IGNITION OF ALUMINUM POWDER WITH
A 2.45-GHz MICROWAVE PLASMA TORCH

A Thesis in
Aerospace Engineering

by

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Abstract

Research was conducted at The Pennsylvania State University to investigate and develop a proof-of-concept aluminum igniter using a 2.45-GHz microwave plasma torch. Using Penn State’s Microwave Plasma Torch design, an argon and helium plasma were generated at 300-W delivered power in both air and steam environments. Injector design iterations allowed for steam, with reduced condensation effects, to become entrained within the plasma and mitigated the presence of air chemistry by employing a fused-quartz chamber. Aluminum powder, carried by argon, was able to enter the plasma volume directly at a relatively steady flow rate drawn from a beneficial pressure drop through the delivery line. It was hypothesized that a region in the microwave-generated plasma would have a temperature greater than or equal to 2300 K, the melting point of aluminum oxide, which exists as an ignition-inhibiting layer in aluminum particles. Preliminary work was performed to study the plasma temperature as a function of axial distance and delivered power via diatomic rovibrational spectra fitting of the NO, OH, and N2 positive system bands from axial spectral measurements. Difference in ignition over the axial measurements was noted to depend on the diffusivity of the working gas, as the broadband continuum from the thermal emission saturated the optical spectrometer when using helium as a plasma starter near the injection tube, but it did not signal that saturation had occurred when using argon as a plasma starter.

Validation of the plasma state was obtained via optical emission spectroscopy with reference to profiles of plasma radicals for helium, argon, air, water, aluminum, and aluminum monoxide. Peak lines of interest for the following elements were studied at particular wavelengths: helium at 587.56 nm; argon at 750.387 nm and 811.531 nm; hydrogen at 656.3 nm (Hα); and a hydroxide band from 250 nm to 340 nm (OH: A2 Σ+ → X2 Π). Validation of the ignition state due to the presence of aluminum powder and steam radicals from the plasma source was achieved through thermal emissions registered via optical emission spectroscopy, as well as material analysis through x-ray diffraction of condensed combustion products that showed the presence of elemental aluminum, corundum or α-alumina, γ-alumina, and δ-alumina, along with other aluminum oxide forms. Initial ignition spectra showed an aluminum line present at 396 nm and an aluminum monoxide band spanning from 450 nm to 550 nm. An estimate of the flame temperature from the thermal emission peak wavelength assuming blackbody and grey-body models revealed $T_F = 3583 \pm 326$ K, which follows a similar pattern found in previous literature for flame temperatures.
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Nomenclature

\( a \) waveguide width dimension, m  
\( b \) waveguide height dimension, m  
\( \bar{B} \) magnetic flux density, T  
\( c_0 \) speed of light, \( 2.99 \times 10^8 \text{ m s}^{-1} \)  
\( C \) capacitance, F  
\( D \) diffusion coefficient  
\( \bar{D} \) electric flux density, C m\(^{-2}\)  
\( \Delta E \) transition energy, eV  
\( e \) elementary charge, \( 1.602 \times 10^{-19} \text{ C} \)  
\( \epsilon \) emissivity  
\( \varepsilon \) permittivity, F m\(^{-1}\)  
\( \bar{E} \) complex electric field, V m\(^{-1}\)  
\( E \) Electron orbit energy, eV  
\( E_{b\lambda} \) Blackbody radiation energy emission, K m\(^{-3}\) s\(^{-1}\)  
\( f \) frequency, Hz  
\( f_c \) cutoff frequency, Hz  
\( G \) conductance  
\( \bar{H} \) magnetic field, A m\(^{-1}\)  
\( i \) circuit current, A  
\( I \) traveling wave current, A  
\( j \) imaginary number, \( \sqrt{-1} \)  
\( k \) wavenumber, m\(^{-1}\)  
\( k_c \) cutoff wavenumber, m\(^{-1}\)  
\( L \) inductance, H  
\( L_P \) plasma dimension, m  
\( m \) mass, kg  
\( n \) electron number density, m\(^{-3}\)  
\( N_D \) Debye sphere number  
\( P \) traveling wave power, W  
\( P_e \) rate of energy gain of electrons, J s\(^{-1}\)  
\( P_L \) power delivered to load, W  
\( R \) resistance, \( \Omega \)  
\( \Re \) real number  
\( v \) circuit voltage, V  
\( v_g \) wave group velocity, m s\(^{-1}\)  
\( v_i \) ion generation rate, s\(^{-1}\)  
\( v_p \) wave phase velocity, m s\(^{-1}\)  
\( V \) traveling wave voltage, V  
\( Z_0 \) characteristic impedance, \( \Omega \)  
\( Z_L \) load impedance, \( \Omega \)  
\( \alpha \) attenuation coefficient  
\( \beta \) phase constant  
\( \gamma \) propagation constant  
\( \Gamma \) reflection coefficient  
\( \Gamma_D \) electron current density, A m\(^{-2}\)  
\( \lambda \) wavelength, in vacuum, m  
\( \lambda_D \) Debye length, m  
\( \mu \) permeability, H m\(^{-1}\)  
\( \tau \) average time between collisions, s  
\( 2\theta \) Scattering angle  
\( \Theta \) reflection coefficient phase  
\( \omega \) frequency, radians  
\( \omega_p \) plasma frequency, radians
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Chapter 1 - Introduction

As one of the most abundant metals on the Earth, aluminum has a variety of uses globally due to its attractive properties—lightweight, moderate strength, recyclability, and affordability. Commercial applications of aluminum range from cooking foil to structural beams, yet one of the most promising applications is in the combustion and propulsion fields with the use of aluminum as a metallic fuel. Solid-rocket propulsion, which was tirelessly developed throughout the 20th century, utilized aluminum as a fuel source, although over the years, several modifications were made in order to generate composite fuels.\(^1\) The most difficult challenge in utilizing aluminum as a fuel source is overcoming the ignition-inhibiting, passive oxide layer.\(^2\) It is the aim of this thesis to demonstrate an alternative to achieving aluminum ignition using a plasma as a starter flame source.

1.1 Motivation for Aluminum as a Fuel Source

Since the development of the Bayer process, which produces alumina from naturally-found bauxite via chemical refinement, and the Hall-Héroult process (see Figure 1.1), which yields aluminum from alumina via electrolysis, worldwide access to aluminum has increased and has also significantly reduced the price and perceived rarity of the metal over the course of a century.\(^3,4\) Aside from the use for alloying and construction, aluminum also gained utility in the field of combustion, especially for solid-rocket propulsion (SRP). Processing solid aluminum into a powdered state, with particle size ranging from micrometers to nanometers, enables its delivery into a combustor design. According to DeLuca et al.,\(^1\) aluminum is one of the most attractive fuels for propulsion systems, given its low density of 2.69 g/cm\(^4\), high energy density of 30 kJ/kg, and relatively low cost.

In terms of propulsion applications, aluminum has also been applied as an additive or fuel enhancer. Young\(^5\) explains that, as aluminum particles are added, the volumetric energy stored in the original fuel is increased, leading to improvements in performance, particularly for atmospheric flight. However, for access to space (i.e., ground to low Earth orbit), mass becomes more critical than volume and, as such, the use of SRP prevails, since it offers a large amount of thrust in a small volume in comparison to what liquid fuel would offer. In order to improve the specific impulse, a parameterization of the propellant composition is altered, in which aluminum, a binding agent, and an oxidizer are located together, and such studies are still ongoing.\(^1\) Research has even been conducted to perform in-situ mining and refining of aluminum from
lunar regolith by NASA in order to establish a self-sufficient lunar base for improved exploration and reduced launch and flight cost.\(^6\)

**Figure 1.1:** Schematic of Bayer and Hall-Héroult processes: bauxite to aluminum\(^3\)

For energy applications, a combustor design with aluminum as fuel has also found appeal. Franzoni et al.\(^2\) demonstrated the feasibility of using water as an oxidizer for aluminum combustion in order to not only generate power, but also as a means of creating hydrogen for additional energy uses. It is also pointed out that the combustion process between aluminum and water has low environmental impact, since no toxic or harmful substance is released. However, if a recycling method were introduced for converting the resulting alumina from the combustion process into aluminum through the Hall-Héroult process, carbon monoxide would be generated.

With the evolving use of aluminum, it is of particular interest to promote this energetic metallic fuel for uses other than structures and containers, and possibly to improve current energy-producing methods as well as propulsive mechanisms.
1.2 A Simplified Model of Aluminum Combustion

A basic combustion process is composed of two reactants: a fuel and an oxidizer. When combined in a chamber at appropriate pressure and temperature, a reaction occurs in which products and heat are generated. In commercial vehicles, gasoline or diesel fuel and air are combined at elevated pressures in several piston-cylinders and the resulting reaction generates work onto the piston—which translates into torque and the rotational work on gears, allowing the wheels of an automobile to propel the vehicle forward—and products such as water vapor and carbon dioxide. This process has been studied using hydrocarbon droplet combustion models.

However, when considering aluminum powder as a fuel, the simplicity and the fidelity of these models does not accurately portray the combustion process.

One of the main differences between hydrocarbons and aluminum powder is the inertness and pacification due to the presence of an oxide shell. In aluminum, the surface exposed to the environment rapidly bonds with the available oxygen and forms a thin layer of aluminum oxide, which is the layer that well defines aluminum’s lack of reactivity and oxidation in contrast to other metals such as iron or copper. The presence of this oxide shell alters the expected temperatures of aluminum, whose melting and boiling points at 1 bar are 933 K and 2791 K, respectively, to a melting point of 2300 K and a boiling point of 3200 K. As such, an additional component must be introduced in order to melt the protective oxide shell. In previous experiments, starter or igniter flames composed of propane (C\textsubscript{3}H\textsubscript{8}), carbon monoxide (CO), methane (CH\textsubscript{4}), hydrogen (H), or cyanogen [(CN)\textsubscript{2}] have been utilized in order to begin a combustion process.

Many of those experiments reported that, as the oxide shell temperature approaches its melting point, the liquid aluminum metal expands and can cause fractures in or fragmentation of the aluminum oxide layer. As the liquid or vapor aluminum metal fuel exits the shell, it rapidly reacts with oxygen and hydroxide (see Figure 1.2), resulting in a two-phase flow with condensed combustion products (CCP). DeLuca et al. confirm that the burning of aluminum occurs through a simultaneous steady diffusion flame from the gas phase and an unsteady reaction due to the presence of the liquid phase, and also note that the aluminum particle size can alter the ignition temperatures.
Figure 1.2: Combustion model of an aluminum particle indicating reactants, products, and heat transfer.

1.3 Application of a Microwave Plasma Torch

Even though starter flames, such as propane flames, have been shown to be capable of igniting aluminum, safer alternatives should be considered if a design is intended for commercial use. Propane gas is highly flammable and must be stored properly within isolated containers. Liquid fuels, such as gasoline, are also highly flammable and, as such, they are carefully stored and isolated in a vehicle to protect the driver and passengers from being harmed during operation. As noted before, aluminum, by nature, is inert and non-reactive due to the oxide shell, although in the powder state, it should not be inhaled. By using a plasma element, which consists of ionized atoms, excited molecules, and energetic electrons, the need for chemically reactive substances is eliminated when considering a starter flame because plasma gas temperatures are capable of matching, if not surpassing, the temperatures of a pilot flame, as observed and discussed herein.

A microwave plasma torch (MPT) is an electrical apparatus that applies a strong, yet localized, electric field via delivered microwave power to a working gas flowing through a region called the applicator. If the electric field strength is greater than the breakdown value for the working gas, a discharge occurs, which forms a plasma plume. The working gas needs not be chemically reactive.
For an MPT to operate properly, various components are required. A power source must deliver power to a magnetron, which is a device that converts source power into microwave-frequency power. A conducting element, such as a waveguide or a coaxial cable, efficiently delivers the microwave energy into a cavity or an applicator. Tuning elements allow for increased power coupling so that majority of the power is delivered to the working gas.

Recent research topics for an MPT and other non-microwave based plasma sources have demonstrated applications, not only for igniting fuels such as hydrocarbons or metals, but also for gasification, metal cutting, and environmental purification. The shared mechanism behind such a range of applications is the generation of ions, electrons, and metastable species within a plasma. This is uniquely attractive to chemical reactions, since combustion is highly dependent on the availability of radicals, such as hydroxyl and atomic oxygen, which a plasma can easily provide due to the resulting abundance of excited species. A steam plasma, as an example, would carry a higher number density of OH and O radicals than other previously studied pilot flames, so that a more complete combustion mechanism could occur between aluminum and the oxidizers. The immediate availability and continued production of excited OH and O radicals from the plasma, and the bulk gas heating from the microwave radiation, would consequently increase the burning speed of the aluminum reaction flame. Also evident is a reduction in ignition delay for metallic fuels, since the resulting stable plasma gas temperature (capable of reaching up to 6000 K) would melt the oxide layer more quickly and completely than the historically-used unstable propane flame (reaching up to 2200 K).

1.4 Contributions

This thesis encompasses the design of an MPT following Penn State’s MPT model and testing of the MPT at atmospheric pressure using helium and argon as working gases. Initial experiments performed by Hammond revealed the feasibility of an MPT in air using argon and he studied characteristics of the resulting plasma with regard to coupling between the injector and the waveguide line, and the temperature profile through diatomic rovibrational spectra. Methods in reducing nozzle erosion were also studied. Through fitting methods for OH and N\textsubscript{2} second positive system, a gas temperature range was found to be 2700–3400 K, which was deemed to have utility for industrial-based applications. Further development of the MPT and testing was carried out by Lani to achieve ignition of ionic liquids and validation of sustained combustion using helium as the working gas without the use of a catalyst.

This MPT iteration allows for aluminum powder to flow somewhat steadily through the injector in the MPT applicator and for steam to become entrained near the applicator to roughly resemble a steam environment.
The use of this proof-of-concept igniter model can improve safety in achieving aluminum combustion for power systems or propulsive systems, which greatly benefit from using an energy-rich fuel by eliminating the need for a reactive gas or liquid based starter flame.

1.5 Thesis Organization

This thesis first covers the motivation for aluminum combustion with recent research history of plasma torches. Chapter 2 discusses the theoretical aspects of the MPT, such as electromagnetic transmission theory and the plasma criterion, a simplified aluminum combustion mechanism, and the optical emission spectroscopy (OES) and x-ray diffraction (XRD) techniques used for analysis. Chapter 3 outlines the necessary apparatus in order to perform experiments, such as a magnetron and waveguide circuit to deliver the microwave power, mass flow controls and meters for the plasma gas and water, and power supplies for steam and microwave generation. Chapter 4 denotes the procedures for achieving plasma ignition, steam entrainment, and ultimately, aluminum ignition. Chapter 5 reveals the initial challenges in achieving ignition and experimental results with regard to the emission spectra and the products of reaction under XRD. Chapter 6 provides a review of the experiment and proposes future work that may benefit from improved aluminum flow control and diagnostic tools.
Chapter 2 – Literature Review and Theory

2.1 Electromagnetic Transmission Theory

In order to understand how the MPT operates, it is necessary to understand the mechanism that describes the propagation of electromagnetic waves, especially microwaves which span from 300 MHz to 300 GHz, through media and conductive bodies. Idealized transmission-line theory demonstrates how a wave travels in a rectangular waveguide with arbitrary dimensions. Utilizing this theory, impedance matching and power delivery are discussed, as they are important characteristics of a microwave circuit, along with the development of a standing wave. These elementary concepts are then further developed for a rectangular waveguide. Finally, since the magnetron operates at a frequency of 2.45 GHz, the cutoff frequency for a rectangular waveguide is also discussed.

2.1.1 EM Propagation along a Transmission Line

Steer demonstrates that a section of a uniform transmission line can be modeled using circuit elements, which describe the primary characteristics to be: resistance, inductance, shunt conductance, and shunt capacitance of the line segment (see Figure 2.1). Mathematically, this model uses $R$, $L$, $G$, and $C$ as resistance, inductance, conductance, and capacitance, respectively, in a per-unit-length measure along the spatial dimension $z$. Steer further applies this model to Kirchhoff’s laws and, by limit definition, the voltage ($V$) and current ($i$) differential equations are obtained.

![Figure 2.1: Transmission line segment (a) and a lumped-element model (b)](image-url)
\[ \frac{\partial v(z,t)}{\partial z} = -Ri(z,t) - L \frac{\partial i(z,t)}{\partial t} \]  
(1)

\[ \frac{\partial i(z,t)}{\partial z} = -Gv(z,t) - C \frac{\partial v(z,t)}{\partial t} \]  
(2)

By further assuming steady-state conditions and transforming to phasor notation, Equations 1 and 2 become

\[ \frac{dV(z)}{dz} = -(R + j\omega L)i(z) \]  
(3)

\[ \frac{dI(z)}{dz} = -(G + j\omega C)V(z) \]  
(4)

where \(\omega\) is the frequency in radians and \(j\) is the imaginary number. The voltage or current wave equations can then be obtained by differentiation and substitution, i.e.,

\[ \frac{d^2 V(z)}{dz^2} - \gamma^2 V(z) = 0 \]  
(5)

\[ \frac{d^2 I(z)}{dz^2} - \gamma^2 I(z) = 0 \]  
(6)

where \(\gamma\) is defined as the propagation constant

\[ \gamma = \alpha + j\beta = \sqrt{(R + j\omega L)(G + j\omega C)} \]  
(7)

and \(\alpha\) is the attenuation coefficient in units of nepers per meter and \(\beta\) is the phase constant in units of radians per meter. Fundamental solutions to Equations 5 and 6 are shown to be

\[ V(z) = V_0^+ e^{-\gamma z} + V_0^- e^{-\gamma z} \]  
(8)

\[ I(z) = I_0^+ e^{-\gamma z} + I_0^- e^{-\gamma z} \]  
(9)
where \( V_0^+, I_0^+ \) indicate the forward wave propagating in the \(+z\) direction and \( V_0^-, I_0^- \) indicate the backward wave propagating in the \(-z\) direction. If a line characteristic impedance is defined, and if Equations 8 and 9 are substituted into Equations 3 and 4, then

\[
Z_0 = \frac{V_0^+}{I_0^+} = -\frac{V_0^-}{I_0^-} = \sqrt{\frac{R + j\omega L}{G + j\omega C}} \tag{10}
\]

Additional parameters include the wavenumber, phase velocity, and wavelength, defined respectively as

\[
k = -j\gamma \tag{11}
\]
\[
v_p = \frac{\omega}{\beta} \tag{12}
\]
\[
\lambda = \frac{2\pi}{|\gamma|} = \frac{2\pi}{|k|} \tag{13}
\]

Since components such as coaxial or waveguide lines generally have minimal losses (i.e., \( R \rightarrow 0, G \rightarrow \infty \)), then the quantities can be reduced to the following set

\[
\beta = \omega \sqrt{LC} \tag{14}
\]
\[
k \approx \beta \tag{15}
\]
\[
v_p = \frac{\omega}{\beta} \tag{16}
\]
\[
\lambda = \frac{2\pi}{\beta} = v_p f \tag{17}
\]

where \( f \) is the frequency in units of Hz. In the interest of understanding how information propagates through a medium, the group velocity is defined to be equal to the phase velocity since losses can be assumed to be negligible in a rigid metallic waveguide, i.e.,

\[
v_g = \frac{\partial \omega}{\partial \beta} \approx v_p \tag{18}
\]

It can be noticed that the phase constant, also denoted as the propagation constant in some literature when losses are minimal, directly affects the speed at which information will travel through a medium, which can never exceed the speed of light in a vacuum. A relationship can be drawn between the permeability \( \mu \) and permittivity \( \varepsilon \) and the wavenumber \( k \), as
\[ k = j\omega \sqrt{\mu \varepsilon} \quad (19) \]

2.1.2 **Impedance Matching and Power**

Since the MPT waveguide circuit can be understood to be a nearly lossless transmission line, the plasma can be modeled as a terminating load, as the microwave power from the magnetron is absorbed by the plasma (see Figure 2.2). If the MPT circuit has a characteristic impedance \( Z_0 \) and phase constant \( \beta \), and if the plasma has a different impedance \( Z_L \), the voltage and current equations as a function of position on the \( z \)-axis must meet the new conditions.

**Figure 2.2**: A terminated transmission line with load \( Z_L \)

By applying the constraint (i.e., boundary condition)

\[ \frac{V_L}{I_L} = \frac{V(z = 0)}{I(z = 0)} = Z_L \quad (20) \]

to Equations 8 and 9, we find

\[ \frac{V(0)}{I(0)} = Z_L = Z_0 \frac{V_0^+ + V_0^-}{V_0^+ - V_0^-} \quad (21) \]

By rearranging Equation 21 in order to solve for a ratio of the forward and backward traveling voltages, we obtain
\[ \Gamma = \frac{V_0^-}{V_0^+} = \frac{Z_L + Z_0}{Z_L - Z_0} \]  \hspace{1cm} (22)

which is the reflection coefficient, also known as the voltage reflection coefficient. Equation 22 can be further manipulated in order to solve for the terminating load impedance if the reflection coefficient is known. \( \Gamma \) has a value range from 0 to 1, where 0 implies no reflection occurs and 1 defines absolute impedance mismatch between the transmission line and the terminating load and complete reflection. As such, Equations 8 and 9 can be modified to include the reflection coefficient, i.e.,

\[ V(z) = V_0^+(e^{-j\beta z} + \Gamma e^{j\beta z}) \]  \hspace{1cm} (23)

\[ I(z) = \frac{V_0^+}{Z_0}(e^{-j\beta z} - \Gamma e^{j\beta z}) \]  \hspace{1cm} (24)

From Equations 23 and 24, the power along the transmission line can be determined. The forward power is

\[ P^+ = \frac{1}{2} \Re[V^+(I^+)^*] = \frac{1}{2} \Re \left[ (V_0^+e^{-j\beta z}) \left( \frac{V_0^+e^{-j\beta z}}{Z_0} \right)^* \right] = \frac{1}{2} \frac{|V_0^+|^2}{Z_0} \]  \hspace{1cm} (25)

where the asterisk denotes the complex conjugate and \( \Re \) is the real component of a complex number. Similarly, the reflected power is defined as

\[ P^- = \frac{1}{2} \frac{|V_0^-|^2}{Z_0} = \frac{|\Gamma|^2}{2} \frac{|V_0^+|^2}{Z_0} \]  \hspace{1cm} (26)

The difference of Equations 25 and 26 yields the total power along the line or power delivered to the load

\[ P_L = P^+ - P^- = \frac{1}{2} \frac{|V_0^+|^2}{Z_0} (1 - |\Gamma|^2) \]  \hspace{1cm} (27)

Since most transmission lines have arbitrary properties, then changing the characteristic impedance of the line itself cannot occur. A similar argument can be made for a specific terminating load. In order to minimize the reflection coefficient, matching networks can be established.
Matching networks can be composed of stub lines, which can be understood as lumped capacitance in circuit terminology. These matching networks are thus placed between the transmission line and the terminating load in order to match the output impedance of the transmission line to the input impedance of the load (Figure 2.3). For the case of an MPT, the 3-stub tuner allows for very delicate and fine tuning to optimize the circuit parameters, often known as the $S$-parameters, with $S_{11}$ denoting the reflection coefficient and $S_{21}$ denoting the transmission coefficient.

![Figure 2.3: A matching network allowing for minimal reflection in a terminated line](image)

2.1.3 Standing Wave in a Transmission Line and the Tunable Short

From Equations 23 and 24, it can be observed that both the voltage and current waves are composed of the sum between the forward-traveling and backward-traveling individual components. Assuming that the transmission line and the terminating load are not perfectly matched, then a standing wave is created, as shown in Figure 2.4.

![Figure 2.4: Standing wave depicting the constructive and destructive interference](image)

Ideally, if the forward and backward wave amplitudes are the same, then there are points or instances in time in which the voltage sum totals to zero. If the amplitudes differ, then the standing wave will have nodes indicating minimum voltage and antinodes indicating maximum voltage. From Equation 23, the magnitude of the voltage can be obtained.
\[ |V(z)| = |V_0^+||1 + \Gamma e^{2j\beta z}| = |V_0^+||1 + \Gamma e^{-2j\beta l}| \] (28)

Note that the substitution \( z = -l \) denotes the distance from the load, located at \( z = 0 \), to the generator. Since the reflection coefficient can be established as a complex number \( \Gamma = |\Gamma|e^{j\Theta} \), where \( \Theta \) is defined as the phase of the reflection coefficient, then Equation 28 can be changed to become

\[ |V(z)| = |V_0^+||1 + |\Gamma|e^{j(\Theta-2j\beta l)}| \] (29)

From inspection, a maximum value occurs if the expression \( e^{j(\Theta-2j\beta l)} = 1 \) and a minimum value occurs if \( e^{j(\Theta-2j\beta l)} = -1 \), as shown in Equations 30 and 31,

\[ V_{\text{max}} = |V_0^+|(1 + |\Gamma|) \] (30)
\[ V_{\text{min}} = |V_0^+|(1 - |\Gamma|) \] (31)

whose respective ratio is known as the voltage standing wave ratio (VSWR). Thus, the VSWR can be related to the reflection coefficient: if \( \Gamma = 0 \), then \( VSWR = 1 \), and if \( \Gamma = 1 \), then \( VSWR = \infty \).

\[ VSWR = \frac{V_{\text{max}}}{V_{\text{min}}} = \frac{1+|\Gamma|}{1-|\Gamma|} \] (32)

For the MPT application, it is imperative to understand where the maxima and minima occur, since a tunable short is capable of altering the position of the circuit length. Equation 29 can be converted to a sinusoidal form using Euler’s formula and solved to find

\[ \Theta - 2\beta l_{\text{max}} = 2n\pi \] (33)

where \( n \) is an integer value \( n = 0, 1, 2, \ldots \) and where \( \beta \) can be substituted using Equation 17 to yield

\[ \Theta - 2n\pi = 2 \frac{2\pi}{\lambda_g} l_{\text{max}} \] (34)

Note that \( \lambda_g \) denotes the wavelength of propagation through air. By further rearranging Equation 34, we obtain
\[
\frac{l_{\text{max}}}{\lambda_g} = \frac{1}{2} \left( \frac{\Theta}{2\pi} - n \right)
\]  

(35)

where \(n\) is still an integer but with reversed count direction. Thus, it can be realized that, since the standing wave is a repeating pattern, by placing the minimum voltage value at the termination of the circuit, past the load location, then the maximum voltage value occurs at a location \(\lambda_g/4\) away from the face of the tunable short.

### 2.1.4 The Rectangular Wave Equation

Although transmission-line theory is simple and functional for the purpose of this project, additional information is necessary in order to understand how waveguide dimensions, shown in Table 2.1, affect the chosen operation frequency. From Maxwell’s equations,

\begin{align*}
\text{Faraday’s Law: } \nabla \times \mathbf{E} &= -\frac{\partial \mathbf{B}}{\partial t} = -\frac{\mu \partial \mathbf{H}}{\partial t} \\
\text{Ampere’s Circuit Law: } \nabla \times \mathbf{H} &= \frac{\partial \mathbf{D}}{\partial t} = \varepsilon \frac{\partial \mathbf{E}}{\partial t} \\
\text{Gauss’s Law for Electricity: } \nabla \cdot \mathbf{D} &= 0 = \nabla \cdot \mathbf{E} \\
\text{Gauss’s Law for Magnetism: } \nabla \cdot \mathbf{B} &= 0 = \nabla \cdot \mathbf{H}
\end{align*}

(36)  
(37)  
(38)  
(39)

the following assumptions are made to find suitable solutions: source-free (no active current or electron density from charges in vacuum, similar to air), linear, isotropic, and homogenous medium (little to no motion of air particles while resting inside the waveguide). Equations 36 through 39 encompass the electromagnetic properties of a wave travelling through a rectangular waveguide. \(\mathbf{E}\) refers to the electric field with units of volts per meter, \(\mathbf{D}\) refers to the electric flux density with units of coulombs per square meter, \(\mathbf{H}\) refers to the magnetic field with units of amperes per meter, and \(\mathbf{B}\) refers to the magnetic flux density with units of teslas.

Rearranging Equation 40 yields the Helmholtz equation for the electric field, and a similar approach is taken for the magnetic field.
Table 2.1: Waveguide band standards and internal dimensions

<table>
<thead>
<tr>
<th>Band</th>
<th>EIA Waveguide band</th>
<th>Operating frequency (GHz)</th>
<th>Internal dimensions ((a \times b, \text{ inches}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>R</td>
<td>WR-430</td>
<td>1.70–2.60</td>
<td>4.300×2.150</td>
</tr>
<tr>
<td>D</td>
<td>WR-340</td>
<td>2.20–3.30</td>
<td>3.400×1.700</td>
</tr>
<tr>
<td>S</td>
<td>WR-284</td>
<td>2.60–3.95</td>
<td>2.840×1.340</td>
</tr>
<tr>
<td>E</td>
<td>WR-229</td>
<td>3.30–4.90</td>
<td>2.900×1.150</td>
</tr>
<tr>
<td>G</td>
<td>WR-187</td>
<td>3.95–5.85</td>
<td>1.872×0.872</td>
</tr>
<tr>
<td>F</td>
<td>WR-159</td>
<td>4.90–7.05</td>
<td>1.590×0.795</td>
</tr>
<tr>
<td>C</td>
<td>WR-137</td>
<td>5.85–8.20</td>
<td>1.372×0.622</td>
</tr>
<tr>
<td>H</td>
<td>WR-112</td>
<td>7.05–10.00</td>
<td>1.122×0.497</td>
</tr>
<tr>
<td>X</td>
<td>WR-90</td>
<td>8.2–12.4</td>
<td>0.900×0.400</td>
</tr>
<tr>
<td>Ku</td>
<td>WR-62</td>
<td>12.4–18.0</td>
<td>0.622×0.311</td>
</tr>
<tr>
<td>K</td>
<td>WR-51</td>
<td>15.0–22.0</td>
<td>0.510×0.255</td>
</tr>
<tr>
<td>K</td>
<td>WR-42</td>
<td>18.0–26.5</td>
<td>0.420×0.170</td>
</tr>
<tr>
<td>Ka</td>
<td>WR-28</td>
<td>26.5–40.0</td>
<td>0.280×0.140</td>
</tr>
<tr>
<td>Q</td>
<td>WR-22</td>
<td>33–50</td>
<td>0.224×0.112</td>
</tr>
<tr>
<td>U</td>
<td>WR-19</td>
<td>40–60</td>
<td>0.188×0.094</td>
</tr>
<tr>
<td>V</td>
<td>WR-15</td>
<td>50–75</td>
<td>0.148×0.074</td>
</tr>
<tr>
<td>E</td>
<td>WR-12</td>
<td>60–90</td>
<td>0.122×0.061</td>
</tr>
<tr>
<td>W</td>
<td>WR-10</td>
<td>75–110</td>
<td>0.100×0.050</td>
</tr>
<tr>
<td>F</td>
<td>WR-8</td>
<td>90–140</td>
<td>0.080×0.040</td>
</tr>
<tr>
<td>D</td>
<td>WR-6</td>
<td>110–170</td>
<td>0.0650×0.0325</td>
</tr>
<tr>
<td>G</td>
<td>WR-5</td>
<td>140–220</td>
<td>0.0510×0.0255</td>
</tr>
</tbody>
</table>

\[
\nabla^2 \vec{E} = -k_c^2 \vec{E} \\
\nabla^2 \vec{H} = -k_c^2 \vec{H}
\]

(40)

(41)

In Equations 40 and 41, \(k_c\) corresponds to the cutoff wavenumber and is defined as \(k_c^2 = \gamma^2 + k^2\). The resulting solutions would depict a sinusoidal wave propagating in the \(z\)-axis, or the longitudinal direction of the waveguide. For a lossless model, such as the lossless transmission line or a coaxial model, the propagation constant is found to be \(\gamma = j\beta\). By correlating to the wavenumber:

\[
\beta = \pm \sqrt{k^2 - k_c^2}
\]

(42)

this relationship is understood with regard to the propagation of the wave due to the \(e^{j\omega t - \gamma z}\) dependence and, if the constant is not real, which occurs if \(|k_c| > |k|\), then the wave’s propagation will rapidly decay, which Steer marks as an evanescent mode. The cutoff wavenumber can be further related to the cutoff frequency of the wave inside a rectangular waveguide from the relationship
\[ f_c = \frac{k_c}{2\pi \sqrt{\mu\varepsilon}} \] (43)

For a rectangular waveguide with transverse cross section \( a \times b \) (see Figure 2.5), modes of propagation can be discussed. In general, several modes exist within a waveguide, but due to the cutoff wavenumber or frequency, some of modes rapidly decay, and no transverse electromagnetic modes (TEM) exist inside the waveguide.

The two principal modes of propagation are called the transverse magnetic (TM) and the transverse electric (TE) modes (see Figure 2.6 and Figure 2.7). The variations are distinguished by the individual variations along the \( x \)-direction and the \( y \)-direction using subscripts \( m, n \). For TM modes, the magnetic field in the \( z \)-direction is zero, but the electric field is not. Therefore, Equation 40 becomes

\[ \nabla^2 E_z = \frac{\partial^2 E_z}{\partial x^2} + \frac{\partial^2 E_z}{\partial y^2} = -k_c^2 E_z \] (44)

Through separation of variables and boundary conditions \((H_z = 0 \text{ and perfectly conducting: } E_z = 0 \text{ for } x = 0, a; y = 0, b)\), Steer\(^\text{16}\) shows that Equation 44 has the resulting solution:

\[ E_z = A \sin(k_c x) \sin(k_y y) e^{-\gamma z} \] (45)

\[ k_{c,m,n}^2 = k_{x,m}^2 + k_{y,n}^2 = \left(\frac{mn}{a}\right)^2 + \left(\frac{mn}{b}\right)^2 \] (46)
Substituting Equation 46 into Equation 43 yields the cutoff frequency.

\[
 f_{c_{m,n}} = \frac{1}{2\pi\sqrt{\varepsilon\mu}} \left[ \left( \frac{mn\pi}{a} \right)^2 + \left( \frac{nn\pi}{b} \right)^2 \right]^{\frac{1}{2}} \tag{47}
\]

For the TM mode, \( m = 1 \) and \( n = 1 \) results in the lowest-order propagation mode within a waveguide.

![Figure 2.6: EM field distribution for the TM\(_{11}\) mode](image)

A similar approach is taken for the TE mode analysis, where the electric field in the \( z \) direction is zero but the magnetic field is not. From Equation 41,

\[
 \nabla_{x}^2 H_z = \frac{\partial^2 H_z}{\partial x^2} + \frac{\partial^2 H_z}{\partial y^2} = -k_z^2 H_z \tag{48}
\]

and by separation of variables, boundary conditions (\( E_z = 0 \) and perfectly conducting: \( E_x = 0 \) for \( y = 0, b \); \( E_y = 0 \) for \( x = 0, a \)), and substitution (\( E_x = -\frac{j\omega\mu}{k_z^2} \frac{\partial H_z}{\partial y} \); \( E_y = \frac{j\omega\mu}{k_z^2} \frac{\partial H_z}{\partial x} \)):

\[
 H_z = B\cos(k_x x) \cos(k_y y) e^{-\gamma z} \tag{49}
\]

Since \( m = 1 \) and \( n = 0 \), or TE\(_{10}\), is the lowest-order mode, and more dominant than TM\(_{11}\),\(^\text{15,16} \) then the transverse electric field equations are shown to be

\[
 E_x = \frac{j\omega\mu k_y}{k_{c_{m,n}}^2} B\cos(k_x x) \sin(k_y y) e^{-\gamma z} \tag{50}
\]
\[ E_y = -\frac{j\omega \mu k_x}{k_{cm,n}^2} B \sin(k_x x) \cos(k_y y) e^{-\gamma z} \] (51)

By applying \( m = 1 \) and \( n = 0 \), \( k_y = 0 \),

\[ k_{c_{1,0}}^2 = \left( \frac{\pi}{a} \right)^2 \] (52)

\[ E_y = -\frac{j\omega \mu a}{\pi} B \sin\left( \frac{\pi x}{a} \right) e^{-\gamma z} \] (53)

If a WR-284 waveguide is used, then \( a = 2.84 \) in or 7.21 cm, so that the cutoff frequency is solved to be \( k_{c_{1,0}} = 2.08 \) GHz.\(^{16}\)

![Figure 2.7: EM field distribution for TE\(_{10}\) mode\(^{16}\)](image)

2.2 Microwave Plasma Theory

Even though it has been theorized that 99% of matter in the universe is composed of plasmas, on Earth and at standard temperature and pressure (STP), the prevalence of plasmas is limited.\(^{17}\) Also known as the fourth state of matter, a plasma, as defined by Chen,\(^{17}\) is a quasineutral gas of charged and neutral particles that exhibits collective behavior. This collective behavior is best contrasted against neutral particles, such as air or water, which rely mostly on collisional phenomena in order to experience translation. Since a plasma consists of charged particles, each of which exhibit local electric and magnetic fields due to motion, and Coulomb forces display dominant effects. However, there are two sets of criteria presented below that must
be met in order to determine whether or not a plasma state is achieved, and what constitutes the formation
of a plasma.

### 2.2.1 Plasma Criteria

In order to define a region with a noticeable degree of ionized particles as a plasma, three conditions must be met. First, the Debye shield length must be significantly less than the plasma characteristic length. Second, the number of particles in a Debye sphere must be significantly greater than unity. Finally, the charged particles cannot collide more frequently with neutral atoms than the oscillation period of a plasma. In other words, the motion of the charged atoms cannot be dominated by hydrodynamic forces over electromagnetic forces, resulting in collective behavior.\(^{17}\)

The Debye length is defined as follows:

\[
\lambda_D = \left( \frac{k_B T_e}{4 \pi n e^2} \right)^{\frac{1}{2}}
\]

where \(T_e\) is the electron temperature, \(k_B\) is Boltzmann’s constant, \(n\) is the number density, and \(e\) is the fundamental charge of an electron. This length can be understood by introducing a positive charge within the plasma: electrons are attracted to the source and ions are repelled, but due to the kinetic energy of the electron, no contact is made, resulting in a shield of electrons around the positive charge. The Debye length can then be understood to be a characteristic distance at which the electric field strength generated from the positive charge is reduced to \(1/e\) \((e = 2.71828)\). Effectively, the length is drawn over a fine sheath that develops in a region of the plasma, at which the thermal energy is relatively close to the electric potential. As such, it is intuitive that the shielding dimension be significantly smaller than the dimension of the plasma itself:

\[
\lambda_D \ll L_p
\]

Aside from the shielding length, the Debye sphere is another important concept, effectively requiring a high number density of charged particles within the enclosure of the sphere:

\[
N_D = \frac{4}{3} \pi n \lambda_D^3
\]
Here, $N_D$ stands for the total number of particles in the Debye sphere. This concept requires that there be a significant number of particles within the sphere.

\[ N_D \gg 1 \quad (57) \]

Finally, in order to demonstrate that the electromagnetic forces primarily govern the motion and shape of the plasma over any other macroscopic force, then the charges inside the plasma must be allowed to oscillate before colliding with any other particles. $\omega_p$ represents the plasma frequency and $\tau$ depicts the average time in between collisions involving charged and neutral particles, which is met by

\[ \omega_p \tau > 1 \quad (58) \]

### 2.2.2 Breakdown Criterion

To understand the process of ionizing and producing a breakdown in the gas, some mechanisms must be understood. Prior to a plasma formation, the main motion that enables a discharge to occur is the electron motion. Since electrons are significantly lighter than ions, their behavior are of upmost importance in the transfer of charges. As such, a balance between the generation of charged particles and collisions that lead to loss of charge is sought.

Since microwaves travelling through a transmission line generate strong electric fields, and because the field also increases in strength, the free electrons in the medium will gain energy proportional to the electric field strength. Brown\textsuperscript{18} describes this relationship as

\[ P_e = ne^2 E_e^2 / mv_e \quad (59) \]

which shows how $P_e$, the rate of energy gain of electrons, is related to the electron number density $n$, the electric field strength $E_e$, mass $m$, and frequency of oscillation $v_e$. Since microwaves operate in the high frequency range, in contrast to DC fields, the principal cause of charge loss is diffusion, where $D$ is the diffusion coefficient for electrons and $\Gamma_D$ represents the electron current density given by

\[ \Gamma_D = -D \nabla n \quad (60) \]
To show a balance between the generation and loss of electrons, Brown\cite{Brown1988} uses the simple continuity equation for electrons,

$$\frac{\partial n}{\partial t} = v_i n - \nabla \cdot \Gamma = v_i n + D \nabla^2 n$$ \hspace{1cm} (61)$$

where the term $v_i n$ is the electron generation rate through ionization. From Equation 61, it can be observed that, as the generation term equals or is greater than the diffusion loss term, the number of electrons increases. A simplified solution\cite{Murdock1977} to Equation 61 shows that

$$n = n_0 e^{(v_i - D)t}$$ \hspace{1cm} (62)$$

The exponential relationship between the electron number density and the generation and extinction terms serves as a means of expressing the Townsend breakdown phenomena, in which an electron avalanche is responsible for the first visible discharge and the imminent ionization of the local gas, leading to the plasma formation. As long as $v_i \geq D$, then the electrons will continue to ionize the environment species within the Debye sphere.

The following can be understood as a collection of elements within a plasma: First and foremost, electrons are overwhelmingly evident, as they give a conductive property to plasmas, and are responsible for the Townsend criterion for discharge and breakdown. Secondly, as the electrons collide with neutral gases, they impart energy onto the target atom, which can consequently lose electrons or cause the atom’s electrons to achieve an excited state. This causes the neutral atom to become either an ion or a metastable species. Thirdly, the resulting ion can then collect an electron to reach neutrality, or collide with a neutral or a metastable species. The collection of electrons, ions, and metastable species, while in the presence of an electric field, then continue to sustain the plasma and its morphology.

### 2.3 Aluminum Combustion Mechanism

Although modeling of the aluminum combustion has proven to be very difficult, as briefly explained in Chapter 1, a simplified reaction mechanism can be used to demonstrate the potential reactive behavior of aluminum, aluminum monoxide, along with other aluminum transients, with available oxidizers such as oxygen and water. Table 2.2 shows the modeled mechanism by Beckstead,\cite{Beckstead1998} which includes surface, gaseous, dissociative, and condensing behaviors.
Aside from the modeled mechanism, it is also of particular interest to understand how aluminum achieves ignition in the first place. The first experiments on metallic fuels were performed by Glassman et al. in the 20th century to explain how the passive oxide shell behaved with increasing heat in the environment. By altering the heat transfer rate between the particle and the environment, the temperature of the surface of the shell is changed and, consequently, the expected behavior of aluminum combustion is noted in Figure 2.8. If the particle size is too large, then the heat transfer through the shell is too slow, which results in no combustion. For an appropriately small particle size, presumably in the range of nanometers to micrometers, the heat transfer through the shell is significantly more prominent.
Figure 2.8: Combustion schematic of an aluminum particle for varying surface temperatures\textsuperscript{19}

Since a starter or ignition flame is required to rapidly increase the surrounding temperature, which in turn affects the surface temperature, it is important to note that not all flames are the same. For a cool or weak flame, even for a small particle size, the resulting surface temperature is much lower than the melting temperature of aluminum oxide, which may result in a slight expansion but overall prevents combustion. For a moderately warm flame, the surface temperature may be approximately equivalent to the melting point of the oxide shell, which results in slow burning and, in turn, can have two potential outcomes: incomplete consumption of the aluminum fuel, still encapsulated by the oxide shell at the end, or nearly complete consumption of the metallic fuel with an empty oxide shell. The final case corresponds to a very hot flame, in which the temperature is so intense that the aluminum metal inside the oxide shell vaporizes, causing the oxide shell to fragment or burst completely, and the individual collections of the aluminum vapor burn through a diffusion flame.\textsuperscript{19} Since the plasma gas temperature would be capable of surpassing the melting point of aluminum oxide, then the latter process would be expected to be observed, enabling the prompt and thorough ignition of most of the aluminum particles.

Corresponding flame temperatures from the aluminum combustion process have also been studied through different methods. Beckstead\textsuperscript{7} noted that a peak flame temperature of 4000 K has been observed in previous research and is readily demonstrated in his computational model of the flame development from an ignited
aluminum particle in the micrometer size range. Lynch et al.\textsuperscript{20} documented a volatilization temperature of 3860 K at 10 atm, 4260 K at 3 atm, and an estimated 4190 ± 200 K at atmospheric pressure through the use of a heterogeneous shock tube. Schloeffel et al.,\textsuperscript{21} through a shock tube experiment, estimated a temperature of 3285 ±10 K. Although no means of directly acquiring temperature through probes is used in this project, an approximation is used to calculate the apparent temperature through Wien’s displacement law, as is discussed herein.

It should be noted that this thesis does not cover the specific interaction between the plasma radicals and the aluminum powder, but merely assumes that an interaction is inevitable due to the presence of steam radicals, which includes water, oxygen, hydrogen, and hydroxide. The resulting emission spectra from aluminum ionization and aluminum reaction is covered in the next section.

2.4 Optical Emission Spectroscopy

An invaluable asset to understanding and characterizing plasmas and the ionized gases within the contained volume is optical emission spectroscopy (OES). OES is specifically useful because it does not physically interact with the plasma, in contrast to probes that are generally used for temperature measurements. Since this is a passive means of acquiring data, then the object of interest must be actively emitting signals in the electromagnetic spectrum. Fortunately, a plasma, as defined previously, is a collection of ionized species that emit photons when a transition occurs between the excited and neutral state.

The process leading from excitation to neutrality causes a photon to be emitted, which is then observed on the electromagnetic (EM) spectrum through OES. Lastly, metastable species in general have the shortest lifespan, as the excited electrons quickly return to their neutral orbit and emit a photon as a result.\textsuperscript{22,23} Since different transitions carry different energy changes, and because the energy of a photon can be correlated to a particular wavelength in the EM spectrum, a spectral graph can be produced by integrating the signal counts over a period of time, with sharp peaks indicating atomic excitation transitions and bands denoting diatomic excitation transitions.

The quantum model, often described as statistical thermodynamics, for transitions, transition probabilities, and resulting emissions is relatively simple for atoms, such as helium or argon. If a diatomic substance, such as nitrogen gas or hydroxide, is considered, then additional understanding regarding the rovibronic transitions is required, as diatomic molecules are capable of exhibiting vibrations due to the bond between the two individual atoms, which can occur simultaneously with rotational energy transitions.
In OES, the emitted photons are collected and studied using an optical spectrometer, as shown in Figure 2.9. Using a fiber optic cable, connected to the input jack (labeled 1), emitted light can be transported with minimal alterations to the aperture of the spectrometer (2). Also known as the slit, this section regulates the spectral resolution achieved. A filter (3) is an optional means of observing a specific wavelength or a limited region from the source spectra. Light is then focused by a collimating mirror (4) onto a grating (5) that diffracts the incoming light into a specific wavelength span. Another focusing mirror (6) allows for the diffracted light to reach a collection lens (7) that causes additional focusing onto the CCD detector (8). The detector then converts the optical signal into a digital signal.

**Figure 2.9:** Interior of an HR4000 spectrometer, courtesy of OceanOptics

### 2.4.1 Argon and helium plasmas in air spectra

Since argon and helium are the easiest working gases to breakdown and ignite for plasma generation, it was deemed ideal to use these two noble gases in order to correlate data obtained from this project to previous research. Due to the presence of air in the plasma environment, additional elements, primarily nitrogen and oxygen, can appear in the plasma emission spectrum. Figure 2.10 shows the argon plasma spectrum in air obtained by Cullen et al.,\textsuperscript{22} noting that argon contains several spectral lines ranging from 700 nm to 850 nm, also tabulated in Table 2.3.
As noted, the presence of the air chemistry is evident within the plasma emission spectra, enabling nitrogen and atomic oxygen to be displayed. Atomic oxygen displays two sets of triplet peaks at 777 nm and 844 nm (see Table 2.4). Both argon and atomic oxygen lines are very sharp, well-defined, and as such lack broadband width, in contrast to the nitrogen lines.

Nitrogen gas has three principal systems for rovibrational broadband transitions: the first negative system (FNS) with a peak emission line at 391.44 nm, the first positive system (FPS), and the second positive system (SPS). In general, the FNS and SPS are the most visible bands in the spectra in the lower UV region. Although additional emissions, such as for molecular oxygen, do exist, given the range of an optical spectrometer, they may not appear at all or the transition energy may simply be very weak in comparison to other bands. Figure 2.11 depicts a diagram showing the transition energies and resulting emission wavelengths, along with the transition locations, for the experiment conducted by Cullen et al.\textsuperscript{22}
Table 2.3: Argon excitation transitions

<table>
<thead>
<tr>
<th>λ (nm)</th>
<th>Transition</th>
<th>$E_i$ (eV)</th>
<th>$E_f$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>696.543</td>
<td>$2p_2^2P \rightarrow 1s_3P$</td>
<td>13.33</td>
<td>11.55</td>
</tr>
<tr>
<td>706.722</td>
<td>$2p_3^2P \rightarrow 1s_3P$</td>
<td>13.30</td>
<td>11.55</td>
</tr>
<tr>
<td>714.704</td>
<td>$2p_4^2P \rightarrow 1s_3P$</td>
<td>13.28</td>
<td>11.55</td>
</tr>
<tr>
<td>727.294</td>
<td>$2p_2^2P \rightarrow 1s_4P$</td>
<td>13.33</td>
<td>11.62</td>
</tr>
<tr>
<td>738.398</td>
<td>$2p_3^2P \rightarrow 1s_4P$</td>
<td>13.30</td>
<td>11.62</td>
</tr>
<tr>
<td>750.387</td>
<td>$2p_1^2S \rightarrow 1s_2P$</td>
<td>13.48</td>
<td>11.83</td>
</tr>
<tr>
<td>751.465</td>
<td>$2p_3^2P \rightarrow 1s_4P$</td>
<td>13.27</td>
<td>11.62</td>
</tr>
<tr>
<td>763.511</td>
<td>$2p_5^2D \rightarrow 1s_5P$</td>
<td>13.17</td>
<td>11.55</td>
</tr>
<tr>
<td>772.376</td>
<td>$2p_7^2D \rightarrow 1s_5P$</td>
<td>13.15</td>
<td>11.55</td>
</tr>
<tr>
<td>772.421</td>
<td>$2p_2^2P \rightarrow 1s_3P$</td>
<td>13.33</td>
<td>11.72</td>
</tr>
<tr>
<td>794.818</td>
<td>$2p_4^2P \rightarrow 1s_3P$</td>
<td>13.28</td>
<td>11.72</td>
</tr>
<tr>
<td>800.616</td>
<td>$2p_6^2D \rightarrow 1s_4P$</td>
<td>13.17</td>
<td>11.62</td>
</tr>
<tr>
<td>801.479</td>
<td>$2p_8^2D \rightarrow 1s_5P$</td>
<td>13.09</td>
<td>11.55</td>
</tr>
<tr>
<td>810.369</td>
<td>$2p_7^2D \rightarrow 1s_4P$</td>
<td>13.15</td>
<td>11.62</td>
</tr>
<tr>
<td>811.531</td>
<td>$2p_9^2D \rightarrow 1s_5P$</td>
<td>13.08</td>
<td>11.55</td>
</tr>
<tr>
<td>826.452</td>
<td>$2p_2^2P \rightarrow 1s_2P$</td>
<td>13.33</td>
<td>11.83</td>
</tr>
<tr>
<td>840.821</td>
<td>$2p_3^2P \rightarrow 1s_2P$</td>
<td>13.30</td>
<td>11.83</td>
</tr>
<tr>
<td>842.465</td>
<td>$2p_5^2D \rightarrow 1s_4P$</td>
<td>13.09</td>
<td>11.62</td>
</tr>
<tr>
<td>852.144</td>
<td>$2p_4^2P \rightarrow 1s_2P$</td>
<td>13.28</td>
<td>11.83</td>
</tr>
</tbody>
</table>

Figure 2.12 shows the obtained spectra by Xiong et al. with helium in an open environment. Since helium has only two valence electrons, the helium lines are less evident and fewer in number than those shown for argon in Figure 2.10. Respectively, Table 2.5 displays the studied helium excitation transitions, with the most probable transition resulting in an emission at 587 nm. It is worth noting that, for a plasma in open air at STP, some systems overlap. As evidenced in Figure 2.12, the hydroxide excitation transition band overlaps with the nitrogen SPS.
Figure 2.11: Simplified transitions for argon, nitrogen, and oxygen species

Table 2.4: Atomic oxygen excitation transitions

<table>
<thead>
<tr>
<th>( \lambda ) (nm)</th>
<th>Transition</th>
<th>( E_i ) (eV)</th>
<th>( E_f ) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>616</td>
<td>4d (5D(^{5,4,3,1})) \rightarrow 3p (5P(_{3,2,1}))</td>
<td>12.7</td>
<td>10.7</td>
</tr>
<tr>
<td>645</td>
<td>5s (5S(<em>{2})) \rightarrow 3p (5P(</em>{3,2,1}))</td>
<td>12.6</td>
<td>10.7</td>
</tr>
<tr>
<td>777</td>
<td>3p (5P(<em>{3,2,1})) \rightarrow 3s (5S(</em>{2}))</td>
<td>10.7</td>
<td>9.1</td>
</tr>
<tr>
<td>845</td>
<td>3p (5P(<em>{0,2,1})) \rightarrow 3s (5S(</em>{1}))</td>
<td>11.0</td>
<td>9.8</td>
</tr>
</tbody>
</table>
2.4.2 Steam and aluminum plasma spectra

Since this thesis deals with using steam as an oxidant, it is also important to study the emission spectra for the hydroxyl–hydroxide transitions and the evident hydrogen lines. Zhao et al. performed an experiment in which a 2.45-GHz microwave source was used to generate a water plasma in a liquid water environment, allowing for clear visualization of only water-related bands and lines. Figure 2.13 shows the primary OH
band spanning from 250 nm to 340 nm and the $H_\alpha$ and $H_\beta$ peak lines located at 656 nm and 486 nm, respectively.

![Water plasma emission spectra from a dc discharge jet](image)

**Figure 2.13**: Water plasma emission spectra from a dc discharge jet$^{24}$

In their study, the dissociation of liquid water molecules is also studied and explained, as the intensity of the electric fields resulting from the microwave power is responsible for the direct creation of ionized elements. Table 2.6 provides the primary forms of radical hydroxide generation and the respective energy thresholds to achieve such an ionization reaction between vibrational transitions noted by $\nu$.

Although active study of aluminum plasma physics is not entirely pervasive, a reference was obtained from Mohamed$^{25}$ who attempted to demonstrate impurities in alloyed aluminum metals through laser-induced breakdown spectroscopy (LIBS) shown in Figure 2.14. In order to confirm the specific values of the peak lines for aluminum, a database created by Sansonetti et al.$^{26}$ was used and tabulated, as provided in Table 2.7.
Table 2.6: Water main excitation system

<table>
<thead>
<tr>
<th>Transition</th>
<th>Peak Wavelength (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Hydroxide</strong></td>
<td></td>
</tr>
<tr>
<td>$A^2\Sigma^+(v = 1) \rightarrow X^2\Pi(v = 0)$</td>
<td>282</td>
</tr>
<tr>
<td>$A^2\Sigma^+(v = 2) \rightarrow X^2\Pi(v = 1)$</td>
<td>289</td>
</tr>
<tr>
<td>$A^2\Sigma^+(v = 0) \rightarrow X^2\Pi(v = 0)$</td>
<td>309</td>
</tr>
<tr>
<td><strong>Hydrogen</strong></td>
<td></td>
</tr>
<tr>
<td>$n = 3 \rightarrow n = 2, H_{\alpha}$</td>
<td>656.3</td>
</tr>
<tr>
<td>$n = 4 \rightarrow n = 2, H_{\beta}$</td>
<td>486.1</td>
</tr>
<tr>
<td><strong>Oxygen</strong></td>
<td></td>
</tr>
<tr>
<td>$3p^5P \rightarrow 3s^5S$</td>
<td>777.1</td>
</tr>
<tr>
<td>$3p^3P \rightarrow 3s^3S$</td>
<td>844.6</td>
</tr>
</tbody>
</table>

Figure 2.14: Aluminum emission spectra acquired from laser-induced breakdown spectroscopy
Two final references for aluminum monoxide lines, evident in aluminum ignition literature, were acquired from Parigger et al.\textsuperscript{27,28} through two separate instances: a combustion experiment and a simulation of the rovibronic transition. Figure 2.15 and Figure 2.16 depict the aluminum monoxide bands, with three primary peaks, the tallest signifying the vibrational transition $\Delta v = 0$ located near 484 nm. As understood with other diatomic spectra, such as nitrogen, main peaks are denoted by vibrational transitions, but each individual broadband region contains smaller peaks, which can be understood as the coupled rotational transitions, giving the behavior the title of rovibrational transition.

![AlO emission lines noting vibrational and rotational peaks via OES\textsuperscript{27}](image)

**Figure 2.15:** AlO emission lines noting vibrational and rotational peaks via OES\textsuperscript{27}
2.4.3 Temperature Measurement through Diatomic Rovibrational Spectra

If a temperature estimation of the entrained plasma gas is desired, then a non-intrusive method must be sought in order to avoid introducing additional substances (i.e., nickel/chromium neutrals and ions from a thermocouple) to the plasma that would alter its profile. Previous experiments regarding plasmas and respective temperature profiles in the axial or radial directions have used the rotational temperature of diatomic gases present in the plasma and evident in the resulting spectra.\textsuperscript{12,13} and Hammond\textsuperscript{8} explains the underlying assumption that the rotational temperature, since the energy levels are tightly spaced and thus react rapidly to thermal changes, can approximate the gas temperature.

A reason as to why this assumption works can be understood by observing the responsible metastable species involved in Penning ionization, where a metastable atom imparts an electron to a neutral molecule via collision. For argon, Hammond\textsuperscript{8} argues that, due to the lifespan of the Ar\((^3P_{0,2})\) metastable, the nitrogen SPS, noted as N\(_2\)(C) and similarly the hydroxide radical OH(A) become evident throughout the volume of the plasma. For helium, Xiong\textsuperscript{23} notes that it is more likely for electron-impact excitation to generate the
OH(A) and N\(_2\)(C) states, and for the helium metastable (2\(^3\) S) to collide with nitrogen to produce the N\(_2^+\) bands. Table 2.7 notes the three primary nitrogen systems generally visible or understood to partake in plasma OES.

<table>
<thead>
<tr>
<th>Transition</th>
<th>Peak Wavelength (nm)</th>
<th>Energy Threshold (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N(_2^+) FNS: B(^2)(\Sigma_u^+) → X(^2)(\Sigma_g^+)</td>
<td>391.44</td>
<td>18.8</td>
</tr>
<tr>
<td>N(_2) FPS: B(^3)(\Pi_g) → A(^3)(\Sigma_u^+)</td>
<td>654</td>
<td>7.35</td>
</tr>
<tr>
<td>N(_2) SPS: C(^3)(\Pi_u) → B(^3)(\Pi_g)</td>
<td>337.14</td>
<td>10.03</td>
</tr>
</tbody>
</table>

With the diatomic rovibronic spectra obtained via OES, a comparison can be made between the resulting lines and respective intensities to the theoretical or simulated bands, which depend on the environmental temperature to generate a profile with rotational and vibrational temperatures for a particular diatomic molecule. Theoretical study, as performed by Hammond,\(^8\) of such a method is outside of the scope of this thesis and, instead, a third-party software, known as Specair, is employed in order to produce a simulated spectrum of the nitrogen systems and of the hydroxide band, comparing the simulated spectrum to the experimental data and recording the matching simulated spectrum’s diatomic rotational temperatures.

### 2.4.4 Wien’s Displacement Law

In 1901, Max Planck published an equation that defined the spectral blackbody emissive power, which Çengel\(^2^9\) defines as the amount of radiation energy emitted by a blackbody at a thermodynamic temperature \(T\) per unit time, per unit surface area, and per unit wavelength about the wavelength \(\lambda\). Also known as Planck’s Law, this relationship is

\[
E_{\lambda}(\lambda, T) = \frac{C_1}{\lambda^5 \left[ \exp(C_2/\lambda T) - 1 \right]}
\]

where \(C_1\) and \(C_2\) are constant coefficients defined as

\[
C_1 = 2\pi \hbar c_0^2 = 3.74177 \times 10^8 \text{ W} \cdot \mu\text{m}^4/\text{m}^2
\]

\[
C_2 = \hbar c_0 / k = 1.43878 \times 10^4 \mu\text{m} \cdot \text{K}
\]

with \(c_0\) represents the speed of light in a vacuum.
Figure 2.17 shows the relationship between the emissive power and the wavelength at varying temperatures. Upon closer inspection, one can note that each isotherm has a peak corresponding to the maximum emissive power, and from that observation, a new simplified relationship can be obtained. This, however, was obtained by Wien through purely classical thermodynamics in 1894 and was known as Wien’s displacement law, but can be derived from Planck’s law.

Figure 2.17: Blackbody emissive power as a function of $\lambda$ and $T$
If we differentiate Equation 63 with respect to the wavelength, while keeping temperature constant, and equating that to zero, then we obtain:

$$\frac{\partial E_{bb}(\lambda)}{\partial \lambda} = C_1 \left[ \frac{C_2}{T \lambda^7} \frac{\exp \left( \frac{C_2}{\lambda T} \right)}{(\exp \left( \frac{C_2}{\lambda T} \right) - 1)^2} - \frac{5}{\lambda^6 \exp \left( \frac{C_2}{\lambda T} \right) - 1} \right] = 0 \quad (64)$$

Multiplying Equation 64 by the term $\lambda^6[\exp(C_2/\lambda T) - 1]$, then we obtain

$$\frac{C_2}{T \lambda} \frac{\exp \left( \frac{C_2}{\lambda T} \right)}{(\exp \left( \frac{C_2}{\lambda T} \right) - 1)} - 5 = 0 \quad (65)$$

Since $C_2$ and $T$ are constants, then a numerical solution for the wavelength can be achieved from Equation 65, such that:

$$\frac{C_2}{T \lambda_{\text{max}}} = 4.96511 \quad (66)$$

Rearranging Equation 66 to solve for the temperature and peak emission wavelength yields Wien’s displacement law:

$$(T \lambda)_{\text{max}} = \frac{C_2}{4.96511} = 2.8978 \times 10^6 \text{ nm} \cdot \text{K} \quad (67)$$

By recognizing that the peak blackbody emission occurs at a specific wavelength, as could be denoted in the thermal emission signature via OES, then a temperature estimation of the emitting body could be obtained. However, as pointed out by Parigger, modifications can be made to Wien’s displacement law to account for emissivity values that vary with wavelength, known as grey-body emissivity:

$$(T \lambda)_{\text{max}} = 2.415 \times 10^6 \text{ nm} \cdot \text{K} \rightarrow \epsilon = \epsilon(1/\lambda) \quad (68)$$

$$(T \lambda)_{\text{max}} = 2.070 \times 10^6 \text{ nm} \cdot \text{K} \rightarrow \epsilon = \epsilon(1/\lambda^2) \quad (69)$$
Equations 68 and 69 then aid in accounting for the fact that thermal emissions from flames do not necessarily embody constant emissivity. Ultimately, Wien’s displacement law could be applied to obtain a flame temperature during aluminum combustion with steam while a relatively steady thermal emission profile, captured by OES, is observed and whose maximum intensity peak can be used to note the wavelength at which the emissive power is the greatest. This wavelength is then used in Equations 67 through 69 to calculate the flame temperature, depending on the emissivity model.

2.5 X-Ray Diffraction

The application of x-ray diffraction, or x-ray scattering, has had profound impact in material sciences and the physical studies of crystalline structure. Akin to how visible light is bent by passing through some objects, or diffracted through media, x-rays undergo a scattering pattern depending on the material it passes through. This phenomenon, upon close study, allows us to identify certain patterns and correlate them to unique crystal structures pertaining to a substance.

Crystals possess an organized structure scheme, whereby the overall repeating pattern can be reduced to a single microscopic symmetric unit, which is then stacked in all directions to mimic the real, macroscopic order of the crystal substance. Note that this process could not be repeated for materials such as glass or fluids, since an orderly structure would not be present.

In order to provide a scattering pattern of the aforementioned sample, a source must be provided. Although light would be diffracted by passing through the substance, due to the wavelength of visible light in the EM spectrum, resolution would be limited and not fine enough to denote intermolecular bonds. X-rays, as stated by van Holde, in contrast, have a wavelength scale sufficiently resolute for resolving atoms separated by the distance of a covalent bond. As such, since a wavelength and intermolecular scale along with a scattered pattern are present, a relationship can be established.

If an x-ray wave is emitted and is incident onto a reflecting plane of an idealized, one-dimensional crystal structure, as shown in Figure 2.18, at an arbitrary angle $\theta$, when a scattered wave results due to the same reflecting plane. The reflecting plane can be thought of as having a repeating pattern in one dimension with a spacing equivalent to $d$ and arbitrary phase. This is useful to establish because the pattern observed is due to the constructive interference between the scattered waves at certain angles.
If the reflecting planes are indeed in arbitrary and equal phase, then a relationship can be drawn between the difference in length of the emitted and scattered waves and the wavelength of the incident x-ray:\(^{30}\)

\[
PD = n \cdot \lambda
\]  

(70)

Due to a geometrical identity step, the path difference is also related to the angle \(\theta\):

\[
\frac{1}{2} PD = d \cdot \sin(\theta)
\]  

(71)

By equating Equations 70 and 71 to each other, then one can obtain Bragg’s law of diffraction:

\[
2d\sin(\theta) = n \cdot \lambda
\]  

(72)

Further development of Bragg’s law to apply to multiple dimensions can be understood through von Laue conditions for diffraction. This also shows that scattering of x-rays occurs not because of a perfectly reflective surface, but because the atoms present are oscillating dipoles.\(^{30}\)

Ultimately, an experimental XRD profile, created from the solid products collected after a combustion process, can be used to identify the individual species, whose reference XRD profiles can be obtained from...
the International Center of Diffraction Data, within the product collection. Regarding Figure 2.19, the experiment involved a reaction between aluminum powder and steam that Lee et al.\textsuperscript{12} carried out, yielding a white and gray solid substance that was collected and studied through XRD. By comparing the experimental profile to the aluminum oxide (also known as alumina, Al\textsubscript{2}O\textsubscript{3}) and aluminum XRD references, a match between unique crystal structures can lead to the justification of a combustion phenomenon.

**Figure 2.19:** (a) Alumina reference (top) and combustion XRD profile (middle) with (b) elemental aluminum reference\textsuperscript{12}

It is also important to note that, aside from α-Al\textsubscript{2}O\textsubscript{3} (alpha alumina or corundum), other transient alumina structures are capable of developing, such as γ-alumina and δ-alumina.\textsuperscript{31} Additional XRD references are provided below, as seen in Figure 2.20.
Figure 2.20: XRD profiles for various transition aluminas used for identification\textsuperscript{31}
Chapter 3 – Design and Experimental Set-Up

In this chapter, the MPT, working gas supply, steam delivery, aluminum delivery devices, and the data acquisition devices are explained in detail and can be observed how they connect to each other in order to achieve aluminum ignition but also record the resulting spectral data.

3.1 Microwave Plasma Torch Experimental Apparatus

As briefly described in Chapter 1, several electrical elements were required in order to design a fully-functional microwave plasma torch. For this experiment, a Daihen SPG-15A High Voltage Module power supply unit (Figure 3.1) and a Daihen SGM-15A 2.45-GHz Magnetron (Figure 3.2) were the primary components for microwave power generation. The SPG-15A uses a 3-phase 200-V\textsubscript{AC} power cable and connects to the magnetron via a high voltage cable, a filament AC cable, a filament control cable, and a detector cable.

The high voltage and AC cables provide the power delivered to the magnetron, and the filament control cable enables the power adjustment knob to alter the power supplied to the magnetron, which ranges from 0 to 1.5 kW.

![Figure 3.1: Daihen SPG-15A Power Supply capable of delivering up to 1.5 kW of total power](image)
The detector cable connects to the SGD-15A Detector and allows for the power supplied to be monitored by the SPG-15A unit. An electrical interlock in the SPG-15A unit requires a separate power supply of 12 V, and a physical interlock requires tightening in order to fully enable power to be supplied to the magnetron.

The Daihen CMC-10 Tuning box (Figure 3.5) is an automatic controller unit for tuning the impedance matching between the load and the source. A voltage supply of 10 V is necessary for operation (Figure 3.3 and Figure 3.4), and the box uses a data cable to control the stub tuners built-in on the magnetron. Since it is an automatic tuning device, a threshold of minimal power reflection was set for the experiment run. However, when excessive impedance mismatch was experienced, the tuning box would not be capable of resolving the reflection. A built-in isolator provides an outlet for reflected power in the magnetron as a safety mechanism.
Figure 3.3: TopWard Dual-Tracking DC Power Supply capable of delivering up to 25 V\textsubscript{DC}

Figure 3.4: Power supplied to SPG-15A interlock and SMA-10A tuner
The microwave power produced was safely and efficiently transported through a series of WR-430 waveguides, ultimately connecting to the 3-stub tuner. From the tuner, a WR-430 to WR-284 reducing adapter was used in order to connect to the tapered WR-284 waveguide, also known as the applicator (Figure 3.6). At the end of the microwave circuit, a tunable short was added, which allows for a coarser adjustment in impedance matching by altering the standing wave peak position. Figure 3.7 shows the schematic of all microwave components.

With regard to safety measures, the following elements were obtained or created to avoid microwave radiation hazards during periods of operation. A NARDA Model 8712 electromagnetic radiation survey meter, capable of detecting power intensities up to 100 mW/cm², proved to be very valuable in leak diagnostics, shown in Figure 3.8.
Figure 3.7: Microwave Power Delivery schematic

Figure 3.8: NARDA survey meter with probe used for measuring microwave radiation leak
OSHA requirements indicated that a value of 6 mW/cm² with safety margin should be used near the MPT and this value was kept under surveillance using the survey meter. A Faraday cage was also constructed using fine stainless steel welded wire mesh in order to contain the microwave radiation within the applicator. A cylindrical cage (Figure 3.9), securely placed on the applicator copper plate seal rest, allowed for relatively complete view access to the working gas plasmas without exceeding radiation levels above OSHA specifications.

Figure 3.9: Cylindrical Faraday cage made from stainless steel wire mesh to contain microwave energy emitted from the applicator
3.2 Working Gas Feed System

Two different, inert gases were used for this experiment: helium and argon. Two Praxair cylinder gas tanks containing ultra-high purity grade helium and argon were purchased. Proper transportation and storage of the cylinders are important prior to using the bottles, since the cylinders are rated to 2000 psi. A pressure regulator, rated to a maximum of 6000 psi, was used to scale down the gas flow to a workable pressure of up to 150 psi (Figure 3.10). Flexible, yet pressure-resistant lines were used to transport the inert gas to the mechanical mass flow controller.

![Figure 3.10: 2000 psi Praxair gas cylinder with pressure regulator installed](image)

In order to accurately read the gas mass flow, a Sierra SmartTrak100 mass flow meter (MFM) was purchased to be used in concert with the mechanical mass flow controller (see Figure 3.11). The MFM contains calibration factors for factory-set gases, which include helium and argon, allowing for seamless integration and utilization. From the MFM, a polytetrafluoroethylene (PTFE) 0.25-in-diameter line allowed for gas to flow to a Y-shaped union in order to reach the applicator through the injector tube. Figure 3.12 depicts a schematic for the gas delivery system.
Figure 3.11: Sierra mass flow meter used to measure helium and argon mass flows

Figure 3.12: Working gas system schematic

3.3 Steam Feed System

A water supply and delivery unit were devised in order to allow steam to enter the applicator environment. A simple, metallic, kettle-like reservoir (Figure 3.13) was filled with mostly deionized water and pressurized from 3–5 psig with nitrogen gas from a K-type cylinder. The nitrogen pressure was first regulated with a pressure regulator down to roughly 50 psi, then with a Paasche R-75 pressure regulator to achieve the 3 to 5 psig range, monitored by a Noshok 30-psi pressure gage. A 50-micron filter was placed
in the line in order to prevent any insoluble products in the deionized water from passing through the feed lines.

![Image](image.jpg)

**Figure 3.13:** Water reservoir with pressurant and delivery ports

In order to measure the quantity of water delivered, a metering unit was required. As such, an ELDEX Stainless Steel Optos 2HM metering pump was utilized, which was capable of delivering flow rates of 0.02 to 40.00 mL/min, shown in Figure 3.14. Additional filters were set to ensure that the water passing through the metering unit did not carry particulates. Polyetheretherketone (PEEK) tubing was used to connect the exit of the filtering line to the inlet of the heating coil. In order to quickly vaporize the liquid water passing through a 0.125 in × 12 ft stainless steel coiled tube, a Power Ten DC power supply unit (Figure 3.15) was connected as a means of providing resistive, or Joule, heating directly onto the metal coil (Figure 3.16). A cylindrical structure was created using a 2-in hollow aluminum cylinder and two aluminum disks, along with insulating material, to support the hot metal coil.
Once the steam coil terminated, the steam was then split by a Swagelok T-splitter. Two 0.125-in copper tubes were connected to the exits of the splitter and inserted into the reaction chamber, which was constructed out of fused quartz to isolate the steam from the open environment and to enable clear visualization of the applicator and its surroundings. The quartz chamber was 12.5 in tall, with an approximate 2-in outer diameter and 0.064-in wall thickness (see Figure 3.17). A restriction was added to the quartz chamber 10 in from the base, as to reduce the outer diameter from 2 in to 1 in and effectively provide a small pressure build-up during testing, resulting in a “chimney” appearance. Two 0.25-in × 3-in quartz ports were added to the chimney 2.4 in from the base angled down and tangential to the curvature of the chamber. This enabled the steam to come in tangentially, creating a vortex shape so that the plasma would remain centered and steam entrainment would be improved.

The quartz chimney was set on the applicator copper plate seal rest and centered through an aperture on a stainless steel shield that rested along the span of the tunable short, the applicator, and the WR-430 to WR-284 transition piece. The need for the shield, also called the waveguide guard, is explained in the next subsection.
Figure 3.15: Steam power supply unit capable of delivering up to 50 V and 40 A

Figure 3.16: Stainless Steel heating coil (red arrow) with structural support and insulator.
Due to the complex geometry of the quartz chimney, a new Faraday cage was constructed using the same material as the first cylindrical cage. Since the waveguide guard was made from stainless steel, it was deemed ideal to make a rectangular cage and to spot-weld the long sides of the cage on the guard for structural stability (reduced wobbling) due to expected height of the cage (17 in). In order to accommodate the steam swirl ports on the chimney, two sections were cut out from the Faraday cage and two separate enclosure mesh shields were made to cover the sections once the quartz chimney was set in place, ultimately allowing the swirl ports to extend outside of the Faraday cage and permit the copper steam delivery tubes.
to be inserted, depicted in Figure 3.18. Figure 3.19 shows the schematic of the components necessary for steam delivery.

**Figure 3.18:** Waveguide cover with steam delivery line, chimney, and rectangular Faraday cage

**Figure 3.19:** Steam delivery system schematic
3.4 Aluminum Feed System

Sieved aluminum powder, with particle sizes in the micrometer range, was added to a two-inch feed system, seen in Figure 3.20. The powder rested in a cavity on the upper section of the cylinder, with an estimated volume of 150 mL. An ultrafine, stainless steel mesh disk was inserted to provide additional sieving at the bottom of the reservoir before aluminum passed through the 0.017-in-diameter orifice port.

In order to drive the aluminum flow, argon was supplied as a pressurant gas from a K-type cylinder. A pressure regulator connected to the cylinder enabled the reduction of the pressure down to 150 psi and, with a Paasche R-75 pressure regulator, the argon pressure, monitored by a Noshok 30-psi pressure gage, would be set to a range between 0 and 15 psig (Figure 3.21).

PEEK tubing was used to connect the exit of the orifice port to the 0.25-in-diameter inlet of a valve. A solenoid fire valve (Figure 3.22), which requires 60-psi gas pressure to operate, was used to quickly enable and disable aluminum flow. The pressurant for the valve was provided by the same nitrogen gas tank used for the steam feed system.

Figure 3.20: Two-inch feed piston-cylinder drawing
The valve outlet was then tightly connected to a capillary-like 0.125-in-diameter stainless steel tube in order to increase the pressure drop in the line. The capillary tube extends to the Y-shaped union, allowing the aluminum powder, argon pressurant, and working gas to reach the applicator through the injector, shown in Figure 3.23.

Since no sufficiently accurate instrument was available to measure small aluminum flow rates, a basic test was performed to estimate a value assuming relatively steady aluminum flow. Using a constant density value of 2.69 g/cm$^3$ (no major density changes were expected since the pressure difference was small), the duration of the flow test, and the volume displaced during the flow test, a flow rate of approximately 2 grams per second was calculated.
In order to protect the magnetron and applicator from exposure to aluminum powder, two stainless steel enclosures were designed and fabricated. The first stainless steel enclosure served to protect the magnetron, while allowing for the magnetron–applicator waveguide connection to remain with a rectangular cut-out.

**Figure 3.22**: Solenoid control valve (red arrow) and fire valve (green arrow) controlled via data computer

**Figure 3.23**: Working gas and aluminum feed union to improve aluminum flow through the injector
The second stainless steel enclosure, also known as the waveguide guard, served to protect the applicator and the tunable short during tests. By connecting the magnetron cover to the waveguide guard with heat-resistant tape, this moderately-protected set-up allowed for repeated experiments with reduced maintenance (see Figure 3.24).

Additional personnel protection was reviewed with regard to handling aluminum powder. A ventilation system within the test environment, respirator masks, protective eyewear, protective gloves, and appropriate clothing were used to avoid excessive inhalation of aluminum powder, as dust was notoriously pervasive. Figure 3.25 shows the components discussed in this section that enabled aluminum powder delivery.

Figure 3.24: Covered MPT system to protect against aluminum powder
3.5 Data Acquisition and Optical Spectroscopy Set-up

In order to monitor the steam temperature, coil temperature, and microwave forward and reflected power from a safe location, a data acquisition system was constructed. Using a previously designed LabVIEW acquisition interface and a data acquisition computer cart, monitoring the tests was possible. Four K-type thermocouples were used: one was attached to a Swagelok union cross in order to measure the temperature of the steam (Figure 3.26), another was welded onto the steam coil to monitor the coil temperature (Figure 3.15), and the last two were placed on the top of the rectangular Faraday cage to measure the temperature of the gases leaving through the quartz chimney exhaust. Two power couplers were connected to the output of the Daihen SPG-15A voltage supply box, which would produce 0 to 5 V for forward and reflected power for external viewing. An additional power coupler was connected to the output of the solenoid valve to monitor the status of the valve when aluminum was introduced into the test procedure. Three video cameras were used to visually monitor the test procedure once the helium or argon plasma was stabilized: one resting roughly 5 feet from the set-up location and two viewing down from the walls. This allowed for test operators to be in a separate room from the test room, since aluminum is a highly energetic fuel.

Figure 3.25: Aluminum delivery system schematic
The final piece of apparatus was the optical spectroscopy set-up. The following elements were used in order to obtain spectra of the plasma and the ignition: an OceanOptics HR4000 optical spectrometer (Figure 3.27), an OceanOptics QP1000-2-UV-VIS fiber optic cable (Figure 3.28), a 1-in collimator for axial measurements (Figure 3.29), and a Dell laptop with OceanView software installed.

A camera tripod was modified in order to support the fiber optic cable and roughly adjust the cable position in order to closely observe the plasma. Due to the expected intensity of chemical reactions, a neutral density filter with 10% transmittance was added in order to avoid saturation of the spectra. For axial measurements of the plasmas, in order to establish temperature profiles, a vertical stand was fixed on the set-up cart and a slide attached to the collimator was used to take measurements with 5-mm spacing per data point. The data were then analyzed with Specair, a software that can simulate the gas temperature in a plasma given the fitted diatomic rovibronic spectra of a molecule, such as nitrogen gas or hydroxide. All the components necessary for data acquisition are shown in Figure 3.30. Figure 3.31 depicts the experimental schematic with all discussed subsystems and a cross-sectional view of the applicator design with the quartz chimney.
Figure 3.27: HR4000 optical spectrometer with SMA port and computer data port

Figure 3.28: UV-VIS OceanOptics fiber optic cable
Figure 3.29: 1-inch collimator on vertically-adjustable support beam for axial spectral measurements
Figure 3.30: OES and data acquisition schematic
Figure 3.31: Complete MPT aluminum igniter schematic with applicator cross-section
Chapter 4 – Experimental Procedure

With the MPT aluminum igniter system fully devised and constructed, steps were designed in order to ultimately allow for an inert gas to generate a plasma, for water to be heated into steam and introduced into the reaction chamber, and for aluminum to be directly exposed to the center of the plasma volume and be ignited.

4.1 Helium/Argon Plasma Start

The first step in producing aluminum ignition was using the MPT and the working gas systems to generate a homogenous plasma plume. Power was provided to the microwave generator after a brief warm-up period during which the microwave generator would perform an internal safety check (see Figure 4.1).

![Figure 4.1: Daihen SPG-15A outputting 556-W of forward power from magnetron detector unit](image)

Any alarm signal from the generator would mean that an element—magnetron, detector, or internal generator issues—would prevent the generator from providing power to the magnetron. The first time the MPT device was set up, tuning and impedance matching were performed in order to maximize forward power delivered to the applicator. Using the display of the tuning box (Figure 4.2), the forward and reflected power were adjusted primarily with the tunable short end.
Figure 4.2: Tuning controller display indicating forward and reflected power prior to plasma ignition

As the tunable short changed the position of the standing wave peak to the injector location, the reflected power began to decrease. With the 3-stub tuning automated by the tuning box, impedance matching was greatly improved, resulting in minimal reflected power, as long as the injector tip in the applicator was above the top surface of the tapered waveguide by no more than 5 mm, otherwise reflection levels would increase due to poor coupling between the waveguide and injector, as noted by Hammond.8

To provide safety precautions against microwave radiation leaking from the aperture on the applicator, two devices were used: a microwave leak detection probe (Figure 4.3) and a custom-made Faraday cage. The probe was calibrated to detect electric field levels up to 100 mW/cm² and placed near the applicator. A cylindrical Faraday cage was designed and placed on the seal support of the applicator copper plate adapters, ensuring a tight fit. Numerous safety measurements indicated that the Faraday cage confined the microwave energy quite well and the probe did not indicate a value greater than 5 mW/cm² near the applicator.

After warm-up and no alarm lights, helium or argon flow was enabled, but not before the mass flow meter was first turned on in order to allow for the device to self-calibrate for approximately 15 minutes. The 2000-psi gas cylinders would then be opened and the pressure would be adjusted using the pressure regulator to achieve 150 psi, which would be delivered to the mechanical mass flow controller (MMFC). Using the MFM, the mass flows were adjusted to initial values of 2 standard liters per minute (slm) for helium and 0.8 slm for argon. With the flow established, power was delivered to the magnetron, starting from no power, with gradual increments using the generator’s power knob, while closely monitoring the forward and
reflected powers. For helium, discharge was observed to occur between 200 W and 250 W of forward power, with stabilization achieved around 300 W. For argon, discharge was observed to occur between 300 W and 400 W of forward power, and stabilization was also achieved around 300 W.

![Survey meter indicating acceptable level of microwave electric field radiation intensity](image)

**Figure 4.3:** Survey meter indicating acceptable level of microwave electric field radiation intensity

After stabilization, it was possible to reduce the power from 300 W to around 120 W, although a loud resonant sound was very audible during the process of reducing the power until a low power setting was found, likely due a breakdown oscillation (the plasma turning off and on very quickly). Once the plasma was observed to be a homogenous volume given the initial mass flow settings, the mass flow was increased until a homogenous threshold was reached (see Figure 4.4 and Figure 4.5), meaning that the plasma morphology would change to an unsteady filament.
Figure 4.4: Diffuse helium plasma plume in open air, $P = 120$ W, $\dot{m} = 4.2$ slm

Figure 4.5: Diffuse argon plasma plume in open air, $P = 130$ W, $\dot{m} = 1.2$ slm
This threshold was affected by the machining efforts on the injector near the tip to reduce surface roughness. As such, the peak mass flow for helium was about 4.0 slm and for argon was about 1.4 slm.

The power to the magnetron was then shut off and the gas flow was set to zero using the MMFC. The cylindrical Faraday cage was removed and the waveguide guard with the rectangular Faraday cage mounted on it was placed over the length of the applicator and centered on the applicator aperture. The quartz chimney was carefully lowered through the rectangular cage and set to rest on the copper plate seal rest, with the steam swirling ports extending out perpendicularly to the narrow dimension of the applicator. The sides of the cage would then be closed with the cut-out stainless steel wire mesh, with a hole large enough to allow the steam ports to remain outside of the cage. Thin and flexible copper wire was used to tighten the cut-out pieces to the cage to reduce microwave leakage.

The process of igniting a helium or argon plasma was then repeated (Figure 4.6 and Figure 4.7), since the MPT was already properly matched. It was noted that the mass flow thresholds seemed reduced while the quartz tube encompassed the plasma region and isolated the plasma from the environment, and that the microwave leak wand detected higher electric field levels in a region very close to the injector below the applicator which was avoided. This was assumed to occur due to a propagation through the gap between the waveguide guard and applicator.

![Image of Helium plasma inside quartz chimney at 300 W of delivered power and about 3 slm](image)

**Figure 4.6**: Helium plasma inside quartz chimney at 300 W of delivered power and about 3 slm
Figure 4.7: Argon plasma inside quartz chimney at 300 W of forward power and roughly 1 slm

4.2 Steam Plasma/Entrainment Start

Prior to enabling water flow, the water level in the reservoir was checked and ensured that it was as full as possible with deionized water. The lid was then closed and, using the Paasche pressure regulator, nitrogen was allowed to pressurize the reservoir to about 3 to 5 psig, mainly to purge the water line of air bubbles. The reservoir exit line was then connected to the PTFE tubing leading to the metering pump, ensuring no air bubbles remain. Once power was provided to the Eldex pump (Figure 4.8), and after a brief warm-up period, the initial water flow was set to 5 mL/min, but not yet started. The Power Ten power supply box (Figure 4.9) was then turned on, allowed to warm up for about twenty seconds, and set to output a voltage of 40 V with a current value of approximately 30 A.

The data acquisition system provided the real-time temperature obtained through the thermocouples connected to the steam coil and the steam line. Once the coil temperature reached 1000 °F, and with a 400-W helium or argon plasma present and stable, water was allowed to flow due to the metering pump from the reservoir into the quartz swirling ports.
Figure 4.8: Eldex pump flow display indicating 20.0 mL/min

Figure 4.9: Voltage and Current displays and knobs on Power Ten steam power supply
It was observed that the initial water delivered did not carry most of the heat, resulting in small amounts of liquid water entering through the ports. However, by allowing the helium or argon plasma to heat the quartz chimney for at least a minute prior to introducing water, any liquid would quickly vaporize.

Water flow increments of 5 mL/min were used while simultaneously monitoring the coil temperature. The steam power supply voltage output was adjusted if the coil was heating too quickly, well above 1000 °F, or if the steam temperature was dropping too fast, below 300 °F. The plasma color was observed to change as well: for helium, the entire plasma would change to a red color (see Figure 4.10), and for argon, a long and thin red line would develop over the upper and middle part of the plasma (see Figure 4.11).

A water flow of 40.0 mL/min was ultimately achieved with a steady temperature around 400 °F for a voltage supply of 48 V and a current supply of 40 A. At these levels, however, a difference in entrainment was observed between helium and argon plasmas. Regardless of the flow value, the helium plasma remained red, whereas the argon plasma’s red region would slowly diminish. The steam plasma was then observed for a short duration to ensure that the steam vortex created by the swirling ports was properly centering the plasma plume and not angling nor providing an unbalanced force.

**Figure 4.10**: Steam plasma with helium working gas, $P = 400$ W
4.3 Aluminum Injection Test

The aluminum two-inch feed reservoir was checked to ensure aluminum powder was fully occupying the permissible volume prior to initiating the test. If the bed level was acceptable, then argon was allowed to enter and pressurize the powder reservoir up to 3 psig controlled by a Paasche knob-based pressure regulator and metered by the Noshok pressure gage (Figure 4.12). It was assumed that the aluminum mass flow would be at its minimal value if a low static pressure value was used.

Figure 4.11: Steam plasma with argon working gas, $P = 400 \text{ W}$
With the steam plasma fully stabilized and the microwave generator set to output 600 W of forward power, a voltage of 5 V was supplied to the solenoid valve as to enable aluminum to travel through the capillary tube, the injector tube, and directly into the plasma volume. A delay would be observed if the delivery lines were initially purged of any aluminum powder (the powder would have to be pushed by the argon and working gas through all the lines).

During the ignition test, aluminum was observed to obscure regions of the quartz chimney in a swirling fashion, likely due to the steam vortex, which would also reduce the apparent luminous intensity of the ignition and reaction processes.

![Figure 4.12: Argon gas pressure gage in the aluminum bed cavity prior to pressurization](image)

Once the end of the operation time was achieved, the microwave generator power was immediately disabled, along with the solenoid valve power. A brief moment was given for the substance still present in the quartz chimney to cool down. The working gas mass flow and the metering pump water flow were then
set to zero. Power to the steam coil was gradually reduced to zero and the pressure in the aluminum bed was reduced to atmospheric pressure.

After the applicator and quartz chimney cooled down, the set-up would be taken down in order to remove any particulates on the applicator, clean the chimney, and purge the aluminum powder in the delivery line. Figure 4.13 shows the condensation of liquid aluminum-steam reaction products and Figure 4.14 shows the cooled condensed products on the quartz chimney after an experimental test run.

![Figure 4.13: Aluminum powder and other products condensing on quartz chimney walls](image)
Figure 4.14: Alumina and aluminum powder accumulation inside quartz chimney
Chapter 5 – Results

5.1 Initial Issues in Testing and Ignition

Although aluminum ignition was achieved in this project, several iterations were taken in order to achieve each phase. Preliminary injector designs showed a significant impact on the electromagnetic coupling between the waveguide and the injector, as well as fluid characteristics for helium and its plasma state and thermal characteristics for steam injection. Additional difficulties emerged when solids and liquids entered the waveguide. Establishing a somewhat steady aluminum-powder flow proved to be very challenging, and when aluminum reached ignition, it was discovered that damage was incurred by the quartz chimney.

5.1.1 Injector Design Iterations

Initial designs for the applicator injector tube comprised of a single, stainless steel, 0.375-in-diameter tube with 0.040-in wall thickness in order to allow a single gas or gas mixture to enter the applicator. The height of the injector tip relative to the top face of the waveguide applicator was varied on the order of a few millimeters to understand the microwave coupling behavior. The tube passed through two copper adapters mounted on the applicator: one which made tight contact with the tube and the other with a 2-in aperture.

During the early stages of igniting a plasma with helium, due to the diameter of the tube, the resulting, voluminous plume would consistently damage the tip of the injector, requiring persistent machining in order to repair the unwanted changes. It was hypothesized that the plasma temperature near the tip was well above the melting point of stainless steel, so an alternative for tube material was considered based on previous torch designs described in the literature. Molybdenum, with higher melting point and lower coefficient of thermal expansion than stainless steel, was chosen for an alternate injector tube design with 0.1875-in diameter and 0.020-in wall thickness.

At the same time, however, several means of introducing steam into the plasma region were explored. The first design called for a coaxial injector with the working gas in the annulus between the outer and inner conductor and the steam in the inner tube (Figure 5.1). Preliminary tests showed a substantial flaw in design, as the plasma volume stability would quickly decay once the steam was introduced and, since the tubes were made of stainless steel, additional machining followed to repair damage. The next iteration comprised of introducing the working gas through the inner tube and the steam through the annulus. Although the
plasma stability improved, the steam flow was inconsistent and condensation developed quickly, which would consequently absorb microwave power and extinguish the working gas plasma.

Figure 5.1: Coaxial injector tube in the applicator

Additional issues developed with the coaxial design for introducing steam into the applicator. By changing the height of the inner tube relative to the position of the outer tube tip, the microwave coupling was altered. If the inner tube tip was positioned below the outer tube tip, plasma ignition was never achieved. However, if the inner tube tip was above the outer tube tip, then a plasma could be generated, but an unwanted and hazardous side effect was discovered through the use of ANSYS’s High Frequency Structural Simulator (HFSS) program: a TEM mode would develop in the annulus as shown in Figure 5.2, resulting in excessive heating of the applicator and the length of the injector tube, which was not entirely modeled in the simulation. Figure 5.3 depicts the coaxial injector without tip height offset, which would allow for frequent ignition due to the magnitude of the E-field (maximum of 50,000 V/m was simulated). Figure 5.4 demonstrates why the gas would never ignite near the tip of the inner conductor, as the electric field was consistently too weak (below 20,000 V/m from simulation) due to the negative offset.

Figure 5.5 shows the overall electric field strength across diameter of the inner conductor tip for each coaxial offset configurations, which explained why ignition of helium and argon could breakdown for no offset and positive offset of the coaxial injector tubes, but not for a negative offset. In order to remove the EM propagation through the coaxial annulus, and to ensure consistent plasma ignition, the change to use a single injector was then executed (see Figure 5.6).
**Figure 5.2**: ANSYS HFSS model displaying E-field strength and mode propagation in annulus for a positive offset

**Figure 5.3**: ANSYS HFSS model displaying E-field strength and limited propagation in annulus, no offset
Figure 5.4: ANSYS HFSS model displaying weak E-field strength above inner conductor tip

Figure 5.5: ANSYS HFSS plot displaying total E-field strength over radial distance of inner conductor
Figure 5.6: Molybdenum injection tube (top) protruding through the applicator (bottom)
The molybdenum tube proved to be resistant to high temperatures and damage as expected when used as part of the torch. Changes to mass flows, however, revealed a unique relationship between the fluid mechanics and electromagnetics involved in the applicator. Due to the roughness of the tube surface, the plasma volume stability would have limits as a function of the working gas mass flow. In other words, the plasma plume would go from a steady and homogenous flame-like appearance for low mass flow rates to an unsteady and single fluctuating filament attached to the edge of the tube wall at high mass flow rates, shown in Figure 5.7.

![Figure 5.7: Unsteady, filamentary helium plasma due to high mass flow rate](image)

Machining allowed for a reduction in the surface roughness in order to improve the working gas flow exiting the injector, but at the same time the electric field strength would diminish, since the strongest fields occur
near sharp areas, such as corners or edges; therefore, a balance between strong electric fields and laminar flow was sought out and ultimately achieved, as previously seen in Figure 4.4 and Figure 4.5.

5.1.2 Quartz Chimney and Steam Injector Ports

Since the coaxial injector for introducing steam was discarded, a different design was studied. Previous literature made use of quartz tubes to better isolate the plasma from the environment in the applicator, and swirling gases through tangential injector ports allowed for centering of the plasma, so a similar approach could enable steam to enter the applicator. The first fused quartz “chimney” allowed for increased steam flow rates, reduced condensation, and allowed overall stable entrainment of water into the plasma and the enclosed environment. The reduction in condensation was believed to be achieved primarily through convective heating between the plasma gas and the walls of the quartz chimney. Other quartz chimneys later revealed that precise machining and fusing techniques were required in order to prevent perturbations to the plasma.

Although the quartz chimney design enabled several visible test runs, the damage caused by molten aluminum and condensation of combustion products on the quartz tube walls would prevent reuse after some time (see Figure 5.8), which would require more chimneys to be manufactured. It must be clarified that the only advantage of using quartz as an isolating chamber is the ability to observe the flames through video and spectroscopy.

Initial use of the ports involved the application of a Swagelok stainless steel fitting to connect the T-splitter to the tube using two stainless steel 0.125-in-diameter tubes. After each test, the tubes would have to be removed in order to properly disassemble and clean the applicator and quartz chimney. Due to the excessive weight of the stainless steel components attached to the chimney, the quartz ports eventually broke and proved difficult to repair (see Figure 5.9). As such, alternatives to using stainless steel were pursued.

First, since the waveguide guard was sturdy, a support was installed for the T-splitter in order to reduce the weight of any metal tubing connecting to the quartz chimney. Second, as a consequence of the Faraday cage design and the quartz ports, the steam metal tubing material was changed from steel to copper, since the tube had to be periodically removed and bent to fit properly. Lastly, all Swagelok fittings were removed from future quartz chimney ports design and simply inserted the 0.125-in-diameter copper tubing inside of the port length. Little to no steam or condensation was observed escaping through the gap between the inner port diameter and the outer metal tube diameter.
Figure 5.8: Etching damage on quartz chimney from molten aluminum after ignition

Figure 5.9: Chimney tube with chipped swirl ports due to stainless steel fittings
5.1.3 Waveguide Applicator Protection

Since the applicator and injector design were fixed on a vertical axis, a means of protecting the inside of the waveguide from aluminum powder was considered. Boron nitride was the first dielectric material chosen because machining a desired geometry was relatively simple and it could withstand high temperatures (Figure 5.10).

![Figure 5.10: Boron nitride two-inch disk placed in aperture to protect the inside of the applicator](image)

However, due to its hygroscopic property, it was quickly ruled out once steam was introduced, since it formed a green-like powder on the surface exposed to the outer environment that became entrained with the plasma (see Figure 5.11). Some other ceramic dielectrics were considered, but most proved to be expensive and very difficult to machine.

A second dielectric material study revealed that quartz might be a suitable candidate, due to its temperature tolerance and hydrophobic properties (Figure 5.12). Although machining was not as simple as boron nitride, properly centered holes were nonetheless achieved through the use of diamond-tipped drill bits and sufficient liquid water.

Initial use of quartz dielectric disks did not successfully prevent water from entering the waveguide when steam was first introduced, but the problem was quickly resolved by increasing the initial power to the steam supply lines. Continued use of quartz dielectric disks proved successful for plasma start and steam entrainment, and although it did keep aluminum powder out, the disk became damaged due to the precipitation of molten aluminum, shown in Figure 5.13.
Figure 5.11: Plasma plume with boron nitride powder and water mixture (green-colored plume)

Figure 5.12: Fused-quartz two-inch disk with a machined centered hole
Most of the damage was superficial, but removing the aluminum proved very difficult, and reusing the disk with some metallic parts present also altered the electric field shape around the injector tip. New quartz disks thus were continuously used for each new set of test runs. It should be noted that the orientation of the set-up (vertically up) was only set for convenience in data acquisition and alternate orientations (using a twist waveguide adapter) were considered for integration into a combustor (horizontal or vertically down orientations).

5.2 Plasma Ignition Achievement

From the procedure discussed in Chapter 4, a plasma plume was achieved in air and steam environments for both helium and argon, as seen in Figure 4.4, Figure 4.5, Figure 4.6, and Figure 4.7. The ignition process
was observed visually and aurally, as microwave power was increasingly supplied to the applicator until a
discharge occurred due to gas breakdown. The steam entrainment within the plasma was observed to cause
a crimson color shift in the plasma volume for helium, with a reduced entrainment effect for argon. These
events were also recorded using OES without a collimator in order to compare the respective gas plasma
spectrum to a reference as a means of confirming plasma ignition.

5.2.1 Helium Plasma Ignition

Helium plasma ignition was primarily characterized through three observations: its apparent emission color
in air, its spectral emission profile, and its low ignition power requirement. As shown in Figure 4.4, the
resulting plasma plume had a purple-red color appearance when exposed to the air, with a small air
recombination region above it, at a microwave power setting of 300 W.

The microwave value at which ignition would first be observed, visually or aurally, was around 250 W. An
audible sound was perceived for microwave powers between 150 W and 280 W, which was assumed to be
related to plasma charge instability resulting in electron currents (sound) to achieve a balance between
positive and negative charges. A low-power plasma setting was found to exist for helium for a range from
100 W and 130 W.

Using the OES setup, without the use of the collimator, an emission spectra for the helium plasma near the
nozzle tip was captured for a microwave power setting of 300 W, as shown in Figure 5.14. The most visible
helium peak was noted to exist at a wavelength of 587.5 nm. Two principal lines were also observed for
the oxygen triplet sets at 777 nm and 844 nm. Bands for the molecular nitrogen systems were also seen:
300 nm to 400 nm for the SPS, and 400 nm to 430 nm for the FNS. Hydroxide was also identified to peak
around 309 nm. Additional investigation of unknown peaks and bands in the helium plasma in air spectrum
revealed the presence of nitric oxide, hydrogen lines, and additional atomic oxygen and nitrogen lines.

For nitric oxide, NOγ: A2Σ+ → X2Π, the bands were found to exist between 200 nm and 300 nm, resulting
in convolution with other molecular nitrogen bands. For hydrogen, Hα and Hβ were observed at 654 and
486 nm, respectively. Additional lines for atomic oxygen were found at 615 nm and 926 nm. Other lines
for atomic nitrogen were located at 648 nm, 742–746 nm, 818–824 nm, 856–870 nm, and 939 nm.

The presence of all the bands in the collected spectrum were taken as a validation of helium-plasma ignition
in the presence of air at atmospheric pressure.
Figure 5.14: Helium plasma emission spectra near the nozzle tip at 300 W with \( \dot{m} = 4.0 \) slm
5.2.2 Argon Plasma Ignition

Ignition of the argon-based plasma proved to require slightly more initial power than helium, generally igniting quickly at around a microwave power setting of 400 W, but similarly stabilizing at 300 W. Unlike helium, in Figure 4.6, argon showed a larger air-recombination plume beyond its plasma volume, as observed in Figure 4.7. Argon in air was characterized by the morphology of the plasma (converging and diverging geometries) and the apparent color (white, with hints of purple and red), noted in Figure 4.5. The resulting plasma was also capable of sustaining itself at a lower-power setting of $P = 130$ W. Due to a change in molecular weight, the new working gas plasma required a lower mass flow rate, with a range of 0.5–1.5 slm, in order to form a homogenous-looking plasma volume.

With the use of OES, the emission spectrum of argon in air was also recorded and studied, as shown in Figure 5.15. Similar bands, in comparison to helium, were found, which included the molecular nitrogen SPS from 300 nm to 400 nm and FNS from 390 nm to 450 nm, hydroxide spanning from 280 nm to 310 nm, with a peak at 309 nm, and nitric oxide gamma ($\text{NO}_\gamma$) from 200 nm to 300 nm. A low continuum formed much more easily with argon as the working gas for the plasma plume, noted across the low-band region of the OES graph (below 700 nm). Several of the argon lines were matched with Table 2.3 and Figure 2.10, although additional lines were found at 549.8 nm, 603 nm, 675 nm, 912 nm, 922 nm, and 965.5 nm. Out of the hydrogen Balmer series, only $\text{H}_\alpha$ was visible at 656 nm. Only two oxygen triplet lines were visible at 777 nm and 844 nm, noticeably weaker in intensity in comparison to Figure 5.14, and only one atomic nitrogen group spanning from 860 nm to 870 nm was noted.

By contrasting the nitrogen systems resulting from excitation between the helium and argon profiles shown in Figure 5.14 and Figure 5.15, it is possible that, from the argument posed by Cullen,$^{22}$ due to the higher energy threshold of the helium metastable (~19.8 eV), more nitrogen SPS rovibrational states were visible, with a possible convolution with the nitric oxide beta bands ($\text{NO}_\beta$) and cyanide (CN), as well as nitrogen monohydride (NH), for a helium-based plasma in air than for an argon-based plasma in air. It can be argued that a helium plasma might more readily excite diatomic molecules than an argon plasma, but further study regarding the plasma species concentration would be required. In general, due to the superior energy carried by helium metastables, the emission lines for the helium plasma in air profile appeared to have greater relative intensity than the respective emission lines for the argon plasma in air profile, both set at the same microwave power levels. It can also be noted that this difference exists from the greater electron temperature achieved in helium plasmas than in argon plasmas in air.$^{24}$
Figure 5.15: Argon plasma emission spectra near the nozzle tip at $P = 300$ W with $\dot{m} = 1.4$ slm
5.2.3 Helium-Based Steam Plasma Spectra

Following the procedural steps in Chapter 4, steam was successfully entrained within the helium plasma due to the quartz chimney, resulting in a reddish plume shown in Figure 4.10. The immediate change to the helium plasma plume in air, aside from the apparent color, was the elimination of the air recombination plume that was visible at 300 W and higher of forward power. This behavior was expected due to the isolating characteristic of the chimney, ideally reducing the influence of air chemistry with the helium plasma by allowing steam to swirl throughout the interior.

Using the optical spectrometer, the emission spectrum of the steam-entrained helium plasma was observed and plotted, as shown in Figure 5.16, noting the initial water flow rate of 10 mL/min with a fixed helium mass flow of 3.0 slm. As noted, the influence of air chemistry was greatly reduced, leaving a weak nitrogen SPS band emission between 300 nm and 400 nm. The hydroxide band was very noticeable in the low UV region of 280 nm to 310 nm, with a primary peak at 309 nm, a secondary peak at 306 nm, and a tertiary peak at 286 nm. Three hydrogen Balmer lines at 656.4 nm, 587.5 nm, and 434 nm, corresponding to $\text{H}_\alpha$, $\text{H}_\beta$, and $\text{H}_\gamma$, were clearly visible, although the gamma line had a much weaker line strength. A single helium line was located at 587.5 nm, and several atomic oxygen lines were found at 615 nm, 777 nm, 844 nm, and 926 nm.

Further studies in changes to the steam-helium plasma spectrum were performed near the nozzle tip, since the water flow was continuously increased until the metering pump reached a maximum value of 40 mL/min. Figure 5.17 displays three different rows of curves, with corresponding values of water volumetric flow of 10 mL/min, 25 mL/min, and 40 mL/min. It was recognized that the intensity of hydroxide bands, the Balmer series, and the oxygen lines decreased with increasing water flow, especially between 25 mL/min and 40 mL/min. Since the steam injection swirling ports had a fixed cross-sectional area, an increase in water flow corresponded to increased velocity of the water particles, which would reduce the residence time inside the plasma volume. As a consequence, fewer water particles would become ionized and less dissociation products, such as hydroxide, hydrogen, and oxygen, were evident.

Since the helium flow was not altered, the presence of helium radicals near the nozzle tip was not diminished by increasing the water flow, even though the line strength at 587.5 nm was generally weak.
Figure 5.16: Steam-helium plasma spectrum at $P = 400 \text{ W}$, with $\dot{m}_{\text{He}} = 3.0 \text{ slm}$, $\dot{V}_{\text{H}_2\text{O}} = 10 \text{ mL/min}$
Figure 5.17: Steam-helium plasma spectrum as a function of water volumetric flow rate at \( P = 400 \) W, where blue is \( \dot{V}_{\text{H}_2\text{O}} = 10 \) mL/min, red is \( \dot{V}_{\text{H}_2\text{O}} = 25 \) mL/min, and green is \( \dot{V}_{\text{H}_2\text{O}} = 40 \) mL/min: (top row) OH band strength decreases for increasing water flow rate; (middle row) H\(_\alpha\) line strength shows change at a flow rate higher than 25 mL/min; (bottom row) O line strength shows increase and then decrease in magnitude for increasing water flow rate
5.2.4 Argon-Based Steam Plasma Spectra

As shown in Figure 4.11, steam was entrained within the argon plasma, but not much like the entrainment with helium, in Figure 4.10. The argon region in the plasma volume was clearly still visible for a gas mass flow of 1.0 slm, water flow of 10 mL/min, and a microwave power setting of 400 W. A relatively thin-appearing region developed at the top of the plasma volume, which was understood to contain water plasma radicals due to the red color shift. It was believed that, due to the density of argon being greater than that of helium, a stronger momentum mismatch occurred between the argon molecules and the water molecules, such that the residence time was too short.

Figure 5.18 depicts the results from OES for the settings described above. As it was with the steam–helium setup, the line strengths of the nitrogen systems were weaker in comparison to the relative intensities of water-based radicals and argon transitions. The reasoning for such a phenomena was again linked to the isolating feature of the quartz chimney and the swirling effect of the steam injection, effectively reducing the air chemistry involved in the plasma plume. Analysis of the spectrographic data revealed a strong presence of the following substances near the nozzle tip: Hydroxide dissociated from water spanning from 280 nm to 310 nm; a weak molecular nitrogen SPS band from 300 nm to 400 nm with a peak at 337 nm; a weak molecular nitrogen ion FNS band from 390 nm to 430 nm; hydrogen Balmer lines at 656 nm, 486 nm, and 434 nm; oxygen lines at 615 nm, 777 nm, and 844 nm and several argon lines matching the expected emissions from Table 2.3, along with additional lines at 550 nm, 603 nm, 867 nm, 912 nm, 922 nm, and 965 nm. The appearance of the nitrogen FNS is not well understood, but it might be due to the presence of various argon metastables.

Figure 5.19 shows the change in the steam–argon emission spectrum as water flow is increased in steps of 15 mL/min. A surprising result was a seeming lack of effect on the hydroxide band strength, since it appeared to be constant regardless of the water flow unlike the effect observed with the steam-helium plasma. Changes in the intensities of the Balmer lines and oxygen lines were evident—weakening in strength as a function of increasing water flow—and similar to changes observed in the steam–helium plasma for increasing water flow near the nozzle tip; therefore, a similar argument for argon and steam can be made that the increasing momentum of water particles quenched and ultimately reduced the residence time of other elements in the plasma, for fixed working gas mass flow and microwave power. Changes in the intensity of the argon lines were very minor, similar to the changes in the helium line intensity. Additional parametric studies with altering the argon mass flow with fixed water flows might reveal complementary information with regard to the quenching effects in a plasma volume due to momentum mismatch between elements in a plasma and its environment.
Figure 5.18: Steam-argon plasma spectrum at $P = 400$ W, $m_{\text{Ar}} = 1.0$ slm, $V_{\text{H}_2\text{O}} = 10$ mL/min
Figure 5.19: Steam-argon plasma spectrum as a function of water volumetric flow rate at $P = 400$ W, where blue is $\dot{V}_{H_2O} = 10$ mL/min, red is $\dot{V}_{H_2O} = 25$ mL/min, and green is $\dot{V}_{H_2O} = 40$ mL/min: (top row) OH band strength remains steady for increasing water flow rate; (middle row) H$_\alpha$ line strength decreases for initial flow rate increase but remains the same thereafter; (bottom row) O line strength initially decreases but remains the same and Ar lines show negligible change in magnitude for increasing water flow rate.
5.3 Validation of Aluminum Ignition

5.3.1 Preliminary Gas Temperature Study

With the 1-in collimator and a vertically-adjustable clamp on a fixed beam, several spectral profiles were acquired over a span of up to 150 mm with 5-mm intervals for helium and argon-based plasmas in air, without steam or aluminum entrainment. The purpose of this procedure served to use the numerous axial spectra for both helium and argon with Specair, a software capable of simulating spectra for various diatomic molecules and consequently fitting experimental data to simulated data as to acquire rotational and vibrational temperatures.

In order to demonstrate changes in the plasma spectrum throughout its length, some of the axial data were compared at two power settings—300 W and 600 W—for both helium and argon plasmas in air, shown in Figure 5.20 through Figure 5.23. At 300 W, a helium-based plasma near the nozzle (4 mm above the injector tip) is almost identical to the profile in Figure 5.14, with the primary elements being molecular nitrogen (SPS and FNS), hydroxide, atomic oxygen, atomic hydrogen, and a small helium line, as discussed earlier. By inspecting the spectrum obtained 10 mm above the starting point, it was evident that the species active and visible in the plume were not as excited, which was likely due to the weakening of the electric field generated by the microwave source, resulting in fewer electron collisions. At 20 mm above the starting point, the primary species involved appeared to be hydroxide, molecular nitrogen (SPS), and atomic oxygen, with a very miniscule emission from helium, where the electron number density is much smaller due to a weaker electric field strength region. Figure 5.3 is a good indicator for how the electric field falls in strength over a distance away from the nozzle tip at 300 W and likely follows a similar pattern for a single injector design.

For a power setting of 600 W, the helium plasma plume was much greater, with a larger region composed of excited air species over the working gas. Near the nozzle tip, the profile is similar to Figure 5.14, but at higher elevations, the presence of excited molecular nitrogen (SPS and FNS), atomic oxygen, atomic nitrogen, atomic hydrogen, and helium all decrease, but at the same time, emissions from nitric oxide gamma and hydroxyl transitions, along with a growing low continuum spanning from 200 nm to approximately 775 nm, remain quite evident even up to 34 mm above the injector tip, shown in Figure 5.21. The low continuum is a weak thermal emission very likely due to convolved emission span of excited molecular and atomic nitrogen, since it is the dominant species in the surrounding environment.
Figure 5.20: Change in spectral profile for helium in air as a function of axial distance, $P = 300$ W
Figure 5.21: Change in spectral profile for helium in air as a function of axial distance, $P = 600$ W
A similar procedure was followed for obtaining axial measurements of an argon plasmas at various power levels over a distance of 150 mm. Prior to analyzing the spectral results, however, it was clearly evident that the argon plasma contained a greater recombination of excited air species, which can be observed in Figure 4.7 and compared to the helium plasma in Figure 4.6, noting the afterglow plume size above the working gas plasma region. Consequently, more data were thus able to be obtained since the overall plasma plume size was taller.

Two sets of data were then taken and compared based on microwave power input and axial position of the collimator with respect to the central axis of the plasma, given a fixed argon mass flow of 1.2 slm. For 300 W of microwave power and at 4 mm above the injector tip, the argon-plasma profile, as observed in Figure 5.22, displayed similar features to those depicted in Figure 5.15: bands and lines from nitric oxide gamma, molecular nitrogen, atomic oxygen, argon, although not very strong hydrogen emissions. At 14 mm above the injector tip, the argon and oxygen emission lines sharply decreased in strength, along with the nitrogen FNS and SPS, although the peak at 337 nm remained evident. Further increase in axial distance revealed even weaker lines from argon and atomic oxygen and growing intensity of the hydroxide and nitric oxide gamma bands, along with a low continuum from the thermal emission from the hot plasma gases.

Increasing the microwave power to 600 W further lengthened the plasma recombination region plume and increased the overall intensity of the thermal emission. A familiar pattern was observed as increments of 10 mm were taken from the initial starting point of 4 mm: the argon and atomic oxygen line strengths were reduced by over 50%, while the bands of the hydroxide and nitric oxide gamma increased, along with the thermal emission broadband collected by the spectrometer. For all cases, the nitrogen SPS peak at 337 nm, which corresponds to a vibrational transition of $\Delta v = 0$, remained clearly visible, while the other vibrational transition peaks rapidly decayed.

Additional axial data was collected at powers ranging from 120 W all the way to 900 W, including 300 W and 600 W, in order to generate varying thermal profiles of the plasma plumes for both helium and argon using Specair. Initial spectral fitting attempts revealed a deviation from local thermal equilibrium (LTE), meaning unequal distributions of the translational ($T_T$), rotational ($T_R$), vibrational ($T_V$), and electronic ($T_E$) temperatures (in LTE, they have the same temperature distribution). As a result, spectral fitting could not be performed for the entire wavelength span captured by the spectrometer. Instead, individual diatomic rovibrational bands, such as those from OH, N$_2$ SPS, or NO$_\gamma$, were considered for spectral fitting using Specair.
Figure 5.22: Change in spectral profile for argon in air as a function of axial distance, \( P = 300 \) W
Figure 5.23: Change in spectral profile for argon in air as a function of axial distance, $P = 600$ W
In order to fit a simulated spectrum to an experimental NOγ band, recorded from a helium plasma emission in air near the injector tip, the following assumptions were made: the translational and rotational temperatures are equal due to the quick relaxation rate between rotational levels at atmospheric pressure; the electronic temperature is approximately equivalent to the electron kinetic energy due to the electron-neutrals collisions; and the vibrational temperature is greater than or equal to the rotational temperature due to a slower relaxation rate in non-LTE condition.

The first iterations quickly showed that no temperature variations in Specair could generate a close spectral fit if only NOγ was considered in the wavelength range from 200 nm to 280 nm as a single radiative species. By inspecting the available diatomic rovibronic spectra in the Specair database, two additional species were discovered to be likely present in the UV region and convolved with NOγ: nitric oxide beta (NOβ) and molecular oxygen (O2 Schumann-Runge).

After assuming an electron temperature of ~2 eV in the plasma glow region, due to the high electric field strength near the injector tip, manual temperature iterations were performed by individually adjusting the vibrational and rotational temperatures. Figure 5.24 shows the simulated diatomic spectrum for $T_R = 3000$ K and $T_V = 3500$ K and the experimental spectrum in the upper UV region (shorter wavelength) for a helium-based plasma in air at an axial position of 4 mm above the injector tip with 500-W of delivered power. Although the temperatures followed a sensible pattern ($T_V > T_R$ for a non-LTE plasma emission), it was not sufficient to justify the local gas temperature, as it was not fully understood if the simulated rotational temperature truly matched the rotational temperature of NOγ due to the presence of two additional species.

Additional case studies were performed to study the temperature sensitivity of the NOγ, NOβ, and O2 fitted spectra with the same experimental settings: helium mass flow of 4.0 slm, delivered power of 500 W, and an axial position of 4 mm above the injector (plasma glow region). The electronic temperature study, shown in Figure 5.25, revealed a low sensitivity of the band spectrum to changes in a temperature range of 10,000 – 30,000 K, with $T_V = 3500$ K and $T_R = 3000$ K. The experimental spectrum appeared to have a better fit for an electronic temperature between 20,000 and 30,000 K (optimization iterations via Specair indicated a closely matching electronic temperature of 24,800 K). The vibrational temperature study, depicted in Figure 5.26, showed a moderate sensitivity of the band spectrum to changes in a temperature range of 3000 – 7000 K, with $T_E = 24,800$ K and $T_R = 3000$ K. A vibrational temperature close to 3000 K (the rotational temperature) appeared to be a desirable match, indicating that the diatomic species in the higher UV region might be close to thermal equilibrium with each other but not necessarily with other diatomic species in the
spectrum. The rotational temperature study, as seen in Figure 5.27, demonstrated a significant sensitivity of the band spectrum to temperatures below 2000 K and low sensitivity to temperatures below the vibrational temperature. A close match between the simulated and the experimental rovibronic band spectra was evident at a rotational temperature closer to 3000 K.

A similar fitting method could be used for the N$_2$ SPS (fitting for the OH in the plasma glow is difficult due to band convolution) or the N$_2^+$ FNS in order to find a potential range of the plasma gas temperature from simulated rotational temperatures. By inspection of Figure 5.21, for an axial location in the plasma afterglow, diatomic fitting of the OH might be simpler due to the reduced presence of molecular nitrogen, although convolution with molecular oxygen appears to be evident in the low-continuum in the UV region. However, additional spectral fitting is not explored in this thesis due to time limitations, but it is still an active area of study for this research topic.

![Specair and Experimental fit comparison](image)

**Figure 5.24:** NO$_\gamma$, NO$_\beta$, and O$_2$ Schumann-Runge convolved band fitting for a helium plasma in air, $\dot{m} = 4.0$ slm, $P_f = 500$ W, $z = 4$ mm ($T_E = 24800$ K, $T_V = 3500$ K, $T_R = 3000$ K)
Figure 5.25: Electronic temperature sensitivity of the NO\(_{\gamma}\), NO\(_{\beta}\), and O\(_2\) Schumann-Runge fitted spectra,
\[T_v = 3500\, \text{K}, \quad T_R = 3000\, \text{K}\]

Figure 5.26: Vibrational temperature sensitivity of the NO\(_{\gamma}\), NO\(_{\beta}\), and O\(_2\) Schumann-Runge fitted spectra,
\[T_E = 24800\, \text{K}, \quad T_R = 3000\, \text{K}\]
Figure 5.27: Rotational temperature sensitivity of the NOγ, NOβ, and O2 Schumann-Runge fitted spectra, $T_E = 24800 \text{ K}, T_V = 3500 \text{ K}$

5.3.2 Aluminum Ignition Imaging and Spectra

Once the aluminum made contact with the steam and working gas plasma by passing through the injector, the volume color changed rapidly from red to intensely bright blue, as observed in Figure 5.28, indicating the ionization and recombination of aluminum neutrals and ions in the plasma. At the same time, the optical spectrometer, with a neutral density filter of 10% transmittance, detected a strong elemental aluminum line at 396 nm and a band of aluminum monoxide from 450 nm to 560 nm for both helium and argon based steam plasmas, as shown in Figure 5.29, near the injector tip. For helium, a hydrogen alpha line and one oxygen triplet line were visible at 656 nm and 777 nm respectively during the initial aluminum ignition phase, but no helium lines due to their weak strength and the thermal emission.

For argon, several of its emission lines were still visible along with a hydrogen alpha line. No bands of hydroxide were visible, an indication that, due to the presence of aluminum monoxide in the spectra, the radical hydroxyl was very likely rapidly reacting with metallic aluminum, overall reducing its lifespan, and thus its intensity, within the plasma region. Figure 5.30 shows the evolution of the reaction spectrum for
helium and argon over a 3-second span, indicating the growing strength of the thermal emission band with some decay in the Al line and AlO bands as the reaction continues to develop. It was noted that an excessive offset from spectral background noise reduction occurred between 510 nm and 700 nm, resulting in intensity values below zero.

**Figure 5.28:** Blue color emission from aluminum injection through a helium-steam plasma at 400 W

After about 5 seconds from the initial aluminum injection, a luminous and large white-yellow region developed across the entire length of the quartz chimney, with a vigorous exhaust plume, observed in Figure 5.31. Due to the presence of excessive mass flow, the unburnt aluminum exited the quartz chimney and immediately reacted with the atmospheric oxygen for approximately 15–20 seconds, resulting in two bright
and burning regions: a reaction of aluminum with the steam radicals inside the chimney and a reaction of aluminum with the air oxidant. A thermal profile therefore was captured via OES, shown in Figure 5.32, for the helium-based steam plasma reaction with aluminum, near the nozzle tip. For argon, a steady thermal profile was not observed near the nozzle tip, which is discussed later. Due to the convolution between the broadband thermal emission and the reactant emission lines, distinguishing the individual species for the helium plasma proved too difficult.

However, by noting the steady emission intensity peak 20 seconds after initial aluminum injection, a flame temperature was estimated from Equations 67 through 69, given a peak wavelength of 741.36 nm, to be $T_f = 3908.76 \text{ K}$ for constant emissivity, $T_{f1/\lambda} = 3257.53 \text{ K}$ for emissivity as a function of $1/\lambda$, and $T_{f1/\lambda^2} = 2792.16 \text{ K}$ for emissivity as a function of $1/\lambda^2$. Given fitting methods to experimental data performed by Parigger, the expected flame temperature would lie in a range between the blackbody flame temperature and the first grey-body flame temperature: $T_{\text{avg}} = 3583 \pm 326 \text{ K}$. A weak oscillating behavior was also observed 30 seconds after aluminum injection: the exhaust plume and luminosity would increase and decrease in intensity over a fraction of the period of operation. After that, the exhaust plume would decrease in size and would become what can be described as a hydrogen flame—a reddish pale flame—with accompanying smoke. It is likely that this oscillation was coupled with the rate at which the metering pump would provide water flow into the reaction chimney. After 40–50 seconds, the microwave power and aluminum flow were shut off and the reaction gradually came to a stop, leaving considerable alumina condensation on the chimney walls.

The most notable difference in aluminum ignition between helium- and argon-based plasmas was the apparent spatial location of the ignition point: the aluminum reaction spectrum for argon remained relatively the same throughout the test fire experiment and little to no condensation was visible on the quartz chimney near the region of the injector tip or the swirling ports, whereas for a helium-based plasma the aluminum reaction grew into a pervasive, purely thermal profile and left CCP throughout the height of the chimney and the helium plasma could not be distinguished from the thermal emission. This, again, was likely due to the greater density and lower diffusivity of argon in contrast to helium, causing the aluminum powder and any CCP to remain in regions well above the nozzle tip area. As such, a flame temperature estimation for argon was not obtained.
Figure 5.29: Aluminum-steam start ignition emission spectra with (top) helium-steam plasma at 400 W and (bottom) argon-steam plasma at 400 W, near nozzle tip, 500 ms after aluminum powder injection.
Figure 5.30: Temporal aluminum initial ignition spectral profiles for helium (top) and argon (bottom) steam plasmas at $P = 600$ W
Figure 5.31: Reaction regions of aluminum and steam/air yielding luminous emission (helium)
5.3.3 X-ray Scattering Profile Analysis

Due to the presence of excess combustion products collected on the quartz chimney walls, several samples were taken and ground into a powder. The powder was then analyzed using XRD at The Pennsylvania State University’s Millennium Sciences Building in order to define the participating substances, following the principle discussed in Chapter 2 for Bragg’s law of diffraction. By using a set of crystalline XRD references, matches were made between several aluminum oxides to the experimental result, shown in Figure 5.34, and aligned in order to observe the peak matches, depicted in Figure 5.35. All references were obtained from the International Center for Diffraction Data (ICDD) through the Material Sciences department.

The closest reference XRD match to the experimental set was alpha aluminum oxide (α-Al₂O₃), also known as alpha alumina or simply corundum. Corundum was noted to be a primary product of aluminum combustion by Lee et al. from the XRD analysis noted in Figure 2.19. The expected process of alumina generation can also be observed through the reaction mechanism laid out by Beckstead in Table 2.2.
Figure 5.33: Hydrogen flame emerging from the quartz chimney exhaust from aluminum-steam reaction (helium)
The second and third closest matches to the experimental XRD profile were transient aluminas defined by a hydroxyl ion in their crystal structure chains\textsuperscript{31}: delta alumina (δ-Al\textsubscript{2.67}O\textsubscript{4}) and gamma alumina (γ-Al\textsubscript{2}O\textsubscript{3}). It can be reasoned that, due to the steam entrainment serving as a provider of hydroxyl through the plasma volume, the prevalence of delta and gamma alumina was evident in the profile obtained from the CCP sample. Additional matches included elemental aluminum (Al), as some unburnt aluminum was also found on the thin region between the CCP and the quartz wall, presumably occurring during initial injection, and other minor aluminum oxides (Al\textsubscript{2}O\textsubscript{2.67}, Al\textsubscript{0.667}O) that allowed for further, yet very minimal, profile matching.

\textbf{Figure 5.34}: XRD results from experimental condensed aluminum reaction products
From the XRD results, a secondary method of recognizing aluminum reaction was perceived and provided additional concrete evidence that using an MPT with helium and entraining steam to provide oxidants enabled the ignition and reaction of aluminum powder. Although no XRD data was obtained for an argon-based MPT experiment with steam, similar CCPs were observed after cleaning the quartz chimney in order to prepare for another fire test, so a similar argument could be made.

**Figure 5.35**: Experimental XRD matching to reference aluminum and aluminum oxide profiles
Chapter 6 – Conclusions

6.1 Summary of Research Conducted

In order to substitute the use of a fuel-based pilot flame for a safer method, a plasma source, provided by a microwave plasma torch designed at The Pennsylvania State University, was integrated with an aluminum power delivery device and a steam supply with an isolation chamber. Using helium or argon, a plasma was established due to the concentrated electric field near the injector tip matching or surpassing the breakdown of the working gas. The resulting plasma was studied through the use of optical emission spectroscopy, ultimately allowing the creation of an axially-dependent temperature profile. Preliminary fitting attempts via Specair revealed non-thermal equilibrium in the plasma glow region and convolution between multiple diatomic air species, requiring manual temperature fittings for individual rovibronic bands. Due to time constraints, a complete gas temperature profile was not achieved.

Entrainment of steam, which was originally generated through resistive heating via a metal coil, was then heavily considered, with multiple design iterations, and successfully added to the plasma environment through the use of a fused quartz tube with a reducing neck at the top and two tangential and angled ports in order to promote swirling within the tube from the steam source. Due to the proximity of the quartz “chimney” to the plasma, the tube walls would quickly warm up, reducing the likelihood of condensation from the delivered steam. Once steam entered the chamber, a change of color, due to the recombination of hydrogen and oxygen, was recorded by the optical spectrometer, confirming that steam radicals would be present, primarily oxygen and hydroxyl.

Aluminum was then delivered into the applicator from a 2-in cylinder piston with industrial-grade argon as a pressurant, through a capillary tube and a union with the working gas to deliver additional momentum, and up the molybdenum injector. With minimal bed pressure, aluminum powder flow remained relatively steady. Upon reaching the plasma volume, the spectrometer recorded intense peaks of aluminum, shortly followed by aluminum monoxide bands and a growing broadband thermal emission. A bright, white-yellow flame developed inside and outside of the quartz chimney visible to the naked eye and photography. It was understood that the flame indicated an exothermic reaction between aluminum and steam oxidants, and its temperature was estimated through Wien’s displacement law, using the stored thermal emission spectrum, to be 3583 ± 326 K which fell in range of temperatures similarly obtained in previous research papers.

After the test fire, the condensed combustion products were collected from the chimney walls, ground into powder, and studied via x-ray diffraction. The analysis revealed a dominating presence of corundum, which
was shown in previous studies to be a primary product of aluminum combustion, and evidence of other transient aluminas, elemental aluminum, and additional aluminum oxide relatives.

6.2 Suggested Future Work

In order to further understand both the plasma source with and without steam entrainment and the reaction between aluminum and steam, added tasks and diagnostic tools can be mentioned. Although raw plasma data from OES enabled the identification of species near the nozzle tip and throughout the plume length at varying powers, specific spatial and temporal species concentration would serve to provide additional understanding as to how aluminum particles interact with the plasma as they travel through its volume, which can be obtained by performing absolute irradiance calibration and testing. Multiple optical spectrometers may also help understand where and when ignition and reaction of the aluminum particles occur by collecting simultaneous data during the early stages of aluminum injection and flame development. A computer-controlled collimator support would also allow for more accurate plasma and thermal spectral data to be evenly collected axially and radially. Similar axial profile data should also be acquired for the working gas plasma with steam entrainment in order to observe temperature changes with a parameterization study on the water flow.

Continued study of LTE and non-LTE plasmas and respective rovibronic fitting methods is necessary if a temperature profile of the plasma glow and afterglow, as a function of distance along the plume length, is to be computed.

Improved measurement of the aluminum flow could be achieved through the use of a Coriolis flow meter, rather than estimating the mass flow through a time-average process. Added control of the aluminum flow would also allow studies of flammability limits and ignition delay for combustion analysis, which could not be achieved through the piston-cylinder device for smaller aluminum flow rates.

A design was briefly studied that would allow for liquid water flow, through an atomizing nozzle, to be quickly dispersed, due pressurization, throughout the reaction chamber in order to eliminate the power supply needed to generate steam, which could reach up to 700 °F, and thus promoting safety during operation. Further design iterations might allow for more feasible experimental tests, but would require sturdier and heavier materials for tighter connections.
References


