Cavity Ignition and Flameholding of High Speed Fuel-Air Flows by a Repetitively Pulsed Nanosecond Discharge

Dissertation

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Abstract

The dissertation presents an experimental study of ignition and flameholding of high speed, room temperature fuel-air flows using a diffuse, large volume, low temperature plasma produced by a repetitive nanosecond pulse discharge sustained in a cavity. Experiments are performed in premixed, partially premixed, and non-premixed ethylene-air and hydrogen-air flows in a pressure range of P = 0.2 – 0.3 atm. The dissertation also incorporates kinetic modeling of plasma assisted ignition of ethylene-air and hydrogen-air mixtures, to study the effect of radical generation in the plasma on ignition delay. The experimental results demonstrate that repetitive nanosecond pulse plasma assisted ignition occurs via formation of multiple arc filaments in the fuel-air plasma, although air plasma remains diffuse and low-temperature until the fuel is added. Comparison of ignition and flameholding achieved in premixed ethylene-air flows using a repetitive nanosecond pulse discharge and a DC arc discharge of approximately the same power (100 W) demonstrated that DC discharge resulted in sporadic ignition and flame blow-off, much lower burned fuel fraction, and significantly lower velocity (35 m/sec) at which ignition is achieved.

For premixed and partially premixed near-stoichiometric ethylene-air flows, ignition and stable flameholding have been achieved up to a flow velocity of 100 m/sec at
P=0.2 atm. During these experiments, nearly complete combustion is achieved. For partially premixed hydrogen-air flows, stable ignition and flameholding at P=0.2 atm has been achieved at flow velocities of up to 100 m/sec and equivalence ratios of φ=0.44-0.96. Time averaged plasma temperature measurements using nitrogen emission spectroscopy showed that the air plasma temperature is within 70° C to 200° C, while plasma temperature in presence of a stable flame is 700-1000° C. During non-premixed combustion experiments in ethylene-air at P=0.2 atm, ignition and stable flameholding is observed up to a flow velocity of 90 m/s at global equivalence ratio of φ=0.1. The highest flow velocity at which stable flameholding is observed in non-premixed hydrogen-air flows at P=0.26 atm is 190 m/sec, at φ≈0.04. Flow choking in the combustor is observed for average flow velocities above 200 m/sec. High frame rate NO Planar Laser Induced Fluorescence (PLIF) imaging and schlieren imaging have been performed to observe the dynamics of fuel-air mixing in the cavity during fuel injection.

Kinetic modeling is used to study the mechanism of low-temperature nanosecond pulse plasma assisted ignition. The reduced kinetic mechanism of plasma assisted ignition of hydrogen has been identified and compared with the full mechanism in a wide range of temperatures and pressures, showing good agreement. Kinetic modeling calculations performed to study the effect of non-thermal radical generation in nanosecond pulse discharge plasma on oxidation/ignition of hydrogen-air mixtures demonstrated that removal of plasma chemical radical generation processes inhibits low-temperature exothermic chemical reactions, thus blocking ignition. It is also observed that presence of radicals produced by the plasma accelerates ignition process significantly.
and reduces ignition temperature. Finally, the kinetic model has been used to interpret the results of flameholding experiments in premixed ethylene-air and hydrogen-air flows.
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Chapter 1: Introduction

1.1 Significance of the problem

One of the most challenging problems in the field of fundamental and applied combustion research is achieving ignition and stable combustion in high speed flows. With the advancement of supersonic/hypersonic aircraft technology, development of supersonic airbreathing engines has become essential. For aircraft cruising at a speed greater than six times the speed of sound (M>6), the air flow velocity in the combustor has to be supersonic to avoid significant stagnation pressure loss (entropy generation) in the supersonic inlet and diffuser upstream of the combustor, excessive heat load, as well as excessive thermal dissociation of oxygen caused by temperature rise during deceleration of freestream air flow to subsonic speed in the diffuser [1], [2]. Consequently, for a combustor of L~1 m length, flow residence time in the combustor becomes very short, about 1 msec. Achieving ignition and combustion within such a short period of time is challenging, since ignition delay time for most fuels can exceed several milliseconds at typical supersonic combustor inlet pressures, temperatures, and Mach numbers (P = 0.6-1.3 atm, T = 500-700 K, and $M_{\text{combustor}} = 1.74-2.8$ for $M_{\text{flight}} = 3.5-6$ [3]; P = 1.2-1.6 atm, T = 1200-1600 K, and $M_{\text{combustor}} = 3-3.6$ for $M_{\text{flight}} = 8-10$ [4]). For example, ignition delay time of stoichiometric hydrogen-air and ethylene-air mixture at 1
atm pressure and temperature of 1000 K are nearly 1 msec [5] and 25 msec [6], respectively, as can be seen in Figure 1.1. Also, at these conditions conventional point source ignition methods may well be inapplicable, due to a relatively slow flame propagation velocity. For instance, laminar flame speed in room temperature stoichiometric ethylene-air [7] and hydrogen-air [8] mixtures at atmospheric pressure, are 70 cm/sec and 2.5 m/sec, respectively (see Figure 1.2), which are much lower compared to the flow velocity. One way of circumventing these problems is to use a pyrophoric gas such as silane (SiH₄), mixed with hydrogen or hydrocarbon fuel, since adding silane drastically reduces autoignition temperature and ignition delay time of the gas mixture and eliminates the need of ignition source to achieve combustion [9]. Although this method has been successfully tested in the scramjet engine of an X-43A hypersonic air-breathing vehicle developed by NASA [9], the highly reactive nature of silane makes it hazardous to carry onboard of an aircraft. Another alternative is to use a cavity to increase flow residence time in the combustor to an extent that it becomes longer than ignition delay time, in order to achieve ignition and stable combustion [1]. The use of cavity recirculation flow would also improve fuel-air mixing. However, it is difficult to achieve stable ignition and combustion over a wide range of temperatures and pressures using a cavity when conventional point source ignition methods are used, since slow flame propagation speed often confines the flame into the cavity. Therefore, it is important to design more effective, large-volume ignition sources capable of igniting the fuel-air flow over a wide range of combustor flow conditions.
Figure 1.1: Left: Ignition delay of stoichiometric hydrogen-air mixture at various pressures and temperatures [5], Right: Ignition delay of ethylene-air at various equivalence ratios, pressures, and temperatures [6].

Figure 1.2: Laminar flame speed in (a) ethylene-air [7] and (b) hydrogen-air [8] at room temperature and atmospheric pressure.
1.2 Conventional ignition methods used in high speed flow combustion

Different types of ignition sources used in high speed flow combustion experiments include (i) pilot flames [10], (ii) spark plugs [3], (iii) plasma torches [4], (iv) flow compression in a bow shock [4], and (v) focused high power laser beams [11]. Pilot flame induced ignition, usually achieved using hydrogen based pilot flame, is not a very reliable ignition source since it is difficult to prevent flame blow out. On the other hand, spark plugs and plasma torches are more reliable. These ignition sources use localized high-temperature plasmas which generate radicals via thermal dissociation of molecules induced by intense local heating. Bow shock induced ignition is specifically used in supersonic combustors. Since this method relies on intense gas heating downstream of the shock to achieve ignition, the shock needs to be strong and stable enough to maintain a stable flame. Laser induced ignition uses a focused high power pulsed laser beam to produce a high-temperature plasma in the focal volume via optical breakdown. Radicals generated in the plasma help achieving ignition in the focal volume. The main limitation of this method is the need to have optical access to the combustor to deliver the laser beam. All these ignition sources produce ignition in a small volume, with subsequent flame front propagation to sustain stable combustion. Since flame propagation speed is of the order of a few meters per second at typical combustion conditions, the chance of flame blow off at high flow velocities becomes significant.
1.3 Nonequilibrium plasma ignition overview

Over the last two decades, considerable amount of research have been conducted to study nonequilibrium plasmas as novel ignition and flame stabilization sources. A review of recent experimental work in this field is given in Refs. [12], [13]. Various types of discharges used to produce nonequilibrium plasma are (a) microwave discharge, (b) RF discharge, (c) gliding arc discharge, (d) pulsed corona discharge, (e) single pulse, nanosecond pulse duration Fast Ionization Wave (FIW) discharge, and (f) repetitively pulsed nanosecond discharge. As opposed to high-temperature plasmas, such as generated in spark and arc discharges, where radical production is due to thermal dissociation of molecules induced by intense local heating [14], the dominant mechanisms of producing radicals in nonequilibrium plasmas is electron impact excitation and dissociation of molecules. It has been observed in previous studies that low-temperature nonequilibrium plasmas generated by high peak voltage, repetitively pulsed, nanosecond pulse duration discharges offer several key advantages over other types of nonequilibrium plasmas used for combustion applications. First, the reduced electric field, E/N, during the pulse is much higher than that achieved in equilibrium plasmas, up to several hundred Td (1 Td=10^{-17} V\cdot cm^2), which results in a significant fraction of the discharge energy going into electronic excitation and dissociation of molecules. Second, these plasmas are known to be more stable at high pressures compared to other types of electric discharges, due to their very low duty cycle, ~1/1000. Basically, electron impact ionization produced by a nanosecond pulse is turned off before ionization instabilities have time to develop, and is repeated before the plasma decays completely. This facilitates generating large-volume,
uniform, and stable repetitively pulsed plasmas [15-23] that can be used as volumetric ignition sources.

It has been observed that the use of nanosecond pulse discharge plasmas can reduce ignition delay in room-temperature methane-air and ethylene-air mixtures by a factor of 2 to 3, compared to spark ignition [24]. However, ignition delay time in plasma-ignited stoichiometric flows at room temperature and near atmospheric pressure is observed to be in the range of 2-10 msec [24]. Ignition delay time measured in quiescent, stoichiometric propane-air mixtures excited by a repetitive nanosecond pulse discharge at P=0.35-2.0 atm and v=30 kHz in a point-to-plane geometry is also observed to be quite long, 7-15 msec [25]. Moreover, previous studies at OSU demonstrated that ignition delay time in premixed, stoichiometric room temperature ethylene-air and acetylene-air flows excited by a repetitive nanosecond pulse discharge at P=0.05-0.08 atm and v=25-50 kHz in a plane-to-plane geometry is in the range of 5-25 msec [26]. These results suggest that to achieve nanosecond pulse plasma induced ignition of high-speed (u~100 m/sec and above, with submillisecond flow residence time in the igniter), room temperature flow in a wide range of pressures would require the use of a cavity to increase flow residence time in the plasma.

1.4 Combustion in high speed cavity flows

In recent years, cavity flows have been used for high speed flow combustion studies to achieve ignition and flame stabilization. An overview of recent numerical and experimental studies on cavity induced ignition and flame stabilization can be found in
Ref. [1]. Basically, when the flow passes over a cavity recess in a combustor wall, a recirculation region is formed inside the cavity, which increases flow residence time and improves fuel-air mixing in the cavity thereby helping ignition and combustion. However, presence of a cavity in a high-speed flow strongly affects pressure, density and velocity distributions inside and outside the cavity, causing total pressure loss. Therefore, it is important to properly design cavity geometry for high speed combustion applications.

Extensive previous studies of the effect of cavity geometry on the flow structure inside and outside the cavity in high speed flows have shown that the length-to-depth ratio (L/D) of the cavity primarily controls the flow pattern inside it. For cavities with L/D approximately less than 10, the shear layer, which is formed when boundary layer separates from the leading edge of the cavity, covers the entire length of the cavity and attaches to the back wall of the cavity (see Figure 1.3(a)). This type of cavity is called an “open” cavity. If L/D approximately greater than 10, then the shear layer is unable to span the entire length of the cavity and reattaches to the bottom of the cavity (see Figure 1.3(b)). This type of cavity is termed a “closed” cavity. In general, a closed cavity induces a greater total pressure loss compared to an open cavity [1]. Therefore, the latter cavity type is preferred for high speed flow combustion applications.
Previous research on cavity flows demonstrated that unsteady motion of shear layer produces pressure oscillations in the open cavity and allows mass flow exchange between the freestream and the cavity. Depending on length-to-depth ratio, pressure oscillations in the open cavity can be categorized into (a) transverse mode, for short cavities ($L/D < 2$ to $3$) and (b) longitudinal mode for long cavities ($L/D > 2$ to $3$). In short cavities, $L/D < 2$, a single main recirculation vortex is formed (see Figure 1.3(a)). The vertical motion of the vortex due to mass flow exchange between the freestream and the cavity produces an acoustic wave. The wave propagates nearly perpendicular to the shear layer when the free stream flow is transonic [27]. On the other hand, in open cavities with $L/D > 2$, two counter-rotating vortices with a flapping shear layer are observed (see Figure 1.3(b)).
Figure 1.3(a)). When the shear layer impinges on the rear wall (aft wall) of the cavity, the freestream flow enters into the cavity, causing pressure rise in the cavity. This pressure rise generates a pressure wave near the rear wall of the cavity that propagates towards the front wall at a local speed of sound and reflects back from the front wall of the cavity. The reflected pressure wave deflects the shear layer upward, thus allowing the fluid to exit the cavity. Once the flow exits the cavity, the shear layer again impinges on the rear wall, causing the freestream flow to enter the cavity, and after that the entire process is repeated. An alternative mechanism suggests that the pressure wave developed by the shear layer impingement creates small vortices at the leading edge of the cavity front wall. These vortices grow as they convect towards the rear wall and cause vertical movement of the shear layer, resulting in mass flow exchange between the cavity and the freestream flow [1]. This cyclic mass exchange between the cavity and the freestream flow induces pressure oscillations in the cavity. The acoustic wave produced by the pressure oscillations in the cavity propagates in the longitudinal direction when the flow is supersonic [27]. Cavity pressure oscillations need to be considered while designing the cavity for high speed combustion application since they may lead to unstable combustion.

Cavity aspect ratio (L/D) also determines flow residence time in the cavity and mass exchange rate between freestream and the cavity. In a small cavity (L/D < 2-3), flow residence time is usually long enough to achieve ignition, but it is difficult to sustain a stable flame because of low mass exchange rate, especially at higher flow velocities (u > 100 m/sec). Increase in the length-to-depth ratio increases mass exchange rate but reduces flow residence time in the cavity. Thus, since flow residence time in the cavity
needs to be longer than ignition delay time to achieve ignition in the cavity, cavities with $L/D = 3$-$5$ are typically used for ignition and flame stabilization in high speed flow.

Another important parameter that affects flow pattern and combustion in the cavity is the aft wall angle (i.e. the angle between the aft wall and the flow direction). It has been observed that decrease in cavity aft wall angle reduces cavity pressure oscillation and stabilizes combustion. However, aft wall angle reduction increases mass flow entrainment into the cavity, thereby reducing flow residence time [28].

### 1.5 High speed flow ignition in cavity flows

Recent interest of U.S. Air Force and NASA in using cavity flows to achieve mixing and flameholding for scramjet combustion motivated numerous studies of cavity induced mixing, ignition, and flame stabilization in high speed flows. In these studies, it has been observed that cavities can be used to achieve ignition and stable flameholding in supersonic flows for various solid, liquid, and gaseous fuels, over a wide range of ignition delay times. Ben-Yakar et. al. [29] conducted an experimental study demonstrating self-ignition and flameholding of solid polymethyl methacrylate (PMMA) fuel in supersonic air flow, at stagnation pressure of 16 atm and stagnation temperature of 1200 K, using a cavity. Owens et. al. [30] studied cavity induced liquid kerosene ignition and combustion in a $M=1.8$ air flow, with kerosene injected upstream of the cavity in the subsonic portion of the flow. In this study, a hydrogen pilot flame located in the cavity was used as ignition source since the flow stagnation temperature (300 to 1000 K) was not sufficiently high for self-ignition. In a recent study, Mungal and Cappelli’s group at
Stanford University [31] measured ignition delay of hydrogen in a cavity in a supersonic air flow (M~2.6) preheated to a static temperature T~ 1300 K, i.e., higher than auto-ignition temperature. Hydrogen was injected upstream of the cavity and flow was ignited using a filamentary repetitively pulsed nanosecond discharge (peak voltage 6-10 kV, pulse width ~15 ns, pulse repetition rate 15-50 kHz). Although auto-ignition was also achieved in this experiment, the use of nanosecond pulse discharge plasma reduced ignition delay time from 80 μsec to 40 μsec. In another study, Leonov et. al. [32] achieved ignition in M=2 non-premixed hydrogen-air and ethylene-air flows at static pressures of 0.2-0.8 atm and low stagnation temperature of 300 K, by using a high power (~1-10 kW) DC arc discharge (with multiple arc filaments) sustained in a cavity, with fuel (hydrogen or ethylene) injected into the cavity. These studies demonstrate that the use of a cavity improves fuel-air mixing and helps achieving stable flameholding in high speed flows over a wide range of flow conditions, therefore, it has significant potential for achieving stable combustion in scramjet engine.

1.6 Optical diagnostics in high speed flow combustion

Optical diagnostics is one of the most powerful and popular techniques used to visualize, and characterize flow field, fuel-air mixing, and flame development in high speed flow combustion. Among various optical diagnostic methods, schlieren imaging and Planar Laser Induced Fluorescence (PLIF) are used widely since they can provide two-dimensional images visualizing flow pattern and spatial extent of reaction/combustion region. Recently, the advancement of high-frame-rate camera
technology made possible to extend these techniques in temporal domain by obtaining a series of flow images during a single run, at a frame rate ranging from a few tens of kHz to a MHz. As a result, time evolution of highly complex flow fields and combustion patterns observed in high speed flow combustion can be captured.

Schlieren imaging is a well known technique of visualizing flow structures in compressible flows. This method uses the variation of refractive index of the flowing medium with density to visualize flows with significant density gradients. It has been extensively used in supersonic combustion studies to visualize shock structure and fuel injection flow patterns [33], [34]. On the other hand, the PLIF technique has been used in various combustion studies for both qualitative and quantitative visualization of combustion processes. Among different PLIF imaging techniques used for different target species, OH PLIF imaging is used most frequently in combustion diagnostics, due to abundance of the OH radical in hydrogen and hydrocarbon flames. OH PLIF has been used to study hydrogen-air combustion in a supersonic wind tunnel [35], [36]. Recently, it has also been used in examining liquid and gaseous hydrocarbon combustion in a scramjet engine combustor [34], [37]. On the other hand, NO PLIF imaging is not a suitable diagnostic tool for combustion study since (i) NO production during combustion remains fairly insignificant until the temperature becomes sufficiently high (> 2000 K) and (ii) NO seeding in reacting flow may strongly affect combustion, by changing auto-ignition temperature and ignition delay time [38]. However, this technique is widely used in flow visualization of NO-seeded supersonic flows.
1.7 Objectives

An overview of previous high speed flow combustion research, described in previous sections, shows that one of the biggest challenges in this field is development of a reliable and efficient ignition source, which can produce ignition and stable combustion over a wide range of pressures, temperatures, and flow velocities. Purely thermal ignition sources, such as spark plugs, DC arc plasmas, and pilot flames are not very efficient for high speed flow combustion, since they initiate ignition in a small volume. On the other hand, nonequilibrium plasmas produced by a high peak voltage nanosecond pulse discharge are observed to accelerate combustion process due to the production of significant amounts of radicals through electron impact excitation/dissociation process. In addition to that, this type of plasma can be produced in a relatively large volume, up to a few centimeters across, thus increasing the size of ignition kernel. Therefore, it is important to study the potential of nonequilibrium plasmas for achieving ignition and flameholding in high speed flows.

The main objectives of the present work are as follows:

1) Experimentally study ignition and flameholding in premixed, partially premixed, and non-premixed ethylene-air and hydrogen-air flows at high flow velocities, using large volume, low temperature, nonequilibrium plasmas produced by a repetitive nanosecond pulse discharge. Study plasma behavior before, during, and after ignition in presence of fuel. Quantify the effect of initial pressure, plasma temperature, and fuel-air mixing on combustion at high flow velocities.
2) Perform kinetic modeling study of plasma assisted combustion of ethylene and hydrogen, to obtain insight into the kinetic mechanism of plasma chemical fuel oxidation and ignition process.

The content of the dissertation is organized in the following way. Chapter 2 describes the design of the experimental facility, design of combustors with different cavity geometries, as well as flow and combustion diagnostics used in the present work. Chapter 3 discusses results of plasma assisted ignition and flameholding experiments, in premixed, partially premixed, and non-premixed flows, performed using combustors with different cavity geometries. Chapter 4 gives a detailed description of the kinetic model used to analyze kinetic mechanisms of plasma assisted combustion in hydrogen-air and ethylene-air. The results of kinetic modeling are discussed in Chapter 5. Finally, Chapter 6 summarizes the results of the present study and provides recommendations for future work.
Chapter 2: Experimental Setup

2.1 High speed combustion facility

A schematic and a photograph of the experimental facility for studies of plasma assisted combustion of high speed flows used in the present work are shown in Figure 2.1. It consists of three main components, (i) experimental test section, (ii) gas delivery system, and (iii) vacuum system. The facility was designed to perform both premixed and non-premixed combustion experiments using gaseous fuels (such as hydrogen and ethylene) and air in a wide range of flow velocities, static pressures, and equivalence ratios. The experimental test section consists of two parts, flow stabilization channel and combustor. The flow stabilization channel is a 15 cm long straight channel having 5 cm x 1 cm rectangular cross section, as shown in Figure 2.2. It has three injection ports, 1 mm in diameter each, located at the bottom wall of the channel to inject fuel into the main air flow and a side wall port to measure static pressure or flow velocity in the channel (see Figure 2.2). The purpose of this channel is to achieve fairly uniform velocity distribution at the combustor inlet. The combustor is the most important part of the experimental setup, where ignition and combustion are achieved. The detailed description of the combustor is given in the next subsection (Section 2.2).
Figure 2.1: High speed combustion facility; (a) schematic diagram, (b) photograph.
The flow stabilization channel is connected to the gas delivery system through a 1 inch diameter, 6 ft long main gas delivery line. The main line delivers either air flow for non-premixed combustion experiments, or a premixed air-fuel flow for premixed combustion experiments. Both air and fuel are supplied from high-pressure cylinders using remotely operated solenoid valves. A flash arrester is placed in the fuel delivery line to prevent flashback. For premixed combustion experiments, fuel is delivered to the main flow delivery line carrying air, and fuel-air flow subsequently passes through an inline flow mixer to improve fuel-air mixing before the mixture enters the test section. For non-premixed combustion experiments, fuel is injected either into the combustor or into the flow stabilization channel shown in Figure 2.1. In case of fuel injection into the flow stabilization channel, fuel is mixed with the air flow to a considerable extent before
entering into the combustor; therefore, in that case combustion occurs in a partially premixed fuel-air flow. During non-premixed combustion experiments, the inline flow mixer was removed from the main delivery line to reduce pressure loss in the gas delivery line, especially at higher flow velocities (u > 100 m/sec). A 1.2 cm long honeycomb made of alumina ceramics is placed 1.5 cm downstream of the flow stabilization channel inlet, to help reduce non-uniformity of the flow exiting the gas delivery line (see Figure 2.1).

In all present experiments, air mass flow rate was measured using a sonic choke (a plate with a small central circular orifice of known diameter) placed in the main delivery line. Two pressure gauges placed upstream and downstream of the sonic choke, as shown in Figure 2.1, were used to determine the pressure ratio across the sonic choke. When the ratio of upstream to downstream pressure exceeds $f(\gamma) = \left(1 + \frac{\gamma-1}{2}\right)^{\frac{(\gamma+1)}{(\gamma-1)}},$ i.e. $f(\gamma) = 1.893$ for air (specific heat ratio, $\gamma=1.4$), then the mass flow rate through the sonic choke can be calculated as follows [39],

$$\dot{m} = \frac{P_0 A^*}{\sqrt{T_0}} \sqrt[\frac{\gamma - 1}{2(\gamma+1)}} \left( \frac{2}{R} \right)^{\frac{(\gamma+1)(\gamma-1)}{\gamma(\gamma+1)}},$$  \hspace{1cm} (2.1)

where $P_0$ and $T_0$ are pressure and temperature of the flow upstream of the choke plate where the flow is near stagnation, $A^*$ is the cross sectional area of the circular orifice in the choke plate, $\gamma$ is the specific heat ratio of air, and $R$ is the gas constant for air. The highest air flow rate used in this work was 28 g/sec, which maintained an average flow velocity of up to 190 m/sec in the test section, at the static pressure of 200 torr. The fuel flow rate was measured using either Omega FMA-A2322 (75 SLM) or Omega FMA-
A1844 (500 SLM) mass flow meters. Since calibration data provided by the manufacturer of mass flow meters have significant uncertainty for light gases such as hydrogen and helium, the mass flow meters were calibrated for hydrogen and helium using a sonic choke. Details of the calibration method are described in Appendix A.

The exit of the test section is connected to a 6-inch diameter vacuum pipe leading to a 110 ft$^3$ vacuum tank. The flow in the vacuum pipe is diluted with atmospheric air through a vent valve, to prevent further combustion in the vacuum tank. The vacuum tank is pumped out using a 200 cfm vacuum pump. The pumping rate was controlled by a valve located at the pump inlet. The vent valve and the pump inlet valve openings are manually controlled, to maintain a nearly constant baseline test section static pressure of 150 torr or 200 torr during experiment. Time-resolved test section static pressure is monitored by high accuracy Omega PX811-005GAV pressure transducers, connected to pressure ports located 8.5 cm upstream and 10 or 12 cm downstream of the high voltage electrode (see Figure 2.1). The pressure transducer readings are collected at a sampling rate of 32 Hz using a computer controlled Omega OMB-DAQ-56 USB data acquisition module. The test section pressure and mass flow rates of fuel and air are varied independently.

2.2 Combustor

Combustors used for different series of experiments in this work differ mainly in geometry and size of the cavity used to achieve ignition and flameholding. Two different cavity geometries, viz. a “small” square shaped cavity with length-to-depth ratio (L/D)
equal to 1 and a “large” rectangular shape cavity with L/D = 3, have been used in combustors employed in this study.

2.2.1 Combustor with a small cavity (L/D=1)

A schematic and a 3D model of the combustor with a square cavity, used for ignition and flameholding experiments, are shown in Figure 2.3. The main objectives of this design were (i) to produce diffuse plasma filling the entire cavity volume, and (ii) to increase the flow residence time in the cavity to achieve ignition and flameholding at high flow velocities. The rectangular cross section (5 cm x 1 cm) flow channel was made of duralumin and had a rectangular cavity (1.9 cm deep and 2.25 cm long in the streamwise direction) machined in the bottom wall of the channel, as shown in Figure 2.3. A 3.2 mm diameter cylindrical high voltage brass electrode was placed in the center of the cavity, perpendicular to the flow direction as shown in Figure 2.3. The electrode was placed inside a 6.4 mm outside diameter alumina ceramic tube, with the gap between the electrode and the tube filled with silicone rubber adhesive. The walls of the main flow channel were covered by 0.65 mm thick alumina ceramic plates, and the cavity walls were covered by 1.6 mm thick macor ceramic plates. Both sets of plates were attached to the walls using silicone rubber adhesive. This was done to preclude secondary electron emission from exposed grounded metal surfaces and the resultant arc filament (“hot spot”) formation in the discharge. This reduced the dimensions of the cavity to 1.8 cm (depth) and 1.9 cm (length). Both the top and bottom walls of the flow channel downstream of the cavity had an expansion angle of 1.5° to allow for expansion of the
combustion product flow in order to avoid thermal choking, as shown in Figure 2.3. A 5 cm x 10 cm rectangular window made of quartz and two 1 cm diameter BK7 glass circular windows were used to obtain optical access to the plasma region in the cavity and to the flow downstream of the cavity (see Figure 2.3).

This test section was designed primarily to operate using premixed fuel-air flow; however, fuel or fuel-air mixture can also be injected into the cavity through a 1.6 mm diameter port located in the bottom wall of the cavity, as shown in Figure 2.3. All the experiments using this test section were conducted in premixed stoichiometric ethylene-air flows, with up to a few per cent of the premixed fuel-air flow diverted from the main flow and injected into the cavity through the injection port in the bottom wall, as shown in Figure 2.3.

Figure 2.3: Plasma assisted combustion test section with a small cavity (L/D=1); (a) schematic diagram (b) 3D model.
2.2.2 Combustor with a large cavity (L/D=3)

A schematic and a 3D model of the combustor with a large cavity, used in the present ignition and flameholding experiments, are shown in Figure 2.4. The combustor consists of a rectangular cross section (5 cm x 1 cm) duralumin flow channel with a 1.9 cm deep and 6 cm long cavity (L/D=3) machined in the bottom wall of the channel. A 60° ramp was provided in the aft wall of the cavity to increase stability of the cavity flow field, which subsequently ensures stable burning in the cavity. It should be noted that using a smaller cavity aft angle could further stabilize the cavity flow field, but it would also reduce flow residence time in the cavity, due to the increase in mass entrainment into the cavity [28]. Therefore, a 60° ramp angle was conservatively selected to ensure that flow residence time in the cavity was longer than ignition delay time. A 3.2 mm diameter cylindrical high voltage brass electrode was placed 1 cm away from the bottom and from the upstream wall of the cavity, perpendicular to the flow direction (see Figure 2.4). The electrode was placed inside a 6.4 mm outside diameter alumina ceramic tube, with the gap between the electrode and the tube filled with a silicon rubber adhesive. The walls of the main flow channel were covered by 0.65 mm thick alumina ceramic plates, and the cavity walls were covered by 1.6 mm thick macor ceramic plates, in order to preclude secondary electron emission from exposed grounded metal surfaces and prohibit resultant arc filament formation in the discharge. This modification reduced the dimensions of the cavity to 1.8 cm (depth) and 5.7 cm (length). Both the top and bottom walls of the flow channel downstream of the cavity have an expansion angle of 1.5° to allow for expansion of the combustion products flow in order to avoid thermal choking. A 5 cm x 10 cm
rectangular window made of quartz and two 1 cm diameter BK7 glass circular windows provided optical access to the plasma region in the cavity and to the flow downstream of the cavity, respectively (see Figure 2.4). The pressure tap in the top wall of the channel downstream of the cavity was connected to one of the pressure transducer described in Section 2.1 to monitor and record pressure history during ignition and combustion.

![Diagram](image)

Figure 2.4: Plasma assisted combustion test section with a large cavity (L/D=3); (a) schematic diagram, (b) 3D model.

The combustor was designed to perform plasma assisted combustion experiments in premixed fuel-air flow regimes. However, experiments were also conducted by injecting fuel into the air flow 16 cm upstream of the cavity through fuel injection ports located in the flow stabilizing section (see Figure 2.1 and Figure 2.2). In these
experiments, the fuel injection flow rate was large enough to choke the injection ports. It should be noted that, during these experiments, the injection jet momentum ratio (i.e. the ratio of the injection flow and the main flow momenta, \( J = \frac{\gamma_j p_j M_j^2}{\gamma_i p_i M_i^2} \), where \( \gamma \), \( p \), and \( M \) are the specific heat ratio, static pressure, and flow Mach number, respectively) was quite high, \( J=35-115 \) in ethylene-air (\( u_{\text{air}}=35-100 \) m/sec) and \( J=50-340 \) in hydrogen-air (\( u_{\text{air}}=20-90 \) m/sec). In addition, the distance from the injection ports to the cavity exceeded the diameter of the injection ports by more than two orders of magnitude. For these reasons, the flow arriving at the cavity can be considered partially premixed.

The combustor described above did not have sufficient optical access to perform PLIF and schlieren imaging; therefore, another combustor with adequate optical access was used for experiments involving these diagnostics. Figure 2.5(a),(b) show schematic and a 3D model of the enhanced optical access combustion test section. This test section has a rectangular cross section (5 cm x 1cm) flow channel with a rectangular cavity (L/D =3, aft wall angle of 60°) machined at the bottom of the channel. The dimensions of the cavity and the high voltage brass electrode geometry and location are the same as those of the combustor described in the previous paragraph. The direction of the flow in Figure 2.5 (a),(b) is right to left, as shown by arrows. One of the key differences of this test section from the previous one is that it has three quartz windows, two in the channel sidewalls and one in the top wall of the channel for enhanced optical access (see Figure 2.5(a),(b)), as opposed to only one quartz window in the side wall of the previous test section (see Figure 2.4). Two rectangular shape side wall windows have the same dimensions, 9.53 cm x 4.45 cm. The dimensions of the top wall window are 10.16 cm x
3.81 cm. All the windows are flush with the walls of the channel and of the cavity. The alumina ceramic tube (6.4 mm outside diameter) covering the high voltage cylindrical electrode was mounted in one of the side windows, using a mushroom shaped macor ceramic insert. The gap between the electrode and the ceramic tube was filled with silicone rubber adhesive. The metal portion of the bottom wall of the cavity, below the cylindrical high voltage electrode, and the adjacent upstream wall of the cavity were used as the ground electrode (Figure 2.5(a),(b)). These walls were covered with 1.6 mm thick macor ceramic plates to avoid secondary electron emission from exposed ground metal surfaces, and resultant arc filament formation in the discharge. All other exposed metal walls close to the high voltage electrode (i.e. the walls of the channel upstream of cavity and the aft wall of the cavity) were covered with 0.65 mm alumina ceramic plates. All the plates were attached to the walls using silicone rubber adhesive. The bottom wall of the flow channel downstream of the cavity had an expansion angle of 3° to allow for expansion of the combustion products flow in order to avoid thermal choking. Two circular windows made of BK7 glass were placed in the two side walls of the flow channel downstream of the cavity (Figure 2.5(a),(b)) to allow visual observation of the flame downstream of the cavity. Similar to the previous combustor (see Figure 2.4), the pressure tap in the top wall of the channel was used to monitor and record pressure history during ignition and combustion. A polycarbonate fuel injector with seven 1.6 mm diameter injection ports, as shown in Figure 2.5(c), was flush mounted in the bottom wall of the cavity to allow fuel injection directly into the cavity (see Figure 2.5(b)). The fuel injector can be rotated over 180°, thus changing the distance between injection ports and
the high voltage electrode. Injection ports were located either 24 mm or 33 mm downstream of the electrode, depending on the injector orientation. This design made possible non-premixed plasma assisted combustion experiments at globally lean conditions. All non-premixed combustion experiments performed in the present work have been conducted using this combustor.

![Combustion Test Section](image)

**Figure 2.5:** Plasma assisted combustion test section with a large cavity (L/D=3) with fuel injector and enhanced optical access; (a) schematic diagram, (b) 3D model, (c) fuel injector assembly.

### 2.2.3 Combustor with a reduced size cavity (L/D=3)

Both combustors described in Figure 2.4 and Figure 2.5 have the cavity size quite large compared to the main flow channel dimensions. This comparatively large cavity produced a significant main flow disturbance at flow velocities beyond 200 m/sec,
causing flow choking upstream of the cavity. Therefore, the combustor shown in Figure 2.4 has been modified to reduce the length and the depth of the cavity by a factor of two each, without changing the cavity aspect ratio (L/D=3) and the aft wall angle, to perform further experiments at higher flow velocities. A polycarbonate injector block, with the same number of injection ports and same spacing between the ports as described in the previous paragraph, has been used to inject fuel into the reduced size cavity. Figure 2.6(a), (b) show a schematic and a 3D model of the modified combustor with a plane electrode geometry used for these experiments. In this configuration, an exposed rectangular copper plate electrode (8.5 mm x 41 mm), flush mounted in the bottom surface of the cavity, was used as a high voltage electrode, while cavity upstream wall and top wall of the combustor were used as a grounded electrode (see Figure 2.6). The grounded electrode was covered with macor ceramic plates.

Figure 2.6: Plasma assisted combustion test section a reduced size cavity (L/D=3); (a) schematic diagram, (b) 3D model. Exposed rectangular plane high voltage electrode is flush mounted in the bottom of the cavity.
2.3 High voltage pulse generator

Figure 2.7 shows a photograph of the high voltage pulsed power supply, developed by Chemical Physics Technologies, used in the present work to produce the plasma in the cavity of the combustor. The pulse generator is capable of producing a series of negative polarity high voltage pulses with 30 kV peak voltage and 14 nsec pulse width (FWHM) at a maximum repetition rate of 100 kHz in a single burst. The power supply can also be operated in repetitive burst mode, when a sequence of pulse bursts, each containing a preset number of high voltage pulses repeated at a particular pulse repetition rate (< 100 kHz), can be produced at a given burst repetition rate. The burst repetition rate is limited by the duty cycle (defined as the ratio of burst “ON” time to burst “OFF” time) of 50%. In other words, the duration of the burst can be no longer than time delay between two successive bursts. In most of the present work, the pulse generator was operated to produce a single burst of high voltage pulses at a 40 kHz pulse repetition rate, in order to produce the plasma in the cavity. However, for some of the experiments, the pulse generator was operated in the repetitive burst mode. Parameters used during repetitive burst mode operation are listed in the Section 3.4.1.2, where the results of such experiments are described. It should be noted that estimated pulse energy coupled to the flow by a single pulse was approximately 2 mJ [22] for the experimental conditions considered in the present work.
2.4 DC arc discharge ignition setup

For qualitative comparison of repetitive nanosecond pulse plasma ignition with conventional ignition methods, a series of experiments has been conducted using a DC arc discharge. The combustor test section used for these experiments is shown in Figure 2.8. The combustor consists of a rectangular flow channel of 1 cm x 5 cm cross section, with a 1.9 cm deep and 1.9 cm long square cavity (L/D=1). A conventional spark plug was placed into the bottom of the cavity, with the electrodes flush mounted with the cavity bottom wall. A 6.4 mm diameter alumina ceramic tube was placed at the center of this cavity to replicate the flow field in the cavity used for nanosecond pulse plasma ignition in the small cavity described in Section 2.2.1. The spark plug was powered by a Glassman 5 kV, 2 A DC power supply connected in series with a 15 kΩ ballast resistor. During operation, a DC arc filament discharge was sustained between the spark plug electrodes to achieve ignition. This combustor was used to ignite premixed ethylene-air flows. In order to obtain optical access to the emission during ignition and combustion in the main flow, a rectangular BK7 glass window mounted in the side wall of the test
section was used. A pressure gauge connected to the pressure tap located 6 cm upstream of the cavity was used to monitor pressure in the combustor ignition and combustion. The same gas delivery system and vacuum system, described in Section 2.1, were also used for these experiments.

![Schematic of combustor test section with a small cavity (L/D=1) used for DC arc discharge ignition experiments.](image)

**Figure 2.8:** Schematic of combustor test section with a small cavity (L/D=1) used for DC arc discharge ignition experiments.

### 2.5 Diagnostics

#### 2.5.1 Flow velocity measurement using Pitot tube

A Pitot tube is commonly used to measure flow velocity in both incompressible and compressible fluid flows. It measures both static pressure (p) and stagnation pressure (p₀) in the flow at a particular location. For compressible flows (0.3 < M < 1), assuming isentropic compression of the flow at the tube entrance, the flow velocity (v) is calculated from these pressure readings using the following equation [39]

\[
v = \sqrt{\frac{2\gamma}{\gamma - 1} \frac{p}{\rho} \left[ \left( \frac{p_0}{p} \right)^{\frac{\gamma - 1}{\gamma}} - 1 \right]},
\]  

(2.2)
where $\gamma$ is the specific heat ratio of the fluid and $\rho$ is the density of the fluid at static pressure $p$ and static temperature $T$. Since Pitot tube measurements give the flow velocity at a particular location in the flow, this technique can be used to obtain a flow velocity distribution. In the present work, this technique was used to determine flow velocity distribution along the spanwise direction at a location near the exit of flow stabilization channel (10 cm upstream of the combustor cavity, see Figure 2.1).

2.5.2 Time resolved OH and CH emission

During the experiments, ignition and flameholding in the flow were detected by monitoring time-resolved OH or CH emission from the flow. For the nanosecond pulse discharge induced combustion experiments reported here, OH emission was used to identify ignition and flameholding. On the other hand, CH emission was used to identify ignition in spark plug induced ignition experiments, since the circular optical access window (made of BK7 glass) of the test section was not transparent to OH emission (see Section 2.4).

OH emission from the plasma and the flame was collected through the quartz rectangular optical access window, using a narrowband pass filter centered at 310±2 nm (band pass 11±2 nm FWHM), a photomultiplier (PMT) tube, and a digital oscilloscope. The response time of this emission diagnostics, approximately 10 µsec, was controlled by using a variable terminator resistor placed between the PMT and the oscilloscope, and set at 50 kΩ. In most of the experiments, emission signal was collected both from the cavity
and from the main flow. However, in some cases emission traces from the cavity and from the main flow were collected separately, by partially masking the optical access window. For CH emission collection at 431 nm, same collection optics described above has been used, except the narrowband pass filter was replaced by a monochromator.

### 2.5.3 Visible emission spectroscopy

Visible emission spectroscopy is used in this work to infer the temperature of the plasma in air and fuel-air flows. The rotational temperature in the plasma sustained in the cavity is inferred from partially rotationally resolved \( v'=0 \rightarrow v''=2 \) and \( v'=1 \rightarrow v''=3 \) bands of \( C^3\Pi_u \rightarrow B^3\Pi_g \) electronic transition of nitrogen. For this, a “best fit” synthetic spectrum generated using accurate nitrogen molecular constants, rotational line intensities, and the experimentally measured slit function of the spectrometer was generated and compared with the experimental spectrum, by varying the rotational temperature. The details of this method can be found in Ref. [40]. In our previous work [22], this method had been calibrated by comparing the synthetic and the experimental \( N_2(C^3\Pi_u \rightarrow B^3\Pi_g) \) emission spectra measured at a low pulse repetition rate in air flow preheated by an in-line flow heater up to \( T=20-180^\circ C \) with thermocouple measurements in the absence of the plasma. This justifies the use of these spectra for accurate temperature measurements. The uncertainty of rotational temperatures inferred from the synthetic spectra is ±30°C.

The emission spectroscopy setup consists of an Optical Multichannel Analyzer (OMA) with a Spectra Physics 0.25 m spectrometer with a 50 \( \mu \)m slit, a 2400 g/mm grating blazed at 500 nm, a PIXIS 256E 1024x256 pixel CCD array camera, and a 5 m
long Thor Labs AFS fiber optic bundle with collimators on each end, providing spectral resolution of about 0.1 nm. The collimators were positioned in front of a rectangular optical access window in the side wall of the combustor and in front of the slit opening of the spectrometer, respectively. Fiber optic link calibration using a 1.3 mm diameter aperture light source showed the collimator signal collection region to be a cylinder 2–3 mm in diameter and approximately 50 mm long. Therefore, emission spectra yield line-of-sight averaged temperature, with the spatial resolution of about 3 mm. The temperature has been measured approximately 3 mm above the high voltage electrode (i.e. 6 mm from the electrode centerline), unless specified otherwise.

2.5.4 FTIR absorption spectroscopy

Fourier Transform Infrared (FTIR) absorption spectroscopy was used in the present work to determine burned fuel fraction and combustion product concentrations. For these measurements, the flow was sampled through one of the two wall sampling ports (static pressure taps) located 10 cm and 50 cm downstream of the high voltage electrode and sent into a 20 cm long, initially evacuated absorption cell with CaF$_2$ windows, as shown in Figure 2.9. The absorption cell was placed into a compartment of a Varian 660-IR FTIR spectrometer (see Figure 2.9). After sampling, the absorption cell was partially evacuated to reduce the cell pressure to 40 torr. Note that the temperature in the absorption cell was close to room temperature since the flow sample rapidly cooled off while passing through the room temperature sampling line. The spectrometer generates absorption spectra in a 2000-3500 cm$^{-1}$ region with a spectral resolution of 1
cm⁻¹. To obtain burned fuel fraction, two absorption spectra were collected by sampling the flow before and during the combustion experiment. Relative intensities of fuel absorption lines in these two spectra are then compared, to infer burned fuel fraction. It should be noted that an extension channel was placed between the combustor and the vacuum pipe in order to sample the flow 50 cm downstream of the high voltage electrode.

2.5.5 Intensified CCD (ICCD) camera imaging

In the present work, gated ICCD camera imaging was used to obtain broadband single-pulse images of the plasma produced by the repetitively pulsed nanosecond discharge, as well as flame images. Images were taken using a PI-MAX ICCD camera with a UV lens (UV-Nikkor 105 mm f/4.5, Nikon). The camera was triggered by a Stanford Research System DG535 four-channel delay/pulse generators, which used a

Figure 2.9: Photograph of absorption cell used for FTIR absorption spectroscopy.
low-voltage TTL pulse output generated by the high-voltage pulse generator 1.25 μsec before each pulse, as synchronization input.

2.5.6 Planar laser induced fluorescence (PLIF) imaging

Figure 2.10 shows the schematic of the experimental setup used for NO PLIF imaging. An ultrahigh repetition rate (up to 1 MHz) tunable burst mode laser with pulse width of 10 nsec was used as the excitation source for the fluorescence imaging. The burst mode laser was built at OSU [41-43] from a commercially available continuous wave (CW) diode pumped Nd:YAG ring laser. The output of this CW laser first passed through a double-pass variable pulse width (from 0.3 to 2.0 msec), flashlamp-pumped pulsed amplifier to produce smooth pulses (0.1 msec) duration, which were then converted to a burst (i.e., a train of pulses) using a dual Pockel cell slicer and subsequently amplified using four additional flashlamp-pumped amplifiers. The output beam at 1064 nm was converted to a third harmonic (355 nm) using a pair of non-critically phase matched Type I Lithium Triborate (LBO) crystals, and passed through an injection seeded optical parametric oscillator (OPO). The output of the OPO was sum-frequency mixed with the residual 355 nm beam to produce an output beam tunable near 226 nm, corresponding to a Q1(7)+Q21(7) line (226.22 nm) of NO excitation transition $X^2\Pi(v''=0)\rightarrow A^2\Sigma^+(v'=0)$, required for NO PLIF imaging. The collimated laser output was directed to the test section using three 2 inch plane mirrors. The collimated beam was then converted to a 50 mm wide, 0.2 mm thick laser sheet using a cylindrical lens and a spherical lens (see Figure 2.10). For all NO PLIF experiments described here, the laser
was operated at 10 kHz pulse repetition rate and burst frequency of 1 Hz. Broadband NO fluorescence signal emitted from the measurement region in the direction perpendicular to the laser sheet was captured using a Princeton Scientific Instruments PSI-IV framing ICCD camera with a UV lens (Nikon Nikkor 105 mm f/4.5). The basic PSI-IV image sensor consists of an $80 \times 160$ array of $115 \times 115$ micrometer pixels, each of which has its own integrated 28-element memory buffer. The camera version used for this work consisted of a pair of such sensors with total available resolution of $160 \times 160$ pixels. A UV-sensitive microchannel plate intensifier provided time gating capability with a minimum exposure time of approximately 10 nsec. Further details of the camera can be found in Ref. [44]. For NO PLIF imaging experiments discussed here, the frame rate and gate width of the camera were set to 10 kHz and 500 nsec, respectively. A Stanford Research System DG535 four-channel delay/pulse generator was used to adjust the camera gate delay gate relative to the laser pulse.

Figure 2.10: Schematic of high frame rate NO PLIF imaging experimental setup.
The same experimental setup as described above (see Figure 2.10) is used to conduct OH PLIF experiments to visualize ignition and flame propagation in the cavity and in the main flow. However, for these experiments OPO of the pulse burst laser was modified to produce a tunable collimated laser beam near 283 nm wavelength, corresponding to OH excitation line Q1(5) (282.75 nm) of $X^2\Pi(v''=0) \rightarrow A^2\Sigma^+(v'=1)$ transition. The ICCD camera described in Section 2.5.5, equipped with an Objectif 100 mm f/2.8 UV lens and a Schott UG11 glass filter combined with WG305 long pass filter, was used to collect single shot OH PLIF images with a camera exposure time of 200 nsec. Both the camera and the laser were triggered by the nanosecond pulse discharge power supply, using Stanford Research System DG535 four-channel delay/pulse generator.

### 2.5.7 Schlieren imaging

Schlieren imaging is used in the present work to visualize mixing of the flow injected into the cavity with the cavity recirculation flow. The schematic of the experimental setup used for schlieren imaging is shown in Figure 2.11. A high-power green LED with a thermoelectric cooler was used as a continuous light source for the schlieren system, and schlieren images were collected using a CMOS camera operated in video mode (exposure time 1.5 ms, frame rate 279 frames per second). The light from the source was converted to 50 mm diameter beam and then directed to the test section using a 3" mirror. Collection optics consisted of one 3" mirror and a 750 mm convex lens, which focused the beam on the plane of knife edge. A series of lenses and a green filter
were used to focus the camera at the center of the test section. With this optical arrangement, camera images visualized a 36 mm x 20 mm flow region in the test section.

Figure 2.11: Schematic of the schlieren system.
Chapter 3: Experimental Results

3.1 Overview

In this chapter, the results of experiments performed using combustors with different cavity geometries described in Chapter 2 will be discussed in detail. Section 3.2 will discuss velocity distribution measurements in the main flow upstream of the combustor. Section 3.3 will discuss the results of combustion experiments performed in the combustor with small cavity (L/D=1) for premixed flow condition. The results of premixed, partially premixed, and non-premixed combustion experiments using combustor with large cavity (L/D=3) will be described in detail in Section 3.4. Section 3.5 will illustrate the results of NO PLIF, schlieren, and OH PLIF imaging experiments performed in this work to visualize injection flow mixing in the cavity and flame development in the plasma region. Finally, Section 3.6 will discuss the results of non-premixed combustion experiments in combustor with reduced size cavity (L/D=3), described in Section 2.2.3.

3.2 Flow velocity distribution upstream of the cavity

The air flow velocity distribution in the experimental test section, in the spanwise direction, was measured 10 cm upstream of the combustor cavity using a Pitot tube, as
described in Section 2.5.1. Figure 3.1 shows flow velocities inferred from the static and stagnation pressures measured by the Pitot tube at several locations across the channel, for different average flow velocities ($u$) calculated from the mass flow rates. In Figure 3.1, dotted trend lines are shown along with the data points for each average flow velocity value to indicate approximate velocity distribution across the flow path. From the plot, it is evident that the velocity distributions at low average velocities are nearly parabolic, and as the average velocity increases, the central part of the velocity distribution becomes more flat. However, the difference between the centerline flow velocity and the average flow velocity is observed to increase with the mass flow rate, which suggests that flow in the channel may choke well before the average flow velocity reaches the speed of sound. Evidence of flow choking was indeed observed when the average flow velocity in the flow channel reached 240 m/sec.

![Flow velocity distributions across the channel 10 cm upstream of the cavity, for several average flow velocities ($u$).](image)
3.3 Ignition and flameholding of premixed ethylene-air flows in a small cavity (L/D=1)

3.3.1 ICCD camera imaging of plasma and flame

Figure 3.2 shows a typical single pulse waveform generated by a high-voltage pulse generator in a premixed ethylene-air flow at ϕ=1, P=70 torr, and u=35 m/sec. The peak voltage of the negative polarity pulse is 27 kV, with the pulse FWHM of 15 nsec. At 40 kHz, the repetitively pulsed waveform has a very low duty cycle, ~50 nsec / 25 μsec, or ~1/500. It is well known that most of the UV/visible emission produced by nanosecond pulse discharges in air (nitrogen second positive bands) decays within several tens of nanoseconds. For example, the results of our previous work [45] showed that N₂ second positive band emission produced by a single 20 kV, 25 nsec pulse in air at 60 torr decreases by three orders of magnitude over 40 nsec, as shown in Figure 3.3. On the other hand, self-sustained hydrocarbon flame emission (OH, CH, and C₂ bands) persists for up to a few milliseconds [46]. However, N₂ emission intensity during and immediately after the pulse is typically much higher compared to the intensity of these flame emission bands. All this suggests a straightforward method of isolating the plasma emission from the flame emission and obtaining plasma and flame images separately, as illustrated in Figure 3.4. The repetitively pulsed waveform shown in Figure 3.4 has been obtained in our previous work [22] using the same pulse generator but a different (plane-to-plane) discharge geometry. To obtain the image of the plasma generated by a single nanosecond pulse, the camera gate, 2 μsec long, was set to open shortly before the pulse and close after the pulse (Gate 1, see Figure 3.4), to collect most of N₂ second positive
emission from the plasma. To obtain the flame image (produced mainly by OH, CH, and C₂ emission), the camera gate was set to open 3 µsec after the pulse and increased to 18 µsec, thus spanning nearly the entire time period between the pulses, 25 µsec for ν=40 kHz and 20 µsec for ν=50 kHz (Gate 2, see Figure 3.4). In addition, the camera gain was increased to compensate for lower flame emission intensity compared to plasma emission. Shorter gate, lower camera gain, and higher N₂ emission intensity allowed nearly complete discrimination of flame emission during Gate 1. On the other hand, rapid N₂ emission decay after the pulse made possible collecting “flame only” emission between the pulses.

Figure 3.2: Typical high-voltage pulse shape. Stoichiometric ethylene-air mixture, P=70 torr, Φ=1, u=35 m/sec, ν=40 kHz.
Figure 3.3: Normalized N₂(C−B) emission intensity as a function of time after the discharge pulse (symbols) and normalized N₂(C) population predicted by the model (lines) [45].

Figure 3.4: Schematic of ICCD camera gate timing. A repetitive pulse waveform [22] is shown for illustrative purposes.
Figure 3.5 shows a photograph of a repetitively pulsed air plasma sustained in the short cavity in the test section at P=150 torr, u=45 m/sec. This photograph was taken using an ordinary digital camera for the pulse burst duration 20 msec long (800 pulses in the burst). It can be seen that the plasma fills most of the cavity volume and appears diffuse, without well-defined arc filaments. Figure 3.5 also shows two ICCD camera images of the plasma taken at the same pressure, P=150 torr, and a lower flow velocity, u=25 m/sec, using camera Gate 1 (see Figure 3.4). These images were taken during pulses #100 and 800 (i.e. at t=2.5 and 20 msec, respectively). It can be seen that, indeed, the plasma fills the region between the electrode and the cavity walls and is diffuse, without well-defined arc filaments. Additional images taken at these conditions, for pulses #1 to #800, demonstrate that the plasma remains diffuse during the entire pulse train.

Figure 3.5: Photograph and ICCD camera images of plasma (Gate 1) sustained in the short cavity in air flow.
ICCD camera images of the plasma and the flame taken in premixed ethylene-air flows at P=150 torr and u=25 m/sec, using the short cavity, are shown in Figure 3.6. Ethylene-air plasma (Gate 1) images for pulses #40 - #200 exhibit multiple arc filaments extending from the high-voltage electrode (see Figure 3.6). Flame (Gate 2) images show that ignition in the cavity occurs after approximately 100 pulses (2.5 msec), with the flame filling the cavity after 140 pulses and coupling to the main flow after 180 pulses. Combustion products exhausting from the cavity and flame propagation into the main flow cause plasma filament extension downstream of the cavity. After the flame couples out, the plasma in the cavity gradually becomes diffuse (pulses #350 and #400). After 400 pulses (10 msec), the flame disappears almost completely (see Figure 3.6). No flame emission was detected between pulses #400 and #1000 (10-25 msec), although the fuel-air mixture was flowing through the test section continuously. Based on the flame images such as shown in Figure 3.6, the upper bound estimate of the total burn time is approximately 7.5 msec (pulses #100 - #400), including about 5 msec of combustion in the main flow (pulses #200 - #400). Summarizing the results of Figure 3.6, (i) the fuel-air plasma in the short cavity is strongly filamentary during ignition and becomes diffuse after all fuel in the cavity is burned, and (ii) the flame in the cavity and in the main flow exists only for a few milliseconds and disappears after the fuel in the cavity is burned.
3.3.2 Time resolved OH emission measurements

Time-dependent OH emission from the main flow, taken at P=150 torr and u=35 m/sec and plotted in Figure 3.7, is consistent with the series of flame images shown in Figure 3.6. It can be seen that the main flow ignites approximately at t=5 msec after the pulse burst is initiated and the flame in the main flow is extinguished approximately at t=10 msec, lasting for about 5 msec. From Figure 3.7, one can also see that the next main flow ignition spike occurs only about 50 msec later, at t=54 msec, although both the fuel-air flow and the plasma were sustained continuously. To test if the repetitive ignition/flame blow-off is due to slow mixing between the cavity and the main flow, a small fraction of the premixed fuel-air flow (up to a few per cent) was diverted from the main
channel and injected into the cavity through the bottom wall, as shown in Figure 2.3. This was done to ensure that some amount of fuel-air mixture would be present in the cavity at all times, so it would not be filled with combustion products for extended periods of time, in case slow mixing with the main flow limits supply of air-fuel mixture.

![Emission intensity (arbitrary units)](Image)

Figure 3.7: Time-dependent OH emission from a plasma-ignited, premixed ethylene-air flow. Short cavity, $\phi=1$, $P=150$ torr, $u=35$ m/sec.

Figure 3.8 compares OH emission oscillograms obtained at $u=60$ m/sec, with (top trace) and without (bottom trace) 0.9% of the main flow rate injected into the cavity. It can be seen that fuel-air injection into the cavity results in a regular (although still repetitive) ignition pattern in the main flow, with considerably shorter delays between ignition events. To confirm that main flow ignition correlates with ignition in the cavity, and to determine whether fuel-air injection results in stable flameholding inside the cavity, time-dependent OH emission from the cavity was monitored separately, using a mask placed on the rectangular optical access window. The results at $P=150$ torr and two
flow velocities, \( u=60 \text{ m/sec} \) and \( 70 \text{ m/sec} \), are shown in Figure 3.9 and Figure 3.10. OH emission traces from the cavity, plotted in these figures, were obtained by subtracting nitrogen second positive band emission measured in air \( (v'-v''=1 \text{ sequence}, v'=1\text{-}4 \text{ bands transmitted through the 310 nm filter}) \) from the raw fuel-air emission oscillograms. From Figure 3.9, it can be seen that at 60 m/sec, injection considerably reduced average delay time between ignition spikes in the cavity, which is consistent with ignition pattern in the main flow at the same flow velocity, with and without injection (see Figure 3.8). Also, from Figure 3.9 it can be seen that flame in the cavity is not sustained continuously even with premixed flow injection. At \( u=70 \text{ m/sec} \), injection into the cavity also substantially reduced time delay between ignition events, both in the cavity and in the main flow (see Figure 3.10). In this case, the average delay time between ignition spikes with injection was noticeably longer than at \( u=60 \text{ m/sec} \), 53-55 msec. Without injection, rare sporadic ignition bursts in the cavity did not couple out to the main flow (see Figure 3.10), which ignited only during the first ignition burst in the cavity or did not ignite at all.

![Emission intensity (arbitrary units) with F/A injection](image)

Figure 3.8: OH emission from a plasma-ignited, premixed ethylene-air flow, with and without fuel-air injection into the short cavity. \( \phi=1 \), \( P=150 \text{ torr} \), \( u=60 \text{ m/sec} \).
Figure 3.9: Time-dependent OH emission from a plasma-ignited stoichiometric ethylene-air in the cavity at $P=150$ torr, $u=60$ m/sec, and $\nu=40$ kHz, with and without injection into the cavity.

Figure 3.10: Time-dependent OH emission from a plasma-ignited stoichiometric ethylene-air in the main flow and in the cavity at $P=150$ torr, $u=70$ m/sec, and $\nu=40$ kHz, with and without injection into the cavity.

These results demonstrate that the rate of mixing between the main flow and the cavity is indeed one of the limiting factors for achieving flameholding in cavity-stabilized high-speed flows, as discussed in Ref. [1]. Basically, the short cavity (length-to-depth ratio of L/D=1) remains filled with combustion products for a long time after ignition.
occurs and flame couples out to the main flow, with the effect becoming more
pronounced at higher flow velocities. Injection into the cavity helps refilling it with fuel-air mixture after ignition. However, a regular repetitive ignition and flame blow-off
pattern was observed even with fuel-air injection into the cavity (see Figure 3.8- Figure 3.10). This behavior may be caused by a flashback in the premixed fuel-air flow,
resulting in fuel burning upstream of the cavity, or by the fuel-air flow rate reduction due
to a sudden pressure rise in the test section during ignition. The latter effect may be
enhanced significantly if the flow burning in the extension channel downstream of the
test section thermally chokes.

3.3.3 Time averaged emission spectroscopy measurements

In this work, plasma temperature in air and fuel-air is measured using nitrogen
emission spectroscopy as described in Section 2.5.3. For all nitrogen emission
spectroscopy measurements described in this section, the emission signal was collected
from the discharge region with the optical fiber collimator placed above or below the
high voltage electrode, as shown in Figure 3.11. Figure 3.12 shows a typical nitrogen
emission spectrum (C$^3$Π, v$'=${0,1} → B$^3$Π, v$''=${2,3}), in the air plasma, for u= 65 m/sec and
P=150 torr, along with the “best fit” synthetic spectrum used to infer plasma temperature.
In this case, best agreement between experimental and synthetic spectra is obtained at
T=480±30 K.
Figure 3.11: Regions of nitrogen emission signal collection in the plasma produced in the combustor with small cavity (L/D=1).

Figure 3.12: Typical experimental N₂ emission spectrum (C³Π, ν'=0,1 → B³Π, ν''=2,3) from the nanosecond pulse discharge and best fit synthetic spectrum. Air, P=150 torr, u=65 m/sec, best fit rotational temperature T = 480 ±30 K.
Figure 3.13 shows air plasma temperatures in the cavity, inferred from nitrogen emission spectra in the range of pressures and flow velocities for which ignition was achieved when fuel was added to the air flow. The emission spectra were collected from region near the top of the cavity, above the high-voltage electrode, except at P=200 torr when an additional series of measurements was taken with the collimator located near the cavity bottom, below the electrode (see Figure 3.11). The emission was integrated over the pulse burst duration of 100 msec. It can be seen that the temperature in the plasma increases with pressure and decreases with the flow velocity. The temperatures measured near the top and near the bottom of the cavity are close to each other, except at very low flow velocities, u≤15 m/sec (see Figure 3.13). The uncertainty of temperature inference from the N$_2$ emission spectra is approximately ±30° C. Note that although the diffuse air plasma temperatures are fairly low, down to 170-220° C at the high end of the velocity range where ignition was achieved (see Figure 3.13), the use of these temperatures to interpret ignition results in fuel-air mixtures may be misleading since adding fuel to the flow results in formation of arc filaments (see Figure 3.6) where the local temperature may well be significantly higher. As expected, 0.9% of air flow injection into the cavity somewhat reduces the air plasma temperature. From Figure 3.14, which compares temperatures of air plasma measured near the cavity bottom with and without injection, one can see that injection reduces the temperature by up to 40° C, down to 150° C at u=70 m/sec.
Figure 3.13: Air plasma temperatures in the cavity at different pressures and flow velocities. The temperature is time-averaged over the pulse burst duration of 100 msec (at P=70-150 torr) and 200 msec (at P=200 torr). Emission is collected with the optical fiber placed at the top of the cavity unless noted otherwise.

Figure 3.14: Air plasma temperatures in the cavity with and without air injection into the cavity at P=150 torr. The temperature is time-averaged over the pulse burst duration of 100 msec. Emission is collected with the optical fiber placed at the bottom of the cavity.
Figure 3.15 shows fuel-air plasma temperatures in the cavity in the range of pressures and flow velocities where ignition was achieved, also averaged over the pulse burst duration of 100 msec. Although it can be seen that the time-averaged temperatures in fuel-air flows are significantly higher than the air plasma temperatures at the same flow conditions, quantitative interpretation of these measurements is extremely difficult because of repeated ignition and flame extinction at low ignition event frequency (see Figure 3.8 - Figure 3.10). Note that the time-averaged fuel-air flow temperature measured at P=200 torr near the bottom of the cavity is consistently lower than near the top, most likely due to rapid heat transfer to the cold cavity walls. We also attempted to use CH emission bands at 431 nm to infer the rotational temperature in the flame. Figure 3.16 shows a typical experimental CH \((A^2\Delta, v'=0\rightarrow X^2\Pi, v''=0)\) emission spectrum collected from the flame for \(u=25\) m/sec and P=70 torr, along with the “best fit” synthetic spectrum, used to infer flame temperature. However, temperatures inferred from CH spectra exceed the values inferred from \(N_2\) second positive system spectra, taken at the same location, by nearly a factor of two. This most likely occurs due to optical thickness, causing significant self-absorption of CH emission, or because electronically excited CH in the flame is formed in chemical reactions, such as, \(C_2H + O_2 = CH (A^2\Delta) + CO_2, C_2H + O = CH (A^2\Delta) + CO,\) and \(C_2 + OH = CH (A^2\Delta) + CO\) [47], which may generate vibrationally and rotationally “hot” products. The later effect does not influence \(N_2\) second positive system emission spectra, since in this case the emitting \(N_2 (C^3\Pi_g)\) state is populated from the ground state \(N_2 (X^1\Sigma_g^+)\) by electron impact. Since the characteristic
electron impact excitation time is much shorter than rotational relaxation time, electron impact excitation “preserves” the rotational distribution of the ground electronic state.

Figure 3.15: Ethylene-air plasma temperatures in the cavity at different pressures and flow velocities. The temperature is time-averaged over the pulse burst duration of 100 msec (at P=70-150 torr) and 200 msec (at P=200 torr). Nitrogen second positive band emission is collected with the optical fiber placed at the top of the cavity unless noted otherwise.

Figure 3.16: Typical experimental CH emission spectrum (A^2Δ, v^'=0→ X^2Π, v^''=0) from discharge region and best fit synthetic spectrum. Air, P=70 torr, u=25 m/sec, apparent best fit rotational temperature T = 2100 ±50 K.
3.3.4 FTIR absorption spectroscopy measurements

In the present study, burned fuel fraction is measured by sampling the flow of combustion products through a wall pressure tap, located 50 cm downstream of the high voltage electrode, into an absorption cell of the FTIR absorption spectrometer, as discussed in Section 2.5.4. Figure 3.17 shows typical FTIR absorption spectra of a stoichiometric ethylene-air mixture, with and without plasma sustained in the cavity. From these spectra, burned fuel fraction (χ) is calculated using the following formula, \( \chi = \left(1 - \frac{I_{\text{abs,2}}}{I_{\text{abs,1}}} \right) \times 100\% \), where \( I_{\text{abs,1}} \) and \( I_{\text{abs,2}} \) are peak absorbance values on a particular fuel rotational-vibrational absorption line, measured without and with plasma, respectively. Burned fuel fraction measured in the present work represents the average of burned fuel fraction calculated using this approach for three different absorption lines at 2988.8, 3077.6, and 3140.2 cm\(^{-1}\). For example, the burned fuel (ethylene) fraction calculated using the spectra shown in Figure 3.17 is 56%.
Figure 3.17: Typical FTIR absorption spectra of the flow sampled 50 cm downstream of the high voltage electrode, with and without plasma. Ethylene-air flow, P=150 torr, u=35 m/sec, $\varphi=1.0$.

Figure 3.18 plots time-averaged burned fuel (ethylene) fraction vs. flow velocity at different combustor pressures. All data in Figure 3.18 have been taken without fuel-air injection into the cavity. It can be seen that burned fuel fraction decreases with the flow velocity, until it approaches near zero when flameholding is no longer achieved (for P=70 torr this occurs approximately at u=14 m/sec, for P=100 torr at u=25 m/sec, and at P=150 and 200 torr approximately at u=65 m/sec). This is consistent with the trend of ignition spike frequency reduction detected from the time-dependent OH emission traces in Section 3.3.2. Lower burned fuel fraction at the same flow velocity at lower pressures, P=70 and 100 torr, could be due to lower energy per pulse coupled by the discharge to the flow [48], less pronounced plasma filamentation [49], and longer ignition delay time [25].
Figure 3.18: Burned fuel fractions at different pressures and flow velocities, without injection into the cavity. Flow sampled 50 cm downstream of the high voltage electrode.

Figure 3.19 demonstrates the effect of flow injection into the cavity on the time-averaged burned fuel fraction at P=150 torr. One can see that injection considerably increases the fuel fraction burned at higher flow velocities, u=50-70 m/sec (up to 30-50%). Note that at u=70 m/sec without injection, no ignition had been detected in the main flow, although several sporadic ignition events (OH emission spikes) had been detected in the cavity at these conditions. However, injecting 0.9% of the total premixed fuel-air flow into the cavity resulted in fairly regular repetitive ignition, with the time-averaged fuel fraction of 25-30%. Note that at these conditions the OH emission duty cycle in the main flow was significantly lower; approximately 10% (see Figure 3.10). This suggests that every time ignition occurred in the main flow, the flame rapidly propagated downstream and to some extent upstream of the cavity, thereby significantly increasing the amount of fuel burned.
3.3.5 Results of DC arc discharge ignition experiments

To provide qualitative comparison of repetitive nanosecond pulse plasma ignition with conventional ignition methods, we also conducted a series of experiments using DC arc discharge ignition. A 100 W DC arc discharge was generated by a spark plug placed in the bottom of the cavity, as described in Section 2.4, and was used to ignite premixed ethylene-air flows at $P=150$ torr and $u=30-40$ m/sec. The results of these experiments are shown in Figure 3.20. It can be seen that at $u=30$ m/sec, ignition spikes in the main flow occur at a very low frequency, approximately 8-10 Hz (compared to 30 Hz frequency obtained at $u=35$ m/sec using a repetitive nanosecond pulsed plasma). As expected, burned fuel fraction using a DC arc discharge at $u=30$ m/sec was also very low, approximately 5%. This is almost an order of magnitude lower than the burned fuel fraction at $P=150$ torr with injection.
fractions obtained using a repetitive nanosecond pulse plasma, 34-37% at \( u=30 \text{ m/sec} \) and 41-56% at \( u=35 \text{ m/sec} \) (see Figure 3.19). At 40 m/sec, ignition spikes using a DC arc discharge became very rare and sporadic (see Figure 3.20), and in most runs (up to several seconds long each) the flow did not ignite at all. Although quantitative comparison of these two ignition methods is hardly possible due to different discharge geometries, this simple test demonstrates superiority of repetitive nanosecond pulse plasma ignition, compared to localized plasma ignition using a high-temperature DC arc filament. This is consistent with pulsed corona ignition of methane-air and ethylene-air mixtures, which resulted in a shorter ignition delay time compared to spark plug ignition [24].

![Graph showing emission intensity over time](image)

**Figure 3.20:** Time-dependent CH emission from a DC arc ignited stoichiometric ethylene-air in the main flow at \( P=150 \text{ torr} \) and different flow velocities. DC discharge power 100 W.
3.4 Ignition and flameholding in large cavity (L/D=3)

From results of Section 3.3, it is evident that the use of a small cavity (with L/D=1), which helps sustaining fairly diffuse volume filling plasmas due to its symmetric geometry and provides long cavity residence time, does not produce stable flameholding at high flow velocities (u > 50 m/sec). This is most likely due to too slow mass exchange between the cavity recirculation flow and the main flow, which does not allow maintaining sufficient supply of fuel-air mixture into the plasma. Thus, the cavity remains filled with combustion products for long period of time after ignition. Therefore, a large cavity with length-to-depth ratio (L/D) of 3 is used for all the experiments in the rest of the present work. In addition, in all experiments discussed in the rest of the dissertation, the main flow delivery line is choked either at the flow stabilization channel entrance or 34 cm upstream of the entrance to preclude the repetitive ignition and flame blow-off pattern observed in Section 3.3. This approach prevented flashbacks from the combustor into the flow stabilization channel and uncoupled the inlet flow rate from the pressure oscillations in the combustor. It should be noted that when the flow was choked at the inlet of the flow stabilization channel, the velocity distribution across the flow channel was observed to be much less uniform than those shown in Figure 3.1. Therefore, to improve flow uniformity across the channel, the choke plate was moved 34 cm upstream of the flow stabilization channel entrance for all experiments described starting from Section 3.4.4.2. Also, during most of subsequent experiments, the extension channel downstream of the test section was removed to prevent the possibility of thermal choking.
3.4.1 Premixed and partially premixed ethylene-air combustion

3.4.1.1 Photographs and ICCD camera images of plasma and flame

Figure 3.21 shows photographs of air plasma and plasma with flame in a premixed, stoichiometric ethylene-air flow at P=150 torr and u=70 m/sec. In Figure 3.21, the air plasma photograph and flame photograph are averaged over the pulse burst durations of 20 msec (800 pulses in the burst) and 100 msec (4,000 pulses in the burst), respectively. From the air plasma photograph, it is apparent that plasma fills the region between the high-voltage electrode and the adjacent cavity walls, and appears diffuse. In the fuel-air mixture, the plasma also appears diffuse, while the flame fills the entire cavity and couples out to the main flow.

Figure 3.21: Left: photograph of air plasma; Right: photograph of plasma and flame in a premixed stoichiometric ethylene-air mixture. P=150 torr, u=70 m/sec, v=40 kHz, flow is right to left.

Figure 3.22 shows typical ICCD camera images of the plasma and the flame in premixed ethylene-air flows at φ=1, at P=175 torr, u=80 m/sec (photo) and at P=150 torr, u=35 m/sec. These images are taken using the same gating scheme as described in Section 3.3.1. The plasma image is taken during pulse #2500, and the flame image is taken between pulses #2,600 and #2,601, i.e. at τ=65 msec. These images demonstrate
again that the fuel-air plasma becomes diffuse after ignition, and remains diffuse as long as the flame is sustained in the cavity. ICCD images of plasma and flame, taken in partially premixed ethylene-air flows (with fuel injected into the flow 16 cm upstream of the cavity, see Section 2.2.2), are shown in Figure 3.23. These images are qualitatively consistent with the images in Figure 3.22. They also show ignition being initiated in initially filamentary plasma, which subsequently transformed to diffuse plasma as the flame is coupling out to the main flow.

Figure 3.22: ICCD images of plasma (Gate 1) and flame (Gate 2). Premixed ethylene-air flow, P=150 torr, u=35 m/sec, φ=1.
Figure 3.23: ICCD images of plasma (Gate 1) and flame (Gate 2) in a partially premixed ethylene-air flow with choked inlet. Long cavity, $\phi=1.0$, $P=150$ torr, $u=70$ m/sec.

### 3.4.1.2 Time resolved OH emission and pressure measurements

Typical OH emission traces obtained in premixed and partially premixed plasma-ignited ethylene-air flows are shown in Figure 3.24, demonstrating stable flameholding in the test section at $P=150$ torr, $u=100$ m/sec during nearly the entire discharge pulse train 0.5 sec long. One can see that the flame also persists for some time after the plasma is turned off at $t=0.5$ sec. From Figure 3.24, it can also be seen that ignition causes significant initial pressure oscillations in the cavity, up to approximately $\Delta P=40$ torr. Note that the pressure oscillation amplitude may be significantly higher than shown in Figure 3.24. The low sampling rate of the pressure acquisition system (52 Hz) may well be insufficient to resolve high-frequency oscillations. At steady state, test section
pressure rise is just a few torr above the baseline level (see Figure 3.24). Ignition and stable flameholding in the long cavity was achieved in both premixed and partially premixed flows, at flow velocities ranging from 35 to 100 m/sec. Most of the experiments, however, have been conducted in premixed flows, since measurements of fuel fraction in non-premixed flows exhibit significant run-to-run variation, both with and without the plasma.

![Figure 3.24: OH emission and pressure traces in ethylene-air flows with choked inlet, premixed and partially premixed. Long cavity, $\phi=0.9$, $P=150$ torr, $u=100$ m/sec.](image)

To determine whether the nanosecond pulse discharge needs to be sustained in the cavity after ignition has been achieved, it was operated in a repetitive burst mode as discussed in Section 2.3, with duty cycle varied from 5% to 50%. Figure 3.25 plots OH emission traces for three different flow velocities, at minimum discharge duty cycle required to sustain continuous combustion. It can be seen that the minimum duty cycle
increases from 9% at u=35 m/sec to 30% at u=70 m/sec, and to 50% at u=80 m/sec. This implies that flameholding at higher flow velocities requires the plasma to be sustained continuously. Note that the estimated discharge power at these conditions is approximately 80 W [22], much lower than the heat of combustion in a stoichiometric ethylene-air flow at u=70 m/sec, 25 kW. This suggests that even after ignition is achieved, radical species generation in the plasma remains a key factor controlling flameholding in high-speed flows, thereby reducing ignition delay time.

![Intensity (arbitrary units)](image)

Figure 3.25: OH emission during discharge operation in repetitive burst mode, at minimum duty cycle providing continuous flameholding. Ethylene-air, long cavity, premixed flow, choked inlet, $\phi=1$, P=150 torr.

3.4.1.3 *Time averaged emission spectroscopy measurements*

Figure 3.27 plots temperatures measured in the air plasma and in plasma / flame in premixed, choked air and stoichiometric ethylene-air flows vs. the flow velocity. For
these measurements, the optical fiber collimator was placed 3 mm above the high-voltage electrode to measure the flow temperature in the shear / mixing layer near the top of the cavity, as shown in Figure 3.26. Since the rotational temperature is inferred from N₂ second positive system bands, it can only be measured close to the high-voltage electrode, because N₂ emission intensity away from the electrode rapidly decreases. N₂ emission was collected over a 0.5 sec interval, and temperatures inferred from the emission spectra represent time-averaged values. Therefore maintaining a stable flame in the test section during the entire emission collection time was critical for accurate flame temperature measurements. From Figure 3.27, it can be seen that air plasma temperatures are fairly low, decreasing from T=200°C at u=35 m/sec to T=100°C at u=100 m/sec. In stoichiometric ethylene-air flows, temperatures in stable flames sustained after ignition range from T=800°C to 1000°C.

Figure 3.26: Region of nitrogen emission signal collection in the plasma produced in the combustor with large cavity (L/D=3).
The ethylene-air flame temperature measurements in the test section provide a simple estimate of the flow Mach number downstream of the test section after ignition. Since the steady-state test section static pressure rise after ignition is only a few torr (see Figure 3.24), the flow density is inversely proportional to the temperature. At the constant mass flow rate in the flow with a choked inlet, the velocity is proportional to the temperature, and the Mach number is proportional to the square root of temperature, $M \sim T^{1/2}$. Therefore heating a fuel-air flow, initially at 100 m/sec, from 300 K to 1200 K approximately doubles the Mach number, from $M \approx 0.3$ in the cold flow to $M \approx 0.6$ after ignition. This shows that after ignition the flow, which continues burning downstream of the cavity, may approach transonic regime and thermally choke. Evidence of thermal choking was apparent during the runs using the extension channel leading to the vacuum system, used for sampling the flow into the FTIR spectrometer. In this case, steady-state
pressure rise in the test section after ignition was quite significant, $\Delta P \approx 30$ torr at $u=35$ m/sec and $\Delta P \approx 50$ torr at $u=70$ m/sec (at the same baseline pressure of $P=150$ torr). At these conditions, the flame was fairly unstable, switching back and forth between stable flameholding (such as shown in Figure 3.24) and repetitive blow-off / ignition (such as shown in Figure 3.8 - Figure 3.10), caused by high-amplitude pressure oscillations due to thermal choking of the flow. Removing the extension channel reduced the steady-state pressure rise, to just a few torr in the entire velocity range, and resulted in stable flameholding. However, without the extension channel, the flow of combustion products could only be sampled 10 cm downstream of the high voltage electrode, compared to 50 cm downstream when the extension channel was used. This shows that combustion products flow sampling far downstream of the cavity requires the use of a gradually expanding extension channel, with the expansion angle suitably chosen to reduce static pressure rise due to heat release during combustion and to prevent thermal choking.

### 3.4.1.4 FTIR absorption spectroscopy measurements

Figure 3.28 plots burned fuel fraction vs. flow velocity for premixed, choked inlet flow using a large cavity. Flow of combustion product was sampled 50 cm downstream of the high voltage electrode, using the extension channel downstream of the combustor. These burned fuel fraction data are compared with those obtained in repetitively ignited flows using the short cavity (see Figure 3.19), which are also plotted in Figure 3.28. It should be noted that achieving stable flameholding was fairly difficult even when the large cavity was used, due to thermal choking of the flow in the extension channel, as
discussed above. Therefore, the flow was sampled only when a stable flame was detected in the test section during the entire run, such as shown in Figure 3.24. In this case, burned fuel fraction at $u=35$-70 m/sec is much higher, 80-85%, consistent with OH emission traces indicating stable flameholding at these conditions (see Figure 3.24), and nearly independent of the flow velocity. This was not the case with combustion in a small cavity where reduction of burned fuel fraction was observed as the flow velocity was increased, both with and without premixed flow injection into the cavity, since combustion was intermittent.

![Burned fuel fraction vs. Velocity](image)

Figure 3.28: Burned fuel fraction in premixed ethylene-air flows for different flow regimes. $\phi=1$, $P=150$ torr, flow sampled 50 cm downstream of the high voltage electrode.

Comparing burned fuel fraction measured 50 cm downstream of the high voltage electrode with that obtained by sampling the flow 10 cm downstream of the electrode shows that only a relatively small fuel fraction, 10-40%, is burned in the test section,
compared to 80-85% burned in the extension channel (see Figure 3.29). This demonstrates that fuel burning in high-speed plasma ignited flows (estimated flow velocity after ignition $u \sim 400$ m/sec) occurs over a fairly long distance, up to a few tens of cm.

Figure 3.29: Burned fuel fraction in premixed, stoichiometric ethylene-air flows with choked inlet vs. flow velocity. Long cavity, $P=150$ torr. Flow sampled into the FTIR spectrometer 10 cm and 50 cm downstream of the high voltage electrode.

### 3.4.2 Partially premixed hydrogen-air combustion

#### 3.4.2.1 ICCD camera imaging of plasma and flame

Hydrogen-air ignition experiments have been conducted in lean, partially premixed flows with choked inlet, using the long cavity. The global equivalence ratio in partially premixed flows was kept fairly low, $\phi=0.44-0.96$, to avoid hydrogen explosion in the vacuum system at the conditions when the plasma was initiated with some delay after the fuel injection flow was started. The delay was necessary to stabilize the reading.
of the mass flow controller in the fuel delivery line after the solenoid fuel shut-off valve was opened. The equivalence ratio was reduced as the air flow velocity was increased. Figure 3.30 illustrates plasma and flame development in a non-premixed hydrogen-air flow at $u=30$ m/sec and global equivalence ratio of $\phi=0.73$. One can see that, similar to images taken in partially premixed ethylene-air flows (see Figure 3.23), the plasma is filamentary in the beginning of the pulse burst, and becomes diffuse after ignition occurs in the cavity and the flame couples out to the main flow.

![Gate 1 (plasma)](image1)

![Gate 2 (flame)](image2)

Figure 3.30: ICCD camera images of hydrogen-air plasma (Gate 1) and flame (Gate 2) in a partially premixed flow during ignition burst. Hydrogen-air, global equivalence ratio $\phi=0.73$, $P=150$ torr, $u=30$ m/sec, long cavity.
3.4.2.2 Time resolved OH emission measurements

Figure 3.31, which plots OH emission traces in partially premixed hydrogen-air flows, demonstrates that after ignition the flame remains stable during the entire pulse burst duration, and persists after the plasma has been turned off, in the entire air flow velocity range tested, \( u = 30 \text{ - } 90 \text{ m/sec} \). Note that hydrogen injection somewhat increases the flow velocity in the channel before ignition. At \( u = 90 \text{ m/sec} \) (before fuel injection) and the global equivalence ratio of \( \phi = 0.62 \) (hydrogen mole fraction of 21\%), the estimated upper bound of flow velocity, assuming perfect fuel-air mixing, is \( u = 110 \text{ m/sec} \).

Figure 3.31: OH emission pressure traces in partially premixed hydrogen-air flows for different flow velocities and global equivalence ratios. Long cavity, \( P = 150 \text{ torr} \), plasma is turned off at \( t = 0.3 \text{ sec} \).
Figure 3.32 plots the OH emission trace at the lowest global equivalence ratio used in the present partially premixed hydrogen-air experiments, $\phi=0.44$ at $u=80$ m/sec. It can be seen that after the plasma is turned off at $t=0.1$ sec, the flame in the test section persists for almost a second, until the fuel is turned off. This result is strikingly different from the results obtained in ethylene-air flows, plotted in Figure 3.25. Indeed, maintaining a continuous flame in a premixed, stoichiometric ethylene-air flow at the same flow velocity ($u=80$ m/sec) required operating the plasma in a repetitive burst mode with the minimum burst duty cycle of 50%. On the other hand, the present results demonstrate that maintaining a continuous flame in non-premixed, lean hydrogen-air flows at $u=80-100$ m/sec, $\phi=0.44-0.64$ does not require sustaining the plasma in the cavity after ignition is achieved. This also suggests that ignition and flameholding in lean, non-premixed hydrogen-air flows, initially at room temperature, can be achieved at significantly higher flow velocities and Mach numbers, at a very low duty burst cycle.

![Figure 3.32: OH emission pressure trace in a partially premixed hydrogen-air flow with choked inlet at $u=80$ m/sec, global equivalence ratio of $\phi=0.44$, short plasma run time (0.1 sec). Long cavity, $P=150$ torr.](image)
3.4.2.3 *Time averaged emission spectroscopy measurements*

Figure 3.33 shows temperature in air and hydrogen-air plasmas inferred from N$_2$ emission spectroscopy at different air flow velocities. Similar to ethylene-air plasma temperature measurements, shown in Figure 3.27, hydrogen-air plasma temperatures have been measured at the condition when a stable flame was sustained in the test section during the entire discharge burst duration of 0.3 sec by collecting N$_2$ emission signal from the plasma region 3 mm above the high voltage electrode (see Figure 3.26). Therefore, these temperatures are time-averaged over 0.3 sec. It can be seen that the air plasma temperatures remain fairly low, T=70-200$^\circ$C, consistent with the results of Figure 3.27. Temperatures in the hydrogen-air plasma / flame are significantly higher, T=700-900$^\circ$C. The flame temperature does not exhibit a strong dependence on the equivalence ratio in the range tested, $\phi$=0.44-0.96.

Figure 3.33: Air plasma and hydrogen-air plasma / flame temperatures vs. flow velocity. Long cavity, non-premixed flow, P=150 torr. Global equivalence ratios are indicated in the plot.
3.4.3 Non-premixed ethylene-air combustion

3.4.3.1 Photographs and ICCD camera imaging of plasma and flame

Figure 3.34 shows photographs of the nanosecond pulse plasma in the air flow and of the plasma / flame in a fuel injection ethylene-air flow. During these experiments, test section pressure was $P=150$ torr, air flow velocity was $u=60$ m/sec, and ethylene was injected into the cavity 33 mm downstream of the high voltage electrode (indicated by an arrow in Figure 3.34), at the global equivalence ratio of $\phi=0.1$. These photographs are taken for the pulse burst duration of 33 msec (1320 pulses in the burst). It can be seen that the plasma appears to fill the volume between the high voltage electrode and the cavity walls, and the flame appears to fill nearly the entire cavity.

Figure 3.34: Left: photograph of air plasma; right: photograph of plasma and flame in a non-premixed ethylene-air flow. $P=150$ torr, $u=60$ m/sec, $\nu=40$ kHz. Flow direction is left to right. Fuel injected into the cavity 33 mm downstream of the high voltage electrode (indicated by an arrow), global equivalence ratio $\phi=0.1$.

Figure 3.35 shows a series of ICCD camera images of the air plasma produced by the repetitive nanosecond pulse discharge at the conditions of Figure 3.34, using camera Gate 1 (see Figure 3.4). These images are taken during different runs, for pulse numbers ranging from 1 to 2000 (i.e. from $t=0$ to 50 msec). From these images, it is apparent that
the plasma indeed occupies the region between the electrode and the cavity walls and is fairly diffuse, except for a few occasional filaments.

Figure 3.35: ICCD camera images of a repetitive nanosecond pulse plasma in air flow. $P=150$ torr, $u=60$ m/sec, $\nu=40$ kHz (time between consecutive pulses 25 $\mu$sec).

ICCD camera images of the plasma (using Gate 1 of Figure 3.4) and the flame (using Gate 2 of Figure 3.4) in fuel injection ethylene-air flows at the conditions of Figure 3.34 ($P=150$ torr, $u=60$ m/sec, global equivalence ratio $\phi=0.1$) are shown in Figure 3.36. In this figure, fuel is injected into the cavity 24 mm downstream of the electrode. Plasma images in ethylene-air exhibit multiple filaments, extending from the high-voltage electrode to the cavity walls, during ignition and flame propagation ( pulses #100 - #320 in Figure 3.36). As the flame fully develops and fills a significant part of the
cavity, the filaments gradually disappear and the plasma becomes more diffuse. This trend is similar to that observed during premixed and partially premixed combustion of ethylene-air, discussed previously (see Sections 3.3.1 and 3.4.1.1). Flame images show that ignition in the cavity begins after approximately 100 pulses (2.5 msec), with the flame filling most of the cavity after 600 pulses (15 msec, see Figure 3.36). Similar plasma and flame development is observed when ethylene is injected into the cavity 33 mm downstream of the high voltage electrode. However, in this case the flame is observed to be less stable, compared to the case when the fuel is injected closer to the plasma.

Figure 3.36: ICCD camera images of plasma and flame in a fuel injection ethylene-air flow. Fuel injected into the cavity 24 mm downstream of the high voltage electrode. P=150 torr, u=60 m/sec, v=40 kHz, global equivalence ratio $\phi=0.1$.  

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3.4.3.2 Time resolved OH emission and pressure measurements

Time-dependent OH emission traces from the cavity during plasma assisted combustion of fuel injection ethylene-air flows are plotted in Figure 3.37. These results are obtained at P=150 torr for different air flow velocities and global equivalence ratios. During these experiments, fuel is injected into the cavity either (a) 33 mm or (b) 24 mm downstream of the high voltage electrode. From Figure 3.37(a), it is clear that when ethylene is injected 33 mm downstream of the electrode, stable flameholding can be achieved at air flow velocities of up to u=70 m/sec. Moving the location of the injection ports closer to the plasma region (24 mm downstream of the electrode) noticeably improves flame stability, and flameholding limit increases up to u=90 m/sec (see Figure 3.37(b)). In addition, moving fuel injection location closer to the plasma also somewhat reduces the optimum value of global equivalence ratio for stable flameholding, from $\phi=0.1$ to $\phi=0.076$. At higher flow velocities (near $u=100$ m/sec), the flame becomes unstable. No ignition has been achieved beyond $u=110$ m/sec. It should be noted that for both injection locations, the flame disappears almost immediately after plasma is turned off (i.e., OH emission rapidly decays to zero, see Figure 3.37(a),(b)).
Figure 3.37: OH emission from plasma-ignited fuel injection ethylene-air flows for different flow velocities and global equivalence ratios. Fuel injected into the cavity (a) 33 mm and (b) 24 mm downstream of the high voltage electrode. P=150 torr, ν=40 kHz, pulse burst duration 0.1 sec.

3.4.4 Non-premixed hydrogen-air combustion

3.4.4.1 ICCD camera imaging of plasma and flame

Figure 3.38 shows ICCD camera images of the plasma and the flame taken in fuel injection hydrogen-air flows at P=150 torr, u=60 m/sec, and global equivalence ratio of φ=0.15. Hydrogen is injected into the cavity 33 mm downstream of the high voltage electrode. From these images, it is evident that, although occasional filaments are detected in the plasma before and during the ignition, the plasma is considerably more diffuse compared to that in ethylene-air (see Figure 3.36). This result is qualitatively consistent with images of ethylene-air and hydrogen-air plasmas obtained in our previous work [50], also showing filament formation in ethylene-air plasmas. Hydrogen-air plasmas are less filamentary, most likely due to high thermal conductivity of hydrogen.
which prevents formation of hot arc filaments. Flame images in the hydrogen-air flow show that ignition occurs after approximately 140 pulses (3.5 msec) and flame fills the entire cavity after 200 pulses (5 msec). After that, the flame propagates downstream of the cavity, unlike in ethylene-air flows where the flame is always observed to be confined into the cavity (see Figure 3.36). No significant changes in plasma and flame development pattern are observed when hydrogen is injected closer to the high voltage electrode (24 mm downstream).

Figure 3.38: ICCD camera images of plasma and flame in a fuel injection hydrogen-air flow. Fuel injected into the cavity 33 mm downstream of the high voltage electrode. P=150 torr, u=60 m/sec, v=40 kHz, global equivalence ratio $\phi=0.15$. 
3.4.4.2 Time resolved OH emission and pressure measurements

Figure 3.39 shows time-dependent OH emission traces from the cavity during plasma assisted combustion of non-premixed hydrogen-air flows. The results are shown at different air flow velocities and global equivalence ratios, for combustor static pressure of (a) P=150 torr and (b) P=200 torr. During these experiments, hydrogen is injected into the cavity 24 mm downstream of the high voltage electrode. From Figure 3.39(a), it is clear that stable flameholding is achieved at air flow velocities of up to u=140 m/sec at P= 150 torr. Increasing combustor static pressure to 200 torr increased the flameholding limit to u=190 m/sec (see Figure 3.39(b)). In addition, increasing the static pressure reduced the minimum value of global equivalence ratio for stable flameholding. At higher flow velocities (u > 140 m/sec at P=150 torr and u > 190 m/sec at P=150 torr) no ignition was observed. Similar results were obtained when fuel injection location was moved further downstream in the cavity (33 mm downstream of the high voltage electrode). In this case, however, the minimum global equivalence ratio needed for ignition and stable flameholding increased by almost a factor of two. Therefore, injection ports location 24 mm downstream of the high voltage electrode was used for hydrogen injection in all subsequent experiments.
Figure 3.39: OH emission from plasma-ignited fuel injection hydrogen-air flows for different velocities and global equivalence ratios. (a) P=150 torr (b) P=200 torr. Pulse burst duration 0.3 sec.

Figure 3.40 shows transient pressure traces in the combustor measured 8 cm upstream and 7 cm downstream of the cavity during combustion, along with the OH emission trace at flow velocity of \( u=156 \text{ m/sec} \) and initial pressure of \( P=200 \text{ torr} \). It is evident that pressures both upstream and downstream of the cavity remain close to baseline value, indicating no significant change in flow velocity after the flow is ignited. Insignificant pressure rise after ignition is due to low global equivalence ratio, \( \varphi=0.037 \) in Figure 3.40. Similar results are observed for other flow velocities, \( u=60–140 \text{ m/sec} \), and initial pressures.
3.4.4.3 *Time averaged emission spectroscopy measurements*

Figure 3.41 plots temperatures measured in the air plasma and in plasma / flame during cavity injected non-premixed hydrogen-air combustion experiments. The results are shown for different flow velocities at the same combustor static pressures as in Figure 3.39 and Figure 3.40, (a) P=150 torr and (b) P=200 torr. For these measurements, the optical fiber collimator was again placed 3 mm above the high-voltage electrode to measure the flow temperature in the shear / mixing layer near the top of the cavity (see Figure 3.26). Since the rotational temperature is inferred from N$_2$ second positive system bands, it can only be measured close to the high-voltage electrode, because N$_2$ emission intensity away from the electrode rapidly decreases. N$_2$ emission was collected over a 0.3 sec interval, and temperatures inferred from the emission spectra represent time-averaged
values. Therefore, maintaining stable flame in the test section during the entire emission collection time was critical for accurate flame temperature measurements. From Figure 3.41, it can be seen that air plasma temperatures for both static pressures are fairly low, below 160°C. On the other hand, temperatures in stable flames sustained after ignition range from T=600°C to 900°C, demonstrating significant additional heat release due to hydrogen combustion.

![Graph showing temperature vs. flow velocity for air and hydrogen-air plasma/plasma flame temperatures at different pressures.](image)

Figure 3.41: Air plasma and hydrogen-air plasma / flame temperatures vs. flow velocity. (a) P=150 torr. (b) P=200 torr. Temperature is averaged over burst duration of 300 msec. Global equivalence ratio (φ) ~ 0.1.

### 3.4.4.4 Lean flammability limits measurements

Figure 3.42 outlines the range of global equivalence ratios for which ignition is achieved in fuel injection hydrogen-air flow, (a) for u=70-140 m/sec at P=150 torr and (b) for u=80-190 m/s at P=200 torr. In Figure 3.42, open symbols indicate the conditions
velocity and equivalence ratio) at which ignition is achieved, and closed symbols indicate conditions at which stable flameholding was reached. From Figure 3.42(a), it can be seen that at P=150 torr and u=70 m/sec, ignition is achieved at a very low global equivalence ratio, \( \phi \approx 0.03 \). As the flow velocity is increased to \( u=130 \) m/sec, the lean global flammability limit increases only slightly, \( \phi \approx 0.05 \). However, the lower bound of global equivalence ratio at which stable flameholding is achieved, represented by solid symbols in Figure 3.42(a), actually decreases as the flow velocity is increased. This most likely occurs due to improved fuel-air mixing in the cavity at higher flow velocities. Similar trend of lean global flammability limit reduction with the increase in flow velocity is observed when the combustor static pressure was increased to 200 torr (see Figure 3.42(b)). However, comparison of Figure 3.42(a),(b) shows that for a given flow velocity, lean global flammability limit reduces with the increase in combustor static pressure. In the present work, the upper bound of global equivalence ratio has not been explored to avoid excessive heat release during combustion in the combustor and in the vacuum system.
3.5 Visualization of fuel-air mixing in the large cavity

To obtain insight into the dynamics of fuel-air flow mixing during fuel injection into the cavity, high frame rate NO PLIF imaging and schlieren imaging have been used. During these experiments, fuel was replaced with NO-seeded nitrogen or helium (for NO PLIF imaging) and helium (for schlieren imaging). In addition, single shot OH PLIF imaging was used to observe ignition and flame development in the plasma region of the cavity.

3.5.1 NO PLIF imaging

Figure 3.43 shows NO PLIF images of NO seeded nitrogen flow injected into the main flow in the cavity. Each set of images is taken during the same run, using a high...
frame rate ICCD camera described in Section 2.5.6, also operated at 10 kHz frame rate.

Nitrogen seeded with 20% NO was injected into the cavity through injection ports located 24 mm downstream of high voltage electrode in presence of a main flow of nitrogen at \( u = 100 \text{ m/sec} \) and \( P = 150 \text{ torr} \). This experiment simulated mixing of ethylene injected into the cavity with the main air flow. The steady state injection flow rate was set to 0.057 g/sec, which was essentially the same as the ethylene injection flow rate in the non-premixed plasma assisted ignition experiments, corresponding to global equivalence ratio of \( \phi = 0.076 \) at which ignition was observed (see Figure 3.37). Figure 3.43(a) illustrates the field of view of the camera, which covers a 30 mm long and 24 mm high rectangular area downstream of the cylindrical high voltage electrode. The sequence of images in Figure 3.43(b), taken in the beginning of injection flow after the solenoid valve opens, visualizes the injection flow path in the cavity recirculation flow and subsequent flow mixing. From these images, it is clear that the injection flow is directed towards the high voltage electrode by the cavity recirculation flow. Once the injection flow rate has reached steady state (within a few seconds after initializing the injection flow), NO PLIF images become diffuse (see Figure 3.43(c)), which suggests apparently uniform distribution of NO in the cavity. However, the estimated optical thickness of the NO-N\(_2\) mixture at these conditions shows that the flow is optically thick, with the characteristic absorption length of \( \sim 2 \text{ mm} \), (see Appendix B for detailed calculations). Therefore, images observed in Figure 3.43(c) are significantly affected by self absorption and subsequent re-emission, which would cause smearing of the flow structure in the images. Because of this, the images of Figure 3.43(c) do not provide sufficient information on the
extent of injection flow mixing with the main flow in the cavity. To make the medium optically thin one would need to reduce the fraction NO in the injection flow significantly (to approximately 1%). However, this would also reduce the fluorescence signal drastically and reduce the signal-to-noise ratio in the images. Therefore, this method of flow mixing visualization can only be used to observe injection flow pattern in the early phase of injection.

Figure 3.43: NO PLIF images of injection flow in the cavity. (a) Field of view of the camera, (b) PLIF images taken at the onset of injection, (c) PLIF images taken at near steady state condition. 20% NO – N\textsubscript{2} flow is injected into the main nitrogen flow. Main flow velocity \(u=100\) m/sec, \(P=150\) torr, steady state injection flow rate = 0.057 g/sec.
Figure 3.44 shows sequences of NO PLIF images at the conditions simulating mixing of hydrogen injected into the cavity with the main air flow in the cavity. In these experiments, helium seeded with 5% NO was injected into the cavity, with the main flow being nitrogen or air, at $u=150$ m/sec and $P=150$ torr to simulate hydrogen-air mixing in the cavity during actual combustion experiments. Similar to the images in Figure 3.43, each set of images in Figure 3.44 is taken during a single run, at 10 kHz laser pulse repetition rate and camera frame rate, with the same camera field of view. The steady state injection flow rate was equal to that of hydrogen injection during the combustion experiment (mass flow rate of 0.038 g/sec, global equivalence ratio of $\varphi=0.079$), at the same test section pressure and flow velocity. Again, images in Figure 3.44(a) show the injection flow path in the cavity after injection is initiated. Similar to Figure 3.43(b), the injection flow is observed to move towards the high voltage electrode (i.e., to the right) following the recirculation flow in the cavity. Once the injection flow rate has reached steady state, NO PLIF images (see Figure 3.44(b)) show nearly uniform distribution of NO fluorescence intensity in the cavity. Again, since the medium was found to be optically thick, with the characteristic absorption length of $\sim 2$ mm (see Appendix B for detailed calculations), these images cannot be used to characterize the mixing of injection flow with the main flow. Although distortion of intensity distribution due to self-absorption and subsequent re-emission could be eliminated by reducing the NO mole fraction in the NO-He mixture to 0.2%, this would reduce the fluorescence signal significantly. Therefore, mixing pattern of injection flow with the main flow at steady state could not be visualized.
Figure 3.44: NO PLIF images of injection flow in the cavity (a) at the onset of injection, (b) at near steady state. Helium seeded with 5% NO is injected into the main air flow (a) or main nitrogen flow (b). Main flow velocity $u=150$ m/sec, $P=150$ torr, steady state injection flow rate $0.038$ g/sec.

3.5.2 Schlieren imaging

Figure 3.45 shows schlieren images of helium injection flow into the recirculation air flow inside the cavity. The imaging area shown in Figure 3.45(a) covers a 35 mm long and 25 mm high rectangular area downstream of the cylindrical high voltage electrode. The sets of schlieren images shown in Figure 3.45(b) and Figure 3.45(c) were extracted from a movie taken using a CCD camera operating at the frame rate of 279 frames/sec (i.e., time delay between two successive frames is 3.6 msec). During the experiment,
helium was injected into the cavity through injection ports located 24 mm downstream of the high voltage electrode, in presence of main air flow of $u=150$ m/sec and $P=150$ torr. The steady state helium injection flow rate was the same as that of hydrogen injection during the combustion experiment (mass flow rate of $0.038$ g/sec, global equivalence ratio of $\phi=0.079$), at the same test section pressure and flow velocity. In order to obtain better image contrast, helium was pre-cooled with liquid nitrogen prior to injection. The steady state injection flow rate was the same as that of NO-seeded helium injection during NO PLIF images experiments described in the previous section. This allows comparison of schlieren images with NO PLIF images shown in Figure 3.44. From the schlieren images shown in Figure 3.45(b), it is evident that at the onset of injection, the injection flow penetrates almost the entire depth of the cavity. However, the depth of injection flow penetration is reduced significantly after a few hundred milliseconds, when the injection flow rate reaches near steady state (see Figure 3.45(c)). Injection flow pattern in this set of images is similar to that observed in NO PLIF images of Figure 3.44.
Figure 3.45: Schlieren images of injection flow mixing. (a) Field of view of the camera, (b) schlieren images at the beginning of injection, and (c) schlieren images 220 msec after the beginning of injection inside the cavity. Liquid nitrogen cooled helium injected into the main flow of air. Main flow velocity $u=150$ m/sec, $P=150$ torr, steady state injection flow rate $= 0.038$ g/sec.
3.5.3 OH PLIF imaging

Figure 3.46 shows a series of single shot OH PLIF images of flame in non-premixed hydrogen-air flow ignited by a repetitive nanosecond pulse discharge ($v = 40$ kHz), at the main flow velocity of 100 m/sec and combustor pressure of 150 torr, using the experimental setup described in Section 2.5.6. Each image was taken in a separate run using an ICCD camera synchronized with the laser and high voltage pulse generator to capture the fluorescence signal during and after the 10 nsec duration laser pulse. The laser pulse was generated 5 μsec after a burst of particular number of high voltage pulses, indicated in Figure 3.46. The ICCD camera gate was set to 200 nsec, which incorporated the laser pulse. Therefore, a long wavelength pass filter described in Section 2.5.6 was placed in front of the camera lens to eliminate the scattered laser light (at 283 nm) from the fluorescence signal. During these experiments, hydrogen was injected into the cavity 24 mm downstream of the high voltage electrode as shown by an arrow in Figure 3.46. All images in Figure 3.46 show a well developed flame extending over a significant part of the cavity, since they were taken a few milliseconds after ignition, which requires about 150-200 high voltage pulses (i.e., 3.75-5 msec burst durations). Attempts have been made to obtain images during and immediately after ignition to identify the location of ignition in the plasma and to visualize subsequent flame propagation. However, the fluorescence signal intensity was too low to detect the onset of the flame, even using maximum camera gain. OH PLIF images of the flame taken during repetitive nanosecond pulse discharge plasma assisted combustion of a non-premixed ethylene-air flow, at flow velocity of 60 m/sec and combustor pressure of 150 torr (see Figure 3.47), have even
lower signal-to-noise compared to hydrogen-air flame images in Figure 3.46. Although, these experiments were conducted at globally lean conditions ($\varphi \sim 0.1$), the local equivalence ratio may well be significantly higher. These results suggest that laser pulse energy ($\sim 0.2 \, \text{mJ}$ in the present work) needs to be increased to visualize flame dynamics during and after ignition. Therefore, no high frame rate OH PLIF imaging experiments were performed in this work.

Figure 3.46: Single shot OH PLIF images of the flame in a non-premixed hydrogen-air flow, acquired after a burst of high voltage discharge pulses. Number of pulses in the burst is indicated in each image. Main flow velocity $u=100 \, \text{m/sec}$, $P=150 \, \text{torr}$, global equivalence ratio $\varphi=0.1$, $\nu=40 \, \text{kHz}$. Red arrow indicates hydrogen injection location in the cavity.
3.6 Ignition and flameholding in reduced size cavity (L/D=3)

All plasma-assisted combustion experiments discussed in the previous sections have been conducted in a cavity with the depth exceeding the main flow channel height. At these conditions, the cavity flow affects the main flow significantly. To reduce the effect of the cavity on the main flow and to study feasibility of combustor scaling, additional experiments have been conducted in the reduced size cavity, with the same length-to-depth ratio, as described in Section 2.2.3.

3.6.1 Photographs and ICCD camera imaging of plasma and flame

Figure 3.48 shows photographs of the nanosecond pulse plasma in the air flow through the combustor at P=150 torr and u=100 m/sec. The photograph was taken for the
pulse burst duration of 20 msec (800 pulses in the burst). It can be seen that, although the plasma appears to be concentrated near the exposed high voltage electrode at the bottom of the cavity, it becomes diffuse as it extends into the main flow.

Figure 3.48: Photograph of the air plasma. P=150 torr, u=100 m/sec, v=40 kHz, flow is right to left.

Figure 3.49 shows a series of ICCD camera images of the air plasma produced by the repetitive nanosecond pulse discharge at the conditions of Figure 3.48, using camera Gate 1 (see Figure 3.4). These images are taken during different runs, for pulse numbers ranging from 1 to 1000 (i.e. from t=0 to 25 msec). From these images, it is apparent that the plasma is filamentary from the very first pulse and filaments become strong after a few tens of pulses. Formation of these filaments could not be prevented since in these experiments the high voltage electrode was not covered with dielectric. When the high voltage electrode was covered with a macor ceramic plate, no plasma could be produced in the cavity, since a strong arc was formed between the high voltage electrode and the surrounding metal combustor test section walls. The arcing occurred through the interface between the electrode and the macor plate covering it.
ICCD camera images of the plasma (using Gate 1 of Figure 3.4) and the flame (using Gate 2 of Figure 3.4) in fuel injection hydrogen-air flows at P=150 torr, u=60 m/sec, and global equivalence ratio of $\phi=0.076$ are shown in Figure 3.50. Fuel was injected into the cavity 22.5 mm downstream of the upstream cavity wall. Plasma images in hydrogen-air exhibit similar filamentary structure as observed in the air plasma in Figure 3.49 before ignition (pulses #30 - #50 in Figure 3.50). However, once the flame was developed in the cavity, the plasma became diffuse, following the same trend as observed previously using a cylindrical high voltage electrode enclosed in a ceramic tube (see Figure 3.30 and Figure 3.38). Flame images show that ignition in the cavity begins
after approximately 50 pulses (1.25 msec), with the flame filling most of the cavity after 100 pulses (2.5 msec).

Figure 3.50: ICCD images of plasma and flame. Non-premixed hydrogen-air flow, P=150 torr, u=100 m/sec, ν=40 kHz, Φ=0.076, flow is right to left.
3.6.2 Time resolved OH emission and pressure measurements

Figure 3.51 shows time-dependent OH emission traces from the cavity during plasma assisted combustion of non-premixed hydrogen-air flows for different air flow velocities and global equivalence ratios, at combustor static pressure of $P=150$ torr. From Figure 3.51, it is clear that stable flameholding was achieved up to a flow velocity of $u=230$ m/sec at $P=150$ torr. It is also observed that, similar to previous hydrogen-air combustion experiments in a large cavity, a self sustained flame existed in the cavity after plasma was turned off. At flow velocities exceeding $u=230$ m/sec, significant static pressure rise was observed upstream of the cavity, which caused the ratio of static pressures measured upstream and downstream of the cavity go beyond choking limit, $(P_{up}/P_{down} > 1.89)$. Therefore, no experiments were performed at $u > 230$ m/sec.

Figure 3.51: OH emission from plasma-ignited fuel injection hydrogen-air flows for different velocities and global equivalence ratios. $P=150$ torr, $\nu=40$ kHz, pulse burst duration 0.1 sec.
Figure 3.52 shows transient pressure in the combustor measured 6 cm upstream and 7 cm downstream of the cavity during combustion, along with OH emission trace at the flow velocity of $u=230$ m/sec and initial pressure of $P=150$ torr. It is evident from the plot that pressures both upstream and downstream of the cavity remained close to the baseline value (within 10 torr), indicating no significant change in the flow velocity after the mixture is ignited. Insignificant pressure rise after ignition is due to low global equivalence ratio, $\varphi=0.033$ at these conditions. Similar results were observed for flow velocities ranging from $u = 100$ m/sec to 200 m/sec.

Figure 3.52: OH emission trace and pressure traces in a non-premixed hydrogen-air flow. Fuel injected into the cavity, $u=230$ m/sec, $\varphi=0.033$. $P=150$ torr, $\nu=40$ kHz, pulse burst duration 0.1 sec.
3.6.3 Time averaged emission spectroscopy measurements

Figure 3.54 plots temperatures measured in the air plasma and in plasma / flame during non-premixed hydrogen-air combustion experiments in the reduced size cavity for different flow velocities, at the same combustor static pressure of P=150 torr. For these measurements, the optical fiber collimator was placed above the high-voltage electrode (see Figure 3.53) to measure the flow temperature in the cavity. N₂ emission was collected over an interval of 100 msec, and temperatures inferred from the emission spectra represent time-averaged values. Therefore, maintaining a stable flame in the test section during the entire emission collection time was critical for accurate flame temperature measurements. From Figure 3.54, it can be seen that air plasma temperatures are much higher (> 500° C) than that observed previously, at the conditions when the plasma was diffuse (see Figure 3.33). Obviously, the high air plasma temperature is due to formation of strong arc filaments, such as shown in Figure 3.49. Temperatures in a stable flame sustained after ignition are observed to exceed 800° C, which is close to the flame temperature measured when diffuse plasma was used to ignite the flow (e.g., see Figure 3.33). This similarity is due to rapid dissipation of filaments after ignition (within 70 pulses, i.e., over 1.75 msec, see Figure 3.50), compared to the emission signal collection time (100 msec). It should be noted that high air plasma temperature suggests that the ignition in this case is predominantly thermal.
3.6.4 Shortcomings of reduced size cavity combustor and possible improvements

The results of present experiments using the reduced size cavity suggest that the electrode design, with high voltage electrode flush mounted in the cavity bottom wall
may be inadequate for producing diffuse plasma in the cavity. In particular, the strong localized electric field near the electrode edges resulted in breakdown through the interface between the ceramic plates covering the electrode, to the grounded metal walls of the test section. This caused arcing between the high voltage electrode and the nearest grounded cavity wall. One way of resolving this problem would be using a cylindrical high voltage electrode configuration as shown in Figure 3.55, similar to that used previously with the large cavity (see Figure 2.5). Although in this case the electrode would occupy some space inside the cavity and would affect the cavity flow pattern, there would be no interface near the electrode, which would greatly reduce the chance of arcing. Also, the combustor needs to be made out of easily machinable dielectric material, such as nylon, with inner walls covered with high temperature resistant macor ceramic plates to protect nylon from heat release during combustion.

Figure 3.55: Schematic of plasma assisted combustion test section with the shallow cavity (L/D=3). Dielectric covered high voltage electrode mounted in one of the side wall windows.
Chapter 4: Kinetic Model

4.1 Kinetic model overview

In the present work, both the flow field and the spatial distribution of power loading in the repetitively pulsed nanosecond discharge are rather complex. Predictive modeling of plasma assisted ignition and flameholding at these conditions requires coupling of the nonequilibrium plasma chemistry model with a 3-D flow code predicting velocity and temperature fields in the test section, as well as fuel-air mixing for non-premixed flows. However, insight into the kinetic mechanism of plasma chemical fuel oxidation and ignition can be obtained by using a relatively simple 0-D hydrogen-air/hydrocarbon-air plasma chemistry model developed in our previous work [23], [45], [46], [51-53]. In short, the model incorporates a nonequilibrium air plasma chemistry model [54], coupled with hydrogen and hydrocarbon fuel (methane and ethylene) dissociation processes in the plasma [45], a hydrogen-oxygen chemistry model developed by Popov [55], and GRI-Mech 3.0 hydrocarbon-air chemistry model [56].

4.2 Air plasma chemistry

The the air plasma model used in the present work contains a set of ordinary differential equations for number densities of neutral species N, N₂, O, O₂, O₃, NO, NO₂,
N₂O, NO₃, charged species e⁺, N⁺, N₂⁺, N₃⁺, N₄⁺, O⁺, O₂⁺, O₄⁺, NO⁺, NO₂⁺, N₂O⁺, N₂O₂⁺, N₂NO⁺, O₂NO⁺, NONO⁺, O, O₂⁻, O₃⁻, NO⁻, NO₂⁻, NO₃⁻, N₂O⁻, and excited species N₂(A³Σ), N₂(B³Π), N₂(C³Π), O₂(a¹Δ), O₂(b¹Σ), O₂(c¹Σ), N(²D), N(²P), O(¹D) produced in the plasma, along with the energy equation for predicting the time-dependent temperature of the mixture [45]. These equations are coupled with the steady, two-term expansion Boltzmann equation for the electron energy distribution function (EEDF) of electrons in the plasma [57]. Experimental cross sections of electron impact electronic excitation, dissociation, ionization, and dissociative attachment processes used in Boltzmann equation are obtained from Refs. [58] and [59]. The Boltzmann equation calculates the rate coefficients of these electron impact processes using cross sections averaged over the EEDF. Chemical reactions of ground state species and excited electronic species, electron-ion recombination and ion-ion neutralization processes, ion-molecule reactions, and electron attachment and detachment processes are also incorporated in the model. Rate coefficients of these processes are obtained from Ref. [54]. The air plasma processes (not including recombination, attachment, and ion-molecule reactions) and the kinetic rates used are listed in Table 4.1. The full list of air plasma processes and their rates can be found in Ref. [54].
<table>
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<tr>
<th>#</th>
<th>Process</th>
<th>Rate</th>
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<td>1</td>
<td>$\text{N}_2 + e^- \rightarrow \text{N}_2(A^3\Sigma) + e^-$</td>
<td>$\sigma^1$</td>
<td>[58]</td>
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<td>$\text{N}_2 + e^+ \rightarrow \text{N}_2(B^3\Pi) + e^-$</td>
<td>$\sigma$</td>
<td>[58]</td>
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<tr>
<td>3</td>
<td>$\text{N}_2 + e^- \rightarrow \text{N}_2(C^3\Pi) + e^-$</td>
<td>$\sigma$</td>
<td>[58]</td>
</tr>
<tr>
<td>4</td>
<td>$\text{N}_2 + e^- \rightarrow \text{N}_2(a^1\Sigma) + e^-$</td>
<td>$\sigma$</td>
<td>[58]</td>
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<tr>
<td>5</td>
<td>$\text{N}_2 + e^- \rightarrow \text{N}(^4\text{S}) + \text{N}(^4\text{S}) + e^-$</td>
<td>$\sigma$</td>
<td>[58]</td>
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<td>6</td>
<td>$\text{N}_2 + e^- \rightarrow \text{N}(^4\text{S}) + \text{N}(^3\text{D}) + e^-$</td>
<td>$\sigma$</td>
<td>[58]</td>
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<tr>
<td>7</td>
<td>$\text{N}_2 + e^- \rightarrow \text{N}(^4\text{S}) + \text{N}(^3\text{P}) + e^-$</td>
<td>$\sigma$</td>
<td>[58]</td>
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<td>8</td>
<td>$\text{O}_2 + e^- \rightarrow \text{O}(^3\text{P}) + \text{O}(^1\text{P}) + e^-$</td>
<td>$\sigma$</td>
<td>[59]</td>
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<td>9</td>
<td>$\text{O}_2 + e^- \rightarrow \text{O}(^3\text{P}) + \text{O}(^1\text{D}) + e^-$</td>
<td>$\sigma$</td>
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<td>[59]</td>
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<td>$\text{O}_2 + e^- \rightarrow \text{O}_2(c^1\Sigma, A^3\Delta, A^3\Sigma) + e^-$</td>
<td>$\sigma$</td>
<td>[59]$^2$</td>
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<td>$\text{N} + \text{O}_2 \rightarrow \text{NO} + \text{O}(^3\text{P})$</td>
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<td>14</td>
<td>$\text{N} + \text{O}_3 \rightarrow \text{NO} + \text{O}_2$</td>
<td>$\leq 2.0\cdot10^{-16}$ cm$^3$/s</td>
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<td>$\text{N} + \text{NO} \rightarrow \text{N}_2 + \text{O}(^3\text{P})$</td>
<td>$1.8\cdot10^{-11}$ cm$^3$/s</td>
<td>[54]</td>
</tr>
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</table>

1 Calculated by the Boltzmann solver from the experimental cross section
2 Three excited electronics levels of $\text{O}_2$, $c^1\Sigma$, $A^3\Delta$, and $A^3\Sigma$, are considered a single excited species, $\text{O}_2(c)$
3 Rate coefficient is calculated from $k_e$ and $k_0$ using expressions in Ref. [54]
4 Ref. [54] assumes $\text{O}_2$ dissociation in this reaction. In the present work, cascade quenching of $\text{N}_2^*$ to a lower electronic level is assumed instead.

Table 4.1: Air plasma processes [45].
Table 4.1 continued

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<td>$9.1 \cdot 10^{-13} \text{ cm}^3/\text{s}$</td>
<td>[54]</td>
</tr>
<tr>
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<td>$N + NO_2 \rightarrow N_2O + O(^3\text{P})$</td>
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</tr>
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<td>19</td>
<td>$N + NO_2 \rightarrow NO + NO$</td>
<td>$2.3 \cdot 10^{-12} \text{ cm}^3/\text{s}$</td>
<td>[54]</td>
</tr>
<tr>
<td>20</td>
<td>$NO_2 + O(^3\text{P}) \rightarrow NO + O_2$</td>
<td>$9.1 \cdot 10^{-12} \text{ cm}^3/\text{s}$</td>
<td>[54]</td>
</tr>
<tr>
<td>21</td>
<td>$O(^3\text{P}) + O_3 \rightarrow O_2 + O_2$</td>
<td>$9.4 \cdot 10^{-15} \text{ cm}^3/\text{s}$</td>
<td>[54]</td>
</tr>
<tr>
<td>22</td>
<td>$NO_3 + O(^3\text{P}) \rightarrow NO_2 + O_2$</td>
<td>$1.0 \cdot 10^{-11} \text{ cm}^3/\text{s}$</td>
<td>[54]</td>
</tr>
<tr>
<td>23</td>
<td>$NO + O_3 \rightarrow NO_2 + O_2$</td>
<td>$2.4 \cdot 10^{-14} \text{ cm}^3/\text{s}$</td>
<td>[54]</td>
</tr>
<tr>
<td>24</td>
<td>$NO + NO_3 \rightarrow NO_2 + NO_2$</td>
<td>$1.7 \cdot 10^{-11} \text{ cm}^3/\text{s}$</td>
<td>[54]</td>
</tr>
<tr>
<td>25</td>
<td>$NO_2 + O_3 \rightarrow NO_3 + O_2$</td>
<td>$3.4 \cdot 10^{-17} \text{ cm}^3/\text{s}$</td>
<td>[54]</td>
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<tr>
<td>26</td>
<td>$NO_3 + NO_3 \rightarrow NO_2 + NO_2 + O_2$</td>
<td>$2.3 \cdot 10^{-16} \text{ cm}^3/\text{s}$</td>
<td>[54]</td>
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<tr>
<td>27</td>
<td>$NO_2 + NO_3 \rightarrow NO + NO_2 + O_2$</td>
<td>$1.1 \cdot 10^{-15} \text{ cm}^3/\text{s}$</td>
<td>[54]</td>
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<td>28</td>
<td>$N + N + M \rightarrow N_2 + M$</td>
<td>$4.4 \cdot 10^{-33} \text{ cm}^6/\text{s}$</td>
<td>[54]</td>
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<td>29</td>
<td>$O(^3\text{P}) + O(^3\text{P}) + N_2 \rightarrow O_2 + N_2$</td>
<td>$3.0 \cdot 10^{-33} \text{ cm}^6/\text{s}$</td>
<td>[54]</td>
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<tr>
<td>30</td>
<td>$O(^3\text{P}) + O(^3\text{P}) + O_2 \rightarrow O_2 + O_2$</td>
<td>$6.7 \cdot 10^{-33} \text{ cm}^6/\text{s}$</td>
<td>[54]</td>
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<tr>
<td>31</td>
<td>$N + O(^3\text{P}) + M \rightarrow NO + M$</td>
<td>$1.0 \cdot 10^{-32} \text{ cm}^6/\text{s}$</td>
<td>[54]</td>
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<tr>
<td>32</td>
<td>$O(^3\text{P}) + O_2 + N_2 \rightarrow O_3 + N_2$</td>
<td>$6.2 \cdot 10^{-34} \text{ cm}^6/\text{s}$</td>
<td>[54]</td>
</tr>
<tr>
<td>33</td>
<td>$O(^3\text{P}) + O_2 + O_2 \rightarrow O_3 + O_2$</td>
<td>$6.9 \cdot 10^{-34} \text{ cm}^6/\text{s}$</td>
<td>[54]</td>
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<table>
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<tr>
<td>34</td>
<td>NO + O(3P) (+ M) → NO₂ (+ M)</td>
<td>$k_\infty=3.0\cdot10^{-11}$ cm³/s</td>
<td>[54]^3</td>
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<td></td>
<td></td>
<td>$k_0=6.3\cdot10^{-32}$ cm⁶/s</td>
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<tr>
<td>35</td>
<td>NO₂ + O(3P) (+ M) → NO₃ (+ M)</td>
<td>$k_\infty=2.2\cdot10^{-11}$ cm³/s</td>
<td>[54]^3</td>
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<td></td>
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<td>$k_0=9.0\cdot10^{-32}$ cm⁶/s</td>
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<tr>
<td>36</td>
<td>NO₂ + NO₂ (+ M) → N₂O₄ (+ M)</td>
<td>$k_\infty=8.3\cdot10^{-13}$ cm³/s</td>
<td>[54]^3</td>
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<tr>
<td></td>
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<td>$k_0=6.6\cdot10^{-34}$ cm⁶/s</td>
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<tr>
<td>37</td>
<td>NO₂ + NO₃ (+ M) → N₂O₅ (+ M)</td>
<td>$k_\infty=1.6\cdot10^{-12}$ cm³/s</td>
<td>[54]^3</td>
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<tr>
<td></td>
<td></td>
<td>$k_0=3.7\cdot10^{-30}$ cm⁶/s</td>
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<tr>
<td>38</td>
<td>N₂(A³Σ) + O₂ → N₂ + O(3P) + O(3P)</td>
<td>$1.7\cdot10^{-12}$ cm³/s</td>
<td>[54]</td>
</tr>
<tr>
<td>39</td>
<td>N₂(A³Σ) + O₂ → N₂(v) + O₂(b¹Σ)</td>
<td>$7.5\cdot10^{-13}$ cm³/s</td>
<td>[54]</td>
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<td>40</td>
<td>N₂(A³Σ) + O₂ → N₂O + O(3P)</td>
<td>$7.8\cdot10^{-14}$ cm³/s</td>
<td>[54]</td>
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<tr>
<td>41</td>
<td>N₂(A³Σ) + O(3P) → NO + N(4D)</td>
<td>$7.0\cdot10^{-12}$ cm³/s</td>
<td>[54]</td>
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<tr>
<td>42</td>
<td>N₂(A³Σ) + N₂O → NO + N + N₂</td>
<td>$1.0\cdot10^{-11}$ cm³/s</td>
<td>[54]</td>
</tr>
<tr>
<td>43</td>
<td>N₂(A³Σ) + N₂O → N₂ + N + NO</td>
<td>$1.0\cdot10^{-11}$ cm³/s</td>
<td>[54]</td>
</tr>
<tr>
<td>44</td>
<td>N₂(A³Σ) + N₂(A³Σ) → N₂ + N₂(3Σg)</td>
<td>$1.6\cdot10^{-10}$ cm³/s</td>
<td>[54]</td>
</tr>
<tr>
<td>45</td>
<td>N₂(A³Σ) + N₂ → N₂ + N₂</td>
<td>$3.0\cdot10^{-18}$ cm³/s</td>
<td>[54]</td>
</tr>
<tr>
<td>46</td>
<td>N₂(A³Σ) + N → N₂ + N(3P)</td>
<td>$5.0\cdot10^{-11}$ cm³/s</td>
<td>[54]</td>
</tr>
<tr>
<td>47</td>
<td>N₂(A³Σ) + O(3P) → N₂ + O(1D)</td>
<td>$2.1\cdot10^{-11}$ cm³/s</td>
<td>[54]</td>
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</table>

Continued
Table 4.1 continued

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<tr>
<td>48</td>
<td>$N_2(A^3\Sigma) + NO \rightarrow N_2 + NO$</td>
<td>$7.0 \cdot 10^{-11}$ cm$^3$/s</td>
<td>[54]</td>
</tr>
<tr>
<td>49</td>
<td>$N_2(B^3\Pi) + N_2 \rightarrow N_2(A^3\Sigma) + N_2$</td>
<td>$5.0 \cdot 10^{-11}$ cm$^3$/s</td>
<td>[45]</td>
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<tr>
<td>50</td>
<td>$N_2(B^3\Pi)</td>
<td></td>
<td></td>
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</table><p>ightarrow N_2(A^3\Sigma) + h\nu$                       | $1.5 \cdot 10^5$ 1/s       | [54]      |
| 51 | $N_2(B^3\Pi) + NO \rightarrow N_2(A^3\Sigma) + NO$                    | $2.4 \cdot 10^{-10}$ cm$^3$/s | [54]      |
| 52 | $N_2(B^3\Pi) + O_2 \rightarrow N_2 (A^3\Sigma) + O_2$                 | $3.0 \cdot 10^{-10}$ cm$^3$/s | [54$^4$] |
| 53 | $N_2(a^1\Sigma) + N_2 \rightarrow N_2(B^3\Pi) + N_2$                   | $2.0 \cdot 10^{-13}$ cm$^3$/s | [54]      |
| 54 | $N_2(a^1\Sigma) + O_2 \rightarrow N_2 (B^3\Pi) + O_2$                 | $2.8 \cdot 10^{-11}$ cm$^3$/s | [54$^4$] |
| 55 | $N_2(a^1\Sigma) + NO \rightarrow N_2 + N + O(3P)$                      | $3.6 \cdot 10^{-10}$ cm$^3$/s | [54]      |
| 56 | $N_2(C^3\Pi) + N_2 \rightarrow N_2(a^1\Sigma) + N_2$                   | $1.0 \cdot 10^{-11}$ cm$^3$/s | [54]      |
| 57 | $N_2(C^3\Pi)ightarrow N_2(B^3\Pi) + N_2$                            | $3.0 \cdot 10^7$ 1/s       | [54]      |
| 58 | $N_2(C^3\Pi) + O_2 \rightarrow N_2(B^3\Pi) + O_2$                      | $3.0 \cdot 10^{-10}$ cm$^3$/s | [54$^4$] |
| 59 | $N_2(X^1\Sigma,v) + N_2 \rightarrow N_2 + N_2$                         | $2.0 \cdot 10^{-15}$ cm$^3$/s | [60]      |
| 60 | $N_2(X^1\Sigma,v) + CH_4 \rightarrow N_2 + CH_4$                       | $1.0 \cdot 10^{-14}$ cm$^3$/s | [60]      |
| 61 | $N_2(X^1\Sigma,v) + C_2H_4 \rightarrow N_2 + C_2H_4$                   | $1.0 \cdot 10^{-14}$ cm$^3$/s | estimate |
| 62 | $N_2(X^1\Sigma,v) + O(3P) \rightarrow NO + N$                         | $5.0 \cdot 10^{-11}$ cm$^3$/s | estimate |
| 63 | $O_2(a^1\Delta) + O_3 \rightarrow O_2 + O_2 + O(3P)$                   | $5.3 \cdot 10^{-15}$ cm$^3$/s | [54]      |
| 64 | $O_2(a^1\Delta) + N \rightarrow NO + O(3P)$                           | $2.7 \cdot 10^{-15}$ cm$^3$/s | [54]      |
| 65 | $O_2(a^1\Delta) + N_2 \rightarrow N_2 + O_2$                          | $3.0 \cdot 10^{-21}$ cm$^3$/s | [54]      |</p>
Table 4.1 continued

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<tbody>
<tr>
<td>66</td>
<td>( \text{O}_2(a^1\Delta) + \text{O}_2 \rightarrow \text{O}_2 + \text{O}_2 )</td>
<td>( 2.2 \times 10^{-18} \text{ cm}^3/\text{s} )</td>
<td>[54]</td>
</tr>
<tr>
<td>67</td>
<td>( \text{O}_2(a^1\Delta) + \text{O}(^3\text{P}) \rightarrow \text{O}_2 + \text{O}(^3\text{P}) )</td>
<td>( 7.0 \times 10^{-16} \text{ cm}^3/\text{s} )</td>
<td>[54]</td>
</tr>
<tr>
<td>68</td>
<td>( \text{O}_2(a^1\Delta) + \text{NO} \rightarrow \text{O}_2 + \text{NO} )</td>
<td>( 2.5 \times 10^{-11} \text{ cm}^3/\text{s} )</td>
<td>[54]</td>
</tr>
<tr>
<td>69</td>
<td>( \text{O}_2(b^1\Sigma) + \text{O}_3 \rightarrow \text{O}(^3\text{P}) + \text{O}_2 + \text{O}_2 )</td>
<td>( 1.8 \times 10^{-11} \text{ cm}^3/\text{s} )</td>
<td>[54]</td>
</tr>
<tr>
<td>70</td>
<td>( \text{O}_2(b^1\Sigma) + \text{N} \rightarrow \text{O}_2(a^1\Delta) + \text{N} )</td>
<td>( 1.0 \times 10^{-13} \text{ cm}^3/\text{s} )</td>
<td>[61] (estimate)</td>
</tr>
<tr>
<td>71</td>
<td>( \text{O}_2(b^1\Sigma) + \text{N} \rightarrow \text{NO} + \text{O}(^3\text{P}) )</td>
<td>( 2.5 \times 10^{-10} \text{ cm}^3/\text{s} )</td>
<td>estimate</td>
</tr>
<tr>
<td>72</td>
<td>( \text{O}_2(b^1\Sigma) + \text{N}_2 \rightarrow \text{O}_2(a^1\Delta) + \text{N}_2 )</td>
<td>( 2.1 \times 10^{-15} \text{ cm}^3/\text{s} )</td>
<td>[54]</td>
</tr>
<tr>
<td>73</td>
<td>( \text{O}_2(b^1\Sigma) + \text{O}_2 \rightarrow \text{O}_2(a^1\Delta) + \text{O}_2 )</td>
<td>( 1.7 \times 10^{-16} \text{ cm}^3/\text{s} )</td>
<td>[54]</td>
</tr>
<tr>
<td>74</td>
<td>( \text{O}_2(b^1\Sigma) + \text{O}(^3\text{P}) \rightarrow \text{O}_2(a^1\Delta) + \text{O}(^3\text{P}) )</td>
<td>( 8.0 \times 10^{-14} \text{ cm}^3/\text{s} )</td>
<td>[54]</td>
</tr>
<tr>
<td>75</td>
<td>( \text{O}_2(b^1\Sigma) + \text{O}(^3\text{P}) \rightarrow \text{O}_2 + \text{O}(^1\text{D}) )</td>
<td>( 2.8 \times 10^{-17} \text{ cm}^3/\text{s} )</td>
<td>[54]</td>
</tr>
<tr>
<td>76</td>
<td>( \text{O}_2(b^1\Sigma) + \text{NO} \rightarrow \text{O}_2(a^1\Delta) + \text{NO} )</td>
<td>( 4.0 \times 10^{-14} \text{ cm}^3/\text{s} )</td>
<td>[54]</td>
</tr>
<tr>
<td>77</td>
<td>( \text{O}_2(c) + \text{O}_2 \rightarrow \text{O}_2(b^1\Sigma) + \text{O}_2(b) )</td>
<td>( 2.9 \times 10^{-13} \text{ cm}^3/\text{s} )</td>
<td>[54]²</td>
</tr>
<tr>
<td>78</td>
<td>( \text{O}_2(c) + \text{N}_2 \rightarrow \text{O}_2(b^1\Sigma) + \text{N}_2 )</td>
<td>( 3.0 \times 10^{-13} \text{ cm}^3/\text{s} )</td>
<td>[54]²</td>
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<tr>
<td>79</td>
<td>( \text{O}_2(c) + \text{O}(^3\text{P}) \rightarrow \text{O}_2(b^1\Sigma) + \text{O}(^1\text{D}) )</td>
<td>( 9.0 \times 10^{-12} \text{ cm}^3/\text{s} )</td>
<td>[54]²</td>
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<td>80</td>
<td>( \text{N}(^2\text{D}) + \text{O}_2 \rightarrow \text{NO} + \text{O}(^3\text{P}) )</td>
<td>( 1.5 \times 10^{-12} \text{ cm}^3/\text{s} )</td>
<td>[54]</td>
</tr>
<tr>
<td>81</td>
<td>( \text{N}(^2\text{D}) + \text{O}_2 \rightarrow \text{NO} + \text{O}(^1\text{D}) )</td>
<td>( 6.0 \times 10^{-12} \text{ cm}^3/\text{s} )</td>
<td>[54]</td>
</tr>
<tr>
<td>82</td>
<td>( \text{N}(^2\text{D}) + \text{NO} \rightarrow \text{N}_2\text{O} )</td>
<td>( 6.0 \times 10^{-11} \text{ cm}^3/\text{s} )</td>
<td>[54]</td>
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Table 4.1 continued

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<th>Reference</th>
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<tbody>
<tr>
<td>83</td>
<td>N((^2)D) + N(_2)O → NO + N(_2)</td>
<td>3.0 (\times) 10^{12} cm(^3)/s</td>
<td>[54]</td>
</tr>
<tr>
<td>84</td>
<td>N((^2)D) + N(_2) → N + N(_2)</td>
<td>6.0 (\times) 10^{15} cm(^3)/s</td>
<td>[54]</td>
</tr>
<tr>
<td>85</td>
<td>N((^2)P) + O(_2) → NO + O((^3)P)</td>
<td>2.6 (\times) 10^{12} cm(^3)/s</td>
<td>[54]</td>
</tr>
<tr>
<td>86</td>
<td>N((^2)P) + NO → N(_2)(A(^3)\Sigma) + O((^3)P)</td>
<td>3.4 (\times) 10^{11} cm(^3)/s</td>
<td>[54]</td>
</tr>
<tr>
<td>87</td>
<td>N((^2)P) + N(_2) → N((^2)D) + N(_2)</td>
<td>2.0 (\times) 10^{18} cm(^3)/s</td>
<td>[54]</td>
</tr>
<tr>
<td>88</td>
<td>N((^2)P) + N → N((^2)D) + N</td>
<td>1.8 (\times) 10^{12} cm(^3)/s</td>
<td>[54]</td>
</tr>
<tr>
<td>89</td>
<td>O((^1)D) + N(_2) → O((^3)P) + N(_2)</td>
<td>2.6 (\times) 10^{11} cm(^3)/s</td>
<td>[54]</td>
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<tr>
<td>90</td>
<td>O((^1)D) + O(_2) → O((^3)P) + O(_2)(b)</td>
<td>3.2 (\times) 10^{11} cm(^3)/s</td>
<td>[54]</td>
</tr>
<tr>
<td>91</td>
<td>O((^1)D) + O(_2) → O((^3)P) + O(_2)</td>
<td>8.0 (\times) 10^{12} cm(^3)/s</td>
<td>[54]</td>
</tr>
<tr>
<td>92</td>
<td>O((^1)D) + O(_3) → O(_2) + O((^3)P) + O((^3)P)</td>
<td>1.2 (\times) 10^{10} cm(^3)/s</td>
<td>[54]</td>
</tr>
<tr>
<td>93</td>
<td>O((^1)D) + O(_3) → O(_2) + O(_2)</td>
<td>1.2 (\times) 10^{10} cm(^3)/s</td>
<td>[54]</td>
</tr>
<tr>
<td>94</td>
<td>O((^1)D) + NO → N + O(_2)</td>
<td>1.7 (\times) 10^{10} cm(^3)/s</td>
<td>[54]</td>
</tr>
<tr>
<td>95</td>
<td>O((^1)D) + N(_2)O → NO + NO</td>
<td>7.2 (\times) 10^{11} cm(^3)/s</td>
<td>[54]</td>
</tr>
<tr>
<td>96</td>
<td>O((^1)D) + N(_2)O → N(_2) + O(_2)</td>
<td>4.4 (\times) 10^{11} cm(^3)/s</td>
<td>[54]</td>
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</table>
4.3 Hydrogen-air chemistry

The hydrogen-air plasma chemical oxidation kinetic model incorporates hydrogen dissociation processes in the plasma and the hydrogen-oxygen chemistry model (22 reactions among H, O, OH, H₂, O₂, H₂O, HO₂, and H₂O₂) developed by Popov [55]. The dominant radical species (O, H, and OH) generation processes in the hydrogen-air plasma are listed in Table 4.2. The rates of electron impact processes in the species concentration equations are predicted using a two-term expansion Boltzmann equation for the energy distribution function of plasma electrons, with electron impact cross sections taken from [58], [59], [62]. The Boltzmann equation was solved for the initial composition of the fuel-air mixture. The list of hydrogen-oxygen chemical reactions and their rates (the full mechanism suggested by Popov [55]) is given in Table 4.3. A reduced mechanism of hydrogen-oxygen chemistry previously developed in Ref. [63] from Popov’s full mechanism using sensitivity analysis is also used in this work. The reduced mechanism reactions are listed in Table 4.4.
<table>
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<td>P1</td>
<td>N₂ + e⁻ = N₂(A₃Σ, B³Π, C³Π, a¹Σ) + e⁻</td>
<td>σ¹</td>
<td>[58]</td>
</tr>
<tr>
<td>P2</td>
<td>N₂ + e⁻ = N(c⁶Σ) + N(c⁶S) + e</td>
<td>σ</td>
<td>[58]</td>
</tr>
<tr>
<td>P3</td>
<td>O₂ + e⁻ = O(3P) + O(3P, 1D) + e⁻</td>
<td>σ</td>
<td>[59]</td>
</tr>
<tr>
<td>P4</td>
<td>N₂(C³Π) + O₂ = N₂(B²Π) + O₂</td>
<td>3.0 · 10⁻¹⁰ cm³/s</td>
<td>[54]</td>
</tr>
<tr>
<td>P5</td>
<td>N₂(a¹Σ) + O₂ = N₂(B³Π) + O₂</td>
<td>2.8 · 10⁻¹¹ cm³/s</td>
<td>[54]</td>
</tr>
<tr>
<td>P6</td>
<td>N₂(B³Π) + O₂ = N₂(A³Σ) + O₂</td>
<td>3.0 · 10⁻¹⁰ cm³/s</td>
<td>[54]</td>
</tr>
<tr>
<td>P7</td>
<td>N₂(A³Σ) + O₂ = N₂ + O + O</td>
<td>2.5 · 10⁻¹² cm³/s</td>
<td>[54]</td>
</tr>
<tr>
<td>P8</td>
<td>H₂ + e⁻ = H + H + e⁻</td>
<td>σ²</td>
<td>[62]</td>
</tr>
<tr>
<td>P9</td>
<td>N₂(a¹Σ) + H₂ = N₂ + H + H</td>
<td>2.6 · 10⁻¹¹ cm³/s</td>
<td>[55]</td>
</tr>
<tr>
<td>P10</td>
<td>N₂(B³Π) + H₂ = N₂(A³Σ) + H₂</td>
<td>2.5 · 10⁻¹¹ cm³/s</td>
<td>[55]</td>
</tr>
<tr>
<td>P11</td>
<td>N₂(A³Σ) + H₂ = N₂ + H + H</td>
<td>4.4 · 10⁻¹⁰ exp(⁻3500/T) cm³/s</td>
<td>[55]</td>
</tr>
<tr>
<td>P12</td>
<td>O(¹D) + H₂ = H + OH</td>
<td>1.1 · 10⁻¹⁰ cm³/s</td>
<td>[55]</td>
</tr>
</tbody>
</table>

¹ Calculated by the Boltzmann solver from the experimental cross sections

² Sum of electronic excitation cross sections (b³Σ, b¹Σ, c³Π, a³Σ, c¹Π, and d³Π)

Table 4.2: Dominant radical species generation processes in hydrogen-air plasma [64].
<table>
<thead>
<tr>
<th>#</th>
<th>Reaction</th>
<th>Forward rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>H + O₂ + M = HO₂ + M</td>
<td>5.8·10⁻³⁰ T⁻⁰.⁸ cm⁶/s</td>
</tr>
<tr>
<td>2</td>
<td>OH + H₂ = H + H₂O</td>
<td>1.7·10⁻¹⁶ T⁻¹.⁶ exp(-1660/T) cm³/s</td>
</tr>
<tr>
<td>3</td>
<td>O + H₂ = H + OH</td>
<td>8.5·10⁻²⁰ T²⁺°.⁶ exp(-3160/T) cm³/s</td>
</tr>
<tr>
<td>4</td>
<td>O + OH = H + O₂</td>
<td>2.4·10⁻¹¹ exp(-353/T) cm³/s</td>
</tr>
<tr>
<td>5</td>
<td>H₂ + O₂ = OH + OH</td>
<td>1.0·10⁻⁹ exp(24180/T) cm³/s</td>
</tr>
<tr>
<td>6</td>
<td>O + HO₂ = OH + O₂</td>
<td>3.0·10⁻¹¹ exp(200/T) cm³/s</td>
</tr>
<tr>
<td>7</td>
<td>OH + HO₂ = H₂O + O₂</td>
<td>4.8·10⁻¹¹ exp(250/T) cm³/s</td>
</tr>
<tr>
<td>8</td>
<td>H + HO₂ = H₂O + O</td>
<td>5.0·10⁻¹¹ exp(-866/T) cm³/s</td>
</tr>
<tr>
<td>9</td>
<td>H + HO₂ = OH + OH</td>
<td>2.8·10⁻¹⁰ exp(-440/T) cm³/s</td>
</tr>
<tr>
<td>10</td>
<td>OH + OH = H₂O + O</td>
<td>2.5·10⁻¹⁵ T⁻¹.¹⁴ exp(50/T) cm³/s</td>
</tr>
<tr>
<td>11</td>
<td>H + OH + M = H₂O + M</td>
<td>6.1·10⁻³⁶ T⁻².⁰ cm⁶/s</td>
</tr>
<tr>
<td>12</td>
<td>H + H + M = H₂ + M</td>
<td>5.14·10⁻³⁰ T⁻¹.⁰ cm⁶/s</td>
</tr>
<tr>
<td>13</td>
<td>O + O + M = O₂ + M</td>
<td>2.37·10⁻³¹ T⁻⁰.⁶³ cm⁶/s</td>
</tr>
<tr>
<td>14</td>
<td>H + O + M = OH + M</td>
<td>1.3·10⁻²⁹ T⁻¹.⁰ cm⁶/s</td>
</tr>
<tr>
<td>15</td>
<td>H + HO₂ = H₂ + O₂</td>
<td>1.1·10⁻¹⁰ exp(-1070/T) cm³/s</td>
</tr>
<tr>
<td>16</td>
<td>HO₂ + H₂ = OH + H₂O</td>
<td>1.08·10⁻¹² exp(-9400/T) cm³/s</td>
</tr>
<tr>
<td>17</td>
<td>HO₂ + HO₂ = H₂O₂ + O₂</td>
<td>3.1·10⁻¹² exp(775/T) cm³/s</td>
</tr>
<tr>
<td>18</td>
<td>OH + OH + M = H₂O₂ + M</td>
<td>6.1·10⁻²⁹ T⁻⁰.⁷⁶ cm⁶/s</td>
</tr>
<tr>
<td>19</td>
<td>OH + H₂O₂ = HO₂ + H₂O</td>
<td>1.3·10⁻¹¹ exp(670/T) cm³/s</td>
</tr>
<tr>
<td>20</td>
<td>H + H₂O₂ = HO₂ + H₂</td>
<td>2.8·10⁻¹² exp(1890/T) cm³/s</td>
</tr>
<tr>
<td>21</td>
<td>H + H₂O₂ = OH + H₂O</td>
<td>1.7·10⁻¹¹ exp(1800/T) cm³/s</td>
</tr>
<tr>
<td>22</td>
<td>O + H₂O₂ = OH + HO₂</td>
<td>5.5·10⁻¹³ exp(2000/T) cm³/s</td>
</tr>
</tbody>
</table>

Table 4.3: Full H₂O₂ chemical reaction mechanisms suggested by Popov [55].
<table>
<thead>
<tr>
<th>#</th>
<th>Reaction</th>
<th>Forward rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1</td>
<td>( \text{H + O}_2 + \text{M} = \text{HO}_2 + \text{M} )</td>
<td>( 5.8 \times 10^{-30} \ T^{-0.8} \ cm^6/s )</td>
</tr>
<tr>
<td>C2</td>
<td>( \text{O + HO}_2 = \text{OH} + \text{O}_2 )</td>
<td>( 3.0 \times 10^{-11} \ \text{exp}(200/T) \ cm^3/s )</td>
</tr>
<tr>
<td>C3</td>
<td>( \text{OH + H}_2 = \text{H + H}_2\text{O} )</td>
<td>( 1.7 \times 10^{-16} \ T^{-1.6} \ \text{exp}(-1660/T) \ cm^3/s )</td>
</tr>
<tr>
<td>C4</td>
<td>( \text{O + H}_2 = \text{H + OH} )</td>
<td>( 8.5 \times 10^{-20} \ T^{2.67} \ \text{exp}(-3160/T) \ cm^3/s )</td>
</tr>
<tr>
<td>C5</td>
<td>( \text{H + HO}_2 = \text{H}_2\text{O + O} )</td>
<td>( 5.0 \times 10^{-11} \ \text{exp}(-866/T) \ cm^3/s )</td>
</tr>
<tr>
<td>C6</td>
<td>( \text{H + HO}_2 = \text{OH + OH} )</td>
<td>( 2.8 \times 10^{-10} \ \text{exp}(-440/T) \ cm^3/s )</td>
</tr>
<tr>
<td>C7</td>
<td>( \text{H + HO}_2 = \text{H}_2 + \text{O}_2 )</td>
<td>( 1.1 \times 10^{-10} \ \text{exp}(-1070/T) \ cm^3/s )</td>
</tr>
<tr>
<td>C8</td>
<td>( \text{O + OH = H + O}_2 )</td>
<td>( 2.4 \times 10^{-11} \ \text{exp}(-353/T) \ cm^3/s )</td>
</tr>
<tr>
<td>C9</td>
<td>( \text{OH + HO}_2 = \text{H}_2\text{O + O}_2 )</td>
<td>( 4.8 \times 10^{-11} \ \text{exp}(250/T) \ cm^3/s )</td>
</tr>
</tbody>
</table>

Table 4.4: Reduced \( \text{H}_2\text{O}_2 \) chemical reaction set obtained from the full mechanism suggested by Popov [55], given in Table 4.3.

### 4.4 Hydrocarbon-air chemistry

To model ethylene-air plasmas, the air plasma kinetic model was combined with either the full GRI Mech 3.0 [56] or a reduced kinetic mechanism (reduced UCSD mechanism) developed in Ref. [65] for ethylene-air combustion, and supplemented with ethylene dissociation by electron impact and in reactions with electronically excited nitrogen molecules. Note that the reduced UCSD mechanism has been obtained from the full ethylene-air combustion mechanism listed in Ref. [65], rather than from GRI Mech 3.0 mechanism, and therefore these mechanisms yield somewhat different results even for thermal ignition of ethylene. It is well known that the GRI Mech 3.0 mechanism is not very accurate when used for kinetic modeling of ethylene-air ignition and flame propagation [56], mainly because it lacks key primary radicals generation/chain initiation.
reactions, such as \( \text{C}_2\text{H}_4 + \text{O}_2 = \text{C}_2\text{H}_3 + \text{HO}_2 \) and \( \text{C}_2\text{H}_4 + \text{HO}_2 = \text{CH}_3\text{CHO} + \text{OH} \).

However, GRI Mech 3.0 is used in the present work to analyze plasma assisted ignition of ethylene-air. This is justified by the fact that in the nonequilibrium plasma, dominant radical generation reactions are those of electron impact dissociation of oxygen and fuel, as well as quenching of electronically excited nitrogen molecules, listed in Table 4.2 and Table 4.7, rather than thermal dissociation.

In the present work, comparison of GRI Mech 3.0, reduced GRI mechanism, and reduced UCSD mechanisms for plasma assisted ignition is done to explore the effect of plasma chemistry on conventional chemical reaction sets, which yield similar results at thermal equilibrium conditions. The reduced GRI mechanism listed in Table 4.5, was developed from GRI Mech 3.0 in Ref. [40] using sensitivity analysis for single pulse nanosecond discharge. The reduced UCSD mechanism reactions are listed in Table 4.6. Cross sections and rate coefficients of electron impact processes and reactions with electronically excited nitrogen were taken from [66-68]. In particular, theoretical electron impact dissociation cross sections of ethylene into \( \text{C}_2\text{H}_3 + \text{H} \), \( \text{C}_2\text{H}_2 + \text{H}_2 \), \( \text{C}_2\text{H}_2 + \text{H} + \text{H} \), and \( \text{C}_2\text{H} + \text{H}_2 + \text{H} \) [66], have been used. In ethylene dissociation reactions by electronically excited nitrogen molecules, the quantum yield for H atom production was assumed to be equal to one, i.e. dissociation into \( \text{C}_2\text{H}_3 + \text{H} \) was assumed. The list of these processes and their rates is also given in the Table 4.7.
<table>
<thead>
<tr>
<th>#</th>
<th>Process</th>
<th>Rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>O + C₂H₄ = CH₃ + HCO</td>
<td>2.08·10⁻¹⁷ T⁻¹.₈³ exp(110.78/T) cm³/s</td>
</tr>
<tr>
<td>2</td>
<td>O + C₂H₄ = H + CH₂CHO</td>
<td>1.11·10⁻¹⁷ T⁻¹.₈³ exp(110.78/T) cm³/s</td>
</tr>
<tr>
<td>3</td>
<td>C₂H₃ + O₂ = HCO + CH₂O</td>
<td>7.60·10⁻⁸ T⁻¹.₃⁹ exp(511.12/T) cm³/s</td>
</tr>
<tr>
<td>4</td>
<td>C₂H₃ + O₂ = O + CH₂CHO</td>
<td>5.03·10⁻¹³ T⁰.₂⁹ exp(5.54/T) cm³/s</td>
</tr>
<tr>
<td>5</td>
<td>O + CH₂CHO = H + CH₂ + CO₂</td>
<td>2.49·10⁻¹⁰ cm³/s</td>
</tr>
<tr>
<td>6</td>
<td>H + O₂ + M = HO₂ + M</td>
<td>7.72·10⁻₃⁰ T⁻₀.₈₆ cm⁶/s</td>
</tr>
<tr>
<td>7</td>
<td>H + O₂ + O₂ = HO₂ + O₂</td>
<td>5.73·10⁻₂⁹ T⁻₁.₂⁴ cm⁶/s</td>
</tr>
<tr>
<td>8</td>
<td>H + O₂ + N₂ = HO₂ + N₂</td>
<td>7.17·10⁻₂⁹ T⁻¹.₂⁴ cm⁶/s</td>
</tr>
<tr>
<td>9</td>
<td>O + HO₂ = OH + O₂</td>
<td>3.32·10⁻¹¹ cm³/s</td>
</tr>
<tr>
<td>10</td>
<td>OH + HO₂ = O₂ + H₂O</td>
<td>2.41·10⁻¹¹ exp(-251.78/T) cm³/s</td>
</tr>
<tr>
<td>11</td>
<td>OH + C₂H₄ = C₂H₃ + H₂O</td>
<td>5.98·10⁻₁₈ T².₀ exp(1258.91/T) cm³/s</td>
</tr>
<tr>
<td>12</td>
<td>HO₂ + CH₃ = OH + CH₃O</td>
<td>6.28·10⁻₁² cm³/s</td>
</tr>
<tr>
<td>13</td>
<td>CH₃O + O₂ = HO₂ + CH₂O</td>
<td>7.11·10⁻₃⁷ T⁻⁷.₆₀ exp(-1777.58/T) cm³/s</td>
</tr>
<tr>
<td>14</td>
<td>O₂ + CH₂CHO = OH + HCO + HCO</td>
<td>3.90·10⁻¹⁴ cm³/s</td>
</tr>
<tr>
<td>15</td>
<td>HO₂ + HO₂ = O₂ + H₂O₂</td>
<td>2.16·10⁻¹³ exp(-820.81/T) cm³/s</td>
</tr>
<tr>
<td>16</td>
<td>HCO + O₂ = HO₂ + CO</td>
<td>2.24·10⁻¹₁ exp(201.43/T) cm³/s</td>
</tr>
<tr>
<td>17</td>
<td>CH₂ + O₂ = H + H + CO₂</td>
<td>9.63·10⁻₁² exp(755.35/T) cm³/s</td>
</tr>
</tbody>
</table>

Table 4.5: Reduced GRI mechanism [40].
<table>
<thead>
<tr>
<th>#</th>
<th>Process</th>
<th>Rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>( H + O_2 = O + OH )</td>
<td>( 5.84 \times 10^{-8} \ T^{-0.70} \exp(8587.78/T) \ \text{cm}^3/\text{s} )</td>
</tr>
<tr>
<td>2</td>
<td>( \text{OH + H}_2 = \text{H} + \text{H}_2\text{O} )</td>
<td>( 1.94 \times 10^{-15} \ T^{1.30} \exp(1827.94/T) \ \text{cm}^3/\text{s} )</td>
</tr>
<tr>
<td>3</td>
<td>( \text{OH + OH} = \text{O} + \text{H}_2\text{O} )</td>
<td>( 4.07 \times 10^{-25} \ T^{3.97} \exp(-2285.17/T) \ \text{cm}^3/\text{s} )</td>
</tr>
<tr>
<td>4</td>
<td>( \text{H} + \text{O}_2 + \text{O}_2 = \text{HO}_2 + \text{O}_2 )</td>
<td>( 2.15 \times 10^{-29} \ T^{-1.20} \ \text{cm}^6/\text{s} )</td>
</tr>
<tr>
<td>4</td>
<td>( \text{H} + \text{O}_2 + \text{H}_2\text{O} = \text{HO}_2 + \text{H}_2\text{O} )</td>
<td>( 5.02 \times 10^{-28} \ T^{-1.70} \ \text{cm}^6/\text{s} )</td>
</tr>
<tr>
<td>4</td>
<td>( \text{H} + \text{O}_2 + \text{CO} = \text{HO}_2 + \text{CO} )</td>
<td>( 4.82 \times 10^{-29} \ T^{-1.70} \ \text{cm}^6/\text{s} )</td>
</tr>
<tr>
<td>4</td>
<td>( \text{H} + \text{O}_2 + \text{CO}_2 = \text{HO}_2 + \text{CO}_2 )</td>
<td>( 1.08 \times 10^{-28} \ T^{-1.70} \ \text{cm}^6/\text{s} )</td>
</tr>
<tr>
<td>4</td>
<td>( \text{H} + \text{O}_2 + \text{N}_2 = \text{HO}_2 + \text{N}_2 )</td>
<td>( 7.17 \times 10^{-29} \ T^{-1.20} \ \text{cm}^6/\text{s} )</td>
</tr>
<tr>
<td>4</td>
<td>( \text{H} + \text{O}_2 + \text{AR} = \text{HO}_2 + \text{AR} )</td>
<td>( 3.58 \times 10^{-29} \ T^{-1.20} \ \text{cm}^6/\text{s} )</td>
</tr>
<tr>
<td>5</td>
<td>( \text{H} + \text{HO}_2 = \text{OH} + \text{OH} )</td>
<td>( 2.82 \times 10^{-10} \ \exp(445.15/T) \ \text{cm}^3/\text{s} )</td>
</tr>
<tr>
<td>6</td>
<td>( \text{H} + \text{HO}_2 = \text{O}_2 + \text{H}_2 )</td>
<td>( 7.11 \times 10^{-11} \ \exp(709.52/T) \ \text{cm}^3/\text{s} )</td>
</tr>
<tr>
<td>7</td>
<td>( \text{OH} + \text{HO}_2 = \text{O}_2 + \text{H}_2\text{O} )</td>
<td>( 4.80 \times 10^{-11} \ \exp(-252.79/T) \ \text{cm}^3/\text{s} )</td>
</tr>
<tr>
<td>8</td>
<td>( \text{HO}_2 + \text{HO}_2 = \text{O}_2 + \text{H}_2\text{O}_2 )</td>
<td>( 5.01 \times 10^{-12} \ \exp(697.44/T) \ \text{cm}^3/\text{s} )</td>
</tr>
<tr>
<td>9</td>
<td>( \text{H}_2\text{O}_2 = \text{OH} + \text{OH} )</td>
<td>( 2.55 \times 10^{-20} \ T^{-1.68} \ \exp(26351.49/T) \ \text{1/s} )</td>
</tr>
<tr>
<td>10</td>
<td>( \text{H}_2\text{O}_2 + \text{M} = \text{OH} + \text{OH} + \text{M} )</td>
<td>( 13.2 \ T^{-2.21} \ \exp(-25497.95/T) \ \text{cm}^3/\text{s} )</td>
</tr>
<tr>
<td>11</td>
<td>( \text{H} + \text{OH} + \text{O}_2 = \text{H}_2\text{O} + \text{O}_2 )</td>
<td>( 61.82 \times 10^{-26} \ T^{-2.0} \ \text{cm}^6/\text{s} )</td>
</tr>
<tr>
<td>11</td>
<td>( \text{H} + \text{OH} + \text{H}_2\text{O} = \text{H}_2\text{O} + \text{H}_2\text{O} )</td>
<td>( 4.25 \times 10^{-25} \ T^{-2.0} \ \text{cm}^6/\text{s} )</td>
</tr>
<tr>
<td>11</td>
<td>( \text{H} + \text{OH} + \text{CO} = \text{H}_2\text{O} + \text{CO} )</td>
<td>( 4.55 \times 10^{-26} \ T^{-2.0} \ \text{cm}^6/\text{s} )</td>
</tr>
</tbody>
</table>

Table 4.6: Reduced UCSD mechanism of ethylene combustion [65].
Table 4.6 continued

<table>
<thead>
<tr>
<th>#</th>
<th>Process</th>
<th>Rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>11</td>
<td>( \text{H} + \text{OH} + \text{CO}_2 = \text{H}_2\text{O} + \text{CO}_2 )</td>
<td>( 9.01 \cdot 10^{-26} \cdot T^{-2.0} \text{ cm}^6/\text{s} )</td>
</tr>
<tr>
<td>11</td>
<td>( \text{H} + \text{OH} + \text{N}_2 = \text{H}_2\text{O} + \text{N}_2 )</td>
<td>( 6.06 \cdot 10^{-26} \cdot T^{-2.0} \text{ cm}^6/\text{s} )</td>
</tr>
<tr>
<td>11</td>
<td>( \text{H} + \text{OH} + \text{AR} = \text{H}_2\text{O} + \text{AR} )</td>
<td>( 3.03 \cdot 10^{-26} \cdot T^{-2.0} \text{ cm}^6/\text{s} )</td>
</tr>
<tr>
<td>12</td>
<td>( \text{OH} + \text{CO} = \text{H} + \text{CO}_2 )</td>
<td>( 7.31 \cdot 10^{-18} \cdot T^{-1.50} \exp(-251.28/T) \text{ cm}^3/\text{s} )</td>
</tr>
<tr>
<td>13</td>
<td>( \text{C}_2\text{H}_4 + \text{O}_2 = \text{C}_2\text{H}_3 + \text{HO}_2 )</td>
<td>( 7.01 \cdot 10^{-11} \exp(28987.14/T) \text{ cm}^3/\text{s} )</td>
</tr>
<tr>
<td>14</td>
<td>( \text{OH} + \text{C}_2\text{H}_4 = \text{C}_2\text{H}_3 + \text{H}_2\text{O} )</td>
<td>( 9.18 \cdot 10^{-19} \cdot T^{2.31} \exp(1491.56/T) \text{ cm}^3/\text{s} )</td>
</tr>
<tr>
<td>15</td>
<td>( \text{O} + \text{C}_2\text{H}_4 = \text{CH}_3 + \text{HCO} )</td>
<td>( 3.74 \cdot 10^{-18} \cdot T^{2.08} \text{ cm}^3/\text{s} )</td>
</tr>
<tr>
<td>16</td>
<td>( \text{O} + \text{C}_2\text{H}_4 = \text{H} + \text{CH}_2\text{CHO} )</td>
<td>( 2.01 \cdot 10^{-18} \cdot T^{2.08} \exp(110.78/T) \text{ cm}^3/\text{s} )</td>
</tr>
<tr>
<td>17</td>
<td>( \text{C}_2\text{H}_4 + \text{HO}_2 = \text{CH}_3\text{CHO} + \text{OH} )</td>
<td>( 3.7 \cdot 10^{-12} \exp(8647.7/T) \text{ cm}^3/\text{s} )</td>
</tr>
<tr>
<td>18</td>
<td>( \text{H} + \text{C}_2\text{H}_4 = \text{C}_2\text{H}_3 + \text{H}_2 )</td>
<td>( 7.45 \cdot 10^{-17} \cdot T^{2.12} \exp(6723.08/T) \text{ cm}^3/\text{s} )</td>
</tr>
<tr>
<td>19</td>
<td>( \text{H} + \text{C}_2\text{H}_4 = \text{C}_2\text{H}_5 )</td>
<td>( 1.79 \cdot 10^{-12} \cdot T^{0.45} \exp(913.97/T) \text{ cm}^3/\text{s} )</td>
</tr>
<tr>
<td>20</td>
<td>( \text{H} + \text{C}_2\text{H}_4 + \text{M} = \text{C}_2\text{H}_5 + \text{M} )</td>
<td>( 5.24 \cdot 10^{-13} \cdot T^{5.57} \exp(2537.96/T) \text{ cm}^6/\text{s} )</td>
</tr>
<tr>
<td>21</td>
<td>( \text{C}_2\text{H}_4 + \text{M} = \text{H} + \text{C}_2\text{H}_3 + \text{M} )</td>
<td>( 4.32 \cdot 10^{-7} \exp(48590.88/T) \text{ cm}^3/\text{s} )</td>
</tr>
<tr>
<td>22</td>
<td>( \text{H} + \text{C}_2\text{H}_3 = \text{H}_2 + \text{C}_2\text{H}_2 )</td>
<td>( 2.01 \cdot 10^{-11} \text{ cm}^3/\text{s} )</td>
</tr>
<tr>
<td>23</td>
<td>( \text{C}_2\text{H}_3 + \text{O}_2 = \text{HCO} + \text{CH}_2\text{O} )</td>
<td>( 2.82 \cdot 10^5 \cdot T^{2.31} \exp(3283.24/T) \text{ cm}^3/\text{s} )</td>
</tr>
<tr>
<td>24</td>
<td>( \text{C}_2\text{H}_3 + \text{O}_2 = \text{O} + \text{CH}_2\text{CHO} )</td>
<td>( 1.16 \cdot 10^{-9} \cdot T^{0.67} \exp(2646.23/T) \text{ cm}^3/\text{s} )</td>
</tr>
<tr>
<td>25</td>
<td>( \text{CH}_3 + \text{O}_2 = \text{OH} + \text{CH}_2\text{O} )</td>
<td>( 5.48 \cdot 10^{13} \exp(4497.83/T) \text{ cm}^3/\text{s} )</td>
</tr>
<tr>
<td>#</td>
<td>Process</td>
<td>Rate</td>
</tr>
<tr>
<td>----</td>
<td>----------------------------------------------</td>
<td>--------------------------------------------</td>
</tr>
<tr>
<td>26</td>
<td>O + CH\textsubscript{3} = H + CH\textsubscript{2}O</td>
<td>1.40\times10^{-10} \text{ cm}^3/\text{s}</td>
</tr>
<tr>
<td>27</td>
<td>CH\textsubscript{2}CHO = H + CH\textsubscript{2}CO</td>
<td>1.05\times10^{37} \text{T}^{-7.19} \exp(22370.82/\text{T}) \text{ 1/s}</td>
</tr>
<tr>
<td>28</td>
<td>C\textsubscript{2}H\textsubscript{5} + O\textsubscript{2} = HO\textsubscript{2} + C\textsubscript{2}H\textsubscript{4}</td>
<td>3.32\times10^{-12} \exp(2513.79/\text{T}) \text{ cm}^3/\text{s}</td>
</tr>
<tr>
<td>29</td>
<td>H + CH\textsubscript{2}CO = CH\textsubscript{3} + CO</td>
<td>1.84\times10^{-17} \text{T}^{-2.0} \exp(\text{1010.15}/\text{T}) \text{ cm}^3/\text{s}</td>
</tr>
<tr>
<td>30</td>
<td>OH + CH\textsubscript{2}O = HCO + H\textsubscript{2}O</td>
<td>6.48\times10^{-14} \text{T}^{0.89} \exp(204.45/\text{T}) \text{ cm}^3/\text{s}</td>
</tr>
<tr>
<td>31</td>
<td>HCO + O\textsubscript{2} = H + CO + O\textsubscript{2}</td>
<td>3.09\times10^{-7} \text{T}^{-1.0} \exp(8551.52/\text{T}) \text{ cm}^3/\text{s}</td>
</tr>
<tr>
<td>31</td>
<td>HCO + N\textsubscript{2} = H + CO + N\textsubscript{2}</td>
<td>3.09\times10^{-7} \text{T}^{-1.0} \exp(8551.52/\text{T}) \text{ cm}^3/\text{s}</td>
</tr>
<tr>
<td>31</td>
<td>HCO + AR = H + CO + AR</td>
<td>3.09\times10^{-7} \text{T}^{-1.0} \exp(8551.52/\text{T}) \text{ cm}^3/\text{s}</td>
</tr>
<tr>
<td>31</td>
<td>HCO + CO = H + CO + CO</td>
<td>7.72\times10^{-7} \text{T}^{-1.0} \exp(8551.52/\text{T}) \text{ cm}^3/\text{s}</td>
</tr>
<tr>
<td>31</td>
<td>HCO + CO\textsubscript{2} = H + CO + CO\textsubscript{2}</td>
<td>7.72\times10^{-7} \text{T}^{-1.0} \exp(8551.52/\text{T}) \text{ cm}^3/\text{s}</td>
</tr>
<tr>
<td>31</td>
<td>HCO + H\textsubscript{2} = H + CO + H\textsubscript{2}</td>
<td>5.87\times10^{-7} \text{T}^{-1.0} \exp(8551.52/\text{T}) \text{ cm}^3/\text{s}</td>
</tr>
<tr>
<td>31</td>
<td>HCO + H\textsubscript{2}O = H + CO + H\textsubscript{2}O</td>
<td>3.71\times10^{-6} \text{T}^{-1.0} \exp(8551.52/\text{T}) \text{ cm}^3/\text{s}</td>
</tr>
<tr>
<td>32</td>
<td>HCO + O\textsubscript{2} = HO\textsubscript{2} + CO</td>
<td>4.98\times10^{-12} \text{ cm}^3/\text{s}</td>
</tr>
<tr>
<td>33</td>
<td>H + HCO = H\textsubscript{2} + CO</td>
<td>1.66\times10^{-10} \text{ cm}^3/\text{s}</td>
</tr>
<tr>
<td>34</td>
<td>OH + C\textsubscript{2}H\textsubscript{2} = H + CH\textsubscript{2}CO</td>
<td>3.15\times10^{-17} \text{T}^{1.0} \exp(-505.07/\text{T}) \text{ cm}^3/\text{s}</td>
</tr>
<tr>
<td>35</td>
<td>HO\textsubscript{2} + CH\textsubscript{3}CHO = CH\textsubscript{3} + H\textsubscript{2}O\textsubscript{2} + CO</td>
<td>6.64\times10^{-12} \exp(8563.60/\text{T}) \text{ cm}^3/\text{s}</td>
</tr>
</tbody>
</table>
4.5 High-voltage pulse energy coupling and heat transfer

The high voltage pulse shape used by the present plasma chemistry model is a Gaussian fit to the experimentally measured voltage pulse shape shown in Figure 4.1. The mathematical expression of the Gaussian fit used is

\[
V(t) = V_n \cdot \exp \left[ -\left( \frac{t-t_n}{\tau} \right)^2 \right] + V_p \cdot \exp \left[ -\left( \frac{t-t_p}{\tau} \right)^2 \right], \tag{4.1}
\]

with \( V_n = -27.5 \text{ kV}, \ V_p = 23 \text{ kV}, \) and \( \tau = 10 \text{ nsec}. \) However, the electric field in the plasma is much lower than the applied electric field, due to strong shielding of the applied voltage caused by the charge accumulation on dielectric covered electrodes after breakdown. The analytical model of energy coupling in nanosecond pulse discharge plasma for plane-to-plane geometry has been developed in Ref. [48]. Briefly, this model incorporates key effects of pulsed breakdown, charge accumulation on dielectric surfaces, and sheath development on nanosecond time scale. The model predicts that energy

<table>
<thead>
<tr>
<th>#</th>
<th>Process</th>
<th>Rate</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>( \text{C}_2\text{H}_4 + e^- \rightarrow \text{products}^* + e^- )</td>
<td>( \sigma )</td>
<td>[66]</td>
</tr>
<tr>
<td>2</td>
<td>( \text{N}_2(A^3\Sigma) + \text{C}_2\text{H}_4 \rightarrow \text{N}_2 + \text{C}_2\text{H}_3 + \text{H} )</td>
<td>( 9.7 \cdot 10^{-11} \text{ cm}^3/\text{s} )</td>
<td>[67]</td>
</tr>
<tr>
<td>3</td>
<td>( \text{N}_2(B^3\Pi) + \text{C}_2\text{H}_4 \rightarrow \text{N}_2 + \text{C}_2\text{H}_3 + \text{H} )</td>
<td>( 3.0 \cdot 10^{-10} \text{ cm}^3/\text{s} )</td>
<td>estimate</td>
</tr>
<tr>
<td>4</td>
<td>( \text{N}_2(C^3\Pi) + \text{C}_2\text{H}_4 \rightarrow \text{N}_2 + \text{C}_2\text{H}_3 + \text{H} )</td>
<td>( 3.0 \cdot 10^{-10} \text{ cm}^3/\text{s} )</td>
<td>estimate</td>
</tr>
<tr>
<td>5</td>
<td>( \text{N}_2(a'^1\Sigma) + \text{C}_2\text{H}_4 \rightarrow \text{N}_2 + \text{C}_2\text{H}_3 + \text{H} )</td>
<td>( 4.0 \cdot 10^{-10} \text{ cm}^3/\text{s} )</td>
<td>[68]</td>
</tr>
</tbody>
</table>

Table 4.7: Ethylene dissociation processes in the plasma [45].
coupled per unit volume of the plasma during the discharge pulse is controlled primarily by the capacitance of the dielectric layers and by the applied voltage pulse shape,

$$Q_{\text{pulse}} \approx \frac{CV_h^2}{2AL} \left(1 + \frac{V_{\text{peak}}^2}{V_h^2} \frac{\sqrt{2\pi}}{\nu_{RC} \tau}\right) = \frac{1}{2} \varepsilon_0 \left(\frac{V_h^2 + V_{\text{peak}}^2}{2l} \frac{\varepsilon_0 L}{\nu_{RC}} \frac{\sqrt{2\pi}}{\tau}\right). \quad (4.2)$$

Figure 4.1: Typical experimental high-voltage pulse shape with Gaussian fit. Ethylene-air, $\phi=1$, $P=70$ torr, $u=35$ m/s, $v=40$ kHz.

In Eq. (4.2), $C=\varepsilon\varepsilon_0 A/2l$ is the capacitance of two dielectric (alumina ceramic) layers covering the electrodes, $\varepsilon$ is the dielectric constant, $l$ is the dielectric layer thickness, $A$ is the electrode surface area, $L$ is the discharge gap between the dielectric walls, $V_{\text{peak}}$ and $V_b$ are peak pulse voltage and breakdown voltage, respectively, $\tau$ is the pulse duration parameter of a Gaussian shape pulse, $V(t)=V_{\text{peak}} \exp\left[-(t/\nu)^2\right]$, $\nu_{RC}=1/RC$ is the RC time constant of the load (i.e. the plasma and the dielectric layers) after the
breakdown, $R = L / e n_e \mu_e A$ is the resistance of the shielded plasma after breakdown, $e$ is the elementary charge, $n_e$ is peak electron density, and $\mu_e$ is the electron mobility. The first and the second terms in Eq. (4.2) account for the energy coupled during breakdown and after breakdown, respectively. Derivation of Eq. (4.2), as well as expressions for breakdown voltage and peak electron density, can be found in Ref. [48]. The coupled pulse energy predicted by the nanosecond pulse discharge model [48], $Q_{\text{pulse}}$, is nearly proportional to the number density, i.e. the energy coupled per molecule, $q_{\text{pulse}} = Q_{\text{pulse}} / N$, remains approximately constant. The coupled pulse energy predicted by this model in room temperature air at $P = 60$ torr was found to be in good agreement with the value inferred from O atom number density measurements by Two-Photon Absorption Laser Induced Fluorescence [51].

To calculate the coupled pulse energy at the conditions of the present experiments, the experimental pulse waveform shown in Figure 4.1 was approximated by a superposition of two Gaussian pulses with $\tau = 10$ nsec, which approximately doubles the second term in Eq. (4.2). Assuming a quasi-1D plane-to-plane geometry for simplicity and using Eq. (4.2) for the alumina ceramic dielectric constant of $\varepsilon = 6.0$, dielectric thickness of $t = 1.6$ mm, and the discharge gap of $L = 5.8$ mm (distance between the ceramic sleeve on the high-voltage electrode and the ceramic plate on the cavity wall, Figure 2.4), the energy coupled per molecule is $q_{\text{pulse}} = Q_{\text{pulse}} / N = 0.55$ meV/molecule, nearly independent of pressure and temperature. In the present model, the peak reduced electric field, $(E/N)_{\text{peak}} \approx 250$ Td, was adjusted to keep the coupled pulse energy per molecule constant during the burst, according to the nsec pulse discharge model of Ref.
Thus, the coupled pulse energy decreases during the burst inversely proportional to the temperature. At these conditions, almost 50% of the coupled pulse energy in an ethylene-air mixture at \( \phi = 0.5 \) is spent on generation of O and H atoms. This simple coupling of the nanosecond pulsed discharge theory and the plasma chemistry model incorporates the most essential effect of coupled pulse energy dependence on voltage waveform, discharge geometry, dielectric plate parameters, and number density.

In the present work, the kinetic model described above is employed using two different approaches:

(a) For single pulse discharge in air, a full set of ionization, electron-ion recombination, ion-ion recombination, electron attachment/detachment, and ion-molecule reactions [54] are used, and concentration equations for all species listed in Section 4.2 are incorporated. In this case, pulse peak voltage is adjusted to obtain the desired discharge energy coupled per molecule. This approach has been used only in air plasmas since charged species kinetics in dry air is well understood, and only for single-pulse discharges, since gradual temperature rise in the burst mode discharges would require significant reduction of pulse peak voltage to keep the coupled pulse energy consistent with the nanosecond pulse discharge model [48]. Such reduction has no physical basis, does not actually occur in the experiment, and reflects inability of the plasma chemistry model to incorporate kinetics of ionization and sheath formation in nanosecond pulse discharges [48].

(b) In the remainder of kinetic modeling calculations, the electron density in the plasma was adjusted to keep the pulse energy consistent with the nanosecond pulse discharge
model prediction. This includes all calculations in burst mode discharges and in fuel-air mixtures. In this case, reactions involving ions are not incorporated in the model, and species concentration equations for electrons and ions are not solved. Instead, the electron density is found from the coupled pulse energy, predicted by the nanosecond pulse discharge model [48].

The kinetic model incorporates the equation for the temperature in the center of the discharge gap, $T_c$, with heat transfer to the walls being the dominant energy loss mechanism,

$$
\rho c_p \frac{dT_c}{dt} = Q_{pulse} \nu - \sum_i h_i \left( \frac{dn_i}{dt} \right) - \lambda(\bar{T}) \frac{T_c - T_w}{(L/\pi)^2},
$$

(4.3)

where $Q_{pulse}$ is the coupled pulse energy per unit volume, $\nu$ is the pulse repetition rate in a burst, $h_i$ are enthalpies of chemical and excited species, $dn_i/dt$ are the rates of species concentrations (in kmole/m$^3$) change in chemical reactions, $\lambda$ is the thermal conductivity, $T_w$=300 K is the wall temperature, $\bar{T}$ is the spatially averaged temperature, and $L/\pi$ is the spatial scale for transient conduction heat transfer. In a transient conduction model with constant thermal diffusivity, the spatial temperature distribution across the plasma can be approximated by a cosine function, $T(x)-T_w \approx \left[ T_c-T_w \right] \cdot \cos(\pi x/L), \ -L/2 \leq x \leq L/2$, which gives the spatially-averaged temperature as $\bar{T} \approx T_w + (2/\pi) \cdot (T_c - T_w)$. If the temperature dependence of the thermal diffusivity is taken into account, the temperature distribution is $T(x)-T_w \approx \left[ T_c-T_w \right] \cdot (1-2x/L)^3$, and $\bar{T} \approx T_w + (3/4) \cdot (T_c - T_w)$. The accuracy of the zero-
dimensional heat transfer approximation has been verified by comparing time-dependent centerline and spatially averaged temperatures predicted by 0-D and 1-D heat transfer equations for the same heating rate, which differ only by a few per cent.

The computer code incorporating the kinetic model described above and used for modeling calculations in the present work is described in greater detail in Ref. [40].

4.6 Model validation

The present hydrocarbon-air and hydrogen-air plasma chemistry models have been validated by comparing with several experimental measurements performed using single-pulse and repetitive pulse nanosecond discharges in non-preheated air and fuel-air mixtures. Figure 4.2, taken from Refs. [51] and [52], show time-dependent Two Photo Absorption Laser Induced Fluorescence (TALIF) O atom concentration measurements in single-pulse and repetitive nanosecond discharges in air and hydrocarbon–air mixtures, along with corresponding predictions from kinetic model, indicating good agreement. Time-resolved temperature measurements and ignition delay time measurements using purely rotational CARS [53] in repetitively pulsed nanosecond discharges in non-preheated air and hydrogen-air mixtures shown in Figure 4.3 also demonstrate close agreement between the experiment and the kinetic model predictions.
Figure 4.2: O atom mole fraction versus time after (a) a single high-voltage pulse in air and in ethylene–air ($\varphi = 0.5$) mixtures at $P = 60$ torr [51], (b) after a series of pulses in air, methane–air ($\varphi = 1.0$) and in ethylene–air ($\varphi = 0.5$) mixtures at $P = 60$ torr and $\nu = 100$ kHz [52].

Figure 4.3: Comparison of CARS temperatures in a repetitively pulsed nanosecond discharge in air and in hydrogen-air at $P = 40$ torr with kinetic model predictions. $\nu = 40$ kHz, burst repetition rate 10 Hz [53].

Specifically, Figure 4.3 demonstrates that the overall energy balance in air and hydrogen-air plasmas (i.e. both the energy input by the discharge and the heat transfer
losses) is reproduced by the model correctly. Figure 4.3 also shows that ignition time, defined as time to reach peak temperature in a reacting fuel-air mixture, is also predicted by the model rather accurately. Finally, Figure 4.2 shows that the total energy fraction going to oxygen dissociation in air and hydrocarbon-air plasmas (both by electron impact and in reactions of electronically excited nitrogen) is predicted by the model correctly.

Recently, the kinetic model has been validated in experiments on ignition of preheated hydrogen-air using repetitive nanosecond pulse discharge. Figure 4.4 compares experimental measurements of time-resolved absolute OH radical concentrations during plasma chemical oxidation/ignition of hydrogen with kinetic modeling, for two different initial mixture temperatures [69]. These plots show that the kinetic model results agree well with the experimental measurements. Although the model somewhat overpredicts OH concentration before ignition, the general trend of OH accumulation during the discharge pulse burst, a sudden OH concentration rise during ignition, and the ignition time are predicted correctly. Comparison of experimentally measured ignition delay in a stoichiometric hydrogen-air mixture with kinetic model predictions for two different initial temperatures and different pulse repetition rates, shown in Figure 4.5 [50], also demonstrates good agreement between experimental and modeling results. Specifically, the model correctly reproduces ignition time reduction as pressure is increased, as well as weak dependence of ignition time on equivalence ratio, except at low pulse repetition rates (see Figure 4.5(a)). Finally, Figure 4.6 [50] compares experimental ignition delay in stoichiometric hydrogen-air at different pressures and two different initial temperatures with kinetic model predictions. The results shows that ignition time predicted by the
model agrees well with experimental results, at pressures up to 150 torr, i.e. close to the combustor pressure for most of the experiments conducted in the present work.

Figure 4.4: Comparison of experimental absolute hydroxyl radical concentration as a function of burst duration at pulse repletion rate of 40 kHz with kinetic model predictions. H₂–air, φ=1.0; (left) P=54 torr at T₀=100 °C and (right) P=68 torr at T₀=200 °C [69].

Figure 4.5: Ignition delay time vs. equivalence ratio at different pulse repetition rates and initial temperatures, T₀=100° C (left) and T₀=200° C (right), in a hydrogen-air mixture [50].
Figure 4.6: Ignition delay vs. pressure for repetitive nanosecond pulse discharge ignition of a stoichiometric hydrogen-air mixture at two different initial temperatures [50].

**4.7 Objectives of kinetic modeling**

The main objective of kinetic modeling in the present work is to identify the dominant kinetic processes affecting plasma chemical oxidation and ignition of hydrogen and ethylene, and to obtain the reduced reaction mechanism that can be used in a flow code for modeling of coupled mixing and plasma / ignition kinetics in actual test section geometry. In addition to that, model predictions using a reduced kinetic mechanism for ethylene-air combustion developed in Ref. [65] are compared with those obtained using a full GRI 3.0 mechanism, for plasma assisted ignition in a wide range of pressures and temperatures.
Chapter 5: Results of Modeling Calculations

5.1 Single pulse nanosecond discharge in air

One of the most serious concerns regarding the use of low-temperature plasmas for plasma-assisted ignition at high pressures (p ~ 0.1-1.0 atm) is rapid plasma decay due to three-body attachment of electrons to oxygen,

\[ O_2 + e + M \rightarrow O^-_2 + M \text{,} \tag{5.1} \]

the rate of which scales quadratically with pressure. The rate coefficients of this reaction are \( k_{\text{att}} = 2.5 \cdot 10^{-30} \text{ cm}^6 / \text{sec} \text{ for } M = O_2 \text{, and } k_{\text{att}} = 0.16 \cdot 10^{-30} \text{ cm}^6 / \text{sec} \text{ for } M = N_2 \) [70]. This gives air plasma decay time, \( \tau_{\text{delay}} \sim \frac{1}{k_{\text{att}}[O_2][M]} \sim 10 \text{ nsec} - 1 \text{ \mu sec} \text{ at } P = 0.1 - 1 \text{ atm, } T = 300 \text{ K, and suggests that a repetitively pulsed discharge at these pressures would need to be operated at very high pulse repetition rates, up to } 1 - 100 \text{ MHz. This issue is addressed in this section.} \]

The kinetic model of air plasma described in Section 4.2 has been used to study the effect of electron concentration decay rate due to negative ion formation by three-body electron attachment in air on radical species generation. This effect has been studied in single-pulse discharges in air at room temperature and different pressures. Figure 5.1 shows electron number density, as well as number densities of dominant positive and
negative ions after a single pulse nanosecond discharge in room temperature air at (a) $P=150$ torr (0.2 atm), and (b) $P=760$ torr (1 atm), for the same coupled pulse energy of $\approx 1$ meV/molecule, which is close to the condition of present experiments. From these plots, it is evident that electron density after the pulse decays more rapidly as the pressure is increased from 150 torr to 760 torr due to negative ion formation by the three-body electron attachment process of Eq. (5.1), with rapid subsequent ion-molecule conversion reactions creating $O^-$ and $O_3^-$ ions. At atmospheric pressure, the electron density decay time is indeed very short, approximately 80 nsec. However, Figure 5.2, which plots O atom mole fraction at the conditions of Figure 5.1, shows that peak O atom mole fraction generated during the pulse remains nearly independent of pressure.

Figure 5.1: Electron number densities and densities of dominant ions in air plasma after a single nanosecond pulse discharge, predicted by the air chemical kinetic model. (a) $P=150$ torr, $T=300$ K, peak voltage= 13.5 kV, $E/N = 20.3 \times 10^{-16}$ V. cm$^2$; (b) $P=760$ torr, $T=300$ K, peak voltage= 53.7 kV, $E/N = 15.9 \times 10^{-16}$ V. cm$^2$. Discharge energy loading per molecule $\approx 1$ meV/molecule.
Discharge energy balance analysis demonstrated that at both pressures, about 40% of the input discharge pulse energy is spent on O atom generation. The O atom decay time is much longer compared to the electron density decay time, and is controlled primarily by the reaction of ozone formation, \( O + O_2 + M \rightarrow O_3 + M \), as well as \( O + O_3 \rightarrow O_2 + O_2 \) reaction. Long O atom decay time, a few tens of microseconds, suggests that operating the pulse discharge in air at pulse repetition rates of a few tens of kHz would result in accumulation of O atoms, even at pressure of \( \sim 1 \) atm. Such accumulation has been detected in air during our earlier experiments (see Figure 4.2(b) [52]).

![O atom mole fraction](image)

**Figure 5.2:** O-atom mole fraction after a single nanosecond pulse discharge in room temperature air, predicted by air plasma kinetic model for two different pressures.
In summary, short electron density decay time in high-pressure, low-temperature air plasmas does not result in significant reduction of radical species yields (such as O atoms). Basically, sufficient amount of O atoms and electronically excited nitrogen molecules are generated during the discharge pulse, before the electrons are lost to attachment, to achieve high efficiency of discharge energy conversion into O atom generation, ~ 40% at atmospheric pressure.

5.2 Nanosecond discharge in hydrogen-air mixtures

In this section, we compare the full mechanism of hydrogen-air combustion chemistry suggested by Popov [55] (see Table 4.3) and the reduced combustion chemistry obtained from Ref. [63] (see Table 4.4). The kinetic modeling results using the full and reduced mechanisms are compared for a single-pulse discharge and a burst mode discharge, for different initial pressures and temperatures. In both cases, the kinetic model also incorporates air plasma processes as well as hydrogen dissociation processes by electron impact and by reactions with electronically excited nitrogen molecules (see Table 4.2). In these calculations, the discharge pulse energy per molecule is 0.28 meV/molecule (estimated energy loading in previous experiments at OSU [51-53]) or 0.55 meV/molecule (estimated energy loading in the present experiment).

5.2.1 Single pulse discharge

Figure 5.3 compares dominant neutral species mole fractions after a single pulse nanosecond discharge in room temperature hydrogen-air, predicted by the plasma
chemical kinetic model using the full set and the reduced set of H$_2$-O$_2$ reactions described in Section 4.3 for two different pressures, (a) P=150 torr and (b) P=760 torr. In these calculations, the discharge pulse energy loading per molecule is 0.28 meV. These plots show that for both pressures, the reduced H$_2$-O$_2$ reaction mechanism predicts very similar time-dependent concentrations of dominant species formed during plasma chemical oxidation of hydrogen (such as O, H, OH, H$_2$O, and O$_3$) to those obtained using the full mechanism. The only difference is the effect of HO$_2$ conversion into H$_2$O$_2$ (not included in the reduced mechanism), which does not significantly affect concentrations of H$_2$O and other species. It should be noted that the steady state mole fraction of the dominant stable oxidation product, H$_2$O, is significantly lower compared to peak mole fractions of the primary radical species, H, O, and OH, especially at P=760 torr (see Figure 5.3). This demonstrates that at the low initial temperature (T=300 K), radical recombination back into H$_2$ and O$_2$, as well as ozone formation (i.e. chain termination processes) dominate over chain branching and chain propagation processes (reactions C4-C8 of Table 4.4). Basically, the use of nanosecond pulse discharge for fuel-air oxidation at low initial temperatures is extremely inefficient, in spite of high radical generation efficiency. At the initial temperature of T=600 K, the full mechanism and the reduced mechanism again show very similar results, except for the relatively minor effect of the H$_2$O$_2$ chemistry, as can be seen in Figure 5.4. Note that at T=600 K, the final H$_2$O mole fraction is significantly higher than the combined mole fraction of primary radicals (H, O, and OH). This demonstrates that at elevated temperatures, chain branching processes begin to dominate over radical species loss in chain termination/recombination reactions.
Figure 5.3: Dominant neutral species mole fractions after a single pulse nanosecond discharge, predicted by the plasma chemical kinetic model. Full reaction set (left) and reduced set (right). Hydrogen-air, $\phi=1$, $T=300$ K.
Figure 5.4: Dominant neutral species mole fraction after a single pulse nanosecond discharge, predicted by the plasma chemical kinetic model. Full reaction set (left) and reduced set (right). Hydrogen-air, $\phi=1$, $T=600$ K.

5.2.2 Pulse burst discharge

Figure 5.5 compares predicted species mole fractions during plasma chemical oxidation of room-temperature stoichiometric hydrogen-air mixture by a repetitive
nanosecond pulse discharge, using the full set and the reduced set of H$_2$-O$_2$ reactions for the same pressures as in Section 5.2.1, P= 150 torr and 760 torr, and initial temperature of T=300 K. In these calculations, energy loss due to heat transfer to the walls is incorporated, using Eq. (4.3) of Section 4.5. These results show again that for both pressures, the reduced mechanism of H$_2$-O$_2$ reaction chemistry predicts nearly the same time-dependent species concentrations during plasma chemical oxidation/ignition of hydrogen as those predicted using the full mechanism. In addition, ignition times predicted using the full and reduced reaction sets are very close to each other. Note that the kinetic model (using both full and reduced reaction mechanisms) predicts ignition time to be nearly independent of pressure in this pressure range, if the initial temperature and the discharge energy per molecule are the same. Similar results were obtained for plasma chemical oxidation of a stoichiometric hydrogen-air mixture at an elevated temperature of T=600 K, as shown in Figure 5.6. In summary, the reduced kinetic mechanism of plasma assisted hydrogen-air oxidation/ignition suggested in Ref. [63] and listed in Table 4.4 remains accurate in a wide range of pressures (P=60-760 torr) and temperatures (T=300 K to ignition temperature).
Figure 5.5: Species mole fractions during fuel-air oxidation/ignition by a repetitive nanosecond pulse discharge at $\nu=40$ kHz, predicted by the plasma chemical kinetic model. Full reaction set (left) and reduced set (right). Hydrogen-air, $\phi=1$, $T=300$ K.
Figure 5.6: Species mole fractions during fuel-air oxidation/ignition by a repetitive nanosecond pulse discharge at ν=40 kHz, predicted by the plasma chemical kinetic model. Full reaction set (left) and reduced set (right). Hydrogen-air, ϕ=1, T=600 K.

Figure 5.7(a) shows time-resolved temperatures predicted by the plasma chemistry model in a ϕ=0.5 hydrogen-air mixture at P=150 torr and initial temperature of
T=300 K, excited by a repetitive nanosecond pulse discharge at ν=40 kHz and $q_{\text{pulse}}=0.55$ meV/molecule, i.e., at the conditions of experiments performed in the present work. The results shown in Figure 5.7(a) have been calculated for the full set of H$_2$-O$_2$ chemical reactions (22 reactions) and for the reduced reaction set, listed in Table 4.4 (in addition to plasma processes listed in Table 4.1 and Table 4.2). It can be seen that temperatures predicted using both reaction sets are nearly identical. Figure 5.7(b) plots major chemical species mole fractions, calculated using the reduced reaction set. Calculations using the reduced reaction set produce nearly identical results. Also, removing reaction C2 from the reduced reaction set (see Table 4.4) produces fairly minor effect on O, OH, and HO$_2$ mole fractions in the beginning of the pulse burst and has almost no effect on ignition delay time. Therefore, reactions C1, C3-C9, in addition to the dominant plasma processes providing a repetitively pulsed source of radical species at low temperatures and listed in Table 4.2 (P1–P12), constitute a fairly accurate reduced plasma / chemistry reaction set. Ignition delay time predicted by the model at these conditions, 4.75 msec (190 pulses) is approximately 50% longer compared to the experimental result, ≈125-135 pulses (3.1-3.4 msec, see Figure 3.30). However, taking into account the simplicity of the heat transfer model used, as well as filamentation of the plasma prior to ignition (see Figure 5.7), we conclude that the agreement is fairly satisfactory.

From Figure 5.7, it can be seen that significant hydrogen oxidation and H$_2$O formation occur well before ignition. Sensitivity analysis shows that initially, at near room temperature, this process is triggered by O and H atom generation in the plasma (reactions P3, P7-P9, P11 of Table 4.2) and occurs almost exclusively via reaction path
C1-C3 (O,H→HO₂→OH→H₂O), with essentially no chain branching (equivalent net reaction is O+H₂→H₂O). In particular, no OH formation via the well known “high temperature” chain branching processes (reactions C4 and C8) occurs at these conditions, due to their high activation energies. Note that HO₂ formation by three-body recombination (reaction C1) initiates the low-temperature reaction path resulting in H₂O production. In this sense, the role of three-body recombination is opposite of that in conventional, high-temperature H₂/air combustion, where it acts as a strong sink. At higher initial temperatures, T=500-600 K, the oxidation kinetics change significantly, and reactions C4-C8, which control chain branching, become sufficiently rapid to come into play. These chain propagation / chain branching reactions result in additional heat release at elevated temperatures (well below autoignition temperature). As a result, plasma chemical hydrogen oxidation into water generates substantial amount of energy prior to ignition, in addition to energy input by the discharge. This, as well as presence of primary radicals (O and H atoms) generated by the plasma, significantly accelerates ignition.
5.2.3 Effect of plasma chemical processes on ignition

In all kinetic modeling calculations discussed so far, the nanosecond pulse discharge plasma produces two different effects, (a) Joule heating of the fuel-air mixture, and (b) generation of chemically active radical species, H, O, and OH (via processes of Table 4.2). To isolate the non-thermal effect of radical generation on fuel oxidation and ignition from the less interesting thermal effect, we conducted a series of calculations with the radical-producing plasma chemical reactions (i.e. reactions listed in Table 4.2) removed from the reaction set. The results are summarized below.

Figure 5.8 plots time-resolved, spatially averaged temperature, $\bar{T}$, in a $\phi=0.5$ hydrogen-air mixture at $P=150$ torr and initial temperature of $T=300$ K, excited by a repetitive nanosecond pulse discharge at $v=40$ kHz and $q_{\text{pulse}}=0.55$ meV/molecule. As discussed above, the temperatures plotted in Figure 5.8 are predicted by the kinetic model.
using (a) the complete set of hydrogen-air plasma and chemistry processes, and (b) only chemistry processes, i.e. with all plasma processes removed. In both cases, the coupled pulse energy per molecule, $q_{\text{pulse}}$, is the same. From Figure 5.8, it can be seen clearly that removal of radical generation processes in the plasma (primarily processes P1-P11 of Table 4.2) completely blocks subsequent exothermic chemical reactions and precludes ignition, which otherwise occurs at $t \approx 4.75$ msec. This demonstrates that generation of O and H atoms in the plasma, due to oxygen and hydrogen dissociation by electron impact and by collisions with electronically excited nitrogen (see Table 4.2), is key to initiating low-temperature exothermic chemical reactions.

![Figure 5.8: Time-resolved, spatially averaged temperature predicted by the model in hydrogen-air mixture excited by a repetitive nanosecond pulse discharge at $v=40$ kHz, for the full set of reactions and for the set with all plasma processes removed. $\phi=0.5$, $P=150$ torr, $T=300$ K.](image-url)
The effect of radical generation in the plasma on hydrogen-air ignition is further investigated by comparing ignition delay time for plasma assisted ignition and for thermal ignition. Figure 5.9 shows ignition delay time for plasma assisted ignition and thermal ignition of a stochiometric hydrogen-air mixture for different initial mixture temperatures. In case of plasma assisted ignition, a burst of discharge pulses repeated at 40 kHz repetition rate, is applied to a hydrogen-air mixture initially at room temperature. The number of pulses in the burst was varied to control the mixture temperature at the end of the burst, and the ignition delay calculated from the end of the burst is plotted vs. the mixture temperature at the end of the pulse burst. On the other hand, for thermal ignition, ignition delay was calculated by setting initial mixture temperature to a value above autoignition temperature. These calculations were performed in absence of heat transfer to the surrounding for both the cases. In addition, the energy release due to Joule heating in the plasma was disabled to observe a purely non-thermal effect of radical generation in the plasma on plasma assisted ignition. It is evident from Figure 5.9 that plasma assisted ignition occurs at temperature significantly lower than thermal ignition, which again emphasizes the importance of radicals produced by high peak voltage pulsed discharge to accelerate ignition process. It should be noted here that enthalpy stored in the radicals (O, H, and OH) produced by the plasma at the conditions (≈3 kJ/kg) is insignificant compared to the sensible enthalpy of the mixture (≈750 kJ/kg). Therefore, energy release during recombination of all these radicals would raise the temperature by only a few degrees. Since the effect of ignition temperature reduction is more significant,
$\Delta T \sim 100$ K, it can only be due to chain reactions of radical species generated in the plasma.

![Graph comparing ignition delay for plasma assisted ignition and thermal ignition](image)

Figure 5.9: Comparison of ignition delay for plasma assisted ignition and for thermal ignition, predicted by the kinetic model in hydrogen-air using the full set of reactions. $\phi=1.0$, $P=150$ torr. Ignition temperature reduction is solely due to radical species generation on the plasma.

### 5.3 Thermal ignition in ethylene-air mixture

This section compares predictions of dominant species concentrations, time-dependent temperature rise, and ignition delay during thermal ignition of ethylene-air obtained using GRI Mech 3.0 mechanism and reduced UCSD mechanism (see Table 4.6) at two different pressures, $P=150$ torr and 760 torr, and different initial temperatures ranging from 1000 K to 2500 K. This has been done to observe how close the predictions of these two mechanisms are for thermal ignition before using them in plasma assisted
ignition kinetic model. These calculations were performed in absence of heat transfer to the surrounding.

Figure 5.10 compares ignition delay time of a stochiometric ethylene-air mixture vs. initial temperature at two different pressures, P=150 torr and 760 torr predicted by the kinetic model using GRI Mech 3.0 and reduced UCSD mechanism. It is evident from these results that ignition delays predicted by these two mechanisms at P=150 torr are close to each other, compared to those results at P = 760 torr. Note that at T < 1500 K (1000 /T ≥ 0.67), ignition delay predicted using GRI Mech 3.0 mechanism is longer compared to that of the reduced UCSD mechanism.

![Figure 5.10: Comparison of thermal ignition time calculated using GRI Mech 3.0 mechanism and reduced UCSD mechanism for two different pressures. Ethylene-air, \( \phi = 1 \).](image-url)
Comparison of dominant species mole fractions predicted by the kinetic model for thermal ignition of a stoichiometric ethylene-air mixture at an initial temperature of 1100 K and two pressures, P=150 torr and 760 torr, using GRI Mech 3.0 mechanism and the reduced UCSD mechanisms is shown in Figure 5.11. In addition, time-dependent mixture temperature at these conditions is plotted in Figure 5.12. From Figure 5.11 and Figure 5.12, it can be seen again that ignition delay time predicted by the reduced UCSD mechanism is shorter than that predicted by the GRI Mech 3.0 mechanism. In addition, the rate of radical species concentrations rise predicted by the reduced UCSD mechanism is significantly more rapid than that predicted by the GRI Mech 3.0 mechanism. This difference is most likely due to the absence of primary radical generation reactions, C\textsubscript{2}H\textsubscript{4} + O\textsubscript{2} = C\textsubscript{2}H\textsubscript{3} + HO\textsubscript{2} and C\textsubscript{2}H\textsubscript{4} + HO\textsubscript{2} = CH\textsubscript{3}CHO + OH (reaction #13 and 17 of Table 4.6) in GRI Mech 3.0 mechanism, which considerably slows down chain reaction initiation in absence of plasma chemical radical generation processes, such as listed in Table 4.2 and Table 4.7. For plasma chemical fuel oxidation/ignition, which is discussed in Section 5.4, absence of these reactions is not critical since radicals, such as O, H, OH, C\textsubscript{2}H\textsubscript{3} etc., are generated in plasma chemical processes, including direct electron impact and reactions of electronically excited nitrogen molecules (see Table 4.2 and Table 4.7).
Figure 5.11: Dominant species mole fractions during thermal ignition of fuel-air, predicted by the kinetic model. GRI Mech 3.0 mechanism (left) and reduced UCSD mechanism (right). Ethylene-air, $\phi=1$, $T=1100$ K.
5.4 Nanosecond discharge in ethylene-air mixture

This section discusses the results of kinetic modeling calculation for plasma chemical ethylene oxidation/ignition using the GRI Mech 3.0 mechanism and the reduced UCSD mechanism. Similar to the plasma chemical kinetic modeling calculation for hydrogen-air described in Section 5.2, the calculations are performed for single pulse discharge and pulse burst discharge. During these calculations, heat transfer loss from the plasma-excited mixture has been incorporated, unless specified otherwise. The discharge pulse energy per molecule is 0.28 meV/molecule for all calculations discussed in this section.
5.4.1 Single pulse discharge

Figure 5.13 compares dominant neutral species mole fractions after a single pulse nanosecond discharge in a room temperature ethylene-air mixture, predicted by the plasma chemical kinetic model using the full GRI reaction mechanism and the reduced kinetic mechanism of ethylene-air combustion described in Section 4.4 (see Table 4.6), for two different pressures, (a) P=150 torr and (b) P=700 torr. These results show that for both pressures, mole fractions of dominant species formed during plasma chemical oxidation of ethylene (such as CO, CO₂, H₂O, CH₂O, and OH) predicted by these two mechanisms are quite different. In particular, the reduced UCSD mechanism predicts much lower mole fractions of CO₂, H₂O, and OH after the discharge pulse, compared to those predicted by the GRI mechanism (see Figure 5.13). For example, steady-state CO mole fraction predicted by the GRI Mech 3.0 mechanism exceeds that predicted by the reduced UCSD combustion mechanism by about a factor of ~5. Further investigation revealed that energy release during plasma chemical oxidation of ethylene at these conditions predicted by reduced UCSD mechanism is much slower than that predicted by GRI Mech 3.0 mechanism and reduced GRI mechanism listed in Table 4.5 of Section 4.4 (see Figure 5.14). This is due to the absence of some of the low temperature heat releasing reactions (reaction #5, 9, 12, 13, 14, 17 of Table 4.5) in the reduced UCSD mechanism of Table 4.6. Similar results are obtained for plasma chemical oxidation of a stoichiometric ethylene-air mixture preheated up to T= 700 K (see Figure 5.15).
Figure 5.13: Dominant species mole fractions after a single pulse nanosecond discharge, predicted by the plasma chemical kinetic model. GRI Mech 3.0 mechanism (left) and reduced UCSD mechanism (right). Ethylene-air, $\phi=1$, $T=300$ K, pulse energy loading 0.28 meV/molecule.
Figure 5.14: Input pulse energy and thermalized energy after a single pulse nanosecond discharge, predicted by the plasma chemical kinetic model using GRI Mech 3.0 mechanism, reduced GRI mechanism, and reduced UCSD mechanism. Ethylene-air, φ=1, T=300 K, pulse energy loading 0.28 meV/molecule.
This result is somewhat unexpected since radical species concentrations predicted by reduced UCSD mechanism during thermal ignition are significantly higher compared to the GRI Mech 3.0 mechanism predictions (see Figure 5.11), i.e. for plasma assisted...
ignition prediction is reversed. Note that the set of air plasma chemical reactions and reactions of ethylene dissociation is the same in both cases. However, fuel-air temperatures in these calculations (T=300 K and 700 K) are significantly lower compared to the temperature range for which both GRI Mech 3.0 and the reduced UCSD mechanism have been validated, 1500 - 2000 K [56] and 1000 - 2500 K [65], respectively, i.e. both mechanisms are compared far outside their range of applicability.

5.4.2 Pulse burst discharge

To verify whether the predictions of the two mechanisms would agree better at higher temperatures (near ignition temperature), an additional series of calculations have been done for a nanosecond pulse discharge operating in burst mode. Figure 5.16 compares dominant species mole fractions during plasma chemical oxidation of a stoichiometric ethylene-air mixture, initially at room temperature by nanosecond pulse discharge operated in burst mode, predicted using GRI Mech 3.0 mechanism and the reduced UCSD mechanism. These results are shown for the same two pressures as in Section 5.4.1. In addition, time-dependent mixture temperature at these conditions is plotted in Figure 5.17. These results show that ignition delay times predicted by the two mechanisms are relatively close (≈11 msec for GRI Mech 3.0 mechanism and ≈20 msec for reduced UCSD mechanism, see Figure 5.17). However, in this case ignition delay time predicted by GRI Mech 3.0 mechanism is shorter compared to the one predicted by reduced UCSD mechanism, which is contrary to the result obtained for thermal ignition (see Figure 5.10 and Figure 5.12). Also time evolution of key species concentrations
predicted by the two mechanisms is quite different. Similar to single pulse discharge cases discussed in Section 5.4.1, the rates of CO$_2$, H$_2$O, and OH concentrations increase before ignition predicted by the reduced UCSD mechanism, are much slower than those predicted by GRI Mech 3.0 mechanism. Again, this completely reverses the trend detected in the thermal ignition modeling calculations (see Figure 5.11). Similar results were obtained for plasma chemical oxidation/ignition of a stoichiometric ethylene-air mixture at an elevated initial temperature (T=700 K), as shown in Figure 5.18 and Figure 5.19.
Figure 5.16: Dominant species mole fractions during fuel-air oxidation/ignition using a repetitive nanosecond pulse discharge at $\nu=40$ kHz, predicted by the plasma chemical kinetic model. GRI Mech 3.0 mechanism (left) and reduced UCSD mechanism (right). Ethylene-air, $\phi=1$, $T=300$ K.
Figure 5.17: Temperature rise during fuel-air oxidation/ignition using a repetitive nanosecond pulse discharge at $\nu=40$ kHz, predicted by the plasma chemical kinetic model using GRI Mech 3.0 mechanism and reduced UCSD mechanism. Ethylene-air, $\phi=1$, $T=300$ K.
Figure 5.18: Dominant species mole fractions during fuel-air oxidation/ignition using a repetitive nanosecond pulse discharge at ν=40 kHz, predicted by the plasma chemical kinetic model. GRI Mech 3.0 mechanism (left) and reduced UCSD mechanism (right). Ethylene-air, φ=1, T=700 K.
The results of modeling calculations comparing plasma chemical fuel oxidation/ignition using the GRI Mech 3.0 mechanism and the reduced UCSD mechanism show that ignition delay time and dominant species concentrations predicted by these two mechanisms are quite different. In particular, the trend observed during thermal ignition, i.e. that reduced UCSD mechanism predicts shorter ignition delay time at $T < 1500$ K and higher radical species concentrations before ignition, is completely reversed for plasma assisted ignition. This demonstrates that the use of reduced kinetic mechanisms for thermal fuel oxidation and ignition to develop plasma-assisted oxidation/ignition reduced mechanisms is not an adequate approach. Instead, kinetic sensitivity analysis should be applied to the full set of reactions, including equilibrium chemistry and plasma chemical processes, as has been done previously to identify the
reduced mechanism of hydrogen-air plasma chemical fuel oxidation/ ignition (see Section 5.2).

Similar to numerical calculations of hydrogen-air ignition (see Section 5.2.3), the effect of radical generation in the plasma on ignition was studied by comparing ignition delay time for plasma assisted ignition and thermal ignition for ethylene-air mixture. Figure 5.20 compares ignition delay time for plasma assisted ignition and thermal ignition of a stochiometric ethylene-air mixture for different initial mixture temperatures using the GRI Mech 3.0 mechanism and the reduced UCSD mechanism. In case of plasma assisted ignition, ignition delay calculated from the end of the burst is plotted vs. mixture temperature at the end of the burst. For thermal ignition, ignition delay was calculated by setting initial mixture temperature to a value above autoignition temperature. For both cases, calculations were performed in absence of heat transfer losses from the mixture. In addition, energy release due to Joule heating of the plasma was turned off to isolate purely non-thermal effect of radical generation in the plasma on plasma assisted ignition. It can be seen from Figure 5.20 that for the same ignition delay time, (a) ignition temperature for plasma assisted ignition is lower compared to thermal ignition, for both mechanisms, and (b) at the same temperature, ignition delay time for plasma assisted ignition is much shorter compared to that for thermal ignition, by about two orders of magnitude at T ~1000 K for the reduced UCSD mechanism. This again emphasizes the importance of radicals produced by high peak voltage pulsed discharge for ignition process acceleration. It should be noted again that although thermal ignition delay predicted using reduced UCSD mechanism is shorter than that predicted using GRI
Mech 3.0 mechanism, the reverse trend is observed in case of plasma assisted ignition (see Figure 5.20).

![Graph showing ignition delay for plasma assisted ignition and thermal ignition predicted by the kinetic model using GRI Mech 3.0 and reduced UCSD mechanism. Ethylene-air, $\phi=1.0$, $P=150$ torr.]

**5.5 Comparison of kinetic model predictions with cavity flameholding experiments**

The present kinetic model has been used to explain why stable flameholding in premixed, stoichiometric ethylene-air flows requires operating the repetitive nanosecond pulse discharge at a high duty cycle (see Figure 3.25), while flameholding in non-premixed, lean hydrogen-air flows is maintained even after the plasma is turned off (see Figure 3.32), as discussed in Section 3.4.1.2. In these calculations the full hydrogen-air
chemistry mechanism (see Table 4.3) and the full GRI Mech 3.0 mechanism have been used. Figure 5.21 plots time-dependent temperatures in ethylene-air and hydrogen-air mixtures with initial temperatures corresponding to the experimental conditions of Figure 3.25 (C₂H₄-air, ϕ=1, u=80 m/sec, T=800°C) and Figure 3.32 (H₂-air, ϕ=0.44, u=80 m/sec, T=700°C), respectively, with and without plasma chemical processes given in Table 4.2. In the model, the discharge energy loading per molecule, q_{pulse}, is the same for both mixtures. From Figure 5.21, it can be seen that, although ignition occurs both with and without the plasma processes, adding them to the model reduces ignition delay time considerably, from τ_{ign}=2.7 msec to τ_{ign}≈0.2 msec in ethylene-air and from τ_{ign}=0.8 msec to τ_{ign}=0.25 msec in hydrogen-air, i.e. ignition delay time reduction in ethylene-air is more significant compared to that in hydrogen-air. This occurs due to more significant energy release in low-temperature chemical reactions among the radical species in C₂H₄-air [23], [46], [51].
Comparing ignition delay time predicted by the model with the flow residence time over the ~6 cm long cavity, $\tau_{\text{res}} \approx 0.8$ msec at $u=80$ m/sec, shows that ignition delay in ethylene-air (without the plasma processes), $\tau_{\text{ign}} = 2.7$ msec, is considerably longer, which explains ethylene-air flame extinction after the plasma is turned off. On the other hand, ignition delay in hydrogen-air (also without the plasma processes), $\tau_{\text{ign}} = 0.8$ msec, is comparable with flow residence time over the cavity, which makes possible flameholding in the absence of the plasma. With the plasma processes taken into account, ignition delay for both mixtures becomes shorter than flow residence time, thus stabilizing the flame. Although these calculations do not take into account rather complex flow and discharge geometry, they demonstrate the critical role of radical generation processes by the nanosecond pulse discharge for flameholding in high-speed flows.
Chapter 6: Summary and Conclusion

This dissertation presents an experimental study of plasma assisted ignition and flameholding of high speed, room-temperature ethylene-air and hydrogen-air flows in the pressure range of $P=0.2-0.26$ atm, using a diffuse, large volume, low-temperature, non-equilibrium plasma produced in a cavity. The plasma is produced by a repetitive, high peak voltage nanosecond pulse discharge. The dissertation also incorporates a kinetic modeling study of plasma assisted ignition of ethylene-air and hydrogen-air mixtures, to investigate the effect of radical generation in the plasma on ignition delay. Previous studies of plasma assisted ignition of high speed flows using a cavity (see Refs. [31] and [32]) used either strong flow preheating (flow static temperature of $\sim1300$ K) or high-power arc discharges to achieve ignition. To the author’s best knowledge, this is the first work where a diffuse, volume filling, low-temperature plasma produced by high peak voltage, repetitive nanosecond pulse discharge is used to ignite high speed flows.

For the experimental study, three different cavity geometries, viz., a small square shape cavity ($L/D=1$), a large rectangular cavity ($L/D=3$), and a reduced size rectangular cavity ($L/D=3$), have been used to achieve ignition and flameholding by increasing flow residence time in the plasma sustained in the cavity. The results of small cavity experiments in premixed stoichiometric ethylene-air flows at $P=0.2$ atm demonstrate that
repetitive nanosecond pulse plasma assisted ignition occurs via formation of multiple arc filaments in the fuel-air plasma, although air plasma remains diffuse and low-temperature until the fuel is added. After ignition, when the flame couples out to the main flow, the plasma becomes diffuse again. It is also observed that the use of a small cavity results in repetitive ignition and flame blow-off, caused by a slow rate of mixing between the main flow and the cavity, which results in combustion products remaining in the cavity for extended periods of time (up to a few tens of milliseconds). To counter this effect, which becomes more pronounced at higher flow velocities (u=50-70 m/sec), a small fraction of the main premixed fuel-air flow (up to 1%) was injected into the cavity. Although this approach considerably reduced delay time between ignition events and increased burned fuel fraction, ignition could not be achieved beyond the flow velocity of 70 m/sec. Two other critical issues which adversely affect flameholding during these experiments are combustion instability caused by feedback between fluctuations of test section pressure and the flow rate and thermal choking of the flow in the extension channel downstream of the test section. These problems have been circumvented by increasing the length-to-depth ratio of the cavity (to L/D=3), choking the inlet air and fuel flows, and removing the extension channel used for combustion products sampling.

The small square shape cavity (L/D=1) combustor has also been used to compare ignition and flameholding achieved in premixed ethylene-air flows using a repetitive nanosecond pulse discharge with that using a DC arc discharge of approximately the same power (100 W) sustained in the cavity of the same geometry. The results showed that the DC discharge resulted in sporadic ignition and flame blow-off at a very low
repetition rate (a few Hz), much lower burned fuel fraction (by about an order of magnitude) compared to that of the repetitive nanosecond pulse discharge, and significantly lower flow velocity at which ignition could be achieved.

Experiments performed using the large rectangular cavity (L/D=3) combustor with the main flow choked upstream of the combustor demonstrated nearly complete combustion in both premixed and partially premixed ethylene-air flows at flow velocities up to 100 m/sec at P=0.2 atm, with high burned fuel fraction (~80-90%) over a wide range the flow velocities. For partially premixed hydrogen-air flows stable ignition and flameholding have been achieved at the same discharge pressure of P= 0.2 atm, for flow velocities of up to u≈100 m/sec and equivalence ratios of $\phi=0.44-0.96$. ICCD camera images of ethylene-air and hydrogen-air plasmas and flames demonstrate the same qualitative plasma and flame behavior as observed in small cavity, i.e. (a) filament formation in the plasma prior to ignition and diffuse plasma formation after ignition, and (b) flame coupling out to the main flow. During these experiments, air plasma temperature was in the range of 70° C to 200° C, while stable flame temperature after ignition was 700-1000° C.

Estimates based on temperature and pressure measurements in premixed ethylene-air flows show that for a flow velocity of $u\approx100$ m/sec ($M\approx0.3$) before ignition, the velocity and Mach number of combustion product in the combustor can reach $u\approx400$ m/sec and $M\approx0.6$. Since combustion in a high speed flow downstream of the cavity occurs over a fairly long distance, up to a few tens of cm, the flow of combustion products in the extension channel downstream of the combustor is approaching transonic
regime and may thermally choke. Evidence of thermal choking, such as significant static pressure rise after ignition and high amplitude pressure oscillations, has been detected when the extension channel was used for sampling of combustion products into the FTIR spectrometer.

When the nanosecond pulse discharge is operated in repetitive burst mode, stable ethylene-air flame in the test section is maintained only at fairly high duty cycles, increasing from 9% at u=35 m/sec to 50% at u=80 m/sec. This implies that flameholding in ethylene-air flows at higher flow velocities requires the plasma to be sustained continuously. However, in hydrogen-air combustion experiments a stable self-sustained flame is observed after the plasma is turned off, as long as the fuel and air supply remain uninterrupted. This suggests that ignition and flameholding in hydrogen-air flows, initially at room temperature, can be achieved at significantly higher flow velocities and Mach numbers, using a very low discharge burst duty cycle.

It has been observed in the present study that to achieve ignition and stable flameholding in premixed and partially premixed ethylene-air and hydrogen-air flows, the equivalence ratio needs to exceed $\varphi \approx 0.5$. As a result, the amount of fuel burned during these experiments at flow velocities near 100 m/sec would be quite significant, thus producing significant heat release in the combustor during operation, up to ~50 KW. Therefore, further combustion experiments have been conducted in non-premixed flows, with fuel injected into the cavity near the plasma. This approach confined the region of combustion mostly to the cavity, reducing the amount of fuel needed to sustain a stable flame and thereby significantly reducing energy release during combustion at high flow.
velocities. During non-premixed combustion experiments in ethylene-air at $P=150$ torr, ignition and stable flameholding is observed at flow velocities up to 90 m/s, at global equivalence ratio as low as $\varphi \approx 0.1$. At higher flow velocities, combustion becomes unstable due to poor fuel air mixing in the cavity. On the other hand, the highest flow velocity at which stable flameholding is observed in non-premixed hydrogen-air flows at the same static pressure ($P=150$ torr) is 140 m/sec with a global lean flammability limit of $\varphi \approx 0.06$. Increasing the static pressure to 200 torr increased the upper limit of flow velocity for stable flameholding to 190 m/sec and reduced lean flammability limit to $\varphi \approx 0.04$. No experiments have been performed at flow velocities above 200 m/sec since flow choking has been observed upstream of the cavity at these conditions. Flow choking caused pressure rise in the combustor when the main flow mass flow rate was increased to reach flow velocities above 200 m/sec. ICCD camera images taken during these experiments again demonstrated that the nanosecond pulse discharge plasma becomes filamentary in presence of fuel before ignition, and becomes diffuse as the flame develops and fills the cavity. Time-averaged temperature measurements in the air plasma and in the plasma in non-premixed hydrogen-air flow again showed that the air plasma temperature remains quite low, below 200° C, whereas in presence of hydrogen injection the plasma temperature increases above 700° C, due to energy release during combustion. Temperature measurements in non-premixed ethylene-air flames have not been performed due to unstable combustion which made it difficult to obtain results with good run-to-run reproducibility.
To observe the dynamics of fuel-air mixing in the cavity during fuel injection, high frame rate NO PLIF imaging and schlieren imaging have been used. NO PLIF images visualized transient mixing of NO-N\(_2\) and NO-He injection flows with the cavity recirculation flow after the onset of injection. However, flow mixing pattern at steady state conditions could not be visualized due to high concentrations of NO in the cavity, which made the medium optically thick. Schlieren imaging was used to visualize the injection flow path inside the cavity in the beginning of injection. At steady conditions, the contrast of schlieren images was not sufficient for injection flow visualization inside the cavity.

In the present work, OH PLIF imaging has been used to detect ignition and flame propagation in the cavity in non-premixed ethylene-air and hydrogen-air flows. Based on the results of these experiments, it has been concluded that the laser pulse energy of 0.2 mJ was not sufficient to detect flame development during plasma assisted ignition, at low global equivalence ratio used in the present work, due to low OH concentrations immediately after the ignition. However, once the flame filled the cavity, the fluorescence signal intensity somewhat increased, allowing flame visualization for hydrogen-air combustion. For ethylene-air combustion, OH PLIF signal was too weak to detect even a fully developed flame.

Since the large rectangular cavity (L/D) combustor could not be used to study plasma assisted ignition and flameholding at flow velocities beyond 200 m/sec, due to flow choking in the combustor. A combustor with a reduced size cavity with same cavity aspect ratio (L/D=3) has been used for further experiments. During these experiments the
high voltage electrode was flush mounted in the bottom wall of the cavity to remove flow obstruction caused by a cylindrical electrode inside the cavity. Although this combustor design allowed increasing the main flow velocity to 230 m/sec without flow choking, the nanosecond pulse discharge was observed to form strong arc filaments in the cavity when the high voltage electrode was not covered with a dielectric plate. The air plasma temperature measurements during these experiments showed that the plasma temperature was quite high, above 500° C, due to the presence of high temperature arc filaments. When the high voltage electrode was covered with a dielectric plate, breakdown was observed between the high voltage electrode and the grounded metal combustor walls via the interface between the electrode and the dielectric plates. As a result, no plasma was produced in the cavity at these conditions. This result suggests that the combustor needs to be manufactured out of easily machinable dielectric material, such as nylon, with inner walls covered with high temperature resistant macor ceramic plates, to protect nylon from heat release during combustion.

In order to obtain insight into the kinetics of radical generation in plasma and its effect on oxidation/ignition of ethylene and hydrogen, a plasma chemical kinetic modeling study has been performed in the present work. First the kinetic model has been used to study the effect of electron attachment processes in a low temperature plasma produced by a single nanosecond pulse discharge in air at P=150-760 torr on efficiency of radical species generation (O atoms). From this study it has been observed that although electrons disappear more rapidly in high pressure air plasma due to three-body attachment to oxygen, this does not result in reduction of O atom yield. In the entire
range of pressures modeled, the discharge is observed to be highly efficient for O atom generation, with nearly 40% of total input discharge energy stored in O atoms.

The kinetic model has also been used to compare the full mechanism of hydrogen-air combustion chemistry with a reduced combustion chemistry mechanism, both for a single-pulse nanosecond discharge and for a burst mode discharge, for different initial pressures and temperatures. From the calculations for a single pulse discharge, it has been observed that the dominant neutral species concentration (such as O, H, OH, H₂O, and O₃) predicted by the reduced mechanism are very close to those predicted by the full mechanism, both at room temperature and near autoignition temperature (at T=600 K) over a pressure range of 150 to 760 torr. It is also observed that at temperatures close to autoignition temperatures, radical species loss in recombination becomes insignificant compared to radical generation via chain branching. The modeling calculation results for pulse burst discharge in hydrogen-air, at the same pressures and initial temperatures also demonstrated that predictions of dominant species concentrations and ignition time by both kinetic mechanisms are very close.

Kinetic modeling calculations performed to study the effect of non-thermal radical generation processes in nanosecond pulse discharge plasma on oxidation/ignition of hydrogen-air mixtures showed that removal of radical generation inhibits low temperature exothermic chemical reactions, thus blocking ignition. Further study of the effect of radical generation in the nanosecond pulse discharge plasma on hydrogen-air ignition, performed by comparing ignition delay time for plasma assisted ignition and for
thermal ignition, again demonstrated that radicals produced in the discharge accelerate ignition process significantly and reduce ignition temperature by nearly 100 K.

Kinetic modeling study of thermal and nanosecond pulse discharge plasma assisted ignition of ethylene-air has been performed to compare concentrations of dominant species formed during oxidation/ignition processes and ignition time predicted by two mechanisms, viz. the GRI Mech 3.0 and the reduced UCSD mechanism. The calculation results showed that for thermal ignition, ignition delay times predicted by these two mechanisms in the temperature range of 1000 – 1500 K are fairly close. It is also observed that thermal ignition delay predicted by reduced UCSD mechanism is shorter than that predicted by GRI Mecha 3.0 mechanism, due to the absence of key chain initiation processes in the latter mechanism, which slows down radical species generation before ignition.

Dominant neutral species mole fractions predicted by these two models for plasma assisted ethylene oxidation, have been observed to be quite different. Specifically, the reduced UCSD mechanism predicts much lower mole fractions of CO$_2$, H$_2$O, and OH after the discharge pulse, compared to those predicted by the GRI Mech 3.0 mechanism. The same trend has been observed for nanosecond discharge operated in the burst mode. Also, ignition delay time predicted by the GRI Mech 3.0 mechanism in these calculations is shorter compared to that predicted by reduced UCSD mechanism. This is completely opposite to the trend observed in thermal ignition modeling calculations. Comparison of ignition delay times predicted by the two mechanisms for thermal ignition and for nanosecond pulse discharge induced ignition of ethylene-air again showed that radical
generated by plasma chemical processes significantly reduce ignition delay time as well as ignition temperature (by ~ 100 - 300 K). It has also been observed that ignition delay predicted by the reduced UCSD mechanism is significantly longer, by almost two orders of magnitude, than that predicted by the GRI Mech 3.0 mechanism, again reversing the trend detected in thermal ignition calculations. This demonstrates that the use of reduced kinetic mechanisms for thermal fuel oxidation and ignition to develop plasma-assisted oxidation/ignition reduced mechanisms is not an adequate approach. Instead, kinetic sensitivity analysis should be applied to the full set of reactions including equilibrium chemistry and plasma chemical processes, as has been done previously to identify the reduced mechanism of hydrogen-air plasma chemical fuel oxidation/ignition.

Finally, the kinetic model has been used to interpret the results of flameholding experiments in premixed ethylene-air and hydrogen-air flows. The modeling calculation results suggest that ignition delay in the ethylene-air mixture at the experimentally measured flame temperature (~700° C) is of the order of the main flow residence time over the cavity, whereas ignition delay in the hydrogen-air mixture at similar conditions is shorter than the flow residence time over the cavity. This explains why the ethylene-air flame was blown off after the nanosecond pulse discharge plasma was turned off; while stable flameholding was achieved in the hydrogen-air flow after the plasma was turned off. According to the kinetic model predictions, plasma chemical radical generation processes reduce ignition delay in the ethylene-air flow to a value below the flow residence time over the cavity, which results in stable flameholding, as indeed observed in the experiments.
The results of the present work demonstrate that the use of a cavity with a length-to-depth ratio of $L/D=3$ allows maintaining a stable flame in high-speed ethylene-air and hydrogen-air flow ignited by repetitive nanosecond pulse discharge. However, significant main flow disturbance induced by the cavity, with the depth comparable to the main flow height, caused flow choking in the combustor at average flow velocities above 200 m/sec. Therefore, in future studies of plasma assisted ignition and flameholding in transonic and supersonic flows, the dimensions of the cavity need to be reduced while keeping the cavity aspect ratio the same. This approach will require redesigning the electrode geometry to accommodate the electrodes inside the reduced size cavity. Although a flat, rectangular shape high voltage electrode flush mounted in the cavity bottom is attractive since it does not disrupt the flow inside the cavity, the results of the present work suggest that this design is not suitable for producing diffuse plasma in the cavity. Therefore a cylindrical electrode, similar to the one used in the large size cavity in the present work, but with a smaller diameter, may need to be used in the reduced size cavity. Also, to avoid arcing inside the combustor, it needs to be manufactured of a machinable dielectric material, such as nylon plastic, with inner walls covered with high temperature resistant macor ceramic plates to protect nylon from heat release during combustion. The future work should also incorporate high frame rate optical diagnostics such as schlieren imaging, NO PLIF, and OH PLIF imaging, to study fuel-air mixing in the cavity before and during combustion, as well as flame development.
References


Appendix A

Calibration of mass flow meters for different gases

Mass flow meters used in the present work have been calibrated by the manufacturer (Omega Engineering Inc.), using nitrogen as test gas, and conversion factors (K factors) have been provided to obtain mass flow rates for other gases from the flow meter reading. Since in the present work, these flow meters have been used to measure flow rates of gases other than nitrogen. They have been calibrated in-house to verify the accuracy of measured flow rates. The calibration has been performed by measuring mass flow rate using a sonic choke of known cross sectional area, for the range of fuel flow rates used during the combustion experiments. The mass flow rate has been calculated from pressures measured upstream and downstream of the sonic choke plate,

\[
\dot{m} = \frac{P_0 A^*}{\sqrt{T_0}} \sqrt{\frac{\gamma}{R} \left( \frac{2}{\gamma + 1} \right)^{(\gamma+1)/(\gamma-1)}}
\]

where \( P_0 \) and \( T_0 \) are pressure and temperature of the flow upstream of the choke plate where the flow is near stagnation, \( A^* \) is the cross sectional area of the circular orifice in the choke plate, \( \gamma \) is the specific heat ratio, and \( R \) is the gas constant. The mass flow rate calculated using this method for a particular gas has been compared with that
obtained using the table of K factors provided by the flow meter manufacturer, for same flow meter reading. Figure A.1 shows the mass flow rate of ethylene measured using both an Omega FMA-A2322 mass flow meter and a sonic choke plate. It is evident from the plot that the flow meter K factor for ethylene is very accurate in the flow rate range of interest. The other flow meter used in present work (Omega FMA-A1844) was not calibrated for ethylene, since it has not been used to measure ethylene flow rate during the combustion experiments. For hydrogen, mass flow rate measured using a sonic choke plate and using the flow meter K factor table turned out to be completely different, for both flow meters used in present work (see Figure A.2). Therefore, both flow meters have been calibrated using sonic choke measurements (see Figure A.3). The trend lines obtained from these data have been used to determine the actual mass flow rate of hydrogen from the flow meter reading during the present combustion experiments. In addition, Omega FMA-A2322 mass flow meter has also been calibrated for helium. Figure A.4 shows comparison between the actual flow rates obtained using sonic choke measurements and the flow meter calibration table provided by the manufacturer, for different flow meter readings. Again, it can be seen that the flow rate obtained using the calibration table is quite different from the actual value. Therefore, the flow meter calibration line shown in Figure A.4, based on sonic choke measurements, was used for helium flow rate measurements in the present work. The discrepancy between the flow rates obtained using a sonic choke plate and the flow meter K factor table for hydrogen and helium is expected, since the flow meter operation manual contains a warning
regarding significant alteration of dynamic response and stability of the flow meter while measuring flow rates of these two gases.

Figure A.1: Comparison between ethylene flow rates obtained using (i) Omega FMA-A2322 mass flow meter K factor table and (ii) sonic choke plate.
Figure A.2: Comparison between hydrogen flow rates obtained using (i) mass flow meter K factor table and (ii) sonic choke plate.

Figure A.3: Hydrogen flow rate calibration plots obtained using sonic choke plate measurements for (a) Omega FMA-A2322 mass flow meter and (b) Omega FMA-A1844 mass flow meter.
Figure A.4: Helium flow rate calibration plot obtained using sonic choke plate measurements for Omega FMA-A2322 mass flow meter, compared with that obtained using manufacturer’s K factor table.
Appendix B

Calculation of optical thickness of the medium for NO PLIF measurements

Optical thickness of a medium is the measure of the fraction of optical signal absorbed in the medium along its path. During the NO PLIF experiments, emitted fluorescence signal from laser-excited NO molecules can be absorbed by surrounding unexcited NO molecules followed by subsequent re-emission. If this process occurs in the medium during the PLIF experiment, then the fluorescence signal collected by the camera would come not only from the region illuminated by laser sheet but also from the surrounding gas volume. Therefore, images obtained at these conditions would not yield actual distribution of NO in the medium in the laser sheet plane. For a medium with NO number density $N_1$, the optical thickness ($L$) is given by the following expression [72]:

$$L = \frac{1}{N_1 f_i \sigma_{ge}(\nu)} \ln \left( \frac{I_0(\nu)}{I(\nu)} \right),$$

where $I_0(\nu)$ is the fluorescence signal intensity at frequency $\nu$, emitted by the laser excited medium, $I(\nu)$ is the fluorescence signal intensity after the signal has traversed
over distance L in the medium, \(f_i\) is the Boltzmann fraction, and \(\sigma_{ge}(v)\) is the absorption cross section of NO molecule.

The absorption cross section [72] is given by

\[
\sigma_{ge}(v) = B_{ge} \cdot h \cdot v \cdot g(v),
\]

where \(B_{ge}\) is the average Einstein B coefficient for NO excitation transition lines \(Q1(7)+Q21(7)\) of \((X^2\Pi(v''=0) \rightarrow A^2\Sigma^+(v'=0))\) resulting in fluorescence, \(h\) is the Plank constant, and \(g(v)\) is the absorption line shape function.

The line shape function is determined considering natural broadening \((\Delta \nu_N)\), collisional or pressure broadening \((\Delta \nu_C)\), and Doppler broadening \((\Delta \nu_D)\) of the fluorescence signal at high pressures (above a few torr), when pressure broadening becomes comparable with Doppler broadening, the line shape function is given by the Voigt profile [72], i.e.,

\[
g(v) = \left( \frac{1}{\Delta \nu_D} \right)^\frac{\ln 2}{\pi} \frac{B}{\pi} \int_{-\infty}^{\infty} \frac{e^{-y^2}}{B^2 + (D - y)^2} dy,
\]

where

\[
B = \sqrt{\ln 2 \frac{\Delta \nu_N + \Delta \nu_C}{\Delta \nu_D}}, \quad (B4)
\]

\[
D = \sqrt{\ln 2 \frac{\nu - \nu_0}{\Delta \nu_D}}, \quad (B5)
\]

\[
\Delta \nu_D = \frac{2 \nu_0}{c} \sqrt{\frac{2 \ln 2 \cdot kT}{m_{NO}}}, \quad (B6)
\]

\[
\Delta \nu_N = \frac{A_{ge}}{2\pi}, \quad (B7)
\]
and \[ \Delta \nu_c = \frac{\sum C_i Z_i}{\pi}. \] (B8)

In Eqs. (B5) - (B7), \( \nu_0 \) is the frequency on the line center, \( A_{eg} \) is the Einstein A coefficient for \( A^2 \Sigma ' (v'=0) \rightarrow X^2 \Pi (v''=0) \) transition of NO molecule, \( k \) is the Boltzmann constant, and \( T \) is the temperature of the gas mixture.

In Eq. (B8), \( Z_{ci} \) represents the rate of collisions of NO molecules with molecules of species \( i \),

\[ Z_{ci} = N_i \sigma_{ai} \left( \frac{8 \pi k T}{\mu_{ai}} \right)^{1/2}, \] (B9)

where \( N_i \) is the number density of species \( i \), \( \sigma_{ai} \) is the effective cross section for collisions between molecules of species \( A \) (i.e. NO molecules) and molecules of species \( i \), and \( \mu_{ai} \) is the collision reduced mass,

\[ \mu_{ai} = \frac{m_A m_i}{m_A + m_i}, \] (B10)

where \( m_A \) and \( m_i \) are molecular masses of NO and species \( i \), respectively.

For collisions between molecules of the same species \( A \),

\[ Z_{ci} = \frac{N_A \sigma_{AA}}{2} \left( \frac{16 \pi k T}{m_A} \right)^{1/2}. \] (B11)

Using Eqs. (B1) - (B11) the optical thickness of the medium has been calculated for both \( N_2 (80\%) - \text{NO (20\%)} \) and \( \text{He (95\%)} - \text{NO(5\%)} \) injection flows in main flow of \( N_2 \).
**N₂ (80%) - NO (20%) injection into main N₂ flow**

Test conditions: P = 150 torr ≈ 0.2 atm, T = 300 K, u = 100 m/sec

N₂ flow rate in the main flow is 560 SLM

Estimated 10% - 15% of the main flow enters the cavity, therefore, N₂ flow entering into the cavity is \( -0.1 \times 560 = 56 \) SLM.

In NO PLIF experiments N₂ - NO injection flow rate = 3 SLM (mass flow rate 0.057 g/sec).

Therefore, NO injection flow rate is \( 0.2 \times 3 = 0.6 \) SLM and N₂ injection flow rate is \( 3 - 0.6 = 2.4 \) SLM.

After the injection flow is mixed with the main N₂ flow entering the cavity, the NO mole fraction in the cavity mixture of N₂ - NO is \( \frac{0.6}{56 + 3} = 1.02 \times 10^{-2} \)

Therefore, N₂ mole fraction in the cavity mixture is \( 1 - 1.02 \times 10^{-2} = 0.99 \)

Using Eq. (B11) for NO - NO collisions,

\[
Z_{CA} \approx (0.2 \times 10^{1325} \times 1.02 \times 10^{-2}) \times \left( \frac{40 \times 10^{-20}}{2} \right) \times \left( \frac{16\pi}{30 \times 1.66 \times 10^{-27} \times 1.38 \times 10^{-23} \times 300} \right)^{1/2} \\
= 2.03 \times 10^7 \text{ sec}^{-1}.
\]

Similarly, for N₂ – NO collisions, using Eqs. (B9) and (B10),

\[
Z_{CB} \approx (0.2 \times 10^{1325} \times 0.99) \times \left( \frac{40 \times 10^{-20}}{2} \right) \times \left( \frac{8\pi}{14.48 \times 1.66 \times 10^{-27} \times 1.38 \times 10^{-23} \times 300} \right)^{1/2} \\
= 4.03 \times 10^9 \text{ sec}^{-1}.
\]

Hence, Eq. (B8) gives collisional broadening

\[
\Delta v_c = \frac{Z_{CA} + Z_{CB}}{\pi} = 1.29 \times 10^9 \text{ sec}^{-1}.
\]
Now, using Eq. (B7) natural broadening, \( \Delta v_N = \frac{A_{eg}}{2\pi} = \frac{9.276 \times 10^5}{2\pi} = 1.48 \times 10^5 \text{ sec}^{-1} \)

The value of the Einstein A coefficient for \( A^2\Sigma^+ (\nu' = 0) \rightarrow X^2\Pi (\nu'' = 0) \) transition of NO molecule used in expression above is obtained from LIFBASE software [73].

Doppler broadening can be obtained using Eq. (B6) in the following way,

\[
\Delta v_D = 2 \cdot \left( \frac{1}{226.502 \times 10^{-9}} \right) \times \sqrt{\frac{2 \ln 2 \times 1.38 \times 10^{-23} \times 300}{30 \times 1.66 \times 10^{-27}}} = 3 \times 10^9 \text{ sec}^{-1}
\]

Once values of \( \Delta v_C, \Delta v_N, \) and \( \Delta v_D \) are calculated, the integral in the Eq. (B3) is then evaluated numerically. This gives \( g(\nu) = 2.183 \times 10^{-10} \text{ sec} \)

Then, from Eq. (B2) we get

\[
\sigma_{ge}(\nu) = 4.27 \times 10^8 \times 6.626 \times 10^{-34} \times \left( \frac{3 \times 10^9}{226.502 \times 10^{-9}} \right) \times 2.183 \times 10^{-10} = 8.12 \times 10^{-20} \text{ m}^2
\]

The value of the Einstein B coefficient for \( Q1(7)+Q21(7) \) lines of \( X^2\Pi (\nu'' = 0) \rightarrow A^2\Sigma^+ (\nu' = 0) \) transition of NO molecule used in expression above is obtained from LIFBASE software [73].

NO number density, \( N_1 = \frac{0.01017 \times 0.2 \times 101325}{1.38 \times 10^{-23} \times 300} = 4.978 \times 10^{22} \text{ m}^{-3} \)

Finally, using Eq. (B1) and using \( \ln \left( \frac{I_0(\nu)}{I(\nu)} \right) = 1 \), we get the optical thickness,

\[
L = \frac{1}{4.978 \times 10^{22} \times 0.1 \times 8.12 \times 10^{-20}} = 2.5 \times 10^{-3} \text{ m} \approx 2.5 \text{ mm}.
\]

Thus, the optical thickness is much less than the width of the cavity (5 cm).
**He (95%) - NO (5%) injection into main N₂ flow**

Test conditions: P= 150 torr ≈ 0.2 atm, T = 300 K, u= 150 m/sec

N₂ flow rate in the main flow is 844 SLM

Estimated 10% - 15% of the main flow enters the cavity, therefore, N₂ flow entering into the cavity is \( \sim 0.1 \times 844 = 84.4 \) SLM

During NO PLIF experiments, He - NO injection flow rate is 28.2 SLM (mass flow rate 0.038 g/sec).

Therefore, NO injection flow rate is \( 0.05 \times 28.2 = 1.41 \) SLM and He injection flow rate is \( 28.2 – 1.41 = 26.79 \) SLM

After the injection flow is mixed with the main N₂ flow entering the cavity, the NO mole fraction in the cavity mixture of He, N₂, and NO is \( \frac{1.41}{84.4 + 28.2} = 0.0125 \)

Mole fraction of He in the mixture is \( \frac{26.79}{84.4 + 28.2} = 0.238 \)

Therefore, N₂ mole fraction in the cavity mixture is 1 - 0.238 - 0.0125 \( \approx 0.75 \)

Using Eqs. (B11) for NO - NO collision,

\[
Z_{CA} \approx (0.2 \times 101325 \times 0.0125) \times \left(\frac{40 \times 10^{-20}}{2}\right) \times \left(\frac{16\pi}{30 \times 1.66 \times 10^{-27} \times 1.38 \times 10^{-23} \times 300}\right)^{1/2}
\]

\[= 2.5 \times 10^7 \text{ sec}^{-1}.\]

Similarly, for He - NO collision using Eq. (B9) and (B10),

\[
Z_{CB} \approx (0.2 \times 101325 \times 0.238) \times \left(\frac{40 \times 10^{-20}}{2}\right) \times \left(\frac{8\pi}{1.875 \times 1.66 \times 10^{-27} \times 1.38 \times 10^{-23} \times 300}\right)^{1/2}
\]

\[= 1.35 \times 10^9 \text{ sec}^{-1}.\]

Then, for N₂ - NO collision using Eqs. (B9) and (B10),
\[ Z_{CC} \approx (0.2 \times 101325 \times 0.7495) \times \left( \frac{40 \times 10^{-20}}{2} \right) \times \left( \frac{8\pi}{14.48 \times 1.66 \times 10^{-27} \times 1.38 \times 10^{-23} \times 300} \right)^{1/2} \]

\[ = 1.5 \times 10^9 \text{ sec}^{-1}. \]

Hence, Eq. (B8) gives collisional broadening:

\[ \Delta \nu_C = \frac{Z_{CA} + Z_{CB} + Z_{CC}}{\pi} = 9.2 \times 10^8 \text{ sec}^{-1}. \]

Now, using Eq. (B7) natural broadening, \( \Delta \nu_N = \frac{A_{eg}}{2\pi} = \frac{9.276 \times 10^5}{2\pi} = 1.48 \times 10^5 \text{ sec}^{-1} \)

The value of \( A_{eg} \) for \( \Lambda^2\Sigma^+ (v'=0) \rightarrow \Lambda^2\Pi(v''=1) \) transition of NO molecule used in above expression is obtained from LIFBASE software [73].

Doppler broadening can be obtained using Eq. (B6) in the following way,

\[ \Delta \nu_D = 2 \cdot \left( \frac{1}{226.502 \times 10^{-9}} \right) \times \sqrt{\frac{2 \ln 2 \times 1.38 \times 10^{-23} \times 300}{30 \times 1.66 \times 10^{-27}}} = 3 \times 10^5 \text{ sec}^{-1} \]

Once values of \( \Delta \nu_C, \Delta \nu_N, \) and \( \Delta \nu_D \) are calculated, the integral in the Eq. (B3) is then evaluated numerically. This gives \( g(\nu) = 2.4 \times 10^{-10} \text{ sec} \)

Then, from Eq. (B2) we get

\[ \sigma_{ge}(\nu) = 4.27 \times 10^8 \times 6.626 \times 10^{-34} \times \left( \frac{3 \times 10^8}{226.502 \times 10^{-9}} \right) \times 2.4 \times 10^{-10} = 9 \times 10^{-20} \text{ m}^2 \]

The value of the Einstein B coefficient for Q1(7)+Q21(7) lines of \( \Lambda^2\Pi(v''=0) \rightarrow \Lambda^2\Sigma^+ (v'=0) \) transition of NO molecule used in expression above is obtained from LIFBASE software [73].

NO number density, \( N_1 = \frac{0.0125 \times 0.2 \times 101325}{1.38 \times 10^{-23} \times 300} = 6.118 \times 10^{22} \text{ m}^{-3} \)

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Finally, using Eq. (B1) and using $\ln \left( \frac{I_0(\nu)}{I(\nu)} \right) = 1$, we get the optical thickness,

$$L = \frac{1}{6.118 \times 10^{-22} \times 0.1 \times 9 \times 10^{-20}} = 1.81 \times 10^{-3} \text{ m} \approx 2 \text{ mm}$$

Again, the optical thickness is much less than the width of the cavity. Therefore, for the NO - N$_2$ and NO - He mixtures to be optically thin, NO mole fraction in the injection flow should not exceed 1% and 0.2%, respectively.
Appendix C

Operating procedure for plasma assisted combustion facility

The following steps need to be followed sequentially to perform plasma assisted combustion experiments using the experimental setup described in Section 2.1:

1. The butterfly valve isolating the high speed combustion tunnel from the vacuum system needs to be fully open, and the vent valve connected to the vacuum system downstream of the butterfly valve needs to be fully closed.

2. The vacuum pump should be turned on while keeping the pump inlet valve fully closed. After the pump is turned on, the valve should be opened (10-20% of full scale) to pump out the vacuum system.

3. The DC power supply for the Omega OMB-DAQ-56 USB data acquisition system (DAQ) for the pressure transducer should be turned on and the voltage should be subsequently set to 10 V. The data acquisition system should always be connected to the Gateway laptop computer by a USB cable. A solid green light on the DAQ indicates a proper connection. Flashing green light or no light indicates an improper connection. However, the green light will be flashing during data acquisition. The laptop computer should remain powered on all the times, since turning it off or restarting it may cause connection problems between the DAQ and the laptop. If
connection problem occurs, the green light on the DAQ will flash a few times when the laptop is booting and then the light will disappear. If connection failure occurs then the laptop computer needs to be restarted.

4. Once the connection between the DAQ and the laptop is made successfully, the software (PDaqView) on the desktop needs to be opened. Since the laptop should be turned on all the time, it is recommended not to close the software after finishing experiments.

5. Once the vacuum system pressure is reached below 200 torr, the air cylinder valve should be opened and desired air flow rate should be set by setting the pressure upstream of the main gas delivery line choke plate to the predetermined value obtained from choked flow calculations. Once the air flow rate is set, the fuel cylinder valve and the fuel line flash arrester should be opened. Then opening the fuel cylinder regulator slowly and controlling the opening of flow metering valve located immediately upstream of the fuel mass flow meter, fuel injection flow rate needs to be set. Once the flow rates are set, air and fuel flow should be turned on and off using remote control operated solenoid valve.

6. Cooling water supply of the high voltage pulse generator (pulser) should be turned on, and then the power supply of the pulse generator should be turned on. The pulse generator coolant pressure should be checked to make sure that it does not exceed 64 kPa. Then the discharge parameters can be set using the front panel of the pulser power supply.
7. Once the pulser parameters are set the vent valve of the vacuum system should be opened partially to bring the pressure close to the baseline operating value (e.g., 150 torr or 200 torr). During the experiment, pressure in the combustor will rise, due to high air flow rate and energy release during combustion. Therefore, the vacuum system pressure should be kept below the desired baseline pressure before starting experiment.

8. To perform the experiment, first the air flow needs to be turned on, and then the fuel flow should be turned on. Fuel flow rate takes a few seconds to reach the steady state value. After the fuel flow becomes steady (indicated by the steady reading of the fuel flow meter), a high voltage pulse burst should be fired. It should be noted that waiting too long after the fuel flow reaches steady state may cause detonation in the vacuum system, producing a loud noise. Fuel supply should be turned off immediately after the end of the high voltage pulse burst. Air should be allowed to flow for a few seconds to cool down the combustor after each combustion run.

9. During combustion, the combustor pressure should be monitored using a pressure transducer and DAQ to make sure that it does not overshoot the baseline pressure by more than 10 torr, since this would alter the flow velocity an the combustor.

10. After each run there should be at least 1 min waiting period before starting the next run.