Section 16.0: Spectrographic Analysis of Combustion Products

The eventual goal of this project was to determine whether or not a plasma torch operating with hydrocarbon feedstocks would be a good ignitor and flameholder in a supersonic combustor. The flame speed of conventional fuels is too low to burn at supersonic velocities. By injecting combustion-enhancing radicals from a plasma torch, it should be possible to enhance the flame speed by increasing the combustion reaction rates. Atomic emission spectrometry was used to search for excited atoms and ions in methane, ethylene and propylene plasma jets to determine if these combustion-enhancing radicals were produced.

In past years, nitrogen and a 1:1 volumetric mixture of hydrogen and argon have been proven to be effective flameholders (Wagner et al., 1987, Kimura et al., 1981 and Weinberg, 1978). Kimura et al. (1981) found that nitrogen plasma proves almost as effective as hydrogen plasma, but based on the input electric power, nitrogen is superior. Nitrogen atoms make good combustion enhancing radicals because of their long life and high energy. According to Hilliard (1979), they react with hydrocarbon fragments to produce HCN and hydrogen atoms, as suggested by the following reaction:

$$CH_n + N \rightarrow HCN + H$$

Hydrogen atoms are key in any combustion enhancement, providing a very basic element required in almost every combustion reaction. They participate in the chain branching reaction:

$$H + O_2 \rightarrow OH + O$$

This reaction is highly endothermic and easily quenched. Therefore, increasing the concentration of hydrogen atoms in a combustion process will speed up and stabilize this reaction. In addition to the effectiveness of nitrogen and hydrogen feedstocks, Kato and Kimura (1996) reported that oxygen feedstocks also have good potential for supersonic combustion applications for hydrogen burning in air, possibly even exceeding that of nitrogen and hydrogen. Mitani (1995) also validated these findings by discovering that the addition of O was found to be 1.5 times more effective than the addition of H for ignition applications involving a plasma torch. These atoms, along with any other specie, can be detected by the way they interact with one another in the flow.

Transition of electrons between the outer electron shells of interacting atoms generates the optical emission spectra. The wavelength of excited specie is related to the energy difference of the electron shells. This wavelength can be measured using a spectrometer, which separates the light into component wavelengths using a diffraction grating. In addition, the light intensity of the particular wavelength is directly related to the number density of the atoms or ions present (Dean and Raines, 1975).

In the tests conducted using the Virginia Tech Plasma Torch, an arc/plasma was the light source to be analyzed. These tests used a monochromator type dispersive spectrometer, one that scans a single wavelength at a time, as opposed to a polychromator. A dispersive spectrometer can also use different mirror and diffractive grating configurations, such as an Ebert, Czerny-Turner or Seya-Namioka mounting. In atomic emission spectrometry, the diffraction grating is used to disperse the incoming light. The amount of dispersion is dependent on the number of grooves in the grating, with higher number of grooves providing increased dispersion, and in turn, higher resolution.

Various detectors can be used to sense radiation emitted from a light source. Photomultipliers are commonly used, but they are only single channel detectors. Multichannel detectors such as photodiode arrays, image dissector tubes, charge-coupled devices and charge injection devices can scan many wavelengths simultaneously, but they lack sensitivity in the UV and VUV range.

16.1: Equipment and Calibration

Spectrographic tests conducted with the Virginia Tech Plasma Torch utilized a 0.5-meter Ebert scanning monochromator with a diffractive grating of 1180 grooves/mm. The full scanning range of the monochromator is from 1900 to 9100 Angstroms (Å), with a resolution of approximately 1Å. A 0.7 meter length of PVC pipe was aimed at the plasma jet in an effort to capture only the light emanated from the arc and plasma jet, rather than light from other sources such as reflections or the flame plume.

Between the PVC pipe and the entrance slit, there were two Oriel absorptive neutral density filters. They were used to reduce the intensity of the light entering the

spectrometer. Although the spectrometer is rather insensitive to light intensity, the photomultiplier tube (PMT) can easily be burned from intense light. These filters had an optical density of 3.0 and a range of sensitivity as seen in Fig. 16.1. It was noted that transmittance dropped off sharply below 3500 Å (350nm, see Fig. 16.1).

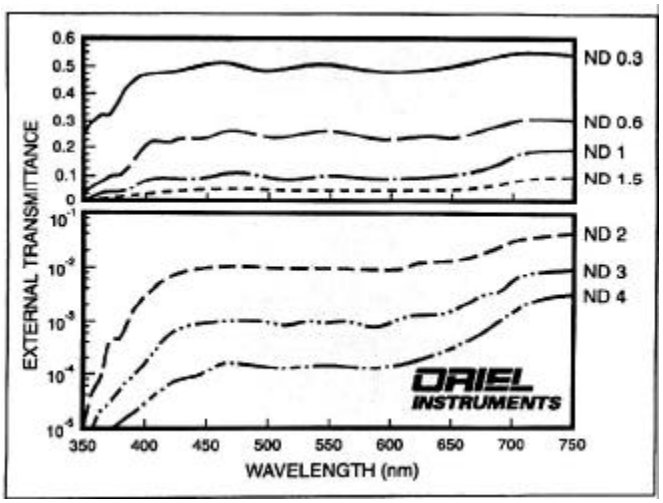


Figure 16.1: Filter Transmittance from Oriel Data Sheet

After passing through the filters, the light traveled through the spectrometer, was dispersed by the grating and left through the exit slit. A Burle PMT was attached to the exit slit to capture the remaining light. This PMT, powered by a 15V supply, had a variable gain potentiometer that was set depending on output intensity. In some cases, after a few tests were conducted, the gain had to be increased to get the same resolution as the previous runs due to desensitization of the PMT. A graph of the spectral response characteristics is given in Fig. 16.2.

A simple resistor was connected across the output leads of the PMT so that the voltage drop across the resistor could be measured. The voltage drop across the resistor was on the order of 0 to 50 mV. The signal conditioning module that was used to measure power supply current was chosen to read the PMT output, since it was designed for a 0-50mV input.

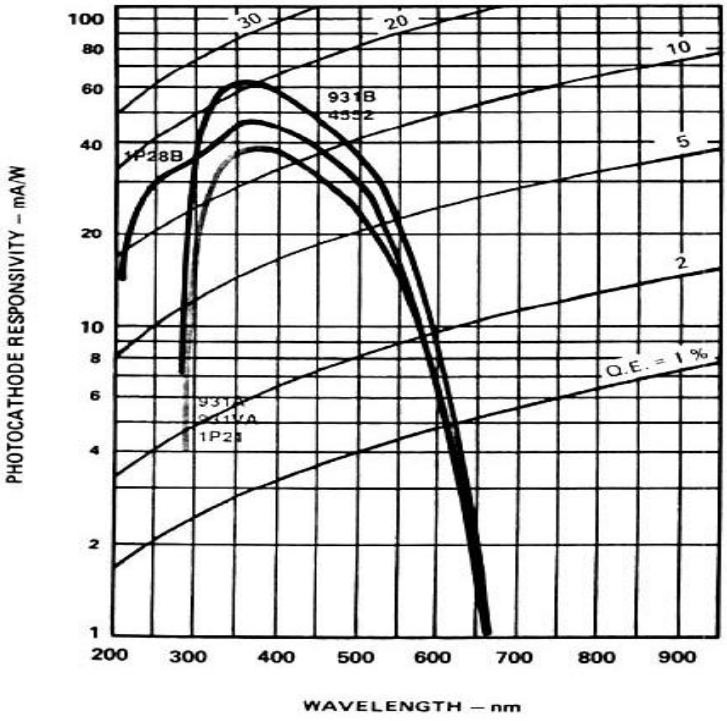


Figure 16. 2: PMT Response Characteristics

It was necessary to check the calibration of the spectrometer to insure that the wavelength counter on the instrument was correct. A 200W Oriel mercury arc lamp was chosen, since a mercury arc has well defined peaks at 2491 Å, 4046 Å, 4358 Å and 5461 Å. After the calibration run was completed, the spectral irradiance data sheet for the Oriel lamp was found to match the computer output of the PMT to within 2.0 Å, indicating that the spectrometer and computer were calibrated. Also noted was the fact that the 2491 Å peak was registered by the DAQ system despite the neutral density filter resolution dropping off below 3500 Å.

16.2: Testing Setup and Procedure

The test procedure started with setting the gas flowrate. In an effort to maintain a chamber pressure of about 210 kPa, methane was run at 24 SLPM and ethylene at 36 SLPM. The current setting on the power supplies was turned to 20%. It was desired to keep the current and chamber pressure constant since it affects the width of the arc. With the flowrate and current set, the torch was started with the HF starter. When the torch

ignited, the HF starter was turned off. Following HF shutoff, the spectrometer scan and DAQ system were started simultaneously. Scanning was completed at a rate of 500 Å/min from 3000 Å to 7000 Å, unless the torch extinguished itself. If the test lasted until the counter reached 7000A, the torch was shut off. After the test, the torch was removed from the test stand and inspected for electrode wear and damage. Electrodes and gas seals were replaced as needed. The test procedure was conducted three more times to verify peaks. In total, eight test runs were conducted - four runs using methane and four runs using ethylene.

Other tests with methane were conducted using different flowrates and current settings than those run in earlier tests to determine if these changes affected radical production. Three tests were conducted, each at 27% current and 30 SLPM. Other tests were conducted, in addition to these, with slower spectrometer scan speeds. These tests were run for small ranges and 50 Å/min to determine if hydrogen atoms were being produced. Earlier runs were conducted to try to discover any general species produced by the torch, but these tests were aimed at specifically determining whether or not hydrogen atoms were present.

Finally, several propylene experiments were conducted. These were designed to determine how heavier and more complex hydrocarbon feedstocks affected the production of species. The instability caused by pure propylene operation prompted use of a mixture of argon and propylene to stabilize the arc. Table 16.1 summarizes each spectrographic test and the conditions under which it was run.

Table 16.1: Spectrographic Test Summary

Test #	Gas	Flowrate	Current	Scan Speed	Purpose
1	Methane	24 SLPM	20%	500 Å/min	General species production analysis
2	Methane	24 SLPM	20%	500 Å/min	"
3	Methane	24 SLPM	20%	500 Å/min	"
4	Methane	24 SLPM	20%	500 Å/min	"
5	Ethylene	36 SLPM	20%	500 Å/min	"
6	Ethylene	36 SLPM	20%	500 Å/min	"
7	Ethylene	36 SLPM	20%	500 Å/min	"
8	Ethylene	36 SLPM	20%	500 Å/min	"
9	Methane	30 SLPM	27%	500 Å/min	Determine how power and flowrate affect radical production.
10	Methane	30 SLPM	27%	500 Å/min	"
11	Methane	30 SLPM	27%	500 Å/min	"
12	Methane	20 SLPM	27%	50 Å/min	Searching for H atoms
13	Methane	25 SLPM	27%	50 Å/min	"
14	Propylene	20-Argon 3-Propy.	27%	500 Å/min	General radical production analysis
15	Propylene	20-Argon 3-Propy.	27%	500 Å/min	"

16.3: Results and Discussion

For each spectrographic test series, spectrographs from each test were compared with each other to verify that the results were repeatable. Peaks found in most or all of the spectrographs were recorded, while stray peaks appearing in only one test were discarded.

16.3.1: Methane Spectrographic Test Results

The output from the PMT for methane tests #1-4 is given in Fig. 16.3. Only the first two runs lasted the entire 4000 Å test range, however, there was little concern since there were no major peaks beyond 5000 Å. The strongest peak occurred at 3854 Å and was confirmed by all four runs. According to a listing of typical flame emission spectra, the strong peak could be C_2 (3852.2 Å), CN (3854.7 Å) or CO_2^+(3853.2 Å) (Dean and Raines, 1975 and Pearse and Gaydon, 1976). For CN or CO_2^+ to form, the methane first had to be broken down into some partial carbon ion while flowing through the arc, then rapidly react with N_2 or O_2 in the air. R©ck and Auweter-Kurtz discovered that CN was

formed when a mixture of nitrogen and methane was used as a torch feedstock (R©ck and Auweter-Kurtz, 1997). A methane plasma interacting with atmospheric nitrogen may also produce the same results. In any event, both C_2 and CN are free radicals associated with combustion enhancement, so their presence is promising.

Another strong peak was observed at 3577 Å. The closest molecular spectra for that wavelength would be N_2 at 3576.9 Å. A listing of other possible molecules present in the methane plasma are found in Table 16.2.

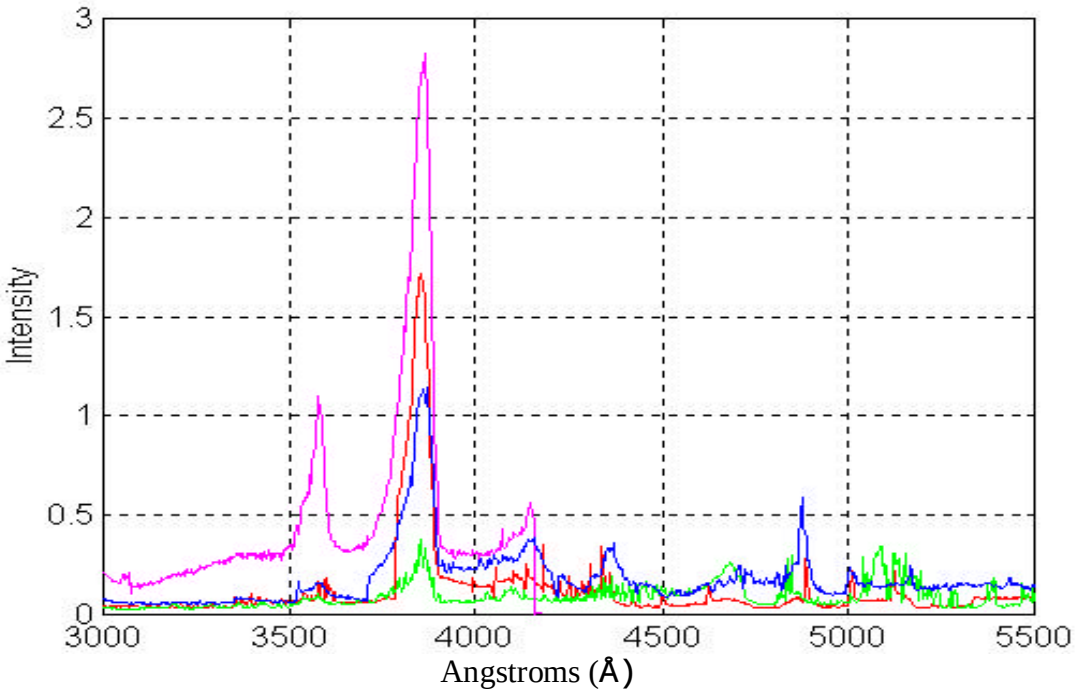


Figure 16.3: Results of Spectrographic Tests with Methane

Table 16.2: Potential Species Production (Methane)

Peak (Å)	Possible Molecule Present – Wavelength (Å)			
3577	N_2 – 3576.9			
3854	CN – 3854.7	CO_2^+ - 3853.2	C_2 – 3852.2	
4335	CO_2 - 4335	OH – 4336.6		
4367	C_2 – 4368.8	C_2 – 4365.2		
4679	O_2^+ - 4678.5	C_2 – 4680.2	W – 4679.04	C – 4678.6
4870 - 4880	H_2 – 4873	O_2^+ - 4877.6	CO^+ - 4879.5	O_2 - 4880

16.3.2: Ethylene Spectrographic Test Results

The data from the ethylene experiments, tests #5-8, in Fig. 16.4 is less clear, but again, a well-defined peak occurs near 3577 Å. As with methane, this peak could be N_2. Since the signal noise in the four runs is greater for ethylene, it is harder to determine exactly where the peaks occur. However, each run was separately analyzed and only peaks that occurred in all four runs were recorded. This method filters out any noise or errant peaks that occurred due to plasma jet fluctuations.

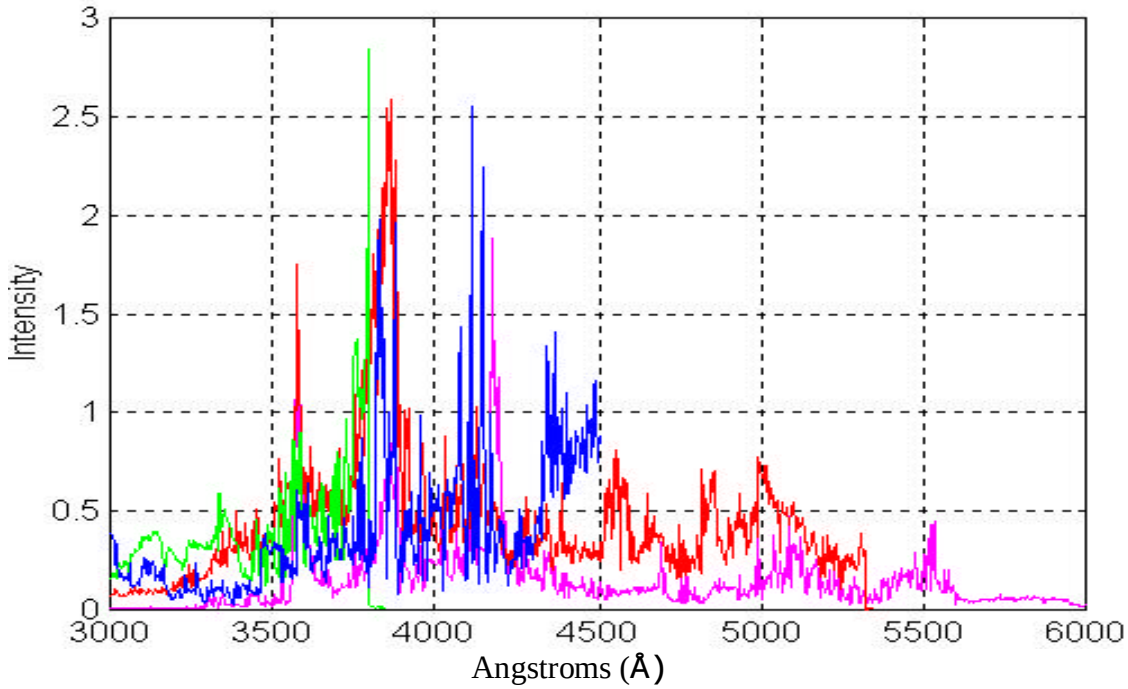


Figure 16.4: Results of Spectrographic Tests with Ethylene

The prominent peaks in Fig. 16.4 are organized in Table 16.3 in increasing wavelength. It should be noted that there were other products that had values near the peaks, but were outside the ±2Å tolerance. Also, there were peaks at 4148 Å and 4691 Å where no molecules could be identified.

Table 16.3: Potential Species Production (Ethylene)

Peak (Å)	Possible Molecule Present – Wavelength (Å)			
3796	CO^+ - 3795.8	NH – 3795		
3860	O_2^+ - 3859.5	N_2 – 3857.9	N_2^+ - 3857.9	CN – 3861.9
3955	CH^+ - 3954.4	CO^+ - 3953.6		
4115	O_2^+ - 4115.8	O_2 – 4114		
4179	O_2 - 4179	CH^+ - 4178.4	H_2 – 4177.1	CN – 4181
5084	H_2 – 5084.8			
5533.5	OH – 5534.1	CO – 5532.5		

16.3.3: Propylene Spectrographic Test Results

Experiments with propylene (tests 14-15) were designed to determine how heavier, more complex particles would react with the arc. It was hypothesized that fewer species would be produced because of the low power of the torch and the relatively high bond strength within the propylene atom. The results of the spectrographic propylene tests are shown in Fig. 16.5.

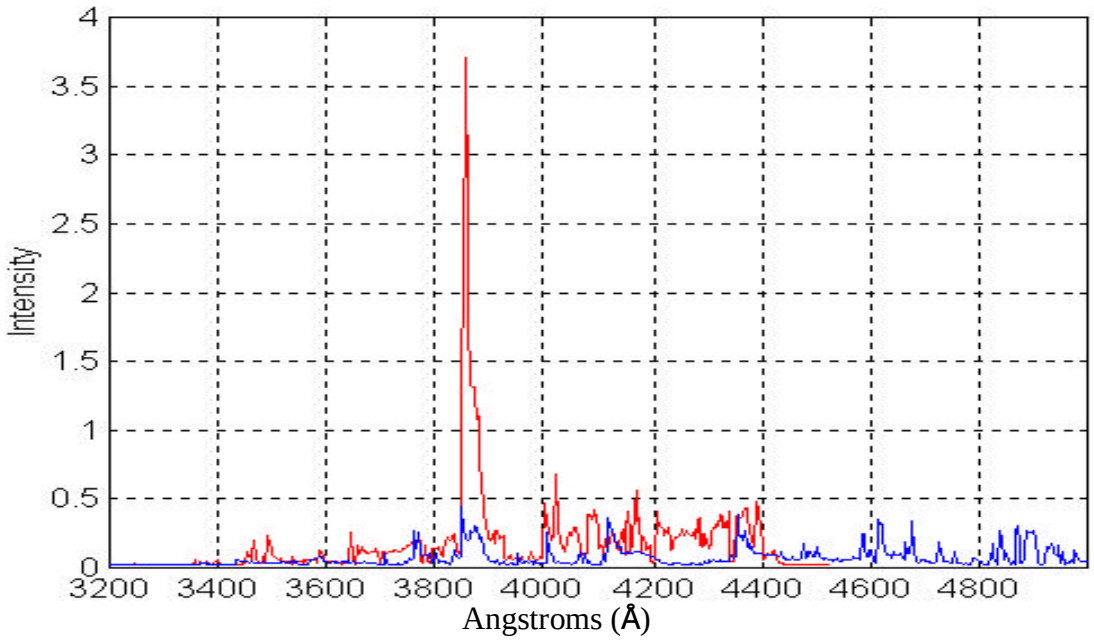


Figure 16.5: Results of Spectrographic Tests with Propylene

Close analysis of the graphs revealed several identifiable peaks. The first occurred at 3858 Å and was a common peak found with both ethylene and methane. The

second peak, much smaller that the first, occurred at 4117 Å, which was close to the peak of 4115 Å found in earlier ethylene tests. Other peaks were found at 3763 Å, 3768 Å and 4354 Å and are summarized in Table 16.4.

Table 16.4: Potential Species Production (Propylene)

Peak (Å)	Possible Molecule Present – Wavelength (Å)		
3763	O^+ - 3762.5	N_2^+ - 3761.6	
3768	W – 3768.5		
*3858	N_2 – 3857.9	N_2^+ - 3857.9	O_2^+ - 3859.5
4117	CO^+ - 4117.3	O_2^+ - 4115.8	NO_β - 4113.6
4354	C_2 – 4353	N_2 – 4355.0	

- indicates a peak already experienced

16.3.4: Power Effects on Radical Production

The experiments designed to determine whether or not different current levels would affect the production of radicals had interesting results (tests 9-11). The results of those tests are shown in Fig. 16.6. By analyzing the data, it was discovered that four new peaks were found, along with one peak that was already observed in previous tests with methane. These peaks and the species they most likely originated from are summarized in Table 16.5.

The peak occurring at 4679 Å was also found in previous tests and according to the data in Table 16.5, is most likely produced by tungsten atoms burned off of the electrodes. The next peak was found at a wavelength of 4337 Å. The species identified by this wavelength, OH, WO, or possibly CO_2, also appeared for other methane and ethylene tests. It appears that changing the power level of the torch does affect the type or amount of species produced. This effect was also observed by Masuya et al. (1993), who discovered that the ignition temperature of the fuel-air stream almost linearly decreased as the input electric power to the plasma torch increased. This result was most likely produced by either an increase in the number of combustion-enhancing radicals or different radicals being produced.

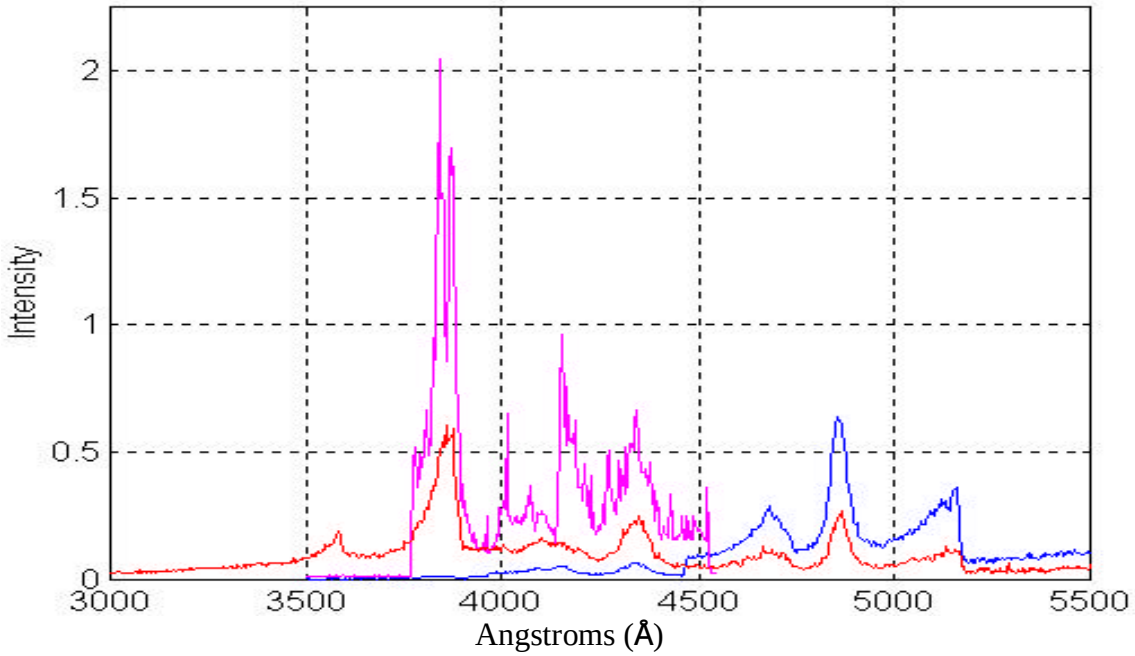


Figure 16.6: Spectrographic Test Results to Determine How Power Affects Radical Production

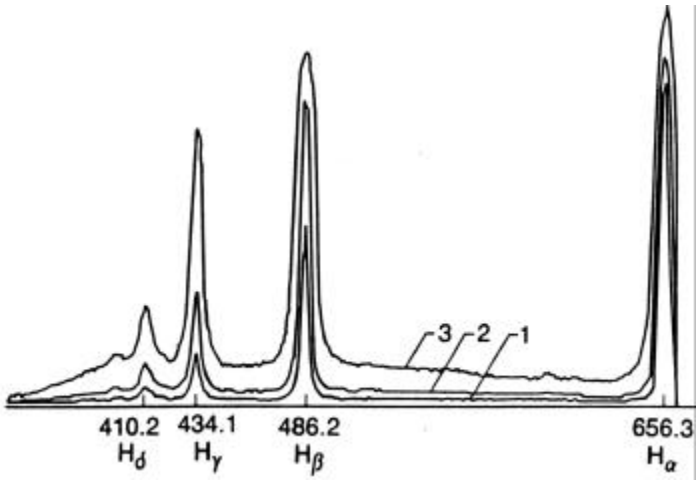
Table 16.5: Peak Summary for Different Methane Current Levels

Peak (Å)	Possible Molecules Present – Wavelength (Å)			
3841	N^+ - 3842.2	CO_2^+ - 3838.8	O_2 – 3841.0	O_2 – 3840.0
4337	OH - 4336.7	CO_2 – 4335.0	WO – 4338.3	
*4679	O_2^+ - 4678.5	C_2 – 4680.2	W – 4679.04	C – 4678.6
4854-4862	W – 4854.1	W – 4863.1	H_β - 4861.3	H_2 – 4856.6
5157	CN – 5156.0			

* - indicates a peak already experienced

16.3.5: The Presence of Hydrogen Atoms

The production of H atoms is very important for combustion enhancement. Even small amounts of H atoms by mass can be as effective as 20% by mass of silane, a pyrophoric compound (Wagner et al., 1986). Hydrogen atoms have been extensively studied and can be detected by scanning the Balmer series with a spectrometer. The first four lines of the Balmer series are shown in Fig. 16.7.



(units in nm)

Figure 16.7: Spectrograph of Balmer Series for Hydrogen (Wagner et al., 1986)

Spectrographic tests conducted by Wagner (1986) on the exhaust spectra of a plasma torch operating on a 1:1 volumetric mixture of argon and hydrogen clearly showed the presence of hydrogen atoms. Slow scan speeds over these wavelength ranges, while the torch was operating on methane (tests 12 and 13), did not produce these lines at all. However, methane tests 9-11 showed a possible presence of the H_β line. It is still feasible that the torch is producing hydrogen atoms, but they may be in such a small quantity or recombine so quickly with other species that they are not easily detected using the given equipment.

It is hypothesized that higher torch power would be needed to more effectively stabilize the arc and break apart the heavier hydrocarbon molecules to produce combustion-enhancing radicals, for the same volumetric flowrates. Denser gases generally have better heat transfer capabilities and will require a hotter arc to locally dissociate the feedstock, for equal volumetric flowrates. As an example, methane tests showed more evidence of the combustion enhancing radicals, OH and C_2, than ethylene, for the same power levels. Propylene tests showed little evidence of producing these radicals. Plasma torches operating on hydrogen can easily produce hydrogen atoms that are excellent for reducing the combustion reaction rates, at much lower power levels than for any hydrocarbon feedstock. The trend appears to be that simple hydrocarbons, or even hydrogen, make the best ignition and flameholding candidates because of their low power requirements and ability to produce desirable radicals. However, for higher power levels, more complex hydrocarbon feedstocks may be just as effective.

16.4: Concluding Remarks

These tests clearly demonstrated that hydrocarbon feedstocks can produce combustion enhancing radicals that are desirable for supersonic combustion applications. The results were repeatable and produced defined peaks which could be used to identify known species. There is positive data supporting the presence of C_2, OH and O_2^+ in the methane plasma exhaust and CH^+, CO^+ and O_2^+ in the ethylene plasma exhaust. Some stable products that appeared were CO_2, H_2, O_2 and N_2. Spectrographic data of the propylene exhaust showed evidence of O^+, CO^+, C_2 and O_2^+.

Increasing the torch power altered the type of species produced from methane. However, the desirable radicals OH and C_2 were still present. Also, evidence of hydrogen atoms was observed in very few circumstances. However, this does not prove that hydrogen atoms are not present. The torch might be producing hydrogen atoms, but they may recombine too quickly, or be present in such minute amounts that they are not detectable with the given equipment.

Recommendations for the future include using a more robust plasma torch designed for operating with pure hydrocarbon feedstocks at higher power levels. The current torch was designed for running simple gases and at power levels between 1-2 kW. A more robust torch design would allow spectrographic experiments to be conducted with more complex hydrocarbons such as JP-4 or kerosene, conducted at higher power levels.

Another future recommendation is the method of "seeding", or deliberately inducing gases into the feedstock that are known to produce desired radicals as in the case described by Harrison and Weinberg (1971). They reported that methane-air mixtures were more effective at flameholding than pure methane, but not as effective as pure nitrogen. However, they stated that at higher levels of power, methane-air mixtures should prove the most effective. From a systems viewpoint, this could easily be accomplished by injecting air into the hydrocarbon feedstock, thereby increasing the likelihood of OH, H and O radicals.