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INVESTIGATION OF PYROLYSIS GAS CHEMISTRY IN AN INDUCTIVELY COUPLED PLASMA FACILITY

A Thesis Presented

by

Corey C. Tillson

to

The Faculty of the Graduate College

of

The University of Vermont

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for the Degree of Master of Science
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Abstract

The pyrolysis mechanics of Phenolic Impregnated Carbon Ablators (PICA) makes it a valued material for use in thermal protection systems for spacecraft atmospheric re-entry. The present study of the interaction of pyrolysis gases and char with plasma gases in the boundary layer over PICA and its substrate, FiberForm, extends previous work on this topic that has been done in the UVM 30 kW Inductively Coupled Plasma (ICP) Torch Facility. Exposure of these material samples separately to argon, nitrogen, oxygen, air, and carbon dioxide plasmas, and combinations of said test gases provides insight into the evolution of the pyrolysis gases as they react with the different environments. Measurements done to date include time-resolved absolute emission spectroscopy, location-based temperature response, flow characterization of temperature, enthalpy, and enthalpy flux, and more recently, spatially resolved and high-resolution emission spectroscopy, all of which provide measure of the characteristics of the pyrolysis chemistry and material response. Flow characterization tests construct a general knowledge of the test condition temperature, composition, and enthalpy. Tests with relatively inert argon plasmas established a baseline for the pyrolysis gases that leave the material. Key pyrolysis species such as CN Violet bands, NH, OH and Hydrogen Alpha (H_α) lines were seen with relative repeatability in temporal, spectral, and intensity values. Tests with incremental addition, and static mixtures, of reactive plasmas provided a preliminary image of how the gases interacted with atmospheric flows and other pyrolysis gases. Evidence of a temporal relationship between NH and H_α relating to nitrogen addition is seen, as well as a similar relationship between OH and H_α in oxygen based environments. Temperature analysis highlighted the reaction of the material to various flow conditions and displayed the in depth material response to argon and air/argon plasmas. The development of spatial emission analysis has been started with the hope of better resolving the previously seen pyrolysis behavior in time and space.

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CHAPTER 1

INTRODUCTION

1.1 OBJECTIVE AND SCOPE

Space travel and planetary exploration missions experience intense thermal loading as they re-enter the atmosphere [28]. The high speed trajectories of these spacecrafts can reach upwards of 15 km/s. These velocities must be reduced greatly to insure safe passage of the spacecraft and its cargo as it passes through atmosphere to its landing. The blunt geometry of modern spacecraft have been used effectively to accomplish this task by dissipating the kinetic energy from velocity to heat through shock wave creation and atmospheric flow friction. The atmospheric molecules absorb the energy associated with friction, ionizing, and forming a chemically reactive plasma around the surface of the spacecraft. The plasma deposits its energy through chemical, convective, and radiative heat transfer. This environment can rapidly damage the re-entry vehicle. To mitigate damage, Thermal Protection Systems (TPS) have been designed and implemented to protect the vehicle from the associated high temperature and enthalpy loads [15]. Size and mass are primary considerations in the design

of spacecrafts, meaning low mass, highly efficient TPS materials are needed. The focus of this study is to quantify and characterize the behavior of on TPS material, Phenolic Impregnated Carbon Ablator (PICA) and its pyrolysis gases in time and space to improve the understanding of the associated gas chemistry between TPS and the re-entry environment. Spectroscopic and thermal measurement techniques are implemented to observe and describe the species and reactions present. The same methods are used to characterize the test conditions for model verification and cross-facility comparisons. The results can be used in conjunction with other studies to help improve and validated new and existing numerical models and TPS design to decrease the size of protection systems while maintaining proper heat dissipation.

1.2 BACKGROUND

Future space missions to Mars and beyond will involve larger mission payloads to pave the way for eventual human exploration activities. The recent, successful Mars Science Laboratory (MSL) Mission demonstrated the limit to our current Entry, Descent and Landing (EDL) technology [24]. At the same time, development of an advanced thermal protection system for the next manned exploration vehicle, Orion, has highlighted limitations to current Thermal Protection Systems (TPS) that have motivated renewed interest in fundamental studies of their performance under atmospheric entry plasma conditions. Figure 1.1 shows a schematic comparing the heat fluxes associated with non-ablative and ablative materials in a high-enthalpy (shock) environment.

Figure 1.1: Heat fluxes associated with non-ablative and ablative material heating [24]

There exist two main varieties of TPS materials; ablative and non-ablative materials. Non-ablative materials include metals, certain ceramics and composites [14]. This paper focuses on the ablative TPS material PICA. PICA has been used on the Stardust mission as well as the MSL mission for protecting the spacecrafts from large thermal loading (MSL heat shield shown in Figure 1.2). The term ablator/ablation refers to method of material removal through melting or vaporization due to the high temperatures and reactive environment of atmospheric re-entry. The ablation process in the re-entry plasma environment is described below [35]

1. As the convective heat flux of the atmospheric flow increases, the surface temperature of the material increases. This creates a conductive heat flux through the material thickness.
2. The material melts/vaporizes/decomposes once the exposes surface temperature exceeds the melting/vaporization temperature. Some of the convective heat flux is dissipated through this event.
3. The interface between the virgin and charred material moves away from the

surface of the material. In the case of PICA, the material pyrolyzes and is expelled against the incoming flow (described later).

4. Steady-state ablation regime is reached once recession of the surface and in-depth virgin-char interface move at a constant rate.

Figure 1.2: PICA heat shield used for Mars Science Laboratory Mission [9]

The UVM facility produces a constant convective heat flux, which is polar to that seen in re-entry, where convective heat flux increases as the vehicle descends into the atmosphere. There are other heat dissipation methods associated with PICA, including re-radiation of heat from the surface, heat storage within the char layer, chemical decomposition through gas molecule decomposition and solid material removal through shear erosion, and convective mass blowing from TPS material.

The last method is the basis for the second main cooling feature of PICA, called pyrolysis. When the material is heated, the energy transfer causes a change in the phenolic resin that is impregnated within the carbon matrix. The heating causes

exothermic chemical reactions to occur, turning the resin into a gas. These gases travel through the matrix to the surface where they meet the oncoming flow, creating a convective cooling mechanism [20] [34]. These gases are referred to as pyrolysis gases.

These two methods make PICA one of the preferred mediums for dissipating kinetic energy and reducing heating along re-entry vehicle surfaces. The combination of ablation, pyrolysis and recession mechanisms provide a reliable TPS that has been demonstrated as sufficient during missions such as Stardust, Mars Science Laboratory, and Orion missions [24].

While these mechanisms serve useful, they are not completely or thoroughly documented nor are their interactions with the reactive atmospheric plasma environment. The expelled pyrolysis gases as well as the ablative char material will interact with the plasma creating further chemical reactions and added heating along the material surface. Some of these reactions have been observed [20] but the validity is called into question. For accurate models to be developed, these interactions and gas chemistry must be observed and recorded in better temporal and spatial resolution. By doing so, the estimation of the TPS size can be refined to use less mass that can be better used for payload.

1.3 PREVIOUS AND EXISTING WORK

There currently exist several numerical modeling codes that are used to model PICA and its linked reactions and temperature/material response. One such package is the Data-Parallel Line Relaxation (DPLR) code developed at NASA Ames Research Cen-

ter. The DPLR code is full three-dimensional CFD solver with models for finite-rate reaction kinetics, thermal and chemical non-equilibrium, accurate high-temperature transport, and ionized flow physics. This makes DPLR a satisfactory solver for use in simulating realistic boundary layer conditions in coupling with TPS materials and their related response [42]. The code has been in use since 2007.

Another prominent solver developed at NASA-Ames is the Fully Implicit Ablation Thermal (FIAT) response program. The code simulates one-dimensional transient thermal energy transport in TPS materials and structure that can ablate from the top surface and decompose within the in-depth char layer [6]. The code is useful in determine B' curves which can be used to determine a pyrolysis and ablative mass flux and blowing rate. Figure 1.3 shows an example B' curve produced by FIAT.

Figure 1.3: B' curves produced by FIAT for PICA at a single pressure [6]

While these numerical models are useful in estimating material and chemical response, their full accuracy has yet to be validated, especially in the boundary layer.

The issues relating the models to the experimental results can be attributed to the defined surface boundary layer conditions as well as the coupling between the fluid modeling and material response codes [12]. These conditions in the boundary layer are often in a non-equilibrium state, leading to differences in models and ground-flight test results. Non-equilibrium conditions remain particularly difficult to simulate, especially in the boundary layer while the pyrolysis process is not completely understood as well. Due to this, many numerical codes assume chemical and local thermal equilibrium in this flow region to solve for heat flux, mass flux, recession rate, shape change, and thermal gradients [16] [7]. Thermochemical analysis of the boundary layer and material can produce gas composition and chemical reaction probabilities at elevated temperatures for pyrolyzed phenolic resin, but the estimates remain subject to improvements [19] [43].

Methods and attempts to improve these codes have been made and are continuing to be made. Tests conducted at NASA Ames' Aerodynamic Heating Facility (AHF) and Interaction Heating Facility (IHF) have given some recent additional knowledge to pyrolysis mechanisms. Extensive tests have been done to study the numerous characteristics associated with PICA and its carbon substrate, FiberForm, such as Effective Heat of Ablation, In-Depth Temperature Response and Thermal Conductivity [34] [8] [3]. These characteristics apply to the thermal response of PICA.

In addition to these results, spectroscopic methods have been developed and tested to observe and describe the pyrolysis gases and their chemical interactions in the boundary layer [29] [41]. These methods have been applied at UVM's ICP Facility in previous studies. Using emission spectroscopy, the pyrolysis species of PICA have been probed. The preliminary emission results of PICA and FiberForm in a variety

of test gases found in this study [36] are shown in Figures 1.4, 1.5, and 1.6.

Figure 1.4: Previous PICA and FiberForm emission results in Argon [36]

Figure 1.5: Previous PICA and FiberForm emission results in Air-Argon [36]

These tests were conducted to determine the prominent pyrolysis gases expelled by PICA. By comparing PICA and FiberForm results for an argon flow in Figure 1.4, it can be seen that CN Violet and C₂ Swan dominate the spectra for PICA but are absent from the FiberForm spectra both at 6 seconds and 60 seconds of plasma exposure. Figure 1.5 shows that CN Violet and C₂ Swan are absent from the PICA spectra in diluted air and CN Violet is seen in the FiberForm. While unexpected,

(a) PICA and FiberForm in Nitrogen at 6s (b) PICA and FiberForm in Nitrogen at 60s

Figure 1.6: Previous PICA and FiberForm emission results in Nitrogen [36]

this could be caused by either the Carbon in the PICA reacting with molecular and atomic oxygen to form CO₂ and CO or caused by the recession of the sample within the holder. Figure 1.6 shows near identical results between PICA and FiberForm samples, most likely due to the dominance of the CN emission from the prominence of both carbon and nitrogen.

The methodology and arrangement behind these tests are repeated and described later. These results provided the starting point for this study. These results allow us to choose specific regions of interest to analyze as well as species of interest, including OH, NH, CN, and H_α. In addition to specific species, the temporal and spatial behavior of said species is investigated.

CHAPTER 2

ICP FACILITY AND EXPERIMENTAL ARRANGEMENT

2.1 UVM 30kW INDUCTIVELY COUPLED PLASMA TORCH

The 30-kW Inductively Coupled Plasma (ICP) Torch Facility at UVM is used to test material samples in high-enthalpy plasma flows for simulation of planetary and atmospheric entry [27]. The current design allows for subsonic operation in an attempt to simulate the hypersonic, post-shock conditions. Despite operating at subsonic flows, the facility produces test conditions that can be related to in-flight conditions seen in re-entry. The 30 kW ICP Torch was designed to simulate the high enthalpy stagnation point heating environment of planetary entry and hypersonic flight. In addition to matching the stagnation point heating, the facility allows for cross-facility comparison due to matching boundary layer edge velocity gradient, enthalpy and total

pressure [10]. Figure 2.1 shows a comparison of in-flight conditions and experimental conditions in the ICP.

Figure 2.1: Comparison of boundary layer formation of atmospheric re-entry flight conditions and UVM ICP test conditions. Non-equilibrium boundary layer formation identified by red dashed line.

While ICP facilities used for high enthalpy testing applications are not new, arc-jet facilities are more common used for re-entry flight simulation. Arc-jet facilities produce molten copper due to electrode attachments, resulting in strong copper emission lines and possible contamination of diagnostic equipment and material samples. ICP torch facilities use magnetic field coupling to produce surface heating, thus eliminating contaminants within the plasma flow. The subsonic nature of the free stream plasma provides a test environment that is closer to local thermal equilibrium (LTE) than arc-heater counterparts. This feature allows for better simulation of chemical characteristics of boundary layer thermodynamics with minimal contaminants [22]. Table 2.1 shows normal facility operating condition [27].

The ICP Torch consists of several main components, the 30 kW radio frequency power supply, the gas injection, test chamber and cooling, and the control system. An

Table 2.1: UVM ICP Torch Facility Specifications

Parameter	Specification
Test Gas	Air, Ar, N ₂ , O ₂ , CO ₂
Power	30 kW @ 2-3 MHz
Cold Wall q_{stag}	10-100 W/cm ²
Enthalpy Range	5-20 MJ/kg ⁻¹
Mach	<0.3 & >1.0
Test Pressure	100 to 200 Torr

overview of the facility is shown in Figure 2.2. The entire system starts by passing the cold test gases from the pressurized cylinders through the gas injection block, where the gas flow is directed into a annular flow pattern by a columnar insert. The flow passes through a 36 mm inner diameter quartz tube. Surrounding the quartz tube is a water-cooled copper induction coil. The coil supports an alternating current of 2-3 MHz powered by the 30 kW power supply. This induces a RF magnetic field that heats and ionizes the gas flow to form a plasma ball. The resulting plasma flows through and out the quartz tube into the stainless steel, PID pressure controlled test chamber. The gas is passed through a heat exchanger and through a vacuum, exhausting through the roof of the building. The details of each of these subsystems is explained further in subsequent sections.

Figure 2.2: Schematic of subsystems within the UVM 30kW ICP Torch Facility. The power supply, plasma chamber, gas injection system, and water cooling systems are shown [Tillson AIAA 5].

The start up procedure for the facility begins with an initial low flow primer gas argon, starting at pressures below 1 torr. Argon is used due to its "soft" properties, in that it is easy to ionize and is reactively inert. Once the power supply is initiated, the argon couples, producing the plasma. The test gas is then slowly fed into the system while increasing power and decreasing argon flow, until the desired test condition is met.

2.1.1 30 kW POWER SUPPLY

The plasma torch is powered by a Lepel Model T-30-3-MC5-TLI-RF induction heating power generator. The generator utilizes standard 3-phase alternating current converted to high voltage direct current that can be adjusted to meet the needs of the designed tests and experiments. The power supply consists of a tank circuit and an oscillator circuit. The tank circuit incorporates a system of capacitors and an induction coil. The oscillating current travels between the capacitors and the induction

coil, causing the coupling of the plasma. The induction coil is cooled by deionized water that flows through the center of the 6 mm tube. The coil wraps around the quartz tube in 6-7 rotations. Energy is passed to the plasma through each of the rotations by the induced RF magnetic field. With each pass, the energy through the coil is gradually dissipated [27].

To account for the tank circuit energy dissipation, the tuned oscillator replenishes the lost energy. These systems work in unison to automatically match the oscillator source frequency with the tank circuit frequency as it changes with the dynamic test conditions. The source current is maintained by small adjustments related to the impedance of the tank circuit, which is done with a tunable grid setting. The oscillator is kept at the resonant frequency by adjusting the grid current loop through transfer of a small amount of power from the tank circuit. Efficiency of the total power system could be increased by making the induction coil and plasma flow the same diameter, but due to space constraints, this would increase the chance of electrical arching between the coil and the plasma, facility, or the coil itself [27].

2.1.2 GAS INJECTION, TEST CHAMBER AND COOLING SYSTEM

The test gases are contained in pressurized cylinders before being passed through individually dedicated MKS M100B Series mass flow controllers into the injection system. Each flow controller is calibrated for a specific test gas, with flow amounts ranging from a maximum of 2 standard liters per minute (slpm) to 50 slpm. After passing through the flow controllers, the gas enters into the injection block, shown in

Figure 2.3a. The block is based on a design by Playez [29]. The gas is mixed within the injector and passes up along the walls of a center brass insert, into the quartz confinement tube. The thin gap between the brass insert and the quartz tube allow for annular alignment of the flow. The end of the brass insert creates a low pressure zone, inducing recirculation allowing for the coupling of the gas. This sustained recirculation allows for the continued coupling of the plasma for the duration of the test. The quartz tube has a melting temperature and resistivity of 2000 K and 10^6 Ohms respectively [27]. In addition to the convective cooling of the incoming gases, this protects the quartz tube from melting and additional failures. Figure 2.3b shows the coupled plasma within the quartz tube.

(a) Schematic of UVM's gas injection block (b) Coupled plasma with quartz tube and induction coil

Figure 2.3: Gas injection block assembly and effective coupled plasma [27]

Upon leaving the quartz tube, the plasma flow enters into the stainless steel test chamber, shown in Figure 2.4. The flow is maintained in a turbulent fluid state for the extent needed to test samples by keeping the operating pressure at 160 torr. The test chamber includes a numerous optical windows (including side and underneath viewing) for data collection from an array of sensors and systems. The chamber also

includes a water cooled base as well as a heat exchanger coil in the top to cool exhaust gases before entering into the vacuum pump.

Figure 2.4: Air-Argon plasma in UVM ICP facility

The entire system is cooled by a recirculating pump and a dedicated heat exchanger. The water lines cool the probe holders, injection block, center brass insert, top of the quartz tube, chamber base, and the chamber heat exchanger. The chamber heat exchanger consists of flanges attached to concentric tubing that moves the remaining heat out of the gas into the water lines. The power supply's cooling loop is independent of the torch cooling since it uses deionized water, but it shares the main heat exchanger with the entire system.

2.1.3 CONTROL SYSTEM

To control the numerous flow, pressure, and temperature settings in the facility, a LabVIEW program was developed to simplify and assist in the process [5]. The gas flow is controlled by slider commands that adjust the mass/volumetric flow into

the chamber. The chamber pressure is kept at a set pressure through the use of a PID (Proportional Integral Derivative) control loop that is directly attached and integrated into the vacuum pump. The cooling line temperatures are monitored in the program by thermocouples installed in the water in-feed and out-feed lines. This feature is useful in monitoring the injector and bass insert temperatures to insure that failure is avoided.

2.2 SAMPLE MATERIAL AND DESIGN

2.2.1 PICA AND MUSHROOM DESIGN

As previously mentioned, the material of interest in this study is Phenolic Impregnated Carbon Ablator (PICA) and its substrate FiberForm. FiberForm is a low density, rigid, carbon matrix that is designed to withstand temperatures up to 2750° C. FiberForm is best utilized when it is oriented such that the matrix and fiber layers run perpendicular to the direction of heating/plasma flow direction. The material has a density of 0.190 g/cm³ on average [11]. A FiberForm sample is shown in Figure 2.5a.

FiberForm serves as the substrate for PICA. To create the final form of the material, a proprietary phenolic resin is impregnated within the FiberForm matrix through a vacuum process. The details of the operation and chemical composition of the resin was not disclosed for this study. The material was provided by Langley Research Center from a previous manufacturing operation. A PICA sample is shown in Figure 2.5b

Figure 2.5: FiberForm and PICA materials tested.

The mushroom geometry of the samples test is shown in Figure 2.6. The geometry has been used in prior studies [36]. The design has a diameter of 1 inch and a total thickness of 1 inch. Only 0.5 inches are exposed while testing. The remaining thickness serves as a stem with a diameter of 0.412 inches. The stem has an included notch that is used to hold the sample in the holder, described later. The corner radius is 0.125 inches. This radius is the same as the heat flux calorimeter used in the lab to ensure comparable test environment diagnostics through matching stagnation point velocity gradients.

Figure 2.6: Mushroom sample geometry

In addition to the density, the porosities of PICA and FiberForm serve as a good indicator of its performance and material characteristics. Using the high resolution microCT scanner at UVM, a plug sample of both materials was scanned. The scanning software includes a porosity calculator. Using this tool the porosity of the PICA and FiberForm was estimated to be 70% and 82% respectively. The cross sectional scan images of both materials are shown in Figure 2.7.

(a) PICA cross-section scan, $\varphi=70\%$ (b) FiberForm cross-section scan, $\varphi=82\%$

Figure 2.7: microCT scans showing sample porosity through cross-section

2.2.2 SAMPLE HOLDER

The material samples were tested using two sample holders; one designed for direct insertion into the plasma, and another designed for instrumentation. The insertion probe is shown in Figure 2.8. The probe was previously designed for testing similar mushroom geometry samples [36]. The holder is water-cooled through concentric copper tubing. The holder runs on a threaded rod that drives the probe into the flow when desired. The holder can be adjusted vertically and horizontally.

Figure 2.8: Water-cooled insertion sample holder

The other sample holder was also designed for a previous study ran in the UVM Plasma Test and Diagnostics Laboratory [27], shown in Figure 2.9. The holder consists of copper tubing with two 135° and one 90° bends to align the hold in the path of the plasma. Like the insertion probe, the gooseneck holder is water-cooled with concentric copper tubing. This probe includes a center tube that allows access for an array of instrumentation. In this study, thermocouples are used in conjunction with the probe to register in-depth temperature behavior.

Figure 2.9: Water-cooled gooseneck sample holder [27]

2.3 EMISSION SPECTROSCOPY

Emission spectroscopy is a simple, non-intrusive diagnostic tool that served as the primary data collection method for this study. Its main purpose was to observe and identify pyrolysis gases and their associated interactive chemistry in the boundary layer and out into the free plasma stream. The method functions by collecting light emitted by atomic and molecular transitions. These transitions occur when an atom or molecule that is in a thermally excited upper energy state returns to its lower energy ground state [16]. These energies expelled can be in the form of rotational, vibrational, and electronic energy transitions. Atomic transitions only happen in electronic transitions while molecular transitions include all described. Figure 2.10 shows a simple diagram of the above energy modes.

Figure 2.10: Energy modes and diagram of molecules and atoms

Key pyrolysis species were identified and studied based on prior investigations and preliminary testing [36]. These species include both atomic elements and molecular compounds that are generated as a product of pyrolysis [33]. Table 2.2 lists the species of interest and their transitions, wavelength locations, oscillator strengths, and Einstein A spontaneous emission probabilities [16] [40] [4]. Figure 2.11 shows a SPECAIR [16] model of the pyrolysis species.

Table 2.2: Pyrolysis Species of Interest and Associated Spectroscopic Constants [16] [40] [4]

	<i>Transition</i>	λ (μm)	f	A_{ul} (sec^{-1})
CN Violet $\Delta v=0$	$B^2\Sigma^+ \rightarrow X^2\Sigma^+$	0.365 - 0.390	3.36×10^{-2}	1.49×10^7
CN Violet $\Delta v=+1$	$B^2\Sigma^+ \rightarrow X^2\Sigma^+$	0.400 - 0.425	2.95×10^{-3}	1.54×10^6
CN Violet $\Delta v=-1$	$B^2\Sigma^+ \rightarrow X^2\Sigma^+$	0.330 - 0.360	6.57×10^{-3}	2.53×10^6
C ₂ Swan $\Delta v=0$	$D^3\Pi \rightarrow A^3\Pi$	0.475 - 0.520	3.05×10^{-2}	7.63×10^6
C ₂ Swan $\Delta v=+1$	$D^3\Pi \rightarrow A^3\Pi$	0.520 - 0.565	1.43×10^{-2}	4.34×10^6
C ₂ Swan $\Delta v=-1$	$D^3\Pi \rightarrow A^3\Pi$	0.430 - 0.475	1.28×10^{-2}	2.75×10^6
OH	$A^2\Sigma^+ \rightarrow X^2\Pi$	0.305 - 0.330	8.00×10^{-4}	1.21×10^5
NH	$A^3\Pi \rightarrow X^3\Pi^-$	0.325 - 0.350	8.00×10^{-3}	N/A
H $_{\alpha}$	$3p^2P^0 \rightarrow 2s^2S$	0.656	6.41×10^{-1}	4.41×10^7
H $_{\beta}$	$4d^2D \rightarrow 2p^2P^0$	0.486	1.19×10^{-1}	8.42×10^6

Figure 2.11: SPECAIR produced plot of pyrolysis species of interest

In addition to pyrolysis species, the atomic transitions of argon were observed in an effort to analyze the LTE conditions and validity in the free stream plasma. Nitrogen molecular bands were studied as well to determine the quality and quantity of contaminants within the stream. The transitions, wavelength locations, and Einstein A spontaneous emission probabilities of these features are shown in Table 2.3.

Table 2.3: Atomic Argon and Molecular Nitrogen Features of Interest and Associated Spectroscopic Constants [16] [26]

<i>Transition</i>		λ (μm)	A_{ul} (sec^{-1})
N ₂ (2+)	C ³ Π → B ³ Π	0.200 - 0.400	2.56 × 10 ⁴
N ₂ ⁺ (1-)	A ² Σ ⁺ → X ² Π ⁺	0.300 - 0.425	1.21 × 10 ⁶
Argon	3s ² 3p ⁵ (² P _{1/2} ⁰)4p → 3s ² 3p ⁵ (² P _{3/2} ⁰)4s	0.738	8.47 × 10 ⁶
Argon	3s ² 3p ⁵ (² P _{3/2} ⁰)4p → 3s ² 3p ⁵ (² P _{3/2} ⁰)4s	0.763	2.45 × 10 ⁷
Argon	3s ² 3p ⁵ (² P _{3/2} ⁰)4p → 3s ² 3p ⁵ (² P _{3/2} ⁰)4s	0.772	5.18 × 10 ⁶
Argon	3s ² 3p ⁵ (² P _{1/2} ⁰)4p → 3s ² 3p ⁵ (² P _{1/2} ⁰)4s	0.794	1.86 × 10 ⁷
Argon	3s ² 3p ⁵ (² P _{3/2} ⁰)4p → 3s ² 3p ⁵ (² P _{3/2} ⁰)4s	0.912	1.89 × 10 ⁷

2.3.1 OCEANOPTICS SPECTROMETER

Two USB-enabled emission spectrometers were used to document the majority of the results of this study. These spectrometers collect a single line-of-sight collection volume, essentially a single point at a given location. Initial tests were performed using an Ocean Optics HR4000CG-UV-NIR spectrometer. While this spectrometer has lower resolution, it enables for large wavelength range collection which is ideal to identify key species to probe with higher resolution emission or diode laser absorption options in further studies. Higher resolution tests with increased UV sensitivity were conducted using either an Ocean Optics HR2000+ spectrometer. Table 2.4 lists the specifications for these two spectrometers.

Table 2.4: Specifications of Spectrometers Used

	HR4000CG-UV-NIR	HR2000+
<i>Wavelength</i>	0.20-1.10 μm	0.20-0.42 μm
<i>Slit Width</i>	5 μm	5 μm
<i>Grating</i>	HC-1 300 G/mm	HC-1 300 G/mm
<i>FWHM</i>	1.65 nm	1.0 nm
<i>Resolution</i>	3648-element	3648-element
	linear-array CCD	linear-array CCD

The experimental setup for collection emission measurements is shown in Figure 2.12a as a top view schematic. The focal volume and subsequent collection volume is indicated by the dashed line. The emission is collected at approximately 2 mm below the 25 mm diameter sample for face emission measurements shown in Figure 2.12b. The emission is collected through a series of reflections, starting at a 50 mm diameter, 300 mm focal length concave mirror then off a 25 mm diameter flat mirror, through a 5 mm diameter aperture onto a 400 μm diameter, 2 m length optical fiber. The aperture can be adjusted as desired to achieve the desire collection volume. The setting chosen was shown to have a high f-number of 36+ and minimized collection angle to 4×10^{-5} steradians [35]. The mirrors are coated in UV-enhanced aluminum to increase the sensitivity in the UV range. The collection path is oriented as a z-fold geometry, where the light path between the sample and spherical mirror is parallel to the light path from the flat mirror to the fiber optic is a 1:1 (600 mm) design from the mirror to the fiber entrance. This yields a near-cylindrical focal volume of 3.34 mm^3 at the face for a 26.57 mm pathlength.

Figure 2.12: *Left:* A top view of the emission spectrometer setup showing the location of the test chamber (1), 25-mm diameter flat mirror (2), aperture (3), lens tube (4), 50-mm diameter, 300-mm focal length concave mirror (5) and fiber optic cable, spectrometer assembly (6). *Right:* Emission collection location given by blue dot

The location of the collection location is determined using a Helium-Neon laser, centered at $0.633 \mu\text{m}$. The HeNe laser is channeled through the optical set up and centered 2 mm below the sample face, centered across the entire diameter.

The uncalibrated setup produces emission measurements in absolute units of counts. Calibration is done using an Oriel Instruments Open Air Model 63966 tungsten filament light source. The optical set-up and tungsten lamp are positioned outside the test facility such that the window, dimensions, and lamp location mimic that of a full test condition. Light from the filament is collected by the spectrometer. This spectra is multiplied by the provided calibrated emission spectra. This gives a calibration file that can be used to transform the emission measurements to intensity units of $\text{W}/(\text{cm}^2 \mu\text{m sr})$. Due to the lack of light provided by the tungsten lamp in the UV and the low response of the spectrometer in the IR, the usable range is limited to $0.30\text{-}0.90 \mu\text{m}$. This procedure is completed with confidence for the HR4000CG-UV-NIR spectrometer. The HR2000+ spectrometer has been tentatively calibrated

using the emitted light from the tungsten lamp in the 0.19-0.42 μm region. While this method does not generate a completely accurate calibration, it does provide a better means of comparison between spectrometers. The full calibration routine and associated calibration files are explained further in Appendix A.

2.3.2 PRINCETON INSTRUMENTS ISOPLANE

Single point emission measurements, while useful to a degree, are limited in that they give little detail on how the complex species of a pyrolyzing ablator interact spatially within a high-temperature boundary layer. A two-dimensional imaging spectrometer has recently been integrated into the UVM ICP facility presenting the ability to acquire spatially resolved emission in this complex region. The Princeton Instruments IsoPlane320 is a 0.32 m, high resolution, multi-grating spectrometer that is capable of not only highly resolving spectral intensity and wavelength, it also utilizes a PIXIS:256 imaging CCD to capture spectra in a planar field [23]. Table 2.5 lists relevant specifics for the general system and available grating options.

Table 2.5: IsoPlane Specifications

<i>Wavelength</i>	See Grating
<i>Slit Width</i>	5 10 μm - 3 mm
	600 G/mm ruled - 300 nm blaze
<i>Grating</i>	600 G/mm ruled - 500 nm blaze
	900 G/mm Holographic - NIR Optimized
	0.142 nm (300 nm blazed)
<i>FWHM</i>	0.140 nm (600 nm blazed)
	0.09 nm (NIR optimized)
<i>Resolution</i>	PIXIS 1024 x 256 (26 mm x 6.7 mm)
	element imaging CCD

A schematic of new imaging configuration along with an illustration of general imaging location near sample surface is given in Figure 2.13. The basic design is similar to that used for the OceanOptics spectrometers. The target collection region was imaged onto the vertical entrance slit of the spectrometer using a z-folded optical collection assembly that incorporated a 300 mm concave mirror, where d_o is 736.6 mm, d_{i1} is 190.5 mm d_{i2} is 330.2 mm. This configuration led to a measurement region of $h=9.5$ mm that was imaged onto the vertical 256 pixels of the CCD. The entrance slit was set to the most narrow value of between 0.01 to 0.02 mm. This slit narrowing allowed for maximum system spectral resolution in this imaging mode. Calibration for this spectrometer is currently in development.

Figure 2.13: *Left:* IsoPlane spectrometer integration schematic., *Right:* Vertical emission collection given by blue dashed line

2.3.3 COMPARISON OF SPECTROMETER RESOLUTION

The spectrometers used in this study offer different spectral ranges, measured intensities, and resolution. As previously mentioned, the HR4000CG-UV-NIR spectrometer has a wide spectral range but with reduced resolution, the HR2000+ covers a smaller spectral range, but has increased sensitivity and spectral resolution in the UV region, and the IsoPlane has a smaller spectral range but the highest signal resolution. Figure 2.14 clearly displays the differences in resolution between the spectrometers. When comparing the NH (A-X) band, the IsoPlane is able to identify individual features on either side of the main band the clearest, while the other spectrometers do not have the same resolution to clearly distinguish without blending the features? signal. The same trend is seen in both OH (A-X) and CN (B-X) bands, especially when considering the HR4000CG-UV-NIR signal which does not show any minor rotational features where as the two higher resolution spectrometers display the features to varying degrees. Each spectrometer continues to serve a purpose; the HR4000CG-

UV-NIR allows for species of interest to be broadly identified, the HR2000+ can be used to better resolve and observe said features and the IsoPlane can be used for high precision and validity final measurements both in a single and multiple line-of-sight configuration [23].

Figure 2.14: *Left Column:* IsoPlane Spectrometer, with an integration time of 0.1 seconds. *Center Column:* HR2000+ Spectrometer, with an integration time of 0.1 seconds. *Right Column:* HR4000CG-UV-NIR Spectrometer, with an integration time of 1 seconds.

2.4 TWO-COLOR PYROMETRY

A two-color pyrometer (model Raytek RAYMR1SCCF) was used to record surface temperature during testing. The pyrometer is oriented underneath the test chamber to aim upwards at the face exposed to the plasma flow. The surface is observed by the pyrometer in two-color mode through a pyrex window with a transmittance of approximately 92% between 0.4 and 2.0 μm . The temperature is determined by

measuring the integrated ratio of two wavebands, one from 0.75 to 0.95 μm and from 0.90 to 1.1 μm . The temperature range for this model is 1000-3000° C. There are questions regarding the pyrometers accuracy when the image is bounced off a mirror, but for this study the imaging is done directly. The instrumentation set-up is shown in Figure 2.15.

Figure 2.15: Pyrometer instrumentation arrangement

2.5 HIGH TEMPERATURE THERMOCOUPLES

In depth temperature for select samples were recorded as well as surface temperature. Type K (Ni-Cr/Ni-Al) thermocouples from Omega were used to measure the material temperature within the sample. The thermocouples have a temperature range of -270°-1372° C. Three thermocouples were positioned along the centerline at approximately 0.12", 0.28", and 0.50" behind the sample face. Figure 2.16 shows the locations.

Figure 2.16: Instrumented thermocouple locations

CHAPTER 3

LOCAL THERMODYNAMIC EQUILIBRIUM

Local thermal equilibrium (LTE) is described as the thermal condition in which the excitation and de-excitation of atomic and molecular species are caused primarily by particle collision instead of radiative or absorption processes [32] [38]. This condition is not complete equilibrium, but rather a quasi-equilibrium state. If the conditions of the plasma are determined solely on collisions, then the atomic and molecular state populations can be assumed to be in their equilibrium states. In this state, the particle's characteristics are governed and defined by the Boltzmann distribution, shown in Equation (3.1). Equations (3.2) and (3.3) shows the simplification of the partition function to g_i through the exponential terms going to 0 or 1 [26] [31]. These equations will define both the upper and lower state number densities as well as the local thermodynamic equilibrium temperature.

$$\frac{n_o}{n_i} = \frac{g_i \exp(\frac{\epsilon_i}{k_B T})}{Q} \quad (3.1)$$

$$Q = Q_{elec} = \sum_j g_j \exp^{\frac{-\varepsilon_j}{k_B T}} \quad (3.2)$$

$$Q_{elec} = g_o \exp^{\frac{0}{T}} + g_1 \exp^{\frac{-134070}{T}} + g_2 \exp^{\frac{-134944}{T}} = g_o + 0g_1 + 0g_2 = g_o \quad (3.3)$$

One of the key assumptions within the Plasma Test and Diagnostics Laboratory is that the ICP torch resides in LTE. The assumption means that the state of the plasma is close to equilibrium before any interaction with a material sample. This simplifies the mathematical and spectroscopic analysis of interactions that occur in the boundary layer and as a result of pyrolysis between the plasma and the sample. If the condition of the plasma is based solely on the collisional interactions of the plasma, then the heat flux associated with the samples is simplified. This allows for radiative, absorption, and black/grey body effects to be either disregarded or minimized.

Previous experiments and studies have looked at the plasma ball and free stream conditions and concluded that the studied states resemble LTE but lack complete validation [18] [29]. This study utilizes argon plasma and varying dilutions as the primary test condition. There has been little investigation into the LTE validity of argon plasmas in the facility, prompting the need for such analysis for this study. Several different evaluations were performed, with the mathematical and spectroscopic theory described below.

3.1 EMISSION SPECTROSCOPY

Emission spectroscopy is a useful tool in the analysis of pyrolysis characteristics due to its minimally invasive set-up and operation, as described in Section 2.3. The process measures and outputs a spectral irradiance of units $\text{W}/\text{cm}^2 \mu\text{m sr}$. This value describes the two-dimensional power density of the emitted light per μm of spectrum per unit steradian. In these units, the spectrum intensity is defined for each individual line strength at each line (or wavelength) position, giving a starting point for number density and temperature analysis.

The methodology used is based on the process defined by Laux [16] and Vancraynest [37]. The process starts with the definition for spectral radiance, Equation (3.4), and the modified Boltzmann distribution expression, Equation (3.5). The upper and ground state degeneracies are expressed as g_i and g_o , the upper and ground state number densities are expressed as n_i and n_o . The state energies are given as $\varepsilon_{ul} = hc\nu_{ul}$, where h is the Planck constant, c is the speed of light and ν is the state energy in units cm^{-1} .

$$E\left[\frac{W}{\text{cm}^3 \text{sr}}\right] = \frac{n_i A_{ul} \Delta\varepsilon_{ul}}{4\pi} \quad (3.4)$$

$$\frac{n_o}{n_i} = \frac{g_i \exp\left(\frac{hc\nu_u}{k_B T}\right)}{g_o} \quad (3.5)$$

The spectral radiance in Equation (3.4) is found using Equation (3.6), where l is the emission pathlength (2.54 cm for material sample tests and 3.8 cm for free stream tests). The desired feature is integrated over a wavelength region that encapsulates

the entire feature. For an atomic feature, this would start before the first indication of signal and end after the signal has decayed. A line shape function can be applied if desired, but was omitted for this investigation.

$$E = \int_{\lambda_1}^{\lambda_2} \frac{I}{l} d\lambda \quad (3.6)$$

This value can be substituted into Equation (3.4) and the upper state number density of the desired species can be solved for, shown in Equation (3.7). This gives a number density in the units of cm^{-3} .

$$n_i = \frac{4\pi}{A_{ul}} \frac{\int_{\lambda_1}^{\lambda_2} \frac{I}{l} d\lambda}{\varepsilon_u - \varepsilon_l} = \frac{4\pi}{A_{ul}} \frac{\int_{\lambda_1}^{\lambda_2} \frac{I}{l} d\lambda}{hc(\nu_u - \nu_l)} \quad (3.7)$$

The upper state number density can be inserted into Equation (3.5). This allows the ground state number density to be full defined by known or measured values, shown in Equation (3.8)

$$n_o = \frac{g_i}{g_o} \frac{4\pi}{A_{ul}} \frac{\int_{\lambda_1}^{\lambda_2} \frac{I}{l} d\lambda}{hc(\nu_u - \nu_l)} \exp\left(\frac{hc\nu_u}{k_B T}\right) \quad (3.8)$$

If the temperature is known, then the number density of a given species can be calculated using Equation (3.8). While this general concept can be applied to either atomic or molecular species, this specific model is derived for atomic analysis based on the integration of atomic line features rather than molecular bands. The number density is largely dependent and sensitive to the temperature at the measured position and condition, leading to widely varying and interesting results. The full analysis of Argon and Hydrogen features and specific constants and energy levels are described and defined in Chapters 4 and 5.

The number density expression can also be used to determine the local thermodynamic equilibrium temperature (T_{LTE}) from an emission measurement. To do so, some simple assumptions are made to simplify the equation and process. The main assumption is that the ground state number density can be defined through the statistical mechanics definition of the ideal gas law, given in Equation (3.9). This expression assumes that at the operating pressure and temperature, the ground state population is filled and in equilibrium. This process, detailed fully later, is best suited for free stream measurements as opposed to emission measurements beneath a sample.

$$P = nk_B T \rightarrow n = \frac{P}{k_B T} \quad (3.9)$$

If the temperature in the above equation is assumed to be the T_{LTE} , then the expression for number density can be used to modify Equation (3.8). This formulation would create an equation that has temperature as the singular variable. Equation (3.10) shows the modification.

$$\chi_{Ar} \frac{P}{k_B T_{LTE}} = \frac{g_i}{g_o} \frac{4\pi}{A_{ul}} \frac{\int_{\lambda_1}^{\lambda_2} \frac{I}{l} d\lambda}{hc(\nu_u - \nu_l)} \exp\left(\frac{hc\nu_u}{k_B T_{LTE}}\right) \quad (3.10)$$

Because temperature is the only variable, the above equation can be solved numerically. The first step is obtaining an expression with the temperature variable on the same side of the equation, as shown in Equation (3.11). While the equation cannot be solved algebraically, it can be solved graphically and numerically. Since the right hand side of the equation is known based on the constants for whichever species is under analysis, the left hand can be reduced, in this case using MATLAB, to find the given temperature.

$$T_{LTE} \exp\left(\frac{hc\nu_u}{k_B T_{LTE}}\right) = \chi_{Ar} \frac{g_o}{g_i} \frac{P}{k_B} \frac{A_{ul}}{4\pi} \frac{hc(\nu_u - \nu_l)}{\int_{\lambda_1}^{\lambda_2} \frac{I}{l} d\lambda} \quad (3.11)$$

This method produces an LTE temperature that is dependent on the spectroscopic constants of the species of interest and the signal acquired experimentally. As mentioned previously, this method works best for free stream measurements due to the lack of recombination, pyrolysis, blowing, and gas chemistry effects typically seen in boundary layer interactions. This method is also a line-of-sight analysis, meaning the temperature is a path average of the entire emission along the chord length collected within the free stream plasma. This average is generally a suitable measurement, but other techniques are known and utilized to further understand the local thermodynamic equilibrium conditions of the plasma, especially in a radial dimension.

3.1.1 ABEL INVERSION

To obtain radial-distributed emission values, an Abel inversion can be applied to the experimental measurements to convert them from a length averaged chord measurement to a radial measurement. The inversion is dependent on axially-symmetric flow. Figure 3.1 shows a top view of the collection configuration. As described in Section 2.3, the emission arrangement collects light along the principal focal axis, with a set path length, of radiance $I(x)$. If the x -position of the radiance is aligned with the center of the flow, the signal is strongest due to the highest temperature flow being confined to the jet core. Outside the jet, the radiance is zero, resulting in no signal collection.

Figure 3.1: Top view of the axially-symmetric plasma. Emission measurements along a chord length, $I(x)$, are converted to radial emission measurements, $e(r)$, by an Abel inversion [17]

In the Abel inversion, the measured radiance is related to the radial emission as described in Equation (3.12). The measured radiance is found by integrating desired features to find an integrated area value of radiance with units W/m^2 .

$$I(x) = 2 \int_r^R \frac{r e(r)}{\sqrt{r^2 - x^2}} dr \quad (3.12)$$

To find the the radial emission radiance, Equation (3.12) is inverted as shown in Equation (3.13). This process is known as the Abel inversion.

$$e(r) = -\frac{1}{\pi} \int_r^R \frac{dI/dx}{\sqrt{x^2 - r^2}} dx \quad (3.13)$$

The full analytical process of the Abel inversion is done as described by Lutz [17]. This process involves fitting the measured radiance with a polynomial fit of 4 - 7 degrees [13], [29], [16]. This process ensures an precise and smooth input into the inversion due to the sensitivity of the radially-distributed emission signal. The inversion was done using the mathematical scheme and MATLAB code written by Lutz. This inversion transforms the measured radiance from an per area value to a pre volume value of W/m³.

The same process as described in Equations (3.4) through (3.11) is used to extract the temperature from the radial absolute emission radiance. Since the radially-distributed spectral radiance values are a per volume measurement, $e(r)$ can be used in place of E in Equation (3.4). With this substitution, the temperature separated expression is shown in Equation (3.14) below, which is solved using the same method given earlier.

$$T_{LTE} \exp\left(\frac{hc\nu_u}{k_B T_{LTE}}\right) = \frac{g_o}{g_i} \frac{P}{k_B} \frac{A_{ul}}{4\pi} \frac{hc(\nu_u - \nu_l)}{e(r)} \quad (3.14)$$

This analysis generates a radial temperature distribution. The previous analyses described calculate a point-wise, path length averaged value that is valid, but potentially less accurate. The Abel Inversion method also details the total temperature gradient that the radial component of the sample experiences.

3.2 ENTHALPY AND TOTAL POWER

3.2.1 THEORETICAL APPROACH

In addition to temperature, the total enthalpy of the free stream can be calculated using measured values and known constants. Temperature is a generalized aspect of the flow, describing the molecular behavior of the ionized gas, but it doesn't fully characterize the conditions of the flow. By determining the enthalpy, the flow conditions can be better characterized. With enthalpy, the heat flux, heating capacity, and heat transfer rates can be defined. The flow conditions can also be compared to other facility's enthalpy conditions.

Determining the total enthalpy requires the calculation of the thermal and dissociation energies of the free stream plasma. One must know the composition and characteristics of the species in the plasma to compute the quantities of these enthalpies. To determine the composition of the plasma, the experimental spectra was compared to a SPECAIR generated simulation spectra at the calculated condition temperature, described later. When the spectrums are matched, the mole density of each species (Argon and contaminants N_2 and O_2) are determined. With the dissociation energies from Vincent and Krueger [38], the total enthalpy can be found. The process is as follows. First, the number densities at the known mole fractions for O_2 and N_2 are determined to affirm the plausibility of the conditions, as shown in Equations (3.15) and (3.16).

$$n_{O_2} = \chi_{O_2} \frac{P}{k_B T} \quad (3.15)$$

$$n_{N_2} = \chi_{N_2} \frac{P}{k_B T} \quad (3.16)$$

Once the condition has been validated, the per molecule mass of oxygen and nitrogen can be found. This determination is later used to turn the dissociation enthalpies into a per mass measure. The calculations are shown in Equations (3.17) and (3.18). N_A is Avogadro's number, 6.022×10^{23} particles per mole.

$$m_{O_2} = \frac{MW_{O_2}}{N_A} \quad (3.17)$$

$$m_{N_2} = \frac{MW_{N_2}}{N_A} \quad (3.18)$$

The per molecule mass can then be used to find the dissociation enthalpies, described in Equations (3.19) and (3.20). These are found using the dissociation energies for oxygen and nitrogen, which have units of 59,500 K and 113,000 K respectively. This value is transformed to Joules by the Boltzmann constant.

$$h_D(O_2) = \frac{\Theta_{O_2} k_B}{m_{O_2}} \quad (3.19)$$

$$h_D(N_2) = \frac{\Theta_{N_2} k_B}{m_{N_2}} \quad (3.20)$$

To find the enthalpy flux, or dissociation power, from these enthalpies, the mass flow of the gases are next determined. This process is shown in Equations (3.21), (3.22), and (3.23). The densities, ρ , are determined at STP with each species respective gas constant ($R_{Ar}=208.1$, $R_{O_2}=259.82$, $R_{N_2}=296.99$).

$$\dot{m}_{Ar} = \rho_{Ar} \dot{V}_{Ar} = \frac{P_{atm}}{R_{Ar} T_{atm}} \dot{V}_{Ar} \quad (3.21)$$

$$\dot{m}_{O_2} = \rho_{O_2} \dot{V}_{O_2} = \frac{P_{atm}}{R_{O_2} T_{atm}} \dot{V}_{O_2} \quad (3.22)$$

$$\dot{m}_{N_2} = \rho_{N_2} \dot{V}_{N_2} = \frac{P_{atm}}{R_{N_2} T_{atm}} \dot{V}_{N_2} \quad (3.23)$$

Equations (3.24) and (3.25) show the calculation of the dissociation enthalpy flux from the above expressions and the dissociation enthalpies.

$$\dot{h}_D(O_2) = h_D(O_2) \dot{m}_{O_2} \quad (3.24)$$

$$\dot{h}_D(N_2) = h_D(N_2) \dot{m}_{N_2} \quad (3.25)$$

To determine the total enthalpy of the plasma, the thermal enthalpy needs to be determined as well. The thermal enthalpy is calculated using the total gas constant for the plasma and the temperature of the plasma, as found using the theory described in Section 3.1. The total gas constant calculation is shown in Equation (3.26) and the expressions for thermal enthalpy and thermal enthalpy flux are shown in Equation (3.27) and (3.28).

$$R_m = \chi_{O_2} R_{O_2} + \chi_{N_2} R_{N_2} + \chi_{Ar} R_{Ar} \quad (3.26)$$

$$h_{th} = \frac{5}{2}R_mT \quad (3.27)$$

$$\dot{h}_{th} = h_{th}(\dot{m}_{Ar} + \dot{m}_{O_2} + \dot{m}_{N_2}) = h_{th}\dot{m}_{total} \quad (3.28)$$

With the total dissociation and thermal enthalpy fluxes calculated, the sum can be taken to find the total enthalpy flux then the total enthalpy by dividing by the total mass flow, shown in Equations (3.29) and (3.30).

$$\dot{h}_{total} = \dot{h}_{th} + \dot{h}_D(O_2) + \dot{h}_D(N_2) \quad (3.29)$$

$$h_{total} = \frac{\dot{h}_{total}}{\dot{m}_{total}} \quad (3.30)$$

3.2.2 POWER SUPPLY APPROACH

In the previous section, the total enthalpy is derived and calculated using known species characteristics and experimentally collected values. A secondary approach using the conditions of the facility power supply can be used to validate the analysis and to find the flow temperature for comparison and validation against previous mathematical methods.

The total power output of the power supply can be easily calculated from the plate amperage and voltage. The total power output is not transferred in full to the plasma. Energy is lost in the form of heat transfer, radiation, and facility cooling. With these parameters, the power transfer coefficient of the power supply is 0.3 [27].

Equation (3.31) shows the calculation.

$$P = \dot{h}_{total} = 0.3I_{plate}V_{plate} \quad (3.31)$$

Since the dissociation enthalpy fluxes are known from Equations (3.19) and (3.20), the thermal enthalpy flux can be found using the total power output of the power supply, shown in Equation (3.32). The expression for thermal enthalpy and thermal enthalpy flux are known as well, meaning the only unknown variable in this approach is the temperature, thus it can be solved for. This equality is displayed in Equation (3.33).

$$\dot{h}_{th} = \dot{h}_{total} - \dot{h}_D(O_2) - \dot{h}_D(N_2) \quad (3.32)$$

$$T = \frac{\dot{h}_{total} - \dot{h}_D(O_2) - \dot{h}_D(N_2)}{2.5R_m\dot{m}_{total}} \quad (3.33)$$

This temperature calculation can be compared to the temperatures found in the emission spectroscopy and abel inversion methods. Each method is different, but having multiple approaches for determining LTE temperature improves the validity of the measurements and the analysis of the pyrolysis species and mechanisms.

CHAPTER 4

LTE ANALYSIS OF TEST CONDITIONS

The materials of focus in this study were tested in a variety of test gases. While a general understanding of the flow conditions are known, a better characterization is needed to validate the results, for comparison across other facilities, and for future modeling purposes. One key aspect of this is determining the LTE conditions of test gas mixtures, specifically the argon, argon/oxygen, and argon/nitrogen mixtures. As previously explained, this distinction allows for several conclusions and analyses to be made.

There are several conditions needed to determine the full characterization of the test gases and mixtures. Temperature is the most straight forward and easiest to correlate. Multiple approaches were used to calculate and verify the free stream temperature. With the temperature known, the flow composition can be found using simulation and modeling software. Finally, with both of these aspects, the flow enthalpy and enthalpy flux (power) can be calculated.

4.1 TEMPERATURE ANALYSIS AND SENSITIVITY

4.1.1 LASER-INDUCED FLUORESCENCE

The first method used to estimate the free stream temperature was two-photon absorption laser induced fluorescence (TALIF). The Plasma Test and Diagnostics Lab utilizes a frequency-doubled Nd:YAG laser system that creates a 532 nm laser. This radiation pumps a dye laser to produce a tunable laser from 600 to 700 nm. This laser is frequency doubled then mixed with residual red light to produce 200 to 233 nm radiation. This wavelength region allows for probing atomic species of interest to the lab [2] [17] [21].

At the desired UV wavelength (in this case, 211 nm for nitrogen), the laser beam is used to induce two-photon excitation [30] in the torch (ICP) and in a microwave discharge flow reactor (MDFR). The laser is scanned across the frequency tripled wavelength range to capture the feature of interest. A Gaussian distribution is fit to the measured sets of data to extract a full-width at half-maximum (FWHM), as seen in Figure 4.1.

Figure 4.1: Sample TALIF scan of nitrogen atom feature at 211 nm over copper in an air plasma [2]

With the FWHMs known, the temperature can be extracted using the simplified process shown in Equations (4.1) through (4.4). The full and detailed process is explained in theses by Lutz [17] and Allen [1].

$$(\Delta \hat{\nu}_{tot,ICP})^2 = (\Delta \hat{\nu}_{D,ICP})^2 + 2(\Delta \hat{\nu}_{laser})^2 \quad (4.1)$$

$$(\Delta \hat{\nu}_{tot,FR})^2 = (\Delta \hat{\nu}_{D,FR})^2 + 2(\Delta \hat{\nu}_{laser})^2 \quad (4.2)$$

$$\Delta \hat{\nu}_{D,FR} = \frac{\hat{\nu}_0}{c} \sqrt{\frac{2k_B T_{FR}}{M}} = \hat{\nu}_0 \cdot 7.162 \times 10^{-7} \sqrt{\frac{T_{FR}}{M}} \quad (4.3)$$

$$T_{ICP} = \frac{M}{(\hat{\nu}_0 \cdot 7.162 \times 10^{-7})^2} [(\Delta \hat{\nu}_{tot,ICP})^2 - (\Delta \hat{\nu}_{laser})^2] \quad (4.4)$$

Using this process, the temperature of a 68.1 g/min argon, 2.5 g/min nitrogen plasma was determined. Four measurements were taken and the resultant temperatures were averaged. One of the scan results is shown in Figure 4.2. The calculated

free stream temperature was found to be 5700 ± 500 K. While it is not exact or precise, this assessment serves as an acceptable starting point for fully characterizing the flow temperature of the prominent test conditions.

Figure 4.2: Sample scan done of 68.1 g/min Argon and 2.5 g/min Nitrogen. Scan temperature of 5352 K calculated

4.1.2 EMISSION BASED TEMPERATURE ANALYSIS

Emission measurements of free stream test conditions were used as second method of determining the free stream temperature of various test conditions. These conditions were 71.4 g/min argon, 71.4 g/min argon and 2.9 g/min oxygen mixture, and 71.4 g/min argon and 2.5 g/min nitrogen mixture. Using the HR4000CG-UV-NIR spectrometer, multiple emission scans were taken for each condition. The argon features of interest were chosen due to there isolation from other features. Table 4.1 shows the features and their respective spectroscopic constants.

Using the integrated signal and spectroscopic constants, the temperature was calculated using Equation (3.9). The spectrum and resultant temperatures for each test case are shown in Figures 4.3, 4.4, and 4.5.

Table 4.1: Argon Spectroscopic Constants and Energy Levels [26]

	g_o	g_i	$A_{ul} (sec^{-1})$	$v_u (cm^{-1})$	$v_l (cm^{-1})$
0.738 μm	3	5	8.47×10^6	107299	93751
0.763 μm	5	5	2.45×10^7	106238	93144
0.772 μm	1	3	1.17×10^7	107492	94554
0.794 μm	1	3	1.86×10^7	107132	94554
0.912 μm	5	3	1.89×10^7	104102	93144

Figure 4.3: Emission spectrum and calculated argon temperatures of argon plasma

Figure 4.4: Emission spectrum and calculated argon temperatures of argon/oxygen plasma

Figure 4.5: Emission spectrum and calculated argon temperatures of argon/nitrogen plasma

Averaging the temperatures of the five probed features gives a strong estimate of the flow temperature for each condition; 6130 K for the argon flow, 5890 K for the argon/oxygen flow, and 5530 K for the argon/nitrogen flow.

It is interesting to note that the argon temperature was the highest despite the lack of more reactive and energetic species. Adding species such as oxygen or nitrogen (or running in pure oxygen or nitrogen) will increase the surface temperature and heat flux applied to a tested sample, as shown later. It is believed that the decrease in flow temperature is associated with the dissociation of the nitrogen and oxygen molecules. Due to its inert qualities, argon serves as a poor third party for molecular recombination (and higher flow temps). Since there is a fixed amount of energy deposited into the flow by the load coil, the dissociation energy reduces the energy fraction directly proportional to temperature. This mechanism is further detailed and validated in Section 4.3.

Uncertainty Analysis

An uncertainty analysis was performed on Equation (3.9) and the subsequent results in each test condition. The analysis was conducted using the second uncertainty procedure described in Appendix B, where uncertainty is determined as a decimal percentage. The four terms that comprise some kind of uncertainty in Equation (3.9) are the mole fraction (χ_{Ar}), pressure (P), the Einstein A coefficient (A_{ul}), and the calculated integrated intensity (I).

The first three terms have uncertainties based on their respective measurement apparatus. The mole fractions are found by means of the mass flow baratrons that have an uncertainty of $(\Delta\chi/\chi) = 0.01$. The pressure is measured by the pressure

transducer that has an uncertainty of $(\Delta P/P) = 0.01$. The uncertainty of the Einstein A coefficients is reported by Wiese [40], each having an uncertainty of $(\Delta A_{ul}/A_{ul}) = 0.25$.

The uncertainty of the integrated intensities is determined by taken the root mean square of the calibration uncertainty ($\Delta Cal/Cal = 0.028$) and the calculation uncertainty (standard deviation) of each feature of interest. The uncertainties of each feature in each condition are shown in Table 4.2.

Table 4.2: Integrated intensity uncertainty ($\Delta I/I$) for each argon line in each condition

<i>Argon Line (μm)</i>	<i>Argon</i>	<i>Argon/N₂</i>	<i>Argon/O₂</i>
0.738	0.039	0.063	0.071
0.763	0.046	0.082	0.077
0.772	0.042	0.074	0.074
0.794	0.045	0.088	0.074
0.912	0.043	0.071	0.079

To determine the effect each term's uncertainty has on the temperature calculation, the term was varied by its uncertainty while the other terms were kept constant. The new temperature was then determined for each feature. This new temperature was compared to the average temperature presented in the previous section to determine the temperature uncertainty with respect to that term, $(\Delta T/T)_x$. This was repeated for each term for each condition. With the temperature uncertainty for each term known for each feature, the total feature temperature uncertainty, $(\Delta T/T)_{feature}$, was calculated using a root mean square average. The results are shown in Tables 4.3, 4.4 and 4.5.

Table 4.3: Temperature uncertainty (term and feature total) in 71.4 g/min Argon

<i>Argon Line</i> (μm)	$(\Delta T/T)_{\chi_{Ar}}$	$(\Delta T/T)_P$	$(\Delta T/T)_{A_{ul}}$	$(\Delta T/T)_I$	$(\Delta T/T)_{feature}$
0.738	0.000415	0.000415	0.0092	0.0016	0.0096
0.763	0.000426	0.000426	0.0094	0.0019	0.0094
0.772	0.000402	0.000402	0.0089	0.0017	0.0091
0.794	0.000396	0.000396	0.0088	0.0017	0.0090
0.912	0.000436	0.000436	0.0097	0.0018	0.0099

Table 4.4: Temperature uncertainty (term and feature total) in 71.4 g/min Argon and 2.5 g/min Nitrogen

<i>Argon Line</i> (μm)	$(\Delta T/T)_{\chi_{Ar}}$	$(\Delta T/T)_P$	$(\Delta T/T)_{A_{ul}}$	$(\Delta T/T)_I$	$(\Delta T/T)_{feature}$
0.738	0.000375	0.000375	0.0083	0.0023	0.0086
0.763	0.000380	0.000380	0.0084	0.0030	0.0089
0.772	0.000363	0.000363	0.0081	0.0026	0.0085
0.794	0.000355	0.000355	0.0079	0.0030	0.0085
0.912	0.000388	0.000388	0.0087	0.0027	0.0091

Table 4.5: Temperature uncertainty (term and feature total) in 71.4 g/min Argon and 2.9 g/min Oxygen

<i>Argon Line</i> (μm)	$(\Delta T/T)_{\chi_{Ar}}$	$(\Delta T/T)_P$	$(\Delta T/T)_{A_{ul}}$	$(\Delta T/T)_I$	$(\Delta T/T)_{feature}$
0.738	0.000397	0.000397	0.0088	0.0027	0.0092
0.763	0.000405	0.000405	0.0090	0.0030	0.0095
0.772	0.000387	0.000387	0.0086	0.0028	0.0091
0.794	0.000381	0.000381	0.0085	0.0027	0.0089
0.912	0.000415	0.000415	0.0092	0.0032	0.0098

With the temperature uncertainty known for each feature, the overall uncertainty for each test condition is determined, again using a root square mean average. The argon temperature measurements have an uncertainty of 0.021 (129 K), the argon/oxygen temperature measurements have an uncertainty of 0.021 (124 K), and the argon/nitrogen temperature measurements have an uncertainty of 0.020 (111 K).

The individual contributions to the total uncertainty indicate that the Einstein A coefficient and intensities are the primary sources of uncertainty, albeit to a small degree. The overall uncertainties add to the validity of the free stream temperatures.

4.1.3 ABEL INVERSION AND RADIAL TEMPERATURE PROFILES

The temperature determined through the previous analyses was found using the path-length averaged spectral radiance. This intensity is a summation of all emission along the collection line of site. This produces a result that is more of an average value rather than a point wise value, necessitating the use of an Abel Inversion.

As described in Section 3.1.1, the process takes the integral of a desired feature's spectral radiance at various locations along the radius and uses a transformation to return a radially distributed emission radiance. The same argon features used in Section 4.1.2 were examined in this approach.

An emission scan every 1 mm for 25 mm and a fifth order polynomial fit were used to extract the radial emission distribution, as shown in Figure 4.6. These intensity values were used with Equation (3.14) to determine the radial temperature distribution, shown in Figure 4.7.

Figure 4.6: Radially distributed emission radiance of free stream argon via an Abel Inversion

Figure 4.7: Radial temperature distribution of free stream argon

In both plots, the behavior of each metric either approaches zero or sharply decreases around 14 mm from the jet center. This is an indicator that the edge of the free stream plasma is approximately 14 mm from the center of the jet at 88 mm above the chamber floor. Figure 4.8 shows the free stream with the stream edge defined at this radius. It is difficult to visually see the edge of the stream but these results best indicate the position in which ionization is no longer sustained.

Figure 4.8: Free stream argon plasma with centerline and radial location of stream edge

To validate the results, the radial temperatures were used to back calculate the radial emission intensity, $e(r)$ using Equation (3.14). The difference between the Abel inverted values and the back-calculated intensity values were found and are shown in Figure 4.9. The plot indicates that the largest difference as determined by the residual in 0.04%, affirming the accuracy of the temperature results.

Figure 4.9: Abel Inverted and Temperature Back-Calculated Radial Intensities Residuals

With these results, the temperature results can be further examined. It should first be noted that the dip and subsequent rise in temperature around and after 14 mm is due to the polynomial fit not being an exact fit. While this induces an inaccurate

result in that region, the results themselves are not of interest. The temperatures determined continue to reaffirm those found in previous analyses. The center line temperatures (0 mm) ranged 5800 K and 6300 K. As the temperature extends radially, it decreases in an increased trend as it approaches the stream edge.

4.2 TEST GAS COMPOSITION AND CONTAMINATION

With the free stream temperature known for each condition, the subsequent composition in terms of mole fractions can be estimated. SPECAIR was used for modeling each condition. Emission spectra was taken using the HR4000CG-UV-NIR and HR2000+ spectrometers at 88 mm from the nozzle, with the focus on the UV range between 0.200 and 0.500 μm . N_2^+ (1-), N_2 (2+), and NO are seen in this range and are the most prominent features for the temperatures and associated mole fractions.

The 71.4 g/min argon flow was the first condition modeled. It was known that there was some level of contamination in the flow based on the presence of molecular nitrogen vibrational bands in the flow spectrum. Using a temperature of 6100 K and a pressure of 160 torr, a model was created as shown in Figure 4.10.

Figure 4.10: Experimental (black) and SPECAIR simulated (orange) emission of 71.4 g/min argon plasma at 6100 K

With the known temperature, the oxygen and nitrogen mole fractions were determined to be approximately $\chi_{O_2} = 0.005$ and $\chi_{N_2} = 0.01$. These numbers are a slight overestimation of the mole fractions if the contamination was an improper seal resulting in an air leak (2 torr base pressure, $\chi_{total} = 0.005$). The model relied heavily on the existence of N_2^+ . Only a minuscule (order of 10^{-6}) amount was needed to simulate the molecular bands seen. This may indicate a few things; one being that the nitrogen is not in complete equilibrium as it remains in an ionized state. Despite all of this, the results are useful, as it gives a rough approximation of the free stream composition.

The process was then repeated for the argon/oxygen mixture previously described. In this condition the temperature was 5900 K and the pressure was 160 torr. The results are shown in Figure 4.11.

Figure 4.11: Experimental (black) and SPECAIR simulated (purple) emission of 71.4 g/min argon and 2.9 g/min oxygen plasma at 5900 K

In the argon/oxygen mixture, the oxygen and nitrogen mole fractions were found to be $\chi_{O_2} = 0.05$ and $\chi_{N_2} = 0.01$. Again, these mole fractions are an overvalue of the expected mole fractions for the mass flow rates, $\chi_{total} = 0.04$. N_2^+ is again present in very small amounts, leading to a strong influence over the nitrogen bands. An interesting observation is the appearance of NO. This can be explained by the presumed air leak in the facility. The mole fraction of NO was found to be 5×10^{-4} .

Finally, the same procedure was used for the argon/nitrogen mixture describe earlier. The temperature was set to 5500 K and the pressure was 160 torr. The successful simulation is shown in Figure 4.12.

Figure 4.12: Experimental (black) and SPECAIR simulated (blue) emission of 71.4 g/min argon and 2.5 g/min nitrogen plasma at 5500 K

The mole fractions of the argon/nitrogen mixture were determined to be $\chi_{O_2} = 0.005$ and $\chi_{N_2} = 0.06$. Once again this is more than the expected mole fractions for the condition flow rates, $\chi_{total} = 0.03$. While the simulated value is more, it still is within a believable range. N_2^+ (10^{-4}) is present in this mixture, as one would expect for a nitrogen based flow.

With the temperature and approximate (and simplified) composition of each mixture known, the flow conditions are nearly fully characterized. The temperature and composition can now be used in tandem to determine the total enthalpy and power of each test gas and mixture. Table 4.6 summarizes the test gas compositions and temperatures.

Table 4.6: Test condition temperature and composition

	T (K)	χ_{O_2}	χ_{N_2}
Argon	6100	0.005	0.01
Argon/O ₂	5900	0.05	0.01
Argon/N ₂	5500	0.005	0.06

4.3 TOTAL ENTHALPY AND POWER

While it is a decent metric for describing a test condition, temperature cannot be used to full characterize the flow. As seen previously, derivations determined that the argon plasma has a higher free stream temperature than the oxygen and nitrogen mixtures, despite the logical thinking that the mixtures will induce higher heating. By finding the enthalpy and total power of each condition, the flow can be better understood and validated, both for testing and future modeling purposes.

The first method used for determining total enthalpy and power was through the use of the dissociation energies of oxygen and nitrogen and by using the mole fractions for each test condition. Table 4.7 gives the mass flows, temperatures, and total gas constants for each test case.

Table 4.7: Test conditions for total enthalpy and power calculation

	$\dot{m}_{Ar}$ (kg/s)	$\dot{m}_{O_2}$ (kg/s)	$\dot{m}_{N_2}$ (kg/s)	T (K)	R_m (J/kgK)
Argon	0.0011	4.4×10^{-6}	7.8×10^{-6}	6100	209
Argon/O ₂	0.0011	4.9×10^{-5}	7.8×10^{-6}	5900	211
Argon/N ₂	0.0011	4.4×10^{-6}	4.7×10^{-5}	5500	214

With these values, the total enthalpy and power (or enthalpy flux) of the free stream flow was calculated using Equations (3.18) through (3.27). An assumption of this analysis was that nitrogen and oxygen were both fully dissociated. In reality, and indicated by the presence of N_2^+ , there is some gas phase recombination that occurs. Due to this, the enthalpies and powers presented may be overestimated. The results are given in Table 4.8.

Table 4.8: Test condition total enthalpy and power

	h_{total} (MJ/kg)	$\dot{h}_{total}$ (KW)
Argon	3.49	3.85
Argon/O ₂	4.00	4.60
Argon/N ₂	4.36	4.99

The findings of the enthalpy and power analysis are more indicative of what is expected of the flow conditions. The nitrogen mixture possessed the largest enthalpy and power of the three test conditions, due to its large dissociation energy (113,000 K). The total enthalpy and power of the oxygen mixture was slightly less. Despite a lower

total enthalpy, it is expected that oxygen will create a higher surface temperature amongst the test materials caused by oxygens high reactivity with carbon.

The second method was completed using the plate amperage and voltage from the power supply. As explained in Section 3.2.2, the total power of the flow is only a fraction, estimated to be 0.3, of the total output power of the power supply. By determining the total power, and temperature, through a secondary method, validity and confidence can be added to the results of other analyses. Table 4.9 presents the results of the power supply approach.

Table 4.9: Test conditions, total power, enthalpy and temperature from power supply analysis

	V (KV)	I (Amps)	P (KW)	$\dot{h}_{total}$ (KW)	h_{total} (MJ/kg)	T (K)
Argon	5.6	2.5	14	4.2	3.78	6730
Argon/O ₂	6.1	2.5	15.25	4.58	3.96	6220
Argon/N ₂	6.2	2.5	15.5	4.65	4.04	5140

In addition to these analyses, the chemical simulation code, Chemical Equilibrium with Applications (CEA), was used to verify the enthalpies in each condition given the known temperatures and mixtures. The results of the three methods are shown in Table 4.10.

Table 4.10: Total enthalpies of various methods (MJ/kg)

	<i>Dissociation Approach</i>	<i>Power Supply Approach</i>	<i>CEA</i>
Argon	3.49	3.78	3.48
Argon/O ₂	4.00	3.96	4.25
Argon/N ₂	4.36	4.04	3.69

The results of the enthalpy analyses show strong agreement in values for the argon and argon/oxygen mixtures, where the values differ by a maximum of 8% for argon and 7% for the oxygen mixture. There is considerable variance between the dissociation/power supply methods and the result calculated by CEA. The reason for this deviation is believed to be sourced from the assumption of full dissociation. Given the determined facility conditions and nitrogens dissociation energy, it would be expected that nitrogen would only have a partially complete dissociation of approximately 0.25 mole fraction of nitrogen atom. This then reduces the actual energy in the system, producing over estimates from the described analyses.

Comparing the power and temperature results show that there is a fair agreement between the different methods, both in value and in trend. The calculated total powers differ by 8% (argon), 0.4% (argon/oxygen) and 7% (argon/nitrogen), while the calculated temperatures varied farther from the values determined in other methods, but the same relative trends exist (argon is the hottest flow and nitrogen is the coolest flow). Since the power transfer coefficient is only an estimate, the power supply approach calculations are as well. More testing is planned to refine the coefficient and the overall validity.

CHAPTER 5

MATERIAL TESTING RESULTS

5.1 SURFACE AND IN-DEPTH TEMPERATURE

Surface and in-depth temperature analysis acts as an adequate way of characterizing the behavior and subsequent reaction of the ablators in high temperature/enthalpy and reactive flows. To analyze the in-depth temperature, Type K thermocouples were placed within two PICA samples, as shown in Figure 5.1. Three tests were conducted, two in an argon plasma, and one in an argon/air plasma. One sample was ran in a 71.3 g/min argon twice. The other sample was ran in an 17.8 g/min argon, 36.8 g/min air plasma.

The placement of the thermocouples is designed so that the tips lie on the centerline at intermediate spacing along the depth. The thermocouple locations for the argon test do not lie directly on the centerline but provide a decent approximation of the equal spacing desired. For subsequent tests, thermocouple alignment was well centered. Figures 5.1c, 5.1d, and 5.1e show cross sectional images taken by the microCT scanner at the tips of the thermocouples indicated in Figure 5.1b

(a) Argon Test Thermocouples Locations - Side View

(b) Air/Argon Test Thermocouples Locations - Side View

(c) Air/Argon Test Thermocouples Location - Top View

(d) Air/Argon Test Thermocouples Location - Top View

(e) Air/Argon Test Thermocouples Location - Top View

Figure 5.1: *A*: microCT scan of thermocouple locations for argon test. Top: 0.51" from front face. Left: 0.20" from front face. Right: 0.16" from front face. *B*: microCT scan of thermocouple locations for air/argon test. Top: 0.51" from front face. Left: 0.27" from front face. Right: 0.14" from front face. *C*: Cross Section image at location (c). *D*: Cross Section image at location (d). *E*: Cross Section image at location (e).

The results of each test are shown in Figures 5.2, 5.3, and 5.4. The PICA sample used in the argon test was ran twice, once for 60 seconds, then again until the thermocouple temperature plateaued. The sample used in the air/argon test was ran for 80 seconds, when the thermocouples exceeded their listed maximum threshold. As expected, the air/argon test produced higher temperatures, presumably due to the high reactivity of air with the PICA material. As seen in Figure 5.3, the ther-

thermocouples reached a plateaued temperature after approximately 75 seconds in the second argon test. The thermocouple 0.51" behind the front face stayed within the pyrolysis temperature zone, while the other two thermocouples at depth reached maximum temperatures in the coking zone, just below the ablation zone [25]. These tests provide a good estimation of the in depth temperature response of PICA throughout the course of related experiments as well as bounding values for the maximum temperatures reached on and in depth by the PICA in the ICP facility at UVM.

Figure 5.2: First Instrumented PICA Test in Argon. Pyrolysis Zone: 523 K-1173 K, Coking Zone: 1173 K-1373 K, Ablation Zone: 1373 K+ [25]

Figure 5.3: Second instrumented PICA test in Argon Pyrolysis Zone: 523 K-1173 K, Coking Zone: 1173 K-1373 K, Ablation Zone: 1373 K+ [25]

Figure 5.4: Instrumented PICA test in Air/Argon mixture. Pyrolysis Zone: 523 K-1173 K, Coking Zone: 1173 K-1373 K, Ablation Zone: 1373 K+ [25]

In addition to in-depth temperature measurements, the surface temperature was measured for each tested condition on PICA and FiberForm. This was done using a high-temperature pyrometer in 2-color mode, as described in Section 2.4. All samples tested in this study were placed 90 mm above the floor of the test chamber. The surface temperatures for each test condition are shown in Figures 5.5 and 5.6.

Figure 5.5: Surface temperature measurements for PICA in each tested condition.

Figure 5.6: Surface temperature measurements for FiberForm in each tested condition.

The solely argon flow produced the lowest surface temperatures, due to argon's inert nature. The highest overall surface temperatures are achieved in FiberForm. This is expected due to the absence of pyrolysis. In both materials, the diluted oxygen environment produced the highest temperature. This again could be expected due to oxygen's highly reactive nature with the carbon substrate, leading to an increase in chemical energy transfer. The diluted CO₂ environment produced the next highest surface temperatures, again likely due to oxygen's reactivity. The diluted nitrogen and air flows yielded similar temperatures, lower than the rest but higher than the argon plasma.

5.2 PICA PUCK EMISSION RESULTS

5.2.1 PICA IN ARGON

Argon plasmas acted as the foundation for the test gases due to its inert characteristics. Samples were tested in a 71.4 g/min argon plasma, at 90 mm above the nozzle (45 W/cm² heat flux. All heat flux results are shown in Appendix C) for varying test durations to establish a baseline for the behavior of pyrolysis species ejected from the PICA material. The samples maintained their original geometry, as seen in Figure 5.7. The char layer depth (lighter gray) varied depending on duration. The mass loss rate of the tests was 0.003 ± 0.0002 grams/second.

Figure 5.7: *Left:* PICA before being exposed to argon plasma (1.955g) *Right:* PICA after being exposed to argon plasma (1.620g)

Emission was taken using the HR4000CG-UV-NIR spectrometer with a 0.5 second integration time. Three tests were ran for durations of 60 seconds, 120 seconds, and 480 seconds. Figures 5.8, 5.9, and 5.10 show the results of these tests.

Figure 5.8: 60 second PICA exposure in argon plasma.

Figure 5.9: 120 second PICA exposure in argon plasma.

Figure 5.10: 480 second PICA exposure in argon plasma.

From the results, several observations can be made to highlight the general characteristics of the pyrolysis gases. First is the large spike in signal seen at the initial insertion of the sample. This has been previously seen in related studies [25] and could be due to the initial temperature shock. The phenolic resin on the surface of the sample pyrolyzes near instantaneously producing a large jump in signal. The presence of hydrogen and NH show a potential interaction between pyrolysis species, seen through similar temporal trends. The strong C₂ Swan signal at the beginning of the test may be caused by stray strands of the carbon substrate ablating.

Another observation is the behavior of the species between 60 and 120 seconds. In this time region, the majority of the known and traced pyrolysis species are quickly dissipated, except for the presence of CN Violet. In all of the tests, the CN Violet signal drops after initial insertion, before ascending at 30 seconds. This may corresponds with the rise in signal of the other pyrolysis species. The CN Violet signal is prominent through the duration of the test, potentially due to the existence of nitrogen contaminants in the environment reacting with the carbon substrate.

Number density analysis was conducted using the hydrogen signal at 0.656 μm . The feature was determined to be a suitable candidate for analysis due to its atomic structure and ability to be simplified. It was believed that hydrogen could be traced then applied to LIF measurements to validate the number density and electronic temperature. Analysis using Equation (3.6) was done using the spectroscopic constants and energy levels shown in Table 5.1.

Table 5.1: Hydrogen Spectroscopic Constants and Energy Levels [40]

	g_o	g_i	$A_{ul} \text{ (sec}^{-1}\text{)}$	$v_u \text{ (cm}^{-1}\text{)}$	$v_l \text{ (cm}^{-1}\text{)}$
H_α	8	18	4.41×10^7	97492	82259

At the estimated boundary layer temperature of 2000 K, the number density of the hydrogen feature was calculated to be on the order of 10^{35} cm^{-3} . When compared to the expectant order of 10^{17} cm^{-3} , the result is abnormal. A possible explanation for this outcome is that hydrogen, and by extension the other pyrolysis species, are not in equilibrium with the ground state. The number density analysis is performed under the assumption of a Boltzmann distribution. If the species is in non-equilibrium, then a Boltzmann distribution is not valid. Due to this, it is believed that the pyrolysis gases exist in a non-equilibrium state in the tested conditions.

These results display the behaviors of the pyrolysis species in a theoretically pure heating environment. With this data, tests in argon with small amounts of reactive species are conducted to observe the pyrolysis behavior in such environments.

5.2.2 PICA IN DILUTED NITROGEN

The first diluted mixture tested was that of argon and nitrogen. Having a diluted mixture allows for more suitable observation of the reactions associated with the reactive flows considering their fast reaction rates. The first test conducted was done by incrementally adding minute amounts of nitrogen at set times through the duration of the test. The purpose of this was to identify the smallest amount of nitrogen needed to facilitate faster reactions of nitrogen-based pyrolysis species, such as CN Violet and NH. Nitrogen was added in increments of 0.6 g/min every 10 seconds to a 71.4 g/min argon plasma, starting with 0 g/min at the start of the test. At 30 seconds, the flow rate was doubled from 1.3 g/min to 2.5 g/min. The results are shown in Figure 5.11.

Figure 5.11: Emission results from incremental nitrogen addition test. The bottom plot shows the instantaneous and cumulative nitrogen flow rates

An interesting observation of note is the change in NH and hydrogen upon the increase in nitrogen from 1.3 g/min to 2.6 g/min. It is seen that NH increases sharply

while hydrogen decreases at a similar rate. This is indicative of any remaining hydrogen reacting strongly with the extra available nitrogen. At this flow rate, it could be expected that hydrogen will be depleted much quicker than in an inert environment. This titration event shows that very little nitrogen is needed to trigger faster hydrogen depletion and faster NH reactions. It can also be noted that the CN Violet signal sharply increases with the final nitrogen addition, likely due to the increased nitrogen reacting with the carbon substrate.

A second test was done with a diluted nitrogen mixture. This test was ran with a steady mixture of 71.4 g/min argon and 2.5 g/min nitrogen with a heat flux of 67 W/cm². Negligible surface recession was observed. The mass loss was 0.004 grams/second. The purpose of this test was to observe the initial transient reactions of the pyrolysis species of interest (NH, CN Violet, and hydrogen) and their long term behavior. Figure 5.12 shows the result of this test.

Figure 5.12: Emission results from static diluted argon/nitrogen mixture.

The figure indicates that the hydrogen in phenolic resin is consumed by the nitrogen from the moment the sample is inserted into the flow. There is a small peak in hydrogen at the beginning of the test, but the signal quickly dissipates, indicating that the hydrogen present has been pyrolyzed. The CN Violet signal saturates for the first 10 seconds of the test as the abundance of nitrogen quickly reacts with the carbon ablator. As the test progresses, the CN Violet signal approaches a plateaued value denoting the only reaction present is that of the nitrogen flow and of the substrate.

5.2.3 PICA IN DILUTED OXYGEN

The next tests were ran with diluted oxygen mixtures. Oxygen induces separate pyrolysis species than nitrogen, making it an equally interesting test condition. Two initial tests were conducted. Instead of incrementally increasing the oxygen in the flow, a set amount was introduced for 10 second increments. Each test had a 120 second duration, with oxygen being present between 10-20 seconds and 70-80 seconds. The first test used 0.7 g/min of oxygen and the second test used 2.9 g/min of oxygen. Emission was collected in the same configuration as described for the nitrogen tests. The results are shown in Figures 5.13 and 5.14.

Figure 5.13: Emission results from lower flow oxygen addition test (0.6 g/min).

Figure 5.14: Emission results from higher flow oxygen addition test (2.9 g/min).

The results from the 0.6 g/min oxygen test show little difference from the argon test explained earlier. There was minimal visual increase in oxygen at the times of delivery. The small quantity of oxygen may not have been strong enough to induce the expected reactions.

In the 2.9 g/min oxygen test, the typical oxygen emission lines at 0.777 μm and 0.845 μm are absent and, instead, strong potassium lines are seen in correlation with the oxygen addition. This may be due to contaminants in the plumbing, but since potassium is a strong radiator, it cannot be assumed that oxygen is not in

the system. In the first oxygen delivery window, no change in pyrolysis species is observed until after removing the oxygen. At this point OH sharply increases while every other species drops to near zero intensity. In the second oxygen delivery window, the pyrolysis gases disappear again, then returning to the trend established prior to oxygen addition.

Similar to the nitrogen configuration, secondary tests were ran with a steady mixture of 71.4 g/min argon and 2.9 g/min oxygen, with a heat flux of 61 W/cm². Surface recession was measured to be approximately 2 mm. The mass loss was 0.006 grams/second. Pre- and post-test conditions of the sample are shown in Figure 5.15.

Figure 5.15: *Left:* PICA before being exposed to argon/oxygen plasma (1.889g) *Right:* PICA after being exposed to argon/oxygen plasma (1.145g)

The purpose was again to observe the initial transient reactions of the pyrolysis species of interest and their behavior over the test duration. Due to the corrosive nature of oxygen, the samples tested experienced recession through the duration of the test (1 mm/minute). This meant that the emission collection scanned a 2 mm region within the boundary layer while pyrolysis simultaneously occurred. Two tests

were ran; one test started emission at 1 mm below the sample face and ended at 3 mm, and the other started at 2 mm and ended at 4 mm. The results of both tests are shown in Figures 5.16 and 5.17.

Figure 5.16: Emission results from static diluted argon/oxygen mixture. Emission collection beginning at 1 mm.

Figure 5.17: Emission results from static diluted argon/oxygen mixture. Emission collection beginning at 2 mm.

Again, similarly to the nitrogen tests, the oxygen based species dominate the initial transients of both tests. Small hydrogen spikes are seen at the beginning, but quickly taper off as the hydrogen reacts with oxygen. Comparing the two tests, it can be seen that the OH signal is stronger closer to the surface of the sample. This is expected, as the hydrogen does not have a chance to extend into the boundary layer because of its reactions with free oxygen.

Another interesting observation is the existence of NH early on in the test. The presence of nitrogen can be attributed to contamination from air leaks in the facility. Some of the hydrogen potentially reacts with this nitrogen to form NH. This could mean that the OH reactions sought in the experiment are less than desired, especially in the 2 mm region of the boundary layer. The NH signal depletes to negligible signal as the OH signal does the same. As the NH decreases, CN Violet signal increases. This may be caused by the nitrogen reacting with the carbon substrate now that the phenolic resin has been pyrolyzed. This trend is seen in both test cases; in the 1 mm test, the CN signal is stronger, while the NH signal is stronger in the 2 mm test.

5.2.4 PICA IN DILUTED AIR

The next logical step after testing diluted nitrogen and oxygen was to test in diluted air. A single, steady flow test was ran in 71.4 g/min argon and 2.5 g/min air flow, with a heat flux of 62 W/cm². The mass loss was 0.003 grams/second. Negligible surface recession was observed. The test and subsequent results are more relatable to re-entry conditions than nitrogen or oxygen alone. Recession was negligible. The results of the test are shown in Figure 5.18.

Figure 5.18: Emission results from static diluted argon/air mixture.

The emission and species tracking display results similar to those seen in the diluted nitrogen and oxygen tests. The NH intensity spikes upon insertion, as does CN Violet and C₂ Swan. CN Violet drops in intensity while OH and NH maintain their intensity as they react with the available hydrogen. As the presumed hydrogen is exhausted, the OH and NH intensities begin to decrease. As more nitrogen becomes available, CN Violet increases in signal, reaching an plateau as the NH signal goes to zero. This all happens within the first 30 seconds. Further analysis and documentation of these 30 seconds could produce fascinating conclusions.

5.2.5 PICA IN DILUTED CO₂

The final tests with PICA were in a diluted CO₂ environment. This is relevant to a Mars atmosphere test. The purpose again was to observe the transient and interactive behavior of pyrolysis gases in a time frame that allowed the reacts to be observed and recorded. The test flow was 71.4 g/min argon and 5.9 g/min CO₂ with a heat flux of

62 W/cm². The mass loss rate was 0.004 grams/second. Minimal surface recession was observed (less than 1 mm). Pre- and post-test sample conditions are shown in Figure 5.19 and emission results are shown in Figure 5.20.

Figure 5.19: *Left:* PICA before being exposed to argon/carbon dioxide plasma (1.878g) *Right:* PICA after being exposed to argon/carbon dioxide plasma (1.355g)

Figure 5.20: Emission results from static diluted argon/carbon dioxide mixture.

The plot indicates that CN Violet is present in the free stream. This is possibly due to an air leak in the facility. At the moment of insertion, NH and OH signals ascend and descend within 5 seconds, while a hydrogen signal is minimal. This short reaction period may be influenced by the increase oxygen and carbon in the system, effectively suffocating the reactions. After the initial increase, the CN Violet intensity begins to decrease at 10 seconds before plateauing around 30 seconds at a value slightly above that seen in the free stream.

5.3 FIBERFORM PUCK EMISSION RESULTS

As previously mentioned, PICA is composed of a carbon substrate, FiberForm, and phenolic resin. FiberForm was tested to serve as a comparison for each test condition, due to its lack of resin and thus pyrolyzing gases. Test conditions, including sample location, emission location, and heat fluxes, were identical to related PICA tests conditions. The FiberForm used was manufactured by Fiber Materials Inc. and sourced from NASA-Ames.

5.3.1 FIBERFORM IN ARGON

Argon plasma was again used as the baseline test condition for FiberForm. The sample was test in a 71.4 g/min argon flow, same as previously used. The mass loss rate was 0.0005 grams/second. The purpose of the test was to image the resultant spectra. With this spectra, the key pyrolysis species and relative strengths can be better understood. The pre- and post- test conditions are shown in Figure 5.21 and the emission results are shown in Figure 5.22.

Figure 5.21: *Left:* FiberForm before being exposed to argon plasma (1.408g) *Right:* FiberForm after being exposed to argon plasma (1.344g)

Figure 5.22: Emission results from FiberForm in pure argon.

The above plot indicates that CN Violet and hydrogen are the only observed species seen in the PICA tests as well. The case of hydrogen may be due to a potential humidity leak though. The hydrogen signal is seen before insertion, implying that it was already in the system before the test commenced. The small peak at the

beginning may be also due to residual moisture on the sample or sample holder. A second test in identical conditions was ran for a longer duration of 480 seconds. This test was done to observe the long term temporal behavior of CN Violet. The results are shown in Figure 5.23

Figure 5.23: 480 second FiberForm exposure in argon plasma.

As explained prior, the appearance of CN Violet may be attributed to the interaction of trace nitrogen in the flow and the carbon material. The note of interest is the strength. The measured intensity is one tenth of that seen in PICA tests. This can provide an approximate measure of the CN Violet contribution from reactions with the flow, essentially a background signal compared to the CN Violet formed as a result of pyrolysis. Calcium and sodium contamination is seen $0.389 \mu\text{m}$, $0.397 \mu\text{m}$, and $0.589 \mu\text{m}$, likely due to machining and handling procedures.

5.3.2 FIBERFORM IN DILUTED NITROGEN

A diluted mixture of 71.4 g/min argon and 2.5 g/min nitrogen was used to test another FiberForm sample. Similarly to the argon test, the purpose was to produce a

control result for comparison to the PICA test in the same condition. The mass loss rate was 0.0006 grams/second. Negligible surface recession was observed. Emission results are shown in Figure 5.24.

Figure 5.24: Emission results from FiberForm in argon/nitrogen test mixture.

Unlike the argon test, CN Violet is the only comparable species present. Unlike the PICA test case where the signal saturated over the first 10 seconds, the CN Violet signal stays consistent through the duration of the test. The CN Violet intensity in the PICA test plateaus to a value very close to the FiberForm test intensity of approximately $0.004 \text{ W/cm}^2 \mu\text{m sr}$. These results suggest that the increased heating induced faster nitrogen based reactions in the PICA to a point where no nitrogen from the sample was left to react. The similar late test intensities indicate that in both cases the CN Violet production was a result of the nitrogen flow and substrate interactions.

5.3.3 FIBERFORM IN DILUTED OXYGEN

A diluted oxygen mixture was next used for testing FiberForm. The test flow was a mixture of 71.4 g/min argon and 2.9 g/min oxygen, same as the PICA tests. Again, the FiberForm sample was tested in similar conditions so that the pyrolysis behavior of PICA could be isolated from other interactions. The mass loss rate was 0.004 grams/second. The pre- and post-test sample conditions are shown in Figure 5.25 and emission results are shown in Figure 5.26.

Figure 5.25: *Left:* FiberForm before being exposed to argon/oxygen plasma (1.156g)
Right: FiberForm after being exposed to argon/oxygen plasma (0.663g)

Figure 5.26: Emission results from FiberForm in argon/oxygen test mixture.

The emission collection location was placed 1 mm below the sample face with the expectation that the sample would recede, allowing emission observation through the depth of the boundary layer. The sample receded approximately 3.5 mm, mean emission was collected from 1 mm to 4.5 mm below the surface through the length of the test.

The results show that CN Violet is again the only species of interest present. The initial intensity is stronger than the intensity in the PICA test but quickly dissipates as the sample surface recedes. The presence of CN Violet can be attributed to trace amounts of nitrogen interacting with the virgin carbon material. The recession of the sample is caused by the oxygen corroding the carbon material, forming CO and CO₂. Unfortunately, the spectrometers used are unable to record far enough into the infrared to observe either species. A diode laser absorption system is needed for proper observation.

5.3.4 FIBERFORM IN DILUTED AIR

A diluted air mixture was chosen as the next test condition, because it acted as a proper combination of the nitrogen and oxygen test, as well as being a comparable condition to earth atmospheric re-entry conditions. The sample was tested in a 71.4 g/min argon and 2.5 g/min air flow. The mass loss rate was 0.0011 grams/second. Surface recession was negligible. The measured emission results are shown in Figure 5.27.

Figure 5.27: Emission results from FiberForm in argon/air test mixture.

Again, CN Violet is seen as the only species of interest present, likely caused by the material's interaction with the nitrogen in the air. The intensity signal decays at a linear rate, similar to the PICA test result but the FiberForm test has a higher intensity. The first 20 seconds of the PICA test showcases many different reactions not seen in the FiberForm test, but both have the same decay trend after that point. This points to the majority of the pyrolysis reactions occurring in that initial period.

5.3.5 FIBERFORM IN DILUTED CO₂

The final FiberForm test was done in a diluted carbon dioxide plasma, consisting of 71.4 g/min argon and 5.9 g/min CO₂. The mass loss rate was 0.0024 grams/second. The pre- and post-test sample conditions are shown in Figure 5.28 and emission results are shown in Figure 5.29.

Figure 5.28: *Left:* FiberForm before being exposed to argon/carbon dioxide plasma (1.144g) *Right:* FiberForm after being exposed to argon/carbon dioxide plasma (0.778g)

Figure 5.29: Emission results from FiberForm in argon/carbon dioxide test mixture.

The CN Violet results of the FiberForm CO₂ test are very similar to the PICA CO₂ test. Both tests have a free stream value of approximately 0.006 W/cm² μm sr and plateau to an approximate intensity of 0.008 W/cm² μm sr. The only difference is the initial jump seen in the PICA test. The CN Violet signal stays constant throughout the duration of the test, presumably due to the lack of extra carbon associated with pyrolysis mechanisms.

5.4 ANALYSIS OF APPROXIMATE PHENOLIC RESIN AND CHAR LOSS VIA CN VIOLET

The presented emission results revealed that CN Violet was present in PICA and FiberForm in each test condition but to varying intensities. With this knowledge and the understanding of the flow compositions, a visual approximation of the resin and

char losses can be created.

CN Violet is formed as a result of the carbon in the phenolic resin or substrate reacting with nitrogen in the flow. It is presumed that there is substantial carbon in the resin, which explains the higher concentrations of the species in the PICA emission results. The intensities of PICA and FiberForm at matching spectral locations and matching flow conditions can be compared using their ratios as well as the difference.

The first set of results come from the argon test condition with a 120 second duration. The results are shown in Figure 5.30, where the top plot shows the ratio of the intensities, the middle plot shows the difference, and the bottom shows the temporal trace of CN Violet for both materials.

Figure 5.30: Comparison of CN Violet features in 120 second duration argon test.

The plot indicates that the majority of the CN Violet produced over the duration of the test is a product of the phenolic resin, since the FiberForm signal remained nearly constant for the duration while the PICA signal varied. It is hypothesized that the variations in behavior are a result of the change in temperature as the pyrolysis

mechanisms are occurring. The graph does not indicate at what point the phenolic resin's contribution to the CN Violet signal ends. The results of the longer duration (480 second) tests were compared to determine this, as shown in Figure 5.31.

Figure 5.31: Comparison of CN Violet features in 480 second duration argon test.

In this test, the ratio of intensities remains a near constant 0.1 from 150 seconds onward and the difference approaches zero as the test concludes. This suggests that the phenolic resin has been consumed in near full by the 150 second point. The FiberForm sample experienced a recession rate of approximately 0.25 mm/min (the PICA sample did not recede). because of the recession, the CN Violet signal is lower than what is expected at the 2 mm location below the sample. However, with this approximation known the results are still conclusive.

The same comparison was carried out for the 120 second duration argon/nitrogen mixture condition. The results are shown below in Figure 5.32.

Figure 5.32: Comparison of CN Violet features in 120 second duration argon/nitrogen test.

The results show a definitive moment in which the phenolic resin has been exhausted. From 60 seconds onward, the ratio approaches 1 and the difference approaches 0, both of which indicate that the same amount of CN is produced by both materials at that instant. This useful as it provides a time measurement of when the pyrolysis is occurring in this condition.

The CN Violet signals in the argon/oxygen conditions were then analyzed, with the results shown in Figure 5.33 below. The data is from the 120 second tests described in the earlier results.

Figure 5.33: Comparison of CN Violet features in 120 second duration argon/oxygen test.

The results of the argon/oxygen mixture condition are interesting owing to the fact that there are numerous different details that influence the pyrolysis and chemical reactions present. These include oxidation, pyrolysis, recombination, and recession. Recession and the oxygen based reactions reduce and affect the production of CN Violet in this condition. The recession rates were approximately 1 mm/min for PICA and 2 mm/min for FiberForm. If the above results are adjusted and scaled to vary with recession, details of the pyrolysis duration is better visualized. The resultant scaling is shown in Figure 5.34.

Figure 5.34: Comparison of CN Violet features with respect to recession in 120 second duration argon/oxygen test.

These results give a better indication of the temporal behavior and length of the pyrolysis mechanisms. The signals become analogous when each sample has receded approximately 0.6 mm (ratio and difference approach 1 and 0 respectively). The corresponding time signature is determined to be 36 seconds using PICA's recession rate in the argon/oxygen mixture. This can be seen as the moment when the phenolic resin's contribution to CN Violet ends, thus the end of pyrolysis. In actuality, this is solely an estimate, as the reactions occurring in an oxygen environment (CO , CO_2 , OH) have a known but unquantified effect on the overall behavior of the pyrolysis mechanisms.

The same analysis was conducted for the argon/air condition. Recession in the FiberForm sample was observed (approximately 0.25 mm/min) was observed, but the amount was considered not to be a factor in the results. The resultant plots are shown in Figure 5.35

Figure 5.35: Comparison of CN Violet features in 120 second duration argon/air test.

At approximately 20 seconds, the intensity ratio and difference reach plateau values of approximately 1.2 and 0 respectively. This again is indicative of the time in which the phenolic resin has been expended thus a duration of the pyrolysis. In addition to these indicators, the trend that the CN Violet signal decreases in similar between the two materials, indicating that the species loss is occurring at approximately the same rate.

Finally, the process was performed on the results from the argon/carbon dioxide mixture. The recession rates in the two materials were similar, thus the recession was not factored into the qualitative analysis. The results are shown in Figure 5.36.

Figure 5.36: Comparison of CN Violet features in 120 second duration argon/carbon dioxide test.

Like in the previous tests, a time is found in which the phenolic resin's contribution to the CN signal ends. At approximately 30 seconds, the intensity ratio and difference approach 1 and 0, both denoting that the contribution to the CN signal is from the char layer from that point onward and not from pyrolysis mechanisms.

5.5 TEMPORALLY AND SPATIALLY RESOLVED STAGNATION LINE EMISSION PROFILES

Single point emission measurements are limited in that they only show a small fraction of detail on how the pyrolysis species interact spatially within the high-temperature boundary layer. Using the IsoPlane spectrometer, the entire boundary layer can be analyzed in specific regions of interest. This allows for in-depth analysis on the chemical and thermal behavior of the species of interest.

This method, developed at UVM, is a new process and still under development. The results provide a highly resolved and precise look into the spatial and temporal behavior of pyrolysis and PICA but there are limitations. The system is not fully calibrated, so emission results are in arbitrary units rather than normalized spectral radiance. There is also a small issue with ghosting or pixel bleeding. These issues do not effect the results presented.

5.5.1 ANALYSIS NEAR $0.656\ \mu\text{M}$

Figure 5.37 center image represents a 0.6157 to $0.6952\ \mu\text{m}$ dispersed onto the 1024 horizontal pixels and about 10 mm imaged onto the 256 vertical pixels with flow going from the bottom of image to top. Top plot of Figure 5.37 gives the uncalibrated emission intensity at 2 mm above the surface at 10 seconds. The surface was easily identified pre-test with the torch off through lamp illumination of the test sample. The interface location lined up quite well with the apparent sharp jump at $y = 0$ mm illustrated in the image. As the sample moves (due to thermal expansion and sample recession) it was necessary to track this interface and set the y value to zero for all frames evaluated in time. The bright glow on the bottom right represents the hot corner of the sample which has a radius of 3 mm. The hot spot, intuitively, resides 1.5 mm off of the surface.

Figure 5.37: Emission results from IsoPlane in $0.656 \mu\text{m}$ region, 2 mm above surface

Emission traces at 1, 2, 3, and 4 mm distances above the surface are given in Figure 5.38. These traces were taken at 10 seconds after sample insertion.

Figure 5.38: Emission results from IsoPlane (from top to bottom): 1, 2, 3, and 4 mm above surface in $0.656 \mu\text{m}$ region.

Normally the only specie of interest to probe in this environment would be the H_α line. However, additional molecular spectra are apparent near $0.672 \mu\text{m}$. This vibrational band comes from NH (A–X) which normally emits near $0.336 \mu\text{m}$. This spectra is present as the grating is currently operating off of center wavelength and at an extreme angle introducing 2nd order dispersion onto the CCD. This presents a unique opportunity to probe both H_α and NH (A–X) within the same horizontal CCD coverage. Figure 5.39 gives vertical distributions of emission at $0.6564 \mu\text{m}$ (to track H_α) in the top row and emission at $0.6721 \mu\text{m}$ (to track NH (A–X)) in the bottom row. Four time instances are represented: 3, 10, 30, and 60 seconds after sample insertion.

Figure 5.39: Comparison of transient H_α (Top) and NH (A-X) (Bottom) results in $0.656 \mu\text{m}$ region.

These plots show an interesting trend in that the peak H_α intensity tends to stand off of the surface and gradually move toward the surface over time as the pyrolysis gases are expelled. The NH (A-X) trend is similar, however there is less of a stand-off from the surface but its spatial location with respect to that of the H_α peak remains relatively constant. First instinct suggests that lower temperature NH (A-X) initially ejects into the boundary layer. Its emission intensity increases as one goes away from the surface and comes to a peak. A declining trend might owe to a region where significant temperature begins to dissociate NH (A-X) into constituent species. The trend of H_α supports this theory as the decline in NH (A-X) signal corresponds to an increase in H_α signal.

5.5.2 ANALYSIS NEAR $0.350\ \mu\text{m}$

Figure 5.40 center image represents a 0.2852 to $0.4137\ \mu\text{m}$ dispersed onto the 1024 horizontal pixels and about 10 mm imaged onto the 256 vertical pixels. Flow is still from bottom of image to top. Top plot of Figure 5.40 gives the emission intensity at 2 mm above the surface at 10 seconds. The surface was easily identified pre-test with the torch off through lamp illumination of the test sample. However, tracking the surface in test was less straight-forward than the $0.656\ \mu\text{m}$ range. Even so, the pre-test interface location lined up quite well with the apparent discontinuity edge in the CN band shown as $y = 0\ \text{mm}$ in the image. As the sample moves (due to thermal expansion and sample recession) it was necessary to track this interface and set the y value to zero for all frames evaluated in time.

Figure 5.40: Emission results from IsoPlane in $0.350\ \mu\text{m}$ region, 2 mm above surface

Emission traces at 1, 2, 3, and 4 mm distances above the surface are given in Figure 5.41. These traces were taken at 10 seconds after sample insertion.

Figure 5.41: Emission results from IsoPlane (from top to bottom): 1, 2, 3, and 4 mm above surface in $0.350 \mu\text{m}$ region.

Figure 5.42 gives vertical spatial trends of lines at $0.3883 \mu\text{m}$ (CN (B-X) $\Delta\nu=0$ in top row), $0.3360 \mu\text{m}$ (NH (A-X) in middle row), and $0.3067 \mu\text{m}$ (OH (A-X) in bottom row). A few seconds after sample is inserted there is a fairly intense distribution of CN. After about 10 seconds one can see that the intensity drops significantly. After about 30 seconds the intensity increases as the trend moves toward the surface. At about 60 seconds the peak intensity is well onto the surface. NH (A-X) trend similar to trend shown in Figure 5.42. This is the same band probed, just with a different grating. OH (A-X) trend is similar to that of NH (A-X) (though less intense). A similar trend with both species suggests that both NH and OH are dissociating off of

the surface to produce H_α . H_α is not produced until OH and NH are dissociated in the higher temperature boundary layer regions.

Figure 5.42: Comparison of transient CN (B-X) (Top), NH (A-X) (Center), and OH (A-X) (Bottom) results in $0.350 \mu\text{m}$ region.

CHAPTER 6

SUMMARY AND CONCLUSIONS

The purpose of this thesis and research was to study and observe the gas chemistry interactions between various atmospheric re-entry conditions and the pyrolysis gases of the TPS material PICA for use in further understanding pyrolysis mechanisms and for numerical model validation. The study began by discussing the current and past research on the material, including spectroscopic, thermal, and modeling results and how more knowledge and information is needed to fully comprehend the behavior of PICA. The UVM 30 kW ICP facility and its diagnostic capabilities were detailed and presented. In addition to the experimental set-up, the theoretical derivations and interpretations of the spectroscopic and thermal analysis were described.

The study consisted of two distinct analyses; test condition characterization and material testing and analysis. The free stream temperatures (centerline and radial distribution), the test gas composition, and total enthalpy and power were determined to characterize specific test conditions (argon, argon/nitrogen, and argon/oxygen mixtures). These metrics are helpful in understanding and explaining specific facets of the material response in various test conditions.

Temperature analysis using LIF, emission spectroscopy, Abel Inversion, and power setting analysis generated results that were in agreement across each method with satisfactory validity corroborated by uncertainty analysis. By determining the composition of each test condition, the quantity of the reactive species were realized, offering an understanding of what flow species are interacting with the pyrolysis gases. The compositions were used in determining the flow enthalpies and powers. The calculated values were in agreement with the expected flow behaviors, where the argon/nitrogen mixture comprised the most heat/power and the argon flow had the least. These metrics yield a more comprehensive characterization than previously reported.

Material analysis was performed on PICA and its substrate FiberForm in the form of temperature and spectroscopic evaluation. Temperature measurements were taken on the surface and in-depth to ascertain the temporal response. The in-depth temperatures provide an upper and lower bound for what temperatures can be achieved by the ICP facility. The surface temperatures show a limited representation of how the material responds in each test condition

Single and multiple line of sight spectroscopy was used to observe the behaviors of pyrolysis gases, specifically OH, NH, CN Violet, and H_{α} . Single line of sight spectroscopy was used to analyze each material in argon, argon/nitrogen, argon/oxygen, argon/air, and argon/ CO_2 mixtures. Argon results show the behavior of the pyrolysis gases in a pure heating environment with no additional reactive species. Nitrogen and oxygen mixtures highlighted the interaction of hydrogen with NH and OH species. Air mixture results illustrated the pyrolysis mechanisms in an environment closest to that seen on earth. The results from the CO_2 mixture exhibit the reactions typically seen in a Martian environment.

Using the emission results of CN Violet, the pyrolysis duration was approximated from the contribution of the phenolic resin to the CN Violet signal. Using the ratio and differences in intensities, the pyrolysis duration of an argon environment lasted around 150 seconds and between 20 and 60 seconds in the reactive specie mixtures.

Multiple line of sight spectroscopy was performed on a PICA sample in an argon plasma. The spectral range was focused on the region encompassing NH, OH and CN Violet, and also focused on the region with H_α and NH. The experiment demonstrated the spatial and temporal behavior and evolution of the pyrolysis species. The initial heating produced blowing deep into the boundary layer before the extent of the species blowing retreated toward the surface. The interaction of H_α and NH was better resolved, showing that NH begins just off the surface then dissociates to hydrogen and nitrogen as it encounters a higher temperature region.

In conclusion, the results presented further the current research and knowledge of PICA and its pyrolysis mechanism through better understanding of the pyrolysis gases and their interactions with each other and reactive test environments. The characterization of plasma conditions adds to the presented validity and allows for better cross facility comparisons and for the verification of simulation conditions. The full scope of the results presented increase the community comprehension of PICA but more work is required. Gas injection for pyrolysis simulation is under development at UVM. This will allow for controlled testing for observation and modeling purposes. Additionally, more multiple line of sight measurements are planned for PICA for better spatial and temporal understanding. In full, all of these results will be useful for the simulation community. They are results that can be used to validate new and more accurate pyrolysis chemistry and non-equilibrium simulation codes.

BIBLIOGRAPHY

- [1] Allen, L, "Characterization of NO Production Over Metallic Surfaces in Air Plasmas Using Laser Induced Fluorescence" (2016). University of Vermont. MS Thesis.
- [2] Allen, L., Meyers, J., and Fletcher, D. "Characterization of NO Production Over Metallic Surfaces in Air Plasmas Using Laser Induced Fluorescence", 47th AIAA Plasmadynamics and Lasers Conference, AIAA Aviation, (AIAA 2016-3380) doi: 10.2514/6.2016-3380
- [3] Bose, D., Skokova, K., Wright, M., and Reuther, J. (2009) "Ground-to-Flight Traceability Analysis of Arcjet Testing for the Crew Exploration Vehicle", 41st AIAA Thermophysics Conference, Fluid Dynamics and Co-located Conferences, doi: 10.2514/6.2009-3845
- [4] Brooke, J. S., Bernath, P. F., Schmidt, T. W., and Bacskey, G. B. (2013) "Line strengths and updated molecular constants for the C2 Swan system". Journal of Quantitative Spectroscopy and Radiative Transfer, 124, 11-20. 2013. doi: 10.1016/j.jqsrt.2013.02.025
- [5] Caird, I., Ma, G., and Sargent, J. (2010) "Control and Monitoring System for ICP Torch System." Norwich University/UVM.
- [6] Chen, Y. K., Milos, F. S., (1999) "Ablation and Thermal Response Program for Spacecraft Heatshield Analysis," Journal of Spacecraft and Rockets, Vol. 36, No. 3, pp. 475-583.
- [7] Driver, D. M. (2011). Improved Predictions of PICA Recession in Arc Jet Shear Tests. 49th AIAA Aerospace Sciences Meeting including the New Horizon Forum and Aerospace Exposition. Orlando: NASA Ames Research Center.

- [8] Driver, D., Carballo, J., Beck, R., Prabhu, D., Santos, J., Cassell, A., Skokova, K., Tang, C., Hwang, H., Slimko, E., Willcockson, W., and Songer, J. (2009) "Arc Jet Testing in a Shear Environment for Mars Science Laboratory Thermal Protection System", 41st AIAA Thermophysics Conference, Fluid Dynamics and Co-located Conferences, doi: 10.2514/6.2009-4230
- [9] Dunbar, B. "Mars Science Laboratory Heat Shield." NASA. 2012. *http : //www.nasa.gov/centers/ames/research/msl_heatshield.html*.
- [10] Fletcher, D. and Playez, M. (2006) "Characterization of Supersonic and Subsonic Plasma Flows", 25th AIAA Aerodynamic Measurement Technology and Ground Testing Conference, Fluid Dynamics and Co-located Conferences doi: 10.2514/6.2006- 3294
- [11] "FiberForm Rigid Insulation | Fiber Materials Inc." Fiber Materials Inc. *http : //www.fibermaterialsinc.com/product/fiberform – rigid – insulation/*.
- [12] Gokcen, T. (2010). Computational Analysis of Arc-Jet Stagnation Tests Including Ablation and Shape Change. Journal of Thermophysics and Heat Transfer, 694-707.
- [13] Gueron, S. and Deutsch, M. A. Fast Abel Inversion Algorithm. (1994).
- [14] Jiang, Z., Liu, Y., and Han, G. (2011). "Conceptual study on non-ablative TPS for hypersonic vehicles", 17th AIAA International Space Planes and Hypersonic Systems and Technologies Conference, International Space Planes and Hypersonic Systems and Technologies Conferences. doi: 10.2514/6.2011-2372
- [15] Laub B. and Venkataphy E., B. L. (2003). Thermal Protection System Technology and Facility Needs for Demanding Future Planetary Missions. International Workshop on Planetary Probe Atmospheric Entry and Descent Trajectory Analysis and Science. Lisbon : NASA Ames Research Center.
- [16] Laux, C. O. (1993). Optical Diagnostics and Radiative Emission of Air Plasmas. Stanford: High Temperature Gas Dynamics Labratory; ME Department; Stanford University.
- [17] Lutz, A., "Experimental Investigation And Analysis Of High-Enthalpy Nitrogen Flow Over Graphite" (2015). University of Vermont. PhD Dissertation.
- [18] Lutz, A., and Fletcher, D.,. "Investigation of Non-Equilibrium Nitrogen Plasmas", 46th AIAA Plasmadynamics and Lasers Conference, AIAA Aviation, doi: 10.2514/6.2015-2961

- [19] Martin, A. and Boyd, I. D. (2010). Chemistry model for ablating carbon- phenolic material during atmospheric re-entry. 48th AIAA Aerospace Sciences Meeting Including the New Horizons Forum and Aerospace Exposition. Orlando: The University of Michigan & NASA Ames Research Center.
- [20] Martin, A., Cozmuta, I., Wright, M., and Boyd, I. (2015) "Kinetic Rates for Gas-Phase Chemistry of Phenolic-Based Carbon Ablator in Atmospheric Air", *Journal of Thermophysics and Heat Transfer*, Vol. 29, No. 2, pp. 222-240. doi: 10.2514/1.T4184
- [21] Meyers, J., and Fletcher, D. "Planar Two-Photon LIF Measurements of Atomic Species in a High-Temperature Inductively Coupled Plasma Environment," (AIAA 2015-2959) 46th AIAA Plasmadynamics and Lasers Conference, 2015
- [22] Meyers, J., Owens, W., and Fletcher, D. (2011) "Near Surface CO₂ Detection in an Inductively Coupled Plasma Facility Using Diode Laser Absorption", 42nd AIAA Thermophysics Conference, Fluid Dynamics and Co-located Conferences. doi: 10.2514/6.2011-3788
- [23] Meyers, J., Tillson, C., and Fletcher, G. (2017) "Temporally and Spatially Resolved Emission of Pyrolyzing Species from a Carbon Phenolic Ablator", 55th AIAA Aerospace Sciences Meeting, AIAA Science and Technology Forum and Exposition
- [24] Milos, F. S. and Chen, Y. K. (2010). "Ablation and Thermal Response Property Model Validation for Phenolic Impregnated Carbon Ablator", *Journal of Spacecraft and Rockets*, Vol. 47, No. 5, pp. 786-805. doi: 10.2514/1.42949
- [25] Minton, T. K. and Bessire, B. K. "Pyrolysis of Phenolic Impregnated Carbon Ablator (PICA)." Early Stage Innovations (NASA). 20 Jan. 2016. Speech.
- [26] "NIST: Atomic Spectra Database Lines Form." NIST: Atomic Spectra Database Lines Form. [http : //physics.nist.gov/PhysRefData/ASD/lines_form.html](http://physics.nist.gov/PhysRefData/ASD/lines_form.html).
- [27] Owens, W., Uhl, J., Dougherty, M., Lutz, A., Fletcher, D., and Meyers, J. "Development of a 30kW Inductively Coupled Plasma Torch for Aerospace Material Testing", (2010) 10th AIAA/ASME Joint Thermophysics and Heat Transfer Conference, Fluid Dynamics and Co-located Conferences. doi:10.2514/6.2010-4322
- [28] Pancrazio, A. (2006). Theoretical and Experimental Study of an ablative TPS Probe in Re-Entry Conditions. Rhode Saint Genese: Van Karmen Institut.

- [29] Playez, M. Titan Atmosphere Plasma Characterization using Spectroscopic Measurement Techniques. Ph.D. thesis, von Karman Institute for Fluid Dynamics (2006).
- [30] Sansonetti, J. E. and Martin, W. C. "Handbook of Basic Atomic Spectroscopic Data." Journal of Chemical Physics Reference Data Vol. 34 No. 4 (2005): 1559-2259.
- [31] Strickler, S. J. "Electronic partition function paradox." Journal of Chemical Education, 43 (7), 364-366. 1966. doi: 10.1021/ed043p364
- [32] Thompson, C. "Analysis of Spectrally Resolved Shock-Layer Emission." Master's thesis, University of Vermont, 2009.
- [33] Tillson, C., Uhl, J., Meyers, J., and Fletcher, G. (2016) "Investigation of Pyrolysis Gas Chemistry in an Inductively Coupled Plasma Facility", 46th AIAA Thermophysics Conference, AIAA Aviation, doi: 10.2514/6.2016-3235
- [34] Tran, H., Johnson, C., Rasky, D., Hui, F., Hsu, M. T., and Chen, Y. (1996) "Phenolic Impregnated Carbon Ablators (PICA) for Discovery class missions", 31st Thermophysics Conference, Fluid Dynamics and Co-located Conferences, doi: 10.2514/6.1996-1911
- [35] Uhl, J. Pyrolysis Investigation in an ICP Torch Facility. Master's thesis, University of Vermont, 2012.
- [36] Uhl, J., Owens, W., Dougherty, M., Lutz, M., Meyers, J., and Fletcher, D. (2011) "Pyrolysis Simulation in an ICP Torch Facility", 42nd AIAA Thermophysics Conference, Fluid Dynamics and Co-located Conferences, doi: 10.2514/6.2011-3618
- [37] Vancrayenest, B., Playez, M., Duchene, L., and Fletcher, D., "Emission Spectroscopy Measurements in a CO₂ Plasma." Project Report.
- [38] Vincenti, W. G., Kruger C. H., "Introduction to Physical Gas Dynamics." Krieger Publishing Co., Malabar, Florida, 1965.
- [39] White, F. M. Viscous Fluid Flow, McGraw-Hill, New York, p. 523, fig. 7-6 (2006)
- [40] Wiese, W. L., Smith M. W., and Glennon, B. M.. "Atomic Transition Probabilities, Volume 1: Hydrogen through Neon." National Bureau of Standards. Washington D.C. Institute for Basic Standards, 1966.

- [41] Winter, M. W, and Auweter-Kurtz, M. (1998). Boundary Layer Investigation in Front of a Blunt Body in a Subsonic Air Plasma Flow by Emission Spectroscopic Means. 7th AIAA/ASME Joint Thermophysics and Heat Transfer Conference. Aberuquerque: Institut fuer Raumfahrtsysteme, Universität Stuttgart
- [42] Wright, M. (2009, October). Data Parallel Line Relaxation (DPLR) Code User Manual Acadia - Version 4.01.1 [PDF]. Moffet Field, California: NASA-Ames Research Center.
- [43] Yakushin, M. I. (2001). An experimental Study of Stagnation Point Heat Transfer from High-Enthalpy Reacting Gas Flow to Surface with Catalysis and Gas Injection. European Symposium on Aerodynamics. Capua.

APPENDIX A

SPECTROMETER CALIBRATION

The uncalibrated setup produces emission measurements in absolute units of counts, which needs to be converted to absolute radiance, with units $\text{W}/\text{cm}^2 \mu\text{m sr}$. Currently, the only spectrometer that has been properly calibrated is the HR4000CG-UV-NIR spectrometer. This was done using an Oriel Instruments Open Air Model 63966 tungsten filament light source. The experimental set-up mimics the set-up for the experimental collection, exhibited in Figure A.1.

Figure A.1: Emission spectroscopy calibration set up [35]

Light from the filament is collected by the HR4000CG-UV-NIR, shown in Figure A.2 in units of counts. This spectra is divided by the provided calibrated emission spectra with units of $\text{W}/\text{cm}^2 \mu\text{m}$, shown in Figure A.3. This gives a calibration file with units of $\text{W}/\text{cm}^2 \mu\text{m}$ counts, shown in Figure A.4. The experimentally collected data is multiplied by this calibration spectra to transform the data from counts to absolute radiance.

Figure A.2: Measured emission spectra of tungsten lamp using HR4000CG-UV-NIR

Figure A.3: Emission data provided by Oriel for tungsten ribbon halogen calibration lamp

Figure A.4: Emission spectroscopy calibration spectra

Due to the lack of light provided by the tungsten lamp in the UV and the low response of the spectrometer in the IR, the usable range is limited to 0.30-0.90 μm . The HR2000+ spectrometer has been tentatively calibrated with the same method using the emitted light from the tungsten lamp in the 0.19-0.42 μm region, shown in Figure A.5.

Figure A.5: Measured emission spectra of tungsten lamp using HR2000+

While this method does not generate a completely accurate calibration, it does provide a better means of comparison between spectrometers. Acquisition of a deuterium arc lamp source for UV calibration is planned to be available in the near term.

APPENDIX B

UNCERTAINTY ANALYSIS PROCEDURE

Uncertainty exists in all measurements taken in various experiments. When those measurements are applied in an equation or derivation, the uncertainty is passed through and is extended to those calculations.

Equation (B.1) shows the derivation for determining uncertainty from measurements and calculations. The basic principle is based on a variation of a least squares mean reduction. Each sigma term within the square root signifies the uncertainty of each measurement technique and the derivative terms denote the uncertainty of each variable as it is passed through the derivation in question.

$$\sigma_A = \sqrt{\sigma_{x_1}^2 \left(\frac{\partial A}{\partial x_1}\right)^2 + \sigma_{x_2}^2 \left(\frac{\partial A}{\partial x_2}\right)^2 + \sigma_{x_3}^2 \left(\frac{\partial A}{\partial x_3}\right)^2 + \dots + \sigma_{x_n}^2 \left(\frac{\partial A}{\partial x_n}\right)^2} \quad (\text{B.1})$$

The determination of uncertainty can be alternatively found by varying the equation in question by the uncertainty percentage in the measurements. For instance, if one variable's uncertainty is $\pm 10\%$, then that value can be varied by that amount in the equation to demonstrate how much of an effect it has on the final product in terms of a percentage, $(\Delta A/A)_{x_i}$.

In this method, the uncertainty of the final measurement with respect to each variable is found. To find the total uncertainty of the measurement, a root mean square average is performed, as shown in Equation (B.2). The final uncertainty is then given in terms of a decimal percentage.

$$(\frac{\Delta A}{A})_{total} = \sqrt{(\frac{\Delta A}{A_{x_1}})^2 + (\frac{\Delta A}{A_{x_2}})^2 + (\frac{\Delta A}{A_{x_3}})^2 + \dots + (\frac{\Delta A}{A_{x_n}})^2} \quad (B.2)$$

APPENDIX C

HEAT FLUX MEASUREMENTS

A simple metric for characterizing each test condition is the use of fully catalytic heat flux measurements. For each test gas/mixture used, the heat flux was determined using a copper slug calorimeter. The calorimeter was positioned in the same location as the PICA and FiberForm tests (90 mm above the chamber floor). The slug calorimeter is shown in Figure C.1.

Figure C.1: Schematic of copper slug calorimeter

The heat transfer rate is measured under the assumption of one dimensional heating through the copper slug. The temperature is recorded using a Type E thermocouple. Figure C.2 shows a sample test and the measured temperature rates of change.

Figure C.2: Sample temperature observation for heat flux calculations

With the rise temperature change quantifies the heating through the slug, and the fall temperature change represents conduction losses through the arrangement. These are used with the copper slug properties and geometry to determine the total heat flux, given in Equation (C.1) where l , ρ , and c_p are the length, density, and specific heat of the copper slug.

$$q = l\rho c_p \left[\left(\frac{dT}{dt} \right)_{rise} + \left(\frac{dT}{dt} \right)_{fall} \right] \quad (C.1)$$

This process was conducted for each static test condition, with the standard deviation, variance. The uncertainty is 0.30. The results are given in Table C.1

Table C.1: Heat flux measurements of test conditions

	q (W/cm^2)	$St.$ $Dev.$	$Var.$
Argon	45.4	3.3	8.4
Ar/N ₂	67.3	2.8	6.0
Ar/O ₂	61.4	3.8	10.9
Ar/Air	61.7	2.7	4.9
Ar/CO ₂	62.3	2.9	5.6

A secondary heat flux approximation is used to strengthen the validity of the above heat flux results using the enthalpy and thermodynamic transport properties of select test conditions. The stagnation point heat flux can be calculated using modified Fay-Ridell method shown in Equation (C.2) [10] below, where Pr is the Prandtl number, ρ and μ are the density and viscosity, $\beta = K \frac{V_\infty}{D}$ ($K = 1.5$ [39], $V_\infty = 152$ m/s [35], $D = 0.0254$ m) is the velocity gradient, h_∞ is the free stream enthalpy, c_p is the specific heat, and T_w is the wall temperature. The test sample geometry yields a velocity gradient of 8976 s^{-1} in the UVM ICP facility.

$$q = 0.76(Pr)^{-0.6}(\rho\mu\beta)^{0.5}(h_\infty - c_p T_w) \quad (\text{C.2})$$

CEA was used to calculate the thermodynamic transport properties of the Argon, Argon/N₂, and Argon/O₂ mixtures, given the conditions presented in Chapter 4. The enthalpies and wall temperatures from Sections 4.3 and 5.1 are used as well. The values for each test condition are given in Table C.2.

Table C.2: Thermodynamic flow properties used for stagnation point heat flux calculation

	Pr	$\rho \text{ (kg/m}^3\text{)}$	$\mu \text{ (Pa}\cdot\text{s)}$	$h_\infty \text{ (J/kg)}$	$c_p \text{ (J/kgK)}$	$T_w \text{ (K)}$
Argon	0.6609	1.64×10^{-2}	1.89×10^{-4}	3.49×10^6	644	1415
Ar/N ₂	0.5497	1.76×10^{-2}	1.74×10^{-4}	4.36×10^6	582	1522
Ar/O ₂	0.6434	1.59×10^{-2}	1.86×10^{-4}	4.00×10^6	731	1573

Using Equation (C.2) and the presented values, the stagnation point heat flux values were determined to be 41.9 W/cm^2 in Argon (8% difference), 62.7 W/cm^2 in Argon/N₂ (7% difference), and 46.1 W/cm^2 in Argon/O₂ (25% difference). While not an exact replication, these results add validity to the experimentally calculated values and tie together the test condition characterization analysis.

APPENDIX D

SAMPLE TEST MATRIX

Test Date	Material	Mass (g, g/s)			Test Gas	Variable Rates	Duration (sec)	Surface Temp (K)	Notes
		Pre	Post	Rate					
20161005	FiberForm	1.121	1.063	0.0005	Argon	N/A	120	~1710	Baseline test in Argon. Used for comparison against PICA results in argon
20161005	FiberForm	1.153	1.020	0.0011	Ar/Air	N/A	120	~1790	Static diluted air test. 2 lpm air. Test results compared against PICA test in argon/air
20161005	FiberForm	1.144	0.778	0.0031	Ar/CO2	N/A	120	~1850	Static diluted CO2 test. 2 lpm CO2 Test results compared against PICA results in argon/CO2
20161006	FiberForm	1.157	1.081	0.0006	Ar/N2	N/A	120	~1800	Static diluted N2 test. 2 lpm nitrogen Test results compared against PICA results in N2
20161006	FiberForm	1.156	0.663	0.0041	Ar/N2	N/A	120	~1890	Static diluted O2 test. 2 lpm oxygen. Test results compared against PICA results in O2

Figure D.1: FiberForm test matrix

Test Date	Material	Mass (g, g/s) Pre Post	Test Gas	Variable Rates	Duration (sec)	Surface Temp (K)	Notes
20160127	PICA	N/A N/A	Argon	N/A	First: 60 Second: 420	Pyrometer Malfunction	Two tests ran. First for 60 sec included emission collection. Potential contamination from material used to image. Second test observed inner temp plateauing. Thermocouples not positioned at desired location. 45 degree TC located off axis and on 60 degree wire. No issue with signal though.
20160216	PICA	2.011 1.672	Ar/N2	0 lpm to 18 lpm in 3 lpm increments every ~15 sec	90	Pyrometer Malfunction	First Incremental N2 addition. N2 dominates immediately (3 lpm) indicating that lower flows need to be controlled to titrate pyrolysis species
20160219	PICA	2.034 1.693	Ar/N2	0, 500, 1000 and 2000 ccm altered every 10 sec	60	Pyrometer Malfunction	Lower flows show that flow between 0 and 1000 ccm has little effect. 1000 to 2000 ccm visual and spectroscopically noticeable
20160302	PICA	2.075 1.735	Ar/N2	1000, 1250, 1500, 1750, 2000 ccm altered every 10 sec	60	Pyrometer Malfunction	Early part of test showed high intensity of nitrogen based species. Slow decrease/depletion through test
20160309	PICA	2.059 1.759	Ar/O2	0 ccm O2 from 0s-10s, 500 ccm O2 from 10s-20s, 0 ccm O2 from 20s-30s	30	~1700	Slight noticeable increase in specie intensity upon addition of O2, not significant. Surface temp constant compared to other tests. Two holes drilled in sample from failed thermocouple installation
20160321	PICA	N/A N/A	Argon	N/A	480	N/A	Test ran to serve as comparison between Carbon based samples. Comparison of CN/C2 traces done. Hydrogen traced as well, significant higher intensity than carbon species. No nitrogen introduced
20160408	PICA	1.955 1.620	Argon	N/A	120	~1720	Re-run of previous pure Argon run for a longer duration, serve as renewing and validating data. Spectrometer collection corrupted by location on sample for first 30 seconds, causing re do of test
20160411	PICA	1.971 1.632	Argon	N/A	120	~1670	New pure Argon baseline for 120 of exposure. Hydrogen signal stronger than Ar/O2 for same exposure times.
20160411	PICA	2.020 1.687	Ar/O2	0 ccm O2 from 0s-10s, 500 ccm O2 from 10s-20s, 0 ccm O2 from 20s-60s. Repeat for second minute	120	~1670	Repeat of 20160309 test for a longer duration. Specie temporal behavior appears to be consistent with previous test O2 test. Not much variation from pure Argon test
20160414	PICA	1.948 1.578	Ar/O2	0 ccm O2 from 0s-10s, 2000 ccm O2 from 10s-20s, 0 ccm O2 from 20s-60s. Repeat for second minute	120	~1700	Similar to 20160309 and 20160411 tests but with a higher flow rate. First O2 addition showed no variation until removal, when Potassium signal spiked. Signal reverted to similar trends shown in pure Argon. Second addition showed spike in Potassium but not Oxygen atom- all other species dropped out in this time. Surface temperature showed increase at O2 addition points
20160503	PICA	N/A N/A	Ar/Air	N/A	60 sec	~2200	Follow up to 20160127 test. Ran in buffered air to induce higher temps and faster pyrolysis evolution
20161005	PICA	1.901 1.541	Ar/N2	N/A	120	~1800	Static diluted nitrogen mixture. 2 lpm nitrogen. Nitrogen based species observed
20161006a	PICA	1.889 1.145	Ar/O2	N/A	120	~1840	Static diluted oxygen mixture. 2 lpm oxygen oxygen based species observed
20161006b	PICA	1.894 1.442	Ar/Air	N/A	120	~1770	Static diluted air mixture. 2 lpm air Nitrogen and oxygen based species observed
20161006c	PICA	1.878 1.335	Ar/CO2	N/A	120	~1790	Static diluted carbon dioxide mixture. 3 lpm CO. Higher rate due to increased baseline reading of flow meter. Carbon and oxygen based species observed
20161006e	PICA	1.902 1.163	Ar/O2	N/A	120	~1830	Repeat of 20161006a test with spectrometer located at 1 mm instead of 2 mm below sample

Figure D.2: PICA test matrix