A Parameter Study of NSD Plasma Assisted Pyrolysis and Oxidation of CH_4 in a Temperature-Dependent Flow Reactor

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1 Introduction

Plasma-assisted ignition and combustion, widely applied in gas turbines, scramjets, and internal combustion engines, has been considered as a promising technique in shortening ignition delay time, improving combustion energy efficiency and reducing emission[1,2]. Many experimental studies in recent years have been carried out to understand the role of non-equilibrium plasma on ignition, flame speed, and flame stabilization. Plasma interacts with combustion via three major enhancement pathways: thermal, kinetic and transport[3]. Zhiyao Yin[4] studied lean fuel-air mixture excited by a repetitively pulsed nanosecond discharge. They used the OH Laser Induced Fluorescence and broadband Coherent Anti-Stokes Raman Spectroscopy to measure the temperature and hydroxyl radical generation in H_2-air, CH_4-air, C_2H_4-air, and C_3H_8-air. The results showed that OH may accumulate during the burst and the experimental results agree well with the kinetic modeling. Khalifeh O, et.al. applied NSD plasma for fuel conversion and effects of different discharge parameters including external electrode length, discharge power, voltage and frequency on CH_4 decomposition have been extensively studied[5]. Their work suggested the maximum 87.2% production of hydrogen from CH_4 decomposition. Zakari E, et.al. experimentally studied plasma-assisted oxidation of hydrogen-oxygen, methane-oxygen, ethylene-oxygen, and propane-oxygen mixtures diluted in argon. The results showed that some products and several radicals were not represented accurately in conventional reaction mechanisms used[6]. For the PAC oxidation of methane-oxygen, Yetter R A research group[7] carried out the temperature-dependent experiments from 420 K to 1250 K in a flat-flat reactor. The reactor pressure was 1 atm. In spite of rigorous investigations, the discrepancy between experimental and numerical results in some temperature environment in this study has not yet to be resolved. Furthermore, parameter roles of NSD discharge in methane pyrolysis and oxidation have not been well studied[3,8].

In this report, a flow reactor experiment system with temperature dependence is described with a spatially movable nanosecond plasma discharge. Experiments are carried out at pressure of 60 Torr and over a temperature range of 298-1173 K using a mixture highly diluted in Helium gas. The conversion of O_2 and CH_4 and the product yields were analyzed from the results in a flow plasma reactor with the gas compositions measured by an off-line Gas Chromatography (GC). The results consist of the quantification of stable product species as a function of temperature, discharge voltage, discharge frequency and pulse width, in order to well compare the effects of NSD parameters in plasma assisted CH_4 conversion kinetics. It is essential to establish detailed experimental data to assess the relevant reaction pathways, to determine the model applicability, and to clarify the rate-limiting steps and competing steps sensitive in temperature-dependent reaction system. This provides a reference for establishing a model for exploring the kinetics mechanism of temperature-dependence.

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2 Experimental methods

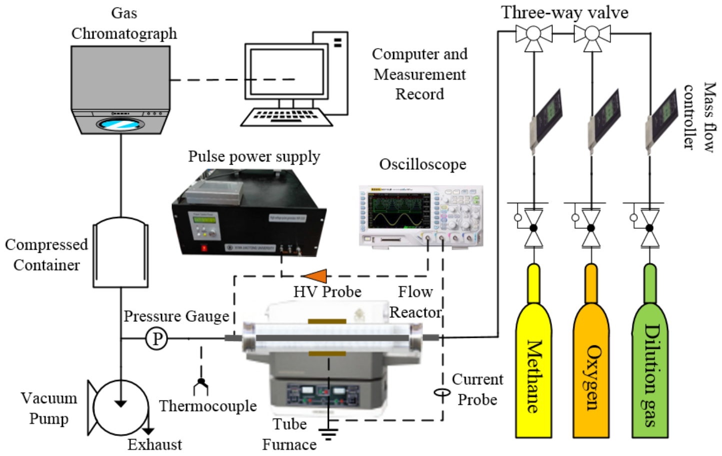
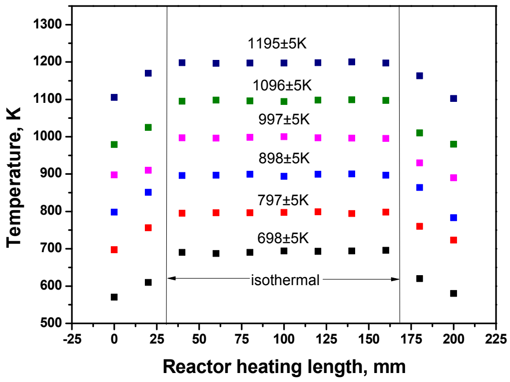


Figure 1 Schematic diagram of experimental setup



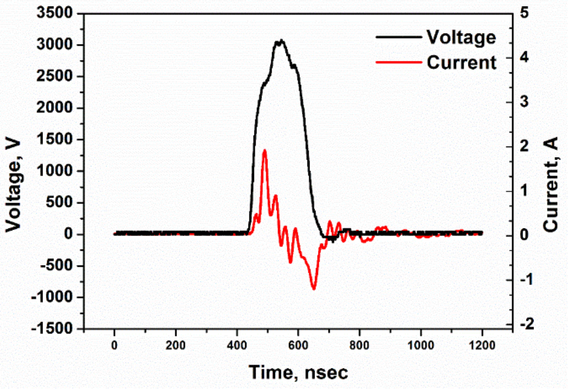


Figure 2 Temperature profiles along flow reactor axis

Figure 3 Voltage and current plots of NSD

As described in Fig.1, methane pyrolysis and oxidation are conducted in a DBD laminar flow reactor, which made of fused-quartz glass. The structure of reactor is wire-cylinder and single dielectric, in order to obtain high conversion rate. The DBD flow reactor is a cylindrical glass vessel with 15 mm I.D. and 19 mm O.D. The copper electrode is wound around the outer wall of the quartz tube to be as a low-voltage electrode of the discharge. The stainless steel as a high-voltage electrode is supported by seals at both ends of the quartz tube and placed in the center of the reactor. The spatially movable thermocouple is placed in the center of the stainless steel to measure the reaction temperature. The quartz glass reactor is placed in the tube furnace to achieve the fixed temperature of the reactant mixture. The flow temperature in the isothermal region is varied in the range of 298-1173 K, as shown in Fig.2. Mixture of methane (99.999%), oxygen (99.999%) and diluent helium gas (99.999%) is flowed through the reactor at a constant flow rate of 500 sccm. The flow rates are controlled using Alicat Scientific mass flow controller, and the experimental pressure is controlled by needle valve. The reaction pressure is fixed to 60 torr to achieve uniform discharges. The high voltage pulse is generated by a high-voltage nanosecond pulse power supply (provided by Xi'an Smart Maple Electronic Technology Company). The applied voltage is measured using a high voltage probe

(RP1018H, 1000:1), and the current is measured using a current probe (CP8030B, 30A/50MHz). Output signal is displayed using oscilloscope (RIGOL DS1104Z, analog channel of 4, bandwidth of 100 MHz and a time resolution of 1 GSa/s). Fig.3 shows the actual discharge voltage and current plots of the nanosecond pulse power supply shown in the oscilloscope. The sample after the reaction is collected by a compression tank. The products of methane pyrolysis and oxidation are measured using a gas chromatograph (GC system, Agilent Technologies 7890B) with a flame ionization detector (FID, Capillary column: HP-PLOT AL2O3 S, 50m × 530μm × 15μm) and a thermal conductivity detector (TCD, 4 mm-φ-stainless steel packed column: Porapak Q, 2 m length). For all species, the FID quantitation error is assumed to be 5% and TCD quantitation error is assumed to be 10%, excluding the uncertainty of the sampling procedure. A gas component sample analysis takes about 22 minutes.

3 Experimental Results

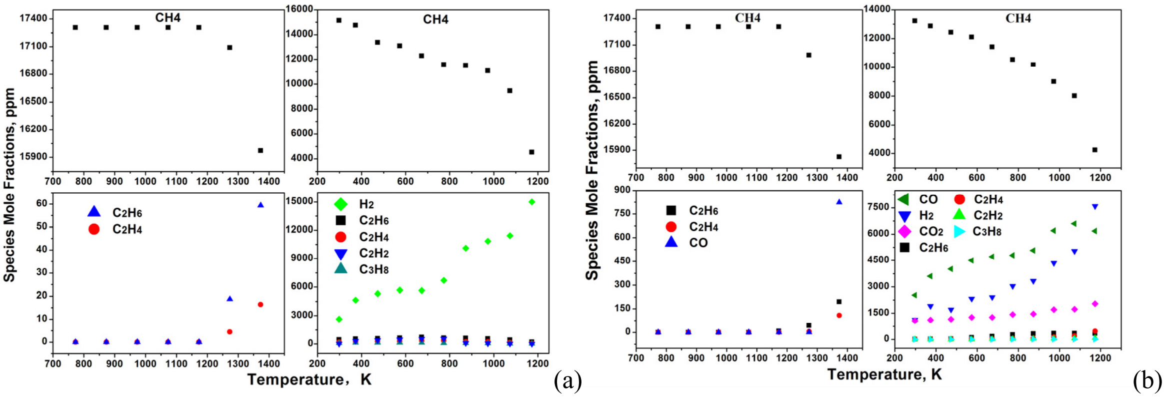


Figure 4 Comparisons of methane consumption and products production for thermal and plasma-assisted CH_4 (a) pyrolysis and (b) oxidation with temperature increasing.

In pyrolysis experimental sets, He is the dilution gas with the fixed flow rate of 490 sccm and CH_4 is the fuel gas with the fixed flow rate of 10 sccm. Replace 20 sccm He in the pyrolysis system with oxygen to form the oxidation system. Fig. 4 shows a comparison of measurement results between thermal and plasma-assisted methane pyrolysis and oxidation. When the reaction temperature is fixed at 1273 K, methane begins to pyrolysis and consumes only 217 ppm. The maximum consumption of methane is correspondingly 1118 ppm. The detectable hydrocarbons are only a small amount of ethane (C_2H_6) and ethylene (C_2H_4). Fuel consumption and conversion is as such very low. However, for the NSD plasma assisted pyrolysis, while the voltage, frequency and pulse width of the power supply are fixed at 5000 V, 30 kHz and 50 ns respectively, pyrolysis and oxidation can occur at room temperature. In the temperature range of 298 K-1173 K, the fuel consumption increases with increasing temperature. At the highest temperature (1173 K), nearly 12784 ppm of methane is consumed and its corresponding conversion rate is 73.87%. The major products of plasma-assisted methane pyrolysis are H_2, C_2H_6, C_2H_4, C_2H_2, C_3H_8. The concentration of H_2 is the largest and increases with temperature increasing. Fig.4 is a brief demonstration of promising features of NSD discharge in a temperature-dependent reaction system of methane conversion. NSD plasma enhances CH_4 pyrolysis and oxidation, especially at low temperature.

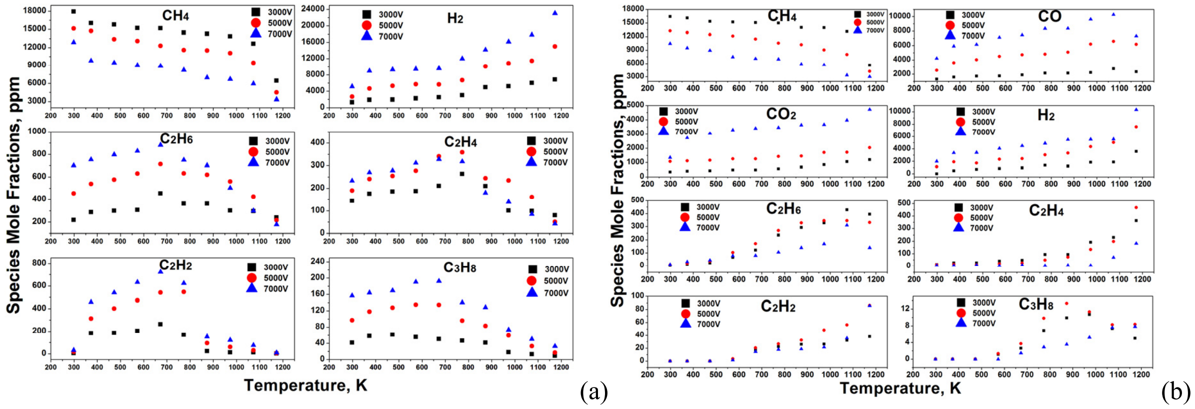


Figure 5 Effect of discharge voltage on (a) pyrolysis and (b) oxidation of CH_4 as a function of temperature.

A prominent aspect of the electric discharge impact in a combustible mixture is that various degrees of freedom of molecules are excited[5]. The types of plasma-excited species are strongly dependent on the electric field strength. Fig.5 shows the effect of discharge voltages (3000-7000 V), i.e., electric field strengths, on plasma pyrolysis and oxidation. For pyrolysis in Fig.5(a), the major products are H_2, C_2H_6, C_2H_2, C_2H_4, C_3H_8 in turn. H_2 increases sharply at temperatures greater than 673 K. At temperature less than 673 K, concentrations of C_2H_6, C_2H_2 and C_3H_8 increase, but decreases at temperature above 673 K. In the temperature range of 298-1073 K, CH_4 decreases gently with increasing temperature. This trend indicates that both the plasma and the thermal reaction promote methane consumption. Comparatively, plasma plays a dominant role. For methane oxidation in Fig.5(b), the concentration of CO reaches a maximum at 1073 K, and then decreases with increasing temperature, eventually converting to CO_2. Furthermore, H_2, CO_2, C_2H_4 and C_2H_2 increase with increasing temperature. C_2H_6 and C_3H_8 increase first and then decrease. When the temperature is greater than 997 K, the consumption of methane is Sharply increased. All the results show the dependence of the products production on electric field strength and the most visible enhancement of NSD plasma in CH_4 pyrolysis and oxidation at low temperature.

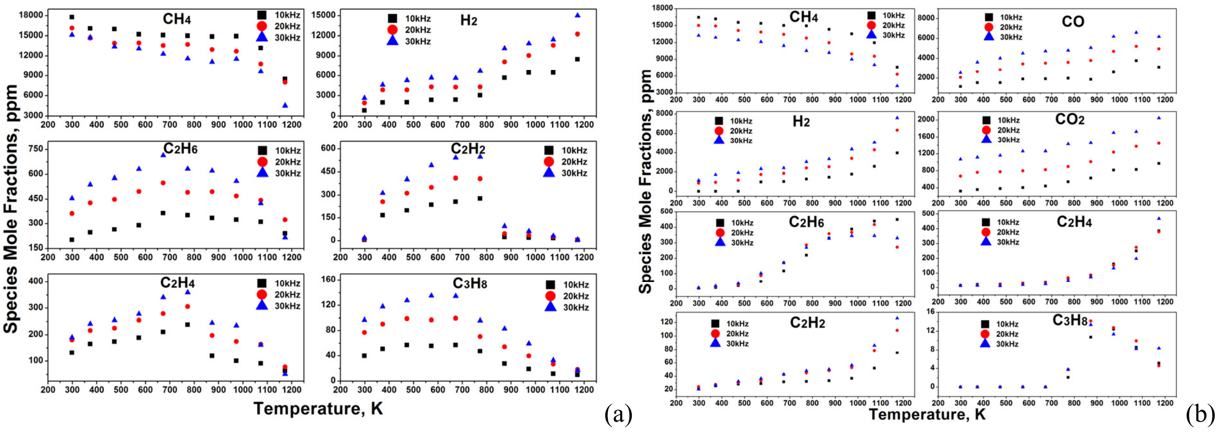


Figure 6 Effect of NSD discharge frequency on (a) pyrolysis and (b) oxidation of CH_4 as a function of temperature.

Fig. 6 shows the effect of frequency of 10-30 kHz for plasma pyrolysis and oxidation. The trends of product concentrations are similar. When the temperature is 1173 K, the CH_4 conversions of 10 kHz, 20 kHz, 30 kHz are 50.9%, 53.7%, 73.9% respectively. It can be seen in Fig.6 (a) that the higher the pulse repetition frequency, the greater the effect on methane pyrolysis. For methane oxidation in Fig.5(b), CO_2,

CO_2 and H_2 are the major species formed. After the mixed gas is added to the oxygen, the fuel consumption is further aggravated compared to the simple pyrolysis. When the temperature is 1173 K, the CH_4 conversions of 10 kHz, 20 kHz, 30 kHz are 56.2%, 63.7%, 75.5%. Discharge frequency presents less impact than the voltage in plasma assisted oxidation process.

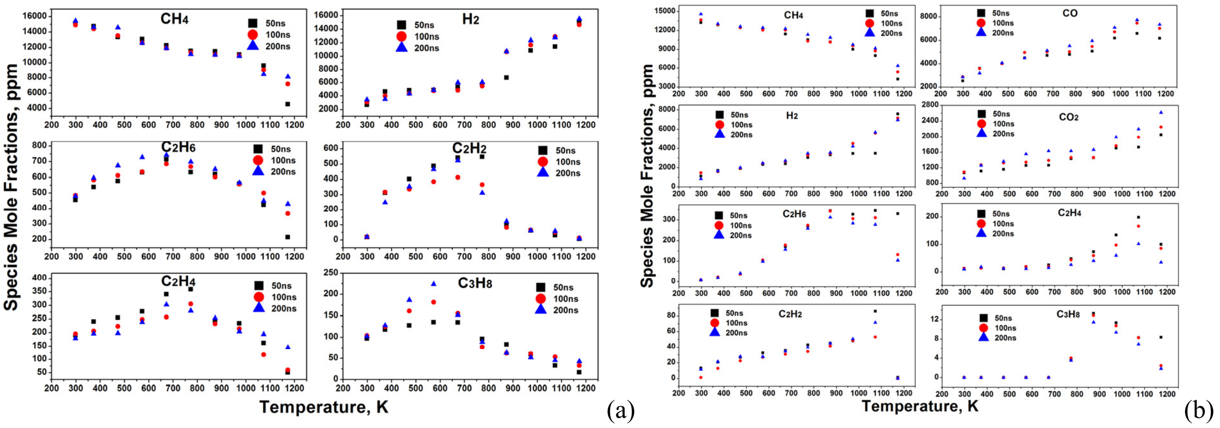


Figure 7 Effect of pulse width on (a) pyrolysis and (b) oxidation of CH_4 as a function of temperature.

Pulse width of NSD discharge is first reported to show its impact on fuel conversion. For methane pyrolysis in Fig.7(a), methane consumption is basically the same at different pulse widths at low temperature. At temperatures greater than 973 K, methane consumption has increased dramatically and conversion rate is maximum at 50ns. When the temperature is 1173 K, the CH_4 conversion of 50 ns, 100 ns, 200 ns is 73.9%, 58.4%, 53.1%, suggesting that the shorter pulse width, the greater the effect on plasma pyrolysis. For methane oxidation in Fig.7(b), at the highest temperature of 1173 K, the CH_4 conversion at pulse width of 50 ns, 100 ns, 200 ns reach 75.5%, 68.9%, 63% respectively. Contrary to the effects of voltage and frequency, the shorter the pulse width, the greater the effect on oxidation. In the high temperature range ($T > 1073$ K), the kinetic effect of the plasma on methane oxidation decreases and accordingly the thermal effect dominates the process.

4 Discussion

At low temperatures, the primary consumption paths of CH_4 are $CH_4 + e \rightarrow CH_3 + H + e$ and $CH_4 + O(1d) \rightarrow CH_3 + OH$. The electron impact dissociative excitation is a dominant route for fuel decomposition. Comparatively, at high temperatures, the concentration of CO begins to decrease and is converted to CO_2 ($CO + OH \rightarrow CO_2 + H$) because of the production of OH radical begining to increase[9]. The chain-branching factor of the thermal reaction dominates and the significance of the plasma reactions reduces. Contrast the methane pyrolysis and oxidation consumption at different temperature, the effect of varied applied voltage on the conversion of methane is maximum, followed by the repetition frequency and pulse width. Increasing the applied voltage can excite a more powerful electric field, which generates higher energy electrons, temperature and electron density. Increasing pulse repetition fruquency can result in less ascent and descent time. Experimental results show that increasing both the applied voltage and pulse repetition frequency can promote CH_4 conversion. The change in pulse width has little effect on methane consumption. The shorter the pulse width, the higher the conversion rate. When the pulse width of the applied high voltage pulse is sufficiently narrow, all the energy of the pulse can be used to destroy the bond of the molecule. But when the pulse width is widened, most of the electrical energy of the pulse is used to heat the gas or surrounding dielectric material instead of breaking the bonds of the gas molecules and rising the temperature of electrons and reactive species production. In this process, since the mean free path is short, the electric energy obtained by the free electrons is small[10]. Therefore, succeeding multi-process would be required and the NSD efficiency can be improved by shortening the pulse rise time and width.

5 Conclusion

The present work reports the quantitatively experimental results in a temperature-controlled $He/CH_4/O_2$ laminar flow reactor, showing the temperature-dependent and parameter-dependent kinetics in plasma assisted methane pyrolysis and oxidation. At first, the comparison in experimental plots shows that plasma can significantly increase fuel consumption and product concentration by kinetic pathway other than thermal pathway at lower temperature. Typically, methane consumptions reach maximums of only 7.7% and 8.6% in thermal enhanced pyrolysis and oxidation experiment at 1373 K. However, application of plasma in methane pyrolysis and oxidation can dramatically increase the conversion rates of up to 80.7% and 82.5% at 1173 K. Then, the effects of NSD parameters including discharge voltage, discharge frequency and pulse width in plasma assisted CH4 conversion kinetics as a function of temperature, are well compared in a temperature-dependent reactive system. The most effective parameter is the applied voltage, followed by the repetition frequency and pulse width. The higher the voltage and frequency are applied, the higher the conversion rates of methane pyrolysis and oxidation are achived. The pulse width is however opposite.

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