Applications and Modeling of Non-Thermal Plasmas

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Chapter 1: Introduction

1.1 Thermal Equilibrium and Chemical Kinetics

Temperature is a measure of the average kinetic energy of the particles in a system. Monoatomic atoms store energy in linear translation, while diatomic and other, more complicated, molecules can also store energy in rotation and vibration. Thermal equilibrium is achieved when energy is evenly spread amongst these modes of internal energy storage. At thermal equilibrium, entropy, or the disorder, of a closed system is maximized. The probability distribution of the energies of each particle in a system with maximized entropy is described by the Boltzmann distribution (Fig. 1A) for systems with discrete energy levels, or as the Maxwellian distribution (Fig. 1B) for systems with continuous energy levels. The system temperature dictates the shape of the corresponding distribution and, at thermal equilibrium, all modes of energy storage are described by Maxwell-Boltzmann distributions of the same temperature.

Figure 1: Vibrational energy distribution (A) and linear translational energy distribution (B) functions for N$_2$ at 300 K (blue), 1500 K (green), and 3000 K (red)
As would be expected, at higher temperatures, more particles occupy higher energy states. These distributions connect microscopic particle behavior to the macroscopic property of temperature\(^1\).

These distributions are useful for predicting the rates of chemical reactions, which occur when individual atoms or molecules collide with sufficient energy to break or form bonds. The rate of the reaction depends on several factors including the concentration of the reactants, pressure, and temperature. For a simple two-body reaction \(A + B \rightarrow AB\), the reaction rate is given by

\[
\frac{d[A]}{dt} = k[A][B]
\]

(1)

Where \([A]\) is the concentration of reactant \(A\), \([B]\) is the concentration of reactant \(B\) and \(k\) is the reaction rate constant. The rate equation becomes more complex for reactions involving more reactants, but in general, increased reactant concentration increases the rate of the reaction since more molecules lead to more collisions\(^2\).

The reaction rate constant \(k\) depends on the collisional cross section \(\sigma(E)\) (that is an energy dependent probability of collision) and the translational energy distribution function \(f(E)\). It may be calculated by the following.

\[
k = \int_{0}^{\infty} \sigma(E)f(E)dE
\]

(2)

Since the Maxwell-Boltzmann distribution predicts that more particles will have higher energy at higher temperatures, reaction rates tend to increase as temperature increases. Though valid for a hard sphere, ideal gas approximation, Eq. 2 ignores factors such as molecular shape, vibration, and dissociation, which can affect the
reaction rate constant. In practice, reaction rate constants are usually determined experimentally.

### 1.2 Overview of Non-Thermal Plasmas and Pulsed Power

When sufficient energy is coupled to a gas, the atoms and molecules ionize creating an electrically neutral, conductive state of matter known as plasma. Plasma can be encountered every day in the form of flames, neon signs, sparks, or lightning. The sun, and all stars, are primarily made of plasma. In the case of flames or stars, intense heat causes ionization, whereas in neon signs, sparks, and lightning, a strong electric field causes ionization. In most practical engineering applications of plasma, the gas is ionized through the application of an electric field.

The breakdown process, that is the process of a gas turning into a plasma, has been widely studied. It is a complex process that is strongly dependent on conditions such as pressure, temperature, gas composition, and most importantly, the ratio of the applied electric field to the number density of particles in the system. This last parameter is known as the reduced electric field, $E/n$, and is proportional to the energy gained by an electron between collisions. The larger the reduced electric field, the more energy is coupled to the electrons in a plasma.

The breakdown process begins when an applied electric field accelerates pre-existing free electrons which then collide into heavy, neutral species. These free electrons are always present in minute quantities due to processes like photoionization and radioactive decay. Because of the large charge-to-mass ratio difference between
electrons and heavy ions, the applied field accelerates the electrons much more rapidly than the heavy ions. The large mass difference between electrons and heavy species makes energy transfer from elastic collisions very inefficient. This keeps the kinetic energy, and thus temperature, of the electrons much higher than that of the heavy species. Plasmas in this state of disequilibrium, where different modes of energy storage of the system have different temperatures, are known as non-thermal plasmas. At a large enough reduced electric field, some of the electrons gain sufficient energy to transfer energy via inelastic collisions. These inelastic collisions lead to rotational, vibrational, and electronic excitation, as well as dissociation, and ionization. Ionizing collisions free more electrons which, in turn, cause more ionization. This chain reaction exponentially increases the number of free electrons, leading to breakdown, in a process known as a Townsend avalanche.  

Unless significant space charges accumulate causing a streamer discharge, the plasma will become a diffuse and uniform glow discharge. Over time, exothermic collisions of electrons with heavy species, as well as electron-ion recombination, increase the temperature of the heavy species (the plasma temperature). As the plasma temperature increases, the number density decreases, which causes the reduced electric field to increase. The rates of both heating processes increase as the reduced electric field increases, driving up the temperature faster than it can be cooled by thermal diffusion. This runaway process, which is spatially non-uniform, causes the diffuse glow discharge to collapse into an arc. The heating causes the temperature of
the gas in the arc to be extremely high, comparable to the temperature of the electrons. Thus, the arc which is now at thermal equilibrium is known as a thermal plasma.

The dissociated, ionized, and electronically excited species generated in the non-thermal plasma are extremely reactive and are useful in combustion enhancement\(^4,5\), materials processing\(^6\), and biomedical applications\(^7\). Production of these species in thermal plasmas is extremely inefficient and would require impractically large temperatures to produce anything useful. This is because most of the energy coupled to a thermal plasma produces heat. Any resulting chemistry is only caused by the increased thermal energy of the particles in the system. However, in a non-thermal plasma, the large temperature difference between the electrons and the heavy species, allows for the plasma to remain relatively cool, while the inelastic electron processes directly lead to excitation, dissociation, and ionization.

Several different methods exist to generate non-thermal plasmas. Of these methods, the use of nanosecond high-voltage pulses is desirable because of the high peak voltage and thus high reduced electric field of the pulses. At low reduced electric fields, the electrons only gain sufficient energy to cause vibrational excitation. At higher reduced electric fields, the electrons gain sufficient energy to cause electronic excitation, dissociation, and ionization. This is because the cross sections for vibrational excitation peak at lower electron energies, whereas the cross sections for electronic excitation, dissociation, and ionization peak at higher electron energies.
Figure 2: Inelastic electron collision energy coupling at different reduced electric fields

For the applications of non-thermal plasmas mentioned above, it is desirable to generate a strongly non-equilibrium plasma over a large volume. However, the glow-to-arc transition quickly thermalizes the plasma and reduces its volume. As the pressure increases, the glow-to-arc transition happens faster. At atmospheric pressure, this transition happens on the order of microseconds. The glow-to-arc transition can be avoided if the high voltage signal is only applied on a timescale shorter than that of the glow-to-arc transition. Thus, non-thermal plasmas produced at atmospheric pressure using nanosecond high voltage pulses are larger in volume, more diffuse, and more uniform in comparison to plasmas generated by other methods. This is another compelling reason for the use of nanosecond pulses to generate non-thermal plasmas.
Chapter 2: Plasma Model Theory

2.1 Overview of the Model

Engineering design fundamentally depends on the ability to understand and predict physical phenomenon. The ability to characterize the effects of design changes is critical for effective implementation and optimization of non-thermal plasmas regardless of the application. The physics of these plasmas is extremely complex, with strong coupling between fluid dynamics, electrodynamics, and chemical kinetics. Phenomenon of interest happen on widely varying time scales, adding additional computational complexity. The required time, money, and computational resources makes high fidelity plasma simulations prohibitively expensive. These simulations can only be performed using state-of-the-art supercomputers. The existence of a model which has sufficient predictive capability without the associated computational demands, is crucial for the continued development of non-thermal plasma technologies.

Most researchers developing plasma simulations are focused on high fidelity models. Few models have been developed for use as a predictive engineering tool. Recently, The Non-Equilibrium Thermodynamics Laboratory at the Ohio State University has developed a 0D kinetic model for this purpose. It is much easier to use compared to other, similar models and is easily accessible because of its implementation through two existing pieces of software: Bolsig+, a free Boltzmann equation solver, and CHEMKIN-Pro, a commercial chemical kinetics package.
The model contains mechanisms for dominant vibrational-to-vibrational (V-V) and vibrational-to-translational (V-T) energy transfer pathways, alongside air plasma and hydrocarbon combustion chemistry. The air plasma mechanism was compiled by the authors of [9]. In the present work, the combustion mechanism used was developed at Lawrence Livermore National Laboratory to model methane-\(n\)-butane flames\(^\text{10}\). Reaction rate constants for the air plasma chemistry and hydrocarbon combustion mechanisms are specified in the Arrhenius form (Eq. 3)

\[
k = AT^\beta \exp\left(-\frac{E_A}{k_B T}\right)
\]

where \(A\) is the collisional frequency, \(T\) is the gas temperature, \(\beta\) is the temperature exponent, \(E_A\) is the activation energy for the reaction, and \(k_B\) is the Boltzmann constant. Reaction rates for V-V and V-T energy transfer are given in a non-Arrhenius form and depend both on the vibrational quantum level and temperature. Most of the parameters for the reaction rate constants were determined empirically. Tabulated rate constants for electron-impact processes are calculated using Bolsig+ as a function of electron temperature (see Section 2.4). These tabulated values are then fitted with a MATLAB post-processor to the following functional form used by CHEMKIN-Pro

\[
k = A T_e^B \exp\left(\frac{C}{T_e} + \frac{D}{T_e^2} + \frac{E}{T_e^3} + \frac{F}{T_e^4}\right)
\]

where \(T_e\) is the electron temperature and \(A, B, C, D, E,\) and \(F\), are the fit coefficients.

The model is set up as an open Perfectly Stirred Plasma Reactor (PPSR) with an inlet and outlet. Temperature dependent thermodynamic data as well as a
mechanism including all relevant reactions and rate constants are input in CHEMKIN format. Temperature, pressure, volume, and mixture composition are specified in the reactor as initial conditions. Inlet composition and temperature are specified to represent ambient conditions. A coupled system of rate equations, one for each specified reaction, is then solved subject to mass, species, and energy conservation using CHEMKIN-Pro (Section 2.2). This is a commercial implementation of CHEMKIN-II, a FORTRAN gas-phase chemical kinetics solver. The computed solutions give the concentrations of any species included in the model, along with the temperature, and electron temperature of the plasma, all as a function of time.

2.2 Governing Equations

The model includes governing equations for mass, species, and energy conservation along with an equation of state. The full details of the governing equations and solution methods are given in [11]. As previously mentioned, the system consists of an inlet, perfectly stirred reactor, and outlet. The specified volume is that of the control volume enclosing the perfectly stirred reactor. This is assumed to be the volume of the plasma discharge. A diagram of the system is shown in Fig. 3.
Figure 3: Diagram of the control volume used in the model

Because only one inlet, one reactor, and one outlet are used in the present work, and because no surface deposition reactions are included, the global mass balance is trivial. The inlet and outlet mass flow rates are identical, thus

\[ \frac{d}{dt} \rho V = \dot{m}_{\text{in}} - \dot{m}_{\text{out}} = 0 \]  

(5)

where \( \rho \) is the global density of the gas in the system and \( V \) is the total volume of the system. The species mass conservation equation is

\[ \rho_k V \frac{dY_k}{dt} = \dot{m}_{\text{in}} (Y_{k,\text{in}} - Y_k) + \dot{\omega}_k V W_k \]  

(6)

where \( k \) denotes the \( k \)th species, \( Y \) denotes the mass fraction, \( \dot{\omega} \) is the molar rate of production, and \( W \) denotes mass fraction.

Two different energy conservation equations are included, one for the gas and one for the electrons. The gas energy equation equates the time rate of change of the
internal energy with terms for energy changes due to heat transfer, boundary work, inlet enthalpy flow, and the enthalpy change of each reaction. This equation governs the temperature of the gas. The heat transfer term is calculated by specifying a heat transfer coefficient, \( h \), an effective heat transfer area, \( A \), as well as an ambient temperature, \( T_0 \), using the following equation.

\[
Q_{\text{loss}} = hA(T - T_0)
\]  

The electron energy equation equates the time rate of change of the total electron energy with the energy loss due to inelastic collisions, the enthalpy of forming and thermalizing new electrons, and an input power profile. This equation governs the temperature of the electrons. The enthalpies of every reaction are contained in the thermodynamic data included in the model. The electron energy loss terms are included with the reaction rate data for each electron impact process.

A first order term is additionally included with the governing equations which returns the state of the system to the inlet conditions. This exponential decay happens with a characteristic time, referred to as the residence time. This residence time is specified in the conditions of the reactor and can be used to include the effects of diffusion and free convection.

### 2.3 The Electron Energy Distribution Function

For electrons in thermal equilibrium, a Maxwellian distribution is used to calculate the rate coefficients of electron impact processes. However, the electrons in non-thermal plasmas are in a state of strong disequilibrium where this Maxwellian
distribution is no longer valid. Instead, the electron energy distribution function (EEDF) must be calculated by solving the electron Boltzmann equation given by Eq. 8

\[
\frac{\partial f}{\partial t} + \mathbf{v} \cdot \nabla f - \frac{q}{m_e} \mathbf{E} \cdot \nabla_v f = C(f)
\] (8)

where \(f\) is the distribution function, \(v\) are the velocity coordinates, \(q\) is the charge of an electron, \(m_e\) is the mass of an electron, and \(E\) is the electric field. \(C(f)\) on the right-hand side of the equation represents the change in the distribution due to different collisional (i.e. electron-impact) processes. The solution of the Boltzmann equation is a six-dimensional probability distribution function for the velocities and positions of the electrons in the system. For realistic systems, the Boltzmann equation is incredibly complex and can only be solved numerically. Even computing numerical solutions is a complicated task and often requires simplifying assumptions to be feasible.

One common solution method is the two-term spherical harmonic expansion method, described in detail in [12]. Briefly, the number of spatial coordinates is reduced by assuming the electric field and collisional probabilities to be spatially uniform. This allows for azimuthal symmetry in velocity space about the direction of the field. The spatial dependence in velocity is reduced to one coordinate, \(\theta\), the polar angle between the velocity and field direction. The spatial dependence in position is also reduced to one coordinate, \(z\), the position along the field direction. The resulting simplified equation is

\[
\frac{\partial f}{\partial t} + v \cos \theta \frac{\partial f}{\partial z} - \frac{q}{m_e} E \left( \cos \theta \frac{\partial f}{\partial v} + \frac{\sin^2 \theta}{v} \frac{\partial f}{\partial \cos \theta} \right) = C(f)
\] (9)
The electric field is assumed to be at steady state, with a transient first order correction to the distribution function to account for electron production from ionization and loss from attachment. The distribution function is then expanded in spherical harmonics in terms of $\cos \theta$, with the weighting coefficients for the expansion determined using Eq. 9. Though higher order terms may be kept for improved accuracy, in the present work, only the zeroth order and first order terms are kept. The zeroth order term represents the isotropic contribution to the distribution while the first order term represents an anisotropic contribution. This approximation fails for large $E/n$ values where the contributions of the higher order terms are non-negligible, or for systems with strong anisotropy.

The authors of [12] created a free Boltzmann equation solver called Bolsig+ which is used in the present work. The gas mixture composition, temperature, and electron collision processes are first specified. Bolsig+ then numerically calculates the EEDF over a specified range of values of the reduced electric field $E/n$ using the

![Figure 4: Numerically calculated EEDF (left) compared to Maxwellian distribution (right) at average electron energies of 1 eV (red), 1.5 eV (green), and 2.5 eV (blue) in air](image)
method described above. Once obtained, the EEDF is integrated along with electron impact cross sections for the specified processes over all electron energies to obtain the rate coefficients in the usual way. Bolsig+ then outputs tabulated values for the rate coefficients as a function of electron energy.

2.4 Global Modeling Assumptions and Validity

The plasma modeling performed in the present work makes many simplifying assumptions. Spatial uniformity of the system is assumed. This applies to any parameter that could potentially have a spatial dependence such as temperature gradients, species concentration, and the electric field. As such, the effects of heat transfer, species diffusion, space charges, and electrodynamics are ignored during the solution of the governing equations. These effects can, however, be approximately accounted for using correction factors which will be discussed later. The present work additionally ignores wall and surface interactions with the plasma, though they can be included in the model.

The chemistry mechanism included with the model is not comprehensive. The model only incorporates basic ion chemistry and limits the reactions for V-V and V-T energy transfer to dominant processes. The role of vibrationally excited species in combustion is neglected. A full list of the included plasma reactions is given in [9].

In addition, most of the empirical reaction rates were determined using measurements taken in low to moderate pressure (1-100 torr) plasmas. This is because the plasmas generated at these pressures are uniform, diffuse, and stable, allowing for
reliable measurements. Though it is assumed that the chemistry mechanism found at these lower pressures is still valid at higher pressures, processes which are negligible at lower pressures may become dominant at higher (e.g. atmospheric) pressure. Because of this, the reaction rates, and thus the model are only known to be valid over the range of pressures at which they were measured.

CHEMKIN-Pro has a bug where the solver crashes if the electron temperature falls too low. To prevent this, the model includes fake heating reactions which maintain the electron temperature at a specified minimum value. To make sure these fake heating reactions don’t couple any energy, the MATLAB pre-processor forces the reaction rates of all electron-impact processes to be zero at the specified minimum electron temperature. However, even though no reactions occur at this minimum electron temperature, the electron energy distribution is affected, changing the energy partitioning and the rates of the different electron impact processes.

The computation time of the model was on the order of a minute or so per pulse. This is much faster than higher fidelity codes which can take days to weeks to run. Though many simplifying assumptions were made, the model still accurately predicted trends seen in experimental data for many different phenomena. This will be discussed in more depth in the next chapter. This speed and accuracy reaffirms the use of this model as a predictive tool for engineering design. In chapter 4, the model will be used to predict and explain the effects of a non-thermal plasma used for combustion enhancement in a rotating detonation combustor.
Chapter 3: Plasma Model Validation

In this chapter, different components of the model will be validated against experimental data. This will allow for increased confidence in the model results later when it is used as a predictive tool for the plasma-assisted rotating detonation combustor. The motivation for validating each component of the model, a summary of experimental details, experiment specific modeling assumptions, and modeling results will be presented for each test case. More details about the diagnostic techniques and experimental setups used can be found in the corresponding referenced journal articles. A full description of the modeling procedure is given in Appendix A.

3.1 Temperature and Vibrational Loading

3.1.1 Introduction and Motivation

Correct determination of the input energy partitioning among the different modes of energy storage is critical for accurate prediction of the rates of electron-impact processes, production of chemical species, and temperature rise in the plasma. In [13], experimental time-resolved measurements of the concentration of the different vibrationally excited states of nitrogen allow for validation of the V-V and V-T energy transfer mechanism included in the model, as well as verification of the correct partitioning of energy to vibrational excitation. Temperature measurements allow for validation of the rate of heating of the plasma filament. Accurate prediction of the plasma temperature rise is important for flow control and combustion enhancement applications.
3.1.2 *Conditions and Modeling Assumptions*

This experiment was carried out in the discharge cell shown in Fig. 5. The nanosecond high voltage pulses were applied to two spherical, bare copper electrodes producing a diffuse filament. This discharge cell was designed to allow for “stable, reproducible, point-to-point geometry with filament dimensions sufficiently small to achieve significant specific energy loading, yet large enough to enable optical diagnostic studies and to reduce mass diffusion effects.”

![Discharge cell used in [13] and [14]](image)

**Figure 5: Discharge cell used in [13] and [14]**

The experimentally measured current and voltage (I-V) waveforms, as well as the current and voltage waveforms used in the model are presented below. The voltage curve was modified to account for a space charge effect known as the cathode fall. During breakdown, the electrons are attracted to the high voltage electrode and the positive ions are attracted to the low voltage electrode. For bare metal electrodes, the electrons form a conduction current, flowing into the high voltage electrode. Positive ions collide with the low voltage electrode, occasionally ejecting electrons through a
process called secondary emission. These ejected electrons continuously neutralize the positive ions, but are produced at a rate slower than the rate of ion collision. Thus, a layer of positively charged ions begins to form. The charge from these ions cancels some of the charge from the high voltage electrode, causing the potential between the electrodes to drop. This voltage drop is the cathode fall. The potential that affects plasma chemistry is the difference between the measured voltage and the cathode fall. Determination of the cathode fall is difficult and, in most cases, can only be estimated. The cathode fall applied to the input voltage in the present work is plotted in Fig. 6.

Figure 6: Experimental (A) and modeled (B) I-V waveforms used in [13]. The blue curve in A is the experimentally coupled energy. The green line in B is the estimated cathode fall.

The power profile inputted into the model was determined by multiplying the current curve with the voltage curve, after subtracting out the voltage drop due to the cathode fall.
The initial conditions for the model are presented in Table I. The mixture was assumed to be dry air with a mole fraction composition of 0.79 N₂ and 0.21 O₂. The discharge was assumed to be of cylindrical geometry with a diameter corresponding to 2 mm, the full-width at half-maximum (FWHM) of the gaussian intensity profile of an image of the filament (Fig. 7) Though significant gas dynamic expansion of the filament is evident (Fig. 7), the filament in the model was assumed to be constant volume and constant pressure.

**TABLE I: Modeling Conditions for [13]**

<table>
<thead>
<tr>
<th>Pressure (torr)</th>
<th>Initial Temperature (K)</th>
<th>Coupled Energy (mJ)</th>
<th>Volume (cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>300</td>
<td>10.2</td>
<td>0.0707</td>
</tr>
</tbody>
</table>

![Image of plasma filament](image)

**Figure 7: ICCD camera image of the plasma filament in [13]**

The characteristic time for radial diffusion, \( \tau \), was estimated to be 6.5 ms using

\[
\frac{1}{\tau} = \frac{D}{(R/2.4)^2} + \frac{v}{R}
\]  

(10)
where \( R \) is the diameter of the filament, \( v \) is the flow velocity of the gas through the discharge cell, and \( D \), the N atom diffusion constant, is 2.4 cm\(^2\) s\(^{-1}\) at the present conditions\(^{13} \). This value of 6.5 ms was specified as the residence time in the reactor. It was assumed that no additional heat or species transfer occurred.

### 3.1.3 Results and Discussion

For all subsequent plots, continuous lines correspond to modeling output, whereas discrete points correspond to experimentally measured values. The model output for temperature and vibrational temperature of the N\(_2\) (\( v = 1 \)) state are given below. The vibrational temperature is found by using the Boltzmann distribution and solving for temperature in terms of the number densities of the ground vibrational state and first vibrationally excited state of N\(_2\).

\[
T_{v=1} = \frac{E_1}{\ln \left( \frac{n_0}{n_1} \right)} \tag{11}
\]

\( E_1 \) is the energy difference between the \( v = 0 \) and \( v = 1 \) vibrational states of N\(_2\), \( n_0 \) is the number density of the ground vibrational state of N\(_2\), and \( n_1 \) is the number density of the first vibrationally excited state of N\(_2\).
The model does a fairly good job of predicting the rise of the temperature of the first vibrational level of N\textsubscript{2} as well as the peak gas temperature. The temperature rise in air discharges is typically a two-stage process. This is seen in the experimental data in Fig. 8. The first temperature rise is due to reactive quenching of electronically excited nitrogen with oxygen, given in the reaction N\textsubscript{2}* + O\textsubscript{2} → N\textsubscript{2} + O + O\textsubscript{15}. This first temperature rise happens faster than the acoustic timescale and leads to a pressure overshoot which forms compression waves. This has applications in active flow control and mixing enhancement and will be discussed later. The second temperature rise is due to energy transfer from vibrational modes to translational modes. In the results of the present work, the temperature during the first stage of heating is overpredicted, while the energy in the second stage is underpredicted. This means that,
in the model, more energy from inelastic electron impact processes was coupled to electronic excitation instead of vibrational excitation. This implies that the modeled reduced electric field is higher than the experimental reduced electric field.

Figure 9: Predicted and measured\textsuperscript{13} number densities of N\textsubscript{2} (blue), N\textsubscript{2}, \textit{v}=1 (green), N\textsubscript{2}, \textit{v}=1 (red), N\textsubscript{2}, \textit{v}=1 (cyan), and N\textsubscript{2}, \textit{v}=1 (purple)

Predicted vibrational loading during and after the plasma is compared against experimentally obtained number densities in Fig. 9. The model does a good job at predicting the number densities of the ground state and first vibrationally excited state of nitrogen. Additionally, it accurately predicts the vibrational loading during the discharge. However, it overpredicts the rate of decay of the \textit{v} = 3 and \textit{v} = 4 vibrational levels of N\textsubscript{2}. There are several reasons to explain this discrepancy. The only vibrational states of nitrogen included in the model are for \textit{v} = 0 to \textit{v} = 8. In reality, there are higher vibrationally excited states of nitrogen that could be relaxing into the
v = 2 to v = 4 states. These higher vibrational levels can additionally be populated by inelastic collisions of electronically excited species. However, the rates of this process are not well understood and reactions involving this process are not included in the model\(^9\). It is also possible that there are unknown mechanisms of energy transfer populating higher vibrational levels of nitrogen. Alternatively, the species measurements could be overpredicted due to experimental error.

Below are the vibrational distribution functions predicted by the model. Since the y-axis is plotted logarithmically, a straight line with a negative slope is indicative of a Boltzmann distribution, and thus equilibrium.

![Figure 10](image)

**Figure 10:** Predicted and measured\(^{13}\) N\(_2\) vibrational distribution function at 50 ns (red), 100 ns (green), and 1 μs (blue)
The model shows good agreement with the experimental results within the first microsecond. However, as previously mentioned, the experimental results show a much slower depopulation of the upper levels when compared to the predictions made by the model. This should not matter much for the present work since no chemistry involving vibrationally excited nitrogen is included in the mechanism other than V-V and V-T transfer. It will, however, affect the temperature rise, which could affect the rates of other processes.

Figure 11: Predicted and measured $^{13}$N$_2$ vibrational distribution function at 100 μs (red), 500 μs (green), and 5 ms (blue)

Since the vibrational loading predicted during the pulse agrees with the experimental data, the energy partitioning during the pulse can be assumed to be validated.
3.1.4 Pressure Overshoot Prediction

Sub-acoustic timescale heating, which is primarily caused by quenching of excited states of nitrogen, produces a pressure perturbation which radially propagates away from the plasma filament. The temperature rise predicted by the current model can be used to predict these pressure perturbations. In [9], the pressure on the centerline of the filament in radial, axisymmetric geometry is estimated by the following

\[ P(t) = P_0 + \rho_0 R [T(t) - T_0] \cdot \exp \left[ -\left( \frac{t}{\tau_{\text{acoust}}} \right)^2 \right] \]  \hspace{1cm} (12)

where \( P(t) \) is the time dependent pressure on the centerline, \( P_0 \) is the initial pressure, \( \rho_0 \) is the initial density, \( R \) is the ideal gas constant, \( T(t) \) is the temperature profile predicted by the model, \( T_0 \) is the initial temperature, and \( \tau_{\text{acoust}} \) is the acoustic timescale.

Figure 12: Predicted pressure overshoot on the centerline of the discharge in [13]
These pressure perturbations excite gas dynamic instabilities and induce turbulence, which is beneficially utilized in plasma-based active flow control\textsuperscript{16}. In addition, these pressure perturbations can be used to enhance fuel-oxidizer mixing in combustion applications\textsuperscript{17,18}. The pressure data produced by this method could potentially be incorporated into computational fluid dynamic (CFD) models of plasma-based actuators. Additionally, it could be inputted back into the 0D model to include the effects of the pressure rise on the kinetics of the plasma.

**Figure 13: Schlieren images\textsuperscript{16} showing compression wave formation at the conditions of [13]**

### 3.2 Air Discharge Kinetics

#### 3.2.1 Introduction and Motivation

Most applications of non-thermal plasmas at atmospheric pressure utilize discharges in air. Thus, validation of the air-plasma chemistry mechanism used in the model is needed if it is to have any usefulness as a predictive tool. The work described in [14] provides experimentally measured, time-resolved concentrations of N, O, and NO number densities during and after a nanosecond pulse in air. This is the data
against which the model will be compared. Both N and O are produced via several pathways including direct electron-impact dissociation and reactive quenching of different excited species. NO is also produced via several different, complex mechanisms. Accurate prediction of the concentrations of all three species should serve as a rigorous test of the accuracy of the model’s air-plasma mechanism.

3.2.2 Conditions and Modeling Assumptions

The modeling conditions and assumptions for this experiment are similar to those of the vibrational loading experiment. The input conditions of the model are summarized below. The filament was measured to be slightly larger than the filament in [13].

<table>
<thead>
<tr>
<th>Pressure (torr)</th>
<th>Initial Temperature (K)</th>
<th>Coupled Energy (mJ)</th>
<th>Volume (cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>300</td>
<td>3.2</td>
<td>0.038</td>
</tr>
</tbody>
</table>

The experimentally measured current and voltage as well as the current and voltage used in the model are presented below. As before, because the electrodes are bare metal, a voltage drop due to cathode sheathing effects is subtracted from the voltage used to calculate the model input power.
The primary difference between the previous experiment and this experiment is the coupled energy. Rapid heating from the large energy deposition of the pulse used in the previous experiment resulted in filament expansion, as seen in Fig. 7. This change in the volume and pressure of the system complicates the kinetics. The lower energy pulse used in [14] is better suited for validation of air kinetics because it “limit[s] both Joule heating of the filament and gas dynamic expansion in the afterglow14.”

3.2.3 Results and Discussion

A plot comparing the modeling results against experimental measurements of [O], [N], [NO], and plasma temperature is given below. The predicted number densities for O, N, and NO are in good agreement with the experimentally measured values.
The model overpredicts the production of O and predicts a faster decay of N and NO. The predicted temperature is much higher than the experimentally measured temperature. However, the diagnostic used for thermometry averages the temperature over a distance across the filament. If the distance was wider than the actual filament, the average would have included a region outside of the plasma, thus decreasing the measured temperature. Lowering the temperature predicted by the model by decreasing the input energy causes the number densities of O, N, and NO to no longer agree with the experimental values. The actual temperature of the filament was likely between the measured and predicted values.
3.3 Combustion Kinetics

3.1.1 Introduction and Motivation

Combustion is a complex, multi-step chemical reaction in which fuel is oxidized. The process starts with initiation reactions that lead to the dissociation of fuel and oxidizer molecules. Some of these dissociated species then form reactive free radicals in chain-branching reactions. The process ends when these free radicals recombine in exothermic, chain-termination reactions.

As previously mentioned, the dissociated species and free radicals produced in non-thermal plasmas make these plasmas well suited for combustion enhancement applications. Modeling predictions of combustion phenomena must be validated, if the model is to be used in development of these technologies. To this end, the temperature rise and generation of hydroxyl (OH) radicals by the plasma should be validated, as both are incredibly important in combustion. The former influences the rates of the combustion reaction and the latter participates in many chain-branching reactions. The experiments described in [20] provide time-resolved, experimental measurements for the temperature and concentration of OH after a burst of pulses, as well as the ignition delay time in various H₂-air mixtures.

3.3.2 Conditions and Modeling Assumptions

For this experiment, the plasma was generated using a burst of nanosecond high voltage pulses in the discharge cell shown in Fig. 16. The width of the copper
electrodes was 14 mm and the length of the electrodes was 60 mm. The gap between the electrodes was 10 mm.

Two different high voltage pulse generators were used. For the OH and temperature measurement experiments, an FID GmbH pulse generator was used. For the ignition delay experiments, a Chemical Physics Technologies (CPT) pulse generator was used. The experimental voltage waveforms for both pulse generators and the power waveforms used in the model for both pulse generators are shown below.

Figure 16: Discharge cell used in the experiments in [20]

Figure 17: Experimental voltage waveforms (A) and coupled energy and reduced electric field for the CPT pulse generator (B) from [20]
The plane-to-plane dielectric barrier discharge used in [20] produced a diffuse, uniform plasma which is closer to the idealized 0D conditions assumed by the model, especially in comparison to the pin-to-pin geometry of the previous two cases. Because the impact of spatial effects is reduced, any discrepancy between the modeling results and the experimental data likely arises from uncertainty in the kinetic mechanism or uncertainty in the input power. However, the long duration of each burst of pulses means that the effects of unknown, long-lived species, as well as steady state effects, may influence the results.
In contrast to the metal electrodes of the previous two modeling cases, the dielectric-covered electrodes prevent the formation of a conduction current and limit the amount of energy coupled per pulse. As before, the ions formed in the plasma still attach to the low voltage electrode during the pulse. However, because of the dielectric layer, the electrons attach to the high voltage electrode instead of entering it. The charges of these ions and electrons cancel and thus there is a negligible cathode fall.

Because of the long duration of both experiments, heat transfer out of the discharge cell needed to be considered. Since the plasma was uniform and diffuse throughout the entire volume, the effects of diffusion were negligible. Conduction through the walls of the discharge cell and subsequent convective cooling by the ambient air were assumed to be the dominant modes of heat transfer in the plane-to-plane discharge. An estimated total heat transfer coefficient of 50 W/m²K was specified to account for this heat loss. This value produced the best modeling prediction for the experimental data.

The conditions for the OH and temperature measurement experiment are listed in Table III. For this experiment, two different hydrogen-air mixtures were ignited using the FID pulse generator, which generated 50 pulse bursts at a frequency of 10 kHz. One set of OH and temperature measurements was made for an equivalence ratio of $\phi = 0.06$ and another set was made for an equivalence ratio of $\phi = 0.12$. The equivalence ratio is defined as

$$\phi = \frac{n_{\text{fuel}}/n_{\text{air}}}{(n_{\text{fuel}}/n_{\text{air}})_{\text{stoich}}}$$  (13)
where the numerator is the molar fuel-to-air ratio of the mixture and the denominator is the stoichiometric molar fuel-to-air ratio for the mixture. Thus, an equivalence ratio of one signifies a stoichiometric mixture. Equivalence ratios less than one correspond to fuel-lean mixtures with excess air and equivalence ratios greater than one correspond to fuel-rich mixtures with excess fuel.

**TABLE III: Modeling Conditions for Temperature and OH Measurements in [20]**

<table>
<thead>
<tr>
<th>Pressure (torr)</th>
<th>Initial Temperature (K)</th>
<th>Coupled Energy (mJ/pulse)</th>
<th>Volume (cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>500</td>
<td>3.2</td>
<td>8.4</td>
</tr>
</tbody>
</table>

The conditions for the ignition delay experiment are listed in Table IV. In this experiment, a stoichiometric hydrogen-air mixture was ignited using the CPT pulse generator which produced a varied number of pulses at 40 kHz. The model was run using 110, 120, 130, and 140 pulse bursts.

**TABLE IV: Modeling Conditions for Ignition Delay in [20]**

<table>
<thead>
<tr>
<th>Pressure (torr)</th>
<th>Initial Temperature (K)</th>
<th>Coupled Energy (mJ/pulse)</th>
<th>Volume (cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>80</td>
<td>473</td>
<td>0.9</td>
<td>8.4</td>
</tr>
</tbody>
</table>

3.3.3 Results and Discussion

A plot of the predicted OH number density and temperatures after the burst of pulses is shown below. The model overpredicts the amount of OH produced in the
microseconds after the burst. This is likely due to uncertainty in the value of the heat transfer coefficient. Because the rates of the different reactions are temperature dependent, if the heat transfer coefficient provided to the model is lower than the heat transfer coefficient of the experimental system, the temperature would be overpredicted and the production of certain species could be overpredicted. Additionally, uncertainty in the coupled energy could also contribute to this excess temperature rise.

Figure 20: Predicted and measured OH (lines and circles) and temperature (dashes and diamonds) in H₂ - air mixtures at ϕ = 0.06 (blue) and ϕ = 0.12 (red)

Accurate prediction of ignition delay is another important measure of the fidelity of the model. Ignition delay, as defined in [20], is “the point where a sharp ‘jump’ in the temperature profile occurs”. As shown in Fig. 22A, this sharp jump
occurs when the temperature reaches approximately 900 K. As such, the time at which the temperature profile rises to 900 K is used to define the ignition delay time in the present modeling work.

Figure 21: Predicted (red) and measured\(^{20}\) (black) ignition delay times in H\(_2\) - air mixture at \(\phi = 1\)

The model output for 120, 130, and 140 pulse bursts agrees very well with the experimentally produced data. However, ignition was achieved using a 110 pulse burst in the experimental work, but was not predicted by the model. This can be explained by the sensitive dependence of ignition on the temperature rise in each pulse, which itself is dependent on the input power waveform. In this case, the lack of ignition is likely due to uncertainty in the reported energy coupled to the plasma. Uncertainty in the dielectric constant of the insulation layer in the discharge cell affects the voltage applied to the plasma and thus coupled energy in the plasma. Additionally, uncertainty
in the heat transfer coefficient could prevent the temperature from reaching the ignition threshold after 110 pulses. Regardless, the model accurately predicted the experimentally measured trend in ignition delay time reduction. As the number of pulses increases, the ignition delay time decreases.

Figure 22: Predicted temperature and OH rise after discharge in H₂ - air mixture at $\phi = 1$ for 110 (red), 120 (green), 130 (blue), and 140 (black) pulses

In Fig. 22A, the sharp temperature rise corresponding to ignition is clearly noticeable for the 120, 130, and 140 pulse cases. It is additionally accompanied by a sharp increase in the number of OH radicals which is shown in Fig. 22B.

The mechanism of non-thermal ignition is illustrated in Fig. 23. Rather than locally producing a hot spot which triggers combustion, as in a thermal spark, non-thermal ignition occurs by the production and accumulation of a large pool of radicals such as OH which subsequently lead to ignition.
Figure 23: Predicted OH rise during and after discharge in H₂ - air mixture at \( \phi = 1 \) for 110 (red), 120 (green), 130 (blue), and 140 (black) pulses

The model successfully predicted a wide range of phenomenon. Though the modeling predictions did not always exactly match the experimental data, it correctly predicted the overall trends in temperature rise and species formation. With the model validated, the next section focuses on using it as a predictive tool to provide theoretical support to the experimental results obtained in hot-fire testing of a plasma assisted rotating detonation combustor.
Chapter 4: Plasma-Assisted Rotating Detonation Combustor

4.1 Detonation Theory

Deflagration and detonation are the two modes of combustion. Normal flames are deflagrations, where the combustion zone propagates at subsonic velocities. In contrast, a detonation propagates at supersonic velocity. The detonation may be modeled as a thin shock wave with a trailing, thicker combustion zone. The pressure and temperature rise generated by the shock wave initiates the combustion process. In turn, the heat released by the combustion sustains the shock wave. This 1D model is known as the Zeldovich, von Neumann, Döring (ZND) model and is frequently used in the analysis of detonations\textsuperscript{19}.

Figure 24: ZND model predictions of various properties illustrating the shock, induction zone, and reaction zone\textsuperscript{21}
The shock wave itself is treated as a discontinuity between pre-shock and post-shock conditions. 1D ideal-gas shock relations, derived using mass, momentum, and energy conservation, can be used to determine the post-shock state given pre-shock conditions. The post-shock state is dependent on initial temperature, pressure, mixture composition, and detonation velocity. This detonation velocity is additionally dependent on the initial mixture composition and temperature. In this model, the detonation is assumed to reach a steady state velocity known as the Chapman-Jouguet (CJ) velocity\textsuperscript{19}.

Because the width of the shock is thin enough, and the change in conditions is assumed to happen fast enough, there is insufficient time for chemical reactions to take place. The detonation induction time is defined as the delay between the shock-induced change in conditions and the time of the maximum rate of heat release by the resulting combustion reaction. This may be multiplied by the detonation velocity to determine a corresponding detonation induction length, that is, the distance between the shock and the flame front.

The structure of real, three-dimensional detonations is decidedly more complex than the ZND model. However, even for these three-dimensional cases, the detonation can still be viewed as a shock wave coupled with a reaction zone. When contained in an enclosure such as a tube, the initially planar shock forms a series of leading and transverse shock waves which collide and interact. These interactions sustain the detonation and form a cellular structure with a characteristic dimension known as the detonation cell size, denoted $\lambda$\textsuperscript{22}. 

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Cell sizes for many different mixtures have been experimentally measured and are related to the detonability (i.e. the sensitivity to detonation) of a mixture. The more sensitive a mixture is to detonation, the smaller the cell size. Because transverse shock interactions are required to sustain detonation, detonations in an enclosure will not form if the characteristic dimension of the enclosure is smaller than the cell size. For rectangular geometries, this dimension is the height of the rectangle. For cylindrical geometries, this dimension is the diameter of the tube.

4.2 Overview of the Rotating Detonation Combustor

Deflagration produces a minimal static pressure loss across the combustion front. In contrast, detonation produces a static pressure gain across the front and reduces entropy rise over the cycle. These aspects of detonation can be used beneficially in pressure gain combustors (PGCs). Current combustors in gas turbine
engines burn fuel through deflagration. It is predicted that replacing these combustors with PGCs would yield efficiency improvements up to fifteen percent\textsuperscript{24}. Because gas turbine engines are widely used in aviation and power generation, an improvement in engine thermal efficiency of one percent would have the same environmental impact as removing more than 1.3 million cars in the United States alone\textsuperscript{25}.

![Figure 26: Comparison of gas turbine thermodynamic cycles using detonative combustion, constant volume combustion, and constant pressure combustion\textsuperscript{26}](image)

The cost savings and environmental impact associated with this improvement in efficiency has garnered substantial interest in the development of PGC technology.

Pulsed detonation combustors (PDCs) were the first practical implementation of PGC technology. In this combustor, a long tube with one closed end is filled with a combustible mixture which is then ignited at the closed end. The combustion front initially propagates towards the open end at subsonic velocities, accelerating as it
progresses. Eventually the combustion front velocity exceeds the speed of sound and becomes a detonation. This process is termed the deflagration-to-detonation transition (DDT)\textsuperscript{27}. The combustion products are then purged before the entire cycle is repeated. Though much work was put into development of PDCs, research into the technology has slowed due to several seemingly insurmountable problems. The immense size of the tubes required for the DDT process makes integration of the combustors into existing engine designs impractical. Additionally, the fill-detonate-purge cycle requires extremely complex valving. Mechanical limits on valving speed restrict the cycle repetition rate to sub-100 Hz frequencies. The resulting large fluctuations in exhaust pressure subject any downstream engine components, such as turbines, to tremendous mechanical stresses, reducing component lifespan\textsuperscript{21}.

Current PGC research is focused on understanding and developing rotating detonation combustors (RDCs)\textsuperscript{28,29}. In the RDC (Fig. 27), a continuous detonation travels circumferentially along an annular combustion channel.

![Figure 27: Front (A), side (B), and cutaway (C) views of a rotating detonation combustor](image)

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Reactants are constantly fed into the channel where they are consumed by each pass of the detonation wave. The RDC is mechanically simple, with no moving parts. It is additionally compact and produces steady exhaust. These attributes make it particularly attractive as a replacement for the combustor in gas turbine engines.

Figure 28: “Unwrapped” RDC CFD solution for temperature (left) and pressure (right). The high pressure (green) zone corresponds to the detonation

Several major technical challenges impede the adoption of RDCs.31 Commercial viability of the technology depends on its ability to readily integrate into existing power generation and aviation infrastructure. In particular, this means that airbreathing RDCs must be able to operate using methane (natural gas) and kerosene (jet fuel) for effective implementation in the power generation and aviation industries. No current RDCs have been successfully run using either methane-air or kerosene-air mixtures. This is attributed to two major problems: reactant detonability and mixing.

Practically usable hydrocarbons such as methane or kerosene have limited detonability and thus have large detonation cell sizes. A table of typical cell sizes for common reactant mixtures is given below. Austin and Shepherd report that the detonation cell size of JP-10 is comparable to that of propane.32
TABLE V: Approximate Detonation Cell Sizes of Various Mixtures

<table>
<thead>
<tr>
<th>Fuel</th>
<th>Fuel-Oxygen (mm)</th>
<th>Fuel-Air (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂</td>
<td>1.4</td>
<td>10</td>
</tr>
<tr>
<td>C₂H₄</td>
<td>0.5</td>
<td>20</td>
</tr>
<tr>
<td>C₃H₈</td>
<td>0.9</td>
<td>60</td>
</tr>
<tr>
<td>CH₄</td>
<td>2.5</td>
<td>280</td>
</tr>
</tbody>
</table>

To date, no RDC with a channel width large enough to support methane detonation has been built. Even if such an RDC were created, the large size of the combustor would make it impractical for many applications.

Designs where fuel and oxidizer are premixed are extremely unsafe, with the potential for flashback causing ignition upstream of the RDC. Because of this, non-premixed designs are favored. However, adequate reactant mixing has proven challenging. Poor mixing prevents local regions from having sufficient fuel or oxygen, decreasing the overall detonability of the reactants. This further increases the detonation cell size.

Non-thermal plasmas present a possible solution to these issues facing the development of the RDC. The generation of reactive species and radicals through inelastic electron impact should increase the detonability of the fuel, thus lowering its cell size. Additionally, the turbulence induced by the compression waves generated by the plasma should enhance mixing, further increasing detonability. Studies at the Naval Postgraduate School utilized non-thermal plasmas to shrink the required size of
PDCs. Their work demonstrated a significant reduction in the DDT length when the mixture was ignited with non-thermal plasma\textsuperscript{36,37}.

The experiment described in the next section focuses on characterizing changes in the behavior of the RDC with the addition of a plasma. The ultimate research goal is to improve the technological feasibility of the RDC with plasma, by expanding its operation to previously non-viable regimes, geometries, and mixtures.

4.3 Experimental Approach

The objectives of the present work are to determine the feasibility of using a non-thermal plasma in an RDC, determine if the plasma affects the behavior of the RDC, and provide preliminary insight into the interaction between the plasma and the detonation. The scope of the present work is to provide proof-of-concept of the plasma assisted RDC, and to lay the foundation for further development and study of the technology.

The experiments were conducted using the RDC at the University of Cincinnati Gas Dynamics and Propulsion Laboratory. A detailed description of the facility is given in [35]. Briefly, their RDC is a heavily modified version of the RDC developed by Shank et. al at the Air Force Research Laboratory [38]. Its modular design allows for easy modification of the geometry of different combustor components including, but not limited to, air injection area, distribution, and location, as well as combustor chamber annulus width. In the present work, air is radially injected inwards while hydrogen is axially injected. The continuous influx of fuel and air is controlled by a system of valves and sensors which are described in [35]. The
reactants are ignited using an initiator tube (Fig. 27) which is fueled with ethylene and oxygen.

Figure 29: University of Cincinnati Twin Oxidizer Injection RDC, full view and cutaway view

Several different high-speed sensors were used to determine detonation behavior. PCB piezoelectric pressure transducers were mounted at P1, P2, and P3 (Fig. 27) on the body of the RDC to capture pressure fluctuations in the air injection slot. This sensor placement is chosen for two reasons. First, the sensors are still close enough to the combustion annulus to accurately capture pressure data resolving the behavior of the detonations. Second, because they are not directly in the combustion annulus, they are not exposed to, and subsequently damaged by, the intense heat produced by the detonation.

The plasma was generated in the RDC using a novel centerbody electrode which was fabricated using MACOR machinable ceramic and aluminum. MACOR was chosen due to its high dielectric strength and thermal properties. The use of MACOR kept project costs low, as it is machinable using normal metal machining techniques. The dimensions of the ceramic were chosen to ensure the discharge was
only generated between the electrode and the outerbody wall. To allow for geometric variation, centerbodies of two diameters, 4 inch and 5.75 inch, were manufactured.

The electrode was powered using a commercial nanosecond high voltage pulse generator (Megaimpulse Ltc. NPG-18). This generator was capable of producing ~10 nanosecond wide pulses up to 40 kV at a frequency of up to 3.5 kHz.

Figure 30: Centerbody exploded view (A), 4 inch centerbody (B), 5.75 inch centerbody (C)

The electrode width was chosen to be wide enough to be easily machined, but thin enough to keep the capacitance between the electrode and outerbody wall low. The capacitance had to be low enough such that the corresponding RC time constant was shorter than the width of the high voltage pulse. CFD models of the RDC show that the detonation only extends several centimeters from the inlet of the combustion annulus. Because the reactive species produced by the plasma disappear quickly, it was decided that the plasma should be generated directly in the path of the detonation
to maximize its effect. As such, the electrode was placed close to the inlet. Its axial position could be adjusted by using ceramic shims of varying width.

The 5.75 inch centerbody produced discharges that radiated from the centerbody to the outerbody. The 4 inch centerbody produced axial discharges that radiated along the centerbody to the baseplate. Photos of the plasma being produced by both centerbodies are shown below in Fig. 31.

![Figure 31: Radial discharges produced by the 5.75 inch centerbody (left) and axial discharges produced by the 4 inch centerbody (right)](image)

Hot-fire tests of the RDC were conducted using hydrogen as the fuel and air as the oxidizer. The use of hydrogen and air in RDCs has been extensively studied and there are many experiments against which the results of the present work can be compared. In addition, the simplicity of the hydrogen and air combustion process allows for faster and more reliable modeling results, since there is increased
uncertainty in the combustion mechanisms of more complex hydrocarbon fuels. The associated detonation cell size of this mixture is around 10 mm.

### 4.4 Results and Discussion

Successful detonation was determined by visual characteristics of the RDC exhaust plume as well as by the data generated by the pressure transducers and ionization probes. The exhaust plume for a deflagration event was several times longer than the exhaust plume of a detonation event as shown in Fig. 32.

![Typical RDC exhaust plume for deflagration (left) and detonation (right)](image)

**Figure 32: Typical RDC exhaust plume for deflagration (left) and detonation (right)**

A large spike in pressure in the signal from the pressure transducer indicated a detonation passing over the sensor. Periodic, large spikes in the pressure trace data were indicative of a detonation.

The behavior of the RDC was grouped into four distinct categories. Detonation was characterized as the presence of consistent, periodic, large spikes in the pressure trace data. Transitionary behavior occurred when stable detonation was initially achieved before being subsequently extinguished. Visually, this behavior was
characterized by a sudden transition from the characteristic exhaust plume of a
detonation, to the exhaust plume of a deflagration. The pressure trace for a
deflagration event, in contrast, did not have any of the pressure spikes associated with
detonation. Outright failure was characterized as the inability of the RDC to initiate
any sort of combustion. In this case, no exhaust plume was formed.

Due to the cyclical loading of the detonation on the ceramic, the 5.75 inch
centerbody cracked during testing. The centerbody was checked after running the first
two tests which corresponded to a stoichiometric mixture with the plasma off then on.
It is unknown at what point the ceramic failed after this test, though it is assumed to
have failed after many more tests were conducted. The cracked ceramic would have
had a substantial impact on the geometry and thus flow field of the RDC, so results of
the tests after the first two runs cannot be entirely attributed to the plasma alone. Thus,
only the data of the first two runs will be presented, though the remaining cases will
still be discussed. The 4 inch centerbody remained intact throughout testing so all
results from that round of experiments will be assumed valid.

Figure 33: Cracking of ceramic due to detonation impulse loading
A map of the behavior of the RDC under different conditions is presented in Fig. 34 below. Each hot-fire test was performed using an air mass flow rate of approximately 0.2 kg/s over a range of equivalence ratios.

![Operating map of the plasma assisted RDC showing detonation (circle), transition (triangle), deflagration (square), and failure (diamond) for the 5.75 inch centerbody (blue) and 4 inch centerbody (red).](image)

**Figure 34: Operating map of the plasma assisted RDC showing detonation (circle), transition (triangle), deflagration (square), and failure (diamond) for the 5.75 inch centerbody (blue) and 4 inch centerbody (red).**

The plasma significantly impacted the behavior of the RDC under certain operating conditions. There was no noticeable difference in operation with the 4 inch centerbody. The channel width with this geometry was sufficiently large to allow for stable detonation over a wide range of equivalence ratios, regardless of whether the plasma was used or not. For the 5.75 inch centerbody, there was noticeable improvement in the operation of the RDC. Previous experiments found the operating map for this geometry to be extremely limited with few conditions leading to
detonation\textsuperscript{39}. The plasma led to stable detonation onset in the $\phi = 1$ and $\phi = 1.2$ runs. This is illustrated in Fig. 35 where without plasma (A) the detonation extinguished, but with plasma (B) the detonation was sustained. At $\phi = 1.4$ the RDC underwent deflagration without plasma. With the plasma, detonation was induced, although it transitioned to deflagration. Even in the case of $\phi = 0.8$ where no detonation occurred, the plasma significantly shrunk the length of the deflagration plume, indicating improved flame holding and combustion stability.

Figure 35: Pressure traces for $\dot{m} = 0.2$ kg/s and $\phi = 1$ without plasma (A) and with plasma (B). Arrow in A indicates detonation extinction, arrow in B indicates stable detonation onset

Because three different pressure transducers were used, the direction of the detonation rotation could be resolved based on the order of the spikes in the pressure
trace signal. As shown in Fig. 36, the direction of each burst of detonation induced by the plasma appeared to be random, though it remained the same within the burst.

![Figure 36: Zoomed in view of pressure traces in Fig. 35B showing detonation direction mode switching](image)

It appears that the plasma is not sustaining the detonation, but rather reinitiating it. However, it is unlikely that the plasma is directly reinitiating detonation. Even with uncertainty in the current and voltage waveforms of the pulse, the coupled energy per pulse is at least three orders of magnitude lower than the critical energy required for direct detonation initiation of hydrogen and air.
A frequency spectrum of each pressure trace signal was produced using a fast Fourier transform algorithm to determine the detonation velocity for each run. The dominant peak in the frequency spectrum around 3 kHz corresponded to the fundamental mode of the detonation rotation. By multiplying this by the circumference of the RDC channel, a detonation velocity of approximately 1500 m/s was determined. There was minimal variation in this velocity between tests with and without the plasma, on the order of a few meters per second.
Figure 38: Spectrogram of the pressure signal in Figure 35B showing consistent dominant detonation rotation frequency of around 3000 Hz

By dividing the circumference of the RDC by time between peaks in the pressure trace signal, the speed of the detonation for each rotation could be determined and plotted. This technique was previously used by Anand et al. as a method for determining the stability of the detonation propagation\(^41\). Unstable detonations will show a large spread in the speed of the detonation from lap to lap. An example wave speed plot is shown below in Fig. 39.
Even in the periods of plasma induced detonation, the wave speed between laps stayed relatively consistent. No noticeable instabilities were found by this method.

4.5 Modeling Predictions

4.5.1 Plasma Assisted Detonation Model Overview

To provide theoretical support to the results described in section 4.4, the behavior of the plasma-assisted RDC was modeled with a reduced order approach, combining the 0D plasma kinetic model with a ZND detonation model implemented through the Caltech Explosion Dynamics Laboratory’s (EDL) Shock and Detonation
Toolbox. The model was run assuming a detonation channel width of ~5 mm, as was the case with the 5.75 inch centerbody.

Because breakdown is more favorable at lower pressure, the discharge was assumed to happen some distance in the low-pressure region in front of the detonation wave. The region preceding the detonation was assumed to be at atmospheric temperature and pressure. It was assumed that the region had been replenished with fresh, perfectly mixed reactant at a specified equivalence ratio. This pressure, temperature, and mixture were input as initial conditions for the plasma model. Because the discharges that were produced were filamentary, they were assumed to be cylindrical in geometry. No imaging equipment was available, so the plasma diameter was assumed to be 2 mm with its height corresponding to the detonation channel width. Based on Fig. 38, the detonation rotation frequency was approximately the same as the pulse frequency. Accordingly, only one input power pulse was specified. Experimental measurements of current and voltage were not possible. Thus, the coupled power was estimated to be 10 mJ, with a power profile corresponding to that of the experiment detailed in [13].

The high voltage pulse length was on the order of nanoseconds and any subsequent plasma chemistry occurred on the order of microseconds. Since both occur much faster than combustion chemistry which happens on a millisecond timescale, it was assumed that the plasma model output could be used as initial conditions for the calculation of the post-shock conditions using the EDL toolbox. The assumed distance between the pulse and the detonation front was divided by the calculated detonation
velocity to yield a corresponding elapsed time between the end of the pulse and the arrival of the detonation. The temperature, and mixture composition predicted by the plasma model at the elapsed time after the pulse were then used as initial conditions to calculate the temperature and OH concentration as a function of distance behind the shock. The induction length was defined as the distance along the temperature profile to the maximum temperature gradient. The ZND model additionally calculated profiles for the heat released behind the detonation as well as the CJ velocity for the specified mixture.

To determine the detonation cell size, a semi-empirical, single parameter model proposed by Ng was used. It posits that the proportionality constant between the detonation induction length and cell size is a function of a non-dimensional stability parameter \( \chi \). This parameter is defined as

\[
\chi \equiv \varepsilon_I \frac{\Delta_I}{\Delta_R}
\]

(14)

where \( \varepsilon_I \) is the reduced activation energy of the induction process, \( \Delta_I \) is the induction length and \( \Delta_R \) is the characteristic reaction length of the mixture. The induction delay time is assumed to exponentially depend on the reduced activation energy. By varying the shock velocity by 1% and determining the corresponding change in the post shock temperature and induction delay time, the reduced activation energy is found with

\[
\varepsilon_I = \frac{E_d}{RT_s} = \frac{1}{T_s} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)
\]

(15)

Because the energy release rate (thermicity) occurs as an approximately Gaussian pulse behind the shock, the characteristic reaction length is calculated as the full width
at half maximum of this profile. The relationship between the induction length and cell size is assumed to be a polynomial correlation given as

\[
\lambda = \left( A_0 + \sum_{k=1}^{N} a_k \cdot \chi^{-k} + b_k \cdot \chi^k \right) \cdot \Delta_I
\]  

(16)

In the present work, only terms up to \( N = 3 \) will be considered. The correlation coefficients obtained using a least-squares fit are given in Table VI.

**TABLE VI: Detonation Cell Size Correlation Coefficients**

<table>
<thead>
<tr>
<th>Coefficients</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>( A_0 )</td>
<td>30.465860763763</td>
</tr>
<tr>
<td>( a_1 )</td>
<td>89.55438805808153</td>
</tr>
<tr>
<td>( a_2 )</td>
<td>-130.792822369483</td>
</tr>
<tr>
<td>( a_3 )</td>
<td>42.02450507117405</td>
</tr>
<tr>
<td>( b_1 )</td>
<td>-0.02929128383850</td>
</tr>
<tr>
<td>( b_2 )</td>
<td>1.026325073064710 \times 10^{-5}</td>
</tr>
<tr>
<td>( b_3 )</td>
<td>-1.031921244571857 \times 10^{-9}</td>
</tr>
</tbody>
</table>

4.5.2 Modeling Results

Cell sizes for H\(_2\)-air mixtures at 300 K over a wide range of equivalence ratios were calculated using the ZND model in combination with the correlation suggest by Ng. The resulting predictions were compared against experimentally obtained detonation cell sizes under the same conditions. The predicted cell sizes show extremely good agreement with the experimental data, especially given that the experimental uncertainty for cell size measurements is usually considered to be a
factor of two\textsuperscript{21}. This baseline prediction serves as sufficient validation of the ability of the model to accurately determine the detonation cell size.

![Graph showing predicted vs. experimental detonation cell sizes](image)

**Figure 40:** Predicted (red) vs. experimental\textsuperscript{33} (blue) detonation cell sizes for H\textsubscript{2}-air mixtures at 300 K for different equivalence ratios

The model was then used to calculate the cell size as a function of distance between the plasma and the detonation. This calculation was performed using initial mixtures with a composition of $\phi = 0.4$, $\phi = 1$, and $\phi = 1.6$. This corresponded to the range of equivalence ratios used in the experimental hot-fire testing. To provide comparison, the cell size for each mixture composition was calculated without the plasma.
Figure 41: Predicted cell sizes for a given distance between the plasma filament and detonation at $\phi = 0.4$ (red), $\phi = 1$ (green), and $\phi = 1.6$ (blue). Corresponding cell sizes without the plasma are plotted as straight lines.

For all cases, a significant decrease in the cell size was observed with the plasma. In the most extreme case, the cell size for the lean mixture was reduced by a factor of almost 130. The stoichiometric mixture cell size was reduced by approximately a factor of 4.5 and the rich mixture cell size was reduced by approximately a factor of 5.5. It appears that the amount of reduction in the cell size remains approximately constant, regardless of the distance between the discharge and the detonation.

The modeling results show some agreement with our experimental results. Because the combustion annulus width with the 5.75 inch centerbody was approximately 5 mm, mixtures with cell sizes less than that should sustain detonation.
In the case of near-stoichiometric mixtures, the experiment agrees with the modeling results. Without plasma, the cell size is too large to sustain detonation, but with plasma the cell size is reduced below the threshold of 5 mm. Additionally, even with plasma, the cell size for the lean conditions was still too large to allow for detonation, which agrees with the experimental findings.

However, the model shows that the rich conditions of $\phi = 1.6$ should have allowed for detonation, when, in reality, detonation did not occur. Since this test using this mixture was conducted near the end of that round of experimentation, it is possible that the centerbody was broken by this point, and the failure was due to changes in the geometry of the RDC. Additionally, the predictions of detonation cell size would only be valid in the region of the plasma filament and not over the entire volume of the combustion region. Diffusion of the reactive species produced in the plasma to the surrounding area would decrease their concentration and likely reduce their impact on the detonation cell size. As such, these model results serve as a best-case estimate of the cell size reduction offered by the chemistry enhancement due to non-thermal plasmas.
Chapter 5: Conclusions and Recommendations

Non-thermal plasmas show potential for use in a wide range of different technologies, from combustion enhancement, to material synthesis, to cancer treatment. Further development of these technologies is reliant upon the ability to predictively model the effects of design changes on the behavior of these plasmas. In the present work, the predictions of a 0D plasma kinetics model were validated against a wide range of experimental data. Temperature, vibrational loading, air kinetics, and combustion kinetics were all validated. It was shown that, although the model output did not exactly match the experimental data, its results were in very good agreement, and in general predicted trends in the behavior of each plasma.

Once validated, this model was utilized as a predictive tool to examine the effects of a non-thermal plasma in an RDC. This non-thermal plasma was generated in the RDC using a ceramic and metal centerbody with nanosecond duration, high-voltage pulses. The plasma caused detonation onset to occur when the channel width was well below the detonation cell size of the hydrogen-air mixture. This effect was the most pronounced at near stoichiometric conditions, with diminishing effects as the equivalence ratio was moved away from unity. No noticeable effects occurred when the channel width was much larger than the detonation cell size. This seems to imply that the effect of the plasma is only relevant for a large area of interaction. Additionally, it seems that the plasma only has an impact when the detonation cell size is larger than the channel width.
These experiments only served as preliminary proof-of-concept for the plasma-assisted RDC. There is still a tremendous amount of work left to determine if the plasma-assisted RDC is practically viable. The current design failed mechanically under the large cyclical impulse loading produced by the detonation. Future designs will likely still need to utilize ceramic due to the unique combination of material requirements for this application, namely high temperature resistance and dielectric strength. However, these designs should utilize a ceramic with better mechanical properties. Ceria-stabilized zirconia has a much higher fracture toughness than MACOR and seems like a promising material candidate\textsuperscript{44}.

Because the breakdown voltage for air at atmospheric pressure is 3 kV per millimeter, the radial discharge generated in the present work is not practical for a combustion channel width larger than tens of millimeters. A pulse generator capable of producing nanosecond pulses of voltages larger than 100 kV at kilohertz repetition rates would be extremely expensive. The immense electromagnetic interference generated by these pulses would also make the technology infeasible for use in aerospace applications. Future work will focus on designing a different electrode that discharges across the air and fuel inlets. This fixed width would be small, allowing for the use of lower voltage, higher repetition rate pulse generators, which should allow for more turbulence and radical generation. Additionally, the breakdown voltage would not depend on the combustion channel width, making it a more versatile design.

The mechanism of the plasma-based enhancement needs to be determined to allow for the creation of more effective designs. Experiments determining if the effect
is primarily chemical kinetic enhancement or mixing enhancement should be performed. High speed imaging plasma-assisted RDC should be performed to capture the detonation and plasma interaction, allowing for better modeling predictions and design iteration. Additionally, the effects of varying plasma voltage, pulse width, and pulse frequency should be optimized through parametric study. These results should be validated using the model.

Obviously, many assumptions were made in the modeling work. Reducing the number of assumptions would greatly improve confidence in modeling results. A method of determining the current and voltage of the discharges in the RDC needs to be developed to allow for accurate measurement of the energy being coupled to the plasma. A full chemistry set including all the excited species and reactions used in the plasma calculations should be integrated into the ZND model. Future modeling work should examine the effects of the plasma on fuel-air mixtures of interest such as methane-air and propane-air mixtures. Beyond kinetic effects, the pressure perturbations predicted by the model could be integrated into CFD models of the RDC flow field.

Finally, once some level of optimization is reached, the plasma-assisted RDC should be run using progressively less detonable mixtures. After hydrogen-air mixtures, ethylene-air mixtures, propane-air mixtures, and methane-air mixtures should be tested. The effects of the plasma on liquid fuels such as JP-10 should additionally be examined. Hopefully, the use of non-thermal plasma will allow for a significant improvement of the technological viability of the RDC.
References


Appendix A: Modeling Procedure

Pre-Simulation

1) Create a project directory
2) Inside the project directory, create directories with the names bolsig, chem, chemkinProj, and processor.
3) Put the required electron impact cross sections into the bolsig folder, put the plasma chemistry, ground state chemistry, and thermos files into the chem folder

Generating Electron Impact Reaction Coefficients

1) Run Bolsig for mixture
   a) Open Bolsig
   b) Click Read Collisions and navigate to the cross-section data file
   c) Select appropriate species and hit OK
   d) Click New run
      i) Normalize mole fraction by hand
      ii) input gas temperature and choose range of E/N values
      iii) Run
   e) Click Save data
      i) Save data to Bolsig folder including .dat extension
      ii) Format is separate tables vs energy
      iii) Uncheck “Selected items only”
2) Edit config.in for processor and run, making sure fits are reasonable
   a) The only file you need to edit is config.in
      i) The variables ending in "File" are all paths to different input or output files, which are documented in the config file
      ii) Leave combineDuplicateBolsigReactions equal to false
      iii) You shouldn't have to mess with kmax, however TeSS may require modifying. I use 0.4 for air buffers, and either 1.0 or 1.5 for argon buffers
      iv) For the first runs, set silent to false. If you are just tweaking the naming of species or changing the combustion mechanism, you can set it to true to speed things up so you don't have to click through the fit plots
      v) Everything beyond that is just renaming of product species so that the neutral chemistry names match with the output of bolsig
b) Next is running the processor. You want to run main.m. It can be run as either a script by pressing run at the top, or as a function.
i) To run it as a script either press run at the top of the editor, or type 'main' into the command window. The processor will run using the file config.in in the current working directory as its configuration file
ii) To run as a function call main('put/path/to/config/file/here.in'); in either the command window or another script. The processor will use the the path passed into it as its configuration file (you should only need to run main as a function if you want to store multiple configuration and chemistry files in the same folder)
iii) If you have silent set to false, every fit MATLAB performs will be plotted for you to inspect. Blue 'x' markers are the bolsig predicted data. You can ignore the green line, but the magenta line is the fit of the data, showing what Chemkin will use as its rate.
   - If the fit looks fine, click on the plot to have the next one fit
   - If the fit is not acceptable you can either start over with step 1, rerunning bolsig with a different number of E/N points, and/or different limits, or you can go into the current bolsig output file and delete some points from this process's output. Usually deleting a couple of the highest energy points can improve the fit. Repeat as necessary
iv) If all fits are acceptable, there is now a Chemkin reaction file at the path specified in the config file of the processor with the fit rates merged with the other chemistry files. Otherwise go back and modify either the configuration file or the bolsig run to improve the fits

Simulation Setup/Pre-Processing

1) Plasma PSR, Inlet, Product
2) Click Update Project
3) Open pre-processor, set working dir to a directory of your choice (likely will be the chemkinProj directory)
4) Add gas phase chem set which was generated by the MATLAB processor, and the thermo file
5) Run pre-processor - check any errors in log file and modify config.in and rerun MATLAB processor as necessary. This will likely include creating thermo file entries for the excited states added by the processor.

6) Set inlet temp/mole fractions
   i) Initial electron temp must be 1 eV to prevent crashing
   ii) Must have initial free electrons, around 1E-10

7) Set up PPSR
   a) Transient Solver
   b) t_end, t_res, T, T_e, P, Vol
   c) Power profile (import from csv)
   d) set initial mole fractions
   e) set default momentum transfer cross-section to 0

**Simulation**

1) Under Solver, choose force positive solution. Time stepping should initially be automatic, but can be manually adjusted to aid in solution convergence.

2) Run Calculations

**Post-Simulation**

1) Click Analyze Results
2) Select Plot Results and click Next Step
3) Use the Units of Measure tab to select the appropriate units for the output data (such as number density instead of mole fraction)
4) Choose the desired data and click process solution data
5) To plot the data within ChemKin, select Display Plot on the prompt that appears
6) To export data, highlight the desired data in the arrays box and click export then save the .csv file
7) Alternatively, this data can be found in the CKSoln.ckcsv file in the working directory. This is just a normal csv file and can be parsed as such using either MATLAB or Excel