J. Plasma Fusion Res. Vol.89, No.4 (2013) 208‐219

小特集 プラズマ支援燃焼の現状と展望

2. Nonequilibrium Plasma-Assisted Combustion: A Review of Recent Progress

SUN Wenting and JU Yiguang*
Department of Mechanical and Aerospace Engineering, Princeton University

（原稿受付：2013年２月19日）

Nonequilibrium plasma assisted combustion has drawn significant attention for its great potential to enhance combustion performance in pulsed detonation engines, gas turbines, scramjets, internal combustion engines, and other lean burn combustion systems. The physical and chemical kinetic processes in plasma assisted combustion involve strong coupling between combustion kinetics and the active radicals, excited species, ions/electrons, and other intermediate species produced specifically by the plasma. In recent years, extensive efforts have been made to develop new combustion techniques using non-equilibrium plasma, as well as new experimental platforms, advanced diagnostic methods, kinetic models, and quantitative experimental databases to understand the underlying interaction between the plasma and combustion mechanisms. This paper will provide a brief review of the recent progress in the studies of experimental phenomena, kinetic mechanisms, advanced diagnostic techniques, and modeling methods to quantify the elementary kinetic processes of plasma assisted combustion.

Keywords:
plasma assisted combustion, plasma combustion chemistry, combustion, advanced diagnostics

2.1 Introduction

2.1.1 Motivation and Overview

About 85% of the world's energy is generated from the combustion of fossil fuels [1]. In the past 30 years, the known reserves of oil and gases have increased by a factor of four owing to the improvements in exploration and extraction technologies [1]. Despite billions of dollars of investment in green energy technology over the last ten years, the production of green energy remains small due to characteristically low energy density and intermittency in service. In addition, the Fukushima nuclear accident makes the option of nuclear energy uncertain. Therefore, combustion will remain the major energy source for applications ranging from civilian life to national security for the foreseeable future. Unfortunately, combustion of fossil fuels not only depletes energy reserves quickly, but also generates huge amount of emissions of CO_2, NO_x, SO_x, and particulates, causing serious concerns of climate change and environmental pollution. As such, the increasing energy demand of the modern world and stringent regulations on combustion emissions pose a grand challenge for the combustion community to renovate conventional combustion technology in order to drastically improve energy conversion efficiency, fuel flexibility, and emissions. To achieve these goals, future advanced engines need to work at higher pressure, lower flame temperature, and leaner conditions, which are often close and even beyond the limit of normal flammability. For example, advanced high hydrogen content syngas turbine engines are required to increase efficiency by 5% to offset the energy cost of carbon capture and decrease NO_x emission to 3 ppm [2]. High altitude unmanned aerial vehicles (UAVs) requires small engines to operate at lean and low pressures, which is close to the flame propagation limit. Hypersonic propulsion systems, such as supersonic combustion ramjet (scramjet) engines [3], need to work in extreme combustion environments where the flow residence time in the combustor is even smaller than the auto-ignition time. At these extreme conditions, the completion of energy conversion in the engine and the extraction of full chemical energy for efficient thrust are strongly restricted. To address these challenges, it is necessary to develop new technologies to enhance and control the performance of the combustion process at near limit conditions. Fortunately, due to the fast ionization and electron impact dissociation processes of non-equilibrium plasma at low temperatures, plasma assisted combustion has become a promising technique to extend combustion limits and enhance combustion efficiency [4-8].

Although many previous studies have demonstrated the effectiveness of plasma to enhance combustion properties phenomenologically, the detailed enhancement mechanisms remain largely unknown. In recent years, extensive efforts have been made to develop new experimental plat-

author's address: Princeton University, Princeton, NJ, 08544, USA

**corresponding author's e-mail: yju@princeton.edu*

forms, advanced diagnostic methods, kinetic models, and quantitative experimental databases to understand the underlying interaction mechanisms between plasma and combustion. Among different approaches, the non-equilibrium plasma is of particular interest for plasma assisted combustion investigations owing to the high production of reactive species while the thermal effect can be minimized. Due to the page limit of this journal, the scope of this review only focuses on non-equilibrium plasma assisted combustion. In this paper, a review of only the recent contributions to the understanding of the fundamental enhancement mechanisms of non-equilibrium plasma assisted combustion is provided. Previous reviews which focused more on the plasma processes and kinetics can be found in [9, 10].

In the first section we will review the experimental observation of plasma assisted combustion in engines. In the second section, we will briefly discuss the major mechanisms of plasma assisted combustion. In the third section, we focus on the recent development of well-defined experimental platforms and the quantified results, including: 1) ignition enhancement through radical generation or catalytic effects, 2) extinction limit enhancement through thermal and kinetic effects via atomic oxygen generation, 3) improved flame stability due to radical production or fuel reforming, 4) flame speed enhancement due to excited oxygen and ozone production. In the same section, we will summarize recent advanced diagnostic techniques and the kinetic modeling of plasma assisted combustion. In the final section, some conclusions are drawn based on recent studies of plasma assisted combustion and a brief remark will be made for the prospects of future research.

2.1.2 Combustion Enhancement by Plasma in Engines

Over the last decade, the application of plasma to improve the performance of combustion has drawn considerable attention for its great potential to enhance combustion in internal combustion engines, gas turbines, pulsed detonation engines, scramjet engines, and lean burn combustion systems [4, 5, 9-16].

In spark ignition internal combustion engines, lean burn combustion is critical to reduce emissions and improve efficiency. Recently, through the collaboration between Princeton University and Imagineering, Inc. in Japan, plasma assisted spark plugs were investigated to improve the ignition performance in single cylinder internal combustion engines [17, 18] as shown in **Fig. 1** (a). The plasma assisted spark plug operates by channeling 2.45 GHz microwave from a commercial magnetron into a non-resistor spark plug. The two electrodes are used as the antenna. Once the spark is formed, the microwave can introduce plasma discharge by coupling the microwave energy into the electrons. It was found that the plasma assisted spark plug can introduce a larger flame kernel, which leads to an overall faster ignition/flame propagation event and thus advancement of peak pressure with about 750 mJ energy addition (150 mJ in standard capacitive spark plug). The experimental results showed that the lean burn limit was extended by 20-30% in terms of the air/fuel (A/F) ratio by using the microwave discharge, according to the coefficient of variation of the indicated mean effective pressure (COV_{imep}) (**Fig.1** (b)). More recently, ignition enhancement by nanosecond pulsed surface dielectric barrier discharge was also demonstrated in a rapid compression machine [19]. The results showed that with the presence of discharge, the ignition delays decreased significantly for methane and n-butane mixtures in the pressure range of 7.5 to 15 atm. Knocking reduction was also reported in knocking-sensitive regimes [19].

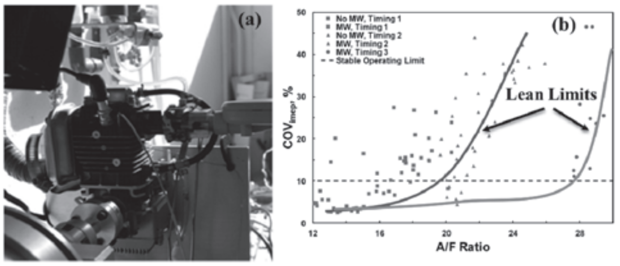

Fig. 1 (a) Direct photograph of plasma assisted 34 cc Fuji engine test setup and (b) the comparison of limits of stable engine operating conditions with and without microwave (MW) discharge [17].

Towards the development of advanced gas turbines, plasma is also used as a new technology to increase the efficiency, reduce the emissions, and improve the stability of flames in the combustion chamber. Serbin et al. [20] showed that a gas turbine combustor with piloted flame stabilization by non-equilibrium plasma can provide better performance, wider turndown ratios, and lower emissions of carbon and nitrogen oxides. Due to the interaction between the unsteady heat release from the flame and acoustics in the combustion chamber, combustion instability is another well-known issue for the design of gas turbines. Moeck *et al.* [21] studied the effect of nanosecond pulsed discharge on combustion instabilities. The authors coupled the discharge at the nozzle exit of a swirl-stabilized combustor and found that the discharges had a strong effect on the pressure pulsations associated with thermoacoustic dynamics. With the consumption of less than one percent of the total power of the flame, the nanosecond discharge can significantly reduce the oscillation amplitude of the acoustic pressure.

As an alternative to jet turbine engines, pulse detonation engines (PDE) have drawn worldwide attention [23]. PDEs utilize repetitive detonations to produce thrust and offer the advantages of less moving parts, higher efficiency, higher thrust, lower weight and cost, and easier scale-up. Despite extensive research in PDEs over the past several decades, it has not been used in practical applications with liquid hydrocarbon fuels. One of the key technical barriers is initiating the detonation wave rapidly and reliably in the engine. Recently, Lefkowitz et al. [22] studied the effect of high-frequency nanosecond pulsed discharges on PDEs as shown in **Fig. 2** (a). By comparing the ignition delay times as well as high-speed imaging of the ignition kernel growth with different igniters (igniter powered by nanosecond pulsed power and conventional multi-spark igniter), they found a significant decrease of the ignition time in the PDE for a variety of fuels and equivalence ratios (Φ). As demonstrated in **Fig. 2** (b), with the same amount of total energy input, higher frequency discharges showed dramatic benefits to initiate flame propagation. **Fig. 2** (c) showed the difference between the nanosecond pulsed plasma igniter and multiple spark discharge (MSD) igniter. With roughly the same amount of total energy consumption, the MSD ignition kernel eventually extinguishes, while the plasma ignited kernel goes on to become a self-propagating flame. In addition, both leaner and richer ignition could be achieved with the help of the nanosecond pulsed igniter. One possible reason of the decrease of the ignition delay is due to the increased energy deposition from the nanosecond pulsed power supply. But the plasma-chemical interaction in the discharge is still not clear.

The arc discharge, also known as plasma jet or plasma torch was also used to increase the temperature of the combustion gases while providing charged species at the same time. As a type of equilibrium plasma, the temperature of a plasma torch is very high, up to 10,000 K. Therefore, plasma torches are a very effective method for combustion enhancement. As one of the most effective methods, plasma jets were extensively studied to enhance combustion, especially combustion/ignition in supersonic combustion environments [12, 24-29]. Takita et al. [24] investigated ignition in a supersonic flow at Mach number about 2.3 using plasma jets (PJ) as igniters as shown in **Fig. 3**. It was found that the plasma jets can successfully ignite and stabilize the flames at supersonic flow conditions for different fuels. The authors also found that different feed stocks for plasma jets can lead to different effectiveness due to different products and elementary reactions. Nevertheless, the quantitative details of the kinetic mechanism of plasma assisted combustion remains not well understood.

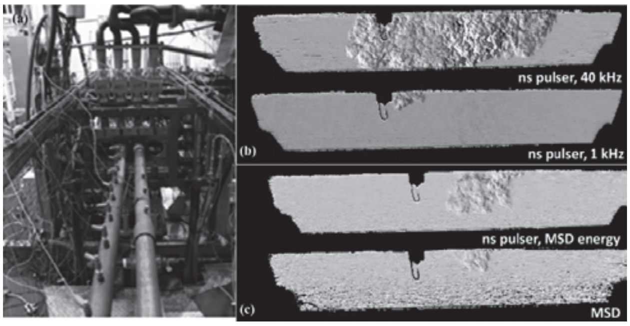

Fig. 2 (a) PDE engine facility at the Air Force Research Lab at Wright-Patterson Air Force Base, (b) Schlieren imaging of nanosecond pulsed discharge igniter in CH_4/air mixture, Φ =1, (c) Schlieren imaging of nanosecond pulsed discharge igniter in CH_4/air mixture, Φ =0.8 [22].

2.2 Mechanisms and Kinetic Processes in Plasma Assisted Combustion

2.2.1 Limiting Phenomena for Combustion — the Ignition and Extinction *S*-Curve

Fuel oxidization is dominated by the rate of the chemical kinetic process. Chemical kinetics is governed by the rates of many elementary reactions via the collisions of molecules and subsequent reactions. From the Arrhenius law [30], the overall rate constant of fuel oxidation can be defined as

$$k \cong Ae^{-E_a/RT} \qquad (1)$$

where E_a the activation energy accounting for the energy barrier required in the collisional process to reach the transition state and make the reaction go forward. T represents the temperature, A the pre-exponential factor that takes into account the translational, rotational, vibrational, and electronic excitation modes and their partition functions, and R the universal gas constant. Note that the Boltzmann factor $e^{-E_a/RT}$ represents the fraction of all collisions that have energy greater than E_a. The applicability of the Arrhenius law is restricted to thermal equilibrium systems.

The large activation energy makes the rate controlling reactions during fuel oxidation strongly temperature dependent. The rate controlling reactions are generally the ones which produce active radicals via a chain-branching process (e.g. $H + O_2 = OH + H$ with activation energy 17,041 cal/mole [31]). An increase of temperature will provide enough energy exchange during molecular collisions to overcome the large activation energy required to accelerate the chain-braining reactions. The onset of $H + O_2 = OH + H$ reaction in an atmospheric pressure combustion system is about 1100 K. As the pressure increases this critical temperature increases due to the strong competition with chain termination reactions at high pressure. Due to the strong dependence of the chain branching reactions on temperature in fuel oxidation (exponential factor in Eq. (1)), the ignition and extinction processes in a combustion system are often described by the classical *S*-curve [32] in **Fig. 4**. The *S*-curve

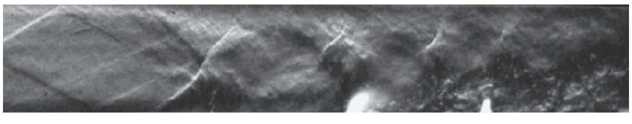

Fig. 3 Schlienren photograph of CH_4 combustion by twin PJs (H_2/N_2-O_2 PJs) [24].

indicates that as the system reactivity increases, the combustion heat release increases and the temperature of the reaction system increases (lower branching in **Fig.4**). At a certain point the temperature becomes high enough to reach the critical temperature of the chain branching reaction (e. g. $H + O_2 = OH + H$), and a self-accelerating ignition process will occur and drive the reaction system to the high temperature flame regime (top branching in **Fig.4**). On the other hand, for a reaction system in the high temperature flame regime, if the heat loss due to flow stretch becomes larger than the heat release, the flame temperature will decrease. When the heat loss becomes so large that there is not enough heat release to sustain the chain branching reactions, extinction occurs. The lean burn limit and the ignition limit in many practical engines are governed by the ignition and extinction limits of the *S*-curve.

To achieve combustion enhancement, the question is : how we can extend the ignition and extinction limits to lower flame temperature or heat release. As indicated by the dashed curve shown in **Fig. 4**, if one can enhance ignition so that the ignition limit becomes lower than the extinction limit, the extinction limit can be removed and combustion can happen at any conditions to realize the energy conversion. Fundamentally, this is equivalent to reducing the activation energy or increasing the temperature in Eq. (1) to remove the strong temperature dependence of the chain-branching process.

Therefore, in order to enhance the chemical kinetic process, the easiest way is to raise the translational temperature which is called "thermal enhancement". However, thermal enhancement is very costly because it has to increase the translational energy of all molecules in the system and excessive thermal heating can drive the chemical equilibrium toward the endothermic reaction direction and result in a decrease of heat release. Another way to enhance fuel oxidation is to reduce the activation energy. This method is called "kinetic enhancement" which has the potential to work more selectively and efficiently because only the rate limiting process is targeted. 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. Obviously, plasma which can produce active radicals and excited species can play a critical role in enhancing combustion both thermally and kinetically. As such, as indicated in **Fig. 4**, the technical questions are how the plasma discharge can modify the ignition and extinction *S*-curve and what are the mechanisms.

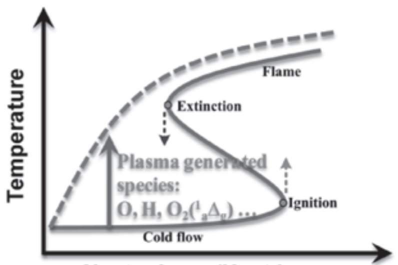

Fig. 4 Schematic of the classical ignition and extinction *S*-curve (solid line) and the stretched *S*-curve (dashed line).

2.2.2 Mechanisms of Plasma Assisted Combustion

Plasma has the potential to enhance combustion by being a source of heat, radicals, excited species, electrons/ions, fuel fragments, and perturbation of flow simultaneously. These many different enhancement pathways are coupled together to cause thermal enhancement, kinetic enhancement, and even transport enhancement via the ionic wind effect, as shown in **Fig. 5**. In addition, the plasma chemistry has very different characteristics compared to the combustion kinetics. As shown in **Fig. 6**, plasma chemistry happens in a time scale on the order of a few to several hundred nanoseconds and at low temperatures (from room temperatures and above). However, the combustion kinetics can only happen at high temperatures at a much longer time scale, from microseconds to milliseconds. If the reactions introduced by the plasma can play an important role in fuel oxidation, the combustion process can be accelerated significantly. The key process in plasma assisted combustion is the kinetic

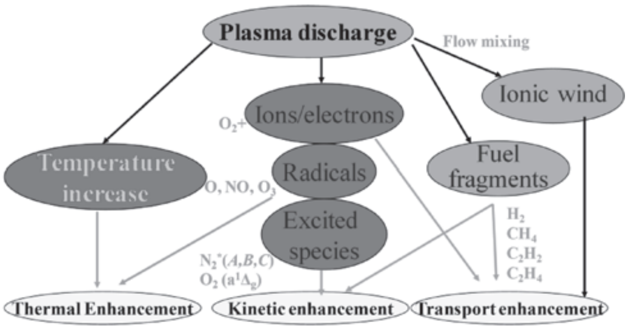

Fig. 5 Possible enhancement pathways of plasma on combustion systems.

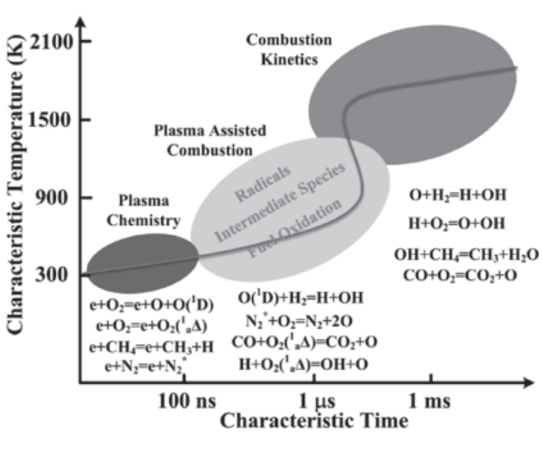

Fig. 6 Kinetic regimes and timescales of a typical plasma assisted combustion process.

coupling between plasma produced long lifetime species with fuel and oxygen at low temperature. As shown in **Fig.6**, this process bridges the fast plasma chemistry process and the high temperature combustion process. Understanding this coupling process is critical to developing an efficient method for plasma assisted combustion.

In order to elucidate the fundamental enhancement mechanisms of plasma assisted combustion at low temperature and near-limit conditions, well-defined experiments to isolate the interactions between different pathways shown in **Fig.5** are necessary [9]. Since both plasma and combustion are very complicated phenomena, an important thing is to minimize the uncertainty of the combustion in the experiment so that the effect of plasma on combustion could be extracted. Otherwise, the study can only be phenomenological.

Another important feature for a well-defined plasma assisted combustion experimental platform is simplicity for kinetic modeling. Since many species generated by the non-equilibrium plasma are not well known and difficult to be quantified, the detailed modeling of plasma assisted combustion is very important to improve our understanding and elucidate the underlying enhancement mechanisms.

2.3 Kinetic Studies of Plasma Assisted Combustion

2.3.1 Experimental Investigations of the Fundamental Mechanisms of Combustion Enhancement

2.3.1.1 Effects of Plasma on Ignition

With the development of plasma technology and laser diagnostics, significant progresses have been made in developing new techniques for plasma assisted combustion and in understanding the enhancement mechanisms of the plasma-combustion interaction. In the 1990s, a new type of plasma discharge known as "Fast Ionization Wave (FIW)" was proposed for non-equilibrium plasma assisted ignition [33]. The FIW was generated by nanosecond pulsed high voltage and could propagate on the nanosecond time scale. Therefore, it could activate the mixture almost instantaneously and uniformly since the characteristic time for ignition is orders of magnitude longer. This type of nanosecond pulsed discharge has three key features [33]: (1) high reduced electric fields (E/N) in the wave front, up to 1000 Td, provides uniform pre-ionization so that the discharge is uniform at relatively high pressure; (2) E/N ratio behind the front is hundreds of Td so that it guarantees high efficiency of the dissociation via excitation of electronic degrees of freedom; (3) the typical time for production of active species by FIW is much less than the typical time of ignition/combustion, which allows one to separate plasma and combustion problems in time/space coordinates.

Significant progress has been made since the emergence of nanosecond pulsed discharge. In 2001, the first work using nanosecond pulsed discharge to assist H_2 oxidation was reported [34]. A very important work by Bozhenkov *et al.* at 2003 was applying nanosecond pulsed discharge in a shock tube to study the plasma-combustion kinetics [35]. The discharge was capable of activating the premixture instantaneously after the reflected shock while not elevating the temperature. Therefore, the kinetic effect from the discharge can be extracted and evaluated. It was found that the nanosecond pulsed discharge can significantly decrease the ignition delay of H_2 and C_1 to C_5 alkanes [36-40]. Along with the experimental work, kinetic models were constructed and numerical simulations were also conducted and had shown that the radical concentrations increased, especially O and H atoms. It was pointed out that O production by plasma was the most effective to enhance ignition [7, 37]. Nevertheless, the experimental results through emission did not agree well with the simulations, and required more detailed kinetic studies. Time-resolved and *in situ* experimental measurements of the dominant radicals and intermediates in the plasma discharge are needed [7].

Another important contribution to advance the understanding of plasma discharges was the quantitative diagnostics of atomic O and OH production in the plasma discharge [8, 41, 42]. Different mixtures in a rectangular quartz reactor were activated by the discharge at different temperatures and pressures. The combustion efficiency with nanosecond pulsed discharge excitation on the flow was investigated and it was found that fuel oxidation occurred even without ignition and flame. The non-thermal fuel oxidation was triggered by plasma-generated radicals. They also conducted experiments at the same conditions by removing the O_2 in the premixture and they found the fuel (ethylene and methane) reduction was very limited. This study demonstrated that the direct electron impact dissociation of fuel in the plasma is a relatively minor effect compared to reactions with species generated in the plasma in the presence of oxygen, such as O and OH. If the discharge involves N_2, a significant amount of NO_x can also be formed. Uddi and co-workers [43] investigated the time production of NO in a nanosecond 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 the catalytic effect [44-46]. The effect of NO in the ignition study was still not investigated in detail in the above-mentioned ignition related works.

Another important work to understand the thermal and kinetic effects of plasma assisted ignition was conducted by Ombrello and co-workers [46, 47]. Different from previous work, the ignition enhancement was investigated in a counterflow burner. The counterflow burner was selected because the counterflow system provides several key benefits, namely minimal buoyancy effects, simplified flame geometry, the 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 advanced laser diagnostics for species and temperatures [48]. Non-equilibrium gliding arc discharge was integrated with the counterflow burner and used to activate the oxidizer side flow. The experiments were conducted at atmospheric pressure and air was 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_x generated from the gliding arc discharge was observed. In this study, NO_x was quantified by Fourier Transform Infrared Spectroscopy (FTIR) and the enhancement of NO_x on H_2/air and CH_4/air diffusion flame ignition was systematically investigated. The catalytic effect of NO_x on ignition in plasma assisted combustion was identified for the first time.

2.3.1.2 Effects of Plasma on Extinction

The effects of plasma on flame extinction were also investigated by the Princeton research group. Ombrello and coworkers studied the effect of gliding arc discharge on flame extinction in a counterflow system at atmospheric pressure [48]. Due to the fast recombination of radicals which were generated by the discharge on the oxidizer side and the rich radical pool produced by the flames, it was found that the effect of the plasma on flame extinction was predominately thermal [48]. Recently Sun *et al.* [49, 50] conducted research about plasma on flame extinction at low pressures (60 Torr) by coupling nanosecond pulsed discharge with the counterflow system as shown in **Fig. 7**.

It was found that the nanosecond pulsed discharge can produce a significant amount of atomic O by activating the O_2/Ar flow on the oxidizer side. The absolute number density of atomic O was measured by Two Photon Laser Induced Fluorescence (TALIF) method [49-52] and then used as a boundary conditions in the numerical modeling [49]. The extinction strain rate measurement together with numerical modeling showed that for CH_4/O_2/Ar diffusion flame, with the increase of discharge frequency on the oxidizer side, the extinction strain rates can be extended significantly. By comparing the extinction strain rates with plasma activation and just heated flow, the thermal effect can be isolated. The results showed that even though the discharge can generate a significant amount of atomic O, most of the atomic O was quenched before reaching the reaction zone at low temperature conditions. More detailed analysis showed that if the oxidizer temperature was higher than a crossover temperature, which was about 900 to 1000 K at low pressure, approximately 80% of the atomic O can be transported to the reaction zone to enhance the flame. Therefore, in order to observe the kinetic enhancement from plasma on flame, the oxidizer temperature must be higher than the crossover temperature to avoid quenching.

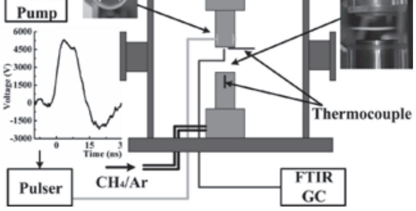

Fig. 7 Schematic of experimental setup [50].

One way to avoid quenching of the radicals is to add fuel into the oxidizer stream. Following this idea, Sun and coworkers [50] blended 2% CH_4 into the oxidizer side flow and activated by the plasma. In this way, the reactive species generated by the plasma reacted with the fuel rather than recombining or quenching. After activation by the plasma, the CH_4 added into the oxidizer flow was oxidized. The concentrations of the products and atomic O were measured by FTIR, Gas Chromatography (GC) and TALIF, respectively. The FTIR and GC measurements showed that with the increase of the discharge repetition frequency, the CH_4 oxidation ratio increased significantly and the production of CO, CO_2, H_2, and H_2O also increased together with the increase of the flow temperature at the nozzle exit. The experimental measurements were also compared with numerical modeling. It was concluded that the modeling deviated significantly from the experiments majorly due to the invalidity of combustion kinetic mechanism at low temperature conditions (below 700 K) and unknown plasma reaction pathways. The path flux analysis revealed that O production by the plasma is the major source to initiate the low temperature CH_4 oxidation. Once O is generated by the discharge, it is consumed rapidly by CH_4 and its intermediate oxidized and dissociated products. Only a small amount of O recombines to O_2. The extinction strain rate measurements showed that with the increase of discharge frequency (CH_4 oxidation ratio), the extinction strain rates were extended significantly. 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.

The study in Ref. [49, 50] demonstrated the effect of plasma-produced species on flame extinction. The experiments successfully isolated the interaction between plasma and flame. However, the missing of the coupling effect minimized the effect of the plasma on the flame due to the short lifetime of reactive species. Thus, the dominant effect of plasma on the reaction zone was not free from thermal enhancement effects. Therefore, it is very important 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, Sun and coworkers [6] subsequently developed a novel well-defined counterflow flame system with an *in situ* discharge using porous electrodes as show in **Fig. 8**. In this way, uniform discharge can be generated between two burners as shown in the embedded picture in **Fig. 8**. The pulse repetition frequency (f) was fixed at 24 kHz, corresponding to an input power of 17.5 W (0.73 mJ/pulse). The pressure was held constant at 72 Torr for all of the experiments.

The ignition and extinction characteristics were studied by measuring the OH* emission intensity in the reaction zone since ignition or extinction happens with an abrupt change of the OH* emission. During the experiments, the strain rate (400 1/s), 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. The relationship between OH* emission intensity as well as reaction zone peak temperature and X_F is shown in **Fig. 9** with (a) X_O = 0.34 and (b) 0.62. The temperatures of the reaction zone were measured by the Rayleigh scattering method. The solid and open symbols 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 in **Fig. 9** (a). Further increase of X_F caused an abrupt increase of OH* emission intensity. 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 which is the fundamental phenomena of ignition and extinction. The local maximum temperature measurement (reaction zone temperature) showed that the value just before ignition was only 897 ± 50 K. With further increasing X_F, ignition occurred and the local maximum temperature increased to approximately 1310 ± 80 K.

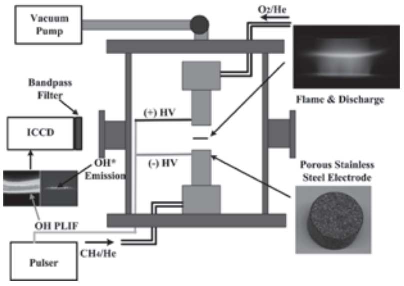

Fig. 8 Schematic of experimental setup integrating counterflow system with *in situ* discharge.

If X_O was increased to 0.62, the ignition and extinction limits (**Fig.4**) merged at X_F =0.09, resulting in a monotonic ignition and extinction S-curve **Fig. 9** (b). The temperature measurements also demonstrated a similar monotonic increase of the local maximum temperatures. The monotonic and fully stretched ignition and extinction 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.

In order to further understand the underlying mechanisms, numerical simulations were conducted at a condition prior to ignition with X_F = 0.16 and X_O = 0.34. The results of path flux analysis showed that CH_4 was predominantly dissociated to CH_3 by H abstraction through collision with OH, electrons, O and H. The major reaction path of CH_3 was the oxidization to CH_2O and finally to HCO, CO and CO_2. OH and H were predominantly generated through reactions be-

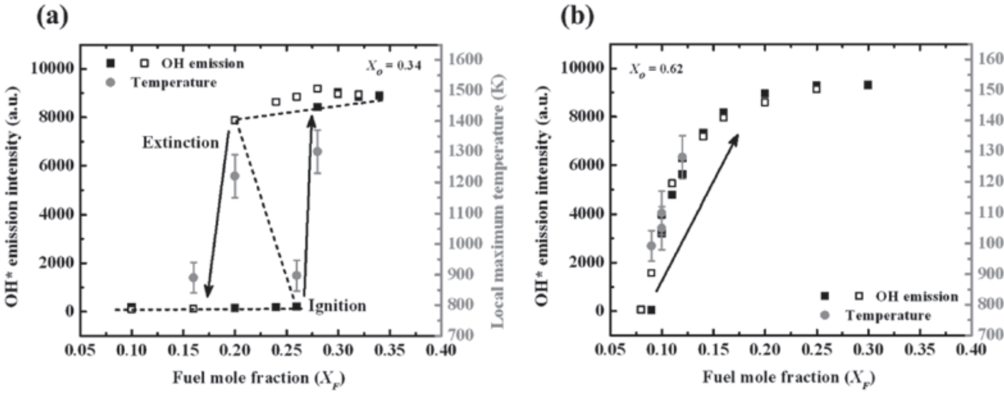

Fig. 9 Relationship between OH* emission intensity, local maximum temperature and fuel mole fraction, f = 24 kHz, a = 400 1/s, (a) X_O = 0.34, (b) X_O = 0.62, (solid square symbols: increasing X_F, open square symbols: decreasing X_F).

tween 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 formation in this experiment was from direct electron impact of O_2, including reactions R1 to R3:

$$e + O_2 = O + O(^1D) + e \tag{R1}$$
$$e + O_2 = 2O + e \tag{R2}$$
$$e + O_2 = O + O(+) + 2e \tag{R3}$$

Once O (^{1}D) and O(+) were produced, they were quickly quenched or recombined with electrons, respectively, to produce O. 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 is the source of radicals, the radical generation from the plasma can change the chain branching effects in the reaction zone. Reaction R1 generated O which reacted with CH_4 to generate CH_3 and OH through reaction R4. Together with reaction R5, the generation of CH_3 promoted reaction R6 to generate H. The generation of H promoted the chain branching reaction R7 to generate OH and O and feed back to build up the radical pool.

$$CH_4 + O = CH_3 + OH \tag{R4}$$
$$CH_4 + OH = CH_3 + H_2O \tag{R5}$$
$$CH_3 + O = CH_2O + H \tag{R6}$$
$$H + O_2 = OH + O \tag{R7}$$

A global reaction can be obtained by adding the above reactions together,

$$e + 2O_2 + 2CH_4 = e + CH_3 + CH_2O + H_2O + OH + O \tag{R8}$$

One can see clearly from the above global reaction that one high energy electron can lead to three radicals and other intermediate species at low temperature.

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 (**Fig. 4**). 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 (R8). The dominant radical formation path was controlled by plasma, rather than the $H + O_2 = OH + O$ reaction. 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.

2.3.1.3 Effects of Plasma on Flame Propagation: effect of O_3 and $O_2(a^1\Delta_g)$

Ombrello and his co-workers developed a lifted flame experimental platform which allowed investigation of the effect of species with long lifetimes generated by the discharge on flame propagation [5, 14, 53]. 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 the lifted flame system in which the flame lift height was very sensitive to flame speed. Therefore, the plasma enhancement effect on flame speed can be clearly identified without a significant amount of energy input. Ozone (O_3) was generated by a dielectric barrier discharge (DBD) cell and measured quantitatively by absorption spectroscopy. Then it was transported to the $C_3H_8/O_2/N_2$ lifted flame. The experiments at atmospheric pressures showed an 8% enhancement in flame speed for 1260 ppm of O_3 addition to the oxidizer [14]. More challenging work [5] was conducted to study the effect of excited O_2 ($O_2(a^1\Delta_g)$) which has an electronic excitation 0.98 eV. $O_2(a^1\Delta_g)$ has a mean radiative lifetime of 2700 s [54] therefore there is the possibility to isolate and transport $O_2(a^1\Delta_g)$ to the flame. The most challenging part of that work was the isolation and the quantification of $O_2(a^1\Delta_g)$. In that study, $O_2(a^1\Delta_g)$ was produced in a microwave discharge and isolated from O and O_3 by NO addition to the plasma afterglow in a flow residence time on the order of 1 s. The concentrations of $O_2(a^1\Delta_g)$ was measured quantitatively through off-axis integrated cavity output spectroscopy [55]. It was found that $O_2(a^1\Delta_g)$ changed the flame liftoff height of C_2H_4 flames. The authors also conducted numerical simulations to investigate the pathways of enhancement. They employed currently published collisional and reactive quenching reactions [56, 57] 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. This work provided an important experimental platform to validate the kinetic mechanisms involving $O_2(a^1\Delta_g)$. More recent modeling work about $O_2(a^1\Delta_g)$ can be found in Ref. [58, 59] and will be discussed later.

2.3.1.4 Effects of Plasma on Flame Stabilization

Employing a coaxial pulsed nanosecond barrier discharge, the C_3H_8/air flame blow-off velocity at atmospheric pressure was investigated by Mintoussov *et al.* [60]. The nanosecond pulsed discharge was applied at the nozzle exit [60]. 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. They found that the principle enhancement mechanism was the change of the initial mixture composition, which resulted in the onset of additional chain reactions in the pre-flame zone. They also concluded that atomic O generated by the discharge played the dominate role to increase the flame propagation velocity.

The stability of turbulent C_3H_8/air flame was studied by Pilla, *et al.* [4]. The nanosecond discharge was applied in the recirculation zone behind the bluff body of the turbulent premixed flame. The plasma can extend the OH spontaneous emission region widely. They found the discharge can significantly improve the stability and efficiency of the flame due to radical generation, such as O, H and OH. Flame stabilization with plasma was experimentally obtained with a low level of plasma power which was only approximately 0.3% of the maximum power of the flame [4]. A very recent work on the same setup revealed that the discharge can significant reduce the lift-off height of the flame due to the generation of radicals from the discharge [61]. The key radical was OH since the life time of atomic O was too short (~25 μs) therefore can't be transported to the reaction zone to enhance the flame. A similar experiment was conducted by Kim et al [62] for CH_4/air premixed flame. Gas chromatography measurements showed that the discharge can reform CH_4 into H_2 and CO. The concentration of H_2 can be up to several hundred ppm level. They concluded that the reforming of CH_4 to produce H_2 and CO played a central role in enhancing flame stability. The authors further investigated the role of H_2 and CO in enhancing the flame stability by conducting experiments with H_2/air mixture. In contrast to CH_4/air case, no significant reduction was seen in the blowout limit for the H_2/air flame. Therefore, they concluded that the radical generation from the discharge did not lead to the enhancement however the CH_4 reformation did.

2.3.1.5 Advanced Diagnostics for Plasma Assisted Combustion

In order to study plasma-assisted combustion and develop the corresponding kinetic models, advanced diagnostics tools are critical to gauge the system. The plasma produces significant amounts of reactive species such as atomic O which affect the combustion dramatically. In order to understand how these plasma produced species affect combustion, advanced diagnostics must be employed and developed to investigate the complicated plasma-assisted combustion systems.

Progress was made in 2009 by Uddi et al. [51] by measuring the absolute atomic O concentration in nanosecond pulsed discharges using the Two Photon Laser Induced Fluorescence (TALIF) technique [49-52]. Ground state atomic O is excited by absorbing two photons at a wavelength of 225.7 nm. The transition between the excited 3p ^{3}P state and the 3s ^{3}S state will release a single photon at 844.6 nm. A similar excitation process exists for Xenon. Xenon can be excited from 5p^6 $^1S_0$ 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. 10**. 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}) [63],

$$N_0 = \frac{S_0}{S_{Xe}} g_{ND} \frac{a_{21}(Xe)}{a_{21}(O)} \left(\frac{\sigma^{(2)}(Xe)}{\sigma^{(2)}(O)}\right) \left(\frac{v_O}{v_{Xe}}\right)^2 \times \frac{1}{F_0(T)} N_{Xe} \tag{2}$$

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, ν_i the photon energies, and g_{ND} the neutral density filter factor. In this way, ground state atomic O can be quantified.

Uddi *et al.* [51] found that the discharge can generate significant amounts of atomic O and the consumption of atomic O was much faster in fuel/air mixtures than in pure air, as shown in **Fig. 11**. So the rapid reaction between fuel and atomic O initiated the combustion and chemical heat release. This technique significantly advanced our understanding about plasma assisted combustion at the elementary reaction level.

It is well accepted that atomic O generation by the plasma has a huge impact on the combustion process. The generation of atomic O includes two major channels. One is

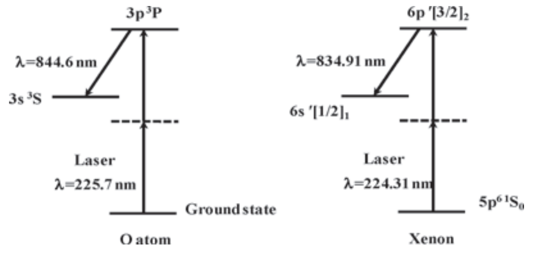

Fig. 10 Schematic of atomic O and Xenon atom energy levels with two photon absorption excitation and fluorescence schematic [64].

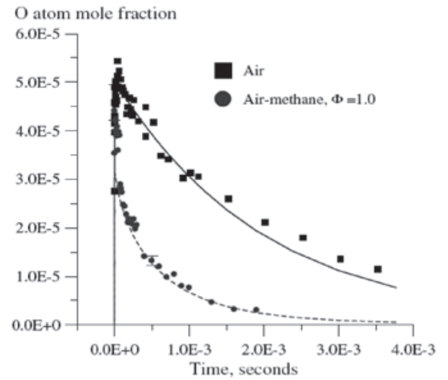

Fig. 11 Atomic O mole fraction vs. time after a single high-voltage pulse in air and in a methane-air mixture at P = 60 torr and Φ = 1.0 [51].

the direct electron impact by collision with electrons. The other one is through collision with excited N_2 (known as $N_2(A)$, $N_2(B)$ and $N_2(C)$) if N_2 is the dilution gas [51, 65]. Significant effort has been made to quantify and study the kinetics of excited N_2. The absolute number density of $N_2(A)$ was measured by Cavity Ring Down Spectroscopy (CRDS) and the densities of $N_2(B)$ and $N_2(C)$ were measured by Optical Emission Spectroscopy (OES) in a nanosecond pulsed discharge at atmospheric pressure in air [65]. A fast two-step mechanism was proposed for atomic O generation [65]:

$$N_2(X) + e = N_2(A,B,C) + e \qquad \text{(R9)}$$

$$N_2(A,B,C) + O_2 = N_2(X) + 2O \qquad \text{(R10)}$$

The electronically excited $N_2(A,B,C)$ are formed by electron impact excitation during a high voltage pulse. Next, they dissociate O_2 via exothermic dissociative quenching reactions, thus producing atomic O and heat release.

Due to the presence of strong electric fields and very short time scales, the temperature measurement in plasma assisted combustion research is a very challenging topic. Zuzeek *et al.* [66] conducted rotational coherent anti-Stokes Raman scattering (CARS) thermometry measurements in a quartz reactor activated by nanosecond pulsed discharge to obtain the time-resolved rotational temperature and O_2 mole fraction. It was found that at low temperature conditions, the heat release was primarily due to the reactions between fuel and O or O and H generated by plasma for C_2H_4/air and H_2/air mixture, respectively.

The detection of excited species can be accomplished through absorption spectroscopy. In the work conducted by Ombrello *et al.* [5], Integrated Cavity Output Spectroscopy (ICOS) [55] was adopted to obtain the absolute concentrations of excited O_2 ($O_2(^1_a\Delta_g)$) by measure the (1,0) band of the $^1_b\Sigma_g^+ - {}^1_a\Delta_g$ Noxon system. The system measured the average number density of $O_2(^1_a\Delta_g)$ across an 82.5 cm long absorption cell. The effective path length was greater than 78 km due to the multiple passes and provided accurate measurements down to 10^{14} molecules/cm^3. Several thousand ppm of $O_2(^1_a\Delta_g)$ produced by a microwave discharge was reported and its effect on flame propagation was then investigated. Mid-IR absorption spectroscopy together with wavelength modulation technique was employed by the Princeton group to study fuel oxidation in a nanosecond pulsed discharge. Recently, Uddi *et al.* [67] developed a mid-infrared miniature Herriott cell with multiple laser passes to conduct *in situ* measurements of temperature and multi-species in a reactor integrated with a nanosecond pulsed discharge. The simultaneous measurements of CH_4, H_2O, C_2H_2 and temperature were successfully carried out with high sensitivity to a few ppm and several Kelvin. This *in situ* diagnostics is a promising technique to understand and develop the kinetic mechanism of plasma assisted combustion.

2.3.2 Development of Kinetic Mechanisms for Plasma Assisted Combustion

Modeling of plasma or combustion problems has been widely investigated and is not to be discussed here. The purpose of this section is to discuss the effort to model plasma assisted combustion. The major challenge of modeling plasma assisted combustion is the lack of detailed kinetic mechanisms. A first step in this attempt is to combine the plasma kinetic mechanisms with combustion kinetic mechanisms and also include the known interactions between plasma generated species and species contained in the combustion kinetic mechanism.

Adamovich *et al.* [15] developed a kinetic model by combining an air plasma model [68] with a hydrocarbon oxidation mechanism (GRI Mech 3.0 [69] or USC Mech II [31]) to model CH_4/air and C_2H_4/air plasmas. The kinetic model supplemented CH_4, C_2H_4, and C_2H_2 dissociation reactions by electron impact and in collisions with electronically excited N_2. The rate coefficients of electron impact ionization, dissociation and electronic excitation are calculated by Boltzmann equation solver using electron impact cross sections which also calculates the electron energy distribution function (EEDF). Similar plasma assisted combustion kinetic models containing H_2, CH_4 to C_5H_{12} were developed by Aleksandrov *et al.* [39] and Starikovskaia *et al.* [34]. Since no reliable cross section data are available for C_3H_8, C_4H_{10} and C_5H_{12}, the authors assumed that these cross sections are similar to those for C_2H_6. Among those kinetic models, the H_2/air plasma model [34] is a detailed state-to-state kinetic model including 750 chemical and 8700 vibrational exchange processes with the participation of 254 species. To the authors' knowledge, the most updated electron impact cross section data can be found in references for O_2 [70], N_2 [71], H_2 [72], CO [73], CO_2 [74], H_2O [75], and simple hydrocarbon molecules (CH_4, C_2H_6, C_2H_4, C_2H_2, C_3H_8, C_3H_6 [76], and n-C_4H_{10} [77] only for ionization).

Uddi *et al.* [51] showed that the kinetic model predictions were in good overall agreement with the experimental data for TALIF O measurements. However, for the fuel oxidation products, different combustion kinetic models had very different predictions and differed by almost one order of magnitude. Since the same set of plasma reactions and rates were used in both cases, the difference between the two kinetic models were from the difference between the reactions and rates used by GRI Mech 3.0 [69] and USC Mech II [31]. As pointed out by Sun *et al.* [50], fuel oxidation kinetic mechanisms are usually not validated at low temperature conditions, so large uncertainties exist at low temperature conditions. In addition, experimental data are scarce to be compared with numerical modeling. It can also be concluded that there are still large amount of missing reaction pathways in the kinetic models, such as electron impact reactions of different fuels, the reactions between excited species and fuel /fuel fragments. The modeling also experiences large gradients of temperature and species concentrations which will affect the EEDF therefore the rate constants of electron impact reactions. Nevertheless, the numerical modeling still provides valuable information to advance our understanding about plasma assisted combustion though large uncertainty exits.

2.4 Conclusions and Prospects

It has been demonstrated that non-equilibrium plasma is a promising technology to enhance the performance of combustion at low temperature, ultra-lean, and high speed flow conditions. Different kinetic enhancement mechanisms were proposed including the effect of ion chemistry, the chemistry of excited species, and the additional production of atoms and radicals [40]. The effect of radical production (such as O, H) from the plasma discharge on ignition and combustion has been widely recognized. Advanced laser diagnostic techniques have also been developed and applied to investigate the production of radicals from the discharge. These techniques significantly improved our understanding. However, the diagnostics are still very challenging for plasma assisted combustion research owing to the large uncertainty and very limited number of species of the measurements. *In situ* quantification of important intermediate species produced during the discharge and combustion process is very critical. Beyond the effect of radical addition, the effect of ion and excited species chemistry is still largely unknown. One example is the excited O_2 ($O_2(^1_a\Delta_g)$). There are many recent efforts to model the effect of $O_2(^1_a\Delta_g)$ on the combustion system [58, 78, 79]. But due to the unknown reaction pathways and rate constants of $O_2(^1_a\Delta_g)$ with hydrocarbons, especially the quenching effect, large uncertainties remain for the models and conclusions. Those species can introduce new unknown reaction pathways into the combustion system and their effects are difficult to quantify. In addition, the electron impacts on hydrocarbons are largely unknown except for some simple molecules. So a challenging target in further fundamental studies is how to isolate the plasma kinetics, which has extremely short time scales as compared with the conventional combustion kinetics. Therefore, different effects can be investigated.

One important feature of plasma assisted combustion is that combustion can be sustained at low temperature conditions where it cannot exist in conventional combustion systems. Since most combustion kinetic mechanisms are not validated at low temperature conditions (below 700 K), the uncertainty of the combustion kinetic mechanisms in this temperature range is very large and difficult to estimate. The development of reliable combustion kinetic mechanisms requires a large amount of data at those conditions which can be easily modeled. With the fundamental understanding of the enhancement mechanisms of plasma on combustion, the plasma itself can be further optimized and tailored to facilitate different applications.

Practical combustion systems always experience a broad range of pressures. The typical working conditions for plasma and combustion systems are not aligned with each other. Most of the research about plasma assisted combustion has been conducted at low pressures (below 1 atm). With the increase of pressure, the instability of plasma discharge starts to develop and will cause a non-uniform structure of the discharge. A reliable high pressure plasma technology is very important towards the application of this technology in practical systems.

Despite the remaining many challenges and unknowns, recent work has demonstrated the principal enhancement mechanisms of plasma assisted combustion. It can be concluded that plasma is a promising technology to enhance ignition and combustion and can be used in novel aerospace application, designing innovative engines and energy conversion systems and enhancing the combustion properties of different fuels.

Acknowledgments

This work was supported by the MURI research grant from the Air Force Office of Scientific Research and the grant FA9550-07-1-0136. The authors would like to acknowledge Mr. Joseph Lefkowitz from Princeton University and Dr. Timothy Ombrello from Air Force Research Lab for helpful discussions.

References

[1] S. Chu and A. Majumdar, Nature **488**, 294 (2012).

[2] R. Schonewald, "DOE Advanced IGCC/Hydrogen Gas Turbine Program at General Electric", 2012 University Turbine Systems Research Workshop, Irvine, CA.

[3] C. Goyne, "Global Hypersonic Program Activities United States of America X-51 Program Activities", AIAA HyTASP Program Committee Inaugural Newsletter (2008).

[4] G. Pilla *et al.*, IEEE Trans. Plasma Sci. **34**, 2471 (2006).

[5] T. Ombrello *et al.*, Combustion and Flame **157**, 1916 (2010).

[6] W. Sun *et al.*, Proc. Combustion Institute **34**, 847 (2013).

[7] I. Kosarev *et al.*, Combustion and Flame **154**, 569 (2008).

[8] E. Mintusov *et al.*, Proc. Combustion Institute **32**, 3181 (2009).

[9] S.M. Starikovskaia, J. Physics D: Appl. Phys. **39**, R265 (2006).

[10] A. Starikovskiy and N. Aleksandrov, Prog. Energy Combust. Sci. **39**, 61 (2013).

[11] C. Cathey *et al.*, Combustion and Flame **154**, 715 (2008).

[12] Y. Matsubara and K. Takita, Proc. Combustion Institute **33**, 3203 (2011).

[13] S.B. Leonov *et al.*, IEEE Trans. Plasma Sci. **39**, 781 (2011).

[14] T. Ombrello *et al.*, Combustion and Flame **157**, 1906 (2010).

[15] I. V Adamovich *et al.*, Plasma Sources Sci. Technol. **18**,

034018 (2009).

[16] W. Kim *et al.,* IEEE Trans. Plasma Sci. **36**, 2898 (2008).

[17] J. Lefkowitz *et al.,* 50th AIAA Aerospace Science Meeting Including The New Horizons Forum and Aerospace Exposition, 9-12, Jan 2012, Nashville, Tennessee, AIAA-2012-1133.

[18] Y. Ikeda *et al.,* 47th AIAA Aerospace Science Meeting Including The New Horizons Forum and Aerospace Exposition, 5-8, Jan 2009, Orlando, Florida, AIAA-2009-223.

[19] S.A. Stepanyan *et al.,* 51st AIAA Aerospace Science Meeting Including The New Horizons Forum and Aerospace Exposition, 7-10, Jan 2013, Grapevine, Texas, AIAA-2013-1053.

[20] S. Serbin *et al.,* 49th AIAA Aerospace Science Meeting Including The New Horizons Forum and Aerospace Exposition, 4-7, Jan 2011, Orlando, Florida, AIAA-2011-61.

[21] J.P. Moeck *et al.,* 51st AIAA Aerospace Science Meeting Including The New Horizons Forum and Aerospace Exposition, 7-10, Jan 2013, Grapevine, Texas, AIAA-2013-0565.

[22] J. Lefkowitz *et al.,* 49th AIAA/ASME/SAE/ASEE Joint Propulsion Conference and Exhibit, 14-17 July 2013, San Jose, California. (Submitted).

[23] F. Schauer *et al.,* 39th AIAA Aerospace Science Meeting Including The New Horizons Forum and Aerospace Exposition, 8-11, Jan 2001, Reno, NV, AIAA-2001-1129.

[24] K. Takita *et al.,* Proc. Combustion Institute **30**, 2843 (2005).

[25] I. Kimura *et al.,* Combustion and Flame **42**, 297 (1981).

[26] K. Takita *et al.,* Proc. Combustion Institute **31**, 2489 (2007).

[27] L.S. Jacobsen, *et al.,* J. Propulsion Power **24**, 641 (2008).

[28] E. Barbi *et al.,* J. Propulsion and Power **5**, 129 (1989).

[29] T.M. Sloane and J.W. Ratcliffe, 21st International Symposium on Combustion, 1986, 1877-1883.

[30] I. Glassman, *Combustion* (New York: Academic Press, 1996).

[31] H. Wang *et al.,* available at http://ignis.usc.edu/USC_Mech_II.htm (2007).

[32] F.E. Fendell, J. Fluid. Mech. **21**, 281 (1965).

[33] S. Samukawa *et al.,* J. Phys. D: Appl. Phys. **45**, 253001 (2012).

[34] S.M. Starikovskaia *et al.,* Combustion Theory and Modelling **5**, 97 (2001).

[35] S.A.. Bozhenkov *et al.,* Combustion and Flame **133**, 133 (2003).

[36] N.B. Anikin *et al.,* Plasma Phys. **30**, 1105 (2004).

[37] I.N. Kosarev *et al.,* Combustion and Flame **156**, 221 (2009).

[38] N.B. Anikin *et al.,* J. Phys. D: Appl. Phys. **39**, 3244 (2006).

[39] N. Aleksandrov *et al.,* Proc. Combustion Institute **32**, 205 (2009).

[40] I.N. Kosarev *et al.,* J. Phys. D: Appl. Phys. **41**, 032002 (2008).

[41] A. Bao *et al.,* IEEE Trans. Plasma Sci. **35**, 1628 (2007).

[42] G. Lou *et al.,* Proc. Combustion Institute **31**, 3327 (2007).

[43] M. Uddi *et al.,* J. Phys. D: Appl. Phys. **42**, 075205 (2009).

[44] T. Amano and F.L. Dryer, Proc. Combust. Inst. **27**, 397 (1998).

[45] Y. Tan *et al.,* Combust. Flame **119**, 346 (1999).

[46] T. Ombrello and Y. Ju, IEEE Trans. Plasma Sci. **36**, 2924 (2008).

[47] T. Ombrello *et al.,* AIAA Journal **46**, 2424 (2008).

[48] T. Ombrello *et al.,* AIAA Journal **44**, 142 (2006).

[49] W. Sun *et al.,* Proc. Combustion Institute **33**, 3211 (2011).

[50] W. Sun *et al.,* Combustion and Flame **159**, 221 (2012).

[51] M. Uddi *et al.,* Proc. Combustion Institute **32**, 929 (2009).

[52] K. Niemi *et al.,* Plasma Sources Sci. Technol. **14**, 375 (2005).

[53] T.M. Ombrello, "Plasma-Assisted Combustion: Systematic Decoupling of the Kinetic Enhancement Mechanisms of Ignition, Flame Propagation, and Flame Stabilization by Long-Lifetime Species", Ph.D dissertation, Department of Mechanical and Aerospace Engineering, Princeton University, 2009.

[54] M. Kasha, *Singlet Oxygen Electronic Structure and Energy Transfer* (CRC Press, Inc., 2000).

[55] S. Williams *et al.,* Optics letters **29**, 1066 (2004).

[56] A.M. Starik and N.S. Titova, Shock **40**, 499 (2004).

[57] N.A. Popov, High Temperature **45**, 261 (2007).

[58] N.A. Popov, Plasma Sources Sci. Technol. **20**, 045002 (2011).

[59] A.S. Sharipov and A.M. Starik, Combustion and Flame **159**, 16 (2012).

[60] E.I. Mintoussov *et al.,* 42nd AIAA Aerospace Science Meeting Including The New Horizons Forum and Aerospace Exposition, 5-8, Jan 2004, Reno, Nevada, AIAA-2004-1013

[61] D.A. Lacoste *et al.,* Proc. Combustion Institute **34**, 3259 (2010).

[62] W. Kim *et al.,* Combustion and Flame **157**, 374 (2010).

[63] M. Uddi, "Non-equilibrium Kinetic Studies of Repetitively Pulsed Nanosecond Discharge Plasma Assisted Combustion", Ph.D dissertation, Department of Mechanical Engineering, Ohio State University, 2008.

[64] W. Sun, "Non-equilibrium Plasma-Assisted Combustion", Ph.D dissertation, Department of Mechanical and Aerospace Engineering, Princeton University, 2013.

[65] G.D. Stancu *et al.,* J. Phys. D: Appl. Phys. **43**, 124002 (2010).

[66] Y. Zuzeek *et al.,* J. Phys. D: Appl. Phys. **43**, 124001 (2010).

[67] M. Uddi *et al.,* 51st AIAA Aerospace Science Meeting Including The New Horizons Forum and Aerospace Exposition, 7-10, Jan 2013, Grapevine, Texas, AIAA-2013-0435.

[68] I.A. Kossyi *et al.,* Plasma Sources Sci. Technol. **1**, 207 (1992).

[69] G.P. Smith *et al.,* GRI-3.0, http://www.me.berkeley.edu/gri_mech/

[70] Y. Itikawa, J. Phys. Chem. Ref. Data **38**, 1 (2009).

[71] Y. Itikawa, J. Phys. Chem. Ref. Data **35**, 31 (2006).

[72] J.S. Yoon *et al.,* J. Phys. Chem. Ref. Data **37**, 913 (2008).

[73] M. J. Brunger and S.J. Buckman, Physics Reports **357**, 215 (2002).

[74] Y. Itikawa, J. Phys. Chem. Ref. Data **31**, 749 (2002).

[75] Y. Itikawa, J. Phys. Chem. Ref. Data **34**, 1 (2005).

[76] T. Shirai *et al.,* Atomic Data and Nuclear Data Tables **80**, 147 (2002).

[77] C.Q. Jiao *et al.,* J. Phys. D: Applied Phys. **40**, 409 (2007).

[78] A.M. Starik *et al.,* Combustion and Flame **157**, 313 (2010).

[79] A.A. Chukalovsky *et al.,* Combustion Sci. Technol. **184**, 1768 (2012).