Non-equilibrium Plasma-Assisted Combustion

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Abstract

As a promising method to enhance combustion, plasma-assisted combustion has drawn considerable attention. Due to the fast electron impact excitation and dissociation of molecules at low temperatures, plasma introduces new reaction pathways, changes fuel oxidation timescales, and can dramatically modify the combustion processes. In this dissertation, the radical generation from the plasma and its effect on flame extinction and ignition were investigated experimentally together with detailed numerical simulation on a counterflow CH\textsubscript{4} diffusion flame. It was found that the atomic oxygen production played a dominant role in enhancing the chain-branching reaction pathways and accelerating fuel oxidation at near limit flame conditions. To understand the direct coupling effect between plasma and flame, a novel plasma-assisted combustion system with \textit{in situ} discharge in a counterflow diffusion flame was developed. The ignition and extinction characteristics of CH\textsubscript{4}/O\textsubscript{2}/He diffusion flames were investigated. For the first time, it was demonstrated that the strong plasma-flame coupling in \textit{in situ} discharge could significantly modify the ignition/extinction characteristics and create a new fully stretched ignition S-curve.

To understand low temperature kinetics of combustion, it is critical to measure the formation and decomposition of H\textsubscript{2}O\textsubscript{2}. A molecular beam mass spectrometry (MBMS) system was developed and integrated with a laminar flow reactor. H\textsubscript{2}O\textsubscript{2} measurements were directly calibrated, and compared to kinetic models. The results confirmed that low and intermediate temperature DME oxidation produced significant amounts of H\textsubscript{2}O\textsubscript{2}. The experimental characterizations of important intermediate species including H\textsubscript{2}O\textsubscript{2}, CH\textsubscript{2}O and CH\textsubscript{3}OCHO provided new capabilities to investigate and improve the chemical
kinetics especially at low temperatures.

A numerical scheme for model reduction was developed to improve the computational efficiency in the simulation of combustion with detailed kinetics. A multi-generation Path Flux Analysis (PFA) method for kinetic mechanism reduction is proposed and validated. In this method, the formation and consumption fluxes of each species at multiple reaction path generations were analyzed and used to identify the important reaction pathways. The comparisons of the ignition delays, flame speeds, and flame structures showed that the PFA method presented a higher accuracy than that of current existing methods in a broad range of initial pressures and temperatures.
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Chapter 1

Introduction

1.1 Motivation

About 85% of the energy we use today is derived from the combustion of fossil fuels. As an effective energy conversion method, combustion has been put to use in human society for thousands of years, with applications ranging from cooking and heating to power generation, industrial processing, transportation and propulsion. As a technology, combustion is an element critical to a wide range of problems, from national security to quality of life.

However, the demands of the modern world on emissions and energy conversion efficiency have pushed traditional combustion technology to challenging limits. Combustion of fossil fuels generates a huge amount of carbon dioxide (CO$_2$), which is widely regarded to be the cause of global warming. New combustion concepts and systems are required to achieve fuel flexibility for alternative fuels, such as biofuels which can be carbon neutral. Combustion also generates a range of air pollutants, including soot, nitrogen oxides (NO$_x$), sulfur oxides (SO$_x$) and unburned hydrocarbons. In order to reduce soot and NO$_x$ emission, energy conversion systems need to work at lower temperatures and leaner conditions even beyond the normal flammability limit. For example, gas turbine engines require leaner burning for reduced emissions. Moreover, limited fossil fuel resources and sharply increased fuel costs require higher efficiencies in conventional combustion systems. Hypersonic propulsion systems, such as supersonic combustion ramjet engines, create environments where the flow residence time in the combustor is on the same order or even smaller than chemical reaction times. Therefore,
the completion of fuel oxidation in the engine and the full extraction of chemical energy for efficient thrust can be challenging.

All these challenges necessitate the development of new technologies to enhance and control combustion processes. Regardless of the mechanical aspect of combustion systems, fuel oxidization is dominated by the chemical kinetic rate. For an elementary reaction, the Arrhenius law [1] states that the reaction rate constant is expressed as

\[ k \approx Ae^{E_a/RT} \]  

(1.1)

where \( E_a \) is the activation energy which specifies roughly the critical energy required for the reaction to occur, \( T \) is the temperature, \( A \) is the pre-exponential factor, and \( R \) is the universal gas constant. It should be noticed that it assumes that the reactants are in thermal equilibrium (equilibrium among translational, vibrational, rotational, and electronic freedom). The energy equilibration among these degrees of freedom is rapid and usually occurs within tens of nanoseconds (vibrational relaxation time scale, estimated from \( O_2 \) at 10 atm, 2000 K [2], [3] and may change significantly for different molecules at different conditions). Therefore translational temperature is usually used to represent the temperatures of the reactants in interest. Rate controlling reaction steps are usually associated with large activation energies. Initiation of fast fuel oxidation is therefore a high temperature phenomenon. In general, the rate controlling processes are chain branching reactions to produce free radicals and accelerate the exothermic oxidation reactions, in such a way that the overall reaction becomes autocatalytic.

From this simple definition of reaction rate constant, different methods can be envisioned to enhance or control the chemical kinetic process of fuel oxidation. The easiest way is to elevate the temperature. This method is called “thermal enhancement”.
However, thermal enhancement can be costly because this method requires the deposition of enthalpy into the system at the onset of the reaction. The increased temperature results in the acceleration of many reactions in addition to the rate controlling reaction steps. So the selectivity of thermal enhancement is very poor.

Another way to enhance fuel oxidation is to increase the pre-exponential factor or reduce the activation energy for the global fuel oxidation reaction. This method is called “kinetic enhancement” which has the potential to work more selectively and efficiently because only the rate limiting process is targeted.

Due to the strong dependence of fuel oxidation rate on temperature, the behavior of ignition and flame extinction can be described by the classical “S-curve” [4] as shown in Fig. 1.1.

![Stretched S-curve](image)

**Fig. 1.1** Representative folded S-curve with multiple solutions and distinct ignition and extinction states

Here, $Da$ is the Damköhler number, defined as the characteristic residence time of the flow divided by the characteristic chemical reaction time of the fuel. It is seen that ignition at a low temperature requires a larger Damköhler number than that of flame...
extinction at a high temperature. As such, for very short residence times or at low temperatures, the Damköhler number can be so small that ignition would become impossible. For example, the ignition delay of a stoichiometric C₂H₄/air mixture at 1 atm and 1000 K is about 240 ms, however, the flow residence time in a scramjet engine is generally less than 1 ms. Therefore, at the above-mentioned temperature and pressure, the flow time is too short for ignition to occur inside the scramjet engine.

In order to achieve ignition or flame stabilization at low temperatures, the characteristic chemical reaction time or the activation energy associated with the global fuel oxidation reaction needs to be reduced. As shown by the dashed curve in Fig.1.1, if one can reduce this activation energy at low temperature, the classical ignition and extinction S-curve can be stretched to make the fuel oxidation to occur under extreme conditions.

Several techniques have been attempted to enhance combustion kinetically. One example is the injection of silane, which is extremely flammable, into a high-speed flow to enhance ignition. This method was proposed in 1980 by NASA[5], [6] and used in X-43 for a Mach 10 flight test in 2005. However, silane is very explosive and causes many concerns for onboard safety. This technique also requires an additional reservoir which needs to be carried and refilled. So the challenge of developing a novel technique to enhance combustion kinetically is to generate reactive species in situ and modify the reaction pathways of fuel oxidation at extreme conditions. Motivated by this desire, plasma was proposed to enhance the combustion system kinetically.

1.2 Plasma and Its Characteristics

Plasma is defined as a collection of free, charged particles which are electrically
neutral on the average and exhibits collective effects [7]. The plasma discussed in this study can be referred as “weakly ionized plasma discharges.” If a strong electrical field is applied, the electrons can be accelerated to high energy states to cause ionization by collision with atoms or molecules in the system. At the same time, the collisions can result in excitation of atoms and molecules into different modes (vibrational, rotational, and electronic excitation), dissociation of molecules. For example, a very common reaction which happens in plasma is the dissociation of molecular oxygen (O₂) upon electron impact [8].

\[ e + O_2 \rightarrow O + O(^{1}D) + e \]  
(R1.1)

where \( e \) is the electron, \( O \) is a ground-state atomic oxygen, and \( O \ (^{1}D) \) is the excited atomic oxygen. So a Plasma is inherently a reacting flow containing a significant amount of reactive species including electrons/ions, excited species, and radicals. This reacting flow can be far from thermodynamic equilibrium.

A very important parameter of plasma is the electron temperature (or energy), \( T_e \). The averaged electron energy determines the rate constant of electron impact dissociation reactions, such as reaction (2). The electron energy \( T_e \) can be determined by the reduced electrical field defined as the electrical field intensity \( E \) divided by particle number density \( N \) [9].

\[
T_e = \frac{\sqrt{3\pi}}{4} \frac{eEL}{\sqrt{\delta}} \approx 0.8 \frac{eEL}{\sigma_r \sqrt{\delta} N}
\]  
(1.2)

where \( e \) is the elementary charge, \( l \) is the mean free path of electrons, \( \delta \) is a coefficient defined as twice the ratio of electron mass to molecular mass, and \( \sigma_r \) is the collision cross section. The reduced electric field is usually expressed using the Townsend unit “Td” which is equivalent to \( 10^{-17} \text{ V·cm}^2 \). A schematic diagram of electron temperatures and
reduced electrical fields is shown in Fig. 1.2 for different types of discharges.

![Graph showing electron temperatures and reduced electrical fields for different discharges]

Figure 1.2: Schematic comparison of electron temperatures and reduced electrical fields for different discharges, DC: direct current discharge; MW: microwave discharge; DBD: dielectric barrier discharge; RF: radio-frequency discharge.

Increasing the reduced electric field increases the averaged electron energy, and this increases the reaction rate constant in general. Figure 1.3 [10] shows an example of the variation of rate constant as a function of the reduced electric field for reaction (2). Also shown in the same plot is the rate constant of several reactions critical to homogeneous gas-phase combustion. It is seen that the rate constants of electron impact reactions are much larger than those of common radical chain-branching and initiation reactions. If plasma-induced reactions can play an important role in fuel oxidation, in principle a combustion process can be accelerated significantly.
Figure 1.3: Rate constants for reactions for dissociation by electron impact at electric field values equal to 100 Td and 200 Td and chain branching reactions [10].

Based on the energy of electrons, ions, and neutral species, the plasma can be categorized as either a non-equilibrium or an equilibrium plasma. If the electron energy (electron temperature, $T_e$) is much larger than the energy of ions (ion temperature, $T_i$), and neutral species (translational temperature, $T$), the plasma is called a non-equilibrium plasma. An equilibrium plasma has $T_e \approx T_i \approx T$. If the working gas is molecular gas, vibrational and rotational temperatures are also important. Rotational-translational energy transfer is very fast, and equilibrium usually can be reached within several collisions due to the low energy levels of rotational excitation. However vibrational-translational energy transfer is slower, especially when the energy difference between vibrational excitation levels is large, and usually takes $10^3$-$10^5$ collisions [11]. So the vibrational temperature, as well as the electronic temperature, is generally considered to be higher than the
translational temperature in non-equilibrium plasmas.

For this research, the non-equilibrium plasma is of particular interest as far as combustion is concerned. In general, non-equilibrium plasma is more effective for reactive species production owing to high electron energies while the translational temperature of the gas can be low.

Beyond radical generation, plasma also produces intermediate species which are not commonly present in a conventional combustion system. These intermediates react differently from what is found in traditional combustion chemistry. For example, approximately one half of the atomic O produced from reaction (2) is electronically excited atomic O (O(^1D)). The rate constant of the O(^1D) + H₂ ⇌ H + OH is approximately 4.4×10¹⁰ cm⁻³s⁻¹ at 300 K [12] which is seven orders of magnitude larger than the reaction for the ground-state O atom. Another example involves the inert gas. Because of electron excitation reactions, the excited inert gas can also be very reactive. For example, excited N₂ can cause O₂ or fuel molecules to dissociate upon collision. Therefore, new reaction pathways can be introduced to affect combustion kinetics.

Another feature of plasma is that the generation of reactive species in situ. In situ and real time generation of reactive species allows the creation of new oxidation pathways that are not possible without plasma. In this way, fuel oxidation can be manipulated and enhanced in a more efficient manner. These characteristics make the plasma an intriguing technique to enhance combustion.

1.3 Background of Plasma-Assisted Combustion

1.3.1 The Effect of Electric Field on Flame

As pointed out in the previous section, a plasma can be referred to as an “ionized
gas” and thermal ionization always exists. Based on the Saha equation [13], charged particle density in a combustion system is typically on the order of $10^{15}$ m$^{-3}$ due to thermal ionization alone. Chemionization is another mechanism responsible for ionization in the flame front where the electron density can reach $10^{17}$ m$^{-3}$ [14]. Flame ionization was first observed by Gilbert in the beginning of 17$^{th}$ century [15]. More than two hundred years later, William Thomas Brande observed the effect of an electrical field on a flame [15]. However, more intense research on charged species in flames started in the early 1900’s [15]. The work by Lewis [16] and Calcote [17] recognized that positive ions were the most important species affected by the electric field. The increased burning velocity and improved stabilization was caused by the movement of positive ions in the presence of an electric field, and this effect was termed the “ionic wind.” In order to mitigate the ionic wind effect, high frequency electric field was proposed by Jaggers and von Engel [18] to suppress the response of ions. They found “…the electrons can acquire only small amounts of energy but sufficient to transfer molecules and radicals from the lowest to higher vibrational states by collisions. This gives rise to an increase in the reaction rate, the burning velocity, and the propagation speed….”. Similar ideas using microwaves to enhance combustion was proposed later by many researchers[19][20]. In the work of Groff and Krage [20], thermal heating of the gas was determined to be the mechanism for flame speed enhancement. With the use of non intrusive laser diagnostics, a Princeton group demonstrated that microwaves can enhance the flame speed by up to 20% [21] due to Joule thermal heating of the flame front. A following work by Michael et al. [22] showed that microwave absorption by the flame front leads to a temperature jump in the reaction zone, and therefore accelerating the flame propagation speed.
Furthermore, other works [23–25] conducted with respect to the electric field effect on flame propagation and stability showed significant enhancement beyond the effect of the ionic wind. Nevertheless, the mechanism for coupling to the flame remains largely unknown. The proposed mechanisms include (1) localized gas heating and enthalpy addition due to the collision between electrons and flame species, (2) vibrational excitation of molecules through electron impact reactions, and (3) direct effects of the electric field on chemical reactions by activating certain species that become important in complete plasma combustion mechanisms [21].

In order to maintain localization of the interaction, the intensity of the electric field used in earlier research efforts was lower than the breakdown voltage. Therefore, both the energy and density of electrons are low. So this technique is only applicable to a system where a flame already exits. Naturally, a stronger electric field beyond breakdown which causes ionization of unignited gas can be applied to introduce larger enhancement. This is the basis behind plasma enhanced combustion.

There have been numerous contributions to plasma-assisted combustion over the world, but only a few of the significant ones are described here.

1.3.2 Early Development of Plasma-Assisted Combustion

Earlier work on applying electric discharges to a combustible mixture dates back to 1904 by Haselfoot and Kirkby [15]. They found the discharge was able to ignite the mixture at low pressure where it would not burn. In a later work, Kirkby [26] applied the electric discharge to a low pressure H₂/O₂ mixture. The chemical effect of H₂O formation by electric discharge and the formation of atomic oxygen (O) was identified. He also suggested that O collided with H₂ to form H₂O directly. In 1924, Southgate [15] applied
an arc discharge to a flame front to enhance the flame. More detailed work about the
anarc discharge was conducted in the 1960s’ [27], [28]. The Arc discharge, also
known as plasma jet or plasma torch, was used to increase the temperature of the
combustion gases while providing charged species at the same time. However, as a type
of equilibrium plasma, the temperature of a plasma torch is very high, up to 10,000 K.
Therefore, although plasma torch is a very effective method to enhance combustion,
thermal enhancement is enormously large and can suppress all other effects. Thermal
enhancement is not efficient because the poor selectivity and excessive thermal heating
can drive chemical equilibrium toward an endothermic direction. As discussed in the
comment section of Chen et al. [28], the combination of chemical heat release and
electrical heating does not appear to have any significant benefit in hypersonic propulsion.
Weinberg pointed out in the reply that “…electrical energy is thermodynamically the
most organized and, accordingly, the most expensive. Any heat or energy drawn from the
system must, therefore, derive chiefly from the chemical component….…” The exchange
clearly suggests that a more energy efficient and selective enhancing mechanism/method
is necessary. Nevertheless, as one of the most effective methods, the plasma jet was
extensively studied to enhance combustion, especially combustion stabilization/ignition
in supersonic combustion environments [29–35]. Among these works, Sloane and
Ratcliffe [35] studied the interaction between plasma jet plumes and the flame using mass
spectrometry. They found the interaction was extremely complex with many species
present simultaneously. In addition to the supersonic flow conditions and presence of
many reactive species, the plasma-flame interaction is extremely complex owing to the
coupling of thermal, kinetic, and hydrodynamic effects. Therefore, well-defined
experiments need to be developed in order to elucidate the fundamental plasma-flame interaction mechanisms.

1.3.3 Recent Progress in Plasma-Assisted Combustion

With the development of plasma technology and laser diagnostics, significant progress has been made in establishing new techniques for plasma-assisted combustion and in understanding the enhancement mechanisms of plasma-combustion interactions. A significant step forward started with the work conducted by a group at the Moscow institute of Physics and Technology (MIPT). In 1996, a type of discharge known as “Fast Ionization Wave (FIW)” was proposed as a tool for plasma-assisted ignition [36]. FIW was generated by nano-second duration high voltage pulses and could propagate on the nanosecond time scale. It could activate the reactive mixture instantaneously since the characteristic time for ignition is orders of magnitude longer. This type of nano-second pulsed discharge has three key features [36]: (1) high reduced electric fields (E/N) in the front of the wave, up to kTd, provide uniform pre-ionization, so the discharge is uniform at relatively high pressure; (2) E/N values behind the front, of hundreds of Td, guarantee high efficiency of the dissociation process via collisions with excited species of electronic degrees of freedom; (3) typical time for the production of active species is far less than the typical time of ignition/combustion, which allows one to separate in time/space plasma and combustion problems.

In 2001, the first work using FIW to assist H₂ oxidation was published [37]. A very important work by Bozhenkov, Starikovskaia and Starikovskii was published in 2003 applying FIW in a shock tube to study the plasma-combustion kinetics [38]. It was shown that FIW was capable of activating the premixture behind the reflected shock
wave nearly instantaneously while not elevating the temperature. Therefore, the kinetic effect from the discharge can be extracted and evaluated. As shown in Fig. 1.4, nanosecond discharge can significantly decrease the ignition delay of H₂ by nearly an order of magnitude. This is one of the first carefully designed experiments to decouple the thermal effect of plasma on combustion and kinetic effect. The uniformity of FIW was confirmed elsewhere [39].

![Graph showing measured ignition delay time vs. gas temperature.](image)

Fig. 1.4 Measured ignition delay time vs. gas temperature.


Along with the experiments, a kinetic model was also developed to simulate the effect of plasma on the combustible mixture. This work demonstrated the efficiency of non-equilibrium excitation over equilibrium excitation in a H₂/O₂/N₂ system as shown in Fig. 1.5. The authors also studied the importance of plasma parameters on the ignition
process.

Fig. 1.5 Calculated ignition delay time of H₂: O₂: N₂ mixture (29.6: 14.8: 55.6) as a function of energy input at P = 1 atm; T₀ = 1000 K; 1 - autoignition; 2 - equilibrium excitation; 3 – non-equilibrium excitation [38].

Since the original work in the early 2000’s, significant subsequent work has been conducted on this platform using different fuels, pressures and temperatures [40–43]. Similar observations were obtained for C₁ to C₅ alkanes. Along with the experimental work, kinetic modeling showed that the radical concentrations increased especially for O and H atom concentrations. The atomic O was shown to be the most effective to enhance the ignition [12], [41]. A comprehensive H₂/air plasma assisted combustion kinetic model was published in 2009 containing over 9000 reactions [37], although the H₂ kinetic model for conventional combustion was significantly updated for high-pressure combustion by a Princeton group [44]. A conventional H₂ combustion model only contains on the order of
10 reactions. The presence of plasma/combustion interactions introduced a great number of new reaction pathways, and the simulation is not affordable for larger hydrocarbons whose kinetic models contain thousands of reactions. Effective mechanism reduction techniques are necessary for practical numerical investigation. The vast differences in time scales of plasma kinetics and combustion kinetics also make the simulation very challenging and multi-time scale modeling for plasma-assisted combustion is necessary.

Despite the earnest efforts of Starikovskii et al, the experimental results measured through optical emission spectroscopy did not agree well with the simulations, and still requires more detailed studies. As pointed out by the authors, time-resolved and in situ experimental measurements of the dominant radicals and intermediates are needed [12]. Therefore, even though the experiments were fairly well-designed, the kinetics have remained a significant issue [45].

Another important contribution to the understanding of plasma discharges and laser diagnostics was made by researchers at Ohio State University. A rectangular quartz reactor was used and the mixture in the reactor was activated by the discharge at different temperatures and pressures. Chintala and co-workers [46] investigated the combustion efficiency using Radio-Frequency discharge excitation on the flow. Fourier Transform Infrared (FTIR) absorption spectroscopy measurement showed fuel oxidation occurred even without ignition and flame. The non-thermal fuel oxidation was triggered by plasma-generated radicals. Similar results were also reported in the same reactor but using the excitation of a nano-second pulsed discharge [47], [48]. Lou et al. [48] pointed out that low temperature plasma chemical fuel conversion and the related flow heating “open the door” to ignition. They also conducted experiments under the same conditions
by removing O$_2$ in the premixture and found the disappearance of the fuel (ethylene or methane) was very limited. This demonstrated that the direct electron impact dissociation of fuel in the plasma is a relatively minor event compared to reactions with species generated in the plasma in the presence of oxygen, such as O and OH. Therefore, in situ diagnostics of plasma generated radicals is essential to understanding the plasma/combustion interaction.

Significant progress was made toward this end in 2009 by Uddi et al. [49]. They were able to measure the absolute O concentration in nano-second pulsed discharges using the Two Photon Laser Induced Fluorescence (TALIF) technique [49], [50]. They found the consumption of O was much faster in fuel/air mixtures than in pure air. So the rapid reaction between fuel and O initiated the combustion process and thus chemical heat release. This technique significantly advanced our understanding of plasma-assisted combustion at the elementary reaction level. Mode details about this technique can be found in Ref. [51] and will be discussed in Chapter 3.

Zuzeek et al. [52] conducted rotational Coherent Anti-Stokes Raman scattering (CARS) thermometry measurement on the same reactor before ignition. They demonstrated that at low temperature conditions, the heat release was primarily due to the reactions between fuel and O or fuel and O and H generated by the plasma discharge in C$_2$H$_4$/air and H$_2$/air mixtures, respectively. Yin et al. [53] studied the ignition delay time by monitoring the intensity of excited OH (OH*) emission at 310 nm, two line OH time resolved temperature, and OH concentrations in a quartz made plasma reactor with H$_2$/air mixture. They found the ignition delay decreased as the number of pulses of high voltage increased and the ignition temperature could be decreased by about 200 K due to the
accumulation of H atoms. They also concluded that H atoms were generated primarily from collisions with electrons or excited N$_2$ with H$_2$. The studies just discussed suggest that plasma discharge can have different kinetic effects for different fuels. Similar OH kinetics were also studied by Wu et al. [54] in mixtures of CH$_4$, C$_2$H$_6$, C$_3$H$_8$ and C$_4$H$_{10}$ with air at atmospheric pressure. The mixtures were preheated to between 400 and 800 K and activated by a pin-to-pin geometry discharge and OH concentrations were measured. It was found that the OH dynamics varied significantly at different initial temperatures for different fuels. The mechanisms are yet to be understood under thermally non-equilibrium excitation. This work also pointed out the importance of fuel dissociation due to collisions with electrons and excited species, such as excited N$_2$ and O$_2$, which is a different conclusion that in the previous work [48].

It is well accepted that O generation by plasmas can have a significant impact on the combustion process. The generation of O includes two major channels. One is direct electron impact. The other is through collision of O$_2$ with electronically excited N$_2$ (known as N$_2$(A), N$_2$(B) and N$_2$(C)) when N$_2$ is present as the dilution gas [49], [55]. Significant effort has been indertaken to quantify the kinetics of excited N$_2$, and a fast two-step mechanism was proposed for O generation [55]. If air was activated by the discharge, significant amounts of NO$_x$ can also be formed. Uddi and co-workers [56] investigated the production of NO in a nano-second pulsed discharge activated reactor. The NO production models agreed reasonably well with the experimental results, but there remained significant uncertainty. Moreover, NO is very important to ignition due to its catalytic effect [57–59]. The effect of NO in the ignition study was still not investigated in detail in the above-mentioned ignition related works. Nevertheless, real-
time measurements of NO formation provided detailed input parameters for future studies. Another important work was conducted by Ombrello and co-workers. Very differently from previous work, ignition enhancement was investigated in a counterflow burner [59], [60]. A counterflow burner was selected because the counterflow system provides four key benefits: minimal buoyancy effects, simplified flame geometry, ability to define a flow velocity gradient (strain rate) on the centerline near the stagnation plane of the two impinging jets, and excellent optical access for laser diagnostics to measure species and temperatures [61]. A non-equilibrium gliding arc discharge was integrated with the counterflow burner and used to activate the oxidizer side of the flow. The experiments were conducted at atmospheric pressure and air was used as the oxidizer. Due to the high pressure and short lifetimes of reactive species, only species with long lifetimes can survive and be transported to the reaction zone. Therefore, only NO\textsubscript{x} generated from the gliding arc discharge was observed. In that study, NO\textsubscript{x} was quantified by FTIR and the enhancement of NO\textsubscript{x} on H\textsubscript{2}/air and CH\textsubscript{4}/air diffusion flame ignition was systematically investigated. The catalytic effect of NO\textsubscript{x} on ignition in plasma assisted combustion was identified for the first time. The enhancement of the gliding arc discharge on flame extinction was also investigated on the same platform at atmospheric pressure [61]. Due to the fast recombination of radicals and the rich radical pool produced by the flames, it was found that the effect of the plasma on flame extinction was predominately thermal [61]. Nevertheless, this is the only study on flame extinction and, up until now, no kinetic enhancement of plasma on flame extinction had been observed.

In follow-up work, Ombrello and his co-workers developed new experiments and
investigated the effect of species with long lifetimes generated by the discharge on flame propagation [59][60]. Very similar to flame extinction, the radical pool produced by the flame was rich and the effect on flame speed was difficult to be observed and quantified in general without a significant amount of energy input. They cleverly chose a lifted flame system in which the flame liftoff height is very sensitive to the flame speed. Therefore, the enhancement of plasma-generated species on the flame speed could be clearly identified without significant amounts of energy input. Ozone (O₃) was generated by a dielectric barrier discharge (DBD) cell and measured quantitatively by absorption spectroscopy and transported to a C₂H₄/O₂/N₂ lifted flame. The experiments at atmospheric pressure showed an 8% enhancement in flame speed for 1260 ppm of O₃ addition to the oxidizer stream [62]. More challenging work [63] was conducted to study the effect of excited O₂ (O₂(¹Δg)) which has an electronic excitation of 0.98 eV. O₂(¹Δg) has a mean radiative lifetime of 2700 s [64]. Therefore there is a possibility to isolate and transport it to the flame. The most challenging part of that work was the isolation and the quantification of O₂(¹Δg). In that study, O₂(¹Δg) was produced in a microwave discharge and isolated from O and O₃ by NO addition to the plasma afterglow for a flow residence time on the order of 1 s. The concentrations of O₂(¹Δg) was measured quantitatively through off-axis integrated-cavity-output spectroscopy [65]. It was found that O₂(¹Δg) enhanced the propagation speed of C₂H₄ lifted flames. However, due to the limitation of lifted flame theory at low pressures, an estimation of 2-3% of flame speed enhancement for 5500 ppm O₂(¹Δg) was observed at reduced pressures (3.61 and 6.73 kPa) [63]. The authors also conducted numerical simulations to investigate the pathways of enhancement. They employed currently published collisional and reactive quenching reactions [66], [67]
and found there was a significant discrepancy in the predicted enhancement due to the lack of quenching reactions of $O_2(a^1\Delta_g)$ by hydrocarbon species. Nonetheless, the work provided an important experimental platform to validate the kinetic mechanisms involving $O_2(a^1\Delta_g)$. More recent modeling work involving $O_2(a^1\Delta_g)$ can be found in Ref. [68], [69].

Employing a coaxial pulsed nano-second barrier discharge, the $C_3H_8/air$ flame blow-off velocity at atmospheric pressure was investigated by Mintoussov et al. [70]. They found the discharge can increase the blow-off velocity significantly by more than twofold with equivalently less than 1% of the chemical power consumed by the discharge. The experiments demonstrated that the reactive species produced by the discharge was the main mechanism for the enhancement. Their one-dimensional modeling also showed that the radical concentration (O) must exceed a critical value to enable the chain-branching reactions.

The stability of turbulent $C_3H_8/air$ flame was studied by Pilla et al. [71]. A nano-second discharge was applied in the recirculation zone of the turbulent premixed flame. They found that the discharge can improve the stability and efficiency of the flame due to radical generation, such as O, H and OH. Similar experiments were conducted by a Stanford group [72] for $CH_4/air$ premixed flame. They found the reforming of $CH_4$ to produce $H_2$ and CO played a central role in enhancing flame stability.

1.4 Questions That Remain

The review of previous research described in section 1.3 has provided a solid foundation for the study of plasma-assisted combustion. The advancements in diagnostics and improved design of the experiments provide opportunities to further investigate
plasma-assisted combustion. However, there are still many unclear aspects about plasma-assisted combustion.

In order to elucidate the fundamental enhancement mechanisms of plasma on combustion, well-defined experiments are necessary. Since both plasma and combustion are complex phenomena, one basic idea is to minimize the uncertainty/unknown factors of the combustion process in the experiment. Therefore the effect of plasma on combustion can be extracted. In other words, combustion itself should be well-defined first with clear boundary conditions and quantitatively measurable properties. Otherwise, the study can only be phenomenological.

Isolation of plasma and combustion either spatially or temporally can significantly simplify the problem. This technique will help to elucidate the underlying species and mechanisms of enhancement. However, the coupling effect between plasma and combustion must be studied beforehand. The coupled enhancement mechanism can also be very different from the results acquired from a “decoupled” study. This is because the reactive species generated by the plasma have very short life times. The experiments designed with the decoupled or isolation approaches cannot observe the effects from those species with a very short time scale.

Detailed modeling of plasma-assisted combustion is critical to improving our understanding and elucidating the underlying enhancement mechanisms. In general, the characteristic time scales associated with plasma and combustion problems are very different. The kinetic models combine all the possible reaction pathways for both plasma kinetics and combustion kinetics and contain a large numbers of species and reactions. It is not straightforward to tackle such a problem numerically. Moreover, the detailed
modeling requires detailed kinetic models for plasma-assisted combustion. However, accurate oxidation kinetics is missing in the plasma society and the plasma kinetics has been neglected in combustion literature for a long time. For example, the electron introduced excitation and dissociation of fuels and quenching of excited species with hydrocarbon molecules are largely unknown. Therefore, the investigation and development of detailed kinetic models for plasma-assisted combustion are ultimately important.

Diagnostic tools are critical to studying plasma-assisted combustion and developing the corresponding kinetic models. For plasma-assisted combustion, the diagnostics become even more challenging as compared to conventional combustion. For example, because of the presence of a strong electric field that is required to generate the plasma, traditional thermocouple measurement for temperature fails. The plasma produces significant number of reactive species such as atomic O which affect combustion dramatically. There are also many intermediate species involved. These species have too short of a lifetime to be measured by most traditional sampling techniques. In order to understand how those plasma produced species affect combustion, advanced diagnostics must be employed and developed to investigate complex plasma-assisted combustion systems.

### 1.5 Motivation and Objectives

As discussed before, plasma has the potential to enhance combustion by being a source to produce heat, radicals, excited species, electrons/ions, and fuel fragments simultaneously. These many different enhancement pathways are coupled together to cause thermal enhancement, kinetic enhancement, and even transport enhancement as
suggested in Fig. 1.6.

In section 1.4, the challenges of designing experimental platforms for plasma-assisted combustion were discussed. In order to simplify the problem and study the effect of individual species on flame, there are two major challenges. The first one is to decouple the various interactions to provide useful, quantitative experimental data. Two of the main pathways that need to be decoupled are thermal and kinetic enhancements. Thermal enhancement has been well studied, but the plasma-produced species and their associated reaction pathways, i.e., the kinetic enhancement pathway, is still largely unknown. Consequently, one of the major challenges is to decouple the complex plasma-flame interactions so that the kinetic contribution of individual species produced by the plasma can be understood at the elementary reaction level. Therefore, a non-equilibrium discharge should be employed, where the translational temperature is only slightly elevated in order to minimize the thermal enhancement in the system. Furthermore, kinetic enhancement has the potential to couple plasma energy more efficiently into combustion systems by generating only critical enhancement species for higher chemical selectivity.

Fig. 1.6 Possible enhancement pathways when plasma is applied to a combustion system
The second major challenge is the ease with which the experiment can be modeled. The species generated by the non-equilibrium plasma are still not well known in combustion chemistry and therefore need further investigation with regard to their inclusion in plasma-flame kinetic models. At the same time, it is very important to quantify the enhancement in the system as well as the types of species present and their concentrations. The measurement of species concentrations can then be used as inputs to compare directly with numerical models to understand the effect of plasma generated species on combustion.

With the understanding of the effect from individual species on the flame, the study of the coupled effects can then be conducted.

The objectives of this dissertation are to develop well-defined plasma-combustion platforms which elucidate the fundamental species and mechanisms involved in plasma-flame interactions using advanced diagnostics and detailed modeling.

The primary objective of this study is to obtain quantitative results of plasma produced species and elucidate their effects on flame extinction and ignition. To accomplish this goal, the discharge was spatially and temporally separated from the combustion reaction zone to avoid the complexity of directly coupling the discharge with the flame. With this approach, the effect of thermal enhancement can be isolated and the kinetic enhancement from the species produced by the plasma can be observed and analyzed. The coupling effect between the plasma and the flame was then investigated using an *in situ* discharge on the combustion reaction zone. At the same time, numerical schemes were developed to explore plasma-assisted combustion kinetic mechanisms.
1.6 Outline of the Dissertation

The research discussed in this dissertation aims to develop a detailed understanding of plasma-flame interactions and to provide quantitative data for elucidating plasma-combustion kinetic mechanisms. Four major contributions were made towards this goal: the development of a well-defined experimental platform to obtain an understanding of the extension of extinction limits due to atomic O and plasma introduced fuel oxidation, the development of a novel plasma-assisted combustion experimental platform to investigate the modification of the S-curve of flame by plasma-flame interaction, the development of a new kinetic mechanism reduction technique for efficient modeling, and lastly the development of diagnostic methods to study the kinetic mechanisms and quantification of H₂O₂ formation in a reacting flow.

In Chapter 2, the experimental platforms are introduced including a counterflow system integrated with a nano-second pulsed discharge in the oxidizer stream, and a novel counterflow system with *in situ* discharge. The numerical models used for the research are also provided.

In Chapter 3, the types of optical diagnostic techniques used in the experiments with a brief overview of how they work are provided.

In Chapter 4, the extension of extinction limits by the nano-second pulsed discharge on diffusion flame is discussed.

In Chapter 5, the extension of extinction limits by the nano-second pulsed discharge on partially premixed diffusion flame is discussed.

In Chapter 6, the modification of the S-curve in a counterflow system with *in situ* discharge is discussed.
In Chapter 7, a Molecular Beam Mass Spectrometer (MBMS) is introduced and used to study the chemical kinetics of dimethyl ether (DME). H$_2$O$_2$ formation was quantified in DME/O$_2$/He mixture using this diagnostic technique.

In Chapter 8, a path flux analysis (PFA) method for mechanism reduction is proposed to tackle complex detailed kinetic mechanism to improve the computation efficiency.

In Chapter 9, the dissertation research is summarized and recommendations for future work are given.
Chapter 2

Experimental Methods and Numerical Models

2.1 Combustion Systems

In this chapter, the counterflow burner and a flow reactor are described as two combustion platforms used in this research.

2.1.1 Counterflow Flame and Burner Design

A counterflow burner was used for the investigation of extinction and ignition in the presence of plasma excitation. The counterflow flame provides a combustion system that has been studied experimentally (e.g., [60], [61], [73], [74]) and numerically (e.g., [75–77]). It provides a well-defined experimental platform for plasma assisted combustion research.

The counterflow burner system is comprised of two opposed jets as shown in Fig. 2.1. If the two jets are oxidizer and fuel, respectively, a diffusion flame can be stabilized between the two nozzles. In general, the nozzles are placed coaxially inside an inert flow shroud to isolate the flame from the ambient conditions. When the momenta of the two jets are balanced, the stagnation plane (location of zero flow velocity) forms approximately in the center of the two nozzles. The flow field outside the mixing layer of the counterflow system is convection controlled (negligible buoyancy) and can be reduced to a one dimensional approximation along the axis of the flow between the two burner nozzles [75]. Therefore, the axisymmetric counterflow system can be described by the following equations [76] by making the stagnation point flow approximation [75].

\[ \frac{da}{dt} = 0 \]  

(2.1)
\[
\frac{d\rho}{dt} + \frac{dU}{dx} = -2\rho G
\]

(2.2)

\[
L(G) = \frac{d}{dx}\left(\mu \frac{dG}{dx}\right) - \rho G^2 + \rho \left(\frac{da}{dt} + a^2\right)
\]

(2.3)

\[
C_p L(T) = \frac{d}{dx}\left(\lambda \frac{dT}{dx}\right) - \sum_{k=1}^{n} \rho Y_k C_{pk} \frac{dT}{dx} - \sum_{k=1}^{n} h_k \omega_k M_k + q_r
\]

(2.4)

\[
L(Y_k) = -\frac{d}{dx}(\rho Y_k V_k) + \sum_{k=1}^{n} \omega_k M_k
\]

(2.5)

Fig. 2.1 Schematic of a counterflow diffusion flame burner system

where \( L(\phi) = d\phi/dt + Ud\phi/dx \), \( t \) is the time, \( x \) and \( r \) denote the axial and radical coordinates, \( u \) and \( v \) are the corresponding components of the velocity, \( U \) is the axial mass flow rate and \( a \) is the stretch rate. In addition, \( G \) is a combined function of the stretch rate and the stream function; \( \rho \), \( T \) and \( Y_k \) are the mass density, temperature, and mass fraction of \( k \)th species, respectively; \( \mu \), \( C_{pk} \), and \( M_k \) denote the mixture viscosity, the constant-pressure heat capacity, and the molecular weight of the \( k \)th species; \( h_k \), \( V_{ks} \) and
$\omega_k$ are respectively the specific enthalpy, the diffusion velocity in the $x$-direction, and the molar production rate of the $k$th species; $q_r$ is the volumetric radiation heat loss.

Under the low Mach number condition [78, the strain rate $a$ can be defined for the oxidizer and fuel flows, respectively, in Eq. (2.6) and (2.7). They serve as the indications of characteristic flow times of a counterflow system,

$$a_o = \frac{2U_o}{L} \left( 1 + \frac{U_f \sqrt{\rho_f}}{U_o \sqrt{\rho_o}} \right)$$

(2.6)

$$a_f = \frac{2U_f}{L} \left( 1 + \frac{U_o \sqrt{\rho_o}}{U_f \sqrt{\rho_f}} \right)$$

(2.7)

The strain rate is the reciprocal of the flow residence time, where $U$ is the speed of the flow, $\rho$ the density of the flow, and $L$ the gap distance between the two burner nozzles. Subscripts $o$ and $f$ refer to the oxidizer and fuel side, respectively. The strain rate presented here is based on global parameters but not on the local flow velocity gradient at the flame front. Therefore, they can be used as parameters of comparison between different experiments. More detailed information about counterflow systems can be found in Ref.[15], [73], [79], [80].

2.1.1a Extinction and Ignition

In Chapters 4 and 5, the counterflow configuration was adopted to study flame extinction. During the experiments (without or with plasma with discharge repetition frequency from 4 to 40 kHz, pressure = 60 Torr), the flow rates on both sides were gradually increased while the momentum balance was maintained. With the increase of flow rate, the flow residence time decreased and at a critical condition, there was no time for combustion to complete, so the flame extinguished. The strain rate at the condition when extinction happened was called the extinction strain rate.
In addition to extinction experiments, the counterflow system can also be used to measure ignition temperatures and flame structures. If the oxidizer side was heated to a high temperature, ignition can be achieved. The ignition temperature can be measured by elevating the oxidizer temperature slowly until a flame appeared while keeping the strain rate constant. The temperature was defined as the temperature along the centerline at the exit of the heated oxidizer nozzle.

In contrast to the conventional approach, in Chapter 6, extinction and ignition were achieved by decreasing and increasing the fuel mole fraction on the fuel side with fixed strain rate and discharge repetition frequency at 24 kHz, pressure = 72 Torr. This is because the in situ discharge modified the reaction pathways in the reaction zone, thus extinction and ignition cannot be controlled just by strain rates and temperatures. In other words, the extinction limit cannot be reached by just increasing the flow rate with the discharge on and the flame was always ignited by the discharge without any electrical heating of the flow.

Both the ignition and extinction experiments can be conducted with and without plasma. It should be noted that with the activation of the plasma, the flow temperature was elevated and flow temperatures changed with varying the discharge conditions. In order to calculate the momentum of the flow, the flow temperature must be specified. Details about the temperature measurements at different discharge conditions are to be discussed in Chapters 4, 5, and 6, respectively, due to the broad ranges of operating conditions of the plasma.

2.1.1b Numerical Methods for Counterflow Systems

Numerical simulations were conducted to validate and quantitatively explain the
experiments. The simulations were computed using OPPDIFF of the CHEMKIN package [81]. In Chapter 4 and 5, the extinction strain rates were calculated using OPPDIFF with a modified arc-length continuation method [76] for plug flow. In order to explain the method, the flame response curve (S-curve) has been presented here as Fig. 2.2.

To calculate the extinction limit at point 3, which is the point at where the Jacobian matrix becomes singular, the computation should start from a solution at point 1 on the upper burning branch (Fig. 2.2). Then, at a position near the extinction limit (point 2), the governing equation is solved to find the strain rate by fixing the flame temperature. For example, as the temperature at 1a is reduced to 2a, the governing equation will find a new solution of strain rate to satisfy the temperature at 2a. The new solution found is point 2. By continually executing this procedure, the solution curve would be obtained and the extinction point 3 can be found without any difficulty. After point 3, by further reducing the flame temperature, the solution moved to the middle burning branch and the lower flame branch (point 4). Note that the middle branch can only be found numerically because the solution is a steady state solution without perturbation. Physically, there are always perturbations in the system to move the flame away from the middle branch to either the upper or lower stable branches. After producing the upper part of the S-curve, the extinction point 3 can be found. More details about this technique can be found in Ref. [76].
2.1.2 Atmospheric Pressure Flow Reactor

In chapter 8, the investigation of chemical kinetics was conducted in a flow reactor. The reactor (as shown in Fig. 2.3) was a cylindrical quartz tube with 17 mm inner diameter (ID), 355 mm in length. It was tightly jacketed within a copper sleeve, and this assembly was placed inside a tube furnace to generate a uniform temperature profile throughout the reactor. A 2 mm ID quartz preheating section at the entrance of the reactor was used to heat the mixture to the reaction temperature within a residence time that was less than 1% of the total residence time of the mixture inside the reactor. The temperature was monitored by a thermocouple inside the reactor, for which no catalytic effect was observed during experiments. Constant temperature profiles were confirmed for all tested flow rates. Due to the heat loss at the reactor exit, ~30 K temperature drop was observed near the reactor exit.
2.2 Plasma System

In this research, the non-equilibrium plasma was generated by a nano-second duration high voltage pulse generator.

2.2.1 Nano-second Pulsed Discharge

In Chapter 4, a nano-second duration high voltage pulse generator (FID FPG 30-50MC4), which is capable of producing 16 kV pulsed polarity (positive and negative) with individual pulse duration of 6 ns at full width half maximum (FWHM), was used to produce the non-equilibrium plasma. The nano-second pulser used in Chapters 5 and 6 has FWHM 12 ns. The frequencies of the two pulsers are adjustable from 0 to 50 kHz. The voltage waveforms measured by a LeCroy high voltage probe (PPE20KV) are shown in Fig. 2.4 (a) and (b). The current through the electrodes was measured with a Pearson Coil (Model 6585). The pulse energy supplied to the discharge was estimated from the time integration of the voltage and current profiles. The characteristics of voltage-current were independent of pulse repetition frequency which ranged from 4 to 40 kHz in the experiments.
The non-equilibrium discharge generated by the nano-second pulser possesses two distinct features [82].

(1) The high reduced electric field (E/N) can efficiently generate ionization, electronic excitation, and dissociation of molecules by electron impact reactions. The rates of these processes have exponential dependence on E/N [9]. This can lead to the generation of large amounts of reactive species at a relatively low power budget compared to other types of discharges.

(2) The short pulse duration greatly improves the stability of the discharge. The characteristic time of the pulsed discharge (several ns) is much shorter than the characteristic time for the development of ionization instability and glow-to-arc transition (~0.1 to 1 ms) [9].

In chapter 4 and 5, the discharges were produced between two copper electrodes (22 mm × 15 mm × 1.5 mm) with a separation distance of 10 mm as shown in Fig. 2.5.
In Chapter 6, the discharge was generated between the two burner nozzles, which were constructed from stainless steel porous plug electrodes (from Mott Corporation) as shown in Fig. 2.6. The electrodes are 25.4 mm in diameter, 2 mm in thickness, and arranged with a separation distance 16 mm.
Fig. 2.6 Direct photograph of the counterflow burner with stainless steel porous electrodes

2.2.2 Kinetic and Numerical Model for the Plasma System

The kinetic model used in this work is an integration of a air plasma model [49] together with USC Mech II [83]. In addition, in order to consider species dissociation by reactions with excited Ar and He, and dissociation of CH$_4$ by electron impact reactions, additional elementary reactions involving the dilution gases (He/Ar) and CH$_4$ were added (Table 2.1). The plasma combustion model incorporates a set of species conservation equations for number densities of neutral, charged, and excited species produced in the plasma: O, O$_2$, O$_3$, e, O$_2$+, O+, O-, O$_2$-. O$_2$(a'$_1\Delta$), O$_2$(b'$_2\Sigma$), O(1D), Ar(+), Ar(3p$^5$(3P$_{3/2}$)4s), Ar(3p$^5$(1P$_{1/2}$)4s), Ar(3p$^5$(3P$_{3/2}$)4p) (Ar* for simplicity, with respective excitation energies
of 11.5, 11.7, and 12.9 eV), He(+), He(2s $^3$S), He(2s $^1$S), He(2p $^3$P), He(2p $^1$P), He(3s $^1$S), and He(4p $^1$P) (He* for simplicity, with respective excitation energies of 19.8, 20.6, 21, 21.2, 22.9, and 23.7 eV), as well as the energy conservation equation to predict the temperature of the mixture. This set of equations are coupled with the steady state, two-term expansion Boltzmann equation for the electron energy distribution function (EEDF) of the plasma electrons using experimentally measured cross sections of electron impact electronic excitation, dissociation, ionization, and dissociative attachment processes. The Boltzmann equation calculates the rate coefficients of the electron impact elementary reactions by averaging the cross sections over the EEDF. The kinetic model also incorporates chemical reactions of excited electronic species, electron-ion recombination reactions, ion-ion neutralization processes, ion-molecule reactions, and electron attachment and detachment processes. Note that the present model does not solve the Poisson equation for the electric field and therefore does not take into account charge separation and sheath formation near the electrode. So in the present work, the reduced electric field (E/N ratio) in the plasma was considered to be an adjustable parameter. In the calculation in Chapter 5, this value was varied until the CH$_4$ concentration (at the nozzle exit, 1 cm away from the end of the discharge region) matched with the experimental results at the burner exit. CH$_4$ concentration was used here to determine the E/N ratio because CH$_4$ concentration measurements had the smallest uncertainty (1% vs. 40% for TALIF of O). Therefore, only the concentrations of CO, CO$_2$, H$_2$O, H$_2$, CH$_2$O, and O from the simulations were compared with the experiments. The model was also employed to calculate the radical/atom (OH and H) concentrations by matching the O concentrations from the simulations with the corresponding experimental values. The
radical concentrations were further used as boundary conditions for extinction limit calculations in Section 3.2 of Chapter 5.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Rate ($\text{cm}^3\text{s}^{-1}$)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>$e + \text{CH}_4 = e + \text{CH}_3 + \text{H}$</td>
<td>$\sigma^a$</td>
<td>[51]</td>
</tr>
<tr>
<td>$e + \text{CH}_4 = e + \text{CH}_4(\cdot)$</td>
<td>$\sigma$</td>
<td>[12]</td>
</tr>
<tr>
<td>$e + \text{CH}_4(\cdot) = \text{CH}_2 + 2\text{H}$</td>
<td>$1.7 \times 10^{-7}(300/T)^{0.5}$</td>
<td>[12]</td>
</tr>
<tr>
<td>$e + \text{CH}_4(\cdot) = \text{CH}_3 + \text{H}$</td>
<td>$1.7 \times 10^{-7}(300/T)^{0.5}$</td>
<td>[12]</td>
</tr>
<tr>
<td>$\text{CH}_4(\cdot) + \text{O}_2 = \text{CH}_4 + \text{O}_2(\cdot)$</td>
<td>$5 \times 10^{-10}$</td>
<td>[12]</td>
</tr>
<tr>
<td>$\text{Ar} + e = \text{Ar}^* + e$</td>
<td>$\sigma$</td>
<td>[12]</td>
</tr>
<tr>
<td>$\text{Ar} + e = \text{Ar}(\cdot) + 2e$</td>
<td>$\sigma$</td>
<td>[12]</td>
</tr>
<tr>
<td>$\text{Ar}^* + \text{O}_2 = \text{Ar} + 2\text{O}$</td>
<td>$2 \times 10^{-10}$</td>
<td>[12]</td>
</tr>
<tr>
<td>$\text{Ar}(\cdot) + \text{O}_2 = \text{Ar} + \text{O}_2(\cdot)$</td>
<td>$1 \times 10^{-10}$</td>
<td>[12]</td>
</tr>
<tr>
<td>$\text{Ar}^* + \text{CH}_4 = \text{Ar} + \text{CH}_2 + 2\text{H}$</td>
<td>$3.3 \times 10^{-10}$</td>
<td>[12]</td>
</tr>
<tr>
<td>$\text{Ar}^* + \text{CH}_4 = \text{Ar} + \text{CH} + \text{H}_2 + \text{H}$</td>
<td>$5.8 \times 10^{-10}$</td>
<td>[12]</td>
</tr>
<tr>
<td>$\text{Ar}^* + \text{CH}_4 = \text{Ar} + \text{CH}_3 + \text{H}$</td>
<td>$5.8 \times 10^{-10}$</td>
<td>[12]</td>
</tr>
<tr>
<td>$\text{Ar}^* + \text{CH}_4 = \text{Ar} + \text{CH}_2 + \text{H}_2$</td>
<td>$5.8 \times 10^{-10}$</td>
<td>[12]</td>
</tr>
<tr>
<td>$\text{Ar}(\cdot) + \text{CH}_4 = \text{Ar} + \text{CH}_3(\cdot) + \text{H}$</td>
<td>$6.5 \times 10^{-10}$</td>
<td>[12]</td>
</tr>
<tr>
<td>$\text{Ar}(\cdot) + \text{CH}_4 = \text{Ar} + \text{CH}_2(\cdot) + \text{H}_2$</td>
<td>$1.4 \times 10^{-10}$</td>
<td>[12]</td>
</tr>
<tr>
<td>$\text{He} + e = \text{He}^* + e$</td>
<td>$\sigma$</td>
<td>[84]</td>
</tr>
<tr>
<td>$\text{He} + e = \text{He}(\cdot) + 2e$</td>
<td>$\sigma$</td>
<td>[84]</td>
</tr>
<tr>
<td>$\text{He}^* + \text{O}_2 = \text{He} + \text{O}_2(\cdot) + e$</td>
<td>$1.5 \times 10^{11}T^{0.5}$</td>
<td>[84]</td>
</tr>
<tr>
<td>$\text{He}^* + \text{O} = \text{He} + \text{O}(\cdot) + e$</td>
<td>$1.5 \times 10^{11}T^{0.5}$</td>
<td>[84]</td>
</tr>
<tr>
<td>$\text{He}(\cdot) + \text{O}_2 = \text{He} + \text{O}(\cdot) + \text{O}$</td>
<td>$0.6 \times 10^{11}T^{0.5}$</td>
<td>[84]</td>
</tr>
<tr>
<td>$\text{He}(\cdot) + \text{O}_3 = \text{He} + \text{O}_2 + \text{O}(\cdot)$</td>
<td>$0.6 \times 10^{11}T^{0.5}$</td>
<td>[84]</td>
</tr>
</tbody>
</table>
He(+) + O_2(\Delta_g) = He + O(+) + O \quad 0.6\times10^{11}T^{0.5} \quad [84]

He(+) + O(1^D) = He + O(+) \quad 2.9\times10^{12}T^{0.5} \quad [84]

He + 2O = He* + O_2 \quad 1\times10^{-33} \quad [84]

He + O(1^D) = He + O \quad 1\times10^{-10} \quad [8]

He* + CH_4 = He + CH + H_2 + H \quad 5.6\times10^{-13} \quad [85]

Table 2.1 List of Ar/He/CH_4 related reactions involved in Ar/He/O_2/CH_4 mixture discharge

*The rate is calculated by the Boltzmann solver using experimentally measured cross-sections, σ

In chapter 6, the in situ discharge happened in a non-homogeneous flow condition crossing from the oxidizer side to the fuel side which is very difficult to model. Therefore, the voltage drops in the sheath regions close to the electrode surfaces were estimated by simulations at the same conditions but with homogeneous compositions [86][87]. The simulation shows that the electric field (E = 7500 V/cm) in the bulk plasma region is nearly constant at different conditions as long as the applied voltage is constant, which was confirmed during the experiments. The typical electron density was approximately 5\times10^{10} cm^{-3} in this study. Because the high voltage pulse is very short (12 ns) compared to the flow residence time, the flame cannot respond to the pulsed perturbation, and the pulsed excitation effect on the mixture is averaged over the fluid particles [82]. Finally, the kinetic mechanism that includes both plasma and combustion kinetics are generated and used by OPPDIF [81] to investigate their interactions.

More details about this model can be found in Refs. [49], [88].
Chapter 3
Diagnostic Techniques

3.1 Laser Diagnostic Techniques

Three optical diagnostic techniques were employed to quantitatively measure the temperatures and radical concentrations (OH and O) in counterflow systems integrated with nano-second pulsed discharge. The Two photon Absorption Laser Induced Fluorescence (TALIF) method was employed in Chapter 4 and 5 to quantify the atomic O production from the discharge. Planar Rayleigh scattering and OH Planar Laser Induced Fluorescence (OH PLIF) techniques were employed in Chapter 6 to measure the temperature distribution and OH number densities, respectively.

3.1.1 Laser Induced Fluorescence (LIF) Method

The laser induced fluorescence method is an inelastic process in which photons are absorbed by the molecules or atoms and then re-emitted at the same or different wavelengths. The absorbed photons excite molecules or atoms to an energy level above the ground state, and then photons are released during the de-excitation process and can be detected. If only one photon was absorbed to generate excitation, it is generally called Laser Induced Fluorescence (LIF). If two photons are absorbed in order to excite the species to a higher energy level, it is called Two photon Absorption Laser Induced Fluorescence (TALIF).

3.1.1a Two Photon Absorption Laser Induced Fluorescence (TALIF)

The Two photon Absorption Laser Induced Fluorescence (TALIF) method, calibrated with Xenon, was used to measure the absolute atomic O concentration produced by the discharge. Ground state atomic O is excited by absorbing two photons at
a wavelength of 225.7 nm. The transition between the excited 3p ³P state and the 3s ³S state will release a single photon at 844.6 nm. Xenon can be excited from 5p⁶ ¹S₀ to 6p'[3/2]2 with two photons at 224.31 nm; de-excitation to 6s' [1/2]₁ corresponds to fluorescence at 834.91 nm. The schematic of atomic O and Xenon atom energy levels is shown in Fig. 3.1.

![Schematic of atomic O and Xenon atom energy levels with two photon absorption excitation and fluorescence schematic](image)

The number density of atomic O \( (N_O) \) was calculated using the following equation in terms of the known number density of Xenon \( (N_{Xe}) \) [51],

\[
N_O = \frac{S_O}{S_{Xe}} g_{ND} \frac{a_{21}(Xe)}{a_{21}(O)} \left( \frac{\sigma^{(2)}(Xe)}{\sigma^{(2)}(O)} \right) \left( \frac{\nu_O}{\nu_{Xe}} \right)^2 \times \frac{1}{F_O(T)} N_{Xe} \\
(3.1)
\]

where \( S_o \) and \( S_{Xe} \) are the observed fluorescence signals for O and Xenon, respectively,

\[
a_{21} = \frac{A_{21}}{A_{21} + Q}
\]

the fluorescence quantum yields \( (A_{21} \) and \( Q \) are spontaneous emission and quenching rates, respectively), \( \sigma^{(2)} \) the two photon absorption cross sections of Xe and O, \( F_O(T) \) the atomic O Boltzmann factor for the lower level of the two photon absorption, \( \nu \)
the photon energies, and $g_{ND}$ the neutral density filter factor ($1.82 \times 10^{-3}$ from manufacturer, Thorlab). These values can be found or easily calculated based on the data in Refs. [50], [51]. It should be noted that the ground electronic state of atomic O is a triplet (not shown in Fig. 3.1), whereas that of Xenon is a singlet. All measurements reported in this study used the atomic O ground state $^3P_2$ component which has the lowest energy level with $F_O = 0.7429$ at 300 K [51].

Fig. 3.2 Schematic of the TALIF setup for atomic O measurement

The schematic of the TALIF system is shown in Fig. 3.2. An Nd:YAG laser was used to generate 532 nm to pump a tunable dye laser operating at ~573 nm. This 573 nm beam was frequency doubled and mixed with the 1064 nm beam of the Nd:YAG laser to get a ~226 nm beam of ~10 $\mu$J/pulse required for the TALIF diagnostics. The UV beam was focused 30 mm ahead of the probe volume (the center of the burner) to avoid saturation. The dye laser was scanned in wavelength to characterize the atomic oxygen fluorescence spectrum. The TALIF signal was focused by a lens with a 300 mm focal length and observed through an 850 nm bandpass filter of 40 nm FWHM using a
Hamamatsu photomultiplier (PMT-R7154 or R636-10). A separate vacuum cell was used to obtain the Xenon atom two-photon fluorescence spectrum. Corrections for the transmission of the vacuum cell and bandpass filter were made to find the atomic O density by the method described in Refs. [50], [51]. The overall relative mole fraction uncertainty of the TALIF measurement was approximately ±40%.

3.1.1b OH Planar Laser Induced Fluorescence (OH PLIF)

The OH PLIF technique was used in Chapter 6 to quantify the OH concentrations. If one photon was absorbed by the OH molecules, fluorescence occurs during the de-excitation process. An energy level diagram of the OH molecule is shown in Fig. 3.3. Different from the atom fluorescence process, the de-excitation processes of molecules also include rotational energy transfer (RET), and vibrational energy transfer (VET) as shown in Fig. 3.3.

Fig. 3.3 Energy level diagram for OH excitation. RET and VET are rotational and vibrational energy transfer, respectively (adapted from [89])
The fluorescence signal, \( S_f \), can be expressed as [90]
\[
S_f = \eta V_c n_{\text{OH}} f_B B_{12} E \phi_f
\]  
(3.2)
where \( \eta \) represents the overall efficiency of the optical setup in collecting fluorescence photons, \( V_c \) is the collection volume, \( n_{\text{OH}} \) is the OH number density, \( f_B \) is the Boltzmann factor for OH molecules in the absorbing state, \( B_{12} \) is the Einstein absorption coefficient, \( E \) is the laser energy, and \( \phi_f \) is the fluorescence quantum efficiency. Since \( \eta \) and \( V_c \) are not well-defined parameters, calibration is required to quantify the OH measurement.

The fluorescence intensity can be calibrated by a known concentration of the species in the combustion system. In general, a transition where excitation from the ground state is insensitive across the range of temperatures in the system is chosen, therefore, only collisional processes need to be considered for the temperature sensitivity. The calibration can be performed in an environment with a known concentration of OH. To accomplish this, a McKenna (or Hencken) burner was used to produce post-flame gases which are in near equilibrium. Then equilibrium calculations can be conducted to compare with the concentration of the species measured in the calibration process. Within the linear regime of excitation, the OH number density \( (n_{\text{OH}}) \) can be calculated as
\[
n_{\text{OH,calibration}} = n_{\text{OH}} \frac{S_{\text{calibration}}}{S_f} \frac{\phi_f}{\phi_{f,\text{calibration}}} \frac{f_B}{f_B^{\text{calibration}}}
\]  
(3.3)

In the study of Chapter 6, the Q1(6) transition \( (X^2\Pi-A^2\Sigma^+(0,0)) \) of OH was excited at the wavelength of 282.93 nm. The fluorescence was collected by an ICCD camera (Princeton Instrument, PI-MAX). A different calibration approach was employed for simplicity. Because the absolute number density is not critical, but the relative change of the number density was of central importance, a counterflow system which was well-
characterized was used as the calibration source and compared with simulations. The calibration was conducted with a CH$_4$ diffusion flame using He as dilution gas. The calibration condition was at pressure ($P$) 72 Torr, strain rate ($a$) 400 1/s, fuel mole fraction ($X_f$) 20%, oxygen mole fraction ($X_o$) 55%, and UV laser power 2 mJ/pulse in order to match the conditions of experiments. The calibration curve is shown in Fig. 3.4.

Fig. 3.4 OH number density calibration curve. The gap distance was 16 mm with oxidizer side nozzle located at 0 mm. $P = 72$ Torr, $a = 400$ 1/s, $X_f = 20\%$, $X_o = 55\%$.

The calibration was then tested in other experiments at different conditions as shown in Fig. 3.5. Good agreement was observed.
Fig. 3.5 OH number density measurement in CH$_4$/O$_2$/He diffusion flame. $P = 72$ Torr, $a = 400$ 1/s, $X_f = 24\%$, $X_o = 55\%$.

3.1.2 Planar Rayleigh Scattering

Temperature is of paramount importance in a combustion system. Traditionally, thermocouples have been used to measure temperatures in a reactive system. However, in the study of Chapter 6, due to the presence of a strong electric field, conventional thermocouples cannot be used to measure the temperature, especially in the reaction zone.

Because of this, the Rayleigh scattering technique was used to measure the temperature distribution in the counterflow system with in situ discharge which will be discussed in Chapter 6.

Different from the LIF technique, the Rayleigh scattering technique relies upon the elastic scattering of light by particles much smaller than the wavelength of light used
to perform the measurement. Since it is an elastic scattering process, there is no energy exchange between the incident light and target particles. Thus, the scattered light is unshifted from its initial wavelength [90]. It is important to notice that the scattered light signal peaks at 90 degrees to the incident light polarization and different particles have different scattering cross-sections for the incident light. The differential scattering cross-section of a particular molecule or atom for Rayleigh scattering at 90 degrees to the incident light is given by [91]

\[
\left( \frac{d\sigma_i}{d\Omega} \right) = \frac{4\pi^2(\mu-1)^2}{\sigma_o^2\lambda^4}
\]

(3.4)

where \(\mu\) is the index of refraction of the gas at STP, \(N_o\) is the Loschmidt number \((2.69 \times 10^{19} \text{ cm}^3)\), and \(\lambda\) is the wavelength of the incident light. The intensity of the Rayleigh scattering, \(I_{\text{Rayleigh}}\), is described by the relation

\[
I_{\text{Rayleigh}} = CIN\Omega \left( \frac{d\sigma}{d\Omega} \right)_{\text{eff}}
\]

(3.5)

where \(C\) is a calibration constant of the collection optics, \(I\) is the incident light intensity, \(N\) is the particle number densities, \(\Omega\) is the solid angle of the collection optics, and \(l\) is the length of the laser beam segment imaged onto the detector, and \(\left( \frac{d\sigma}{d\Omega} \right)_{\text{eff}}\) is the effective scattering cross-sections. In a reacting flow, the gas composition is very complex and the cross-sections can vary significantly. The effective scattering cross-sections can be calculated using the following mole fraction weighted scattering cross-sections of different molecules or atoms in the flow.

\[
\left( \frac{d\sigma}{d\Omega} \right)_{\text{eff}} = \sum X_i \left( \frac{d\sigma_i}{d\Omega} \right)
\]

(3.6)

In this study, only major species (He, O$_2$, CH$_4$, CO, CO$_2$ and H$_2$O) were considered.
during the calculation of effective cross-sections and these values can be found in Ref.[92]. The flow composition was calculated using OPPDIF [81] to calculate the effective cross-sections.

The interaction of light with particles is a function of species concentrations, scattering cross-sections, and particle density (temperature). Therefore, with known effective cross-sections, particle density (temperature) can be derived from Eq. (3.5). However, the values of $C$, $I$, $\Omega$ and $l$ are not well-defined so calibration is still required to extract the quantitative results. The calibrations are conducted by comparing the signals with that from measurements with known composition, temperature and pressure to remove the uncertainty from $C$, $I$, $\Omega$ and $l$.

The Rayleigh scattering measurement was conducted with an Nd:YAG laser at 532 nm and the signals were collected with an ICCD camera (Princeton Instrument, PI-MAX) with a narrow band filter near 532 nm. A total of 1500 images were accumulated and averaged to obtain a high signal to noise ratio. The maximum uncertainty of the Rayleigh scattering temperature measurements is found to be $\pm$ 80 K, dependent on the measurement location. Figure 3.6 shows the temperature profiles measured by Rayleigh scattering and compared with simulations with and without the in situ discharge in a counterflow flow system used in the work of Chapter 6.
Fig. 3.6 Temperature profiles in a counterflow CH₄/O₂/He diffusion flame with and without in situ discharge, $X_O = 53.5\%$, $X_f = 20\%$, $a = 400 \text{ 1/s}$, $P = 72 \text{ Torr}$ (symbols: experiments, lines: simulation)

3.2 Molecular Beam Mass Spectrometry

In Chapter 7, a Molecular Beam Mass Spectrometer (MBMS) was used to investigate the chemical kinetics of low temperature oxidation of DME/O₂/He.

A direct photograph of MBMS system is shown in Fig. 3.7 and the schematic of the experimental system is shown in Fig. 3.8.
The MBMS system consists of a vacuum chamber (part I and II) with one water-cooled sampling nozzle, one skimmer, and an Electron Impact-Reflection Time-of-Flight (EI-RTOF, Jordan TOF Products, Inc., part III) mass spectrometer with a mass resolution of $m/\Delta m = 500-1000$. The two-stage pumped chamber includes a molecular beam compartment (part I) pumped by a turbo pump (3200L/s, Edwards Inc.) and an ionization compartment (part II) pumped by a turbo pump (1600L/s, Edwards Inc.). Pressures in the differential and ionization chambers are set at $\sim 10^{-4}$ Torr and $\sim 10^{-7}$ Torr, respectively. In order to obtain better vacuum in the RTOF, another turbo pump with 300L/s pumping rate is added to the flight tube. The nickel skimmer is located 12 mm downstream of the quartz sampling nozzle. The openings of quartz nozzle and nickel skimmer are 0.1 mm and 1 mm, respectively. The molecular beam formed after the skimmer is ionized by an electron gun (e-gun) with electron energy tuned to 30 eV to improve signal/noise ratio in the experiments. The ionized molecules are then extracted into the flight tube of RTOF by a pulsed extraction field (10-100 μs), which is triggered by a DG535 pulse generator (Stanford Research System Inc.). Accelerated ions are reflected in the reflector and detected by a Micro Channel Plate (MCP) detector. The ion signal from the MCP is amplified by a VT120C-P pre-amplifier (AMETEK) and recorded by a GHz P7888-2.
multi-scaler (FAST ComTec GmbH).

Fig. 3.8 Schematic of experimental setup, part I and II: differential pumped chamber and ionization vacuum chamber, part III: Time-of-light mass spectrometer

Calibration of the MBMS was conducted by flowing mixtures with known compositions for He, H₂, CO, CO₂, and DME. The ion signal \( S_i \) for a given species was determined by the concentration of the species \( \chi_i \), mass discrimination factor \( D_i \), and ionization cross section \( \sigma_i \) in Eq. 3.7. The mass discrimination factor \( D_i \) was only dependent upon the mass of the ion and the ionization cross section \( \sigma_i \) was a constant with given electron energy (30 eV) in the experiments. So the ion signal \( S_i \) was a linear function of species concentration. In order to avoid the uncertainty caused by the fluctuation in the emission of the e-gun, all the ion signals were normalized by the intensity of the helium ion signal.

By flowing gas with known composition, the mass discrimination factors and cross sections were measured for different species. The uncertainty of the calibration of He, H₂, CO, CO₂ and DME were within 3%.

\[
S_i = D_i \cdot \sigma_i \cdot \chi_i
\]  

(3.7)

\( \text{H}_2\text{O}_2 \) was also directly calibrated in this study. Liquid \( \text{H}_2\text{O}_2 \) solution (30.8% wt.
in H₂O, Sigma-Aldrich) was injected into a vaporizer and vaporized by heated He dilution. The vapor was sampled and used for calibration of H₂O₂. Due to the fast surface decomposition reactions of H₂O₂, to O₂ and H₂O were always observed. Therefore, O₂ was also quantified and the actual H₂O₂ concentration was corrected according to the relation 2H₂O₂ = O₂ + 2H₂O. The uncertainty in the calibration of H₂O₂ was 6%. For CH₃OCHO and CH₂O, only the mass discrimination factors were measured and the ionization cross sections were taken from Ref.[93].
Chapter 4

Effects of the Non-equilibrium Discharge on Diffusion Flame Extinction

4.1 Introduction

One of the potential applications for plasma to enhance combustion is to improve the flame stability and extended the extinction limits. Unfortunately, for plasma assisted extinction limit extension, few quantitative experiments have been conducted. A recent study of extinction limit enhancement by a non-equilibrium gliding arc with Rayleigh scattering and laser induced fluorescence measurements of temperature and OH concentration, respectively, [61] showed that the extinction limit enhancement by a low temperature gliding arc discharge was only a thermal effect. However, a nano-second repetitive discharge produces atomic oxygen efficiently; this, coupled with an increase in temperature as well as the decrease of pressure may slow down radical recombination to a sufficient degree, which may allow the observation of kinetic enhancement to extinction limit. The question becomes whether the effect of atomic oxygen on flame extinction is different at higher atomic oxygen concentrations and elevated temperatures. If so, how do we quantitatively demonstrate and understand this effect in a well defined experiment?

The goal of the work in this chapter was to develop a sub-atmospheric pressure counterflow burner integrated with a nano-second non-equilibrium plasma system to decouple the plasma-flame interaction and reduce radical quenching. This system will provide a tool to answer the above questions and to study the effects of O production on the extinction limit.

The work contained in this chapter was published in the Proceeding of
4.2 Experimental Method

A schematic of the experimental system is shown in Fig. 4.1. The experimental setup consisted of a counterflow burner, which was located in a low pressure chamber of 406 mm diameter and 629 mm height. The inner tubes of the counterflow burners were 20 mm inner diameter, and the outer tubes of the inert argon curtain were 28 mm inner diameter; both were made of quartz. The separation distance of the oxidizer and fuel burner nozzles was 20 mm. The argon flow isolated the flame from the environment and provided cooling for the burner. A honeycomb plate was placed inside the tube to ensure a uniform flow field at the nozzle exit. Two parallel bare copper electrodes were located inside the tubes of the upper (oxidizer side) burner and the ends of the electrodes were 10 mm away from the nozzle exit to avoid electric interaction with the thermocouple and allow the diffusion to smooth any non-uniformity until the nozzle exit. Because the pressure of the experiments is very low, diffusion is fast and the effect of the electrode inside the tube on the flow field near the centerline of the burners is negligible. The electrodes were 15 mm × 22 mm in dimension and the edges were smoothed to avoid the concentration of electric field and spark breakdown. The separation distance between the two electrodes was 10 mm. A nano-second pulse generator (FID FPG 30-50MC4) was used to generate the non-equilibrium plasma; this device is capable of producing 32 kV pulses with individual pulse duration of 6 ns (full width at half maximum, FWHM). To
examine the effect of the plasma repetition rate, the frequency of the pulser was adjusted up to 40 kHz. A typical pulse voltage waveform, characterized with the aid of a LeCroy high voltage probe (PPE20KV), is embedded in Fig. 4.1. The current through the electrodes was measured with a Pearson Coil (Model 6585). The energy supplied to the discharge per pulse was estimated by the integration of the voltage and current in terms of time by assuming a resistive load. The energy provided to the discharge is approximate 0.67 mJ per pulse, corresponding to average power of 3.4, 13.4 and 26.8 W at 5 kHz, 20 kHz and 40 kHz repetition frequency, respectively. During the experiments, the peak amplitude of the voltage was fixed at 7 kV as shown in Fig. 4.1.

At first, a nano-second pulsed non-equilibrium plasma system was integrated with the counterflow diffusion flame burner. The O₂/Ar ratio was fixed at 0.28:0.72, while the CH₄ concentration in Ar varied from 0.3 to 0.36. The pressure was held constant at 60 Torr. The extinction strain rates were then measured by fixing the fuel mole fraction and
gradually increasing the flow velocity until extinction was observed. During the experiments, momentum balance between the two nozzles was always maintained to keep the stagnation plane and the flame in the center of the two burner nozzles. At the same time, temperatures were measured by two thermocouples at the exits of the two burners with careful consideration of electric field interaction (In order to avoid the interaction of electric field to the thermocouples, the electrodes inside the tube were located 10 mm away from the nozzle exit where the thermocouple was located to measure the oxidizer boundary temperature. The thermocouple measurement was also confirmed by the NO thermometry method [95] and they were in good agreement. A typical NO fluorescence spectrum and its comparison with the modeling are shown in Fig. 4.2 in order to determine the flow temperature.

Fig. 4.2 Determination of stream temperature by multi-peak fitting of NO fluoresces at the burner exit downstream of O₂/Ar (0.28/0.72) discharge, f=24 kHz (the thermocouple reading is 533 K)
Because of the simplicity and the need for frequent measurements of the temperature, thermocouple measurement was employed in this work. Then, a Xe calibrated two photon absorption laser induced fluorescence (TALIF) method was used to measure the absolute atomic oxygen concentrations at the burner exit. After that, the flame extinction was modeled using the measured flow temperature with atomic oxygen concentration, and the kinetic pathways were analyzed.

4.3 Results and Discussions

4.3.1 Uniform Nano-Second Non-Equilibrium Pulsed Discharge

Figure 4.3 (a)-(e) shows images of flames with and without the nano-second non-equilibrium pulsed discharge at 8 kPa. The pulser repetition frequencies were increased from 5 kHz to 40 kHz. The discharge was uniform in the transverse direction of the electrodes and no visible filamentary structure was observed for repetition frequency from 5 kHz to 40 kHz. Fig. 4.3 (d) and (e) show a visible plasma jet issuing from the burner exit and reaching the reaction zone. The pulsed discharge in Ar/O₂ produces excited Ar (Ar*), as well as multiple oxygen containing species including O, O₃, O₂(v), O(¹D), O(¹S), O₂(a³Δg), O₂(b¹Σg), etc. It is clear that O₂(a³Δg) and O₂(b¹Σg) have longer lifetimes compared to other electronically excited species (see Ref. [62], [63] for related quenching rates). These two species have low excitation energy (0.98 and 1.6 eV, respectively) and can emit photons at orange and red wavelengths (dimol emission of O₂(a³Δg) [96]) when quenching occurs. It is also known that both excited and metastable Ar, which have an excitation energy of about 11 eV, and excited atomic O emits radiation between 650 and 750 nm [97]. Overall, the emission in the afterglow of an Ar/O₂ discharge is produced from the relaxation processes of excited species like Ar*, O(¹D),
O(\(^1\)S), \(O_2(a^1\Delta_g)\), and \(O_2(b^1\Sigma_g)\). During the relaxation processes, ground state atomic oxygen can be produced. Therefore, the visible emission indicates that there exist significant concentrations of excited species, radicals, and atoms between the nozzle exit and the reaction zone that need to be quantitatively examined.

![Fig. 4.3 Images of flames at \(X_{CH4}=0.36, X_{O2}=0.28\) with balance of argon, \(a=178\) s\(^{-1}\), \(d=20\) mm, \(P=60\) Torr (a) without discharge (b) \(f=5\) kHz (c) \(f=10\) kHz (d) \(f=20\) kHz (e) \(f=40\) kHz](image)

### 4.3.2 TALIF Measurements of Absolute Concentration of O

A plasma discharge in Ar/O\(_2\) mixtures can generate electrons, ions, atomic oxygen, \(O_3\), electronically and vibrationally excited \(O_2\), and excited Ar. In our experiments, the focus is on the role of atomic oxygen, which is one of the most important radicals produced by nano-second plasma. A TALIF system, calibrated using a Xe reference measurement, was used to determine the absolute atomic oxygen concentration at the oxidizer-side burner exit. The dependence of the measured atomic oxygen concentration on the pulse repetition frequency is plotted in Fig. 4.4 where it is shown that O concentration increased with the increase of the pulse repetition rate.
Fig. 4.4 Dependence of average atomic O concentration at the burner exit on the pulse repetition frequency

For repetition rates below 5 kHz, atomic O concentration was very low. A previous study by Uddi et al. [51] showed that the characteristic decay time of atomic oxygen in O₂/He plasma at 60 Torr and 300 K was ~3 ms. In this experiment, the distance between the end of electrodes in the burner to the exit of the burner is 1 cm, and the characteristic flow velocity in our experiments is ~100 cm/s. Therefore, the residence time is approximately 10 ms. As such, it is probable that the atomic oxygen generated by the discharge already decayed to a concentration not detectable by TALIF before reaching the exit of the burner. However, when the repetition frequency was increased to 40 kHz, $N_O \approx 1.1 \times 10^{16} \text{ cm}^{-3}$ (5000±750 ppm) at the burner exit. The increase in O concentration originates mainly from the increase of electron number density and also from the increase of the discharge temperature as well as the decrease of flow residence time. Note that at a higher repetition frequency, a higher flow velocity is required to
reach flame extinction. In order to adapt the flow conditions for extinction measurements, the flow velocity for 5 kHz and 20 kHz was 100 cm/s, while for 40 kHz it was 200 cm/s.

4.3.3 Enhancement of Flame Extinction Limit

The extinction strain rates of CH$_4$/O$_2$ diffusion flames were measured with and without plasma ($f$=5 kHz, and 20 kHz). A definition of global strain rate

$$ a_o = \frac{2U_o}{L} \left( 1 + \frac{U_f \sqrt{\rho_f}}{U_o \sqrt{\rho_o}} \right) $$

(4.1)

was adopted and compared with numerical simulations. Here $U$ is the flow velocity, $\rho$ the flow density, and $L$ the separation distance between the two burner nozzles. The subscripts $o$ and $f$ refer to the oxidizer and fuel sides, respectively. Figure 4.5 shows the dependence of extinction strain rates on fuel mole fraction with and without plasma discharge at different repetition plasma rates at 60 Torr. It is shown that the extinction strain rate increased with the increase of fuel mole fraction. In addition, with the increase of the pulse repetition frequency, Fig. 4.5 shows a significant increase of extinction limit extension. The extension of the extinction limit for $f$=5 kHz is about 25%, while for $f$=20 kHz the enhancement was approximately 90%.

In order to understand the mechanism of the extinction limit enhancement, we did the following: 1) measured the extinction limit by raising the oxidizer temperature via an electrical heater without plasma; and 2) computed the extinction limit with the measured temperature and O concentration at the oxidizer nozzle exit. By comparing these additional experimental and numerical results with the baseline extinction limit, we can understand to what extent the observed extinction limit enhancement was from the thermal and the kinetic mechanisms. The measured oxidizer temperatures at the repetition
frequency of \( f = 5 \) kHz and 20 kHz were 398 K and 528 K, respectively.

Fig. 4.5 Dependence of extinction strain rate on fuel mole fraction for different plasma repetition rates at 60 Torr

Figure 4.6 shows the comparison of the measured extinction limits with the nano-second plasma discharge and the electrical heater set to the same temperatures as well as the simulation results with (dashed line) and without (solid line with symbols) atomic oxygen production for repetition rates of \( f = 20 \) kHz at 60 Torr. The measurements showed that for the repetition rate of 5 kHz, the enhancement by the nano-second discharge and the electrical heater at the same oxidizer temperature of 398 K were approximately equal. This result implies that the enhancement at a low pulse frequency was predominately a thermal effect. This result is reasonable because the TALIF measurements (see Fig. 4.4) showed that there was little atomic oxygen at the exit of the
burner when the repetition frequency was 5 kHz. However, when the repetition rate was increased to 20 kHz, Fig. 5 shows that the extinction limit by nanosecond plasma was about 10% higher than that by the electrical heater at the same oxidizer temperature of 528 K, indicating that the existence of atomic oxygen may enhance the extinction limit by promoting the chain-branching reactions. The extinction limit of plasma assisted CH₄-air combustion was modeled using the measured atomic oxygen concentration and the temperature using OPPIDIFF of the CHEMKIN package [81] with a modified arc-length continuation method [76] for plug flow with USC Mech II [83]. All the simulations were performed at 60 Torr with a fixed fuel stream temperature at 300 K. The temperatures of the oxidizer side was set as 528 K, 398 K, and 348 K, respectively, for plasma discharge frequencies of $f=20$ kHz and 5 kHz and without the activation by plasma. The atomic oxygen concentration with plasma discharge at 20 kHz was 1200 ppm (the uncertainty of the TALIF measurement is approximately 40% [49], 40% increase of O concentration in calculation resulted an increase of extinction strain rate by less than 0.5%). The results are also plotted in Fig. 4.6. The figure shows that the model well reproduced the extinction limit without plasma discharge. The results also show that at 20 kHz, the predicted kinetic enhancement by 1200 ppm atomic O addition was only 2.5%, which was still below the kinetic enhancement observed in the experiment (3% uncertainty), suggesting the presence of additional kinetic enhancement pathways. The above comparison demonstrates clearly that non-equilibrium plasma discharge can enhance flame stabilization kinetically via the production of atomic O and other excited species (Excited O₂ is unlikely the reason due to the fast quenching effect of atomic O).
To further understand the effects of atomic oxygen addition and oxidizer temperature on the extinction limits, extinction strain rates were computed at different oxidizer temperatures (but constant fuel side temperature of 300 K) and atomic oxygen concentrations at constant pressure of 60 Torr. As shown in Fig. 4.7, the extinction strain rates increases substantially with the increase of oxidizer temperature and atomic oxygen concentration. The results also reveal that at higher oxidizer temperature, the kinetic enhancement of atomic oxygen becomes more significant. Figure 4.8 shows the detailed atomic oxygen profiles at the extinction limits for different oxidizer temperatures with 5000 ppm atomic oxygen addition at the oxidizer side at 60 Torr. Here, the fuel-side origin is located at x=0 cm, and the oxidizer-side origin is located at x=2 cm. The figure
shows that with the increase of oxidizer temperature, more atomic O could be transported to the reaction zone. At 900 K, nearly 80% of atomic O could reach the reaction zone to enhance the flame. With a further increase of temperature to 1000 K, a significant increase of radical production is predicted. Therefore, there is a crossover temperature between 900 K and 1000 K that governs the transition from radical termination to branching process.

Fig. 4.7 Simulation of the dependence of extinction strain rates on oxidizer-side temperatures with and without atomic oxygen addition

To understand the transition process from radical termination to branching with atomic oxygen addition, the consumption and production pathways of the atomic oxygen and related radicals were analyzed at the preheat zone for two different temperatures, 398
K and 1000 K, with 5000 ppm atomic oxygen addition. The major consumption and production paths of atomic oxygen at these two temperatures are shown in Fig. 4.9 (solid line with symbols for 1000 K and dashed line for 398 K).

![Fig. 4.8 Distributions of O mole fraction in the flame zone and on the side of oxidizer stream for different temperatures with 5000 ppm O addition at the extinction limits](image)

The above pathways represent 90% of the atomic O consumption. At 398 K, the major atomic O consumption reactions were O+OH=H+O2, HO2+O=OH+O2 and the two recombination reactions from O and O2 to O3. The summation of these four reactions leads to a global reaction of HO2+4O=H+2O3. This result indicates clearly that at low temperatures atomic O is terminated to form O3. However, Fig. 4.9 shows that at 1000 K the addition of atomic O promotes the chain branching reactions O+H2=H+OH and O+H2=H+OH as well as the chain propagation reactions and HO2+O=OH+O2. The overall reaction becomes HO2+H2+O=3OH, which implies that the addition of one
atomic O converts the less reactive radical HO₂ and H₂ (which originates from the fuel leakage near the extinction limit) to three active OH radicals. Therefore, the kinetic enhancement of atomic O production from plasma has different impacts on extinction limit enhancement, depending strongly on the temperature. Figures 7 and 8 show that there is a crossover temperature between 900 K and 1000 K, above (below) which the kinetic enhancement by atomic O production is governed by chain-branching (chain termination) reactions. The above analysis and experimental results provide a good explanation to the controversial conclusions made for different experimental conditions for plasma assisted flame speed enhancement.

Fig. 4.9 Calculated rates of elementary reactions related to atomic O consumption and production with oxidizer temperatures at 398 K (dashed line) and 1000 K (solid line), respectively, and 5000 ppm atomic O addition (oxidizer exit at 2 cm) at 60 Torr

4.4 Conclusion

A well-defined platform to study the effect of atomic oxygen production by non-
equilibrium plasma on the extinction limits was developed by integrating a counterflow burner with a nano-second pulsed discharge. Low pressure experiments demonstrated that the increase of plasma repetition rate increased dramatically the extinction limit of Ar diluted CH₄/O₂ diffusion flames. The TALIF measurement of absolute concentration of atomic O showed that the atomic O production also increased with the increase of plasma repetition rate, and at a pulse repetition rate of 20 kHz, the concentration of atomic O was observed to be 1200 ppm; this value was also employed in numerical simulations as a boundary condition. Comparison between plasma assisted combustion and electrically heated combustion at the same temperature confirmed that at low pulse repetition rate the enhancement of extinction limit was dominantly thermal, but that there was a kinetic effect of the atomic O at a high pulse repetition rate. Moreover, the comparison between experiment and numerical modeling with the measured temperature and atomic O concentration suggests that there were possibly additional kinetic effects from other excited species. Numerical simulations and kinetic path analysis further revealed that at higher temperature, more atomic O can be transported to the reaction zone to enhance the flame. There is a crossover temperature between 900 K and 1000 K, above (below) which the kinetic enhancement by atomic O production is governed by chain-branching (chain termination) reactions. The present results provide a good explanation to the conclusions made in different experimental conditions for plasma assisted flame speed enhancement and suggest that in order to achieve a significant kinetic enhancement of flame stabilization from atomic O, the plasma discharge or gas flow temperature needs to be above the critical crossover temperature.
Chapter 5

Kinetic Effects of Plasma-Assisted Methane Oxidation on Partially Premixed Flame Extinction

5.1 Introduction

In Chapter 4, a nanosecond pulsed discharge system has been integrated into the oxidizer side of a counterflow flame configuration, in order to obtain a simplified plasma/flame interaction. The experimental results revealed that the extinction limit of diffusion flames can be significantly extended by applying the discharge on the oxidizer side to produce O. However, considering a practical application, where the flow condition is controlled by the intensive turbulent mixing, partial/full oxidation of the pre-mixture with plasma would be one of the important factors that dominate the flame/plasma interactions. In this case, it is important to investigate how the chemical reactivity of the pre-mixture can be induced or promoted through the plasma/flame interactions, particularly in the low temperature regime (< 1000 K). Moreover, due to a dearth of quantitative data, the current plasma combustion kinetic mechanism for ignition [49] remains untested for low temperature CH$_4$ oxidation. Consequently, it is essential to provide quantitative measurements of species not only to validate of current kinetic models but also to advance the fundamental understanding of kinetic aspects of plasma/flame interactions.

Accordingly, the goal of the present study was to investigate the effect of plasma assisted CH$_4$ oxidation at the low temperature regime on the extinction limits of diffusion flames with partially premixed oxidizer in the counterflow configuration. The species concentrations have been measured with TALIF for O and Fourier Transform Infrared
(FTIR) spectroscopy and Gas Chromatography (GC) for stable intermediate species in order to characterize the performance of nanosecond pulsed discharge in a partially premixed oxidizer stream and to validate the current plasma-combustion kinetic model. This model has been validated further against the experimental measurements of extinction limits. Path flux analyses have also been conducted to identify and understand the important CH$_4$ oxidation pathways in plasma assisted combustion.

The work contained in this chapter was published in Combustion and Flame [98]:

W. Sun, M. Uddi, S. H. Won, T. Ombrello, C. Carter, Y. Ju, “Kinetic effects of non-equilibrium plasma-assisted methane oxidization on diffusion flame extinction limits” 2012 Combustion and Flame, 159(1) 221-229

5.2 Experimental Methods and Kinetic Modeling

5.2.1 Partially Premixed Counterflow Flame System with Nano-second Pulsed Discharge

A schematic of the experimental system is shown in Fig. 5.1 which is nearly identical with the setup used in the study of Chapter 4. The setup consisted of a pair of counterflow burners that were located in a low pressure chamber with a volume of 81 L. The inner diameters of the reactant and co-flow nozzles were 20 and 28 mm, respectively. The burner separation distance of the opposed nozzles were maintained to be equal to the nozzle diameter, 20 mm, to avoid the perturbation of the boundary condition from thermal expansion. The co-flowing inert (Ar) curtain provided the isolation of the flame from the environment and burner cooling as well. A honeycomb plate was placed inside the reactant nozzles to ensure that the flow field was uniform. The counterflow nozzles were made of quartz, and two parallel bare metal electrodes (a copper alloy that is corrosion resistant to avoid the catalytic effect of copper) were located inside the tubes of
the upper nozzle. The electrodes were 15 mm × 22 mm × 1 mm (thick) and were separated by 10 mm (inset in Fig. 5.1). The electrode edges were smoothed to avoid the local concentration of electric field and dielectric breakdown. The front ends of the electrodes were 10 mm away from the exit to avoid electrical interaction with the thermocouples. The experimental pressure was 60 Torr, the diffusion time scale (approximately 1 ms, estimated by $l^2/D$, where $l$ was the electrode thickness, and $D$ the diffusivity ($\sim 10^{-3}$ m$^2$/sec) of O$_2$ at 300 K and 60 Torr) was much shorter than the flow residence time (approximately 10 ms). Thus, the diffusion was sufficiently fast, and the effect of the electrodes on the flow field inside the tube was negligible. To ensure that the stagnation plane was formed in the middle of the two burner exits, the momenta of the two reactant streams were matched. During the experiments, He and Ar were used as dilution gases for the partially premixed oxidizer stream (He can improve the uniformity of the discharge [99], but it was difficult to maintain the flame if He was used as the only dilution gas due to the large thermal diffusivity at low pressure. Thus in our experiments, a He and Ar mixture was used as the diluent). The composition of the oxidizer stream was fixed at O$_2$/Ar/He/CH$_4$ (0.26:0.32:0.4:0.02) to observe the effect of CH$_4$ doping in the oxidizer. The fuel stream was CH$_4$ diluted by Ar (fuel mole fraction varied from 0.2 to 0.4). A nanosecond pulse generator (FID FPG 30-50MC4) was used to generate the non-equilibrium plasma to activate the partially premixed oxidizer stream. The pulse generator is capable of producing repetitive 32 kV pulses with pulse duration of 12 ns, full width at half maximum (FWHM). The frequency of the pulse generator is adjustable from 1 to 50 kHz. A typical voltage waveform measured by a LeCroy high voltage probe (PPE:20KV), is embedded in Fig. 5.1. The current through the electrodes was measured.
with a Pearson Coil (Model 6585). The pulse energy supplied to the discharge was estimated from the time integration of the voltage and current profiles and found to be approximately 1.27 mJ/pulse. The characteristics of voltage-current were independent of pulse repetition frequency. Therefore, average powers were calculated to be 5.1, 12.7, 25.4, 38.1 and 50.8 W at the respective frequencies of 4, 10, 20, 30 and 40 kHz. The amplitude of the voltage was fixed at 5.3 kV for all tested experimental conditions, as shown in Fig. 5.1.

Fig. 5.1 Schematic of experimental setup

The direct image of the nanosecond repetitive discharge is shown in Fig. 5.2 (a) at a pulse repetition frequency of 30 kHz. The optical emission spectrum of the discharge is shown in Fig. 5.2 (b). Figure 5.2 (b) shows strong emissions from excited O, OH, HCO, CH, He, and Ar, which indicated the radical formation from CH$_4$ oxidation during the discharge. It was also observed that the strongest emissions were from excited Ar and O (750 nm and 777.4 nm, respectively) and the intensity of all emission lines increased with
the increase of pulse repetition frequency. Thus, the plasma assisted CH\textsubscript{4} oxidation was presumed to be affected by the pulse repetition frequency, and the excited Ar and O may play an important role in the CH\textsubscript{4} oxidation. The intensity of excited He emission was not strong, however; this is because the excitation energy of He is relatively high (19.8 eV) compared to that of Ar (11.5 eV). Detailed discussions of the kinetic process will be given in the next section.

Fig. 5.2 Discharge at Ar/He/O\textsubscript{2}/CH\textsubscript{4} (0.32/0.4/0.26/0.02 by volume), \(d=20\) mm, \(f=30\) kHz, \(P=60\) Torr, (a) direct image, (b) optical emission spectrum

The extinction strain rates were measured by fixing the fuel mole fraction and increasing the flow velocity gradually until extinction occurred. At the same time, temperatures at the burner exits were measured simultaneously using thermocouples. One thermocouple (380 \(\mu\text{m}\) bead diameter) was fixed at the exit of the lower fuel nozzle, and another movable thermocouple was used to monitor the temperature at the exit of the upper nozzle. The movable thermocouple was coated with MgO and covered with a grounded Nickel-Chrome sheath (with 1 mm outer diameter) to remove the electromagnetic interference from the discharge.
The major products (CH$_4$, CO, CO$_2$, CH$_2$O, and H$_2$O) from the plasma assisted CH$_4$ oxidation in the oxidizer stream were measured by using an FTIR spectrometer (Nicolet Magna-IR 550). A quartz probe with an inlet diameter 1 mm was placed axially at the oxidizer side nozzle exit and was attached to a heated line (to avoid H$_2$O condensation) of the FTIR spectrometer. The pressure and temperature in the FTIR system were held constant at 31 Torr and 393 K, respectively. For H$_2$ measurement, a micro GC system (INFICON 3000) was used. The calibrations were performed by flowing sample gas with known species concentrations through the FTIR or GC at conditions identical to those of the experiments. The relative mole fraction uncertainties of sampling measurements were found to be less than ±1% for CH$_4$, CO, CO$_2$ and ±5% for H$_2$O and H$_2$. The uncertainty of the CH$_2$O measurement was ±80 ppm. The sampling was also performed by using a quartz probe with 6 mm diameter. The results were identical with that of 1 mm diameter probe which indicated the uniformity of the properties of the counterflow system in the center region and the validity of one dimensional approximation.

5.2.2 Computational Approach with Plasma-Combustion Kinetic Model

Both the kinetic model and physical model to simulate the nano-second pulsed discharge were already discussed in Chapter 2. Please refer section 2.2.2 for details.

5.3 Results and Discussions

5.3.1 Effects of Discharge Repetition Rate on Species Concentrations from Plasma-Assisted CH$_4$ Oxidation

FTIR and GC instrumentation were used to quantify the major stable products of the low temperature plasma assisted CH$_4$ oxidation by sampling at the center of the
nozzle exit in the oxidizer stream using quartz probe. Typical FTIR absorption spectra are shown in Fig. 5.3 (a)-(f). Figure 5.3 (a) shows the FTIR absorption spectra without the discharge. The CH$_4$ absorbance spectrum is seen clearly and shows no effects of any CO$_2$ and H$_2$O entrainment from the environment. With the presence of the plasma discharge, the absorbance spectra of CO, CO$_2$, H$_2$O and CH$_2$O appeared due to the plasma assisted CH$_4$ oxidation. Moreover, as shown in Fig. 5.3 (b)-(f), with the increase of discharge pulse repetition frequency (or equivalently, discharge power), the concentrations of CO, CO$_2$ and H$_2$O increased significantly, and at the same time, the concentration of CH$_4$ decreased. The dependence of the measured concentrations of CO, CO$_2$, H$_2$, H$_2$O, and CH$_2$O on the plasma pulse repetition rate is shown in Figs. 5.4-5.6. In order to validate the plasma flame model, the predicted species concentrations are also plotted in Figs. 5.5 and 5.6. In all the FTIR measurements, it was confirmed that the carbon closure with the measured species was 95%, demonstrating that the measurements captured the major carbon containing species in the plasma assisted CH$_4$ oxidation. It was also observed that carbon black deposited on the electrodes and sampling quartz probe during the experiments and that the minor carbon loss was caused by the formation of carbon black in the plasma discharge. As shown in Figs. 5.4 and 5.5, with the increase of pulse repetition frequency, the CH$_4$ concentration decreased significantly, and nearly a mole fraction of 0.9 of CH$_4$ was oxidized at pulse repetition frequency $f= 40$ kHz. At the same time, the concentrations of CO, CO$_2$ and H$_2$O increased monotonically with $f$. With the increase of CH$_4$ oxidation ratio, the oxidizer temperature at the nozzle exit also increased significantly (423±3 K, 613±5 K, 743±5 K, 843±5 K and 933±8 K at $f= 4$ kHz, 10 kHz, 20 kHz, 30 kHz, and 40 kHz, respectively). Note that the concentration of H$_2$ after low
temperature plasma assisted CH$_4$ oxidation remained very low (less than 2000 ppm). The peak concentration of H$_2$ occurred at a pulse repetition frequency $f=20$ kHz. The low value of peak H$_2$ concentration compared to H$_2$O concentration suggests that the plasma assisted combustion was not dominated by fuel reforming into H$_2$ and CO, as will be discussed later. A low peak concentration for CH$_2$O at $f=10$ kHz was also observed during the experiments, as shown in Fig. 5.6. It is shown in both Figs. 5.5 and 5.6 that the model captured the correct trend of the relationship between the species concentrations and pulse repetition frequency, but the kinetic model over-predicted CO (up to 44%), CH$_2$O (up to a factor of 6) and H$_2$ (up to a factor of 3), and under-predicted CO$_2$ (up to 89%) by volume, indicating that the model underestimated the overall reactivity in the oxidizer stream.

Fig. 5.3 FTIR spectrum with different pulse repetition frequencies at Ar/He/O$_2$/CH$_4$ (0.32/0.4/0.26/0.02 by volume), $P=60$ Torr; (a) no plasma, (b) $f=4$ kHz, (c) $f=10$ kHz, (d) $f=20$ kHz, (e) $f=30$ kHz, and (f) $f=40$ kHz
Fig. 5.4 Dependence of CH₄ concentrations and oxidization ratios on pulse repetition frequency

Fig. 5.5 Dependence of species concentrations at the burner exit on pulse repetition frequency (experiments: solid symbol and solid line; simulations: open symbol and dashed line)
Fig. 5.6 Dependence of species concentrations at the burner exit on pulse repetition frequency (experiments: solid symbol and solid line; simulations: open symbol and dashed line)

In order to identify the important CH₄ oxidation pathways and understand the kinetic processes in the plasma assisted CH₄ oxidation mechanism, path flux analysis was performed for a pulse repetition frequency $f = 40$ kHz, and the results are shown in Fig. 5.7. Methane was dissociated to CH\(_3\) mainly by H abstraction with OH, O and H produced via the plasma discharge. Methane also decomposed to CH\(_3\), CH\(_2\) and CH via collisions with an electron, Ar(+) and Ar* (reactions (R5.1)-(R5.6)). The formed CH\(_3\), CH\(_2\) and CH were oxidized further to CH\(_2\)O, HCO, CO and finally CO\(_2\) as shown in Fig. 5.7 (a). The dominant reaction pathway from CH\(_3\) to CH\(_2\)O was through reaction CH\(_3\) + O = CH\(_2\)O + H. A small amount (5.3%) of CH\(_3\) was oxidized to CH\(_3\)O majorly through reaction CH\(_3\) + HO\(_2\) = CH\(_3\)O + OH. Among those reaction paths, a total of a mole fraction of 0.12 of CH\(_4\) was decomposed by collisions with electrons, Ar(+) and Ar*. 

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Molecular hydrogen is another important product of plasma assisted CH₄ oxidation because it can affect greatly the ignition and extinction processes via its fast oxidation chemistry. The reaction path of H₂ is shown in Fig. 5.7 (b). The dominant formation path of H₂ was through H abstraction reactions with CH₄, CH₂O, HO₂, HCO, CH₂ and CH₃. The formation of H₂ via H+HO₂=H₂+O₂ clearly indicates the nature of low temperature chemistry. This reaction plays an important role at low temperature and high pressure when HO₂ concentration is high [100]. Another formation path of H₂ was through CH₄ decomposition by Ar*, but only 1.2% of H₂ was formed through this reaction path. Moreover, the concentration of H₂ increased at low pulse repetition frequency, due to the increased H abstraction reaction by H radicals; at high frequency, H₂ concentration then decreased via increased reactivity at higher temperature. Therefore, the concentration of H is important to determining the concentration of H₂. The reaction paths of H and O are also shown in Fig. 5.8 (a) and (b). Only 11.7% of H was formed via the decomposition of CH₄ by electron impact and excited species collisions through reactions (R5.1) to (R5.5). The major contribution to H formation was from reaction CH₃ + O = CH₂O + H. Thus, O concentration is crucial to determining H concentration.

\[
\text{CH}_4 + \text{e} = \text{CH}_3 + \text{H} + \text{e} \quad \text{(R5.1)}
\]

\[
\text{CH}_4 + \text{Ar}(+) = \text{CH}_3(+) + \text{H} + \text{Ar} \quad \text{(R5.2)}
\]

\[
\text{CH}_4 + \text{Ar}^* = \text{CH}_2 + \text{H} + \text{H} + \text{Ar} \quad \text{(R5.3)}
\]

\[
\text{CH}_4 + \text{Ar}^* = \text{CH}_3 + \text{H} + \text{Ar} \quad \text{(R5.4)}
\]

\[
\text{CH}_4 + \text{Ar}^* = \text{CH} + \text{H}_2 + \text{H} + \text{Ar} \quad \text{(R5.5)}
\]

\[
\text{CH}_4 + \text{Ar}^* = \text{CH}_2 + \text{H}_2 + \text{Ar} \quad \text{(R5.6)}
\]
The reaction path of O is shown in Fig. 5.8 (b). Approximately 54% of O was formed through collisions between O$_2$ and electrons/Ar*. Among all the three major O production paths, 33.5% was from direct electron impact dissociation of O$_2$, 20.4% from O$_2$ collisions with Ar*, and 33.6% from the H+O$_2$=OH+O branching reaction. Note from Fig. 5.8 (a) that the initial H radicals for the branching reaction are formed from the reaction of O with CH$_3$, which is itself produced by the direct plasma discharge in the partially premixed CH$_4$/O$_2$ stream. Therefore, it can be concluded that O production by plasma is the major source to initiate the low temperature plasma assisted CH$_4$ oxidation. Moreover, the partial CH$_4$/O$_2$ premixing increases H production and accelerates the chain branching process. Once O is generated by the discharge, it is consumed rapidly by CH$_4$ and its intermediate oxidized and dissociated products (CH$_3$, CH$_2$, CH$_2$O, HCO, HO$_2$ and H$_2$). It is shown in Fig. 5.8 (b) that the major consumption path of O is to generate OH and H, which are important to the CH$_4$ oxidation process. OH and H then further react with fuel and its fragments, which become the dominant reaction paths of the fuel decomposition. Only a small amount (0.6%) of O recombines to O$_2$ (Surface recombination reaction of O was not considered in this study. This was accounted for by measuring the O concentration at the center of the nozzle and comparing with the simulations). Note that the reaction path from O to O$_3$ is negligible in this study due to the high temperature conditions. Furthermore, the concentrations of reactive oxidant ions (O$_2$*, O-) are several orders of magnitude lower than O, and thus their effects are also negligible. This indicates that when the discharge is applied to the premixture of fuel and oxidizer, O can be consumed more efficiently by the fuel and its intermediate oxidation and dissociation products rather than through recombination. Based on the above analysis,
it is clear that O production within a plasma discharge in a partially premixed fuel and oxidizer is critical for H₂ and H formation and subsequent CH₄ oxidation. Therefore, in order to predict other species, O formation through the collision-induced O₂ dissociation by electrons and excited species needs to be accurately predicted. In addition, to improve the CH₄ oxidation efficiency (the consumption efficiency of O), the plasma discharge needs to be implemented in a partially premixed lean fuel/oxidizer mixture.

In order to determine the concentration of O and compare with the kinetic model prediction, the Xenon calibrated, Two Photon Absorption Laser Induced Fluorescence (TALIF) method was used. The relationship between O concentration and pulse repetition frequency (for a flow velocity of 200 cm/s) with and without fuel premixing is plotted in Fig. 5.6. For plasma discharge in a partial premixture of fuel and oxidizer, it is shown that with the increase of pulse repetition frequency, the O concentration increased, but the increase was very low, less than 300 ppm even at \( f = 40 \) kHz (note that the TALIF detection limit can be as low as several ppm [49]). The low rate of increase of O production versus \( f \) suggests that the cause is rapid CH₄ oxidation at high plasma repetition frequency by the induced chain reactions (shown in Fig. 5.8 (b)). To demonstrate this fact, the O concentration without fuel premixing was also measured at the same condition. Figure 5.6 shows that the concentration of O increased sharply from 530 ppm to 2700 ppm when the pulse repetition frequency increased from 4 kHz to 40 kHz. This result confirmed that the increased CH₄ oxidation at high plasma frequency was due to the increased production of O. The simulation results of O and CH₂O concentrations are also shown in Fig. 5.6, together with the experimental measurements of CH₂O concentration. The calculated concentrations of O and CH₂O intersected with
the experimental results, but the deviations became large at $f=40$ kHz.

As analyzed, the model under-predicted the concentration of CO$_2$, and over-predicted CO and H$_2$, which indicated an overall lower reactivity of the mixture. For O and CH$_2$O prediction, the kinetic model significantly under-predicted their concentrations at low pulse repetition frequency and over-predicted the concentrations at high pulse repetition frequency. This may be due to the missing reaction paths involving peroxide species at low temperature and those involving interactions of excited species with hydrocarbon species and its products. For example, the HO$_2$ + X (X=H, OH) reaction rates have large uncertainty at low temperature, and the OH + O + M = HO$_2$ + M reaction, which is not included in the current combustion mechanism, may become important at low temperature [51]. In addition, a fraction of O atoms was excited to O($^1$D), which is much more reactive, especially at low temperature conditions. But, unfortunately,
reactions involving O(\(^1\)D) and hydrocarbon species are not well characterized and are absent in the current kinetic model (except O(\(^1\)D) + H\(_2\) = H + OH \cite{12}, which is 10\(^7\) faster than O + H\(_2\) = H + OH at 300 K). The formation of CH\(_2\)O was primarily from the reaction CH\(_3\) + O = CH\(_2\)O + H. If the concentration of O was over-predicted (or under-predicted), the concentration of CH\(_2\)O would also be over-predicted (or under-predicted). Likewise, H\(_2\)O can react with O(\(^1\)D) via the H\(_2\)O + O(\(^1\)D) = 2OH reaction and can also be dissociated by electrons and Ar\(^*\) to generate OH and H. The generation of OH can accelerate the oxidation of CO.

![Reaction paths flux analysis for (a) H and (b) O at \(f=40\) kHz](image)

The kinetic model also showed the formation of C\(_2\)H\(_6\) (\(~200\) ppm), but the C\(_2\)H\(_6\)
absorption spectrum was not observed in the FTIR experiments. Previous research in a lean CH₄/air discharge [46] also showed no C₂H₆ formation, and thus the reaction CH₃ + CH₃ = C₂H₆ was over-estimated or the consumption path of C₂H₆ was under-estimated at low temperatures. Furthermore, it is known that the current kinetic mechanism has not been validated below 700 K. More quantitative experimental data at low temperature conditions are thus required to improve the predictability of the kinetic mechanism.

5.3.2 Extinction Strain Rates Measurement and Computation

The extinction strain rates of the CH₄/O₂ diffusion flames were measured without and with plasma (at f=4, 10, 20, 30, and 40 kHz). A definition of global strain rate was adopted and compared with numerical simulations. Here $U$ is the speed of the flow, the density of the flow, and $L$ the gap distance between the two nozzles. The subscripts $o$ and $f$ refer to the oxidizer and fuel side, respectively. The use of global strain rate was found to be appropriate for mechanism validation [73], and the global strain rates were used in this study for both experiments and simulations.

In this experiment, the composition of the partially premixed oxidizer stream was fixed at a volume ratio of 0.02/0.26/0.32/0.4 for CH₄/O₂/Ar/He. The fuel stream was composed of CH₄ and Ar, and the CH₄ mole fractions varied from 0.2 to 0.4. During the measurements, the fuel mole fraction was fixed, and the flow velocity of both sides increased gradually. With the increase of flow velocity, the strain rate increased, and the flame had less residence time to complete the CH₄ oxidation and thus extinguished when the strain rate was above a critical value. This critical strain rate at flame extinction was
recorded as the global extinction strain rate. Figure 5.9 shows the relationship of extinction strain rates and fuel mole fractions without plasma and with plasma at pulse repetition frequencies of $f=4$ and 10 kHz (with oxidizer temperature $T_o = 423\pm4$ K and $613\pm5$ K, the oxidizer side flow rates were among 1.92~2.18 SLPM and 2.22~2.41 SLPM at fuel mole fractions from 0.34 to 0.4, respectively). Extinction strain rates without CH$_4$ addition ($O_2$/Ar/He ratio of 0.28/0.32/0.4) were also presented in Fig. 5.9 as reference. The experiments were compared further with numerical simulations. All simulations were performed by setting the boundary conditions using the measured temperatures and species concentrations (using FTIR, GC and TALIF instruments). The concentrations of H and OH were estimated from the simulation by matching the computational and experimental values of O concentrations, as discussed in section 5.1. It was noticed that the extinction strain rate was sensitive to the CH$_4$ mole fraction in the oxidizer stream because this determines the heat release rate in the reaction zone. Thus, the failure to update the species concentrations information as the boundary condition may cause approximately 15% larger calculated extinction strain rates in the simulations. The results in Fig. 5.9 show that with CH$_4$ addition, the extinction strain rates were extended significantly and the oxidizer temperature after the plasma activation was higher (613 K and 548 K with and without CH$_4$ addition at $f=10$ kHz, respectively). It is also shown that with the increase of the pulse repetition frequency, $f$, there was a significant increase of extinction limit enhancement and the measured extinction strain rates agree well with the computed values. The present results indicate that the plasma generated CH$_4$ oxidation plays an important role for the extension of flame extinction limit. This is because when the flame approaches extinction, there was not enough
residence time for the CH$_4$ to complete the oxidation reactions to release the chemical heat. However, plasma can dramatically accelerate the CH$_4$ oxidation to release the chemical energy at low temperature. The prompt chemical heat release extended the extinction limit.

Fig. 5.9 Dependence of extinction strain rate on fuel mole fraction at the fuel side under different experimental conditions

It was noticed that during the plasma assisted CH$_4$ oxidation process, part of the CH$_4$ was reformed into H$_2$ and CO. Molecular hydrogen can extend the extinction limit through its fast chemistry, and previous research [72], [101] showed that plasma induced fuel reforming, producing a H$_2$/CO mixture, can enhance the flame stability. Therefore, it is important to examine how the fuel reforming affects the extinction. The present experiment showed that the H$_2$ formation by non-equilibrium plasma discharge was low.
As such, the plasma reforming effect only played a minor role in the extension of the extinction limit. Of course, the H$_2$ yield depends on the discharge characteristics and fuel concentration in the mixture. It is necessary to understand whether fuel reforming or CH$_4$ oxidation is more effective in increasing flame stabilization.

Fig. 5.10 Comparison of extinction strain rates of fuel oxidation and fuel reforming effect under a constant enthalpy condition for the oxidizer stream of Ar/He/O$_2$/CH$_4$ (0.32/0.4/0.26/0.02 by volume), $P=60$ Torr

Because plasma can cause both CH$_4$ oxidation and reformation, simulations of the individual effects of plasma assisted CH$_4$ oxidation and CH$_4$ reforming were performed and compared in Fig. 5.10. Here, part of the fuel (CH$_4$) in the oxidizer stream was assumed to be ideally oxidized to H$_2$O and CO$_2$ for Case 1 and reformed to H$_2$ and CO in
Case 2 under a constant enthalpy constraint (a few hundred K temperature increase was along with the fuel reforming, depending on the reforming ratio). It is shown that extinction was enhanced for both cases, but the enhancement from the plasma assisted CH$_4$ oxidation (Case 1) is much larger than that of CH$_4$ reforming. This is because when the flame was approaching extinction, the residence time was too short to complete the reactions. That is, CH$_4$ and its reformation products in the oxidizer stream cannot react completely to release the chemical enthalpy in the reaction zone in Case 2, but the chemical enthalpy was already released in Case 1 before reaching the reaction zone. Therefore, plasma assisted CH$_4$ oxidation is more effective in increasing the extinction limit than CH$_4$ reforming.

Fig. 5.11 Dependence of extinction strain rate on pulse repetition frequency at a fuel side CH4 mole fraction of $X_f=0.2$, an oxidizer side volumetric composition of Ar/He/O$_2$/CH$_4$ (0.32/0.4/0.26/0.02), and $P=60$ Torr
The extinction strain rate measurements and simulations were also conducted at \( f = 20, 30 \) and 40 kHz (with oxidizer temperature \( T_o = 743\pm5 \) K, 843±7 K and 933±8 K, the oxidizer side flow rates were 1.66 SLPM, 1.89 SLPM and 1.92 SLPM, respectively, and with measured and calculated boundary conditions as described above) by fixing the fuel mole fraction and are shown in Fig. 5.11. With the further oxidation of CH\(_4\) (increased \( f \)) in the partially premixed oxidizer stream, the extinction strain rates increased significantly. With further increase of \( f \), the experimental and simulation results deviated, which may indicate that there are additional reaction paths to enhance the flame extinction. Nonetheless, the maximum deviation was small at approximately 10%. Moreover, the peak concentration of H\(_2\) was 1751 ppm at \( f=20 \) kHz, and the extinction limit enhancement from H\(_2\) was only 5.3%. Thus, the dominant enhancement mechanism for the extinction limit is plasma-induced prompt CH\(_4\) oxidation.

### 5.4 Conclusions

The present experiments employing a nanosecond plasma discharge in a partially premixed counterflow flame showed that plasma assisted CH\(_4\) oxidation at low temperature (60 Torr) can extend the extinction limits dramatically. It was found that the main cause of the combustion enhancement was due to a kinetic-thermal effect of prompt CH\(_4\) oxidation and heat release by plasma generated species. Although plasma assisted combustion led to partial CH\(_4\) reforming to H\(_2\) and CO, numerical simulations showed that the effect of CH\(_4\) reforming on combustion enhancement was mainly through the rapid H\(_2\) chemistry but only played a minor role compared to the prompt CH\(_4\) oxidation.

The results also showed that O production by the plasma discharge was the main contributor to the prompt CH\(_4\) oxidation at low temperature and that partial premixing of
fuel in the oxidizer stream led to a dramatic decrease of O concentration due to its rapid consumption by CH₄ oxidation. The path flux analysis showed that O was generated primarily by the discharge via direct electron impact dissociation of O₂ and O₂ collisions with electronically excited species. In addition, the results also showed that the electron impact and excited species collisional dissociation of fuel also contributed approximately a mole fraction of 0.1 of the radical production.

The extinction strain rates from experimental measurements agreed well with the numerical simulations at low pressure. Comparison of measured and predicted species concentrations in plasma assisted CH₄ oxidation showed that the low temperature plasma combustion kinetic model reasonably predicted the O and CH₂O formation, but the model over-predicted the concentrations of CO, H₂O, H₂ and under-predicted the concentration of CO₂. In order to improve the predictability of the plasma flame kinetic model, the elementary reaction rates of O production by electron impact and excited species collision need to be revisited. In addition, more experimental validation data in flow reactors of CH₄ oxidation at temperatures between 300 K and 700 K with radical addition are necessary.
Chapter 6
Effects of the \textit{In Situ} Non-equilibrium Discharge on Flame Ignition and Extinction

6.1 Introduction

Due to the complexity of directly coupling of the discharge with the flame, most of the experiments have been designed to isolate the direct coupling effect between the discharge and the flame, either temporally [38], [43], [47], [49], [54] or spatially [53], [62], [63], [71], [72], [101], [102] in order to elucidate the kinetic roles of species produced by the plasma. This isolation methodology has provided the unique advantage for the fundamental investigation on the kinetic role of plasma assisted combustion since the species generated by the plasma can be measured and transported to the combustion system, therefore isolating the effect of individual species. In Chapter 4 and 5, a well-defined counterflow system integrated with a nano-second pulsed discharge has been developed by applying the discharge on the oxidizer stream, and the effects of the discharge on the counterflow diffusion and partially premixed CH$_4$ flame extinction were studied. Subsequent studies have revealed that the radicals/excited species generated by the plasma cannot be easily delivered to the main reaction zone, either because of the predominant recombination/quenching or due to the reactions with the doped fuel. Thus, the dominant effect of plasma on the reaction zone was not free from thermal enhancement effects, which would make the quantification of the kinetic enhancement mechanism difficult.

Motivated by this observation, in this chapter, the objective is to investigate the direct coupling effect between plasma and a flame, where plasma kinetics pathways
would modify the flame kinetic pathways. In order to focus on the kinetic performance of the plasma/flame interaction, a novel well-defined counterflow flame system with an \textit{in situ} discharge has been developed as introduced in Chapter 2. Direct kinetic coupling effects have been investigated both by experiments and numerical modeling. Further chemical kinetic aspects of the plasma/flame interaction are discussed through detailed flux analysis.

Part of the work contained in this chapter was published in the Proceeding of Combustion Institute [103]:


6.2 Experimental Methods and Numerical Models

6.2.1 Counterflow Flame and \textit{in situ} Nano-Second Pulsed Discharge Systems

A schematic of the experimental system is shown in Fig. 6.1. A counterflow burner was located in a low pressure chamber. Both the fuel and oxidizer nozzles of the counterflow burner were made of stainless steel with a 25.4 mm inner diameter. At the nozzle exits, stainless steel porous plugs (2 mm thickness) were placed to provide the uniform velocity profiles and to serve as the electrodes. The separation distance of the oxidizer and fuel burner nozzles (electrodes) was maintained at 16 mm. The oxidizer- and fuel-side electrodes were connected to the positive high voltage and the negative high voltage, respectively. The discharge could be generated between the two nozzles as shown in Fig. 6.1. The high voltage pulse was generated by a pulse generator with pulse
duration of 12 ns (full width at half maximum, FWHM) and adjustable frequency. The voltage was measured by a high voltage probe (LeCroy, PPE20KV) and kept constant as 7.6 kV during the experiments. The current through the electrodes was measured with a Pearson Coil (Model 6585). The characteristics of voltage-current were found to be independent of the mixture compositions of the fuel and oxidizer sides. The pulse energy supplied to the discharge was estimated from the time integration of the voltage and current profiles and was found to be about 0.73 mJ/pulse. The pulse repetition frequency \( f \) was fixed at 24 kHz, corresponding to an input power of 17.5 W. In order to improve the uniformity of the discharge, helium (He) was used as the dilution gas for both the fuel (CH\(_4\)) side and the oxidizer (O\(_2\)) side. The pressure was held constant at 72 Torr for all of the experiments.

Fig. 6.1 Schematic of experimental setup

The temperature profiles were measured by the Rayleigh scattering technique
discussed in Chapter 3, employing the second harmonic Nd:YAG laser beam at 532 nm. The laser sheet beam was produced by the combination of cylindrical lenses (focal length -50, 50 and 100 mm) to obtain two-dimensional images between the two nozzles of the counterflow burner. The temperatures close to the burner surface (boundary temperatures) were measured by a thermocouple with three coating layers. The thermocouple was coated by magnesium oxide (MgO) on the surface and encapsulated by a metal sheath. So the electromagnetic effect from the pulsed discharge on the thermocouple could be removed. Finally, an aluminum oxide sheath (OD 3 mm) was used to cover the metal sheath to remove the effect from the ionized environment [104][105]. The thermocouple measurements were compared with Rayleigh scattering and other thermocouple measurements, with and without discharge, respectively. The uncertainty of the thermocouple measurements was found to be ± 20 K.

6.2.2 Uniformity of the Discharge and the Excited OH Emission from the Reaction Zone

The experiments were conducted by flowing a He/O$_2$ mixture from the top nozzle, and a He/CH$_4$ mixture from the bottom nozzle. The high voltage pulse applied on the electrodes could generate a uniform discharge between the two nozzles. The uniformity of the discharge could be confirmed by the single shot images from the ICCD camera (576-G/RB-E, Princeton Instruments) with a 50 ns gate, as shown in Figs. 6.2 (a)-(b). It can be noted that no “hot spot” or filamentary discharge was observed with and without the flame, which allowed for a one-dimensional approach in the numerical simulations. Figure 6.2 (c)-(d) also shows direct photos taken with a digital camera (Nikon, D40X) for the O$_2$ concentration ($X_0$) on the oxidizer side of 0.4. At the fixed strain rate, $a = 250$ 1/s, by gradually increasing the CH$_4$ concentration on the fuel side, $X_f$, the mixture is ignited.
at $X_F = 0.25$, and the resulting stable diffusion flame is shown in Fig. 6.2(c). Then by decreasing $X_F$, extinction is observed at $X_F = 0.14$, Fig. 6.2(d).

Fig. 6.2 (a) ICCD image at $X_O = 0.4$ and $X_F = 0.25$ diffusion flame and discharge, 50 ns gate; (b) ICCD image at $X_O = 0.4$ and $X_F = 0.14$ discharge, 50 ns gate; (c) direct photo of (a), 50 ms exposure time; (d) direct photo of (b), 50 ms exposure time, $P = 72$ Torr, $f = 24$ kHz, $a = 250$ l/s

Considering that the ignition in the counterflow burner with heated air occurs generally at high temperatures (> 1200 K) [60] and typical temperature variation of the current plasma configuration was below 1000 K [94], [98], the above observation raises two fundamental questions. Firstly, what is the chemical kinetic mechanism for the ignition by the plasma? Secondly, how does the plasma and flame chemistry interact, thus changing the mechanisms of flame initiation and stabilization? In order to answer
these two questions, the ignition by the plasma as a function of $X_F$ was investigated by monitoring the intensity of excited OH (OH*) emission as the flame or ignition marker [53], [106] using the ICCD camera with a narrow bandpass filter, centered at 307±2 nm (10±2 nm FWHM). In order to suppress the emission of excited He at 315 nm, the ICCD camera gate (30 µs in all OH* emission measurements) was delayed by 5 µs after the initial discharge pulse. A typical OH* emission ICCD image is also embedded in Fig. 6.1. A flat reaction zone or flame between the nozzles can be identified clearly. The ignition and extinction limits were measured by varying $X_F$ at several values of $X_O$ in order to investigate the change of flame regimes with the activation of plasma. Finally, the chemical kinetic analysis was performed in order to address the plasma assisted ignition mechanism. In order to compare the difference between OH* and OH density, OH Planar Laser Induced Fluorescence (OH PLIF) was used to measure the distribution of OH. The $Q_1(6)$ transition of OH was excited at the wavelength of 282.93 nm. More details about OH PLIF technique can be found in Chapter 3.

6.2.3 Kinetic Modeling of Plasma-Flame Interaction

The challenge of the modeling study of the plasma/flame interaction was whether the experimental observation could be properly simulated using a one-dimensional approximation. Although the diffusion flame in the counterflow configuration has been rigorously studied with a one-dimensional approximation [73], [79], [80], there still exists the open question on the validity of one-dimensional approximations for plasma properties. For example, the plasma properties, such as reduced electric field (defined as the local electric field strength, E, divided by the local number density, N) and species concentrations, may not be uniform in the radial direction of the counterflow burner. No
detailed two- or three-dimensional computations have been done yet for plasma-flame systems due to the complex interaction of plasma/flame chemistry. Nevertheless, in our experiments, the OH* profiles appeared to be uniform in the center region of the counterflow burner; this observation therefore rationalizes the one-dimensional approximation.

The kinetic mechanism was generated by the combination of a plasma kinetic model [49] and the combustion kinetic model, USC Mech II [83]. The details of the kinetic model and physical model were discussed in Chapter 2.

6.3 Results and Discussion

6.3.1 Observations of the S-Curve transition

The ignition and extinction characteristics were studied by measuring the OH* emission intensity since ignition or extinction happens along with an abrupt change of the OH* emission. The integration of the OH* emission intensity across the reaction zone was used as a marker for comparisons of different cases/conditions. During the experiments, the strain rate (400 1/s, with flow residence time of approximately 2.5 ms), $X_O$ and the discharge frequency ($f = 24$ kHz) were held constant, while the CH$_4$ mole fraction on the fuel side, $X_F$, was varied. With varying the $X_F$, the thickness of the reaction zone was nearly a constant as marked by the OH* emission profile. For the first case, $X_O$ was fixed at 0.34. The boundary temperatures of the oxidizer side and fuel side were $650 \pm 20$ K and $600 \pm 20$ K, respectively, and nearly constant through all the experiments with the fixed discharge frequency and experimental pressure. The relationship between OH* emission intensity as well as reaction zone peak temperature and $X_F$ is shown in Fig. 6.3. The solid and open symbols in Fig. 6.3 represent the
respective increasing and decreasing of \( X_F \). By starting from \( X_F = 0 \) and increasing \( X_F \) until it equaled 0.265, the OH* emission was negligible compared to the background noise, and no reaction zone was observed. Further increase of \( X_F \) caused an abrupt increase of OH* emission intensity (from 0 to 8000 a.u.). This phenomenon was also identified by the appearance of a visible flame, indicating that ignition occurred. After ignition, further increase or decrease of \( X_F \) only caused very limited increase or decrease of the OH* emission intensity, respectively. But if \( X_F \) is decreased to less than 0.20, an abrupt decrease of the OH* intensity was observed and the visible flame emission disappeared, indicating the extinction. This hysteresis of OH* emission intensity between ignition and extinction forms an S-curve of the flame [107], which is the fundamental phenomena of ignition and extinction. Similar curve can also be obtained by varying the discharge frequency with constant \( X_F \) and \( X_O \). If the discharge frequency was below 1 kHz, no ignition can be observed due to the quenching of radicals between two discharge pulses.

The local maximum temperature measurement (reaction zone temperature) showed that the value just before ignition was only 897 K, which was approximately 300 K higher than the boundary temperatures. The uncertainty of this measurement was about \( \pm 50 \) K due to the repeatability of the experiments. With further increasing \( X_F \), ignition occurred and the local maximum temperature increased to approximately 1310 K. At \( X_F = 0 \), the temperature distribution by Rayleigh scattering was nearly uniform without any local peak between the two burner nozzles, mostly due to the high diffusivity of helium at low pressure. The difference of temperature profiles with and without fuel flow indicated clearly i) the existence of the coupling effects between the plasma and combustion
chemistry for fuel oxidation and ii) the consequent heat release at low temperatures to initiate ignition.

![Graph showing the relationship between OH* emission intensity, local maximum temperature and fuel mole fraction.]

Fig. 6.3 Relationship between OH* emission intensity, local maximum temperature and fuel mole fraction, $X_O = 0.34$, $P = 72$ Torr, $f = 24$ kHz, $a = 400$ 1/s (solid square symbols: increasing $X_F$, open square symbols: decreasing $X_F$)

It has been shown in Chapter 5 that plasma can initiate the CH$_4$ oxidation at low temperatures due to O generation from the discharge. More O generation will further enhance the fuel oxidization and ignition. Therefore, similar experimental observations were made by increasing $X_O$ to 0.55 and 0.62 at the oxidizer side to increase O production. The results are shown in Figs. 6.4 and 6.5, respectively. Compared to the results with $X_O = 0.34$ (Fig. 6.3), it was found that the hysteresis between ignition and extinction still existed for $X_O = 0.55$, but both the ignition and extinction points were pushed to lower
fuel concentrations and become closer to each other: ignition was achieved at $X_F = 0.14$ and extinction did not occur until $X_F$ was decreased to 0.1.

![Graph showing relationship between OH* emission intensity, local maximum temperature and fuel mole fraction, $X_O = 0.55$, $P = 72$ Torr, $f = 24$ kHz, $\alpha = 400$ 1/s (solid square symbols: increasing $X_F$, open square symbols: decreasing $X_F$).](image)

Identical results were obtained by measuring the absolute OH number densities using OH PLIF in the reaction zone as shown in Fig. 6.5 with and without plasma. Without plasma, the OH concentration was significantly lower than that of with plasma and extinction happened at $X_F = 0.2$ without plasma.
Fig. 6.5 Relationship between OH number density with and without plasma, local maximum temperature and fuel mole fraction, $X_O = 0.55$, $P = 72$ Torr, $f = 24$ kHz, $a = 400$ 1/s (solid square symbols: increasing $X_F$, open square symbols: decreasing $X_F$)

With a further increase in $X_O$ to 0.62, the ignition and extinction points merged at $X_F = 0.09$, as shown in Fig. 6.6, and a monotonic ignition and extinction S-curve was formed. The temperature measurements also demonstrated a similar monotonic increase of the local maximum temperatures. The monotonic and fully stretched S-curve could be explained by the fact that the plasma generated reactive species caused a transition of flame stabilization mode from the extinction-controlled to the ignition-controlled modes. This means that the extinction limit did not exist by the plasma/combustion chemistry interaction, thus the chemistry of flame stabilization was fully dictated by the ignition limit.
Fig. 6.6 Relationship between OH* emission intensity, local maximum temperature and fuel mole fraction $X_F = 0.62$, $P = 72$ Torr, $f = 24$ kHz, $a = 400$ 1/s (solid square symbols: increasing $X_F$, open square symbols: decreasing $X_F$)

As a comparison, the pure thermal effect on the $S$-curve transition was investigated with numerical simulations by increasing the boundary temperatures of both the fuel and oxidizer sides as shown in Fig. 6.7. It showed that the disappearance of ignition/extinction hysteresis could be observed at the extremely high boundary temperature of 1350 K. The electric power requirement to achieve 1350 K for both fuel and oxidizer is generally on the order of a kilowatt, which is significantly higher than the power consumption of 17.5 W by the plasma system.
Fig. 6.7 Relationship between maximum local temperature with heated flow and fuel mole fraction $X_O = 0.62$, $P = 72$ Torr, $f = 24$ kHz, $a = 400$ l/s

6.4 Numerical Modeling Results

The numerical simulations were conducted at the condition of $X_F = 0.16$ and $X_O = 0.34$ for the fuel and oxidizer sides, respectively, in order to analyze the plasma reactions prior to ignition and consequent formation of a flame. Without the plasma, no reaction (flame) could exist at this condition. With the presence of plasma, significant amounts of O, H and OH were generated as shown in Fig. 6.8 (a); also shown are the measured and computed temperature profiles. Within the uncertainty of experiments ($\pm 50$ K), the Rayleigh scattering measurement of the temperature agreed with the simulation. The deviations between the simulation and experiment close to the boundaries were larger since the Rayleigh scattering signals were inevitably overwhelmed by scattering from the
burner surfaces. The temperature peaked near the stagnation plane, indicating the location of the main reaction zone. The O concentration peaked on the oxidizer side due to the direct electron dissociation of O\textsubscript{2}, whereas the H peaks on the fuel side due to the electron dissociation of CH\textsubscript{4}. The generation of O and H further stimulates the fuel oxidization to release chemical enthalpy, resulting in the temperature increase. The increased temperature in the reaction zone caused an increase of reduced electric field because of the constant electrical field (E) and decreased gas number density (N). Therefore, the increased E/N accelerated the direct electron impact reactions, as shown in Fig. 6.8 (b), as the rate constants of direct electron impact reactions peaked also where the temperature peaked. The direct electron impact reactions further increased the heat release in the reaction zone. Therefore, it can be summarized that a positive feedback loop between the reaction zone and the discharge could be established by applying an *in situ* discharge to the system. Even though there was no flame, significant amounts (up to several thousand ppm level) of H\textsubscript{2}O, CO, CO\textsubscript{2} and H\textsubscript{2} were already formed in the reaction zone, which indicated the earlier heat extraction from the fuel by the plasma/combustion chemistry interaction.
Fig. 6.8 (a) Radicals and temperature profiles without flame $X_F = 0.16$, $X_O = 0.34$, $P = 72$ Torr, $f = 24$ kHz, $a = 400$ l/s (fuel side at 0 mm, oxidizer side at 16 mm) (b) Rate constants of selected reactions for (a)
In order to identify the important pathways of the radical generation and understand the kinetic processes in the plasma stimulated CH$_4$ oxidation mechanism, path flux analysis was performed; the details was shown in Fig. 6.9.

Fig. 6.9 Path flux analysis (a) CH$_4$ consumption pathways (red arrows: dominant reaction pathway) (a) OH and H formation pathways (b) reaction pathways of O, $X_F = 0.16$, $X_O = 0.34$, $P = 72$ Torr, $f = 24$ kHz, $a = 400$ l/s

Approximately 7.3% of the CH$_4$ was ionized, but the quick charge transfer process between CH$_4$(+) and O$_2$ canceled the effect of CH$_4$ ionization. CH$_4$ was predominantly dissociated to CH$_3$ by H abstraction through collision with OH, electrons, O and H. Approximately 24.5% of the CH$_3$ recombined to C$_2$H$_6$ due to the high concentration of CH$_3$ close to the fuel side. The major reaction path of CH$_3$ was the

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oxidation to CH$_2$O and finally to HCO, CO and CO$_2$. OH and H were predominantly generated through reactions between O and fuel/fuel-fragments. Therefore, it can be concluded that O was the initiation source of fuel oxidization and determined the population of the radical pool.

The dominant formation pathway of O was from direct electron impact of O$_2$, including reactions (R6.1) to (R6.3), and 57.9% of O was formed through these pathways:

$$\text{e} + \text{O}_2 = \text{O} + \text{O}(^{1}\text{D}) + \text{e} \quad \text{(R6.1)}$$

$$\text{e} + \text{O}_2 = 2\text{O} + \text{e} \quad \text{(R6.2)}$$

$$\text{e} + \text{O}_2 = \text{O} + \text{O}(+) + 2\text{e} \quad \text{(R6.3)}$$

Once O($^{1}\text{D}$) and O($+$) were produced, they were quenched and recombined with electrons quickly to produce O, respectively. Another two important formation pathways of O were from collisions between O$_2$ and He ions (He($+$)). Once O was formed, it reacted with CH$_4$ and its fragments to generate OH and H to further oxidize CH$_4$; only a small fraction of O recombined to form O$_3$ and O$_2$.

Since plasma was the source of radicals, the radical generation from the plasma could change the chain branching effects in the reaction zone. In order to demonstrate the change of branching effects in the reaction zone, the flux of radical generation was examined at constant $X_F = 0.16$ while varying $X_O$; the results are shown in Fig. 6.10. As the strongest radical generation reaction, reaction (R6.1) was chosen as the representative radical source from the plasma. Reaction (R6.1) generated O which reacted with CH$_4$ to generate CH$_3$ and OH through reaction (R6.4). Together with reaction (R6.5), the generation of CH$_3$ promoted reaction (R6.6) to generate H. The generation of H promoted the chain branching reaction (R6.7) to generate OH and O and feed back to build up the
radical pool.

\[
\begin{align*}
\text{CH}_4 + O &= \text{CH}_3 + \text{OH} \quad \text{(R6.4)} \\
\text{CH}_4 + \text{OH} &= \text{CH}_3 + \text{H}_2\text{O} \quad \text{(R6.5)} \\
\text{CH}_3 + O &= \text{CH}_2\text{O} + \text{H} \quad \text{(R6.6)} \\
H + O_2 &= \text{OH} + O \quad \text{(R6.7)}
\end{align*}
\]

Fig. 6.10 Relationship of branching effects and O$_2$ concentration on the oxidizer side with fixed CH$_4$ mole fraction at $X_F = 0.16$

It is shown in Fig. 6.10 that by increasing $X_O$, the chain branching reaction (R6.7) increased significantly, thus creating the larger radical pool population. Without plasma, the flame chemistry could not sustain the chain branching reaction below the crossover temperature for the flames, exhibiting hysteresis between ignition and extinction.
However, the plasma enabled the chain branching reaction to be sustainable even at low temperatures by the positive loop between fuel oxidation and regeneration of the radical pool. Thus, the strong radical pool significantly decreased the global activation energy for fuel oxidation at low temperatures. Finally, the excessive production of radicals from the plasma diminished the hysteresis between ignition and extinction.

6.5 Plasma-Assisted Low Temperature Chemistry on Ignition

As shown in Fig. 6.9, the oxidation path of CH₄ is relatively simple and does not contain any low temperature kinetics. In order to examine the effect of plasma on the low temperature chemical kinetics, dimethyl ether (DME) was employed as the fuel in the following study (detailed kinetic study of DME can be found in Chapter 7). By replacing CH₄ with DME and repeating the experiments, similar folded S-curves were observed by recording the OH PLIF. However, OH can only be used to characterize high temperature chemistry rather than low temperature chemistry. Therefore, CH₂O PLIF [108], [109] excited by photons at 355 nm from a Nd: YAG laser was used to characterize the effect of plasma on low temperature chemistry. The relationship between CH₂O PLIF and fuel mole fraction is shown in Fig. 6.11 and Fig. 6.12 at $f = 24$ kHz, $X_O = 0.4$ and $X_O = 0.6$, respectively. With the increase of the fuel mole fraction, the CH₂O PLIF increased indicating the increase of CH₂O concentration. If the DME concentration on the fuel side was larger than 9% at $X_O = 0.4$, ignition happened along with a sharp decrease of CH₂O PLIF signal intensity. Once ignition happened, further increase or decrease of DME mole fraction, the CH₂O PLIF signal didn’t change much. If the DME mole fraction was smaller than 7% at $X_O = 0.4$, extinction happened along with an increase of CH₂O PLIF signal intensity. Similar results can also be observed at $X_O = 0.6$ as shown in Fig. 6.12.
with ignition and extinction occurred at lower fuel mole fractions. By comparing the S-curves between CH$_4$ and DME, this raises two fundamental questions. First, what is the formation pathway of CH$_2$O? Second, at what condition the hysteresis between ignition and extinction can be removed for DME as the fuel?

Fig. 6.11 Relationship between CH$_2$O PLIF and fuel mole fraction $X_O = 0.4$, $P = 72$ Torr, $f = 24$ kHz, $a = 250$ 1/s (solid square symbols: increasing $X_F$, open square symbols: decreasing $X_F$)
Before ignition happened, there are two possible formation pathways for CH$_2$O. One is the decomposition of DME introduced by the electron impact as described by reactions (R6.8) and (R6.9). The other possible reaction pathway is from the low temperature chemical reaction chain as described by reactions (R6.10), (R6.11) and (R6.12).

\[
e + \text{CH}_3\text{OCH}_3 = e + \text{H} + \text{CH}_3\text{OCH}_2 \quad \text{(R6.8)}
\]

\[
\text{CH}_3\text{OCH}_2 = \text{CH}_3 + \text{CH}_2\text{O} \quad \text{(R6.9)}
\]

\[
\text{CH}_3\text{OCH}_2 + \text{O}_2 = \text{CH}_3\text{OCH}_2\text{O}_2 \quad \text{(R6.10)}
\]

\[
\text{CH}_3\text{OCH}_2\text{O}_2 = \text{CH}_2\text{OCH}_2\text{O}_2\text{H} \quad \text{(R6.11)}
\]
In order to examine the two possible formation pathways of CH$_2$O, experiments with fixed DME mole fraction while varying the O$_2$ mole fractions on the oxidizer side were performed and the result was shown in Fig. 6.13. Starting with no O$_2$ in the system, weak CH$_2$O PLIF signal was observed comparing with the background noise. However, by adding O$_2$ in the oxidizer stream, the CH$_2$O PLIF signal increased significantly. With the increase of O$_2$ mole fraction, the CH$_2$O PLIF signal also increased. From the result shown in Fig. 6.13, it can be concluded that the CH$_2$O formation was dominantly due to the reaction pathway involving reactions (R6.10), (R6.11), and (R6.12) which is sensitive to O$_2$ concentration. Therefore, the CH$_2$O formed before the ignition and after extinction was caused by the low temperature kinetics of DME. The ignition and extinction were the transition between the regimes where low temperature chemistry or high temperature chemistry controlled.

The difference between CH$_4$ and DME is that DME has strong low temperature kinetic whereas CH$_4$ does not. So with the increase of CH$_4$ mole fraction in the experiments as presented in Fig. 6.4 to 6.6, the increased radical production only enhanced the high temperature reaction pathway. Using DME as the fuel, there are two reaction pathways competing for the radicals produced from the plasma. Therefore, in order to achieve the smooth transition between ignition and extinction, the radical concentrations generated from the plasma must be high enough. So the reaction fluxes for the low temperature pathway and the high temperature pathway can be comparable at low temperature conditions. With an attempt to increase the productivity of radicals, the discharge frequency was increased to 34 kHz and the results were shown in Fig. 6.14. As
shown in Fig. 6.14, a monotonic S-curve without hysteresis between ignition and extinction was successfully achieved by increase the production of radicals. Therefore, a smooth transition between low temperature chemistry and high temperature chemistry was realized.

Fig. 6.13 Relationship between CH$_2$O PLIF and O$_2$ mole fraction with fixed 5% DME mole fraction, P = 72 Torr, f = 24 kHz, a = 250 l/s
Fig. 6.14 Relationship between CH₂O PLIF and fuel mole fraction $X_O = 0.6$, $P = 72$ Torr, $f = 34$ kHz, $a = 250$ $1/s$ (solid square symbols: increasing $X_F$, open square symbols: decreasing $X_F$)
Fig. 6.15 Homogeneous ignition calculation with DME/O₂/He (0.3%/10%/89.7%) at P = 72 Torr with and without 1000 ppm O addition at 650 K

It was believed that the low temperature chemistry was slow and not important for most practical applications. However, this study demonstrates that the low temperature chemistry can be extremely fast with the assistance of plasma. The dominate effect of the plasma on the low temperature chemistry is to provide radicals to initiate the reactions at low temperature conditions. In order to demonstrate this “radical addition” effect, homogeneous ignition calculations were conducted by SENKIN [110] with DME/O₂/He (0.3%/10%/89.7%) at P = 72 Torr, constant temperature at 650 K with and without 1000 ppm O addition. The results were shown in Fig. 6.15. Without the O addition, the low temperature chemistry was “slow” and the characteristic time was as long as 1 second. However, with 1000 ppm O addition, the formation of CH₂O occurred within 1 ms and 3
orders of magnitude change of characteristic time scales was observed. Therefore, due to the prompt radical generation from the plasma, the low temperature chemistry can be significantly accelerated and play an important role in practical combustion systems into which turbulent mixing may introduce additional radicals.

6.6 Conclusion

A novel well-defined plasma assisted combustion system with an *in situ* repetitive nano-second pulsed discharge integrated into counterflow flame has been developed by placing porous electrodes at the ends of the burner nozzles. Uniform discharge was generated between the two nozzles of the counterflow burner in CH₄/O₂/He diffusion flame. The new system provided an ideal platform to study the kinetic enhancement with the *in situ* discharge directly in the reaction zone so that the maximized kinetic enhancement effect by plasma could be observed at the increased reduced electrical field (E/N) in the reaction zone. The Rayleigh scattering temperature measurements have shown that the *in situ* discharge could dramatically reduce the CH₄ ignition temperatures as low as approximately 900 K. Unlike the conventional S-shaped ignition curve, a new stretched ignition to flame transition ignition curve was observed by measuring the excited OH* emission and OH concentration. At $X_0 = 0.34$ with fixed discharge frequency, a conventional S-curve with a clear hysteresis between the ignition and extinction limits was observed. However at higher oxygen concentration of $X_0 = 0.62$, a direct transition of ignition and extinction diagram without the hysteresis was observed. The transition from the conventional to the fully stretched S-curves revealed that the radical pool population produced by the plasma significantly changed the chemical kinetic pathways of fuel oxidation, thus modifying the characteristics of ignition and
extinction and the flame stabilization mechanisms. A kinetic model for plasma assisted methane/oxygen combustion has also been developed based on the assumption of constant electrical field strength. Numerical results demonstrate that O generation from the plasma was the dominant pathways to create the radical pool, such as H and OH. The path flux analysis revealed that the plasma and the subsequent interaction between plasma and combustion chemistries enabled the chain branching reaction to be sustainable even at low temperatures. The excessive production of radicals from the plasma decreased the global activation energy and removed the hysteresis of ignition and extinction. The results suggest that in situ repetitive non-equilibrium plasma assisted combustion can accelerate low temperature fuel oxidation at a high E/N ratio and can be potentially used to enhance ignition and combustion in high speed propulsion systems.

By employing DME as the fuel, CH₂O formation was used to characterize the low temperature chemistry in counterflow diffusion flames with in situ discharges. It was demonstrated that the radicals generated by the plasma can significantly accelerate the low temperature chemistry to form CH₂O. There was competition between low temperature reaction pathway and high temperature reaction pathway for the radicals produced from the plasma. With the increase of radical productivity, a direct transition of ignition and extinction diagram without the hysteresis was also observed. This observation generalizes the results in the study of CH₄ for larger hydrocarbon fuels which exhibit two stage ignition characteristics and promotes the importance of low temperature chemistry in practical application conditions.
Chapter 7

Measurements of H₂O₂ in Low Temperature Dimethyl Ether Oxidation

7.1 Introduction

Plasma-assisted combustion is a promising technology to improve the performance of combustion with different fuels in engines. In the study of Chapters 4 through 6, as one of the most studied fuel, CH₄ was employed as the fuel. However, CH₄ kinetics is different from other hydrocarbon fuels owing to its unique molecular structure. With the increasing concerns of energy sustainability and climate change, studies of oxygenated fuels for advanced engine applications have drawn great attention. A notable interest has been to improve the combustion performance of next generation fuels, such as biofuels. However, the understanding of biofuel kinetics is still very limited, especially in the low temperature regions. Therefore, before we investigate how plasma affects the combustion of biofuels, it is very important to understand the kinetics of biofuels first.

Dimethyl ether (DME), which can be synthesized from natural gas, coal, or biomass in large scale [111], has a great potential as a diesel fuel substitute for achieving lower carbon and particulate emissions [112], [113]. Moreover, DME is the simplest ether and exhibits two-stage kinetic behavior. It has become one of the most important research targets for understanding the impact of oxygenated fuels and two-stage kinetics on autoignition, flame dynamics, emissions, and turbulent combustion. Recent direct numerical simulations of DME/air stratified HCCI combustion have demonstrated that the heat release rate and scalar dissipation timescales are strongly affected by two stage kinetics and H₂O₂ addition.

In 2000, Fischer, Curran, and Dryer [114], [115] developed a comprehensive
model for DME low, intermediate, and high temperature oxidation that reproduced well the results of jet-stirred reactor [116–118], shock tube ignition delay [119], and flow reactor speciation [120] experiments. More recently, low and high pressure DME flame experiments have been conducted [121–124]. Detailed species profiles in low pressure flat flames and flame speeds at high pressure were measured. Large discrepancies in both atmospheric and high pressure flame speeds were also reported [117]. The recent flat flame experiments using both molecular-beam synchrotron photo-ionization and electron-ionization mass spectrometry provided more detailed distributions of intermediate species in low pressure flames (25 torr) and the results showed that predictions of some minor intermediates such as methanol are significantly different from the experimental results [120]. However, the flat flame experiments of DME were limited to high temperatures and low pressure conditions where low and intermediate temperature chemistry plays no role.

In high temperature oxidation in flames, DME oxidation and unimolecular decomposition are relatively well understood. Below 900 K and at higher pressures, the oxidation and decomposition kinetics of DME are very complex. Unfortunately, experimental data of intermediate species at elevated pressures are very scarce, hindering quantitative validation of low temperature kinetics. Recent shock tube experiments and ab initio dynamics simulations [125] showed that there is a roaming radical formation path in the thermal decomposition of dimethyl ether, which increases its low temperature reactivity. The rate coefficient for the CH₃OCH₃ + H reaction was also measured and a new rate expression was obtained with an evaluation of the experimental data from 273 to 1465 K.
It is well known that H$_2$O$_2$ plays a dominant role in the “hot ignition” transition from low temperature to intermediate temperature kinetic behavior. At low temperatures, H$_2$O$_2$ also acts as an indicator of H abstraction from fuel by HO$_2$ [126]. Thus, the production of H$_2$O$_2$ is an excellent indicator of the low temperature activity, especially at higher pressures. Furthermore, H$_2$O$_2$ formed during local flame extinction and present in exhaust gas recirculation can dramatically change kinetic behavior in turbulent reacting systems. Therefore, it is of a great importance to quantitatively measure H$_2$O$_2$ formation in low temperature combustion and to further validate kinetic mechanisms against such data. To date, many experiments have attempted to measure H$_2$O$_2$ directly by using UV and mid-infrared absorption techniques [127]. However, quantitative direct measurements of H$_2$O$_2$ in a reacting system remain extremely difficult due to the overlaps of absorption lines of H$_2$O$_2$ with other species in the UV and broadening of H$_2$O lines in the mid-infrared. Although molecular beam mass spectrometry [121] is a powerful tool for detecting H$_2$O$_2$, the concentration of H$_2$O$_2$ in low pressure flat flames is very low, and has not been well characterized in such experiments. As H$_2$O$_2$ is a much more significant intermediate at higher pressures, it is important to develop an alternative experimental method to quantitatively measure H$_2$O$_2$ (as well as other intermediate species). The low temperature and higher pressure oxidation of DME is an ideal system for investigating such possibilities and success can lead to significantly improved characterization of the two stage ignition behavior of DME.

The goals of this study are to develop a new experiment approach to investigate the low temperature chemistry of DME at atmospheric pressure using a flow reactor and a combination of Molecular Beam Mass Spectrometry (MBMS) and micro gas
chromatography (µGC). Firstly, the detection of H₂O₂ is investigated and a direct calibration is performed. MBMS quantification of several other species is then cross-validated by directly-calibrated µGC methods. Secondly, H₂O₂ and other intermediate species are measured in flow reactor experiments over a temperature range from 490-740 K at atmospheric pressure. The effect of CO₂ third-body effect on DME oxidation is also examined. Finally, the experimental results are compared with model predictions with recent update of the rate constant of CH₃OCH₃ + H. Path flux analyses are conducted and the mechanism uncertainties are examined and discussed.

The work contained in this chapter was published in the Proceeding of Combustion Institute [128]:


7.2 Experimental Methods and Kinetic Models

7.2.1 Molecular Beam Mass Spectrometry (MBMS) Systems and the Flow Reactor

The schematic of the experimental system is shown in Fig. 7.1 and details about the MBMS system can also be found in Chapter 3. For cross-validations, a micro Gas Chromatograph (µGC) system (INFICON 3000) is also used to measure O₂, CO and CO₂ by standard methods using calibrations based on accurate (+2%) gas mixture standards. The sample for µGC measurement was collected at the center of the reactor exit with a cooled stainless steel needle to quench the reactions. The results are compared in the following section with MBMS results.

A typical molecular beam mass spectrum of DME/O₂/He low temperature
oxidation is shown in Fig. 7.2. The spectrum is a function of nominal masses (mass/charges) and counts of ions. Because the cross sections of second ionization are orders of magnitude smaller than first ionization at the range of electron energy in the experiments, the electrical charge is generally one and secondary ionization need not be considered. As shown in Fig. 7.2, DME ions, O$_2$ ions, and He ions could be identified clearly together with other ions. Fragments of DME, for example, CH$_3$OCH$_2$, were also observed. However, the signal ratio between DME and the fragments was constant. Therefore, the noise generated by the fragmentation could be removed by post processing.

![Fig. 7.1 Schematic of MBMS experimental setup, part I and II: differential pumped chamber and ionization vacuum chamber, part III: Time-of-Flight mass spectrometer, part IV: flow reactor (the temperature profiles inside the reactor are shown as the insert) The reactor (part IV in Fig. 7.1) was a cylindrical quartz tube as discussed in Chapter 2. Sampling was conducted at the reactor exit, taking care to minimize heat loss and back diffusion. Measured temperature profiles (shown as the insert in Fig. 7.1) along]
the reactor were used for numerical modeling.

Fig. 7.2 Mass spectrum of DME/O₂/He (0.02/0.1/0.88) at T = 590 K and P = 1 atm

In this study, two different mixture compositions were investigated. The first case (Case 1) was DME/O₂/He (0.02/0.1/0.88) and the second case (Case 2) was DME/O₂/CO₂/He (0.02/0.1/0.2/0.68). In Case 2, CO₂ was used to study the sensitivity of low temperature DME oxidation to the third-body collisional efficiencies. For both cases, the flow residence time was fixed at 1.7 sec (at 1 atm). The temperature of the reactor was varied from 490-740 K while the mass flow rate was adjusted in order to maintain a constant residence time.

7.2.2 Kinetic Modeling

Two kinetic models for DME (Zhao et al.[120], Yasunaga et al. [129], [130]) were used in this study with an updated H + DME reaction rate coefficient [125]. Model
predictions were initially compared with each other using a zero-dimensional, isothermal flow reactor assumption and the experimentally measured temperature profiles. Zero-dimensional modeling results were obtained using SENKIN [81] and are reported alongside experimental data in Figs. 7.3-7.6. The reaction residence time of the calculations was set to 1.7 sec in agreement with experimental residence time assuming a plug flow. The difference between these two zero-dimensional modeling results is noted to be minimal.

Fig. 7.3 Major species measurements by GC and MBMS at different temperatures and numerical modeling for (a) O₂, (b) DME, (c) CO, (d) CO₂, case 1: DME/O₂/He (0.02/0.1/0.88), case 2: DME/O₂/CO₂/He (0.02/0.1/0.2/0.68), P = 1 atm, residence time = 1.7 s
Prompted by an interest to include insight into effects of the multidimensional flow field as well as the radial and axial diffusive transport on the experimental results, two-dimensional axisymmetric simulations of the reactor were also performed for Case 1, using the model of Zhao et al. [120]. The simulations solved the mass, momentum, and energy conservation equations assuming isothermal, non-reacting wall boundary conditions, and a uniform inlet velocity. The predictions for centerline parameters at the exit of the reactor are compared with the zero-dimensional results and experimental data in Figs. 7.3-7.6.

![Fig. 7.4 H₂O₂ measurement by MBMS at different temperatures and numerical modeling, case 1: DME/O₂/He (0.02/0.1/0.88), case 2: DME/O₂/CO₂/He (0.02/0.1/0.2/0.68), P = 1 atm, residence time = 1.7 s](image-url)
Fig. 7.5 H$_2$ measurement by MBMS at different temperatures and numerical modeling, case 1: DME/O$_2$/He (0.02/0.1/0.88), case 2: DME/O$_2$/CO$_2$/He (0.02/0.1/0.2/0.68), P = 1 atm, residence time = 1.7 s
Fig. 7.6 Measurements by MBMS at different temperatures and numerical modeling for
(a) CH$_2$O, (b) CH$_3$OCHO, case 1: DME/O$_2$/He (0.02/0.1/0.88), case 2: DME/O$_2$/CO$_2$/He
(0.02/0.1/0.2/0.68), P = 1 atm, residence time = 1.7 s

7.3 Results and Discussion

7.3.1 Experimental Species Quantification

Figure 7.3 shows the temperature-dependent species profiles measured from both
µGC (only for Case 1) and MBMS, together with the modeling results. Fig. 7.3 (a) and (b)
show that the concentrations of O$_2$ and DME first decrease and then increase with
increasing temperature, indicating the region of negative temperature coefficient behavior
characteristic of two-stage chemical kinetic behavior. For Case 1, the O$_2$ concentrations
measured by the µGC and the MBMS agree well, with peak reactivity appearing at ~590
K. Due to the ion mass overlap of DME and HCOOH (which was produced during fuel
oxidation), no DME measurements were quantified from the MBMS or are shown in Fig.
3(b). Figure 3(c) and 3(d) display the measured and predicted CO and CO$_2$ data as
function of reaction temperature. Again, good agreement between the µGC and MBMS
measurement for CO and CO$_2$ is observed. The present agreement for Case 1 µGC and
MBMS cross-validation experiments suggests MBMS quantification for species not included in the cross-validation should also be accurate end-to-end experimental measurements.

For Case 2, 20% CO\textsubscript{2} was employed as dilution gas instead of helium to examine third body collisional effects. Both models predict lower formation of CO for Case 2. The MBMS measurements also show lower CO formation compared to Case 1. Due to the extremely high concentration of CO\textsubscript{2} in case 2, CO\textsubscript{2} evolution from the reaction cannot be accurately quantified.

As one of the most important species for low and intermediate temperature chemistry, H\textsubscript{2}O\textsubscript{2} is quantified directly in a high (above vacuum) pressure system for the first time, as an oxidation product in the flow reactor for both Case 1 and Case 2. Consistent with Fig. 7.3, the H\textsubscript{2}O\textsubscript{2} measurements (in Fig. 7.4) show significant formation of H\textsubscript{2}O\textsubscript{2} at temperatures as low as 530 K. The H\textsubscript{2}O\textsubscript{2} concentration peaks at a reaction temperature of ~590 K for both cases. For Case 2 (20% CO\textsubscript{2} dilution), the concentration of H\textsubscript{2}O\textsubscript{2} is higher than for Case 1, likely due to the change of the overall collisional efficiency effects for H + O\textsubscript{2} (+ M) = HO\textsubscript{2} (+ M).

MBMS-quantified H\textsubscript{2} is shown in Fig. 7.5, while CH\textsubscript{2}O and CH\textsubscript{3}OCHO concentrations are reported in Fig. 7.6.

7.3.2 Modeling Results

As shown in Fig. 7.3 to Fig. 7.6, zero-dimensional simulation with the Zhao et al. model [120] shows reasonably good qualitative agreement with experiments about both the window and peak of low temperature reactivity, including agreement with measured H\textsubscript{2}O\textsubscript{2} concentrations. However, the Yasunaga et al. model [129], [130] shows higher
reactivity over a wider temperature region for most species considered. Significant deviations between both models and the experiment were observed for H$_2$/CO$_2$ and CH$_2$O concentrations above 625 K and below 625 K, respectively.

Comparison of the two-dimensional simulation results to the associated zero-dimensional predictions and the experimental results show that the two-dimensional nature of the reactor flow substantially affects observations at the axial exit of the reactor. Above 600 K, the predictions of species concentrations at the centerline are found to be in good agreement with experiment for O$_2$, DME, CO, H$_2$O$_2$, CH$_2$O, and CH$_3$OCHO, further reinforcing the importance of simulating the two-dimensional character of the experiment. Large deviations between the predictions and the experimental results still exist for H$_2$ and CO$_2$ at negative temperature coefficient conditions above ~625K, while deviations for CH$_2$O are evident below this temperature. These discrepancies may suggest missing mechanistic pathways or need for additional rate coefficient refinement to bring model into parity with experiment. It should further be noted that simulation of low temperature chemistry conditions (~525K-600K) requires additional rigor in specifying boundary conditions to account for the possibility of regions in which local axial gradient effects become significant. Moreover, the physical transition between the preheat region and the main body of the reactor was not considered in the current two-dimensional modeling.

7.3.3 Path Flux Analysis

To illuminate reasons for the H$_2$/CO$_2$ discrepancy between modeling and experiment, reactant flux analysis was performed at 680 K using the Zhao et al. model [120] under zero-dimensional modeling assumptions. At this temperature, two-
dimensional modeling suggests significantly reduced effects due to diffusion and flow field. This fact, coupled with the demonstrated convergence of two-dimensional and zero-dimensional concentration predictions (Fig. 7.3-7.6), and the objective here for describing general features of the reacting DME system, justifies the present zero-dimensional path analysis discussed below.

Fig. 7.7 Path flux analysis for (a) DME (b) H$_2$O$_2$, with DME/O$_2$/He = 0.02/0.1/0.88, T = 680 K, P = 1 atm, residence time = 1.7 s
The flux analysis is illustrated in Fig. 7.7 at 680 K for Case 1. The reaction of DME with O₂ to form CH₃OCH₂ and HO₂ initiates the reaction chain. However, as shown in Fig. 7.7 (a), DME mainly decomposes after the initiation reaction through H abstraction reactions by OH, H, and HO₂ to produce CH₃OCH₂. Hydroxyl radicals are found to be the dominant H abstracting species (82%) followed by H radicals (15%). The resulting CH₃OCH₂ radicals further react with O₂ to form CH₃OCH₂O₂. One consumption path of CH₃OCH₂O₂ (2.3%) produces CH₃OCH₂O and CH₃OCHO via disproportionation. Very small amounts of CH₃OCH₂O₂ (0.4%) produce CH₃OCH₂OH, though there are no destruction routes for CH₃OCH₂OH to smaller species in the current kinetic model. The major consumption path of CH₃OCH₂O₂ (97.3%) is isomerization to CH₂OCH₂O₂H. The CH₂OCH₂O₂H mainly decomposes (76.6%) to produce CH₂O. Another reaction path of CH₂OCH₂O₂H (23.4%) is through O₂ addition to form O₂CH₂OCH₂O₂H, followed by decomposition to HO₂CH₂OCHO, production of OCH₂OCHO and then HOCH₂OCO. HOCH₂OCO decomposes to CO and HOCH₂O. HOCH₂O decomposes to HCOOH which further oxidizes to CO and CO₂. The predicted dominant reaction path of DME is clearly controlled by isomerization and decomposition reactions of the CH₃OCH₂O₂ oxygen adduct at this temperature.

Significantly higher concentrations of CO₂ and H₂ were measured in the experiments than predicted by modeling. As shown in Fig. 7.7 (a), there are four major reaction pathways producing CO₂. Roughly 79% of the CO₂ produced is formed from CO oxidation, with the remainder coming from larger, doubly-oxygenated DME fragments. Since the oxidation kinetics for CO→CO₂ are well established, it appears these other non-CO production pathways for CO₂, involving decomposition of CH₃OCO,
HOCH₂OCO and HCOOH, may be responsible for under prediction of CO₂ by the model. Present kinetic model parameters for reactions involving these species may require revision, or perhaps additional pathways for non-CO generated CO₂ are missing from the kinetic model. Nearly all of the H₂ formation comes from H abstraction reactions from DME (54.8%) and CH₂O (37.1%), and consequently the rate coefficients of these two reactions are sensitive for the prediction of H₂ formation. Roughly 98% of H atom production comes from unimolecular decomposition of HOCH₂O. As in the case of CO₂, present model kinetic parameters along the DME, CH₂O, or HOCH₂O pathways, or missing pathways, may explain the differences observed between experiment and model prediction. Additional discrepancy noted earlier for CH₂O prediction is consistent with this observation.

During the oxidation of DME, significant amounts of H₂O₂ are formed. H₂O₂ is primarily formed (75%) through HO₂ + HO₂ → H₂O₂ + O₂, as shown in Fig. 7.7(b). HO₂ is primarily formed by O₂ + HCO and O₂ + H. Nearly 80% of the HO₂ formed is converted to H₂O₂, while only 11% is converted to an OH radical. As shown in Fig. 4, the model prediction of H₂O₂ concentration is slightly higher than experiments, suggesting higher concentrations of H and/or HCO predicted in the modeling. By replacing 20% He with 20% CO₂ as dilution (Case 2), the path flux analysis remains essentially unchanged. The model predicts lower formation of CO, and H₂ and higher production of H₂O₂ due to the change of third body efficiency for H + O₂ (+M) = HO₂ (+M) reaction. The experiments also showed that the production of CO and H₂ decreases. The Zhao et al. model [120] predicts very well the experimentally observed relative change in H₂O₂ concentration between Case 1 and Case 2.
7.4 Conclusion

The formation of H$_2$O$_2$ from the oxidation of DME at low temperature (490-750K) has been studied using a heated atmospheric pressure flow reactor with quantitative species determination by micro Gas Chromatograph (µGC) and Molecular Beam Mass Spectrometry (MBMS). Two conditions with DME/O$_2$/He/CO$_2$ at 0.02/0.1/0.88/0 and 0.02/0.1/0.68/0.2 have been investigated at a fixed flow residence time of 1.7 sec. As an important intermediate product of low and intermediate temperature chemistry, H$_2$O$_2$ was directly measured by the MBMS for the first time in a high (above vacuum) pressure reacting system together with O$_2$, CO, CO$_2$, H$_2$, CH$_2$O, and CH$_3$OCHO. Both zero-dimensional and two-dimensional simulations were conducted by employing two kinetic models, and their results compared with experiments. Comparison of two-dimensional and zero-dimensional modeling results suggests that the two-dimensional description of the experiments may be necessary to capture flow and diffusion physics at the conditions of this study.

The experimentally measured concentration of H$_2$O$_2$ was reasonably well predicted by the simulations. Moreover, comparisons of measurements of other species such as O$_2$, DME, CO, and CH$_3$OCHO with modeling results also demonstrate that the models predict reactivity of DME reasonably well at these conditions. Discrepancies in the experimental and modeled H$_2$, CO$_2$, and CH$_3$O profiles indicate some missing mechanistic features or need for improved rate coefficient determinations in the kinetic models. In any case, the quantitative measurements of H$_2$O$_2$ and other intermediate species provide important targets to further improve low temperature kinetic models of DME oxidation.
Path flux analysis was conducted at 680 K, to show that DME mainly reacts through H abstraction reactions with OH and H. The dominant reaction pathways of the resulting radicals involve isomerization and decomposition reactions of CH₃OCH₂O₂ and CH₂OCH₂O₂H that eventually yield CO and HOCH₂O. HOCH₂O further decomposes to HCOOH and followed by decomposition to CO and CO₂. CH₂O and CH₃OCHO are also noted as intermediate species leading to the formation of CO and CO₂. The experimentally measured CO₂ concentrations were higher than the model predictions above ~625 K. The decompositions of HOCH₂OCO and HCOOH, which were not related with CO formation but CO₂ formation, were responsible for the under prediction of CO₂. The H atom generation reactions and abstraction reactions for DME and CH₂O may also need to be revisited to improve the prediction of H₂ formation.
Chapter 8

A Multi-Generation Path Flux Analysis Method for the Reduction of Detailed Chemical Kinetic Mechanisms

8.1 Introduction

The kinetic mechanisms for plasma-assisted combustion are very complex and very challenging to be employed in modeling because they may include thousands of species and tens of thousands of reactions as discussed in Chapter 1. Unfortunately, even only for a combustion problem of large hydrocarbon fuels, the number of species and reactions involved is still huge as indicated in Fig. 8.1.

Fig. 8.1 Size of selected detailed and skeletal mechanisms for hydrocarbon fuels together with the approximate years when the mechanisms were complied (adapted from Lu et al. [131]).

Therefore, it is critical to have an effective mechanism reduction method to reduce the size of detailed kinetic mechanism. With such a huge detailed kinetic
mechanism, the employment of large detailed mechanisms in numerical simulation demands huge amount of CPU time. Although the available computational power is growing rapidly, a direct numerical simulation of turbulent combustion of hydrocarbon fuels with a detailed chemical kinetic mechanism at practical engine conditions remains challenging. Therefore, in order to make the numerical simulation of reactive flow computationally affordable and comprehensively accurate, the development of computational approaches for rigorous reduction of detailed mechanisms is essential.

Various mechanism reduction methods have been proposed to generate a reduced kinetic mechanism. The first approach is the sensitivity and rate analyses [132–134]. Although this method is very effective, it provides neither the timescales of different reaction groups nor the possible quasi-steady state (QSS) and partial equilibrium groups without good human experience. The second approach is the reaction Jacobian analysis which includes the Computational Singular Perturbation (CSP) method [135–137] and the Intrinsic Low Dimensional Manifold (ILDM) [138]. The CSP method obtains eigen-values and eigen-vectors of independent reaction modes, so that the fast and slow modes can be ranked by using the eigen-values. In the ILDM method, the low dimensional manifold is identified based on the decomposition of the Jacobian matrix of the chemical source term with the constraints of element and enthalpy conservations. Although these approaches can effectively identify the timescales of different reaction groups and the QSS species, it requires significant computation time to conduct Jacobian decomposition and mode projection and is significantly more complex to implement. To achieve efficient calculations of fast mode species, a third approach, the parameterization method, was proposed [139–142]. One example is the In-Situ Adaptive Tabulation (ISAT) [139].
The basic idea of ISAT is to integrate the chemical source term and store the information in a binary tree data structure as the simulation is being performed in-situ. ISAT is efficient if the flame structures are close to those created in the tabulated database. However, for non-premixed turbulent combustion involving a large kinetic mechanism with a broad temperature and concentration gradient distributions, time consumption in table buildup and the difficulties in data retrieval from a high dimensional table lookup lead to reduced advantage of ISAT in comparison to direct integration [143]. The fourth method is to use the reaction-rate or reaction path relations as a measure of the degree of interaction among species. The advantages of this kind of method are simple and fast, requiring minimal user interaction with the reduction process. Bendtsen et al. [144] adopts the reaction matrix with each of whose elements $P_{ij}$ defined as the net production rate of species $i$ from all reactions involving $j$ to establish a reduced reaction pathway (or mechanism). The set of important species is selected by going through the reaction matrix following the reaction path that connects one species to another that is most strongly coupled with it. The reduced mechanism is then completed by including a number of reactions such that for each of the selected species, a certain percentage of the total production or consumption rate (threshold value) of that species is kept in the reduced mechanism. Similar selection procedures are used in Directed Relation Graph (DRG) method [145], [146] and Directed Relation Graph method with Error Propagation (DRGEP) [147] by using the absolute and net reaction rates, respectively. However, the use of absolute reaction rates in DRG makes the relation index not conservative (the interaction coefficient or relation index is the ratio of species flux). DRGEP [147] employed the absolute net reaction flux to include error propagation across multi-
generations. However, for the indirect relations, DRGEP only pick up the strongest reaction path which cannot identify the species flux physically when the intermediate species are more than one in parallel. Moreover, another problem of DRGEP is that the definition of the interaction coefficient fails to identify the relation between the species that have both fast production and consumption rate, such as species having catalytic effect. A typical example is the NO\textsubscript{x} catalytic effect on ignition enhancement [60], in which NO\textsubscript{x} plays a role of catalyst and has a small net reaction rate but contributes significantly to the acceleration of ignition delay time. Another example is that a reaction path which has very long reaction chains with equal reaction rates. The definition of interaction coefficient of DRGEP may also be problematic [148]. In order to improve the accuracy of DRG and DRGEP method, a combination of DRG or DRGEP with species sensitivity was adopted [148], [149]. Unfortunately, the addition of sensitivity analysis is very computationally expensive. Furthermore, all the above methods are based on the analysis of one-generation direct flux/reaction rates. In order to improve the prediction of reaction fluxes, a multi-generation flux analysis including both consumption and production pathways are needed.

In this paper, we developed a Path Flux Analysis (PFA) method based on multi-generation fluxes to reduce the detailed chemical kinetic mechanism with improved model reduction accuracy compared to DRG method with the same size of a reduced mechanism. At first, the methodology of the PFA method is presented and analyzed. The method are tested by the simulations of ignition delay time of homogeneous mixtures, the extinction curves in a perfectly stirred reactor (PSR) and compared with the results of DRG and detailed mechanism. Then the reaction path analyses are conducted for n-
decane and methane ignition problem with the NOx catalytic effect to validate the method.
The accuracy of the present model is also demonstrated by comparing the steady and
unsteady flame propagation speeds and structures with those of DRG and the detailed
mechanism. Finally, the reduced mechanism is integrated with the Hybrid Multi-Time
Scale (HMTS) method for the modeling of the unsteady spherically propagating flames
of n-decane-air mixtures. A significant increase of computation efficiency is achieved.
The present method is an extension of the previous work of Ref.[144], DRG [145], [146]
and DRGEP [147].

The work contained in this chapter was published in Combustion and Flame [150]:

of detailed chemical kinetic mechanisms” 2010 Combustion and Flame, 157(7) 1298-
1307

8.2 Path Flux Analysis Method

The goal of mechanism reduction is to identify species which are important to the
target species. Therefore, it is crucial to define the importance index (interaction
coefficient) of each species in the mechanism. In the DRG method, the direct interaction
coefficient is defined as [145]:

\[
I_{AB}^{DRG} = \frac{\sum_{i=1}^{\text{species}} \left| v_{i,j} \delta_{i,j} \right|}{\sum_{i=1}^{\text{species}} \left| v_{i,j} \right|} \tag{8.1}
\]

\[
\delta_{i,j}^j = \begin{cases} 
1 & \text{if the } i \text{th elementary reaction involves species } B \\
0 & \text{otherwise}
\end{cases}
\]

\[
\omega_{i,j} = \omega_{f,i} - \omega_{b,i} \tag{8.2}
\]
where \( \nu_{A,i} \) is the stoichiometric coefficient of species \( A \) in the \( i^{th} \) reaction. \( \omega_{f,i} \), \( \omega_{b,i} \), and \( \omega_{i} \) are the forward, backward, and net reaction rate of the \( i^{th} \) reaction, respectively. \( I \) is the total number of elementary reactions. The magnitude of \( r_{AB}^{DRG} \) shows the dependence/importance of species \( B \) to species \( A \) \[145\].

To initiate the selection process, a set of pre-selected species (e.g. \( A \)) and a threshold value \( \varepsilon \) need to be specified. If \( r_{AB}^{DRG} < \varepsilon \), the relation between \( B \) and \( A \) is considered to be negligible. On the other hand, species \( B \) is selected when \( r_{AB}^{DRG} \geq \varepsilon \).

However, because the direct interaction coefficient is not conservative, one drawback of this method is that only the first generation (directed relation) of the pre-selected species is considered. In the point view of reaction flux, both the first generation and the second generation or the higher generations are important.

In this study, instead of using the absolute reaction rate, we use the production and consumption fluxes to identify the important reaction pathways. The production and consumption fluxes, \( P_A \) and \( C_A \), of species \( A \) can be calculated as following:

\[
P_A = \sum_{i=1}^{I} \max(\nu_{A,i} \omega_{f,i}, 0)
\]

\[
C_A = \sum_{i=1}^{I} \max(-\nu_{A,i} \omega_{b,i}, 0)
\]

And the flux of species \( A \) related with species \( B \) can be calculated as

\[
P_{AB} = \sum_{i=1}^{I} \max(\nu_{A,i} \omega_{f,i} \delta_{B}^{i}, 0)
\]

\[
C_{AB} = \sum_{i=1}^{I} \max(-\nu_{A,i} \omega_{b,i} \delta_{B}^{i}, 0)
\]

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Here $P_{AB}$ and $C_{AB}$ denote, respectively, the production and consumption rates of species $A$ due to the existence of species $B$.

In order to consider the conservative flux information, we introduce a different definition of the interaction coefficients, which contain the flux information for both the first and second generation. Note that although in the present studies, only two generation fluxes are considered, the method can be extended to any generations. Nevertheless, with the increase of the number of generations, the computation time is proportional to $(\text{species number})^{\text{generations}}$.

The interaction coefficients for production and consumption of species $A$ via $B$ of first generation are defined as:

$$r_{AB}^{\text{pro-1st}} = \frac{P_{AB}}{\max(P_A, C_A)}$$  \hspace{1cm} (8.7)

$$r_{AB}^{\text{con-1st}} = \frac{C_{AB}}{\max(P_A, C_A)}$$  \hspace{1cm} (8.8)

By using the production and consumption fluxes of the first generation, The interaction coefficients which are the measures of flux ratios between $A$ and $B$ via a third reactant ($M_i$) for the second generation are defined as:

$$r_{AB}^{\text{pro-2nd}} = \sum_{M_i} r_{AM_i}^{\text{pro-1st}} r_{M_iB}^{\text{pro-1st}}$$  \hspace{1cm} (8.9)

$$r_{AB}^{\text{con-2nd}} = \sum_{M_i} r_{AM_i}^{\text{con-1st}} r_{M_iB}^{\text{con-1st}}$$  \hspace{1cm} (8.10)

The summation here includes all possible reaction paths (fluxes) relating $A$ and $B$. 

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In theory, different threshold values can be set for different interaction coefficients. For simplicity, we can lump all the interaction coefficients together and set only one threshold value,

\[
r_{AB} = r_{AB}^{\text{pro-1st}} + r_{AB}^{\text{con-1st}} + r_{AB}^{\text{pro-2nd}} + r_{AB}^{\text{con-2nd}}
\]  

(8.11)

The coefficient defined above is used to evaluate the dependence/importance of species B to species A in the present study.

To demonstrate the strategy of the present model, a schematic of flux transfer between A and B via other reactants (\(M_i\)) is depicted in Fig. 8.2.

Suppose species A is a pre-selected reactant (the target), and \(M_1\) to \(M_8\) are the intermediate species which connect species A with products B, C, D, X and Y. For the sake of simplicity of analysis, one can assume no accumulation of the intermediate
species. The values on the arrows are the ratios of the flux of species $A$ to each product (i.e. the percentage of species $A$ changed to other species). Let us assume our goal is to select 5 or 6 species to construct a reduced mechanism from the above diagram. In order to do so, for the DRG method, the threshold value should be $\varepsilon = 0.205$ and species $M_5$ to $M_8$, $C$ and $D$ are the selected 6 species ($M_5$ and $M_6$ are selected first; and then from $M_5$ and $M_6$, $M_7$ and $M_8$ are selected; finally, from $M_7$ and $M_8$, $C$ and $D$ are selected). For the DRGEP method, the threshold value should be $\varepsilon = 0.146$ and the selected species are the same with DRG method (It should be noted that DRGEP does not do iteration during the selection process. The selection process for DRGEP is that $M_5$ and $M_6$ are selected through their direct relations with species $A$. Then $M_7$ and $M_8$ are selected through indirect relations via $M_5$ and $M_6$, respectively. Finally, $C$ and $D$ are selected via intermediate species $M_5$ and $M_7$, $M_6$ and $M_8$, respectively). For the PFA method, the threshold value should be $\varepsilon = 0.215$ and species $M_1$ to $M_4$, and $B$ are the selected 5 species (for simplicity, PFA only chooses 5 species here. First species $B$ is selected through the indirect relation via intermediate species $M_1$ to $M_4$ and then from $B$, the intermediate species are identified). Simple calculations can show that both DRG and DRGEP only capture 29.4% target flux, but PFA can capture 66.4% target flux. The above analysis is just one example. Similar results can be observed from many other cases and we will not list them in this paper. The important thing is that a reduction scheme which has more accurate representation of the species flux will lead to a better reduced mechanism.

In addition, from the demonstration in Fig. 8.2, it is also seen that the interaction coefficient defined in PFA is conservative (the interaction coefficient of two species is equal to the ratio of the flux between these two species). To give an example, let us pick
up one reaction path, $A-M_1-B$ and assume this is the only reaction path in the mechanism that is related with $A$ and $B$. Consider the following two possible cases, one is that only part of species $A$ are converted to $B$ through $M_1$ and the other is all species $A$ are converted to $B$ through $M_1$.

Case 1: at a specific time interval, 100 units of species $A$ change to $M_1$, and at the same time, 99 units of species $M_1$ are converted to $B$, and this is the only reaction path of species $M_1$. It is obvious that the flux from $A$ to $B$ is 99 units. We can calculate the flux ratio using our definition in Eq. 10 as the following.

$$r_{AB}^{\text{pro-2nd}} = \frac{C_{AM1}}{\max(P_A, C_A)} \times \frac{C_{M1B}}{\max(P_{M1}, C_{M1})} = \frac{100}{100} \times \frac{99}{100} = 99\%$$ (8.12)

Therefore, our flux definition also gives the same 99% flux of species $A$ changing to species $B$. This agreement implies that the definition of our present second generation interaction coefficient (flux ratio) is physically meaningful.

Case 2: at a specific time interval, 100 units of species $A$ change to $M_1$, and at the same time, 101 units of species $M_1$ change to $B$ and this is the only reaction path of species $M_1$. The overall reaction flux from $A$ to $B$ is 100 units. By using our definition in Eq.10, we can calculate the flux ratio as the following.

$$r_{AB}^{\text{pro-2nd}} = \frac{C_{AM1}}{\max(P_A, C_A)} \times \frac{C_{M1B}}{\max(P_{M1}, C_{M1})} = \frac{100}{100} \times \frac{101}{101} = 100\%$$ (8.13)

The predicted results are also in consistent with the real flux from species $A$ to species $B$. This above comparison also clarifies the physical meaning of the present definition of interaction coefficient (flux ratio). Therefore, in both Case 1 and Case 2, PFA gives correct indirect interaction coefficients between two correlating species.
Similar results can be obtained for other multi-reaction paths. Therefore, compared to DRG and DRGEP, the present PFA method is more accurate to reproduce the reaction path flux and to develop a reduced mechanism and reaction paths based on more rigorous flux analysis.

8.3 Results and Discussion

8.3.1 Generation of Reduced Mechanisms for Combustion of n-decane and n-heptane/air Mixtures

To evaluate the PFA method, ignition delay time, the extinction curves in a perfectly stirred reactor of n-decane and n-heptane-air mixtures are examined by using the high temperature n-decane mechanism with 121 species [151], [152] and the PRF (primary reference fuel) mechanism with 116 species [152]. Both PFA and DRG are used to generate reduced mechanisms at a similar size and compared with the detailed mechanisms. For n-decane, the reduced mechanisms generated by PFA and DRG have, respectively, 54 and 55 species (further reduction will reach the limit of the methods). For n-heptane, the reduced mechanisms generated by PFA and DRG both have 56 species. In the generation of reduced mechanisms, the pre-selected species in both PFA and DRG are n-decane or n-heptane, oxygen, and nitrogen. The ignition delay time of homogeneous mixtures and the extinction curves in a perfectly stirred reactor are computed, respectively, by using the reduced mechanisms generated from PFA and DRG.

For the ignition test, SENKIN [110] is used to calculate the homogeneous ignition delay time at constant pressures. The initial mixture equivalence ratios are 0.5, 1, and 2, pressures are 1 and 20 atmospheres, and temperatures are varied between 1200 and 1700 K. For all calculations, the ignition delay time is defined as the time when the
temperature increases 400 K from the initial temperature. For the PSR simulations, the inlet temperature is 500 K and the reactor pressures are changed from 1 to 20 atmospheres.

The ignition delay times and the PSR temperature dependence on flow residence time predicted by detailed mechanism and the reduced mechanisms for n-decane are compared in Fig. 8.3 and Fig. 8.4, respectively. It is clearly seen that with even a smaller number of species in the reduced mechanism generated by PFA, the results are much more accurate than that generated by DRG, particularly at lower temperatures and high pressures for ignition and lean and rich conditions for PSR. Similar results are also observed for n-heptane ignition and extinction. The ignition delay times for n-heptane are shown in Fig. 8.5. Again, the reduced mechanism generated by PFA reproduces accurately the ignition delay time and PSR temperature dependence from the detailed kinetic mechanism. However, the discrepancy of DRG increases at lower temperatures in a broad range of pressures.

To demonstrate that the improvement of PFA over DRG is not for a particular size of reduced mechanism, Fig. 8.6 shows the relations between the number of species in the reduced mechanisms of n-decane and the discrepancies of ignition delay time predicted by DRG and PFA methods at 1200 K, 1 and 20 atmospherics. It is seen that PFA improved the prediction accuracy significantly in a broad range of species numbers especially when the number of species in the reduced mechanism is less than 73. Therefore, the improvement of PFA in generating reduced mechanism is consistent with our flux analysis and is originated from the better prediction of species fluxes.
Fig. 8.3 Comparison of ignition delay times of lean, stoichiometric, and rich n-decane-air mixtures for various temperatures and pressures predicted by using reduced mechanisms generated by PFA and DRG as well as detailed mechanism.
Fig. 8.4 Comparison of PSR-simulations of lean, stoichiometric, and rich n-decane-air mixtures for various temperatures and pressures predicted by using reduced mechanisms generated by PFA and DRG as well as detailed mechanism.
Fig. 8.5 Comparison of ignition delay times of lean, stoichiometric, and rich n-heptane-air mixtures for various temperatures and pressures predicted by using reduced mechanisms generated by PFA and DRG as well as detailed mechanism.
Fig. 8.6 Ignition delay time comparisons of detailed and reduced mechanisms with different sizes of reduced mechanisms

8.3.2 Reaction Path Flux Analysis

The above ignition and PSR temperature dependence results showed that the reduced mechanism generated by PFA (with $\varepsilon = 0.47$) can reproduce the detailed mechanism much better than DRG (with $\varepsilon = 0.265$). In order to understand the difference in the accuracy of reduced mechanisms, it will be interesting to examine the impact of species selection on reaction path flux by DRG and PFA. In the two reduced mechanisms for n-decane, most of the species are the same, however, PFA selected some intermediate species such as $\text{C}_{10}\text{H}_{21}-2$, $\text{C}_{10}\text{H}_{21}-3$, $\text{C}_{10}\text{H}_{21}-4$, $\text{C}_{10}\text{H}_{21}-5$, $\text{C}_{4}\text{H}_{9}$, $\text{C}_{3}\text{H}_{6}$, but DRG chose species such as $\text{C}_{9}\text{H}_{19}-1$, $\text{C}_{9}\text{H}_{19}-5$. Are the species chosen by PFA more important? In
order to answer this question, the process where these species are selected should be examined. For example, in the homogeneous ignition problem, at $P = 1$ atm, $\tau = 4.67 \times 10^{-5}$ s, $T = 1197$ K, the reaction path of n-decane is shown in Fig. 8.7. The numbers on the arrows in Fig. 8.7 denote the ratios of flux of that species from Eq. 8.10. We can see that $C_{10}H_{22}$ was first converted to $C_{10}H_{21}-2$, $C_{10}H_{21}-3$, $C_{10}H_{21}-4$ and $C_{10}H_{21}-5$ through H abstraction reactions. Then, these species were changed to small species $C_{4}H_{9}$ and $C_{3}H_{7}$. Even though the flux to each species which is the product of $H$ abstraction reaction is not significant (that is why DRG fails to identify these intermediate species), simple calculations show that about 60% of the n-decane decomposes through these abstraction reactions and then decomposes to $C_{4}H_{9}$ and $C_{3}H_{7}$ via beta scission. Since PFA considers indirect reaction pathways, by starting from the fuel, $C_{4}H_{9}$ and $C_{3}H_{7}$ were selected and then the intermediate species ($C_{10}H_{21}-2$, $C_{10}H_{21}-3$, $C_{10}H_{21}-4$ and $C_{10}H_{21}-5$) were captured. As a result, at least 60% of the fuel flux was captured by PFA at that point. This real example also confirmed the schematic theoretical example which we presented in Fig. 8.2. Since the H abstraction reaction becomes more important at lower flame temperatures, the discrepancy between the reduced mechanism and the detailed mechanism will increase at lean and rich conditions without considering these reactions and their related species.
Another issue which we argued above is that an important property of a mechanism reduction model is to capture the catalytic species which have a relatively small net reaction path flux. For example, the two catalytic species (A and B) in the following two reactions with both large comparable reaction rates are important to the oxidation of M, but have small net reaction flux.

\[ A + M_1 \rightarrow C + B \]  \hfill (8.14)

\[ B + M_2 \rightarrow C + A \]  \hfill (8.15)

As a result, the concentrations of A and B don’t change significantly. A typical example of these reactions are the catalytic effect of NO/NO\(_2\) in the ignition of hydrocarbon fuels [60]. To make the analysis simple, one can assume A and B which form the catalytic cycle are only involved in reaction (Eq. 8.14) and (Eq. 8.15) which have almost the same reaction rate \(P_A = C_A\). Species \(M_1\) (and \(M_2\)) have very large
production rates \( P_{M,i} \) from other reactions. Under the definition of interaction coefficient of DRGEP [147] as described below:

\[
R_{AB} = \max_{\text{all paths}} r_{AB,p}
\]

Where \( p \) means different reaction paths, \( M_i, M_{i-1} \) are different intermediate species. The final interaction coefficient is \( R_{AB} \), the maximum value of the product of interaction coefficients for all possible reaction paths. Simple calculations can show that the direct interaction coefficient for \( A \) and \( B \) is zero.

\[
r_{AB}^{\text{DRGEP}} = \frac{|P_{AB} - C_{AB}|}{\max(P_A, C_A)} = 0
\]

The interaction coefficients for \( A \) and \( B \) through intermediate species \( C \) is also zero because \( r_{AC} \) is zero like \( r_{AB} \).

The interaction coefficients for \( A \) and \( B \) through intermediate species \( M_1 \) (or \( M_2 \)) is

\[
r_{AB,i} = r_{AM_i} \times r_{M_i,B} = \frac{C_{AM_i}}{\max(P_A, C_A)} \times \frac{C_{M_i,B}}{\max(P_{M_i}, C_{M_i})} = \frac{C_A}{C_A} \times \frac{C_{M_i,B}}{P_{M_i}} \approx 0
\]

It is obvious that the interaction coefficient between \( A \) and \( B \) given by DRGEP is nearly zero and the catalytic effect which is very important may not be identified. However, as shown below, by using the present production and consumption fluxes, the PFA method can capture this important path effectively.
As an example, PFA was applied on the ignition S-curve calculation of plasma assisted methane ignition (GRI-3.0 [153]) in Ref. [60] to identify the important reaction paths. The S-curve was shown in Fig. 9 in Ref. [60] and reproduced here as Fig. 8.8 (b). The temperature is 900 K. The reaction path analysis of the fuel at the highest temperature position between the two counterflow burners is shown as Fig. 8.8 (a). The catalytic effect of NO/NO2 can be easily captured. The direct interaction coefficient between NO and NO2 is about 0.99 and this means that the major reaction path for NO and NO2 are the catalytic reaction cycle. The addition of NO can change the reaction path significantly through reaction (Eq. 8.21)-(Eq. 8.24) to change the fairly inactive CH3O2 and HO2 to active radicals. PFA showed clearly that after the addition of NO, the dominant reaction path for CH3O2 is reaction (Eq. 8.21). The introduction of NO2 also added another reaction channel for CH3 and CH3 was oxidized to CH3O by reaction (Eq. 8.22).

\[
CH_3O_2 + NO \rightarrow CH_3O + NO_2 \tag{8.21}
\]
\[
CH_3 + NO_2 \rightarrow CH_3O + NO \tag{8.22}
\]
\[
HO_2 + NO \rightarrow OH + NO_2 \tag{8.23}
\]
\[
H + NO_2 \rightarrow OH + NO \tag{8.24}
\]

The reaction path of reaction (23)-(24) is not shown in Fig. 8.8, but PFA showed about 40%-50% NO (vary with positions) were consumed by reaction (23) which agrees well with the results in Ref. [60]. Note that DRG will capture the same species as PFA because GRI-3.0 is a small mechanism which does not have many parallel reaction pathways. However, the interaction coefficients of DRG do not provide any physical...
information of the species flux other than relation factor.

Fig. 8.8 (a) Ignition pathway of CH$_4$ at the highest temperature point, (b) $S$-curve response for 12% CH$_4$ in N$_2$ vs preheated air with 10,000 ppm NO as a function of maximum temperature and strain rate

8.3.3 Modeling of Steady and Unsteady Flame Propagations Using Reduced Mechanisms

To further verify the mechanism generated by PFA, the reduced mechanisms for n-decane and n-heptane are used to simulate the one-dimensional, quasi-steady freely propagating planar flames, and the unsteady outwardly propagating spherical flames via PREMIX [154] and A-SURF (an adaptive simulation of unsteady reactive flow code developed at Princeton University) [155], [156], respectively. The laminar flame speeds predicted by the detailed and reduced mechanisms are shown in Figs. 8.9 and 8.10. The initial temperature and pressure of the pre-mixtures are 500 K and 1 atm, respectively.
Fig. 8.9 The laminar flame speed as a function of equivalence ratio for n-decane/air mixtures at 500 K and 1 atm
Fig. 8.10 The laminar flame speed as a function of equivalence ratio for n-heptane/air mixtures at 500 K and 1 atm

It is seen that the prediction from reduced mechanisms generated by PFA and DRG agrees well with that from the detailed chemistry, although some small deviations exist on fuel rich side. The mechanisms generated by PFA also showed better predictions especially for fuel lean case. In order to see more detailed information of the prediction by reduced models, the temperature and species distributions are examined for stoichiometric n-decane and air mixture flame, as shown in Figs. 8.11 and 8.12.

We can see the distribution of temperature and the mole fractions of major species such as C_{10}H_{22}, O_2, CO, and CO_2 predicted by the reduced mechanisms are exactly the
same as that of the detailed mechanism. For intermediate species, Fig. 8.12 shows that the deviations of the species profiles for the reduced mechanism generated by DRG are larger than that of PFA for CH$_2$O, CH$_3$ and HO$_2$. This may explain the better reproduction of the flame speeds calculated by the mechanism generated by PFA.

Fig. 8.11 Temperature and major species profiles for a stoichiometric n-decane/air mixture at 500 $K$ and 1 $atm$
Fig. 8.12 Species profiles for a stoichiometric n-decane/air mixture at 500 K and 1 atm

In order to examine the effect of unsteadiness and diffusion transport of flame propagation on the validity of reduced kinetic mechanism, the reduced and detailed models are used to simulate unsteady outwardly propagating spherical flames for n-decane/air mixtures. If ignition is initiated by a hot spot in the center of the flame and the flame will propagate outwardly spherically. Figures 8.13 and 8.14 show the relations of spherical flame front location with time and the flame propagating speed with flame front location with different equivalence ratios. It is seen that the reduced mechanisms work extremely well for most of the cases and that the reduced model generated by PFA still works better than DRG. For the lean case (equivalence ratio = 0.7) where the mechanism generated by DRG has large deviations, the mechanism generated by PFA can still have a very good prediction of the detailed mechanism.
Fig. 8.13 Flame front location as a function of time for propagating spherical n-decane/air flames
8.3.4 Analysis of Error Propagation in PFA Method

From the aforementioned comparisons and applications we can see that the mechanisms generated by PFA can reproduce the results of detailed mechanisms successfully. It is also very important to examine the propagation of the errors introduced by the mechanism reduction. The errors will be introduced by removing the species and eliminating the reaction pathways in the detailed mechanism. In this section, the errors introduced by the mechanism reduction will be analyzed at different reduced mechanism sizes (different reduction levels).
The averaged error introduced by mechanism reduction of PFA method on the computation of ignition delay times as a function of threshold value are shown in Fig. 8.15. The computation was conducted for one atmosphere stoichiometric n-decane/air mixture from 1200 K to 1700 K. We can see in Fig. 8.15 that, with the increase of the threshold value of the PFA method (decreased number of species in the reduced mechanism), the averaged error increases. When the threshold value is larger than 0.65 (the number of species in the reduced mechanism is less than 43), a significant error will be introduced and the mechanism will fail to reproduce the ignition delay times. Similar phenomena were observed in the DRG method. When the threshold value is less than 0.2, the error introduced by the reduction is small (compared to the experimental uncertainty). However, when the threshold value is larger than 0.2 (the number of species in the reduced mechanism is less than 74), significant computation error is observed. A further examination of the reduced mechanism showed that, at this threshold several important species such as C\textsubscript{3}H\textsubscript{5}CHO, C\textsubscript{3}H\textsubscript{5}O were removed by the DRG method. Because numerical simulations are mainly limited by the number of species in the reduced mechanism, the corresponding number of species in the reduced mechanisms as a function of threshold value was also shown in Fig. 8.15. As the number of species in the reduced mechanism decreases, the introduced error in ignition delay time increases. With the same number of species in the reduced mechanism, the mechanism generated by PFA always has a better prediction accuracy than the one generated by DRG. As we see in Fig. 8.15, when the number of species was less than 74, the mechanism generated by DRG introduced a significant error (20%) indicating that some important species were removed. However, for the PFA method, the error remained to be small (compared to the
Experimental uncertainty) until the number of species was less than 43. Therefore, the PFA method has better prediction of the important pathways than the DRG method.

![Graph showing averaged error of ignition delay predicted by reduced mechanisms and the number of species in the reduced mechanism as a function of the threshold value for a stoichiometric n-decane/air mixture at 1 atm](image)

In order to demonstrate the accuracy of PFA to reproduce the reaction fluxes, PFA are compared with DRG at a comparable size of the reduced mechanism for the ignition delay time and an important path flux from n-decane to C_5H_11-1. The reduced mechanisms generated by PFA and DRG contained 54 and 55 species, respectively. Note that at this reduction level, the error of PFA in the prediction of the ignition delay time is about 10%, which is well below the uncertainty of the experimental data [152]. The evolution of temperatures and flux ratios of the fuel molecule, C_{10}H_{22} to one of its fragments, C_5H_11-1 calculated by the detailed mechanism, and the reduced mechanisms generated by PFA and DRG are shown in Fig. 8.16. We can see the predicted temperature
profiles are nearly identical for the detailed mechanism and the reduced mechanism generated by PFA, even though the flux ratios from C_{10}H_{22} to C_{5}H_{11}-1 are deviated up to 20% between detailed and reduced mechanisms. However, the mechanism generated by DRG method predicted large derivation in temperature history and the flux ratio. Similar results were also observed for other important pathways. Therefore, in limiting cases PFA has a better prediction of the important reaction fluxes than DRG.

![Graph showing temperatures and fuel decomposition flux ratios as a function of time in detailed and reduced mechanisms for a stoichiometric n-decane/air mixture at initial temperature 1200 K and 1 atm.](image)

Fig. 8.16 Temperatures and fuel decomposition flux ratios as a function of time in detailed and reduced mechanisms for a stoichiometric n-decane/air mixture at initial temperature 1200 K and 1 atm

One thing should be pointed out is that the PFA method is based on reaction path analysis. Target species which have weak chemical coupling (flux) to the pre-selected species may not be captured. One example is the NOx formation problem. PFA will remove NOx species because of the weak flux pathway from the oxidizer to NOx. However, this weakness can be fixed by choosing NO, NO2 or N2 as a pre-selected...
species when NO\textsubscript{x} formation is an important target.

Finally, the error introduced by the mechanism reduction is also examined in the computation of laminar flame speeds. Figure 8.17 shows the laminar flame speeds of stoichiometric n-decane/air mixture at 500 K and 1 atm as a function of different reduction levels. It is interesting that the errors introduced by mechanism reduction at different reduction levels are not monotonic with the number of species in the reduced mechanism. The errors remain small (within 4\%) for all reduced mechanisms with species number larger than 50.

![Figure 8.17](image)

**Fig. 8.17** The laminar flame speed and the error predicted by the reduced mechanism as a function of number of species in reduced mechanism for a stoichiometric n-decane/air mixture at 500 K and 1 atm

**8.3.5 Integration of PFA with Multi-Time Scale Method**

To further improve the computation efficiency, the reduced mechanism is integrated with a Hybrid Multi-Time Scale method (HMTS) [157]. By using the HMTS
method, the computation times of ignition delays of stoichiometric n-decane/air were approximately 10% of those by using the ODE solver [158], which is used in the CHEMKIN- SENKIN [24] package. More detailed comparisons can be found in Ref. [157]. In this paper, the simulation results of flame front location as a function of time for the propagating spherical stoichiometric n-decane/air flame are compared by using the ODE solver [158] and the HMTS method. It is clearly seen from Fig. 8.18 that the results computed by the ODE solver and the HMTS method agree very well. By integrating the reduced mechanism and HMTS method, a significant increase of computation efficiency is observed. The results suggest that the integration of the dynamic multi-timescale (MTS) model with the PFA mechanism reduction approach is promising to increase dramatically the computation efficiency in the direction numerical simulations involving large kinetic mechanisms.

Fig. 8.18 Flame front location as a function of time for propagating spherical n-decane/air flames by ODE and HMTS methods
8.3.6 Application of PFA on Large Scale Detailed Kinetic Mechanisms

The PFA method was used to reduce a detailed kinetic model for h-heptane with 1034 species [159]. A reduced model with 128 species was generated and compared with the detailed model. Figure 8.19 showed the comparison of ignition delays time for both detailed and reduced models. The reduced mechanism with 128 species is sufficiently comprehensive to reproduce both the ignition delay time at the negative temperature condition (NTC) region. This reduced model permitted and was employed in a modeling study of a homogeneously charged compression ignition HCCI engine [160].

![Graph showing comparison of ignition delay times for various temperatures and pressures predicted by using reduced mechanisms generated by PFA and detailed mechanism.](image)

Fig. 8.19 Comparison of ignition delay times of stoichiometric n-heptane-air mixtures for various temperatures and pressures predicted by using reduced mechanisms generated by PFA and detailed mechanism.
8.4 Conclusion

A multi-generation path flux analysis method to generate reduced mechanisms is presented and validated. The methodology extends the effectiveness of the existing DRG method and can identify the important multi-generation pathways and species in catalytic cycles. Different sized reduced mechanisms for n-decane and n-heptane ignition, extinction, and steady and unsteady flame propagation are generated and examined. Comparison between the present PFA method and the DRG method for ignition and flame propagation show that with the same or smaller sized reduced mechanisms, PFA has better accuracy than DRG to reproduce ignition and extinction of n-decane and n-heptane mixtures in a broad temperature and pressure range. The simulation of unsteady spherical flame initiation process demonstrates that the PFA generated reduced mechanism also work well for unsteady combustion processes involving non-equilibrium flame structures and diffusion transport. A further increase of computation efficiency is achieved by the integration of the PFA method and the multi-timescale method for the detailed modeling of n-decane and n-heptane flames.
Chapter 9
Summary and Recommendations

9.1 Summary

In this dissertation, the fundamental mechanisms of kinetic enhancement of plasma assisted combustion were investigated systematically and quantitatively by using advanced laser diagnostics and detailed kinetic modeling. A new \textit{in situ} plasma discharge integrated with a counterflow flame system was developed to enable observation of new flame regimes and ignition-extinction transitions in plasma-assisted combustion. A flow reactor integrated with a molecular beam mass spectrometry system was developed to detect intermediate species in low temperature fuel oxidation. A multi-generation path flux analysis method was developed to generate reduced kinetic mechanisms. Quantitative experimental data of ignition, extinction, and fuel oxidation were obtained and compared with numerical modeling to understand the plasma-combustion interactions. The research comprises of three major parts. The first part, detailed in Chapters 4 and 5, aimed to develop a well-defined experimental platform for plasma-assisted combustion by integrating a nano-second pulsed discharge with a counterflow burner to decouple the interaction between the plasma and flame. The second part, Chapter 6, was motivated by the work of Chapters 4 and 5, and aimed to investigate the coupled effects of the plasma and flame by integrating the well-known counterflow burner with the nano-second pulsed discharge. The third part, Chapters 7 and 8, aimed to developed new measurements and kinetic modeling methods to study the fundamental chemical kinetics of large fuel molecules and achieve increased computation efficiency with detailed chemical kinetic models.
In Chapter 4, it was found that for CH₄/O₂/Ar diffusion flames, a nano-second pulsed discharge in the oxidizer stream resulted in significant extension of flame extinction strain rates. The TALIF measurements showed that both the atomic O concentration produced by the plasma and the oxidizer stream temperature increased with the increase of the pulse repetition frequency for a constant peak plasma voltage. Moreover, the experimental results revealed that the plasma-activated oxidizer significantly magnified the reactivity of diffusion flames and resulted in an increase of extinction strain rates through the coupling between thermal and kinetic effects. Numerical computations showed that O quenching strongly depends on the oxidizer stream temperature. The kinetic effect of O production by a non-equilibrium plasma discharge on the enhancement of flame extinction limits was demonstrated, for the first time, at high repetition frequencies with elevated oxidizer temperatures. The reaction paths for radical production and consumption were analyzed. It was concluded that in order to achieve significant kinetic enhancement on flame stabilization by atomic O production, the plasma discharge temperature needs to be above the critical crossover temperature which defines the transition point from radical termination to radical chain-branching.

In Chapter 5, the effect of the plasma discharge on low temperature fuel oxidation and the extinction of partially premixed flames were investigated by blending 2% CH₄ into the oxidizer stream of a counterflow system. The experiments showed that non-equilibrium plasma can dramatically accelerate the CH₄ oxidation rate at low temperature. The rapid CH₄ oxidation via plasma-assisted combustion resulted in fast chemical heat release and extended the extinction limits significantly. Furthermore, experimental results
showed that partial fuel mixing in the oxidizer stream led to a dramatic decrease of O concentration due to its rapid consumption by CH₄ at low temperatures. The products of plasma assisted CH₄ oxidation were quantified by the TALIF, FTIR, and GC diagnostic techniques. The product concentrations were then used to validate the plasma-assisted combustion kinetic model. The comparisons showed the kinetic model over-predicted the CO, H₂O, and H₂ concentrations and under-predicted CO₂ concentration. A path flux analysis showed that O generated by the plasma was the critical species for extinction enhancement. In addition, the results showed that O was produced mainly by direct electron impact dissociation reactions and collisional dissociation reactions of electronically excited molecules with O₂.

Based on the work presented in Chapters 4 and 5, the idea of decoupling the interaction between plasma and flame significantly simplified the problem and isolated the effect of even single species produced by the discharge. However, it turns out that the lifetimes of reactive species generated by the plasma are too short to produce enough coupling between plasma chemistry and flame kinetics. Therefore, in Chapter 6, a novel in situ plasma discharge combustion system using a counterflow diffusion flame was developed to study the direct coupling kinetic effects of non-equilibrium plasma on flame ignition and extinction. A uniform discharge was generated between the burner nozzles by placing porous metal electrodes at the nozzle exits. The ignition and extinction characteristics of CH₄/O₂/He diffusion flames were investigated by measuring excited OH* and ground state OH by optical emission spectroscopy and OH PLIF, respectively, at constant strain rates and O₂ mole fractions on the oxidizer side while changing the fuel mole fraction. It was found that ignition and extinction occurred with an abrupt change of
OH* emission intensity at lower O2 mole fraction, indicating the existence of the conventional ignition-extinction S-curve. However, at a higher O2 mole fraction, it was found that the in situ discharge could significantly modify the characteristics of ignition and extinction and create a new monotonic and fully stretched ignition S-curve. The transition from the conventional S-curves to a new stretched ignition curve indicated clearly that the active species generated by the plasma could change the chemical kinetic pathways of fuel oxidation at low temperature, thus resulting in the transition of flame stabilization mechanism from extinction-controlled to ignition-controlled regimes. The temperature and OH radical distributions were measured experimentally by the Rayleigh scattering technique and PLIF technique, respectively, and were compared with modeling. The results showed that the local maximum temperature in the reaction zone, where ignition occurred, could be as low as 900 K. The chemical kinetic model for the plasma-flame interaction has been developed based on the assumption of constant electric field strength in the bulk plasma region. The reaction pathway analysis further revealed that atomic O generated by the discharge was critical to controlling radical production and promoting the chain branching effect in the reaction zone for low temperature ignition enhancement.

By replacing the CH4 with DME, similar results were observed. However, DME has strong low temperature chemistry, as do most large hydrocarbon fuels. So CH2O PLIF was employed to study the effect of plasma on the low temperature chemistry. It was observed that significant amounts of CH2O were produced before ignition and after extinction due to the low temperature reaction pathways. This was because the radicals generated from the plasma significantly accelerated the low temperature kinetics. Due to
the competition between low temperature reaction pathways and high temperature reaction pathways, higher productivity of reactive species in the plasma was required to stretch the S-curve to remove the hysteresis between ignition and extinction towards a new flame regime.

One feature of plasma-assisted combustion is to achieve fuel oxidation and energy conversion at low temperatures. In the studies described in Chapters 4 through 6, CH₄ was employed as the fuel due to its simplicity. However, CH₄ is not a practical transportation fuel and has no low temperature chemistry. For low temperature chemistry, one of the most important species is H₂O₂ which acts as a marker for low temperature kinetic activity. Therefore, it is very important to quantify the formation of H₂O₂ during the fuel oxidation process. The study presented in Chapter 7, reports for the first time, direct measurements of H₂O₂ in helium-diluted DME oxidation in an atmospheric pressure flow reactor, using a MBMS. The fuel used in this study, DME, is a candidate for the next generation of biofuels. This work provided a platform to study plasma-assisted biofuel energy conversion in the future. Also reported in this study is the measurement of other intermediate species concentrations in the temperature range of 490 to 750 K. The experimental results were compared to two different DME kinetic models, under both zero-dimensional and two-dimensional physical model assumptions. The results confirm that low and intermediate temperature DME oxidation produces significant amounts of H₂O₂. Peroxide, as well as O₂, DME, CO, and CH₂OCHO profiles are reasonably well predicted, though profile predictions for H₂/CO₂ and CH₂O are poor above and below ~625K, respectively. The effect of the collisional efficiencies for the H + O₂ + M = HO₂ + M reaction on DME oxidation was investigated by replacing 20% He
with 20% \( \text{CO}_2 \). Observed changes in measured \( \text{H}_2\text{O}_2 \) concentrations agree well with model predictions. The new experimental characterizations of important intermediate species including \( \text{H}_2\text{O}_2 \), \( \text{CH}_2\text{O} \), and \( \text{CH}_3\text{OCHO} \), and a path flux analysis of the oxidation pathways of DME support that kinetic parameters for decomposition reactions of \( \text{HOCH}_2\text{OCO} \) and \( \text{HCOOH} \) directly to \( \text{CO}_2 \) may be responsible for model under-prediction of \( \text{CO}_2 \). The H abstraction reactions for DME and/or \( \text{CH}_2\text{O} \) and the unimolecular decomposition of \( \text{HOCH}_2\text{O} \) merit further scrutiny towards improving the prediction of \( \text{H}_2 \) formation.

As discussed in Chapter 1, the detailed chemical kinetic models for large hydrocarbon fuels are often very large and contain huge numbers of species and reactions. The presence of plasma kinetics makes the kinetic models even more complex. The content of detailed chemical kinetic models is already beyond the capability of current computational facilities. Therefore, it is very important to develop effective and automatic mechanism reduction methods to reduce and simplify the detailed kinetic models so they can be used in numerical simulations. In Chapter 8, a direct Path Flux Analysis (PFA) method for kinetic mechanism reduction is proposed and validated by using ignition delay times, perfectly stirred reactors, and steady and unsteady flame propagation rates of \( \text{n-heptane} \) and \( \text{n-decane}/\text{air} \) mixtures. The formation and consumption fluxes of each species at multiple reaction path generations are analyzed and used to identify the important reaction pathways and the associated species. The formation and consumption path fluxes used in this method retain flux conservation information and are used to define the path indexes for the first and the second generation reaction paths related to a targeted species. Based on the indexes of each reaction path for
the first and second generations, different sized reduced chemical mechanisms which contain different numbers of species are generated. The reduced mechanisms of n-heptane and n-decane obtained by using the present method are compared to those generated by the direct relation graph (DRG) method. The reaction path analysis for n-decane is conducted to demonstrate the validity of the present method. The comparisons of the ignition delay times, flame propagation speeds, flame structures, and unsteady spherical flame propagation processes showed that with either the same or significantly less number of species, the reduced mechanisms generated by the present PFA method are more accurate than that of the DRG method in a broad range of initial pressures and temperatures.

9.2 Recommendations for Future Work

Based on the work presented in this dissertation, there are several areas where detailed experiments and numerical modeling can significantly improve our understanding about how plasma enhances combustion.

9.2.1 Effects of Other Plasma Produced Species

Plasma discharges can produce numerous types of species which are not present in conventional combustion systems. Current studies mainly focus on the effect of radical productions on combustion. These radicals include O, H and OH, all of which are very reactive and can enhance the fuel oxidation directly. However, the discharges also produce a great number of other reactive species, such as excited inert gas (N₂, He, and Ar). The excitation energies are quite high (above 5 eV for N₂, and 10 eV for Ar and He). As shown in Fig. 9.1, the excitation energy is much higher than the chemical bond energy of most hydrocarbon fuels. Hence, the excited species contain a significant amount of
energy, and are capable of dissociating a fuel molecule in a single collision. This phenomenon can lead to drastic changes in the transport and chemical properties of the combustible mixture. Currently, studies into the effect of excited species are very limited.

Fig. 9.1 Potential energy diagram

Electrons in the non-equilibrium discharge also contain high kinetic energies. The large mobility of electrons also results in high frequency of collisions between electrons and molecules. However, the kinetics of electron impact dissociation of most hydrocarbon molecules is poorly understood.

The discharge also produces NO\textsubscript{x} if the inert gas is N\textsubscript{2}. It must be realized that NO\textsubscript{x} is an air pollutant and may become a barrier to application of plasma-assisted combustion in engines.

In summary, the electrical discharge introduces new reaction pathways and these pathways have to be studied in detail for us to fully understand plasma-assisted
combustion. It is also necessary to know that, among the numerous new species, only a small amount of them will have a significant impact on the combustion process. It is necessary to develop numerical tools to reduce the modes and facilitate our investigations, such as the Path Flux Analysis method to simplify the detailed models.

9.2.2 Advanced Diagnostics

Many of the new reaction pathways are introduced by the reactive species produced by plasma. These species, such as the O atom, are usually associated with ultra short lifetimes. Quantitative detection of these species is critical to improving our understanding. Through the study of plasma-assisted combustion, laser diagnostics, such as LIF and TALIF techniques, show unsurpassed advantages as a non-intrusive, in situ, sensitive and fast response technique. As discussed in section 9.2.1, there are many other species produced by the plasma that need to be studied. In order to understand their effects on combustion, diagnostics to quantify these species is the key starting point to fully understanding plasma-assisted combustion kinetics. Advanced techniques, such as laser absorption spectroscopy, will be the new tools to advance our understanding. One example is the recent progress of quantification of HO₂ using Faraday Rotation Spectroscopy (FRS) with mid-IR lasers. The development of IR lasers brings new vitality to laser absorption spectroscopy and its application.

9.2.3 New Plasma Technology

As it is named, plasma-assisted combustion integrates plasma and combustion together. Unfortunately, the working conditions of these two technologies are not aligned with each other. In general, the non-equilibrium plasma favors working at low pressure conditions. Higher pressure will cause thermal instability and collisional thermalization.
However, combustion systems work at high pressure conditions for most of the time. Therefore, developing methods to generate stable, uniform non-equilibrium plasma under practical combustor conditions is a challenging question for fundamental researches. The fundamental question is whether one can sustain plasma at high pressures without uncontrollable discharge. It is necessary to point out that with the increase of pressure (particle number density), the energy density required for ionization and excitation increases too. This new type of plasma must also be generated with a reasonable energy budget compared to the power of combustion system. This is a huge challenge not only for the combustion society, but also for the plasma society.

Motivated by this desire, nano-second or even pico-second pulsed discharges were proposed to avoid the development of instability and reduce the energy consumption. To the author’s knowledge, the highest pressure reported to obtain uniform non-equilibrium plasma was 2 atm by Starikovskaia et al [39]. Another example of the development of plasma technology is Atmospheric Pressure Glow Discharge (APGD). In 2000, Park and co-workers [161] developed a new cold atmospheric pressure plasma source with radio frequency power. Since that, a significant amount of research has been conducted to explore this type of plasma source with different working gases, such as Ar, N₂, O₂ and air. More work to develop new plasma sources and control the properties of the plasma is expected in the future. With improved understanding of both plasmas and combustion, the success of tailoring the plasma system for combustion applications is promising.

9.2.4 Well-Defined Plasma-Assisted Combustion Experimental Platforms

Most of the studies of plasma-assisted combustion in the past have described
plasma as a “magic black box” which enhanced combustion significantly. In order to push forward this technology, quantitative results must be extracted from the experiments to advance our understanding about plasma-assisted combustion. Only in this way, new reaction pathways can be identified and investigated. Therefore, it is extremely important to design well-defined experimental platforms to produce quantitative data.

Based on this idea, the counterflow system was chosen as the experimental platform in this research because of the simple flame structure to decouple the hydrodynamic effect, good optical access and well-developed numerical models. Another example of a well-defined experimental platform is a shock tube with nano-second pulsed discharge [39]. Shock tubes have been widely used in the combustion society to investigate the chemical kinetics of different fuels. With the integration of advanced diagnostic techniques, such as laser absorption spectroscopy, this platform can play a very important role in the study of fundamental enhancement mechanisms of plasma on combustion.
References


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