

Hydrogen Yield Results from Experimental Arc Pyrolysis of Methane

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Although hydrogen is an attractive fuel for a hypersonic airbreathing vehicle in terms of reaction rate, flame temperature, and energy content per unit mass, the substantial tank volume required to store hydrogen imposes a drag penalty to performance that tends to offset these advantages. An alternative approach is to carry a hydrocarbon fuel and convert it on-board into a hydrogen-rich gas mixture to be injected into the engine combustors. To investigate this approach, a 5.6 kW plasma-cutting torch was modified to perform arc pyrolysis experiments. The outlet gas flow was sampled and subsequently analyzed using gas chromatography. The experimental apparatus converted the methane feedstock almost completely into carbon, hydrogen and acetylene. Unfortunately, the energy consumption of the apparatus was too excessive to be feasible for a flight vehicle. However, other researchers have reformed hydrocarbons using an arc process with much less input electrical power.

I. Introduction

Hydrogen has often been touted as the fuel of choice for airbreathing hypersonic vehicles. The very high reaction rate of hydrogen-air combustion is the primary reason for this choice. For a scramjet vehicle, the fuel must be mostly burned in the very brief time before it exits the combustion chamber. In terms of energy output per unit mass, hydrogen has the highest output of any fuel. Accordingly, because specific impulse is defined as the uninstalled thrust divided by the fuel weight flow rate, the low mass of hydrogen tends to yield higher specific impulse than other fuels. However, the key disadvantage of hydrogen is its low density (Fig. 1). In fact, the energy content per unit volume of liquid (or even slush) hydrogen is significantly lower than liquefied methane. Some authors have expressed profound doubts about the feasibility of a hydrogen-fueled airbreathing SSTO vehicle, due to the drag resulting from the large volume required to store this fuel¹. Emanuel and Golovichev² argued that although hydrogen is a fine choice for a rocket launch system, it is a poor choice for an airbreathing single stage to orbit vehicle. This argument is based on the following points: For a rocket vehicle, the force opposing the engine thrust is mainly the vehicle weight. In contrast, the thrust of an airbreathing vehicle is primarily opposed by aerodynamic drag. Because drag depends strongly on volume, fuel volume has a much more significant effect on performance of an airbreathing vehicle than fuel weight. A large fuel volume results in either a large vehicle frontal area, which will produce excessive wave drag, or a very long slender vehicle, which

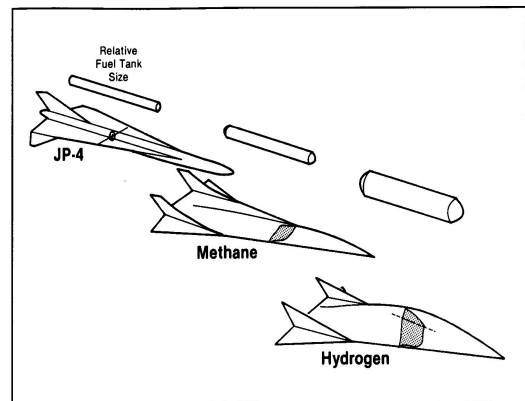


Figure 1. Relative Fuel Volume Requirements

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tends to create excessive skin friction drag. This results in a vehicle with marginal net thrust that cannot accelerate quickly while in the atmosphere. In addition, the difficulty involved with the storage and handling of 20 K cryogenic hydrogen is a secondary disadvantage to its use as a fuel.

The on-board reformation of a hydrocarbon into a hydrogen-rich gas mixture is a concept that attempts to exploit the fast reaction rate and high flame temperature of hydrogen combustion while retaining the lower volume requirements of hydrocarbon. Two methods of obtaining hydrogen from a hydrocarbon are steam reforming and pyrolysis. Steam reforming of methane involves the following reaction:



Using this process would require the vehicle to carry water, which may add undesirable weight to a vehicle. Moreover, this reaction also requires a catalyst.

Methane pyrolysis takes place in the absence of an oxidizer by the following endothermic reaction:



The equation above is grossly simplified; in practice other products are likely to be formed depending on conditions.

The conventional approach to pyrolyze methane would be to heat the gas to a temperature of 700 to 1200 °C. However, if a heat exchanger is used for this process, the hydrocarbon flow passages will become fouled with solid carbon and soot. This problem is commonly known as coking. One approach to preventing coking is to use a partially oxidized fuel, such as methanol, which would tend to form gaseous CO instead of solid carbon or soot, as it is pyrolyzed³. Coking is not only a problem in regard to heat exchanger blockage and heat transfer, but this substantial mass of the carbon needs to be ejected out of the vehicle for better performance. Of course, it would be much more advantageous to exploit the chemical energy available from the carbon by burning it.

An alternative approach to thermally pyrolyzing a hydrocarbon in a heat exchanger is to use an electric arc heater to pyrolyze the fuel. This approach is the subject of this investigation which was originally sponsored by MSE Technology Applications. MSE-TA's interest in fuel reformation is part of their efforts to analyze and develop the Russian vehicle concept known as AJAX. The complete details of the AJAX concept have not been publicly revealed by its originators. For this reason, much of the research published by others on AJAX involves some degree of speculation. In regard to fuel reformation, MSE-TA was interested in examining the premise that arc heaters could act as fuel injectors for the AJAX combustor. The configuration was perceived to be very similar to a Linde arc heater (Huels-type) (Fig. 2)

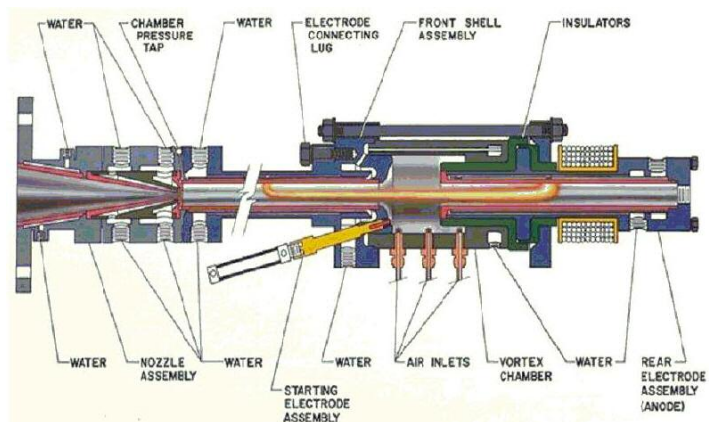


Figure 2. Linde Arc Heater

with the hydrocarbon gas being injected between the electrodes. The hot flow of pyrolysis products would expand through the arc heater nozzle directly into the combustor. This idea is not entirely peculiar, hydrocarbon fed plasma injectors have also been proposed for scramjet engines as a source of ignition promoting radicals. The combustion kinetics of the very hot pyrolysis products would be expected to be very fast, not only for the liberated hydrogen, but also for the carbon and hydrocarbon species. Bruno et al.³ have predicted that the ignition delay for pyrolyzed methanol products is shorter than the delay for hydrogen injected at 500 K. In this manner, the non-hydrogen pyrolysis products become valuable sources of combustion heat as well.

II. Experimental Approach

A. Previous Experiments

The arc pyrolysis experiments at UTA were intended to be performed with a Thermal Dynamics F-5000 arc heater due to its close similarity to a Linde arc heater⁴. However, the Robicon 1.6 MW DC power supply for the arc heater suffered a breakdown only one second into the arc heater's initial run with methane. Although, no steady data was obtained in this test run due to the power supply failing while the arc heater was still in its starting transients,

some useful findings were made. The primary finding was that there was no carbon or soot accumulation on the water-cooled electrode surfaces up to the F-5000's nozzle. Every surface immediately downstream of this location had a thin, yet highly visible, layer of carbon (Fig3). Raman spectral analysis of this very fine black powder indicated it was composed entirely of graphite. Had the arc heater discharged into air rather than a vacuum, this carbon in all probability would have burned. The fluid and thermal conditions in the arc heater along with the Huels electrode geometry appears to have suppressed the build-up of carbon. The high temperature of the flow probably keeps most of the carbon in a gaseous state, and whatever carbon happens to contact the cold electrode walls is swept away by the intense shear of the swirling gas flow. Accordingly, it is conceivable that an arc heater injector could be made that would have no difficulty with carbon accumulation. This assertion is consistent with the results of Hruby et al.⁵, who developed a small, low-pressure arcjet thruster with hollow electrodes that could run indefinitely on methane without carbon creating a flow blockage or electrical short.

Because the damage to the Robicon arc heater power supply was too expensive to have repaired in the short term, the hydrocarbon pyrolysis experiments were continued using a modified industrial plasma-cutting torch. The modified Hypertherm Powermax 600 unit (Fig.4) has only about 1/300th the electrical power of the arc heater facility, but we expected the physical and chemical phenomena occurring within the small torch to be fairly similar to a larger scale case.

The Hypertherm torch unit is nominally rated at 5.6 kW, with an operating voltage of 50-320 V, a variable current output of 20-40 A, and a supply flow rate of approximately 6 scfm. The modifications to the Hypertherm torch were made to address potential safety problems. Unlike the arc heater, the small cutting torch is cooled by gas flow rather than water flow. Only a portion of the gas flow going into the torch head (model PAC123T) actually goes in close proximity to the arc. Most of the gas flow is used for cooling and confining the cutting jet. A surprising aspect to the Hypertherm torch head is that some of the gas flows back into the plastic handle. This presents no problem if one is using air or nitrogen that the torch is designed to use, but is a considerable fire hazard if a fuel gas is substituted. Therefore it was necessary to remove the handle and enclose the back portion of the torch head so that the combustible gas could be contained and vented outside. As an additional precaution, the torch head enclosure also had a continuous flow of argon going into it. The gas control plumbing was taken out of the plasma torch power supply as an additional safety measure. To prevent the pyrolysis products from burning, the plasma torches were discharged into an evacuated test cabin. This practice has been followed for this entire study.

Just prior to MSE-TA's contract deadline, a few pyrolysis experiments were performed with the Hypertherm torch. As previously reported, the emission spectra of the pilot jet of the torch running with a methane feedstock did imply the presence of hydrogen, however, it was difficult with our limited background to surmise much else from the spectral data⁴. From these initial experiments, the strongest evidence for hydrogen liberation actually came from the associated production of free carbon from the brief arc heater run.

B. Development of Water-Cooled Anode Apparatus

The pilot jet mode of the Hypertherm unit is a feature of the torch that allows it to operate without transferring the arc to a work piece, which is particularly helpful when cutting expanded- metal. However, the unit will only deliver 12 amps in this mode, until the jet contacts a conductive workpiece, which allows the arc to transfer to it. Once the arc is transferred, the power supply will deliver the current selected on the dial, from 20 to 40 A.

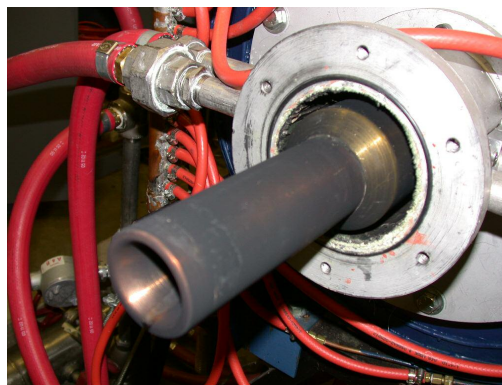


Figure 3. Carbon Deposits on Cold Trap Downstream of Nozzle



Figure 4. Hypertherm Plasma Cutting Unit

Therefore, to utilize the full power of the Hypertherm unit, it was necessary to make an anode for the arc to transfer to. The design of this anode component was heavily influenced by prior experience in fabricating water-cooled calorimetric total enthalpy probes for the arc heated wind tunnel. These probes, which are adapted from the Greyrad design (Fig. 5), feature nested tubes that direct the internal water flow to impinge at the probe tip, just opposite the stagnation point of the external gas flow⁶. This method of cooling is extremely effective and allows the probes to dwell indefinitely in an arc-heated flow stream. Accordingly, the anode cooling water jacket has the same water passage configuration as a Greyrad probe. The other aspects of the anode design were motivated by a desire to avoid any further modification of the Hypertherm torch head. The insulator portion of the torch head has a threaded end for attaching a bypass flow directing shell around the torch nozzle. A brass adaptor piece was made to screw onto this thread and also block the bypass flow around the nozzle. The copper anode block attaches to the adaptor with four non-conductive (PEEK) screws. A gasket seals between the anode block and the adaptor piece and also electrically isolates these parts from each other. The face of the anode is situated 0.0313 inch from the tip of the nozzle and features a countersunk flow orifice. The 0.0625 in. diameter anode orifice is considerably larger than the 0.038 in diameter of the nozzle orifice. Past the anode orifice, the flow area abruptly increases to the inside of a ¼-in. copper gas tube. At this location, four ports were installed to permit pressure measurements, observation of the emission spectra, and the injection of a secondary gas flow. The anode section was instrumented with temperature transducers for making calorimetric measurements in the same manner as a Greyrad probe. The entering and leaving water temperatures were measured along with the leaving gas temperature. A turbine flow meter was used to measure the cooling water flow. Accounting for the gas mass flow was complicated by the design of the Hypertherm torch head, which diverts an unknown

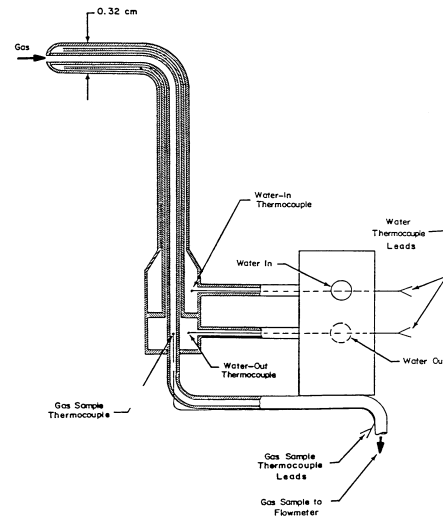


Figure 5. Greyrad Calorimetric Total Enthalpy Probe

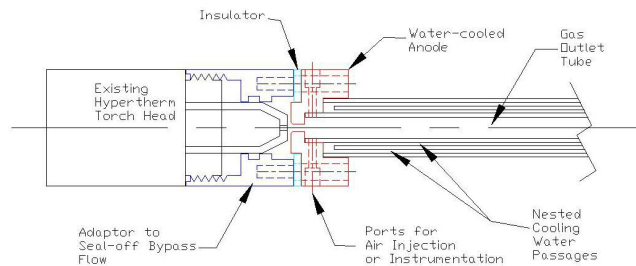


Figure 6. Anode Attached to Hypertherm Torch

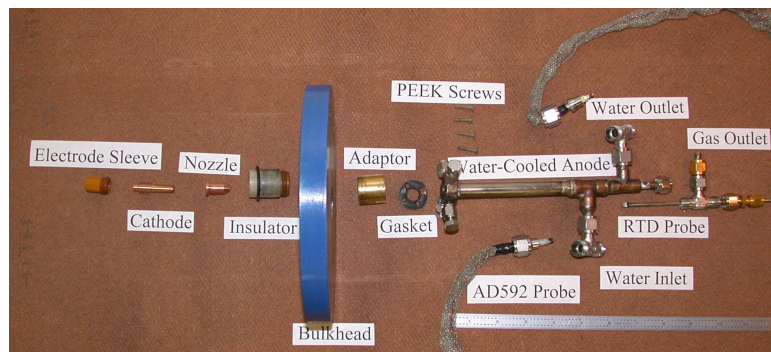


Figure 7. Disassembled Arc Pyrolysis Apparatus

portion of the gas flow for purposes other than being arc-heated. For example, drag force from the gas flow is actually utilized to move the cathode tip from being in contact with the inside nozzle surface (in order to initiate the arc) to a proper gap for maintaining a stable arc. When the gas flow is stopped, the cathode tip is pushed forward by a spring to rest against the inside nozzle surface. For this reason, it seemed that blocking all the gas flows except the

nozzle flow from the torch head would have caused it to not function properly. Moreover, altering the way the arc initiates probably would necessitate some rather time consuming modification to the power supply controls. The approach that we took was to try to determine the relevant mass flow at the gas tube exit rather than at a gas inlet. Of the large variety of methods for measuring the mass flow of a gas, most (if not all) require knowledge of the gas properties, which further requires knowledge of the chemical composition of the gas. This issue was not considered an obstacle since determining the outlet gas composition is a main objective of this investigation. One advantage to using the small-scale torch is that the entire outlet flow can be readily diverted into a portable sample container.

C. Technique for Chemical Analysis of Pyrolysis Products

Our previous efforts to determine chemical composition relied on acquiring the emission spectra of the arc-heated gas emerging from the torch nozzle. We soon discovered that photospectroscopic data tends to be much more informative in a qualitative rather than quantitative sense. Accordingly, we sought a more suitable chemical analysis technique. Mass spectroscopy was considered first, however, the university's chemistry department does not have a mass spectrometer capable of detecting hydrogen. The most suitable technique available was found to be gas chromatography. Analyzing collected gas samples using gas chromatography (GC) gives quantitative results and makes identifying chemical species much more straightforward. The primary disadvantage to this approach is that it does not indicate what species are present in the vicinity of the arc, but instead reveals the products after cooling has occurred. Chromatographic and spectrographic plots happen to look visually similar in that they consist of a series of sharp peaks along a horizontal axis. However, the two kinds of plots represent two entirely different phenomena. Chromatographic separation is the results of differences in the degree to which the components of a mixture are hindered in passing through an adsorptive media. The identity of a substance is determined by the time required for its peak to appear. The retention time for an unknown component of a mixture is compared with the retention time of a known substance (referred to as a standard) injected under the same conditions to determine the component identity. To determine the volume fraction of a component, the area under the peak is compared to the area for a known volume of a standard.

Detecting hydrogen using gas chromatography does require some departure from the more commonly encountered GC set-up. Hydrogen is not detectable by a flame-ionization detector, so the somewhat less sensitive thermal conductivity detector (TCD) must be used instead. The TCD measures the conductivity difference between a mixture of a sample component and the carrier gas with the conductivity of the carrier gas alone. In regard to a carrier gas, helium gives the best results for most analyses, but it produces anomalous detector output when mixed with hydrogen⁷. For this reason, argon was substituted as the carrier gas. The large difference in thermal conductivity between argon and hydrogen provides excellent contrast for detecting hydrogen, but provides less sensitivity for other gases. The UTA chemistry department provided access to a Gow-Mac Series 350 GCTCD. All the chromatography analysis sessions were performed using an 8 ft. long column packed with HayeSep Q (divinylbenzene).

D. Set-Up and Testing of Apparatus

Once the anode was completed, the first trial runs were conducted using nitrogen gas. After resolving minor problems with the apparatus operating on nitrogen, runs with methane were attempted. For these beginning experiments, the arc would flash on momentarily but not sustain when methane was supplied to the torch at the same pressure (120 psig) as the earlier nitrogen tests. At first, the problem was mistakenly attributed to a pressure switch on the Hypertherm power unit turning-off the power right after the gas started flowing. Eventually, the difficulty was discovered to have a more fundamental cause: the endothermic pyrolysis reaction was extracting energy to the extent that no part of the flow was hot enough to have sufficient ions and free electrons to support an arc. The solution was to reduce the supply pressure so that there would be less mass flow relative to the electrical power input. In addition, lowering the gas density also makes it easier to ionize. For the supply pressure range of 40 to 60 psig, the torch was able to maintain an arc when fed with methane. However, the torch voltage fluctuated considerably during all the pyrolysis test runs in contrast to the nitrogen runs, which displayed very steady arc voltages. This arc instability is consistent with the experience of other researchers who have directly arc-heated hydrocarbons in plasma torches. The voltage data given in this paper are values averaged for the length of the test run. The torch power supply generally managed to maintain a constant current during the experiments. Test run time was limited to less than ten seconds to minimize damage to the apparatus. In particular, the orifice of the uncooled nozzle would tend to distort under prolonged heating, directing the flow out of line with the anode orifice and gouging the anode face.

The electromagnetic noise produced by the Hypertherm power supply and torch was a persistent difficulty in regard to making pressure and temperature measurements. The severity of this interference was not anticipated since thermocouple and millivolt-output pressure transducers had been successfully used on the much more powerful arc heater facility (albeit, after a great deal of effort involving shielding, amplification and active filtering). Moreover, the Hypertherm unit was selected specifically because it does not rely on a very noisy high voltage, high frequency circuit to initiate the arc. This potential source of trouble was vividly appreciated since the arc heater facility originally had a 10,000V high frequency igniter that was so damaging to integrated circuitry that it was abandoned in favor of a different arc initiation technique. Purchasing voltage output pressure transducers allowed readable signals to be acquired, however there was not such an immediate solution to cleaning-up the thermocouple signals beyond the measures of shielding, amplification and filtering that were installed from the outset. Accordingly, we were prompted to try alternative temperature transducers: RTD's and Analog Devices AD592 temperature sensing integrated circuits. The AD592 transmits a current signal that is proportional to the temperature (273 μ A corresponds to 273K), which is much less susceptible to EMI than a thermocouple voltage signal⁸. The main concern in using these alternative temperature transducers was achieving a sufficiently fast response time. For this reason, instead of purchasing an off-the-shelf RTD probe with an enclosed element, we made our own probes with exposed elements. In order to improve the response time of the AD592's, we filed-away most of the plastic case around the integrated circuit. The AD592's are potentially slightly more accurate than a platinum RTD, less expensive and also require less signal conditioning. However, the AD592 is limited to less than 105 °C, so the chips were used for the cooling water flow and the RTD was used for the gas tube flow. A circuit based on an Analog Devices ADT70 integrated circuit chip was used to condition the signal from the RTD⁹. The ADT70 was designed specifically for this application of RTD signal conditioning. Having been replaced by AD592's, the type T thermocouples originally installed on the anode to measure the rise in water temperature, were relocated outside the test cabin to where the water lines pass through the top lid. Due to being farther away from the torch, and having the shielding augmented by 1/2" thick steel test cabin lid, the thermocouples produced a ΔT signal that was no longer obscured by noise. The response of the sheathed thermocouples was slightly faster than the trimmed-down AD592's, but both kinds of transducers were quick enough to show some thermal response to voltage fluctuations.

Having settled the problem with sustaining the arc, the outlet flow was routed to a solenoid valve, which would divert the flow to a sample bag when energized. When not energized, the valve allowed the flow to dump into the evacuated test vessel. A 5-micron filter was installed upstream of the solenoid valve to remove any carbon particles from the flow before it was dumped or sent to the sample bag. Foil sample bags were used to contain the samples rather than Tedlar bags, which are permeable to hydrogen. The SKC foil bags were certified to hold hydrogen for at least five days; however, in practice they seemed to retain a consistent mixture for months.

III. Results and Discussion

A. Gas Sample Composition

For all the analysis runs of gas samples from methane pyrolysis, only three peaks were observed: a very prominent hydrogen peak followed by a barely detectable methane peak, and a small acetylene peak arriving much later (Fig.8). All of the successful GC analysis runs of the gas samples

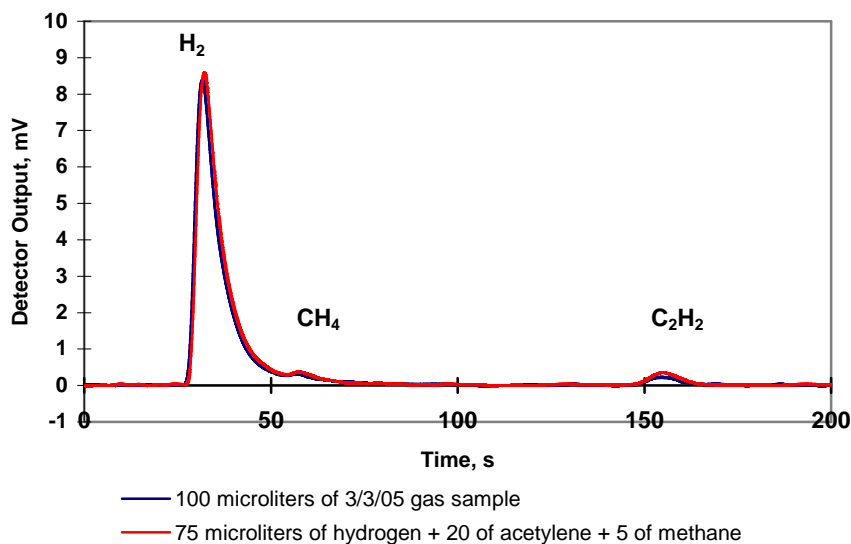


Figure 8. Comparison of Gas Sample with Standards Mixture

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consistently produced plots that closely resemble Fig. 8. Perhaps due to the limitations of making manual injections and/or the instrument, the methane peak always appeared on top of the tail of the hydrogen peak. Some effort was made in exploring different instrument settings in an attempt to improve the degree of component gas separation and optimize the detector output. However, none of the other settings that were tried worked any better than the settings selected for the second chromatography session which were the following: 72°C column temperature, 97°C detector temperature, and a flow rate of 20mL/min of argon carrier gas. Subsequent GC sessions in which data was collected had approximately these same settings. As shown in Fig. 8, the identities of the gases creating the peaks were confirmed by injecting a known mixture of hydrogen, methane, and acetylene. When the plots of an unknown gas sample and the mixture standards are overlaid, the retention times match and the areas are similar. The acetylene standard was obtained from a cutting torch bottle and has some hydrogen and air contamination. This contamination artificially boosts the hydrogen peak when a mixture of standards is drawn into the syringe and injected. The hydrogen concentration data presented in this paper were obtained using only hydrogen standards for comparison rather than a mixture of standards. Ten gas sample runs were made and these samples were analyzed during twelve chromatography sessions. The chromatograph was given typically three to four hours to warm-up to thermal equilibrium conditions, however the column temperature still tended to drift upward a few degrees C during the data collection time period when samples were being injected.

The hydrogen composition of the samples ranged from 78 to 88 percent by volume (Table 1.). The margin of error for a particular volume determination appears to be typically 2 to 5%. The concentration values presented in the data tables are generally averages from several injections often over many GC sessions. The volume concentrations of methane and acetylene could not be calculated accurately due to the lowered sensitivity of the GCTCD using argon rather than helium as the carrier gas, and the low resolution of the portable data recorder that was used to acquire the detector output. However, by inspecting the paper GC plots, it was not difficult to discern the approximate volume of methane or acetylene when injections of known standard volumes produced peaks both higher and lower than the unknown volume, effectively bracketing the unknown volume. To derive a reaction equation or product mole fraction estimates (Table 2.), methane was assumed to comprise only 2% of the gas sample volume, which appeared to be fairly typical for the samples analyzed. With this assumption for methane and having an accurate measurement of the hydrogen volume, the acetylene volume fraction was estimated by subtracting the hydrogen and methane volumes from the total injected volume.

Table 1. Hydrogen Content of Gas Samples

Test Run	Operating Point		Injection Pressure	H ₂ Volume Fraction of Gas Sample	H ₂ mole fraction of total products
6/17/04	39.8 A	142V	55 psig	0.84	0.69
7/15/04	33.5A	171V	55 psig	0.80	0.72
8/17/04	37.9A	159V	50 psig	0.86	0.69
9/30/04	34A	? V	42 psig	0.78	0.72
11/29/04	32.4A	158V	50 psig	0.80	0.71
3/3/05	31.7A	150V	45 psig	0.82	0.70
3/22/05	28.2A	154V	40 psig	0.88	0.68
4/5/05-1	24.4A	148V	42 psig	0.86	0.69
4/5/05-3	40.2A	111V	42 psig	0.87	0.69
4/5/05-4	21.0A	91V	42 psig	0.85	0.72

analyzed. With this assumption for methane and having an accurate measurement of the hydrogen volume, the acetylene volume fraction was estimated by subtracting the hydrogen and methane volumes from the total injected volume.

B. Comparison of Experimental Results with CEA Predictions

Methane pyrolysis simulations were conducted with the NASA CEA code for a range of temperatures and pressures relevant to the plasma torch experiments. However, the GC results are not directly comparable to CEA predictions because the gas samples are at atmospheric temperature and pressure rather than at the conditions specified for the CEA code reactions. As the specified reaction temperature is increased beyond 2500 K (for 3 atm), atomic hydrogen and C₂H appear in the CEA predictions, which would not be present in a room temperature gas sample. For the purpose of making a more relevant comparison, the CEA predictions were extrapolated to account for atomic hydrogen recombining to form diatomic hydrogen and atomic hydrogen combining with C₂H to form acetylene. This extrapolation was performed by assuming that all the C₂H combines with an equal amount of atomic hydrogen to form additional acetylene. The remaining atomic hydrogen is then assumed to recombine to form additional diatomic hydrogen. In addition, the multi-atom carbon species are arbitrarily added to the single carbon

mole fraction, because these different carbon forms are not distinguished in the experimental analysis. The results of this extrapolation are given in Fig. 9 for 3 atm, which approximately matches the pressure of the test runs. If the bulk temperature of the reaction is in the 3000 to 3750 K range, then the predictions are roughly consistent with the GC analysis of the samples. For higher and lower temperature ranges, the CEA code results do not agree with the proportions of acetylene and carbon found experimentally. Comparisons with the CEA calculations are further complicated by the fact that plasma torches do not produce a uniform flow temperature, but instead typically have a highly peaked temperature distribution, with the maximum temperature at the centerline often being twice the average temperature. Therefore, the reactions inside a plasma torch would actually occur over a wide range of temperatures rather than at a single characteristic temperature.

Most of the test runs were configured for an Ocean Optics USB2000 photospectrometer to view the spectra through an optical fiber connected to a port in the anode block. Unfortunately, these attempts to obtain spectral data were thwarted by carbon immediately blocking the optical path through the hole. In an effort to circumvent this problem, an uncooled anode block was coupled to the torch, and an optical fiber was mounted on a bracket to view the free jet exiting the truncated anode. Because of difficulties in obtaining the gas temperature at the anode entrance in a calorimetric manner, we sought to determine the temperature by applying Wien's displacement law to the underlying Planck distribution of the emitted spectra. By inspection, the peak of the distribution seemed to coincide with a wavelength of around 524 nm, corresponding to a temperature of 5530 K, for the entire range of torch operating currents. The molecular and atomic spectral peaks on top of the continuous blackbody distribution obscure the precise peak

Table 2. Moles of Pyrolysis Products from One Mole of Methane

Test Run	Carbon	Hydrogen	Acetylene	Methane
6/17/2004	0.41	1.65	0.27	0.04
7/15/2004	0.11	1.50	0.42	0.04
8/17/2004	0.50	1.69	0.23	0.04
9/30/2004	0.18	1.53	0.39	0.04
11/29/2004	0.27	1.57	0.35	0.04
3/3/2005	0.34	1.61	0.16	0.04
3/22/2005	0.57	1.73	0.19	0.04
4/5/05-1	0.49	1.69	0.23	0.04
4/5/05-3	0.53	1.71	0.22	0.04
4/5/05-4	0.36	1.66	0.26	0.04

Table 3. Estimated Mole Fractions from Test Runs

Test Run	Carbon Fraction	Hydrogen Fraction	Acetylene Fraction	Methane Fraction
6/17/04	0.174	0.694	0.114	0.017
7/15/04	0.054	0.723	0.205	0.018
8/17/04	0.203	0.687	0.093	0.016
9/30/04	0.085	0.715	0.182	0.018
11/29/04	0.120	0.707	0.156	0.018
3/3/05	0.147	0.701	0.136	0.017
3/22/05	0.226	0.682	0.077	0.015
4/5/05-1	0.201	0.688	0.095	0.016
4/5/05-3	0.213	0.685	0.087	0.016
4/5/05-4	0.154	0.716	0.113	0.017

the optical path through the hole. Unfortunately, these attempts to obtain spectral data were thwarted by carbon immediately blocking

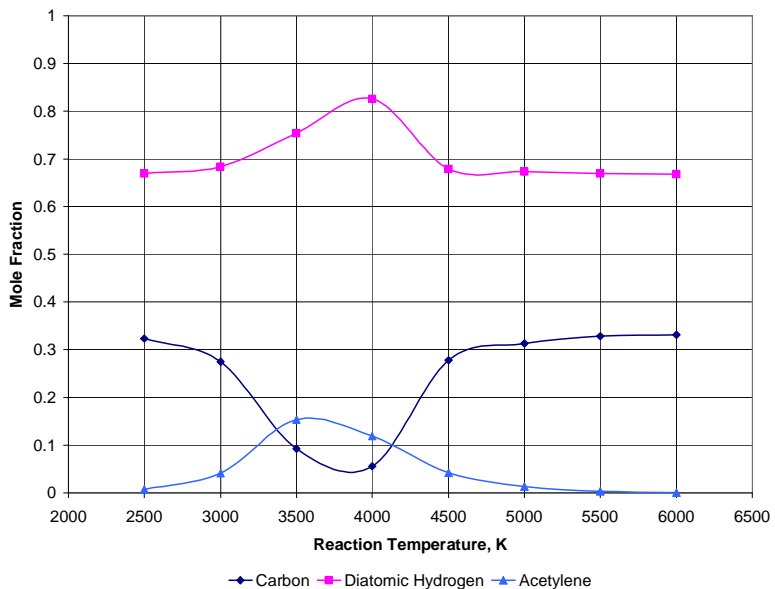


Figure 9. Extrapolated CEA Predictions for 3 atm

wavelength. Accordingly, this recently obtained value is considered highly approximate (± 500 K) and preliminary, since not all factors affecting this measurement technique have yet been sufficiently contemplated.

C. Power Consumption of Apparatus

The hydrogen yield does not seem to vary with power level or any other immediate parameter. If there is such an influencing factor, it is subtle enough to be hidden by the error scatter in the measurements and analysis. This lack of a correlation could be due to the flow being heated to the extent that an arc can be formed and sustained, which is considerably more than what is required to achieve complete pyrolysis. Thermal pyrolysis only requires temperatures of 700 to 1200 °C, whereas the temperature of the arc plasma can be 12,000 °C or more. For the case of the Hypertherm torch, the proportion of gas actually being directly heated by the arc may be much higher than what is typical for a Huels or segmented arc heater. For these arc heaters, only a small percentage of the total gas flow actually passes through the arc plasma; the great majority of the flow is heated indirectly by the arc¹¹. For example, the plasma yarn of the F-5000 is only 1/8" in diameter (at 800A), which is quite small as compared with the 1" anode barrel inside diameter and the 0.6875" diameter nozzle throat. In contrast, for the Hypertherm torch, the arc passes through the narrow 0.038" diameter nozzle orifice along with the entire flow subjected to the pyrolysis reaction.

Although these experiments demonstrated the feasibility of achieving almost complete pyrolysis in a very compact space, the power consumption was far above what could be considered feasible for a flight vehicle. In only one test run was the torch power input lower than the amount of power that could be produced from burning the same mass flow of methane (Table 4). This particular, 21A run seemed to be close to the margin of the arc being extinguished rather than sustained, because a similar 20A run prior to this did fail to sustain the arc. This poor utilization of the input power for the apparatus is not surprising given that the design was improvised rather than being refined to minimize power requirements. Furthermore, injecting additional methane downstream of the arc to exploit the high temperature of the arc-heated flow in order to thermally pyrolyze more methane has not yet been attempted with this apparatus. However, other plasma arc experiments and processes have been developed that show much more promising levels of power consumption (Table 5). For example, the Kaevner process used at the Karbomont facility reports energy consumption of 100.7 MJ per kg-mole of hydrogen¹². In bench scale tests, the GlidArc process produced 1 mole of hydrogen and 0.22 mole of acetylene with 330 kJ (the author anticipated considerable improvement with further development)¹³. The Kaevner and GlidArc devices appear much less suitable than an arc heater as a high discharge velocity fuel injector. Data from John Prebola's thesis suggests that his plasma torch consumed 40-75 MJ per kg-mole of H₂ (assuming complete pyrolysis occurred), but the arc appears to have been quite unstable judging by the large fluctuations in voltage¹⁴. These results suggest that pyrolysis by the direct arc-heating of a hydrocarbon is less practical than introducing a hydrocarbon downstream of an arc to be thermally pyrolyzed in the "tail flame" of a

Table 4. Apparatus Power Requirements

Test Run	Methane Mass Flow Rate, kg/s	Heat Rate Available from Burning Methane, kJ/s	Torch Power Input to Pyrolyze Methane, kW
7/15/04	6.71×10^{-5}	3.36	5.65
8/17/05	5.62×10^{-5}	2.81	6.02
11/29/04	3.68×10^{-5}	1.84	5.13
3/3/05	2.92×10^{-5}	1.46	4.77
3/22/05	4.64×10^{-5}	2.32	4.33
4/5/05-1	6.23×10^{-5}	3.12	3.61
4/5/05-3	5.81×10^{-5}	2.91	4.45
4/5/05-4	5.18×10^{-5}	2.59	1.91

Table 5. Energy Input for Various Hydrogen Generation Techniques

Data Source	Energy Required to Produce a kg-mole of H ₂ , MJ/kmol
7/15/04 Test Run	881.4
8/17/04 Test Run	1,015.1
11/29/04 Test Run	1,422.2
3/3/05 Test Run	2,917.4
3/22/05 Test Run	866.0
4/5/05-1 Test Run	685.0
4/5/05-3 Test Run	867.6
4/5/05-4 Test Run	432.1
Kvaener Process	100.7
Benchtop GlidArc	330
Prebola - Virginia PolyTech	40-75
Theoretical Water Electrolysis	285.8

different arc-heated gas. In this situation, the arc will be much more stable than in a hydrocarbon gas and the hydrocarbon does not have to be excessively heated in order to provide the conditions necessary to support an arc. As a case in point, the developers of the Kaevner process abandoned directly heating a hydrocarbon with the arc to arc-heating hydrogen and then injecting a hydrocarbon downstream. When using a tail flame to perform the pyrolysis, a Huels arc heater could prove to be very competitive with the Kaevner and GlidArc processes in regard to energy consumption. In 1986, John Poole of Plasma Materials, Inc. patented a Huels-type plasma torch that demonstrated a 90% transfer of the arc energy to a hydrogen gas flow (with the remaining 10% heating the cooling water)¹⁵. This torch can also operate over a much broader range of flow rates than other arc heaters (a 10:1 ratio of the highest to lowest gas flow rates). With these advanced characteristics, this torch design would serve as an excellent basis for further development of the concept of a pyrolyzing fuel injector.

IV. Conclusion

This study experimentally demonstrated that methane can be pyrolyzed almost completely in a very compact space with a plasma torch, yielding a hydrogen mole fraction of approximately 0.7 of the total products. Some approximate agreement was observed between the experimental results and predictions from the NASA CEA code for the temperature range of 3000 to 3750 K. However, this limited accordance is based on assuming the predicted atomic hydrogen in the CEA results combines with C₂H to form additional acetylene and with itself to form additional diatomic hydrogen. Unfortunately, the pyrolysis torch apparatus required too much electric power to demonstrate any feasibility for incorporating into a flight vehicle due to the necessity of heating the gas excessively in order to sustain an arc. However, other researchers have demonstrated a more feasible level of power consumption for their arc pyrolysis devices, which suggests that a well-designed plasma torch could be a viable pyrolyzing fuel injector for a hypersonic airbreathing vehicle.

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