Plasma-Assisted Low-Temperature Combustion: Kinetics and Stability
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Introduction

Non-equilibrium plasmas provide a promising solution for advanced engine design, fuel reforming and material synthesis \[1-2\]. Recent studies have shown that plasmas can kinetically enhance low-temperature combustion (below 700 K) more than high temperature combustion (above 1050 K) \[2\]. The active species produced from plasma including O(\(^1\)D), O, O\(_2\)(\(^1\)\(\Delta_g\)) and O\(_3\) provide new reaction channels for combustion kinetics, the reaction rates of which greatly exceed those of typical combustion rate-limiting reactions at low temperature. Therefore, with strong plasma intensity, i.e., high radical production from plasma, one can observe or establish self-sustained cool flames at atmospheric pressures \[3-4\].

To understand such kinetic enhancement from plasma involved in low-temperature combustion, different channels for reactions between excited plasma species and fuels should be investigated quantitively. Previous studies mostly focused on O\(_2\)(\(^1\)\(\Delta_g\)) and O\(_3\) assisted ignition \[3, 5-7\]. Despite high reactivity, O(\(^1\)D) reactions with fuels, especially biofuels, are less studied. Such reactions are extremely fast (\(~1\) \(\mu\)s) but products have different reactivities. Therefore, the branching ratios of multichannel reactions between O(\(^1\)D) and fuels are crucial for understanding kinetics in plasma-assisted low-temperature combustion.

Chemically-active ions, excited species, radicals produced by plasma have strong enhancement on low-temperature combustion. Vice versa, low-temperature combustion processes will affect the formation and consumption of charged particles, plasma energy transfer, and thus modify the plasma thermal instability mechanism. According to classical gas discharge theory \[8\], this mechanism can be demonstrated by a closed chain which can be started from any step as:

\[ n_e \uparrow \rightarrow (jE) \uparrow \rightarrow T \uparrow \rightarrow N \downarrow \rightarrow (E/N) \uparrow \rightarrow \nu_i (E/N) \uparrow \rightarrow T_e \uparrow \rightarrow n_e \uparrow \]

Clearly there is a positive feedback of the perturbation of electron number density (\(n_e\)) linked by Joule heating (\(jE\)), gas temperature (\(T\)), gas number density (\(N\)), electric field strength (\(E\)), ionization rate (\(\nu_i\)) and electron temperature (\(T_e\)). \(\uparrow\) and \(\downarrow\) denote the increase and decrease of the physical properties, respectively.

This mechanism works well in noble gases and air at low pressure \[9\]. However, the appearance of fuel oxidation at low temperature will enable electron-impact fuel
ionization, combustion heat release and low-temperature combustion chemistry. All these further influence temperature \( (T) \), electron number density \( (n_e) \) and reduced electric field \( (E/N) \). There is a knowledge gap in understanding chemical-kinetic effects on plasma stability from combustible mixtures. A new thermal-chemical stability theory and detailed plasma-combustion kinetic model will greatly advance plasma-controlled ignition and plasma-assisted low-temperature combustion technology.

Current Work

(i) Kinetic Studies of Excited Singlet Oxygen Atom \( O(1^D) \) Reactions with Methanol and Ethanol

Electronically excited singlet oxygen atom \( O(1^D) \) is one of the most reactive species produced in non-equilibrium plasma. In the present study, the branching ratios of the reactions between \( O(1^D) \) and alcohols are determined with infrared laser diagnostics in a multi-pass photolysis flow reactor. Quantitative time-resolved \( HO_2 \) profiles are measured with mid-IR Faraday rotation spectroscopy (FRS), while OH radicals are measured from direct absorption spectroscopy (DAS). The branching ratios of \( O(1^D) \) reactions with \( CH_3OH \) and \( C_2H_5OH \) and missing pathways for \( HO_2 \) formation are determined by comparing experimental data with simulation results from the updated HP mech \(^{[10]} \).

(ii) Stability Analysis for Plasma Thermal-Chemical Instability

The present study extends Raizer’s analysis to combustion mixtures where more chemical kinetic pathways are available. To derive an analytical expression for stability criterion, several assumptions are made for simplicity: radicals and ions are in quasi-steady states (QSS); plasma in the contraction process is quasi-neutral; the cathode and anode sheaths are stationary; convection and diffusion are zero-dimensional. The eigenmatrix from the governing equations is obtained analytically and the plasma instability growth rate is analyzed using eigenvalues and complex eigen-pairs. Several kinetic couplings including electron-impact ionization of fuels, electron attachment to oxygen, electron-impact endothermic fuel pyrolysis reactions, and electron energy transfer to vibrational states are identified in the current stability analysis.

Future Work

In the future, the branching of \( O(1^D) \) reactions with more biofuels will be validated by measuring more intermediate species including \( CH_2O \) and \( H_2O \) and various pressure conditions up to 1 atm. The current stability analysis for plasma thermal-chemical instability will lead to a new stability diagram where the limiting conditions of instability
onset will be predicted. By using detailed plasma-combustion kinetics and transport properties, computationally efficient modeling for plasma thermal-chemical instability and non-equilibrium plasma assisted ignition will be developed and validated by theoretical predictions and experimental results from time-dependent electron number density and temperature measurements.

Reference