Fundamental Mechanisms, Predictive Modeling, and Novel Aerospace Applications of Plasma Assisted Combustion

Overview of OSU research plan

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MURI Kick-Off Meeting
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Task 1: Low-to-Moderate (T=300-800 K) temperature, spatial and time-dependent radical species concentration and temperature measurements in nanosecond pulse plasmas in a variety of fuel-air mixtures pressures (P=0.1 - 5 atm), and equivalence ratios (φ~0.1-3.0)

Goal: Generate an extensive set of experimental data on radical species concentrations and temperature rise; elucidate kinetic mechanisms of low-temperature plasma chemical fuel oxidation and ignition using kinetic modeling. Bridge the gap between room-temperature data (low-pressure gas discharges) and high-temperature data (shock tubes)
Test Bed #1: High-temperature, high-pressure nanosecond pulse discharge cell

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High-pressure discharge cell inside a tube furnace (6 inch bore, up to T=1200°C)
Premixed fuel-air flow (~1 m/s), preheated in the furnace, from 0.1 atm to a few atm
Repetitive nanosecond pulse discharge plasma: 20-40 kV, 5-25 nsec, 10 Hz to 100 kHz
Optical access (LIF, TALIF, CARS, CRDS) on the sides
Fuels: hydrogen, methane, ethylene, propane, pentane, methanol & ethanol vapor
Repetitive nanosecond pulse plasma for kinetic studies:

Air, P=60 torr, ν=40 kHz, 40 msec burst, 1 μsec gate

- Some filamentary structure in pulses #1 and #2
- Uniform air plasma during subsequent pulses, at P=40-100 torr
Repetitive nanosecond pulse plasma for kinetic studies: Ethylene-air, P=40 torr, φ=1, ν=40 kHz

• Nearly uniform plasma during entire burst (except pulses #1 and #2)
• Ignition does not occur, likely due to rapid wall cooling
• Pressure is low – can this experiment be done at higher pressures?
Repetitive nanosecond pulse plasma for kinetic studies: Ethylene-air, \( P=60 \) torr, \( \phi=1 \), \( \nu=40 \) kHz

• Uniform plasma during first few tens of pulses (except pulses #1 and #2)

• Well-defined filaments form in pulse #100, persist for several hundred pulses

• After ignition occurs, flame fills entire discharge volume, and plasma becomes uniform again

• Filamentation likely due to ionization / heating instability

• This is unacceptable: need to keep the plasma uniform during entire burst

• We know that preheating will improve plasma uniformity

• Sustaining plasma in a heated cell will allow measurements at higher pressures
Time-resolved species concentrations: O and H atoms
(Two-Photon Absorption LIF with Xe and Kr calibration)

Previous results: O atoms in air, methane-air, and ethylene-air at P=60 torr (single-pulse and burst mode, initially at T=300 K)

Objective: measure time-resolved O and H atoms in nsec pulse discharge plasmas in H\textsubscript{2}-air and C\textsubscript{x}H\textsubscript{y} air mixtures, at P ~ 0.1 - 1 atm, T=300-800 K

Outcome: kinetic mechanism of low-temperature plasma fuel dissociation and oxidation (specifically rates of O atom generation in the plasma and O atom reactions with fuel species)
Work currently underway: OH in methane-air and ethylene-air at P=60 torr (single-pulse and burst mode, initially at T=300 K)

Objective: measure time-resolved OH in nsec pulse discharge plasmas in H₂-air and CₓHᵧ air mixtures, at P ~ 0.1 - 1 atm, T=300-800 K

Outcome: kinetic mechanism of low-temperature plasma fuel oxidation (specifically rates of H atom abstraction from fuel species)
Time-resolved species concentrations: NO
(LIF with calibration using known NO-N₂ mixture)

Previous results: NO in air, methane-air and ethylene-air at P=60 torr
(single-pulse, initially at T=300 K). State-of-the-art kinetic models cannot
explain time-resolved data. Possible effect of N₂(X,v) + O reaction.

Objective: measure time-resolved NO
in nsec pulse discharge plasmas in H₂-air and CₓHᵧ air mixtures, at P ~ 0.1 - 1 atm, T=300-800 K

Outcome: kinetic mechanism of low-
temperature plasma fuel oxidation
(specifically O₂ dissociation vs. NO
formation in N₂* reactions)
Time-resolved, spatially resolved temperature (purely rotational CARS)

Previous results: time-resolved temperature in air and ethylene-air at P=40 torr (burst mode, initially at T=300 K). Evidence of significant additional heat release in fuel-air, compared to air.

Objective: measure temperature in nsec pulse discharge plasmas in H₂-air and CₓHᵧ air mixtures, at P ~ 0.1 - 1 atm, T=300-800 K.

Outcome: kinetic mechanism of low-temperature plasma chemical energy release in exothermic fuel oxidation reactions with radicals.
Test Bed #2: Flat flame McKenna burner with nanosecond pulse discharge

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Flame

HV electrode

5-15mm

~1-5 mm

McKenna burner

Wire mesh HVE

Burner surface

Measurement locations (resolution < 200 μm)

Flat flame burner inside a six-arm cross vacuum chamber (8 inch bore)
Premixed fuel-air flow (~0.1-1.0 m/s) with N₂ co-flow, P=10-40 torr
Repetitive nanosecond pulse discharge plasma: 20-40 kV, 5-25 nsec, 10 Hz to 100 kHz
Optical access (LIF, TALIF, CRDS) on two perpendicular axes
Fuels: hydrogen, methane, ethylene, propane, pentane, methanol & ethanol vapor

Laboratory for Advanced Fluid Dynamics and Combustion Research
Steady, laminar, low-pressure flat flames allow spatially-resolved measurements of temperature and species concentrations.

- Minimize transport influence; isolate kinetic effects.
- Can investigate full range of temperature conditions (from below 500 K to 2000 K) by adjusting measurement position (i.e., height above burner).
- Typical spatial scale ~5-20 mm, spatial resolution <200 µm.
- Straightforward integration of nsec discharge plasma into a low-pressure flame facility and study of plasma effects (i.e., measurements with plasma “off” and “on”).

Steady, laminar, 30 Torr, 1-D flame.
Previous low-pressure flame results (LIF): 
P=10-40 torr; CH₄, C₂H₆, C₃H₈, C₄H₁₀; φ=0.6 -1.4

Flame temperature from rotational structure of OH A-X (1,0) band near 282 nm

Spectral features used for profiles of flame species:
CH A-X (0,0) at 435 nm  NO A-X (0,0) at 226 nm
Previous low-pressure flame results (LIF):

\( P = 10-40\) torr; \( \text{CH}_4, \text{C}_2\text{H}_6, \text{C}_3\text{H}_8, \text{C}_4\text{H}_{10} \); \( \phi = 0.6 - 1.4 \)

Spatially-resolved measurements of radicals to understand high-temperature flame chemistry, help kinetic model development

Kinetic modeling: GRI-Mech 3.0

We will look at the region upstream of the flame where coupling between plasma kinetics and flame chemistry is most important
Objective: Examine coupling of plasma and combustion kinetics in a 1-D low-pressure flame. Use spatially-resolved species concentration and temperature measurements by LIF (OH, H, O, and CH) and CRDS (HO₂, HCO, CH₃) to study the effect of quasi-steady (RF) and repetitively pulsed nsec discharge plasmas on low-temperature chemistry and coupling with the flame zone.

Outcome: Kinetic mechanism of low-temperature plasma chemical fuel oxidation and energy release, and its effect on flame speed and burn rate. Specifically, boundary between “low-T” and “high-T” chemistry by measuring HO₂ radical concentration, at the conditions when O₂ is electronically excited.

\[
O₂ + H \rightarrow OH + O \quad \text{(high temperatures)}
\]
\[
O₂ + H + M \rightarrow HO₂ + M \quad \text{(low temperatures)}
\]

CRDS diagnostics will be used in both “test bed” experiments, (I) high-T, high-P nsec discharge plasma cell, and (II) low-P flame / plasma cell.
Thrust 2. Kinetic model development and validation

Task 8: Development and validation of a predictive kinetic model of non-equilibrium plasma fuel oxidation and ignition, using experimental results of Thrust 1

Goal: Identify key mechanisms, reaction, and rates of plasma chemical fuel oxidation processes for a wide range of fuels, pressures, temperatures, and equivalence ratios. This is absolutely essential to predictive capability of the model.
Current state of the art: hydrocarbon-air, low-temperature plasma chemistry kinetic model

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• **Air plasma model**: equations for ground state species ($N$, $N_2$, $O$, $O_2$, $O_3$, $NO$, $NO_2$, $N_2O$), charged species (electrons and ions), and excited species ($N_2(A^3\Sigma)$, $N_2(B^3\Pi)$, $N_2(C^3\Pi)$, $N_2(a^{1}\Sigma)$, $O_2(a^1\Delta)$, $O_2(b^1\Sigma)$, $O_2(c^1\Sigma)$, $N(2D)$, $N(2P)$, $O(1D)$) produced in the plasma.

• **Two-term expansion Boltzmann equation** for plasma electrons

• **Fuel-air plasma**: model combined with GRI Mech 3.0 $C_xH_y$ oxidation mechanisms, supplemented with fuel dissociation by electron impact and in reactions with electronically excited nitrogen

• **Peak E/N adjusted for pulse energy** to be same as predicted by the nanosecond pulse discharge model

We have absolutely no reason to trust the model predictions: GRI Mech 3.0 (or any other combustion mechanism) is not designed to work at low temperatures (starting at $T=300$ K)

Confidence in the model can be provided **only by detailed kinetic measurements** such as discussed in Thrust 1 plan
Here is what we know so far: dominant radical and energy release processes in C$_2$H$_4$-air predicted by the model

<table>
<thead>
<tr>
<th>O atom generation</th>
<th>Fuel energy release</th>
</tr>
</thead>
<tbody>
<tr>
<td>$N_2 + e^- = N_2(A^3Σ^-) + e^-$</td>
<td>$O + CH_2CHO = H + CH_2 + CO_2$</td>
</tr>
<tr>
<td>$N_2 + e^- = N_2(B^3Π^-) + e^-$</td>
<td>$H + O_2 + M = HO_2 + M$</td>
</tr>
<tr>
<td>$N_2 + e^- = N_2(C^3Π^-) + e^-$</td>
<td>$O + HO_2 = OH + O_2$</td>
</tr>
<tr>
<td>$N_2 + e^- = N_2(a^{1}Π^-) + e^-$</td>
<td>$OH + HO_2 = O_2 + H_2O$</td>
</tr>
<tr>
<td>$O_2 + e^- = O(3P) + O(3P,1D) + e^-$</td>
<td>$OH + C_2H_4 = C_3H_3 + H_2O$</td>
</tr>
<tr>
<td>$N_2(C^3Π) + O_2 = N_2(a^{1}Π^-) + O_2$</td>
<td>$HO_2 + CH_3 = OH + CH_3O$</td>
</tr>
<tr>
<td>$N_2(a^{1}Π^-) + O_2 = N_2(B^3Π^-) + O_2$</td>
<td>$CH_3O + O_2 = HO_2 + CH_2O$</td>
</tr>
<tr>
<td>$N_2(B^3Π^-) + O_2 = N_2(A^3Σ^-) + O_2$</td>
<td>$O_2 + CH_2CHO = OH + HCO + HCO$</td>
</tr>
<tr>
<td>$N_2(A^3Σ^-) + O_2 = N_2 + O + O$</td>
<td>$HCO + O_2 = HO_2 + CO$</td>
</tr>
<tr>
<td><strong>Fuel dissociation</strong></td>
<td>$CH_2 + O_2 = H + H + CO_2$</td>
</tr>
<tr>
<td>$C_2H_4 + e^- = products + e^-$</td>
<td></td>
</tr>
<tr>
<td>$N_2(A^3Σ^-) + C_2H_4 = N_2 + C_2H_3 + H$</td>
<td></td>
</tr>
<tr>
<td>$N_2(B^3Π^-) + C_2H_4 = N_2 + C_2H_3 + H$</td>
<td></td>
</tr>
<tr>
<td>$N_2(C^3Π^-) + C_2H_4 = N_2 + C_2H_3 + H$</td>
<td></td>
</tr>
<tr>
<td>$N_2(a^{1}Π^-) + C_2H_4 = N_2 + C_2H_3 + H$</td>
<td></td>
</tr>
<tr>
<td><strong>O atom decay</strong></td>
<td></td>
</tr>
<tr>
<td>$O + C_2H_4 = CH_3 + HCO$</td>
<td></td>
</tr>
<tr>
<td>$O + C_2H_4 = H + CH_2CHO$</td>
<td></td>
</tr>
<tr>
<td>$C_2H_3 + O_2 = HCO + CH_2O$</td>
<td></td>
</tr>
<tr>
<td>$C_2H_3 + O_2 = O + CH_2CHO$</td>
<td></td>
</tr>
<tr>
<td>$O + O_2 + M = O_3 + M$</td>
<td></td>
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<tr>
<td>$O + O_3 = O_2 + O_2$</td>
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</tbody>
</table>
Model validation summary: so far so good…
… but no surprise if the model fails at some point

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O atom mole fraction

- Air
- Air-methane, $\varphi=1.0$

Time, seconds

0.0E+0 1.0E-3 2.0E-3 3.0E-3 4.0E-3

0.0E+0 1.0E-5 2.0E-5 3.0E-5 4.0E-5

P=60 torr, $v=100$ kHz

- air
- air/CH$_4$, $\varphi=1.0$
- air/C$_2$H$_4$, $\varphi=0.5$

Number of pulses

0 20 40 60 80 100

1E+16 1E+15 1E+14

P=40 torr, $v=40$ kHz

- Air
- Air, model
- Fuel-air, $\varphi=0.1$
- Fuel-air, $\varphi=0.1$, model
- Fuel-air, $\varphi=1.0$
- Fuel-air, $\varphi=1.0$, model

Need a lot more data from Thrust 1 for extensive model validation

Outcome: a self-consistent low-temperature fuel-air plasma chemical mechanism
Task 10: Characterization and modeling of nsec pulse discharges

Goal: Prediction of E/N and electron density in the plasma, individual pulse energy coupled to the plasma, and their scaling with pressure, temperature, pulse waveform, and mixture composition
Two-pronged approach to plasma assisted ignition modeling

Predictive modeling of energy release rate and ignition delay time in low-temperature, repetitive nanosecond pulse fuel-air plasmas requires:

- E/N in the plasma, individual pulse energy coupled to the plasma, and their scaling with pressure, temperature, pulse waveform, and mixture composition
- Air plasma and fuel-air plasma chemistry: reactions among ground state species, excited species and radicals generated in the plasma, and their effect on energy release rate

These two problems require separate analysis:

- Nsec pulse plasma / sheath models cannot incorporate detailed reactive plasma chemistry: too many species (~100) and reactions (~1,000)
- Detailed plasma chemistry models (quasi-neutral) cannot incorporate repetitive, nsec time scale sheath dynamics and plasma shielding

Approach:

- Predict plasma E/N and coupled pulse energy using nsec pulse plasma / sheath model
- Incorporate results into fuel-air plasma chemistry model
Previous results: Repetitive nsec discharge pulse energy measurements

Nitrogen, $P=300$ torr, $\nu=100$ kHz

Nitrogen, $P=350$ torr, $\nu=100$ kHz

0.3 seconds after start (pulse # 30,000)

Pulse energy 11 mJ/pulse
Discharge power 110 W

Nitrogen, $P=650$ torr, $\nu=100$ kHz

What are the electric field and the electron density?
Previous results:
Analytic nsec pulse discharge plasma / sheath model

- Equations for electron and ion number density
- Poisson equation for the electric field
- Plane-to-plane discharge geometry
- Voltage pulse: Gaussian fit to experimental waveform
- Dielectric plate charging / plasma shielding

**Analytic solution:** time-dependent electron density and electric field in the plasma, coupled pulse energy

Excellent agreement with numerical solution, experimental data
Previous results:
Analytic nsec pulse discharge plasma / sheath model

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\[ Q_{total} = Q_{break} + Q_{after} \approx \frac{1}{2} C_{load} V_{peak}^2 \left[ \left( \frac{V_0}{V_{peak}} \right)^2 + \frac{\sqrt{2\pi}}{V_{RC} \tau_{pulse}} \right] \]

- Coupled pulse energy scales with the number density, can be increased by increasing peak voltage, reducing pulse duration

- Excellent agreement with numerical solution, experimental data
Objective: measure time- and space-resolved electric field and electron density in nsec pulse discharge plasmas using psec CARS and Thomson scattering; comparison with the model

Outcome: predictive capability for electron impact kinetic processes in the plasma
Thrust 4. Studies of diffusion and transport of active species in representative 2-D reacting flow geometries

Task 12: Ignition and flameholding in nonequilibrium plasma cavity flows at low static temperatures

Goal: Determine viable approaches to flameholding in high-speed flows using low-temperature plasmas. We simply cannot process the entire flow with the plasma!
Previous results: cavity ignition in premixed ethylene-air flows by nsec plasma (25 kV, 20 nsec, 40 kHz)

Fuel-air, 200 torr, 50 m/s

Air, 200 torr, 50 m/s

Pulse #140, Pulse #180, Pulse #350

#140 to #141, #180 to #181, #350 to #351

Air, 150 torr, 25 m/s

Fuel-air, 150 torr, 25 m/s

Diffuse plasma in air, filamentation in fuel-air during ignition, diffuse plasma after ignition
Previous results: cavity ignition and flameholding in premixed and non-premixed ethylene-air flows by nsec plasma

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• Ignition and stable flameholding in both premixed and non-premixed flows up to 100 m/sec (global φ=1 in both cases)
• 80-90% burned fuel fraction
• Plasma power ~100 W, combustion energy release 35 kW
• After ignition, plasma needs to be “on” at all times (flame blow-off without plasma)
Ignition and flameholding in nonequilibrium plasma cavity flows

Objectives:

• Further studies of cavity ignition and flameholding by repetitive nsec pulse plasmas in fuel injection flows (hydrogen and hydrocarbons)

• High frame rate (10-20 kHz) NO and OH PLIF imaging of ignition process using burst mode laser

• Increasing flow velocity beyond 100 m/sec, operating at low global equivalence ratios (\(\phi=0.1-0.2\))

• Comparison with kinetic modeling calculations using reduced plasma chemical ignition mechanism. Plasma flameholding mechanism after ignition – thermal or not?

Outcome: Demonstration of true predictive capability of the model