Modeling and Simulation of Plasma-Assisted Ignition and Combustion

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Summary of 2012-2013 Progress

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Plasma Flow Reactor

Air Plasma
- self-consistent simulations of pulsed nanosecond discharges in air.
- detailed validation with experiments and analytical model results.
- demonstration of volumetric plasma heating and radical production of critical importance in combustion applications.

Ignition of H$_2$-, CH$_4$-, and C$_2$H$_4$-Air Mixtures
- critical assessment of plasma kinetic models through comparison of OH decay rates after a burst of nanosecond pulses below ignition threshold temperatures (~500 K).
- importance of local plasma chemistry effects over heat transport in achieving “volumetric” ignition using pulse nanosecond discharges.
- detailed parametric studies on the sensitivity of nanosecond plasma ignition to pressure, eq. ratio, pulsing frequency, burst size, initial temperature, and dielectric properties.

Ignition of Heavy Fuels (n-Heptane)
- effect of nanosecond plasma on the two-stage n-heptane ignition process.

Plasma-Coupled Premixed Flames
- construction of plasma flame kinetic mechanisms, including electron impact dynamics of all major species in flame environments (both reactants and products).
- effect of species and temperature gradients in the flame zone on the spatial characteristics of the plasma (E/N, electron density etc.)
- focus on plasma radical generation in the preheat zone and the impact on overall flame characteristics.


4. S. Nagaraja and V. Yang, “Numerical Investigation of Nanosecond Plasma Assisted Ignition of $H_2$, $CH_4$- and $C_2H_4$-Air Mixtures” to be submitted to Combustion and Flame.

Model Assumptions

- Plasma fluid with drift-diffusion approximation.
- Two temperature model: electrons at $T_e$ (defined using mean energy); ions and neutrals at gas temperature, $T_{gas}$
- Lookup table for electron transport and rates using two-term expansion for electron Boltzmann equation (BOLSIG).
- Solution to mean-energy equation to update electron coefficients at each time step.
- Uniform pre-ionization in the discharge volume. No photo-ionization source term.

 Governing Equations

- **Continuity**
  \[
  \frac{\partial \rho}{\partial t} + \frac{\partial \rho u_i}{\partial x_i} = 0
  \]

- **Momentum**
  \[
  \frac{\partial \rho u_i}{\partial t} + \frac{\partial (\rho u_i u_j)}{\partial x_j} = -\frac{\partial p}{\partial x_i} + \frac{\partial \tau_{ij}}{\partial x_j} + F_{i_{EHD}}
  \]

- **Energy**
  \[
  \frac{\partial \rho \Omega}{\partial t} + \frac{\partial [(\rho \Omega + p) u_i]}{\partial x_i} = -\frac{\partial q_i}{\partial x_i} + \frac{\partial (u_i \tau_{ij})}{\partial x_j} + S_g
  \]

- **Species Continuity**
  \[
  \frac{\partial n_k}{\partial t} + \nabla \cdot J_k = S_k
  \]

- **Equation of State**
  \[
  p = \sum_{i=1}^{\text{N-1}} \rho Y_i R_i T_{gas} + \rho Y_e R_e T_e
  \]

- **Electron Energy**
  \[
  \frac{\partial n_e}{\partial t} + \nabla \cdot J_e = S_e; n_e = n_e \bar{e}
  \]

- **Electric Potential**
  \[
  \nabla (\varepsilon \varepsilon_0 \nabla \phi) = -e(n_+ - n_- - n_e)
  \]

- **Electric Field**
  \[
  \vec{E} = -\nabla \phi
  \]

Validity of the BOLSIG approach to calculate electron rate coefficients, among other assumptions, has been validated through comparison of species density (O and OH), temperature and input energy with experiments.
Nanosecond Plasma Assisted Ignition and Combustion Multi-Scale Modeling Framework

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PLASMA DISCHARGE DYNAMICS
- Plasma Chemistry
  - Ionization, Excitation, Dissociation, Recombination

FLOW AND COMBUSTION DYNAMICS
- Ignition and Combustion Chemistry
  - Radical initiation, Chain propagation, termination, Fuel oxidation

- Solution Algorithm
  - Electric field Implicit LU decomposition
  - Electron energy Implicit GMRES
  - Electron and gas transport coefficients
  - Plasma species and flow conservation equations

- Ionization wave propagation
- Electrical breakdown
- Cathode sheath formation
- Electron impact dynamics

- Quenching of excited species
- Ion recombination
- Gas heating

- Cumulative effects of multiple discharge pulses
- Convective and diffusive transport
- Ignition and combustion
Strategies for Computational Efficiency

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Adaptive Time-Stepping

- $\Delta t$ varies between $10^{-13}$ - $10^{-12}$ s
- Semi-implicit treatment of the Poisson equation to circumvent the stiffness arising from tight coupling between electric field and electron density.

- $\Delta t$ fixed at $10^{-9}$ s.
- Electron energy equation and Poisson equation are not solved since electric field effects become negligible and the space charge density rapidly decay as the applied voltage ends.

Multi Time-Scale Treatment of Chemical Source Term

- Speedup by 40% is seen by using the multi time-scale treatment of chemical source terms, but not orders of magnitude speedup observed in combustion simulations without plasma discharge.
- At high pulsing frequencies, the savings with using HMTS reduce because more time spent in simulating electric field transients during breakdown in each voltage pulse.

* Gou et al., Combustion and Flame 157 (2010) 1111–1121
Strategies for Computational Efficiency
plasma combustion chemistry optimization

charged species densities at center of discharge gap

O, H and OH densities at center of discharge gap

full chem: 35 species, 287 reactions  
optimized chem: 19 species 111 reactions

- simulated a burst of 8 nanosec pulses with detailed mechanism.
- removed species with peak mole-fraction less than 10^{-8}
- ensured that E/N, electron and radical species densities and temperature (in both space and time, all within 10%) are accurately predicted by the reduced mechanism.
- provides a speed-up of ~ 4 times with H_2-air plasma ignition.
- expect greater savings with large C\textsubscript{x}H\textsubscript{y} mechanisms and 2D/3D simulations.
OSU Plasma Flow Reactor
40 - 160 torr, 300 - 500 K, 1 - 100 kHz

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measurements

- time resolved O density using TALIF (uncertainty +/- 30%)
- time resolved NO density using LIF (uncertainty +/- 30%)
- time resolved OH density using LIF (uncertainty +/- 20%)
- time resolved temperature using rotational CARS and/or LIF thermometry
- ignition delay time from OH* emission rise
- ICCD imaging of discharge structure and flame kernel evolution.

ICCD images of discharge structure

Front View (2 cm × 1 cm)

Air : 373 K, 60 torr, 40 kHz

Side View (6 cm × 1 cm)

H₂ - Air : 40 kHz

C₂H₄ - Air : 40 kHz
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OSU Plasma-Coupled Premixed Flat Flame

Facility

Burner Configurations

Wiremesh HVE
Flame
Pulse Discharge Generator

2 cm

Premixed Mixture

Measurements

- spatially resolved OH density using LIF
- spatially resolved temperature using five-line OH thermometry.

“direct coupled” configuration

Plasma off
Plasma ON

“plasma upstream” configuration

Plasma off
Plasma ON

Facility

Burner Configurations

“direct coupled” configuration

Plasma off
Plasma ON

“plasma upstream” configuration

Plasma off
Plasma ON

- low pressure 1D flame (20 - 30 torr)
- H$_2$/O$_2$/N$_2$, CH$_4$/O$_2$/N$_2$ and C$_2$H$_4$/O$_2$/N$_2$ premixed flames
- FID pulser: 14 kV peak voltage, 7 ns FWHM, ~3 mJ/pulse
• coupled energy, temperature and O atom density predicted by the 1D model are within 20, 5 and 10% of experimental data, respectively.
• coupled energy remains fairly constant with pulse number, increasing linearly with pressure, and nearly independent of pulsing rates.
• O atom production via electron impact dissociation and quenching of excited N$_2$ by O$_2$ is captured accurately along with subsequent decay via formation of O$_3$ over ms timescales.
Detailed Physics over ns-ms Timescales
air discharge (60 torr, 300 K, 40 kHz, 100 pulses)

- plasma heating effect is about 0.5 - 1K/pulse in air and nearly independent of pulsing frequency (as a function of pulse number).
- rapid gas heating produces weak acoustic waves which propagate into the gas volume from both ends. The strength of these waves becomes weak as overall temperature rises from heat release from quenching of excited species.
- a fairly uniform temperature profile develops in the plasma volume after several discharge pulses, owing to slow but steady (~0.5 K/pulse) heat release primarily from relaxation of excited species.
- repetitive pulsing results in efficient production of atomic oxygen through electron impact dissociation during discharge pulses, and quenching of excited nitrogen species by oxygen.
- volumetric radical generation and heating by pulsed discharges are of great significance for ignition and flame stabilization purposes.
Nanosecond Pulsed Dielectric Plasma in H₂-Air Mixtures

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**model geometry**

- discharge gap
- quartz dielectric
- Kalrez dielectric

**operating conditions**

- Pressure: 40 - 160 torr
- Temperature: 373 - 600 K
- Pulsing Frequency: 10 - 40 kHz
- Gap width: 1 cm
- Initial Electron Density: $10^7$ cm⁻³
- Dielectric thickness (Quartz): 1.75 mm
- Dielectric thickness (Kalrez): 1.58 mm
- Dielectric Constant (Quartz): 4.3
- Dielectric Constant (Kalrez): 4 - 9

**applied waveforms**

- Dashed lines: measurements
- Solid lines: curve fit

**voltage and current**

- **Applied Voltage**
- **Gap Voltage**
- **Conduction Current**

**Objectives**

- comparison of OH density with measurements after a burst of 50 pulses.
- assess the accuracy of kinetics model at low temperature, pre-ignition conditions
- detailed investigations of NS plasma ignition physics and chemistry.
- sensitivity of ignition process to key system parameters and material properties.

**H₂-Air Plasma Combustion Kinetics**

**H₂/O₂/N₂ Combustion**


<table>
<thead>
<tr>
<th>Chain Initiation</th>
<th>Chain Branching</th>
<th>Three Body Reactions</th>
<th>NOX Reactions</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{H}_2 + \text{O}_2 \rightarrow \text{HO}_2 + \text{H} )</td>
<td>( \text{HO}_2 + \text{H} \rightarrow \text{OH} + \text{OH} )</td>
<td>( \text{H} + \text{O}_2 \rightarrow \text{O} + \text{OH} )</td>
<td>( \text{N}_2 + \text{O} \rightarrow \text{N} + \text{NO} )</td>
</tr>
<tr>
<td>( \text{H}_2 + \text{O}_2 \rightarrow \text{OH} + \text{OH} )</td>
<td>( \text{HO}_2 + \text{H} \rightarrow \text{H}_2\text{O} + \text{O} )</td>
<td>( \text{O} + \text{OH} \rightarrow \text{H} + \text{O}_2 )</td>
<td>( \text{N} + \text{O}_2 \rightarrow \text{NO} + \text{O} )</td>
</tr>
<tr>
<td>( \text{H}_2 + \text{M} \rightarrow \text{H} + \text{H} + \text{M} )</td>
<td>( \text{HO}_2 + \text{O} \rightarrow \text{O}_2 + \text{OH} )</td>
<td>( \text{O} + \text{H}_2 \rightarrow \text{H} + \text{OH} )</td>
<td>( \text{NO} + \text{HO}_2 \rightarrow \text{NO}_2 + \text{OH} )</td>
</tr>
<tr>
<td>( \text{H}_2 + \text{OH} \rightarrow \text{H}_2\text{O} + \text{H} )</td>
<td>( \text{H} + \text{OH} \rightarrow \text{O} + \text{H}_2 )</td>
<td>( \text{H} + \text{OH} \rightarrow \text{O} + \text{H}_2 )</td>
<td>( \text{O} + \text{O} + \text{M} \rightarrow \text{O}_2 + \text{M} )</td>
</tr>
<tr>
<td>( \text{O} + \text{H}_2\text{O} \rightarrow \text{OH} + \text{OH} )</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**H₂/N₂/O₂ Plasma**

<table>
<thead>
<tr>
<th>Dissociation/Excitation</th>
<th>Ionic Reactions</th>
<th>Quenching of Excited Species</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{N}_2 + \text{e} \rightarrow \text{N}^\left(4\right)\text{S} + \text{N}^\left(2\right)\text{D} + \text{e} )</td>
<td>( \text{N}_2 + \text{e} \rightarrow \text{N}_2^+ + \text{e} + \text{e} )</td>
<td>( \text{N}_2\left(A^\left(3\right)\right) + \text{O}_2 \rightarrow \text{N}_2 + \text{O} + \text{O} )</td>
</tr>
<tr>
<td></td>
<td>( \text{N}_2 + \text{H}_2 \rightarrow \text{HN}_2^+ + \text{H} )</td>
<td>( \text{N}_2^\left(A^\left(3\right)\right) + \text{O} \rightarrow \text{N} + \text{NO} )</td>
</tr>
<tr>
<td></td>
<td></td>
<td>( \text{N}_2\left(A^\left(3\right)\right) + \text{H}_2 \rightarrow \text{N}_2\left(A^\left(3\right)\right) + \text{H}_2 )</td>
</tr>
<tr>
<td>( \text{O}_2 + \text{e} \rightarrow \text{O} + \text{O} + \text{e} )</td>
<td>( \text{H}_2\text{O}^+ + \text{e} \rightarrow \text{H}_2\text{O}^+ + \text{N}_2 )</td>
<td>( \text{N}_2\left(A^\left(3\right)\right) + \text{O} \rightarrow \text{N} + \text{NO} )</td>
</tr>
<tr>
<td>( \text{H}_2 + \text{e} \rightarrow \text{H} + \text{H} + \text{e} )</td>
<td>( \text{H}_3\text{O}^+ + \text{e} \rightarrow \text{H}_2\text{O} + \text{H} )</td>
<td>( \text{O}^\left(1\right)\text{D} + \text{H}_2 \rightarrow \text{OH} + \text{H} )</td>
</tr>
</tbody>
</table>

- **Nonequilibrium Plasma Chemistry**
- **Low Temperature Radical Chemistry**
- **High Temperature Combustion Chemistry**

- Low temperature (500-1000 K) uncertainties in many key chain branching reactions.
- Detailed chemistry mechanism has 35 species and 287 reactions.
- Reduced chemistry mechanism has 19 species and 111 reactions.
**E/N and Electron Density Evolution**

\[ P_i = 80 \text{ torr}, \ T_i = 500 \text{ K}, \ f = 60 \text{ kHz}, \ \Phi = 1.0, \ \text{FID Pulser} \]

- **Periodic steady-state peak value** ~370 Td
- **Electron density at center** (60 pulses) peak value ~2 \times 10^{12} \text{ cm}^{-3}

- **Breakdown voltage at these conditions occurs at** ~10 kV
- **Sharp spike in current is seen at breakdown before it drops rapidly from the plasma shielding.**
- **Plasma excited species production happens only during a short duration of** ~5 ns when E/N is high.
- **E/N and electron density reach a periodic steady state after ~8 pulses.**
- **Nanosecond discharge efficiently generates radicals and excited species during each pulse because of high peak E/N.**
Decay Rates of O, H and OH after a 50 pulse burst in H₂-air

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$P_i = 100$ torr, $T_i = 500$ K, $f = 10$ kHz, FID pulser

- **OH density at center of discharge gap**
- **O and H density at center of discharge gap**

- Model predictions for OH are within 10% of measurements in H₂-air mixtures, including both peak value and decay rates.
- O production is highly sensitive to changes in eq. ratio, increasing by ~50% when $\phi$ is decreased from 0.12 to 0.06.
- H and OH are relatively insensitive, changing by ~10% when eq. ratio is doubled.

Key low temperature pathways for consumption of O and recirculation of H and OH:

\[
H + O_2 + M \rightarrow HO_2 + M \quad O + HO_2 \rightarrow OH + O_2
\]

\[
H + HO_2 \rightarrow OH + OH \quad OH + O \rightarrow H + O_2
\]
How is ignition achieved with nanosecond plasma?

\( P_i = 80 \) torr, \( T_i = 500 \) K, \( f = 60 \) kHz, \( \Phi = 1.0 \), FID pulser, 115 pulses \( \sim 2 \) ms

- heat transport plays a minor role. local plasma chemistry effects are critical in producing “volumetric” ignition
- secondary peaks in OH density near the boundaries is generated from HO\(_2\) which has accumulated due to low temperatures

**temperature evolution vs time**

- nearly simultaneous ignition at different locations

**spatial evolution of OH and temperature**

- creates a pool of O, H, and OH radicals

**nanosecond plasma pulses**

**(linear heating regime)**
- increases temperature to a threshold value of \( \sim 700 \) K

**(nonlinear heating regime)**
- partial fuel oxidation is triggered

**ignition and complete fuel oxidation**

- secondary peaks in OH density near the boundaries is generated from HO\(_2\) which has accumulated due to low temperatures
Spatial Evolution of Radicals during H₂-Air Ignition

\( P_i = 80 \text{ torr}, \; T_i = 500 \text{ K}, \; f = 60 \text{ kHz}, \; \Phi = 1.0, \; \text{FID pulser, 115 pulses} \sim 2 \text{ ms} \)

- A small increase in temperature near ignition significantly increases the chain branching reaction rates.
- Radical concentration profiles are much steeper than the temperature distribution, with well pronounced maxima near the centerline.
- Both O and H densities increase by ~3 times within 0.4 ms near ignition, with OH density increasing by 4 times.
- Low temperatures at the boundaries because of heat losses aid the accumulation of HO₂ which generates OH. The secondary peaks in OH profiles near the boundaries result from this pathway.
H$_2$-air pulsed nanosecond plasma ignition
what can we infer from emission images?

OSU Experiment

\[ P_i = 104 \text{ torr}, \quad T_i = 473 \text{ K}, \quad f = 40 \text{ kHz}, \quad \Phi = 1.0, \quad \text{CPT pulser} \]

- ignition first observed near edges, due to higher electric fields
- within 0.1 ms, ignition observed all along the centerline.
- the entire volume ignited within 0.4 ms of first detected flame emission.

- the present 1D model simulates a particular cross-section.
- although the 1D model cannot capture edge effects, it is able to explain the spreading of the ignition kernel from the centerline towards the boundaries.
- predictions are in line with observations that local plasma chemistry dominate over heat transport effects
Nanosecond Plasma Ignition vs Thermal Ignition
is there any difference?

$P_i = 80$ torr
$T_i = 500$ K
$f = 60$ kHz
$\Phi = 1.0$
FID pulser
115 pulses

species evolution at center for
NS ignition

\[
\begin{align*}
N_2 + e & \rightarrow N_2(A^3, B^3, C^3) \\
H_2 + e & \rightarrow H + H \\
O_2 + e & \rightarrow O + O
\end{align*}
\]

\[
\begin{align*}
N_2(A^3) + O_2 & \rightarrow O + O(D) \\
N_2(B^3, C^3) + H_2 & \rightarrow H + H
\end{align*}
\]

\[
\begin{align*}
O + OH & \rightarrow H + O_2 \\
O + HO_2 & \rightarrow OH + O_2 \\
H + HO_2 & \rightarrow OH + OH
\end{align*}
\]

\[
H_2 + OH \rightarrow H_2O + H
\]

ignition delay times with nanosecond plasma and a volume heat source

- the high activation energy chain initiation reactions are replaced by electron impact reactions with NS plasma.
- for the same input energy, thermal ignition delay is \(~60\%\) higher.
- plasma generated radicals trigger heat release from fuel oxidation at \(~700\) K, as opposed to auto-ignition temperature of \(~960\) K under same conditions.
Effect of Burst Size and Dielectric constant on Ignition

ignition delay vs # pulses in burst

\[ P_i = 80 \text{ torr}, \; T_i = 473 \text{ K} \]
\[ f = 40 \text{ kHz}, \; \Phi = 1.0, \; \text{CPT pulser} \]

ignition delay sensitivity to eq. ratio

\[ P_i = 80 \text{ torr}, \; T_i = 500 \text{ K} \]
\[ f = 60 \text{ kHz}, \; \text{FID pulser} \]

- there is a minimum # of pulses in burst, below which no ignition is observed.
- ignition characteristics are highly sensitive to dielectric properties.
- uncertainty in the dielectric constant values should be considered during the validation process.
- ignition delay reduction with increase in burst size is especially pronounced for lean mixtures.
Effect of Pressure and Pulsing Rates on H₂-Air Ignition

- \( T_i = 473 \text{ K}, f = 40 \text{ kHz}, \phi = 1.0, \text{ CPT pulser} \)

- Ignition delay reduction with increase in pressure is well reproduced by the model.
- Increase in pressure results in nearly linear rise in input energy per pulse because of its dependence on number density. Faster addition of energy results in more rapid ignition at higher pressures.
- The nonlinear trend of number of pulses required for ignition as a function of pulsing frequency is not reproduced by the model.
- The model predicts that input energy per pulse is nearly independent of pulsing frequency, which may not be true.
- Lowering of input energy, because of residual electron density effects, with rise in pulsing rates may explain the observed nonlinear trend.
OH Density Decay after 50 Pulse Burst in CH₄-, and C₂H₄-Air Mixtures

**CH₄-air**

- GRI Mech 3.0 has been validated extensively in 1000-2500 K and 25 torr to 10 atm range.
- USC Mech has been validated in 900-2500 K and 16 torr to 10 atm range.
- Model consistently over-predicts OH density by ~50% in CH₄-air mixtures.
- Growth rate is correctly predicted in C₂H₄-air mixtures, but the decay rate is slower than measurements.
- Low temperature uncertainty in chain reactions may be the primary reason for deviations.

**C₂H₄-air**

- Different CH₄- and C₂H₄-air combustion chemistry integrated with plasma kinetics are being tested to assess their relative performance on predicting low temperature radical production/decay.

**Ongoing Work**

- GRI Mech 3.0 has been validated extensively in 1000-2500 K and 25 torr to 10 atm range.
- USC Mech has been validated in 900-2500 K and 16 torr to 10 atm range.
- Model consistently over-predicts OH density by ~50% in CH₄-air mixtures.
- Growth rate is correctly predicted in C₂H₄-air mixtures, but the decay rate is slower than measurements.
- Low temperature uncertainty in chain reactions may be the primary reason for deviations.

**Present Model**

- GRI Mech 3.0
- CH₄/N₂/O₂ plasma
- NOX reactions
- USC Mech
- C₂H₄/N₂/O₂ plasma
- NOX reactions

**Present Model Experiment**

- CH₄-air (64 species)
- C₂H₄-air (70 species)

**Experimental Conditions**

- \( P_i = 100 \text{ torr}, \ T_i = 500 \text{ K}, \ f = 10 \text{ kHz}, \ \text{FID pulser} \)
Nanosecond Plasma Ignition of nHeptane-Air
(in collaboration with Wenting Sun)

Objective

- understand the effect of NS plasma on n-heptane-air ignition chemistry through self-consistent simulations.
- investigate the effect of radical addition to the “low temperature” and “high temperature” steps of the 2-stage ignition process.

1st stage
R-H → R (H abstraction)
R + O₂ → RO₂ (exothermic)
RO₂ → HO₂, H₂O₂, CH₂O etc.

2nd stage
H₂O₂ → 2OH
CH₂O → CO, H₂O
CO → CO₂

Temperature

1st stage
R-H → R (H abstraction)
R + O₂ → RO₂ (exothermic)
RO₂ → HO₂, H₂O₂, CH₂O etc.

2nd stage
H₂O₂ → 2OH
CH₂O → CO, H₂O
CO → CO₂

Objective

- understand the effect of NS plasma on n-heptane-air ignition chemistry through self-consistent simulations.
- investigate the effect of radical addition to the “low temperature” and “high temperature” steps of the 2-stage ignition process.

nC₇H₁₆-air plasma combustion kinetics (154 species)

C₇H₁₆/N₂/O₂ combustion
(LLNL reduced mech + NOX reactions)

n-C₇H₁₆ + OH → 2-C₇H₁₅ + H₂O
C₇H₁₄OOH ↔ C₇H₁₄O + OH
C₂H₃ + O₂ → CH₂CHO + O
CH₂O + OH ↔ HCO + H₂O
H + O₂ ↔ O + OH
H₂O₂ + M → OH + OH + M

C₇H₁₆/N₂/O₂ plasma reactions*

e + N₂ → N₂(A³, B³, C³, a¹) + e

N₂(A³) + O₂ → N₂ + O + O

N₂(A³) + C₇H₁₆ → N₂ + C₇H₁₅ + H

e + N₂ → N + N(²D) + e

N₂(A³) + C₇H₁₆ → N₂ + C₇H₁₄ + H₂

e + O₂ → O + O(D) + e

N₂(A³) + C₇H₁₆ → N₂ + C₇H₁₃ + CH₃

e + C₇H₁₆ → C₆H₁₃ + CH₃ + e

O(¹D) + C₇H₁₆ → C₇H₁₅ + OH

e + C₇H₁₆ → C₅H₁₁ + C₂H₅ + e

* C₇H₁₆ (electron impact and with excited species) reaction rates estimated from C₃H₈ based plasma reactions.
Nanosecond Plasma Ignition of nHeptane-Air
Effect of NS Pulses on 1st Stage Delay Time

**Model Geometry**
- Discharge gap
- Quartz dielectric
- Kalrez dielectric

**Operating Conditions**
- \( P_i = 160 \) torr
- \( T_i = 600 \) K
- \( f = 60 \) kHz
- \( \Phi = 1.0 \)
- 8 kV Gaussian pulses
- 10 ns duration

**Temperature Evolution**
- Application of 6 NS pulses significantly accelerates 1st stage temperature rise (by ~ 10 times)

**O, H and OH Density Evolution**

**Self-acceleration** of low temperature chemistry
- Addition of small amount of radicals accelerates the H abstraction step
- \( \text{RO}_2 \) produces more radicals which accelerate the whole process further

**Chemical Reactions**
- \( \text{R-H} \rightarrow \text{R} \rightarrow \text{RO}_2 \rightarrow \text{CH}_2\text{O, HO}_2, \text{H}_2\text{O}_2 \)
Nanosecond Plasma Ignition of nHeptane-Air
Effect of NS Pulses on Overall Ignition Delay Time

School of Aerospace Engineering

operating conditions

\[ P_i = 160 \text{ torr} \]
\[ T_i = 600 \text{ K} \]
\[ f = 60 \text{ kHz} \]
\[ \Phi = 1.0 \]
8 kV Gaussian pulses
10 ns duration

“staggered” application of NS pulses

only a few NS pulses sufficient to rapidly trigger 1st stage temperature rise

25 NS pulses are applied after the 1st stage to reduce the overall ignition delay

• the “staggered” application of NS pulses result in ~ 40% reduction in ignition delay time
• it is evident that the 2nd stage is less sensitive to radical addition by NS pulses than the 1st stage.
• heating provided by the NS pulses after the 1st stage accelerate the decomposition of H$_2$O$_2$ and reduce ignition delay.

\[
\text{H}_2\text{O}_2 + M \rightarrow \text{OH} + M
\]

• inclusion of NOX catalytic reactions change the predictions by ~5% because of following new OH generation pathways.

\[
\text{NO} + \text{HO}_2 \rightarrow \text{NO}_2 + \text{OH}
\]
\[
\text{NO} + \text{CH}_3\text{O}_2 \rightarrow \text{NO}_2 + \text{CH}_2\text{O} + \text{OH}
\]
Nanosecond plasma coupled premixed flame

**CH₄-air**

### School of Aerospace Engineering

#### physical setup

- Wiremesh HVE
- Flame
- Pulse Discharge Generator
- 2 cm premixed mixture

#### operating conditions

- Pressure: 25 torr
- Inlet Temperature: 650 K
- Eq. ratio: 1.07
- Gap width: 4.0 cm
- Initial Electron Density: $10^7$ cm⁻³
- -15 kV peak voltage
- 7 ns FWHM
- Mdot: 0.00377 kg/m²·s

### applied voltage

![Voltage waveform](image)

#### validation of flame model with CHEMKIN solution

- GRI Mech 3.0 + CH₄/N₂/O₂/CO/CO₂ plasma + NOX chemistry

#### CH₄-air plasma flame kinetics (75 species)

- electron impact processes of both reactant (CH₄, O₂, N₂) and product species (H₂O, CO, CO₂) considered.

- **Equations:**
  
  $N_2 + e \rightarrow N_2(A^3, B^3, C^3, a^1) + e$

  $O_2 + e \rightarrow O + O + e$

  $CO + e \rightarrow CO^* + e$

  $H_2O + e \rightarrow O^- + H_2$

- **Questions:**
  - what are most important plasma pathways pertaining to H₂O, CO, CO₂?
  - is plasma species production in preheat zone more important than downstream?
Plasma Coupled Premixed CH₄-Air Flame

\[ P_i = 25 \text{ torr}, \, T_i = 650 \text{ K}, \, \Phi = 1.07 \]

high E/N (100 - 600 Td) and high electron densities (~1e13 cm⁻³) allow for efficient radical generation by NS pulses in preheat zone, where they may provide significant benefit.

- high E/N downstream of the flame can be attributed to high temperatures and low number density.
- E/N in the preheat zone reaches ~ 600 Td at 22.5 ns. Plasma radical generation in this zone may have a significant impact on flame characteristics.
- sharp peak in the E/N profile at 20 ns at the right boundary indicates the cathode sheath region.
- electron density distribution is fairly uniform in the entire domain reaching peak value of \(2 \times 10^{13} \text{ cm}^{-3}\) at 27.5 ns.
- total input energy during the pulse was 2.7 mJ

note that radicals (O, H, OH etc) concentration in the flame zone is already of the order 10,000 ppm, so plasma cannot make much impact.

preheat zone
flame zone

20 ns
7.5 ns
17.5 ns
22.5 ns
the production rates of $N_2(A_3)$ and $N_2(B_3)$ in the preheat zone is about 2 times higher than downstream because of higher $N_2$ number density.

- electron impact dissociation of $O_2$ in the preheat zone results in $\sim$30 times increase in O atom density within 30 ns
- the excited species are quenched rapidly after the pulse resulting in further production of O and other radicals

ongoing work

- we are performing longer timescale simulations to understand the effect of repetitive application of discharge pulses on flame dynamics.
- the effect of NS discharges on H$_2$-air, CH$_4$-air and C$_2$H$_4$-air premixed flames are being investigated.
- close collaboration with OSU group is pursued for obtaining greater insight through experiments and high fidelity modeling
Where we go from here?

High fidelity 1D numerical tools for construction and validation of robust plasma combustion kinetic models

• detailed studies of the plasma coupled premixed flame system for a variety of fuels.
• development of the counterflow plasma flame simulation framework.
• close collaboration with other MURI team members for model validation and critical assessment of the plasma combustion kinetic models

2D/3D simulations of nonequilibrium plasma in complex flow environments

• High fidelity simulations of single filament discharge in 2D with detailed chemistry.
• Large Eddy Simulation (LES) of H₂ jet in supersonic O₂ crossflow in the presence of a nanosecond plasma source.
• theoretical framework to understand plasma-flow interactions.