Development of a Novel Supersonic Hybrid Non-equilibrium Plasma Reactor for Efficient and Tunable Co-Production of Hydrogen and Value-Added Solid Carbons

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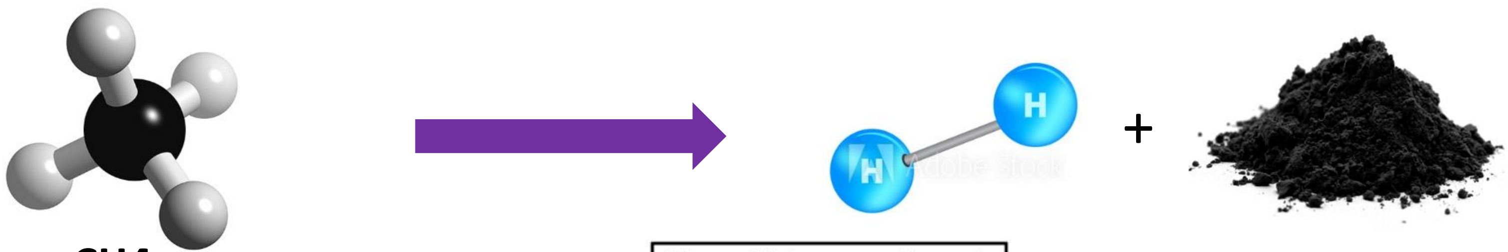
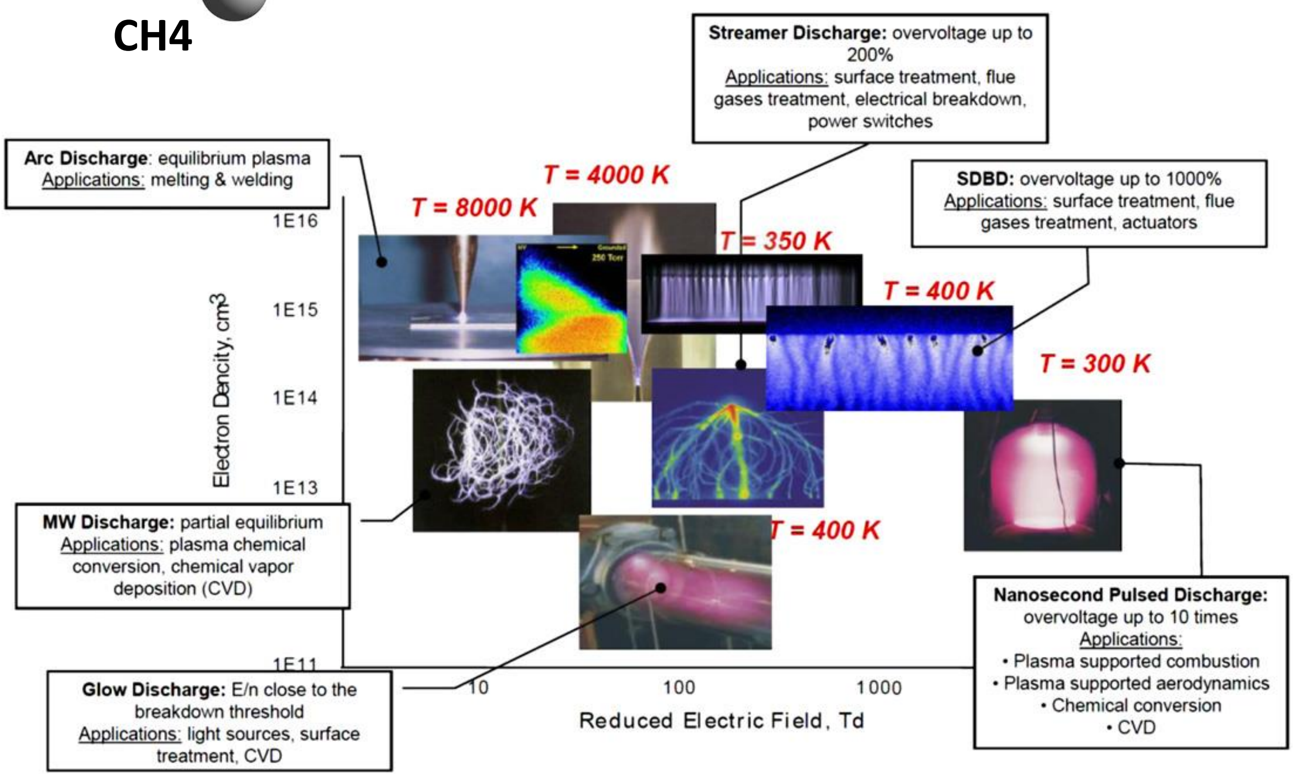
Objective

Develop an innovative supersonic non-equilibrium plasma reactor for efficient and tunable production of hydrogen and solid carbons from methane.



CH4



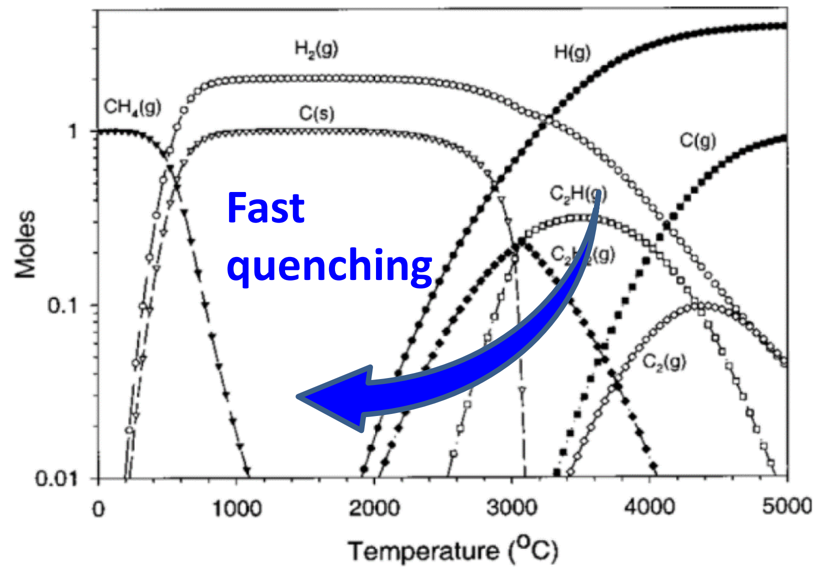
Idea: N.E. Plasma + supersonic quenching

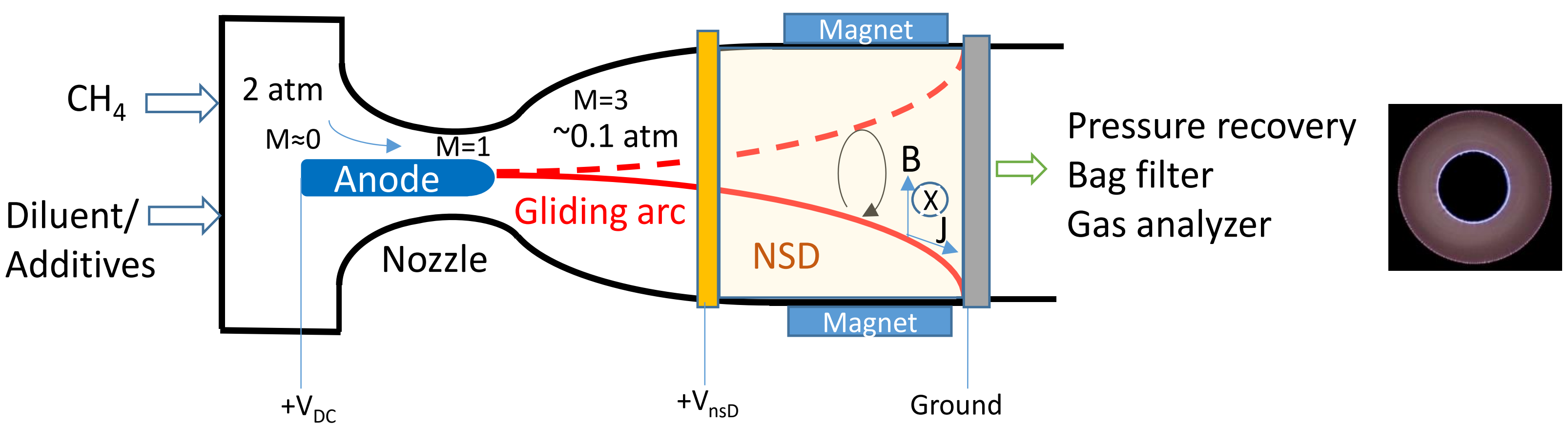
Using non-equilibrium plasma and rapid quenching to achieve high selectivity, controllability, and yield

Equilibrium synthesis
- High temperature, low selectivity
- Low temperature, low yield

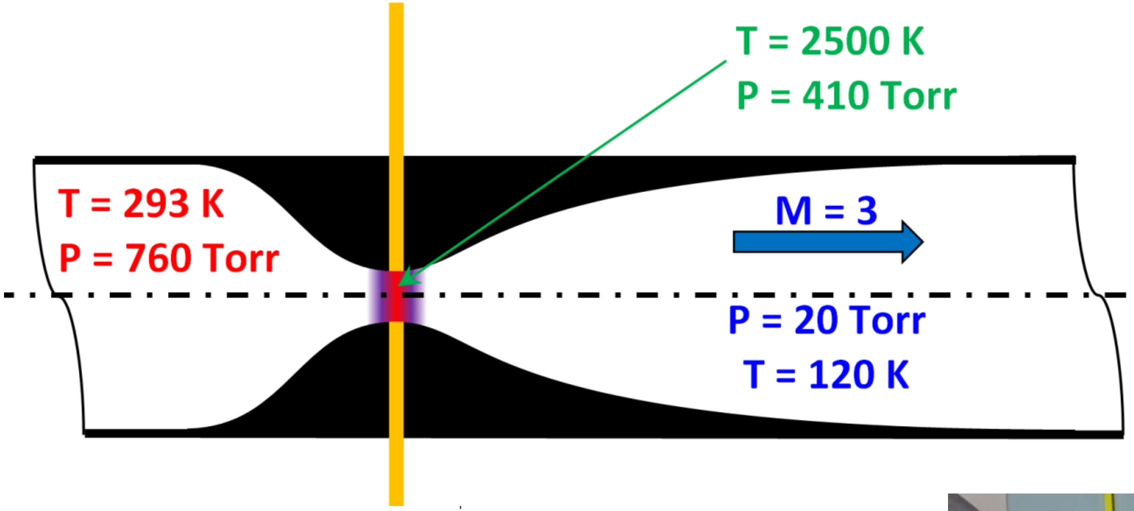
Shifting Equilibrium
- Supersonic nozzle for fast quenching

Non-equilibrium plasma synthesis
- High electron temperature: reactivity
- Lower temperature: high selectivity
- High electron number: high yield
- Supersonic flow: high plasma uniformity, fast reaction quenching, high throughput

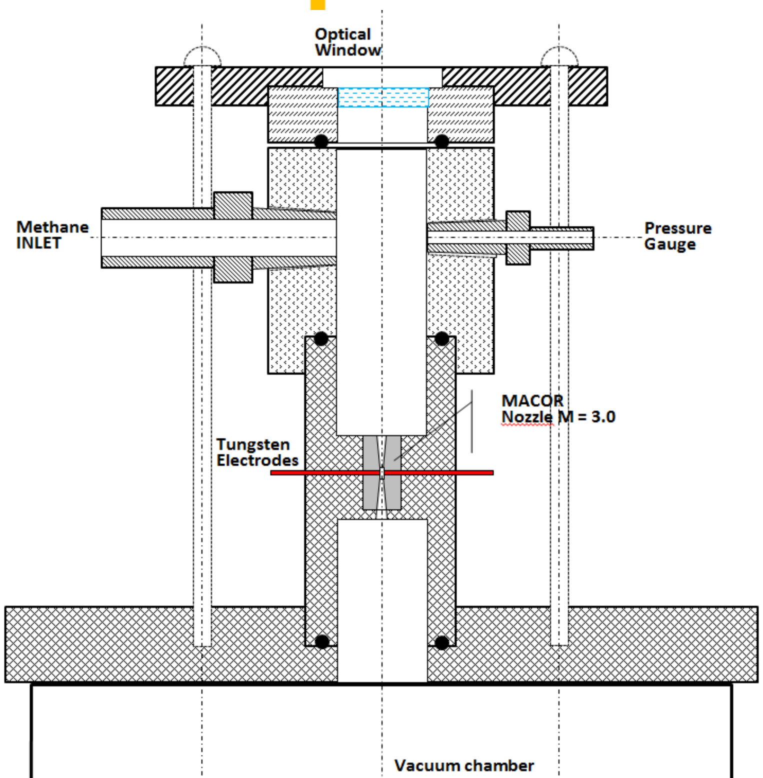


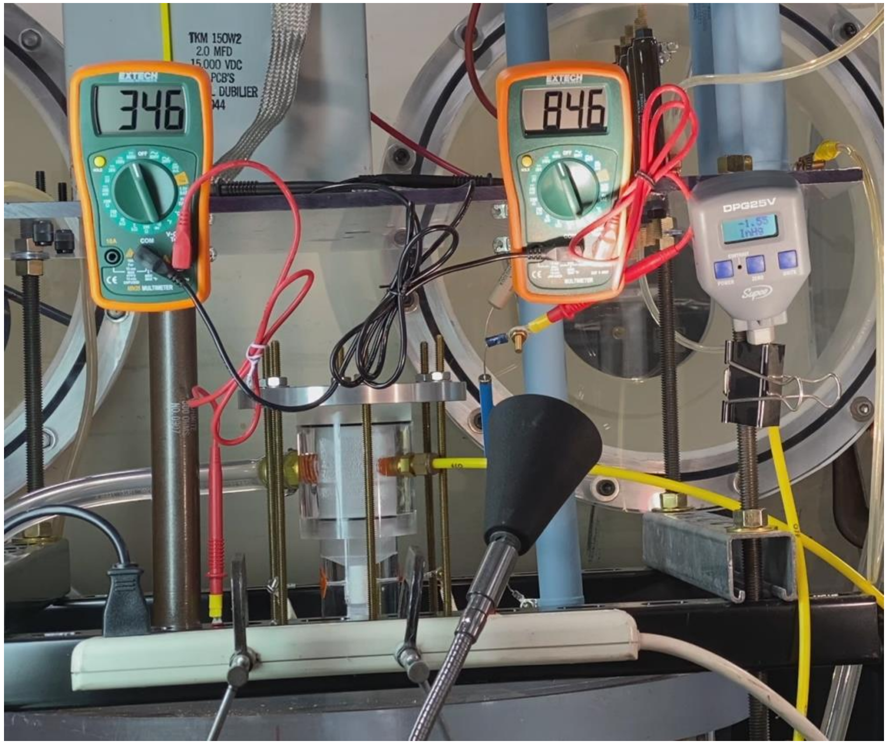


Reactor design and development

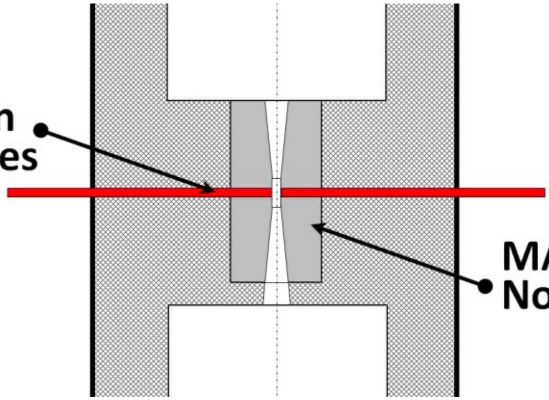


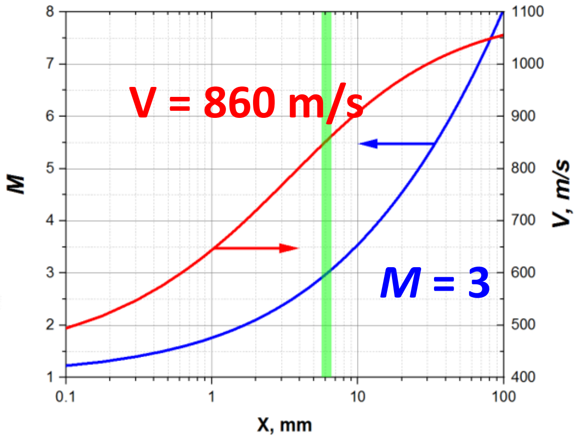
- Nozzle diameter d_0: 1.3 mm,
- Nozzle exit d_e: 3.2 mm,
- Nozzle length: 2 mm + 7 mm
- Nozzle residence time: 8 µs
- Mach number: 3

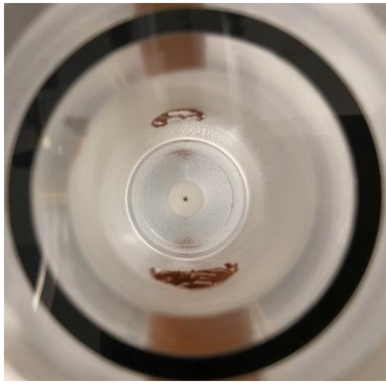




ns-Periodic Discharge Development in Supersonic Methane Flow

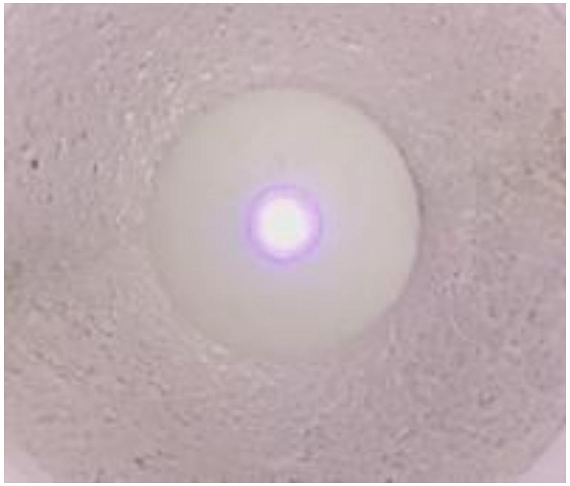


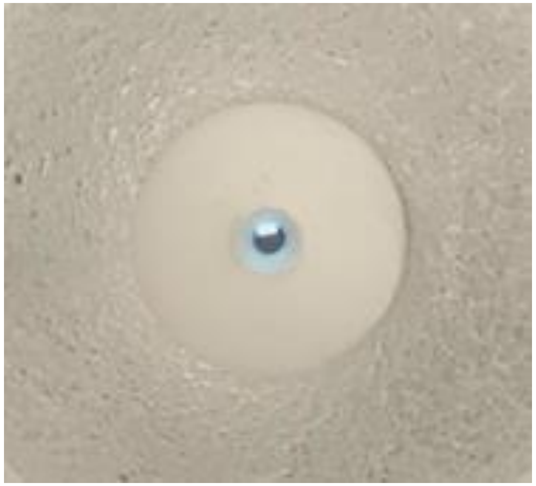




M = 0, $\rho = 0$

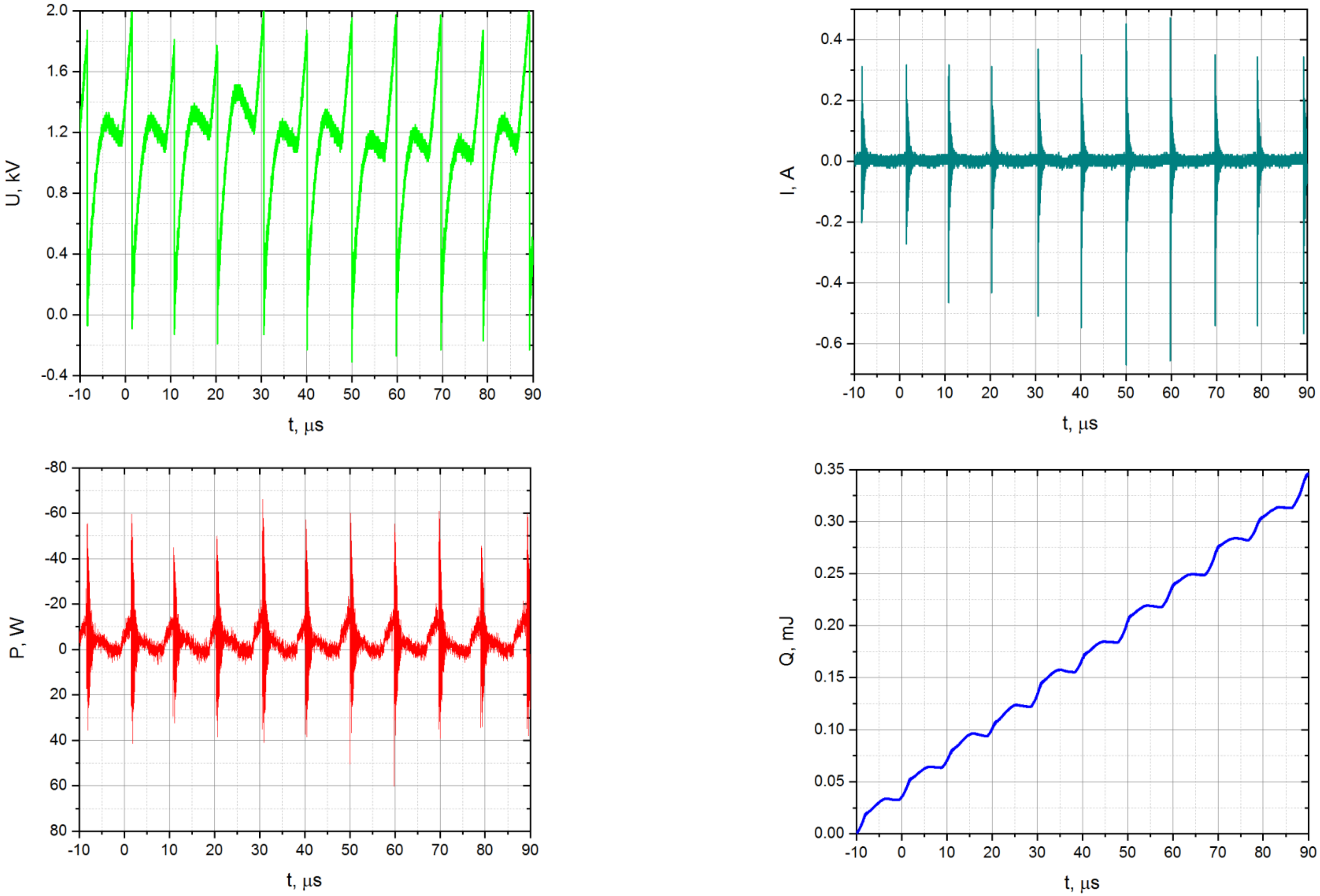
M = 3, $\rho = 0.58\ \rho_0$





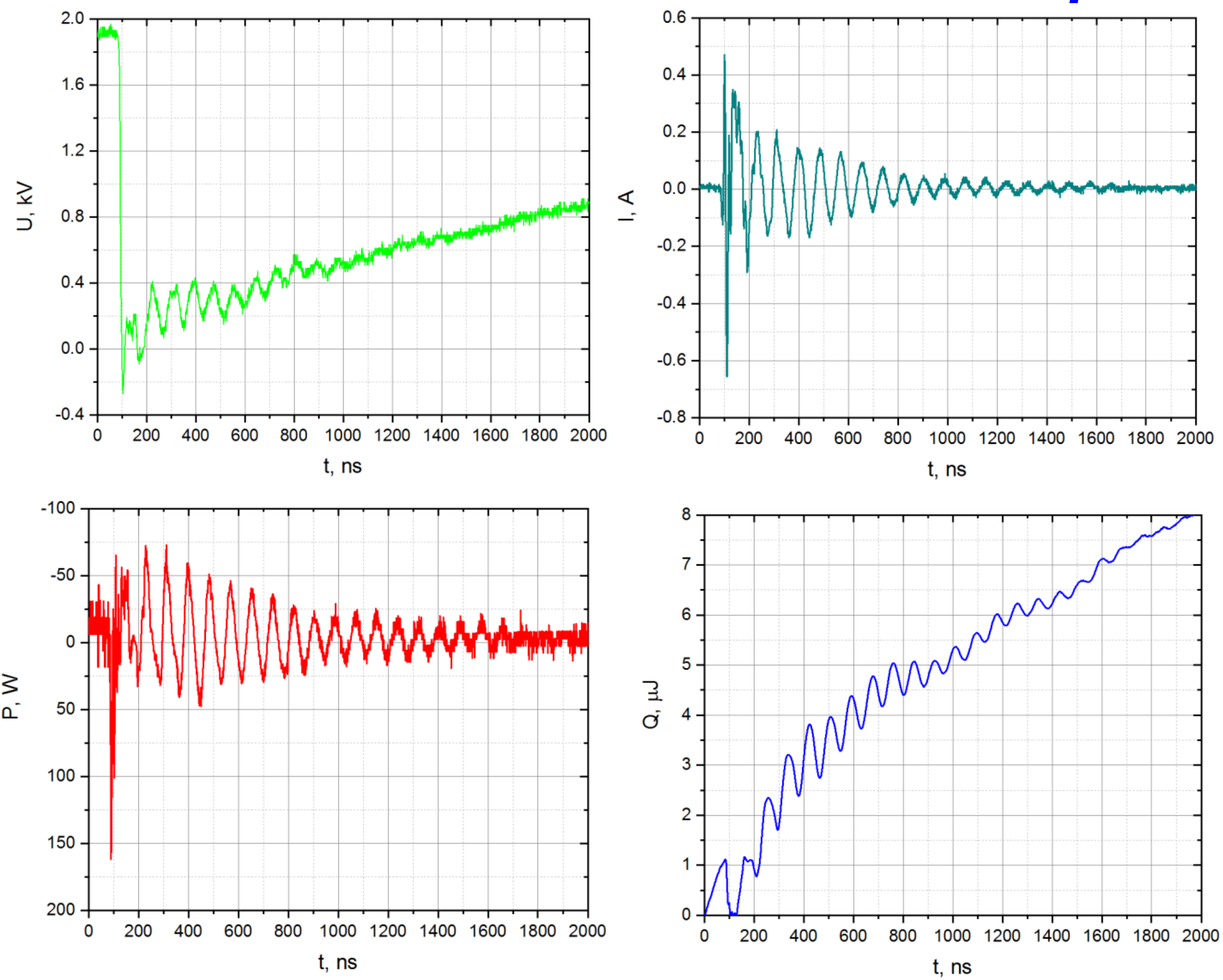
ns-Periodic Discharge in Methane Flow.

f = 120 kHz, U = 2 kV, P_{mean} = 3.5 W



ns-Periodic Discharge in Methane Flow.

f = 120 kHz, U = 2 kV, P_{peak} = 150 W



Plasma volume
V ~ 0.02 mm^3

Discharge frequency
f = 120 kHz

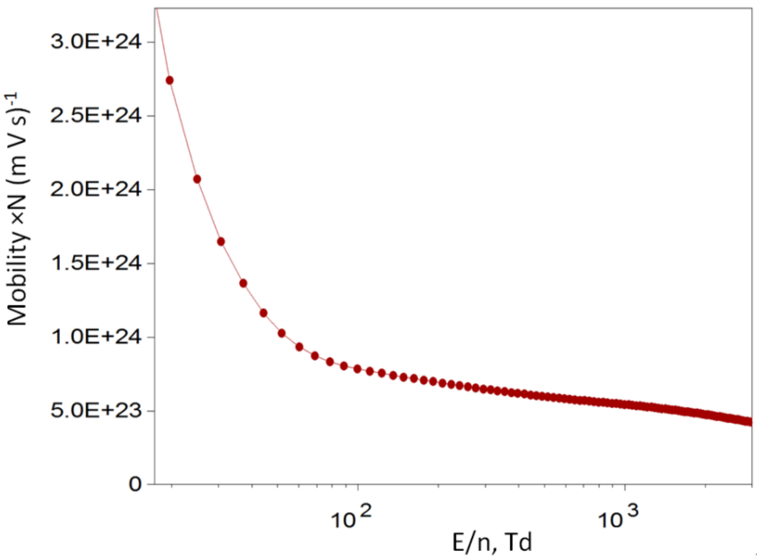
Gas density
in discharge region
$\rho = 0.58\,\rho_0$

Gas velocity
in discharge region
v = 430 m/s (M = 1)

Energy release
E = 0.037 mJ

Temperature increase
$\Delta T = E/C_v$ = 3950 K

ns-Pulse Discharge Modeling
Methane, U = 2 kV, P = 410 Torr, H = 1.3 mm

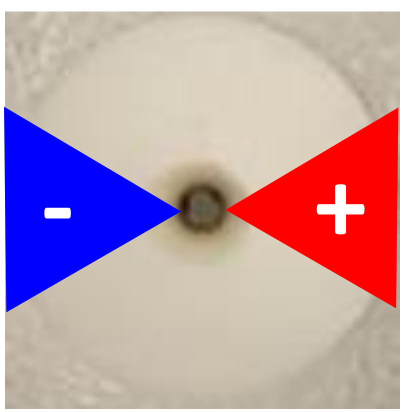


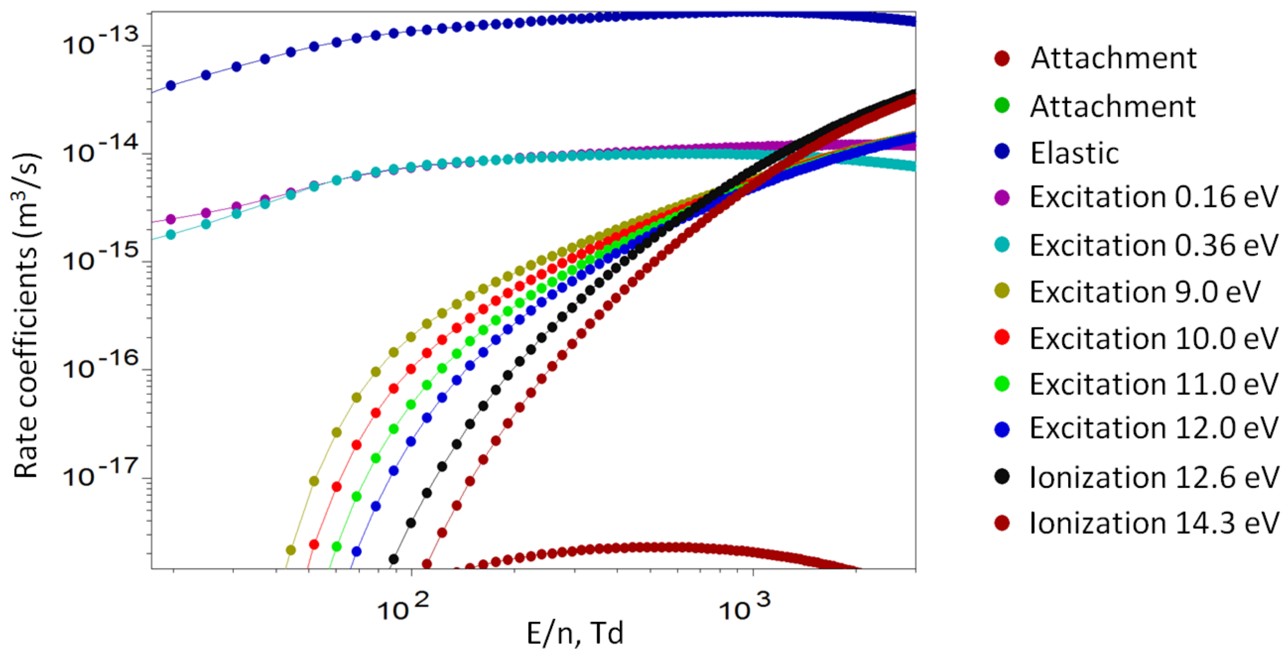
$$\frac{\partial n_\mathrm{e}}{\partial t} + \mathrm{div}\,(\vec{v}_\mathrm{e} \cdot n_\mathrm{e}) = S_\mathrm{ion} + S_\mathrm{photo} - S_\mathrm{att} - S_\mathrm{rec}^\mathrm{ei}, \qquad (1)$$

$$\frac{\partial n_\mathrm{p}}{\partial t} = S_\mathrm{ion} + S_\mathrm{photo} - S_\mathrm{rec}^\mathrm{ei} - S_\mathrm{rec}^\mathrm{ii}, \qquad (2)$$

$$\frac{\partial n_\mathrm{n}}{\partial t} = S_\mathrm{att} - S_\mathrm{rec}^\mathrm{ii}, \qquad (3)$$

$$\Delta\varphi = -\frac{e}{\varepsilon_0}\left(n_\mathrm{p} - n_\mathrm{e} - n_\mathrm{n}\right). \qquad (4)$$





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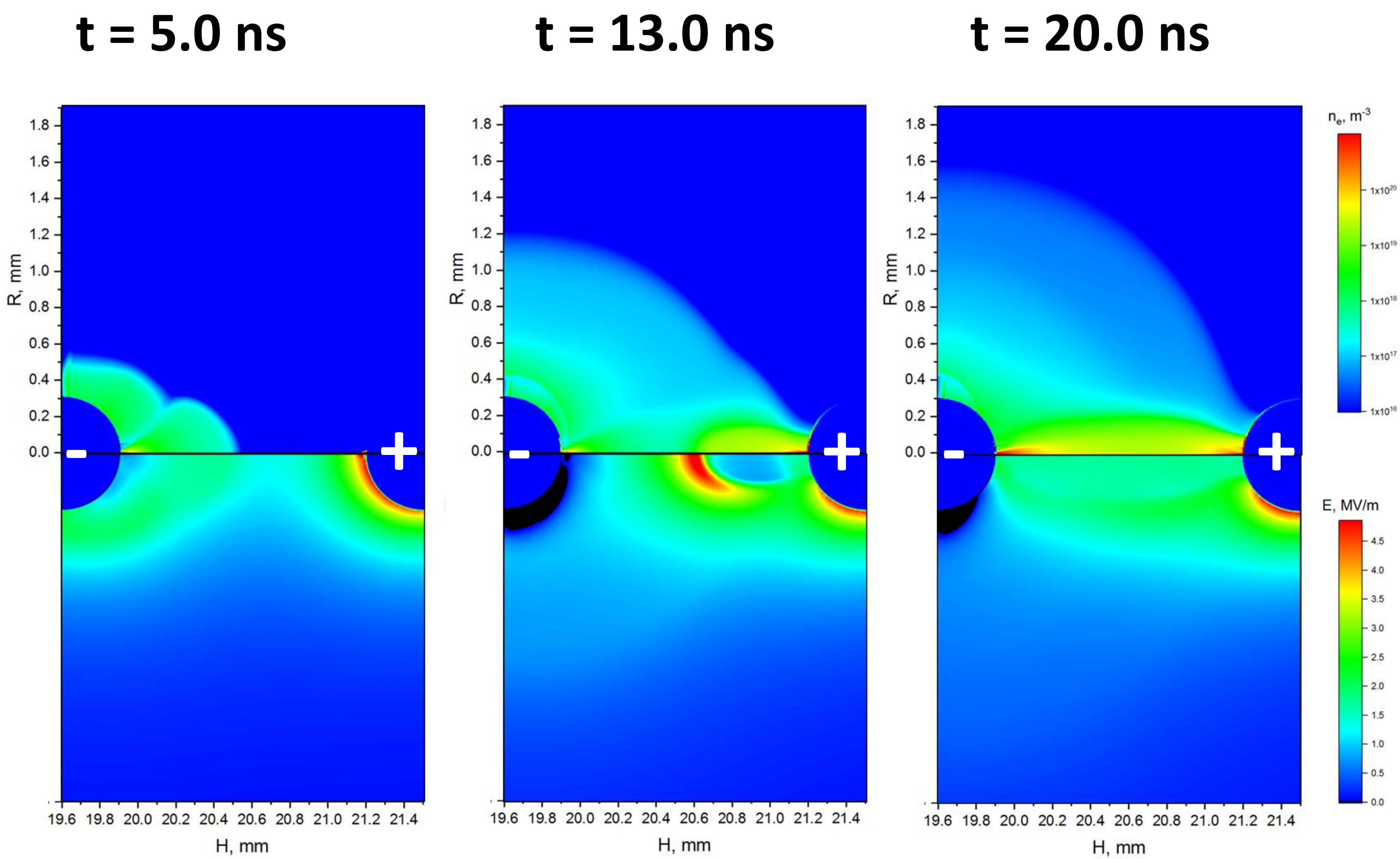

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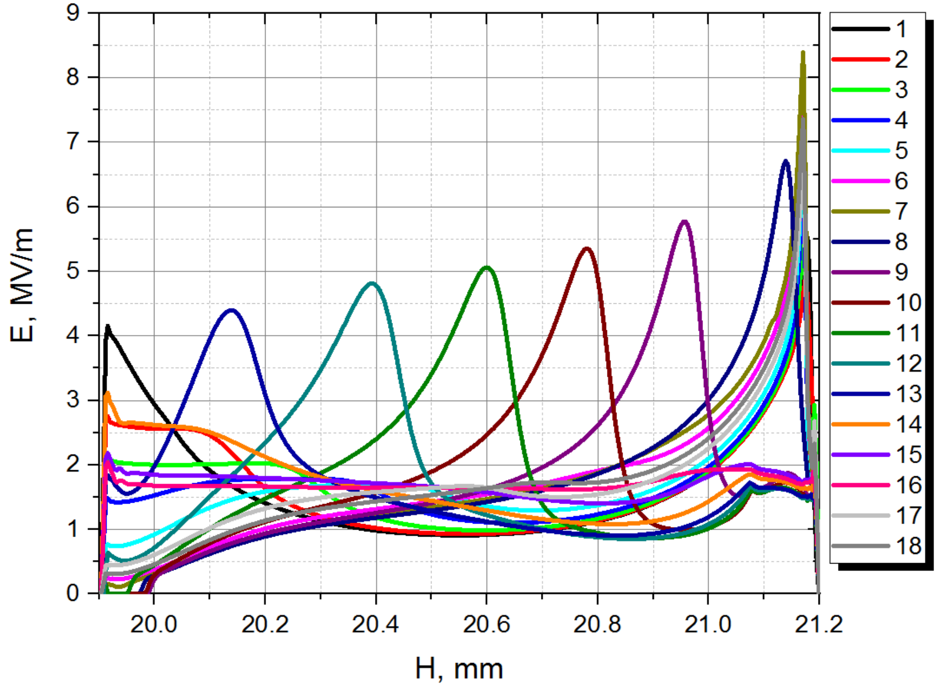
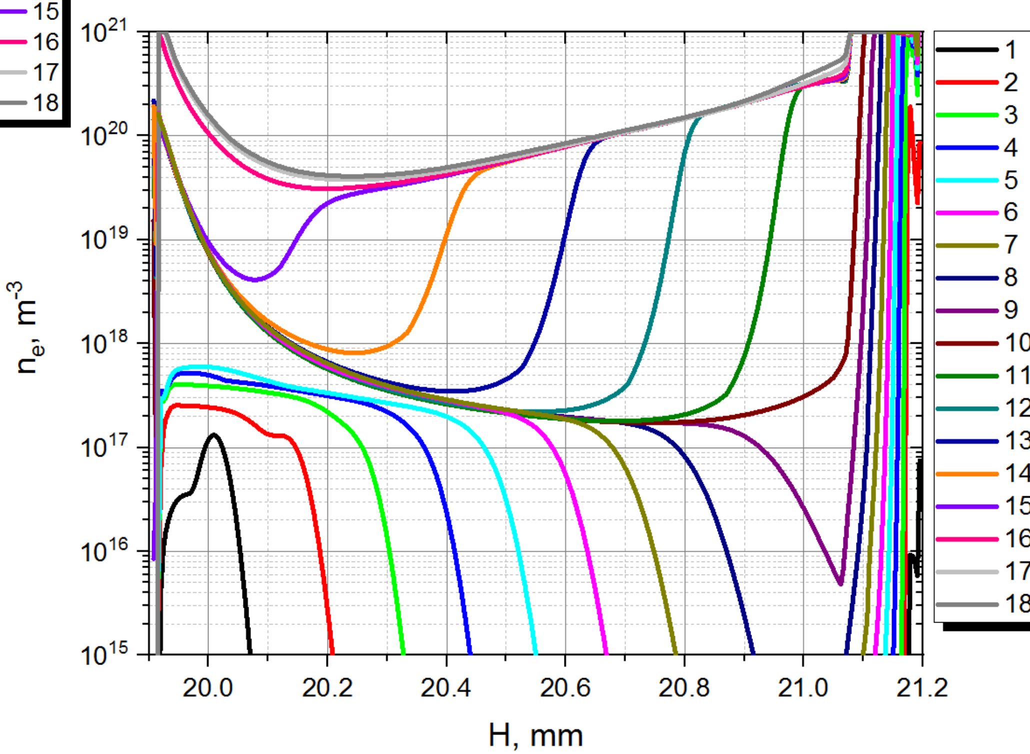
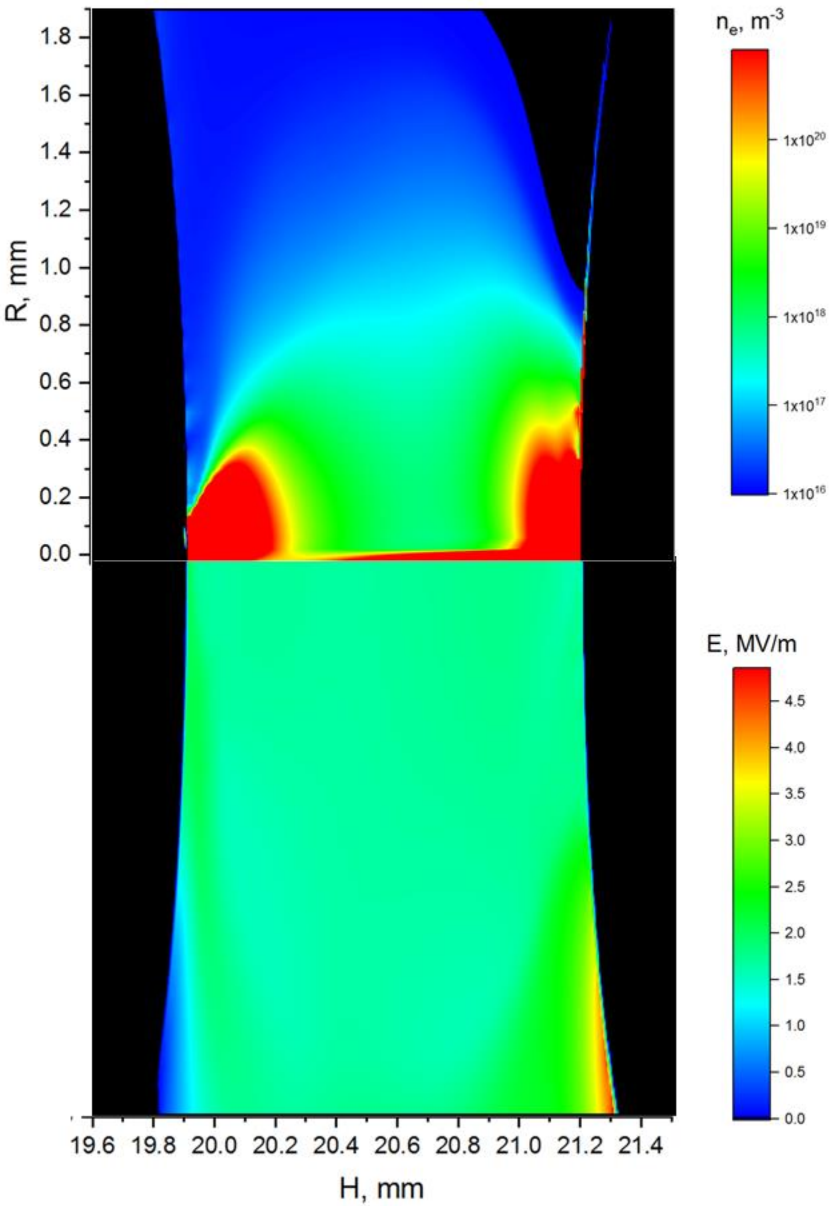


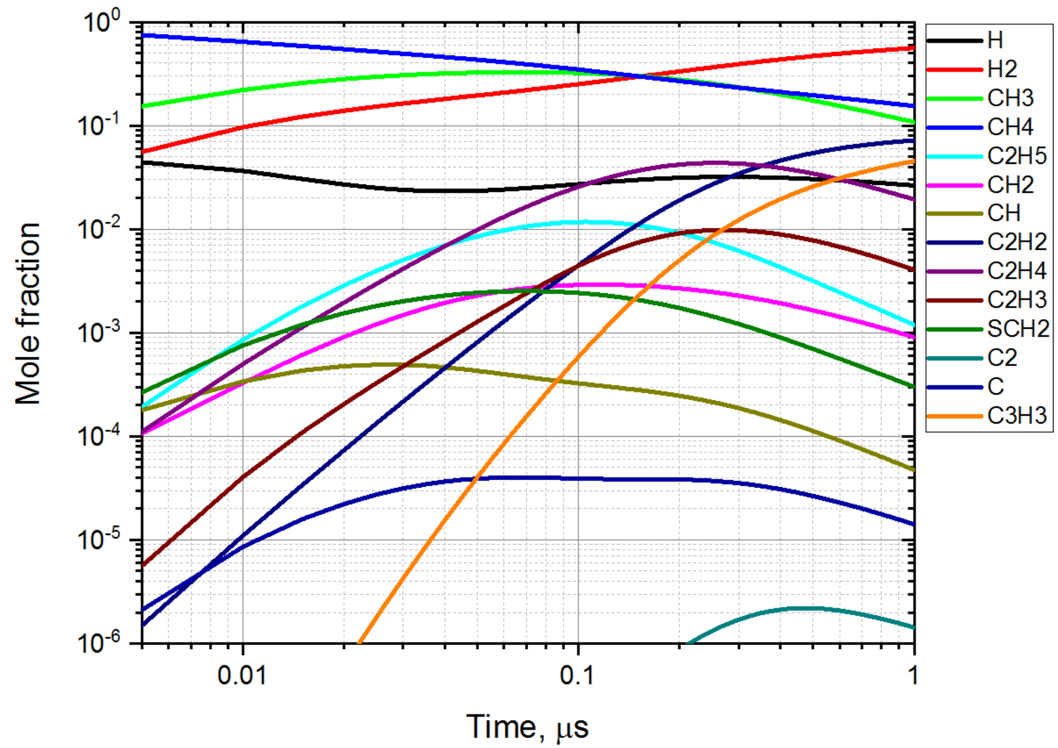
Distribution of electric field along the discharge axis. Time in nanoseconds.



Distribution of electron density along the discharge axis. Time in nanoseconds.

Supersonic nozzle flow modeling: Ultra-fast Gas Heating and Cooling





Supersonic regime: M = 3

Frozen mixture composition

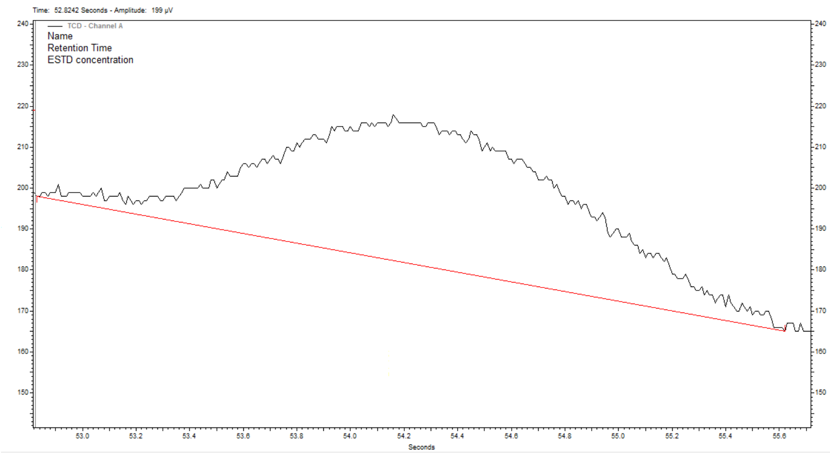
V(plasma) = 0.002 mm^3; V(gas) = 7 mm^3

Estimated hydrogen production for P = 3.5 W

$G(H_2) = G(CH_4) * V(plasma)/V(gas) =$

$= \mathbf{4.3 \times 10^{18}}$ **molec/s**

Hydrogen Production Measurements



Subsonic regime: M = 1

$G(H_2) = 1.9x10^{18}$ molec/s

Energy for hydrogen production

$E(H_2)$ = 3.2 eV/molec = 154 MJ/kg = 43 kWh/kg

Energy for methane dissociation

$E(CH_4)$ = 1.6 eV/molec

GC Gas Composition Measurements

Supersonic regime: M = 3

$G(H_2) = 2.9x10^{18}$ molec/s

Energy for hydrogen production

$E(H_2)$ = 2.1 eV/molec = 101 MJ/kg = 28 kWh/kg

Energy for methane dissociation

$E(CH_4)$ = 1.05 eV/molec

Energy for hydrogen production by electrolysis $E(H_2)$ ~ 259 MJ/kg = 72 kWh/kg

Energy of hydrogen combustion E_c ~ 140 MJ/kg = 39 kWh/kg

Conclusions

- A new supersonic non-equilibrium plasma reactor for controlled methane reforming and H_2/carbon synthesis is assembled and tested.
- Nonequilibrium plasma is generated in supersonic 100% methane flow. Measurements of discharge parameters show that a pulsed spark plasma can reach T = 4000 K for transient chemical reforming.
- Detailed 2D plasma dynamics modeling demonstrates the geometry of the plasma channel. Estimated hydrogen production is $G(H_2) = 4.3\times10^{18}$ molec/s for P = 3.5 W discharge.
- Hydrogen production has been measured using gas chromatography. It was shown that the energy efficiency of hydrogen production in supersonic expanding flow by pulsed spark is 28 kWh/kg of hydrogen. Theoretical estimation is 19 kWh/kg of hydrogen.

Future plans

Experiment:

1) Discharge in supersonic methane flow – stability and power increase
2) Detailed analysis of products – heavy hydrocarbons and black carbon

Modeling:

1) Nonequilibrium supersonic plasma flow with detailed chemistry
2) Dynamics of nanoparticles formation

Diagnostics:

1) Thomson scattering measurements of plasma density
2) Hybrid fs/ps CARS measurements of gas temperature