In Situ Plasma Activated Low Temperature Chemistry and Subsequent S-Curve Transition in DME/Oxygen/Helium Mixture

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Abstract

The effect of plasma activated low temperature chemistry on the ignition and extinction of a Dimethyl Ether (DME)/O2/He diffusion flame was investigated in a counterflow burner with in situ nanosecond pulsed discharge at 72 Torr. A uniform discharge was generated between the burner nozzles by placing porous metal electrodes at the nozzle exits. The ignition and extinction characteristics of DME/O2/He were studied by employing CH2O Planar Laser Induced Fluorescence (PLIF) at constant strain rates and O2 mole fraction on the oxidizer side while changing the DME mole fraction. Contrary to the conventional understanding, strong low temperature reactivity was observed for DME with non-equilibrium plasma activation even at 72 Torr. At lower O2 mole fraction, it was found that with the increase of DME mole fraction on the fuel side, the CH2O PLIF intensity increased significantly before ignition and decreased rapidly after ignition. Moreover, at higher O2 mole fraction and discharge repetition frequency, 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 with a smooth transition between low temperature chemistry and high temperature chemistry. The transition from the conventional S-curves to a new stretched ignition curve at high plasma repetition rate demonstrated that the plasma could dramatically change the chemical kinetic pathways of DME oxidation by activating the low temperature chemistry. The chemical kinetic model for the plasma-flame interaction was developed based on the assumption of constant electric field strength in the bulk plasma region. Both experiments and modeling revealed that the plasma activated low temperature chemistry had a much shorter time scale comparing with that of thermally activated low temperature chemistry. The radical production analysis showed that atomic O generated by the discharge was critical to controlling the radical production. The radical production from the plasma at low temperatures significantly accelerated both the low temperature and high temperature kinetics.

1. Introduction

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]. 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 CO2, NOx, SOx, 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. 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 [2–6].

Over the few last years, plasma assisted combustion has drawn considerable attention for its potential to enhance combustion performance in internal combustion engines, gas turbines, and scramjet engines. Significant progress has been made in developing new techniques for plasma assisted combustion and in understanding the underlying mechanisms of the plasma-combustion interaction [2], [7–11]. However, due to the complexity of the interaction between plasma and flame kinetics, the fundamental kinetic enhancement mechanisms are still not well understood.

Recently, much work has been conducted to understand the role of plasma generated species on ignition [7], [8], [12], flame speed enhancement [3], [13], flame stabilization [2], [10] and extinction [11], [14]. For ignition studies, the reduction of ignition delay times by nano-second pulsed discharges has been reported by applying the pulsed discharge prior to the arrival of the shockwave in a shock tube [8], [15]. The results showed that the ignition delay times could be reduced by about an order of magnitude with the action of plasma. A recent study [12] on the ignition of H2-air mixture has been also conducted by flowing the mixture through a plasma activated quartz made square flow tube. Ignition delays were measured by monitoring the emission from excited OH (OH*) after the termination of the discharge. The reduction of ignition delays has been explained by the heat release through the reactions of H2 with plasma generated species (O, H and OH). The efforts on quantitative understanding of the enhancement mechanism through the plasma/flame interaction has been made by several research groups [3], [13], [16], [17]. Ombrello and co-workers experimentally isolated singlet oxygen (O2(a1Δg)) and ozone (O3) from other plasma related species and have shown that both (at concentrations of several thousand ppm) can enhance flame speeds by a few percent [3], [13]. Enhancement of flame stability by a non-equilibrium plasma in partially premixed systems have been observed for lifted flames [2], [10].

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 [8], [9], [15], [18], [19] or spatially [2], [7], [10–14], [17], [20]. 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. Recent 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 [11], [14]. 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, a novel well-defined counterflow flame system with an in situ discharge was recently developed and the effect of in situ discharge on CH4 diffusion flame was investigated [4]. The results revealed that due to the radical production, the in situ discharge can significantly modify the combustion properties of CH4 flame to remove the hysteresis between ignition and extinction. However, the oxidation path of CH4 does not contain any low temperature kinetics which exists for large hydrocarbon fuels. So the question raised by the different kinetics is how in situ plasma interacts with the low temperature chemistry therefore modifying the combustion properties of larger hydrocarbon fuels. The objective of this study is to investigate the direct coupling effect between plasma and low temperature chemistry. In order to examine the effect of plasma on the low temperature chemical kinetics, dimethyl ether (DME) was employed
as the fuel in this study. 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.

2. Experimental Methods

The experimental setup and characterization were described elsewhere [4] in details and were only briefly summarized here. A schematic of the experimental system is shown in Fig. 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. 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 frequencies ($f$) were fixed at 24 kHz or 34 kHz during the experiments, corresponding to an input power of 17.5 W or 24.8 W. In order to improve the uniformity of the discharge, helium (He) was used as the dilution gas for both the fuel (DME) side and the oxidizer (O$_2$) side. The pressure was held constant at 72 Torr for all of the experiments.

![Fig. 1 Schematic of experimental setup](image)

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 [20, 21]. The thermocouple measurements were compared with Rayleigh scattering [4] and other thermocouple measurements, with and without discharge, respectively. The uncertainty of the thermocouple measurements was found to be ± 20 K. CH$_2$O Planar Laser Induced Fluorescence (PLIF) [21], [22]
excited by photons at 355 nm from a Nd: YAG laser was used to characterize the effect of plasma on low temperature chemistry.

3. Results and Discussion

3.1 Observations of the ignition and extinction S-Curve

The ignition and extinction characteristics were studied by measuring the CH$_2$O PLIF intensity since hot ignition or extinction happens along with an abrupt change of the CH$_2$O PLIF. The intensity of the peak CH$_2$O PLIF signal across the reaction zone was used as a marker for comparisons of different cases/conditions. During the experiments, the strain rate (250 1/s, with flow residence time of approximately 4 ms) [1], $X_O$ and the discharge frequency ($f = 24$ kHz) were held constant, while the DME mole fraction on the fuel side, $X_F$, was varied. The boundary temperatures of the oxidizer side and fuel side were 650 ± 20 K and 600 ± 20 K, respectively, and nearly constant through all the experiments with the fixed discharge frequency and experimental pressure. The relationship between CH$_2$O PLIF and fuel mole fraction is shown in Fig. 2 and Fig. 3 at $f = 24$ kHz, $X_O = 0.4$ and $X_O = 0.6$, respectively. With the increase of the fuel mole fraction, the CH$_2$O PLIF increased indicating the increase of CH$_2$O 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 CH$_2$O PLIF signal intensity. Once ignition happened, further increase or decrease of DME mole fraction, the CH$_2$O 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 CH$_2$O PLIF signal intensity. Similar results can also be observed at $X_O = 0.6$ as shown in Fig. 3 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. 2 Relationship between CH$_2$O PLIF signal 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 $X_F$)](image-url)
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 (R1) and (R2). The other possible reaction pathway is from the low temperature chemical reaction chain as described by reactions (R3), (R4) and (R5).

$$e + \text{CH}_3\text{OCH}_3 = e + \text{H} + \text{CH}_3\text{OCH}_2 \quad (\text{R1})$$

$$\text{CH}_3\text{OCH}_2 = \text{CH}_3 + \text{CH}_2\text{O} \quad (\text{R2})$$

$$\text{CH}_3\text{OCH}_2 + \text{O}_2 = \text{CH}_3\text{OCH}_2\text{O}_2 \quad (\text{R3})$$

$$\text{CH}_3\text{OCH}_2\text{O}_2 = \text{CH}_2\text{OCH}_2\text{O}_2\text{H} \quad (\text{R4})$$

$$\text{CH}_2\text{OCH}_2\text{O}_2\text{H} = \text{CH}_2\text{O} + \text{CH}_2\text{O} + \text{H} \quad (\text{R5})$$

### 3.2 The S-Curve transition and Numerical Analysis

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. 4. 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. 4, it can be concluded that the CH$_2$O formation was dominantly due to the reaction pathway involving reactions (R3), (R4), and (R5) 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 Ref. [4], 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. 5. As shown in Fig. 5, 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. 4 Relationship between CH₂O PLIF and O₂ mole fraction with fixed 5% DME mole fraction, P = 72 Torr, f = 24 kHz, a = 250 1/s](image)

![Fig. 5 Relationship between CH₂O PLIF and fuel mole fraction X₀ = 0.6, P = 72 Torr, f = 34 kHz, a = 250 1/s (solid square symbols: increasing Xᵢ, open square symbols: decreasing Xᵢ)](image)

It has been a common understanding that the overall reaction rates in the low temperature chemistry were so slow thus may not be relevant to the 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 [23] employing a DME kinetic mechanism [24] 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. 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.

Fig. 6 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

4. Conclusions

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. The system provided an ideal platform to study the kinetic enhancement of different fuels with low temperature chemistry by using the in situ discharge directly in the reaction zone.

With DME as a testing fuel, it was found strong low temperature reactivity occurred with non-equilibrium plasma activation even at 72 Torr. CH₂O PLIF measurements showed that significant amount of CH₂O was formed with plasma activation before ignition. The plasma activated low temperature chemistry significantly changed the ignition and extinction characteristics of DME. The results showed that there was strong competition between low temperature reaction pathways and high temperature reaction pathways for the radicals produced from the plasma. With the increase of radical productivity via plasma activation, 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. It was also demonstrated that the radicals generated by the plasma can significantly accelerate the low temperature chemistry. This observation generalizes the results in previous study of CH₄ to larger hydrocarbon fuels which exhibit two stage ignition characteristics and promotes the importance of low temperature chemistry in practical application conditions.

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References