Modeling and Simulation of Plasma-Assisted Ignition and Combustion

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To establish a comprehensive computational and theoretical framework capable of predicting the impact of nonequilibrium plasmas on ignition and combustion of premixed and non-premixed reacting mixtures.

- Multi-dimensional simulations of high-speed, low-pressure, and high-enthalpy flows.
- Multi-time scale modeling of detailed plasma/flame chemistry.
- Extensive validation using data from ignition and flame experiments with laminar flows.
- State-of-the-art turbulence closure schemes based on large-eddy simulation (LES) and direct numerical simulation (DNS) techniques.
1. **Further improvements in the discharge model** such as using exact experimental waveforms and comprehensive treatment of flow dynamics.

2. **Pulsed nanosecond dielectric barrier discharge (DBD) model development and validation** with 1D analytical results in N\(_2\) and experimental data in air.

3. **H\(_2\) -Air ignition simulations** with pulsed nanosecond DBD and comparison with OSU experimental ignition delay and OH measurements.

4. Effects of nanosecond plasma on a **burner stabilized H\(_2\) -air premixed flame**.
Survey of Nanosecond Plasma Models
1D dielectric barrier discharge

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1. Adamovich et al. (Phys. of Plasmas, 2009)
3. Poggie et al. (AIAA ASM meeting, 2012)

Model Features
- Drift diffusion assumption, single pulse simulation
- Chemistry Mechanism
  - Model 1 ($\text{N}_2$): two-species (positive ion, electron)
  - Model 2 (air): three-species (positive ion, negative ion, electron)
  - Model 3 (air): multiple species (15 species + 42 reactions)

Capabilities:
- Models 1 and 2 were used to study charge accumulation in boundary sheath, shielding of plasma and drop in gap voltage after breakdown. Ionization and energy deposition efficiencies in the sheath as compared to the quasi-neutral plasma region were explored.
- Principal goal of Model 3 was to study how input electrical energy is rapidly transformed (over roughly 1 ns) at breakdown into ionization products, dissociation products, and electronically excited particles, and how thermalization occurs over a relatively longer time-scale (roughly 10 $\mu$s). Bulk gas motion from rapid heating was studied using the momentum equation.

Constraints:
- No electron energy equation (electron energy assumed constant or function of E/N).
- Simplistic chemistry in Models 1 and 2. Production of active species during and after the applied voltage pulse cannot be calculated.
- Plasma fluid equations not coupled with gas conservation equations in Models 1 and 2.
- Cumulative effect of multiple pulses on plasma heating and radical production were not studied.
Survey of Nanosecond Plasma Models
2D simulations

Model Features and Capabilities

- **Drift diffusion assumption, single pulse simulations**
- Propagation of cathode streamers was studied with Model 1 in air in a wide range of pressures (300 - 760 torr) using relevant kinetics (7 species + 15 reactions) important in short timescales (25 ns).
- Parallel adaptive mesh refinement was demonstrated with Model 2. A simple 2-species chemistry model was used to simulate streamer propagation during a nanosecond pulse.
- The interaction of surface nanosecond discharges with supersonic premixed H₂ – O₂ flow of relevance to plasma assisted ignition and combustion was studied with Model 3. A single trapezoidal pulse of 10 ns with detailed chemistry (16 species + 87 reactions) was used to generate the discharge.

Constraints:

- No electron energy equation in Models 1 and 2. (electron energy assumed constant or function of E/N).
- Cumulative effect of multiple pulses on plasma heating and radical production were not studied in any model.

Plasma-Assisted Combustion Modeling Framework

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, $T_{gas}$.
- Electron transport and rates using two-term expansion for the electron Boltzmann equation (BOLSIG).
- Solution to the electron energy equation used to update electron coefficients at each time step.
- Uniform pre-ionization in the discharge volume. No photo-ionization source term.

Governing Equations

**Species Number Density**

$$\frac{\partial n_k}{\partial t} + \nabla \cdot J_k = S_k$$

$S_k = \sum_{i=1}^{N_k} R_{ik}$  \hspace{1cm} \text{source term from chemical reactions}$

$$J_k = q_k \mu_k n_k E - \nabla (D_k n_k) + n_k u_f$$

$k^{th}$ species flux \hspace{1cm} drift of charged species in electric field \hspace{1cm} diffusion term \hspace{1cm} convection term

$q_k$: charge number, +1 for positive ions, -1 for negative ions and electrons, 0 for neutral species.

**Electron Energy Density**

$$\frac{\partial n_e}{\partial t} + \nabla \cdot J_e = S_e ; n_e = n_e \bar{E}$$

$$J_e = -\mu_e n_e E - \nabla (D_e n_e) + n_e u_f$$

$$S_e = -(3k_B/e)n_e \nu_{el} (T_e - T_g) - \sum_{i=1}^{N_e} \Delta E_i R_{ie} - \bar{J}_e \cdot \bar{E}$$

$\Delta E_i$: heat of $i^{th}$ electron impact reaction (eV)

$n_e$: electron energy density (eVm$^{-3}$s$^{-1}$)
Plasma – Assisted Combustion Modeling Framework (Cont’d)

**Governing Equations**

### Electric Potential Equation

\[
\nabla.(\varepsilon \varepsilon_0 \nabla \varphi) = -e(n_+ - n_- - n_e)
\]

\[\vec{E} = -\nabla \varphi\]

**semi – implicit form of potential equation**

\[
\nabla.(\varepsilon \varepsilon_0 + e \mu_e n_e \Delta t) \nabla \varphi = -e(n_+ - n_- - n_e + \Delta t[\nabla^2 (D_e n_e) + S_e])
\]

\[n_e^{m+1} = n_e^m - \Delta t[\nabla.(\mu_e n_e \nabla \varphi)]^{m+1} - \Delta t[-\nabla^2 (D_e n_e) + \nabla.(n_e \vec{u}_j) - S_e]^m\]

- electron number density at (m+1)th time-step is estimated using species continuity equation
- It is plugged into RHS of Poisson equation for improved estimate of space charge density.
- Notice that as \(\Delta t \to 0\), original Poisson equation is obtained.
- This modification alleviates time-step restriction arising from strong coupling between electron density and electric field during breakdown.


### Flow Conservation Equations

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

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

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

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

\[\Omega = h - \frac{p}{\rho} + \frac{u_i u_j}{2} + e n_e\]

\[h = \rho \sum_k Y_k \{h_k^0 (T_{ref}) + \int_{T_{ref}}^{T} C_{p,k} (T')dT'\}
\]

\[\tau_{ij} = \mu_v \left( \frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i} - \frac{2}{3} \delta_{ij} \frac{\partial u_p}{\partial x_p} \right)
\]

\[q_j = -\lambda \frac{\partial T}{\partial x_j} + \rho \sum_k h_k Y_k U_{k,j} + J_e
\]

\[F_{EHD}^i = e E_i \left[ \sum_{k=1}^{N_p} (n_{+,k}) - \sum_{k=1}^{N_n} (n_{-,k}) - n_e \right]
\]

\[\dot{Q} = \sum_{k=1}^{N} q_k \vec{j}_k \cdot \vec{E}
\]
**Modeling of Plasma -- Assisted Combustion Closure of Governing Equations**

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**Electron Transport and Chemistry Closure** ($\mu_e, D_e, \mu_\varepsilon, D_\varepsilon, k_{ei}$):

- Solution of the Boltzmann equation (BOLSIG software) with two term expansion for an ensemble of electrons is used to obtain electron transport coefficients as functions of electron mean energy.

\[
\frac{\partial f}{\partial t} + v \cdot \nabla f - \frac{e}{m} E \cdot \nabla_f f = C[f]; \quad f(v, \cos \theta, z, t) = f_0(v, z, t) + f_1(v, z, t) \cos \theta
\]

- Boltzmann equation

\[
\mu_e = -\frac{(2e/m)^{1/2}}{3N} \int_0^\infty \frac{\epsilon}{\sigma_m} \frac{\partial F_0}{\partial \epsilon} d\epsilon
\]

- electron mobility

\[
D_e = \frac{(2e/m)^{1/2}}{3N} \int_0^\infty \epsilon F_0 d\epsilon
\]

- electron diffusion coefficient

\[
k_{ie} = (2e/m)^{1/2} \int_0^\infty \epsilon \sigma_k F_0 d\epsilon
\]

- electron impact reaction rate constants

**Graphs:**
- Electron transport coefficients
- Electron impact ionization coefficients for O$_2$ and N$_2$ in air
- Townsend ionization coefficient in N$_2$
Gas transport and thermodynamic properties:

- Species properties are expressed as polynomial functions of gas temperature.
- Electronically excited species for which data is not available are assumed to have same properties as ground state species.
- Ion mobilities are obtained from literature *, with diffusion coefficients calculated using Einstein relation.

Specific heat

\[ C_{p,k} = a_{0,k} + a_{1,k}T + a_{2,k}T^2 + a_{3,k}T^3 + a_{4,k}T^4 \]

Thermal conductivity

\[ \log(\lambda_k) = b_{0,k} + b_{1,k} \log(T) + b_{2,k} [\log(T)]^2 + b_{3,k} [\log(T)]^3 \]

Viscosity

\[ \log(\eta_k) = c_{0,k} + c_{1,k} \log(T) + c_{2,k} [\log(T)]^2 + c_{3,k} [\log(T)]^3 \]

Mixture viscosity and thermal conductivity

\[ \nu = \sum_{i=1}^{N} \frac{X_i \eta_i}{\sum_{j=1}^{N} X_j \phi_{ij}} ; \quad \lambda = \sum_{i=1}^{N} \frac{X_i \lambda_i}{\sum_{j=1}^{N} X_j \phi_{ij}} \]

Inter collision parameter

\[ \phi_{ij} = \frac{[1 + (\eta_i / \eta_j)^{1/2} (W_j / W_i)^{1/4}]^2}{[8(1 + W_i / W_j)]^{1/2}} \]

Turbulence Closure?

- Turbulence closure needs more groundwork, since plasma discharge turbulence interaction is poorly understood.
- For example, how do electric field fluctuations affect velocity fluctuations and temperature fluctuations?
Nanosecond Plasma Assisted Ignition and Combustion
Multi-Scale Challenges in Modeling

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PLASMA DISCHARGE DYNAMICS

- Plasma Chemistry
  - Ionization, Excitation, Dissociation, and Recombination

FLOW AND COMBUSTION DYNAMICS

- Ignition and Combustion Chemistry
  - Radical initiation, Chain propagation and termination, Fuel oxidation

Time

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

µs
- Quenching of excited species
- Ion recombination
- Gas heating

ms
- Cumulative effects of multiple discharge pulses
- Convective and diffusive transport
- Ignition and combustion

Solution Algorithm

- Calculate electric field
  - Implicit LU decomposition
- Calculate electron energy
  - Implicit GMRES method
- Update electron and gas transport coefficients

solve plasma species and flow conservation equations
- 2nd order Strang splitting method
- Explicit RK4 for convection – diffusion.
- Implicit dense matrix solver for stiff source term integration.

- Time-step during breakdown of order of $10^{-13}$ s. Simulation over multiple pulses at this time-step is infeasible.
- Necessary to use combination of implicit and explicit methods which reduce parallel computational efficiency.
- Stiff source terms and large plasma chemistry mechanisms result in computationally intensive Jacobian evaluations at every time-step at every grid point.
- Resolution of cathode sheath requires grid spacing of order of 10 µm.
Nanosecond Plasma Assisted Ignition and Combustion
Model Improvements for Better Computational Efficiency

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- $\Delta t$ varied between $10^{-13}$ s - $10^{-12}$ s
- A semi-implicit version of Poisson equation is used in order to alleviate 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 goes to zero.

Multi Time-Scale Treatment of Chemical Source Term*

- Speed up of upto 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.
- The stiff electron continuity and energy equations during breakdown (in each pulse) use a large fraction of the CPU time. Increase in pulsing frequency reduces the savings in CPU time.
- 2D and 3D simulations will examine the advantages of the multi time-scale scheme in more detail.

Gou et al., Combustion and Flame 157 (2010) 1111–1121
ICCD images of discharge structure

Front View
Air : 373 K, 60 torr, 40 kHz

Side View
H₂ - Air : 40 kHz

C₂H₄ - Air : 40 kHz
Discharge appears to be non-uniform at room temperature and low pulsing frequencies, especially from front view.

Preheating (about 100 °C – 200 °C) has been demonstrated to improve uniformity, as seen in OSU experiments.

Is discharge uniformity determined by diffusion rates of residual charges for pulsed mode operation?

At what pressure and temperature can we assume uniformity for modeling purposes?

Need more analysis and self-consistent 2D modeling to get conclusive answers.
Pre – heating has been demonstrated to improve discharge uniformity in H₂ – air, CH₄ – air and C₂H₄ – air mixtures.

A 1D model is sufficient to describe the breakdown physics, and detailed chemical pathways self-consistently for volume filling NS – DBD in 50 torr – 100 torr.

The dielectric shielding effect is modeled self-consistently by solving for the gap voltage using below equation (Poisson equation boundary condition)

\[ \frac{dV_{app}}{dt} = (1 + \frac{2l}{\varepsilon L}) \frac{dV_{gap}}{dt} - \frac{2le}{\varepsilon_0 \varepsilon L} \int_0^L (J_+(x,t) - J_-(x,t) - J_e(x,t))dx \]

Boundary Conditions

\[ \bar{J}_{+,s} \cdot \hat{n}_s = \frac{1}{4} n_+ \left( \frac{8k_BT_g}{\pi m_+} \right)^{\frac{1}{2}} + a \mu_+ n_+ \bar{E} \cdot \hat{n}_s \]

\[ \bar{J}_{-,s} \cdot \hat{n}_s = \frac{1}{4} n_- \left( \frac{8k_BT_g}{\pi m_-} \right)^{\frac{1}{2}} + (a-1) \mu_- n_- \bar{E} \cdot \hat{n}_s \]

\[ \bar{J}_{e,s} \cdot \hat{n}_s = \frac{1}{4} n_e \left( \frac{8k_BT_e}{\pi m_e} \right)^{\frac{1}{2}} - a \sum_k \gamma \bar{J}_{+,s}; \cdot \hat{n}_s + (a-1) \mu_e n_e \bar{E} \cdot \hat{n}_s \]

\[ \bar{J}_{e,s} \cdot \hat{n}_s = (\frac{5}{2} k_BT_e) \left[ \frac{1}{4} n_e \left( \frac{8k_BT_e}{\pi m_e} \right)^{\frac{1}{2}} + (a-1) \mu_e n_e \bar{E} \cdot \hat{n}_s \right] - a (\frac{5}{2} k_BT_{se}) \sum_k \gamma \bar{J}_{+,s} ; \cdot \hat{n}_s \]

\[ a = 1 \text{ if } E.n < 0, \text{ and } a = 0 \text{ otherwise} \]
Ion Joule heating during discharge pulse occurs close to the cathode boundary. Heat transfer at the gas-dielectric interface need to analyzed to obtain an accurate boundary condition for the gas energy equation.

At the gas-dielectric interface, \(-k_{\text{gas}}(dT/dx) = -k_{d}(dT/dx)\)
Assuming dielectric is a semi-infinite solid,
1. Constant heat flux boundary condition gives
   \[ T_b(t) = \frac{(T_0 + G(t)*T_1)/(1 + G(t))}{1} \]
2. Constant temperature boundary condition gives
   \[ T_b(t) = \frac{(T_0 + 0.5*G(t)*T_1)/(1 + 0.5*G(t))}{1} \]

where, \( G(t) = \frac{4k_{\text{gas}} \sqrt{\left(\alpha_d t / \pi \right)}}{k_d \Delta x} \)

Heat Transfer parameter, \( G \) is negligibly small (less than 0.1) until ~2 ms, which indicates that the boundary is in reality closer to isothermal than adiabatic conditions.
1D Nanosecond DBD Model Validation

i. Comparison with quasi-1D analytical model results (Adamovich et al. 2009) in N$_2$ at 60 torr and 300 K.

ii. Comparison with the OSU plasma flow reactor measurements of coupled pulse energy, O atom concentration and temperature in air.
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Quasi-1D Analytical Model (Adamovich et al. 2009)

Model Geometry

- plasma fluid equations for a positive ion and electron under drift-diffusion approximation are used along with Poisson equation for electric field in one-dimension.
- Further simplifications are made by neglecting electron-ion recombination and ion motion for discharge timescales (ns).
- simple time-dependent equations are obtained for electric field in sheath \( n_e \approx 0 \), \( E_s \) and electric field in quasi-neutral plasma \( n_e \approx n_+ \), \( E_p \).
- the model demonstrates that the coupled energy is primarily a function of breakdown voltage and capacitance of dielectric layers and it is directly proportional to number density.
- closed form expressions are obtained for time-dependent electric field and electron density in plasma, electric field in sheath, sheath boundary location and coupled pulse energy.

\[
\frac{\partial n_+}{\partial t} + \frac{\partial \Gamma_+}{\partial x} = v_i n_e - \beta n_+ n_e ; \quad \Gamma_+ = \mu_+ n_+ E - D_+ \frac{\partial n_+}{\partial x}
\]

\[
\frac{\partial n_e}{\partial t} + \frac{\partial \Gamma_e}{\partial x} = v_i n_e - \beta n_+ n_e ; \quad \Gamma_e = -\mu_e n_e E - D_e \frac{\partial n_e}{\partial x}
\]

\[
\frac{\partial^2 \phi}{\partial x^2} = -\frac{e}{\varepsilon_0} (n_+ - n_e) ; \quad E = -\frac{\partial \phi}{\partial x}
\]

\[
Q_{\text{pulse}} \approx \frac{1}{2} C \left[ V_b^2 + V_{\text{peak}}^2 \frac{\sqrt{2\pi}}{(\tau/RC)} \right] = \frac{1}{2} \frac{\varepsilon_d \varepsilon_0 A}{2l_d} \left[ V_b^2 + V_{\text{peak}}^2 \frac{\sqrt{2\pi}}{(\tau/RC)} \right]
\]
The present model predicts well with analytical results obtained by Adamovich et al. (2009, Phys. Plasma).

just after breakdown (92 ns), positive charge accumulation on dielectric layer near right electrode shields the discharge volume from further rise in applied voltage, resulting in sharp drop in field in plasma.

The analytical model uses experimental curve fits for electron transport and ionization rates, whereas the present model uses BOLSIG solution. This may explain differences in predictions for coupled energy and field in the cathode sheath.
Coupled energy predicted by the present model is within 20% of experimental data.
Coupled energy remains fairly constant with the pulse number, slightly decreasing beyond pulse #50 with noticeable rise in temperature.
Both temperature and O atom predictions agree well with measurements. Temperature rise in the discharge volume is about 0.5 K – 1 K/pulse in air.

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.
1D Nanosecond DBD model detailed predictions in air

Operating Conditions:
- Initial Pressure: 60 torr
- Initial Temperature: 300 K
- Pulsing Frequency: 40 kHz
- Gap width: 1 cm
- Initial Electron Density: $10^7$ cm$^{-3}$
- Dielectric thickness: 1.75 mm
- Dielectric Constant: 4.3
- Pulse Duration: 100 ns, FWHM: 12 ns
- Peak Voltage: -22.5 kV and +17.5 kV

Model Geometry

Applied Waveform
Plasma Air Chemistry Mechanism Sensitivity Study

**Operating Conditions:**
- Pressure: 60 torr
- Temperature: 300 K
- Gap width: 1 cm
- Initial Electron Density: $10^7$ cm$^{-3}$
- Dielectric thickness: 1.75 mm
- Dielectric Constant: 4.3
- Pulse Duration: 24 ns, FWHM: 5 ns
- Peak Voltage: 20 kV

**Model Geometry**

**Full chemistry mechanism:** 41 species, 485 reactions
- $\text{N}_2$, $\text{N}_2(\text{A}^3)$, $\text{N}_2(\text{B}^3)$, $\text{N}_2(\text{C}^3)$, $\text{N}_2(\text{a}^1)$, $\text{N}$, $\text{N}^{(2\text{D})}$, $\text{N}^{(2\text{P})}$, $\text{O}_2$,$\text{O}_2(\text{a}^1)$, $\text{O}_2(\text{b}^1)$, $\text{O}_2(\text{X})$, $\text{O}$,$\text{O}^{(1\text{D})}$, $\text{O}^{(1\text{S})}$, $\text{N}^+$, $\text{N}_2^+$, $\text{N}_3^+$, $\text{N}_4^+$, $\text{O}^+$, $\text{O}_2^+$, $\text{O}_4^+$, $\text{NO}^+$, $\text{N}_2\text{O}^+$, $\text{NO}_2^+$, $\text{O}_2^+\text{N}_2$, $\text{O}^-$, $\text{O}_2^-$, $\text{O}_3^-$, $\text{O}_4^-$, $\text{NO}^-$, $\text{N}_2\text{O}^-$, $\text{NO}_2^-$, $\text{NO}_3^-$, $\text{O}_3$, $\text{NO}$, $\text{N}_2\text{O}$, $\text{NO}_2$, $\text{NO}_3$, $\text{N}_2\text{O}_5$, $e$

**Reduced Mechanism:** 21 species, 176 reactions
- $\text{N}_2$, $\text{N}_2(\text{A}^3)$, $\text{N}_2(\text{B}^3)$, $\text{N}_2(\text{C}^3)$, $\text{N}_2(\text{a}^1)$, $\text{N}$, $\text{N}^{(2\text{D})}$, $\text{O}_2$,$\text{O}_2(\text{a}^1)$, $\text{O}_2(\text{b}^1)$, $\text{O}$,$\text{O}^{(1\text{D})}$, $\text{O}^{(1\text{S})}$, $\text{N}_2^+$, $\text{N}_4^+$, $\text{O}_2^+$, $\text{O}_4^+$, $\text{O}_2^-$, $\text{O}_3$, $\text{NO}$, $e$
positive and negative space charge accumulation at the cathode and anode sheath boundaries respectively causes the gap voltage to drop and field in the plasma rapidly falls to zero after primary breakdown.

- electrode polarities reverse during the voltage pulse due to bipolar nature of the applied waveform.
- approximately 30% of pulse energy is coupled in the two secondary peaks of E/N. Most of this energy goes into vibrational excitation since E/N < 100 Td.
- We have not considered vibrationally excited species in chemistry model since experimental measurements have shown vibrational temperature is low (~1200 K) for this discharge configuration.
Electron Density and Energy Evolution
(Air Discharge, 60 torr, 300 K)

• electron density is fairly uniform over the entire volume after breakdown ~ $2 \times 10^{12} \text{ cm}^{-3}$, except near the edge of cathode sheath layer where it reaches values of $4 \times 10^{13} \text{ cm}^{-3}$.
• however electron density rapidly drops in the cathode sheath, which is ~ 0.1 mm in thickness.

• electron energy in quasi-neutral plasma is about 10 eV during breakdown, which results in rapid ionization and electronic excitation through electron impact reactions.
• In the sheath near right electrode, electron energy peaks at 70 eV resulting in rapid gas heating.
By the end of the voltage pulse, $N_2^+$ is almost completely transformed to $N_4^+$ via three-body reaction and to $O_2^+$ via following charge exchange reaction:

\[ N_2^+ + N_2 + M \rightarrow N_4^+ + M \]
\[ N_2^+ + O_2 \rightarrow O_2^+ + N_2 \]

Decay of electron density occurs primarily through dissociative recombination of $O_2^+$ and $N_2^+$ and attachment reactions with $O_2$ forming $O_2^-$:

\[ O_2^+ + e \rightarrow O + O \]
\[ N_2^+ + e \rightarrow N + N \]
\[ e + O_2 + O_2 \rightarrow O_2^- + O_2 \]

Electronically excited $N_2$ during the initial breakdown phase is produced via electron impact excitation.

Quenching of these excited species by $O_2$ is an important pathway for production of ground state and excited oxygen atoms, given in the following equation:

\[ N_2(A^3, B^3, C^3, a^1) + O_2 \rightarrow N_2 + O + O(^1D, ^4S) \]
Atomic oxygen is mainly produced via electron impact dissociation of $O_2$ during the voltage pulse and quenching of excited $N_2$ after the pulse.

- **O atom production**
  - $44\%$: $O_2 + e \rightarrow O + O(\overset{1}{D}, \overset{4}{S}) + e$
  - $56\%$: $N_2(A^3, B^3, C^3, a^1) + O_2 \rightarrow N_2 + O(\overset{1}{D}, \overset{4}{S})$

Formation of ozone via three - body reaction is one of the primary destruction pathways for O atom. The other two - body reaction becomes dominant when sufficient ozone is present in the mixture (after 2 ms).

- $O_2 + O + M \rightarrow O_3 + M$
- $O_3 + O \rightarrow O_2 + O_2$
Ion Joule heating results in rapid heating during voltage pulses.
Note that this Joule heating occurs only for ~3 ns after primary breakdown.
Joule heating is observed at both boundaries due to bipolar nature of the voltage pulse and switching of electrode polarities in between the pulse.
Plasma Heating Mechanism (long timescales)
(Air Discharge, 60 torr, 300 K, 40 kHz)

- Plasma heating effect is about 0.5 K – 1 K/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.

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Wall heat loss in time gap between voltage pulses

Heating rates in cathode layer during a voltage pulse

Uniform “hat shaped” temperature profile after ~100 pulses
Summary of NS DBD model results in air

- A self-consistent 1D model of pulsed nanosecond dielectric barrier discharges has been established and validated against experimental measurements in air and analytical results in N₂.
- Significant heating rates (upto 40 K/pulse) are observed in sheath layer near electrode boundaries during breakdown due to Ion Joule effect. However, heat losses in time gap between the discharge pulses effectively remove all this thermal energy.
- 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.
preheated H₂ – Air Ignition with pulsed nanosecond DBD

Model Geometry

Operating Conditions:
- Gap width: 1 cm
- Initial Electron Density: $10^7$ cm$^{-3}$
- Dielectric thickness: 1.75 mm
- Dielectric Constant: 4.3
- Pulse Duration: 100 ns, FWHM: 12 ns
- Peak Voltage: -22.5 kV and +17.5 kV

Applied Waveform

H₂ – Air Plasma Combustion Chemistry (Popov, 2008 and Adamovich, 2009)
(35 species, 248 reactions)

N₂, N₂(A³), N₂(B³), N₂(a¹), N₂(C³), N, N(2D), N₂+, N₄+, O₂, O₂(a¹), O₂(b¹), O, O(1D), O(1S), O₃, O₂+, O₄+, O₂-, H₂, H, H₂(a³), H₂(b³), H₂⁺, H₃⁺, HO₂⁺, HN₂⁺, H₃O⁺, NH, NO, OH, HO₂, H₂O₂, H₂O, E
• Input energy during the voltage pulse is 0.26 meV/molecule.
• 60 % of the energy is coupled before 40 ns, most of which is spent in ionization, electronic excitation and dissociation, since E/N ~ 400 - 700 Td in the plasma volume.
• HN$_2^+$ is the dominant positive ion in H$_2$ - air mixture, formed via N$_2^+$, N$_4^+$ and H$_3^+$ ions during the discharge pulse. Its concentration starts dropping when significant H$_2$O formation occurs after ~ 0.1 ms leading to formation of H$_3$O$^+$.

$$N_2^+ + H_2 \rightarrow HN_2^+ + H ; N_4^+ + H_2 \rightarrow HN_2^+ + H + N_2$$

$$H_3^+ + N_2 \rightarrow HN_2^+ + H_2 ; HN_2^+ + H_2O \rightarrow H_3O^+ + N_2$$
• OH is a key radical primarily produced by a NS discharge via following pathways

\[
R1 \quad O(^1D) + H_2 \rightarrow OH + H \\
R2 \quad H + HO_2 \rightarrow OH + OH \\
R3 \quad O + H_2 \rightarrow OH + H
\]

Dominant pathway for H and OH production from low temperature (300 K - 600 K) plasma, when R3 is slow (Popov, 2008)

• OH decay through reaction with H_2 is one of the main pathways for water formation

\[
R4 \quad OH + H_2 \rightarrow H_2O + H
\]

• Model predictions of OH compare reasonably well with measurements. Uncertainties in measurements and uncertainties in rate constants of key chain reactions, and 3D discharge structure (though fairly uniform) may be main reasons for departure.
Species evolution in plasma volume
(x = 0.5 cm location)

- Repetitive pulsing results in efficient production of key radicals such as O, H and OH, which leads to rapid production of H\textsubscript{2}O reaching ~ 0.1 % mole fraction by 1 ms.
- O atom is produced, as in air, primarily via electron impact dissociation during voltage pulses, and when excited N\textsubscript{2} species are quenched by O\textsubscript{2}.
- O(\textsuperscript{1}D) is the key excited species produced by the discharge which reacts rapidly with H\textsubscript{2} to give OH and H. This pathway dominates over electron impact dissociation and quenching of excited N\textsubscript{2} by H\textsubscript{2}, for H atom production.
Primary OH atom production pathways at x = 0.5 cm for nanosecond DBD in H₂-air

\[ O + H_2 = OH + H \]
\[ H + HO_2 = OH + OH \]
\[ O(1D) + H_2 = OH + H \]

Primary H₂O production pathways at x = 0.5 cm for nanosecond DBD in H₂-air

\[ H + HO_2 = H_2O + O \]
\[ OH + H_2 = H_2O + H \]
\[ OH + HO_2 = H_2O + O_2 \]
\[ OH + OH = H_2O + O \]

\[ R4 \quad OH + H_2 \rightarrow H_2O + H \]

Most important pathway for H₂O formation in low temperature plasmas

- Note that reaction of OH with HO₂ which is very important for high temperature combustion chemistry plays only a minor role here, especially at smaller timescales.
Nanosecond - DBD in H₂ - Air
Repetitive Pulsing (104 torr, 373 K, 15 kHz, φ = 1)

- Repetitive pulsing results in uniform generation of active species such as O, OH and H.
- Uniform species and temperature profiles provide strong evidence for volumetric ignition in the entire volume by non-thermal plasmas as opposed to traditional “hot-spot ignition” by spark igniters.
Ignition delay of H₂ - air mixture subjected to nanosecond DBD has been calculated for pressures between 40 torr - 100 torr, and equivalence ratios between 0.4 - 1.4.

The model predictions of ignition time and temperature at different equivalence ratios and pressures agree well with experimental measurements.

Ignition delay dependence on equivalence ratio is more pronounced at lower pressures. At 84 torr, ignition delay at $\phi = 0.4$ is 7.5 ms, with minimum value of 6.5 ms at $\phi = 0.8$. It is nearly independent of equivalence ratio at 104 torr.

Decrease in ignition delay with pressure is more drastic at 373 K initial temperature, than at 473 K.
H₂ – Air Ignition with pulsed nanosecond DBD
60 torr, 100 kHz, 600 K, φ = 1

- Ignition is observed at about 0.48 ms after 48 voltage pulses. It is consistent with experimental data (ignition at 40 kHz, 60 torr, 473 K achieved after ~ 250 pulses)
- Operating at high pulsing frequency combined with higher initial temperature of 600 K results in rapid ignition.
- Ignition occurs over the entire volume simultaneously except near the electrodes where heat loss keeps the temperature low.

Main channels for H formation from plasma:

O(^{1}D) + H₂ → H + OH
H₂ + e → H + H + e
N₂(A³) + H₂ → H + H + N₂

Main channels for O formation from plasma:

O₂ + e → O + O + e
N₂(A³) + O₂ → O + O + N₂

Subsequent oxidation to form water:

OH + HO₂ → H₂O + O₂
OH + OH → H₂O + O
OH + H₂ → H + H₂O
Summary of Nanosecond DBD assisted H$_2$ - air ignition results

School of Aerospace Engineering

- 1D simulations of NS - DBD in preheated H$_2$ - air mixtures demonstrate that ignition occurs nearly simultaneously in the entire plasma volume owing to uniform temperature profiles from plasma chemical heat release.

- The H$_2$ -air chemistry model consisting of 35 species and 248 reactions has been validated against ignition delay, and OH LIF measurements.

- O($^{1}$D) is the key excited species produced by the discharge which leads to efficient production of H and OH at low temperatures.

- With repetitive pulsing, plasma heating rate of ~ 2K/pulse is observed which accelerate the chain branching process and production of H$_2$O.

- The key chemical pathways identified in H2 - air ignition with plasma should be expected to play important roles in ignition and combustion of hydrocarbon fuels as well.
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Objective:
Study the two – way coupling between nanosecond plasma and premixed laminar flame structure.

OSU Experiment

Facility

Burner Configurations

Schematic

low pressure flat flame

“direct coupled” configuration

“plasma upstream” configuration

Plasma off

Plasma ON

Plasma off

Plasma ON
**Plasma Flame Interaction**

**Simulation Methodology**

“direct coupled”

**Model Geometry**

- CHEMKIN data is used as initial conditions for plasma discharge – flame solver.
- Water based cluster ions (H₃O+, H₂O+, O₂+H₂O, H₃O+(H₂O), H₃O+(H₂O)₂, H₃O+(H₂O)₃) have been included in plasma flame chemistry, since water is present in significant quantity in combustion products.
- High temperature of combustion products can be expected to reduce energy coupled during discharge pulses.
- This modeling effort compliments the OSU experiments with the Mckenna flat flame burner - plasma discharge platform.

**CHEMKIN simulation, H₂ – air (100 torr, φ = 1, (pu)ᵢₙ = 0.005 g/cm²-s )**

H₂ – Air Plasma Flame Chemistry (40 species, 274 reactions) (Popov, 2008 + Adamovich, 2009 + Alexandrov, 2010)

N₂, N₂(A3), N₂(B3), N₂(a⁻¹), N₂(C3),N, N(2D), N₂+, N₄+, O₂, O₂(a¹), O₂(b¹), O, O(¹D), O(¹S), O₃, O₂+, O₄+, O₂⁻, H₂, H, H₂(a3), H₂(b3), H₂⁺, H⁺, HO₂⁺, HN₂⁺, NH⁺, NO⁺, OH⁻, HO₂, H₂O₂, H₂O, H₃O⁺, H₂O⁺, O₂+H₂O, H₃O+(H₂O), H₃O+(H₂O)₂, H₃O+(H₂O)₃, E
A negative polarity Gaussian waveform of 8 kV peak voltage was applied to the top electrode.

The energy coupled to the plasma was 0.98 mJ/pulse. Note that the discharge volume is much bigger ~98 cm², as compared to flow reactor. Hence, energy coupled at each cross section is lower.

Peak E/N at the center of plasma volume is ~340 Td.

Discharge structure is not as homogeneous as in nanosecond DBD due to rather large variations in temperature, and species densities along the axis.
dominant charge species evolution at x = 1 cm from burner exit

spatial profiles of $H_3O^+(H_2O)_3$ and $HN_2^+$ in the discharge domain

spatial profiles of excited $N_2$ species and $O(^1D)$

- Note that $H_3O^+(H_2O)_3$ is the dominant positive ion in regions where water is present in significant mole fraction.
- It's formed through the three-body reaction, which can be an important source of plasma heating:

$$H_3O^+(H_2O)_2 + H_2O + M \rightarrow H_3O^+(H_2O)_3 + M$$

- It can be a contributor to H atom production through the recombination reaction:

$$H_3O^+(H_2O)_3 + e \rightarrow H + 4H_2O$$

- The nature of charge distribution in the domain is very peculiar because of large variation in species composition across the flame.
- To the left, the plasma develops like in a $H_2$ - air mixture with $HN_2^+$ being the dominant positive ion.
- As we move across the flame, increase in water concentration results in $H_3O^+(H_2O)_3$ being the dominant positive ion.
A small temperature rise of 3 - 4 K is seen mainly in between \( x = 0 \) cm and \( x = 1 \) cm. The heat release from quenching of excited species generated by plasma is able to increase the temperature in the pre-heat zone, but not much downstream of the flame. H atom mole fraction shows about 1% increase at \( x = 0.8 \) cm from the burner exit. It is presently unclear if this is due to the temperature rise or if it’s a non-thermal effect.
Further Studies

plasma flame interaction

• Multiple discharge pulse simulations of H$_2$ – Air burner stabilized flame to develop deep insight into plasma flame interactions.

• Formulate strategies to decouple and study chemical effects of discharge vs. thermal effects.

• CH$_4$ – Air burner stabilized flame plasma model is being setup to make direct comparison with OSU experiments and identify thermal and non-thermal effects of plasma on flame structure.

2D discharge simulations

• 2D plane – plane discharge simulations with detailed chemistry in air and H2 – Air to study and identify key parameters affecting discharge non-uniformity.

• 2D single filament nanosecond discharge simulation at 1 atm. and higher pressures with special focus on vibrational non-equilibrium.
Derivation of semi–implicit form of electric potential equation

\[
\frac{\partial n_e}{\partial t} + \nabla \cdot \vec{J}_e = S_e
\]

electron continuity equation

\[
\vec{J}_e = -\mu_e n_e \vec{E} - \nabla (D_e n_e) + n_e \vec{u}_f ; \vec{E} = -\nabla \varphi
\]

electron continuity flux and electric field

\[
\frac{n_e^{m+1} - n_e^m}{\Delta t} = -[\nabla \cdot \vec{J}_e - S_e]^{m+1}
\]

electron density estimate at \((m+1)\)th timestep

\[
n_e^{m+1} \approx n_e^m - \Delta t[\nabla (-\mu_e n_e \vec{E})]^{m+1} - \Delta t[\nabla (-\nabla (D_e n_e) + n_e \vec{u}_f) - S_e]^m
\]

\[
n_e^{m+1} = n_e^m - \Delta t[\nabla (\mu_e n_e \nabla \varphi)]^{m+1} - \Delta t[-\nabla^2 (D_e n_e) + \nabla (n_e \vec{u}_f) - S_e]^m
\]

Poisson equation for electric potential

\[
\nabla (\varepsilon_0 \nabla \varphi)^{m+1} = -e(n_+ - n_- - n_e)^{m+1}
\]

improved estimate of RHS of Poisson equation

\[
-e(n_+ - n_- - n_e)^{m+1} \approx -e(n_+ - n_-)^m + e(n_e)^m
\]

\[
-e(n_+ - n_- - n_e)^{m+1} \approx -e(n_+ - n_-)^m + e n_e^m - e \Delta t[\nabla (\mu_e n_e \nabla \varphi)]^{m+1} - e \Delta t[-\nabla^2 (D_e n_e) + \nabla (n_e \vec{u}_f) - S_e]^m
\]

\[
\nabla (\varepsilon_0 \nabla \varphi)^{m+1} = -e(n_+ - n_- - n_e)^m - e \Delta t[\nabla (\mu_e n_e \nabla \varphi)]^{m+1} - e \Delta t[-\nabla^2 (D_e n_e) + \nabla (n_e \vec{u}_f) - S_e]^m
\]

\[
\nabla ([\varepsilon_0 + e \Delta t \mu_e n_e] \nabla \varphi)^{m+1} = -e(n_+ - n_- - n_e)^m - e \Delta t[-\nabla^2 (D_e n_e) + \nabla (n_e \vec{u}_f) - S_e]^m
\]

final semi–implicit form of electric potential equation
Fraction of electron power going into different energy modes