

## 論文の内容の要旨

### On Radical Quenching Mechanism Based on PLIF Measurement of OH Generated with Pulsed Arc Discharge (パルスアーク放電で生成した OH の PLIF 計測に基づく化学的消炎機構の解明)

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#### Abstract

In the rapid development of technology and society, consumption of portable power is increasing and requires more on conventional battery technology. Development of battery technology can hardly pace the growing demand due to its limited energy density. Contrarily, microscale combustion is promising in application for portable power generation and other fields such as micro thruster and heat source, due to the attractive high energy density of hydrocarbon fuels. However, flame quenching is rigorous in microscale and the quenching mechanism becomes the key point for wider application.

Recent studies on flame quenching in microscale reveal the significance of wall thermal and chemical effects. For flame quenching, wall thermal effect is dominant at lower wall temperature while the wall chemical effect becomes important at higher wall temperature. As to comprehensive wall chemical quenching investigation, little achievement has been obtained recently. At high wall temperature, more detailed data should be necessary for wall chemical quenching study. In methane flame experiments, complicate reactions among large number of co-existing species significantly increase the difficulty in mechanism elucidation and the mechanism transition for radical generation from low to high wall temperatures hinders pure wall chemical quenching elucidation. Therefore, a simpler method for radical generation on demand is preferred for more detailed investigation.

Electrical discharge for OH radical generation is proposed. Since initiation of electron-impact water dissociation is simpler and much fewer radicals co-exist, the mechanism is greatly simplified for wall chemical quenching investigation. In addition, micro OH-PLIF (Planar Laser Induced Fluorescence) is used for radical distribution detection.

As pioneering attempt to adopt long-duration pulsed discharge in combustion study, method of pulsed arc discharge in this work can also be applied for specific study in micro combustion, such as mechanism development/validation and ignition/extinction study, etc.

This dissertation is divided into 6 chapters, including the introduction and conclusions. Details of each chapter is introduced below:

#### Chapter 1

Background of portable energy consumption as well as microscale combustion application is first introduced. Then fundamental of flame quenching and wall thermal/chemical effect on flame behavior are investigated. Quenching distance measurement based on methane flame points out the insufficiency of flame method for wall chemical quenching study. Simpler radical field generated by electrical discharge on demand is proposed. Discharge schemes of interest are compared and pulsed arc discharge method is

selected for more uniform radical field. For objective of wall chemical quenching mechanism elucidation, approach of micro OH-PLIF is employed. Finally, the outline in this dissertation is listed.

## Chapter 2

In this chapter, principle of LIF of OH/acetone is briefly introduced. To investigate wall chemical effects by electrical discharge, specific quartz chamber and test quartz plate are designed for detection of OH spatio-temporal distribution over various wall materials and temperatures. The chamber has function of introducing test gas flow, installing electrode, protecting electrode from oxidation, matching quartz plate for surface material exchange and detecting PLIF signal. Quartz plates with ~100nm-thick films supplies specific chemical boundary condition while the thermal boundary condition is unchanged. Tungsten electrode can be bent to specific shape and the distance from test electrode to wall can be adjusted.

For OH fluorescence capture, the experimental setup has other components for discharge, laser sheet formation, laser excitation and fluorescence capture, laser energy synchronization, external infrared heating, flow control and electrode monitor. Highest voltage of 5 kV and discharge current of 20 mA is available between electrodes with gap of 2mm, and the pulse frequency is 2 Hz with discharge duration from 100 ms to 250 ms. Timing acquisition scheme in LIF system is updated for fluorescence capture frequency of 2 Hz. Humid nitrogen flow with adjustable water vapor fraction lower than 2.03% at atmosphere is introduced into chamber as well as acetone mixture. Quartz plate installed in chamber could be externally heated to 900 °C by infrared lamp heater and electrodes are arranged within 1 mm from the plate surface. Due to significance of electrode position and wall position in narrow space, a monitor camera is employed to monitor/update the position of electrodes and wall due to probable thermal expansion of quartz chamber and experimental variation.

Laser shot energy are collected and synchronized with LIF images to eliminate uncertainty by its fluctuation. During discharge, trigger noise induced by electromagnetic wave cannot be avoided, but noise-induce laser shot can be eliminated by time position examination of laser pulse. In OH PLIF calibration, acetone PLIF data accounting for laser sheet energy distribution in this work compensates the non-uniform laser excitation of OH field. OH PLIF uncertainty after processing of synchronization, average and calibration is less than ~3% if 200 or more LIF images are averaged.

## Chapter 3

In this chapter, characteristic of discharge-based OH field is investigated by LIF/PLIF method.

First, LIF of discharge-based OH field are captured by using ~2mm-diameter laser beam to examine influence of discharge variable on OH generation. Detailed transition lines can all be found in the OH emission spectrum and linearity between excitation laser energy and fluorescence intensity is verified. Uniformity of flow field in chamber with high flow rate of 400 sccm/min is examined by acetone PLIF. At steady state of OH field in 100ms-long discharge, discharge voltage has little influence on OH generation amount since voltage between electrodes greatly decreases after electrode gap is bridged and it affects little on electron energy for water dissociation. Change of water vapor fraction lower than 2% in

volume is found to have no influence on OH generation amount; On the contrary, discharge current associated with electron density affects it almost linearly. Therefore, it seems more feasible to generate OH field in various concentrations by controlling discharge current.

Second, OH temporal and spatial evolution is observed by micro PLIF measurements in discharge duration of 250 ms, without usage of external heater. OH generation field is unsteady within time lag of  $\sim 100 \mu\text{s}$  due to weak arc stability during glow-to-arc transition. Arc is able to self-stabilize after  $\sim 150 \mu\text{s}$  and the OH field reaches equilibrium within 1 ms after discharge starts. OH field variation after 1 ms indicates that OH generation field is sensitive to experimental conditions such as electrode tip curvature. After discharge ends, the OH field rapidly decays within 0.5 ms.

#### Chapter 4

In this chapter, basic theory of homogeneous and heterogeneous reaction that governs OH spatio-temporal distribution is introduced. Hydrogen reaction mechanism simulates the OH behavior in discharge/diffusion zone, while radical reactions at platinum or inert wall are described by specific surface reaction mechanisms. OH generation rate is basically proportional to electron density while overall water dissociation rate in CFD software of Fluent includes the electron density and is estimated by comparing different magnitudes of order with experimental measurement. OH behavior is numerically investigated in one-dimension and two-dimension diffusion scheme.

Calculation in 1D diffusion scheme helps to preliminarily examine homogeneous reaction mechanisms, by comparing with OH PLIF measurements. Overall water dissociation rate around 1000 is estimated. Preliminary simulation examines the influence of inlet gas temperature, wall temperature, water vapor fraction and initial sticking coefficient. Higher inlet temperature renders higher OH concentration mainly in the front of radical diffusion zone by accelerating OH generation and diffusion, while wall temperature mainly affects the OH distribution close to wall. Water vapor fraction less than 5% has no influence on OH generation, in accordance with experimental observation. Simulation of initial sticking coefficient reveals a higher radical destruction rate at higher wall temperature of  $900^\circ\text{C}$ .

2D diffusion simulation for more accurate OH distribution re-estimates the water dissociation rate as 1500 and the boundary conditions are optimized to fit the discharge physics. Result of 2D diffusion simulation is applied in model validation in wall chemical quenching elucidation.

#### Chapter 5

In this chapter, wall effect is investigated based on micro PLIF measurement between electrode and test walls.

First, absolute OH concentration in discharge is derived by identical laser sheet excitation of OH field in flame and discharge. Identical maximum of fluorescence intensity shows that OH concentration by discharge could be in the same order as that in flame and reaches  $10^{-5} \text{ mol/L}$  if discharge current is 20 mA.

Temporal development of OH field with use of external heater is observed within time lag of 100 ms from low to high wall temperatures. Results indicate that OH field reaches its equilibrium after time lag of 10 ms.

The wall temperature influence on OH distribution in discharge is observed at identical time lags and wall materials. Wall temperature is found to be significant at lower wall temperature than 500 °C and affects the OH distribution little at higher wall temperature. Wall thermal effect in discharge is similar to that in flame, but the mechanism is different: In discharge wall temperature governs OH diffusion/recombination while in flame it mainly affects OH generate at lower temperature.

For wall chemical effects, OH distribution over platinum, alumina and quartz starts to have larger difference at higher wall temperature than 700 °C and the results qualitatively agree with flame test: alumina is the most inert while quartz can quenching radical at high wall temperatures.

Clearer wall chemical effects are observed by employment of patterned wall of alumina/quartz to eliminate error induced by discharge arc shift, etc. OH distribution over alumina and quartz has little difference at wall temperature of 500 °C while the difference starts to be evident at higher wall temperature than 700 °C. In comparison with 2D diffusion simulation of normalized OH mole fraction, since surface reaction is adsorption-controlled process, initial sticking coefficient of alumina and quartz is estimated to be 0 and ~0.01, respectively. In addition, wall chemical effects of alumina and quartz are preliminary investigated and compared with flame test at various wall temperatures.

For more accurate analysis of wall chemical effects, chemical action is employed to reveal the significance of diffusion in affecting OH distribution. Higher action in vicinity indicates the wall mainly affects near-wall OH distribution and higher action for quartz than alumina reveals the radical destruction at the quartz surface. In addition, chemical action is used to estimate initial sticking coefficient of alumina and quartz, indicating higher sensitivity and accuracy.

Diffusion coefficient is included in chemical action to compensate temperature influence on diffusion and radical destruction rate on quartz at different wall temperatures are compared for direct wall chemical quenching investigation.

Chemical action in flame and discharge is compared at identical wall thermal/chemical boundary conditions. Action in flame in vicinity of ~0.2 mm from wall is on the whole lower than that in discharge, induced by gas-phase radical generation. Additional radical generation in flame has side effect on wall chemical quenching observation; therefore, discharge method is better for pure wall chemical effect elucidation.

At the end, advantages of longer-duration pulsed discharge method are highlighted and the potential application for specific study in microscale combustion is outlined.

## Chapter 6

In the last chapter, conclusions of wall chemical quenching mechanism investigation based on OH field generated by pulsed arc discharge are listed.