

# DEUTERIUM AND CARBON-13 TAGGING STUDIES OF THE PLASMA PYROLYSIS OF COAL

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## INTRODUCTION

High temperature arc or plasma pyrolysis of coal produces acetylene as the principal hydrocarbon product<sup>1-6</sup>. Furthermore, yields of acetylene in a hydrogen atmosphere are enhanced a factor of three over those achieved in an argon atmosphere. Consistent with the experimental results, thermodynamic data show that acetylene is the only stable hydrocarbon molecule above 1500°C, and below about 1200°C its thermodynamic stability decreases rapidly<sup>7,8,9</sup>; experimental evidence also supports that high temperature acetylene-containing hydrocarbon streams must be quenched rapidly in order to prevent decomposition to carbon black<sup>10</sup>.

During the duration of a program to convert coal to acetylene carried out at Avco/Systems Divisions Laboratories, a number of high temperature arc reaction concepts were tested. The initial conversion scheme utilized coal as the consumable anode of a DC arc, and the process schematic is shown in Figure 1. The consumable anode pyrolysis of coal has been described in detail in Reference 5, but here, briefly, crushed coal, typically 10-20 mesh, is fed into an electrical discharge sustained between a graphite cathode and the coal at a feed rate consistent with the surface pyrolysis rate. The rapid heating occurring at the surface pyrolyzes the coal, and the hydrocarbon products formed are quenched downstream of the arc zone by injecting a gas in order to preserve the acetylene produced in the discharge region. The solid residue, consisting of char and any unreacted coal, spills over the sides of the anode feed tube.

A schematic diagram of the experimental reactor showing the coal feed tube, gas quenching ports, and the product sampling positions is given in Figure 2. The gas sampling tubes were located at sequential positions downstream of the arc zone in order to determine if any acetylene decomposition were occurring in the gas stream. Simultaneous sampling at all three positions shown in Figure 2 produced identical results (although probing of the high temperature arc zone with a small diameter, water-cooled tube produced higher acetylene concentrations indicating that some decomposition was occurring even before the gas reached the first sampling position; the yield and decomposition data that are reported subsequently were obtained from downstream sampling positions and, thus, are not confused with ultra-high quench rate ambiguities).

Hydrocarbon product analyses were carried out on an F&M 700 chromatograph using a Porapak Q column and a flame ionization detector. (Other gases such as CO, H<sub>2</sub>S, COS, CS<sub>2</sub>, etc., were determined on a F&M 720 thermal conductivity chromatographic unit data using argon and hydrogen as quench gases are given in Figure 3, and the data show that at all power levels studied the yield of acetylene is 2-3 times greater with hydrogen as the quench medium.

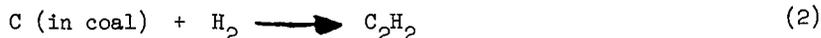
Pyrolysis of coal with consequent formation of acetylene in an inert plasma environment is evidence that the carbon and hydrogen present in the coal are reacting, i.e.,



although Equation (1) is obviously an oversimplification of acetylene formation, and no mechanism is implied.

Several explanations for the higher yields found with hydrogen can be proposed, viz.,

1. hydrogen generates additional acetylene from the carbon in coal via solid carbon-gaseous hydrogen reaction, a yield contribution which is absent in an inert atmosphere, i.e.,



2. hydrogen is a more effective coolant or preserver of acetylene than is argon because of mass transfer or thermal conductivity considerations,

or

3. hydrogen acts as some chemical reactant in the quenching step, preventing the decomposition of acetylene to carbon black.

The most obvious explanation for the improved acetylene yields found with a hydrogen quench is Postulate 1, viz., additional reactions occurring between carbon in the coal and the gaseous hydrogen environment, and this reaction contribution was subsequently tested by reacting char and hydrogen. Hydrogen-free char (collected from previous arc-coal tests) was reacted in the arc environment; however, acetylene yields were only minimal<sup>5</sup>, far below the levels required to explain the factor of three difference between the argon and hydrogen results shown in Figure 3.

Other experiments in the consumable anode, arc reactor showed that if no quench were used, acetylene yields were very small with substantial carbon black formation on the reactor walls, indication that decomposition of acetylene in the product stream was occurring, again in agreement with the thermodynamic data and other experimental evidence.

The coal pyrolysis scheme underwent a number of modifications in both reactor design and reaction philosophy during the course of the program. It was found, for example, that one of the most serious causes of acetylene decomposition (in either the argon or hydrogen case) was the contact between the incandescent surface char layer and the acetylene which was generated below the surface. Examination of large char particles showed that carbon black was present in the pores of the structure<sup>6</sup>. Feeding hydrogen up through the coal resulted in increased yields, up to about 18% (based on total coal), but, finally, certain materials erosion problems shifted emphasis from the consumable anode concept to a plasma reactor shown in Figure 4. The reactor description and operation have been covered fully in Reference 10, but here, again briefly, powdered coal, typically -100 mesh, is carried downward via hydrogen through a magnetically rotated arc region, at a velocity of a several hundred ft/sec. A few inches downstream the hydrocarbon stream is quenched (and several alternatives employing coal, or a hydrocarbon, or solely hydrogen were tested). Acetylene yields and electrical energy consumptions in this reactor approached economically viable levels; in the rotating arc reactor hydrogen still produced substantially higher acetylene yields than did an argon quench.

In order to separate the acetylene forming step from the acetylene preserving step in this coal pyrolysis scheme, and also in order to determine quantitatively the role of hydrogen in the process, tests were carried out in which acetylene was injected into a carbon-free plasma stream, experiments designed to simulate only the "quenching-preserving" step. In the quenching studies, as in the coal tests, the decomposition of acetylene in an argon plasma was again found to be much greater than in hydrogen. Figure 5 gives the results of acetylene decomposition experiments, which have been previously reported<sup>10</sup>, and shows that about 60% of the initial acetylene decomposes with an argon quench while with a hydrogen quench only about 10-12% of the acetylene decomposes.

As a result of the large differences in results with hydrogen and argon, other quench gases, viz., helium, nitrogen, and deuterium, were subsequently tested in an attempt to separate chemical effects from physical ones. For example, if gas diffusivity and thermal conductivity are important parameters in preserving acetylene as an intact species, acetylene decomposition in hydrogen, helium, and deuterium would be essentially the same because all three gases possess essentially identical mass and heat transport properties. If on the other hand, the heat capacity of the quench medium, i.e., its energy absorption and dissociation capability, were the important consideration, hydrogen, deuterium, and nitrogen would produce identical quenching results (ignoring for now nitrogen's somewhat higher stability relative to hydrogen). Finally, if chemical reactions between  $C_2H_2$  and  $H_2$  were in operation during the quenching step,  $H_2$  and  $D_2$  results would be identical. In addition to gas chromatography high resolution mass spectroscopy was carried out with the deuterium samples. The deuterium results, which have been reported previously<sup>11</sup>, showed that substantial H-D exchange was occurring in the acetylene molecule.

Finally as a means of determining reactions in operation during the acetylene quenching step, "heavy" acetylene,  $C_2^{13}H_2$ , and "normal" acetylene,  $C_2^{12}H_2$  were admixed and injected into the plasma quenching simulator so that carbon-carbon triple bond interaction at high temperature could be studied.

## RESULTS AND DISCUSSION

A series of experiments to separate the complex reactions of acetylene generation and acetylene preservation occurring during the arc pyrolysis of coal was carried out as an integral part of the coal pyrolysis studies in the rotating arc reactor. In order to study the quenching reaction, acetylene was injected into a high temperature plasma stream, free of coal and char particles. A plasma generator attached to a 2" copper, water-cooled tube as shown in Figure 6 was used for the quenching studies. Acetylene was injected into the plasma stream about 1/2" from the nozzle, and a gas sampling tube was located about 12" downstream of the plasma generator; again as in the previous reactors, the gas sampling probe was purposely located far downstream of the plasma and injection position in order to allow all decomposition reactions to occur, eliminating the probing ambiguities described earlier. The acetylene concentration in the plasma was about 7%, closely approximating the concentration obtained in the rotating arc reactor. The entire plasma system was connected to a very large capacity rotary vacuum pump so that tests at various total reaction pressures could be carried out.

Tests were made, then, to determine the effect of operating pressure on decomposition and to determine the effects of using different gas quenches on preserving acetylene. Both sets of results are given in Figure 7. Most extensive testing was carried out with hydrogen, and it is seen that decomposition is a function of total pressure, but reaches only about 30% at 1 atm. Figure 7 also shows that decomposition of acetylene in both hydrogen and deuterium is identical at the two pressures studied, and, furthermore, shows that the decomposition is low relative to the other gases used, helium, argon, and nitrogen. The data in Figure 7 bring out then that hydrogen (and chemically-similar deuterium) has some other effect in preserving acetylene, effects not explainable by merely the physical properties of thermal conductivity, diffusivity, or heat capacity.

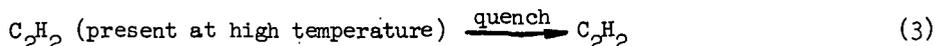
There was no way to determine chromatographically if the acetylene molecules sampled in the hydrogen quenched stream were the identical molecules injected into the plasma, and hence mass-spectrometric analysis of the deuterium gas samples was carried in order to determine if the composition consisted of  $C_2H_2$  or of some deuterated species (and although it would have been possible, no effort was given to chromatographic separation of deuterated acetylenes). The analyses of the deuterium samples showed that H-D interaction to form  $C_2HD$  and  $C_2D_2$  was occurring during the plasma quenching step. Table I gives the measured composition of acetylene in the product gas for the deuterium plasma-deuterium quench set of tests.

TABLE I  
ISOTOPIC ACETYLENE COMPOSITION

<u>Species</u>	<u>Composition</u> <u>(% of Undecomposed <math>C_2H_2</math>)</u>
$C_2H_2$	1.1%
$C_2HD$	15.1%
$C_2D_2$	83.5%

As Table I shows, 99% of the  $C_2H_2$  molecules have exchanged with  $D_2$  to form  $C_2HD$  and  $C_2D_2$ .

A number of workers in very high temperature acetylene formation-decomposition studies have invoked radical recombinations to explain the fact that acetylene compositions "greater than equilibrium" were achieved in their studies. Flooster and Reed<sup>12</sup> postulated that high temperature equilibrium favors two carbon species,  $C_2H_2$  and  $C_2H$ , and that during the quenching sequence two mechanisms contributed to the acetylene measured in the product, viz.,



Their model was based upon estimates of the thermodynamic properties, and their experimental results agreed well with the model of a  $C_2H$  radical. Other workers after Flooster and Reed, viz., Baddour and Iwasyk<sup>13</sup> and Baddour and Blanchet<sup>14</sup> also invoked the  $C_2H$  mechanism to explain their results of reacting hydrogen with carbon in a consumable anode arc reactor.

An equilibrium diagram for the carbon-hydrogen system is given in Figure 8 and shows that  $C_2H_2$  and  $C_2H$  are, in fact, the most prevalent carbon species at high temperature\*. Although calculated from free energy considerations to be present in relatively high concentrations, the  $C_2H$  radical, on the other hand, has not yet been experimentally verified to be present in any quantity. A quenching mechanism which both rapidly cools  $C_2H_2$  and requires a recombination of a non-interconvertible  $C_2H$  radical with H does not explain the presence of large amounts of  $C_2D_2$  in the product stream, i.e., if  $C_2H$  maintains its identity at high temperature, only  $C_2HD$  (along with the preserved<sup>11</sup>  $C_2H_2$ ) could be formed during the quenching step; however, the data in Table I show that 83% of the  $C_2H_2$  has exchanged to  $C_2D_2$ , and a random recombination of radical and atomic species was found to correlate the results.

Conservation of energy considerations, however, preclude the dissociation of all the species into atoms and/or radicals. For example, most of the tests in the plasma reactor were carried out at input power levels of about 15 kw; with a  $H_2$  (or  $D_2$ ) flow of 4.95 SCFM used in the tests, the average gas enthalpy was only about 40 kcal/gmol, much, much less than the 100 kcal/gmol required to dissociate even hydrogen alone (not including the dissociation of acetylene to  $C_2$  and H). In spite of the impossibility of dissociating all the molecules to  $C_2$ , H, and D species, however, there is presented in Table II the predicted statistical concentrations of H- and D-exchanged acetylenic molecules, based upon the recombination of such species, and it is seen that the agreement is very good.

TABLE II  
ISOTOPIC COMPOSITION OF ACETYLENE

<u>Species</u>	<u>Measured Composition</u>	<u>Predicted Composition</u> <u>(Based Upon Combination of <math>C_2</math>, H, &amp; D)</u>
$C_2H_2$	1.1	0.5
$C_2HD$	15.1	13.2
$C_2D_2$	83.5	86.0

\*Figure 8 was calculated for a C/H ratio of 1/4, i.e., for methane, using JANAF data<sup>9</sup>.

As a final study of the decomposition-recombination reactions of acetylene which could aid in the elucidation of the acetylene preservation mechanism in hydrogen, mixtures of carbon isotope acetylenes,  $C_2^{12}H_2$  and  $C_2^{13}H_2$ , were injected into a hydrogen plasma stream, and analysis of the gas product again was determined by high-resolution mass spectroscopy. If the carbon-carbon triple bond maintained its integrity, only  $C^{12}$  and  $C^{13}$  acetylene should be present in the product stream; if, on the other hand, the triple bond were entering into the decomposition-preservation reactions, an interaction to form  $C^{13}C^{12}H_2$  would be measured in the product.

For the  $C^{12}$ - $C^{13}$  experiments the plasma reactor was also operated at about 0.5 atm with approximately a 50/50 mixture of the isotope acetylenes injected into the plasma stream. Gas chromatographic and high resolution, mass spectroscopy analyses were carried out on the samples. Gas chromatograph showed again that only about 10% of the original acetylene disappeared to carbon black (and the decomposition result is shown as a solid dot in Figure 7). Mass spectrograms of both the initial and final product acetylene streams are given in Figure 9. Figure 9 shows that some  $C^{12}C^{13}H_2$  was present in the starting material (because the heavy acetylene could be obtained only as 90%  $C^{13}$  acetylene). A mass spectrogram of the final composition, obtained with the plasma generator operating at 15 kw, a power level identical to that of the deuterium tests, is also compared to the initial spectrogram in the figure, and a large increase in the  $C^{12}C^{13}H_2$  peak is evident.

Acetylene compositions are given in Table III.

TABLE III  
ISOTOPIC COMPOSITION OF ACETYLENE

<u>Species</u>	<u>Composition %</u>	
	<u>Initial Mixture</u> <u>(Power Off)</u>	<u>Final Mixture</u> <u>(Quenched)</u>
$C^{12}_2H_2$	47.6	30.6
$C^{12}C^{13}H_2$	11.9	48.5
$C^{13}_2H_2$	40.5	20.9

If 100% of  $C^{12}$  and  $C^{13}$  reacted, the calculated  $C^{12}C^{13}H_2$  concentration would be 49.6% as shown in Table IV; the measured concentration of 48.5% indicates, therefore, that a 97% exchange occurred based upon the statistical model; again, however, energy considerations (with the plasma stream possessing only a maximum of 40 kcal/gm) preclude such a simple model.

TABLE IV  
ISOTOPIC ACETYLENE COMPOSITION

<u>Species</u>	<u>Measured (%)</u>	<u>Calculated (%)</u>
C <sup>12</sup> <sub>2</sub> H <sub>2</sub>	30.6	29.2
C <sup>12</sup> C <sup>13</sup> H <sub>2</sub>	48.5	49.6
C <sup>13</sup> <sub>2</sub> H <sub>2</sub>	20.9	21.2

A mechanism based upon sequential collisions will be presented.

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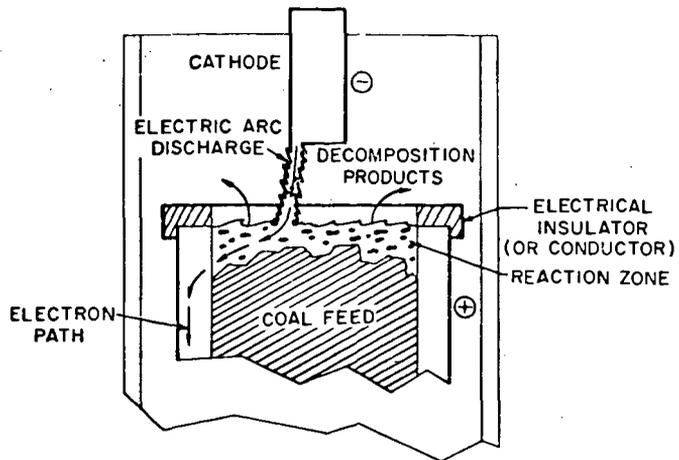
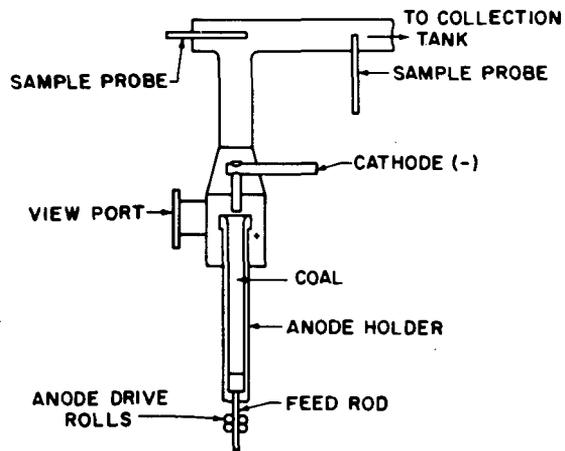


Figure 1 SCHEMATIC OF COAL CONVERSION ARC PROCESS



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Figure 2 ARC COAL REACTOR

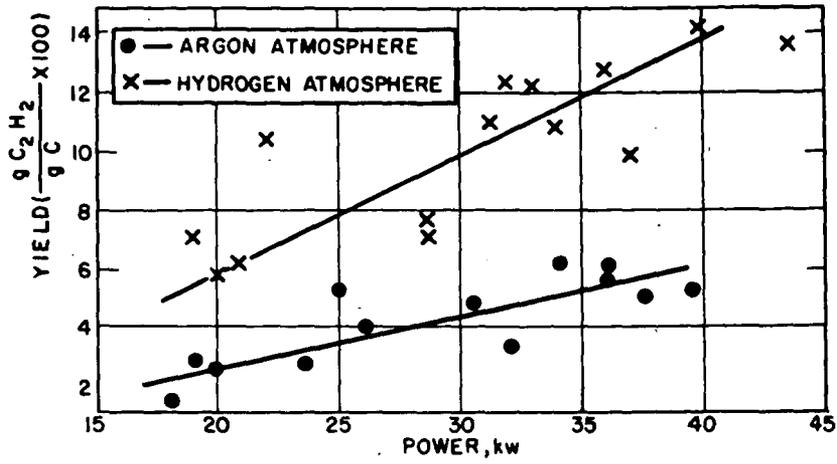


Figure 3 EFFECT OF ATMOSPHERE ON ACETYLENE YIELD

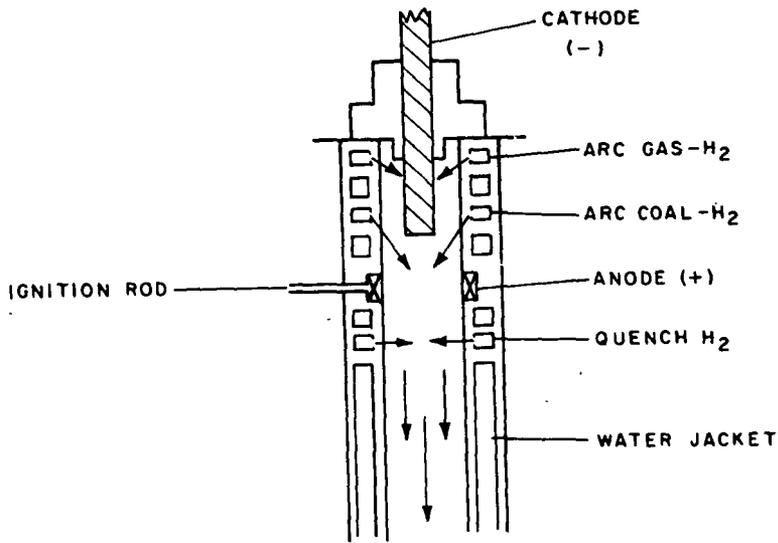


Figure 4 ROTATING ARC-REACTOR

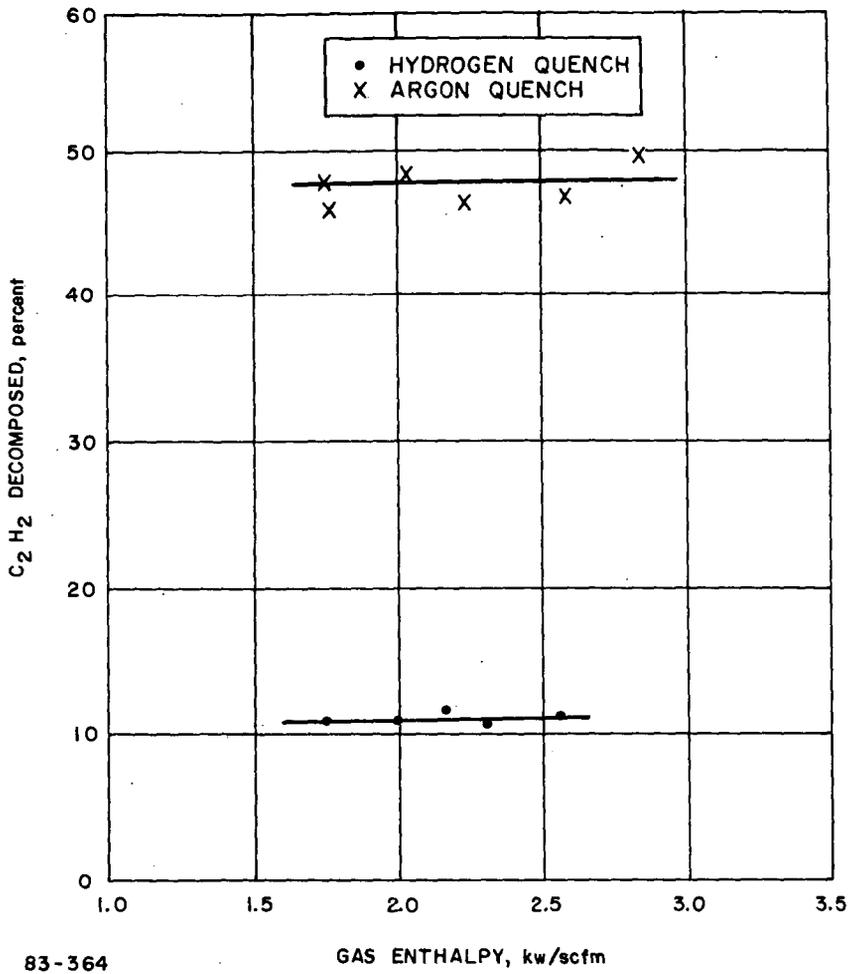


Figure 5 DECOMPOSITION OF ACETYLENE IN QUENCH SIMULATOR

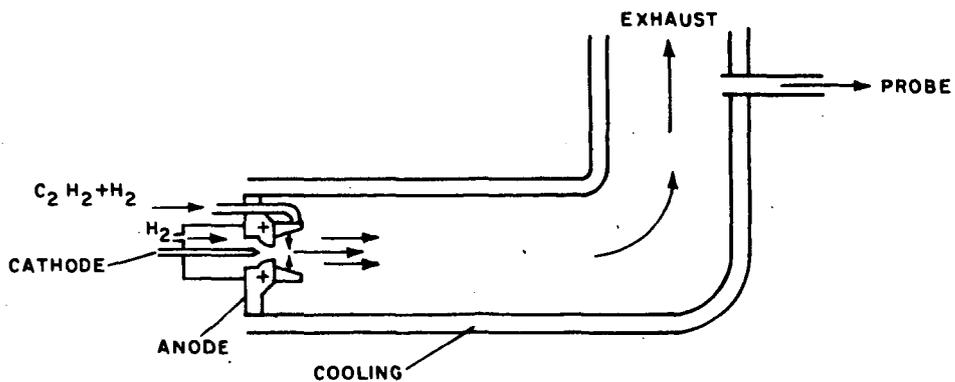


Figure 6 QUENCH SIMULATOR

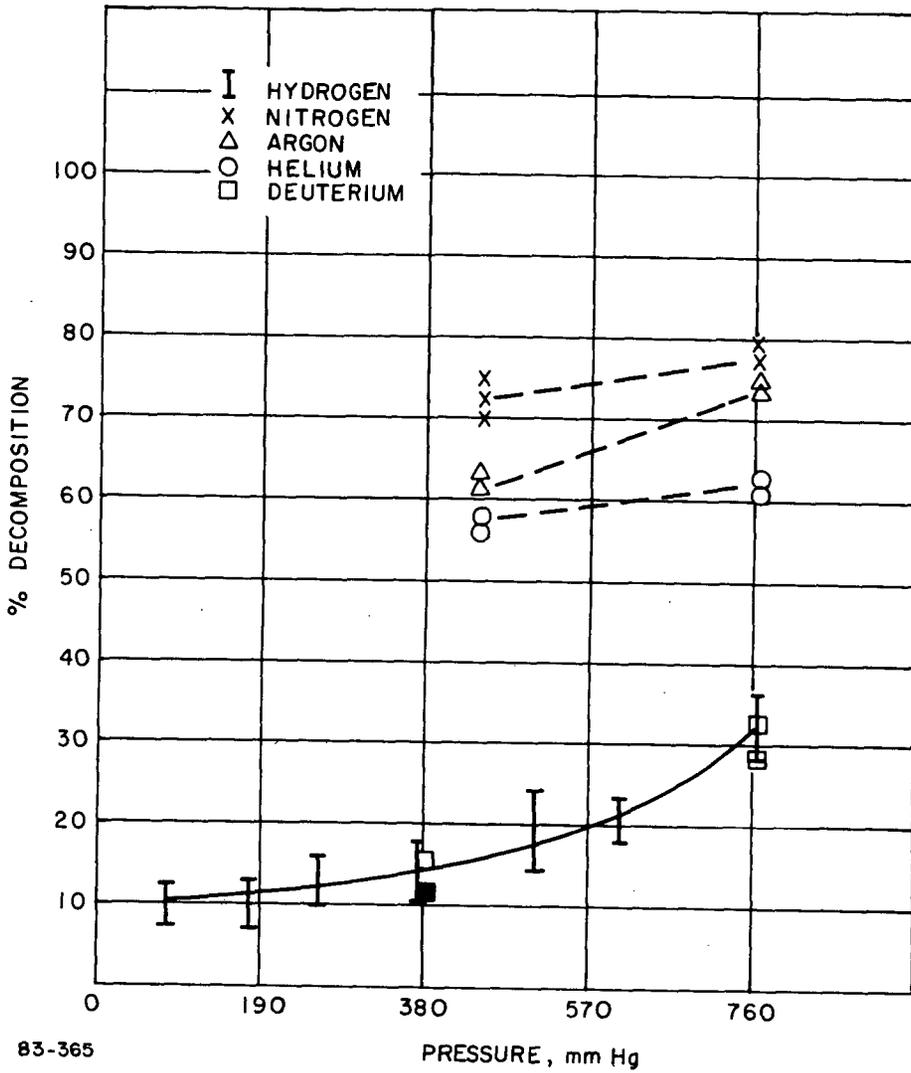
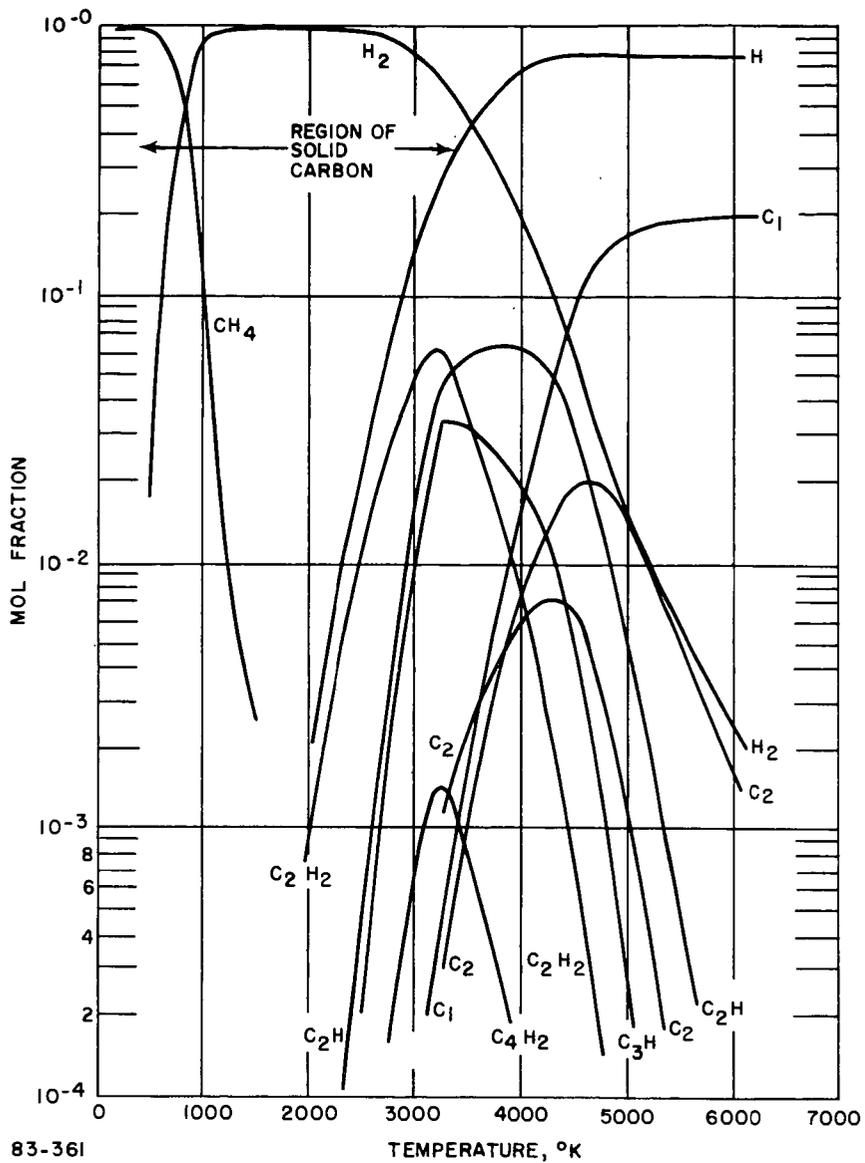
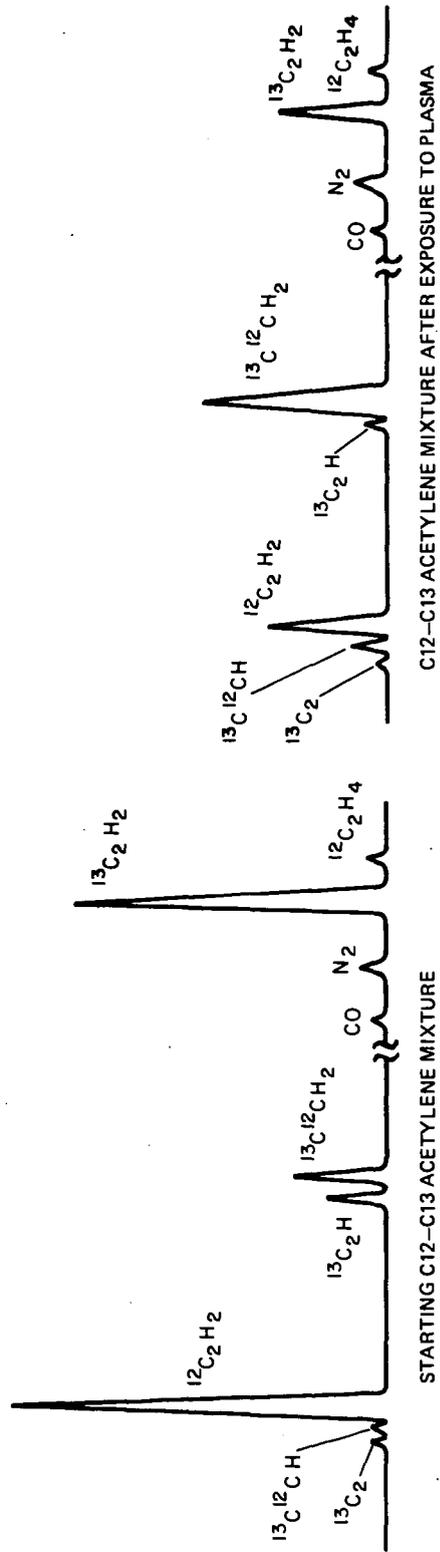


Figure 7 DECOMPOSITION OF ACETYLENE IN VARIOUS GASES





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Figure 9 MASS SPECTRA OF ACETYLENE MIXTURE