coal Conversion to Acetylene in Prototype Reactor with Deuterium Quench

Species	Measured Distribution	Calculated Distribution	Measured - Calculated
C_2H_2	55%	43.5%	+11.5
C_2HD	38.8	44.8	- 6.0
C_2D_2	6.6	11.6	- 5.0

This experiment was similar to a previous experiment (Table V) in that hydrogen was used as the arc gas and deuterium was added downstream. The differences between the measured and calculated values again indicate the higher reactivity of the arc gas. Nonetheless, it is to be noted that the quench gas was identified in 45% of the acetylene product. If the quench gas had been argon or other relatively inert gas, no viable compound would have been formed in these reactions and the high temperature acetylene species,,C_2 and C_2H, would have decayed to carbon. Similarly, consecutive exchange reactions could not occur with inert gas present.

CONCLUSIONS

Conclusions about the decomposition of acetylene in a hydrogen atmosphere that can be drawn from the series of deuterium plasma reactions can be summarized as follows:

1. Reaction mechanisms which require undisassociated C_2H_2 or a C_2H entity cannot be substantiated.

2. Calculations which utilize a route involving a C_2 intermediate can be used to predict the product distribution.

3. At low gas enthalpy levels, only a small percentage of the hydrogen in the coal takes part in acetylene formation. As power is increased, more hydrogen is liberated from the coal for acetylene formation.

4. Although the results show that the arc gas is more reactive than the quench gas, they also show that the quench reacts chemically in preserving acetylene. For this reason, the use of a hydrogen quench is important in obtaining high acetylene yields.

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