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In-situ Production of High Energy Nano- Fuels by Laser Ablation

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Nano-Fuels

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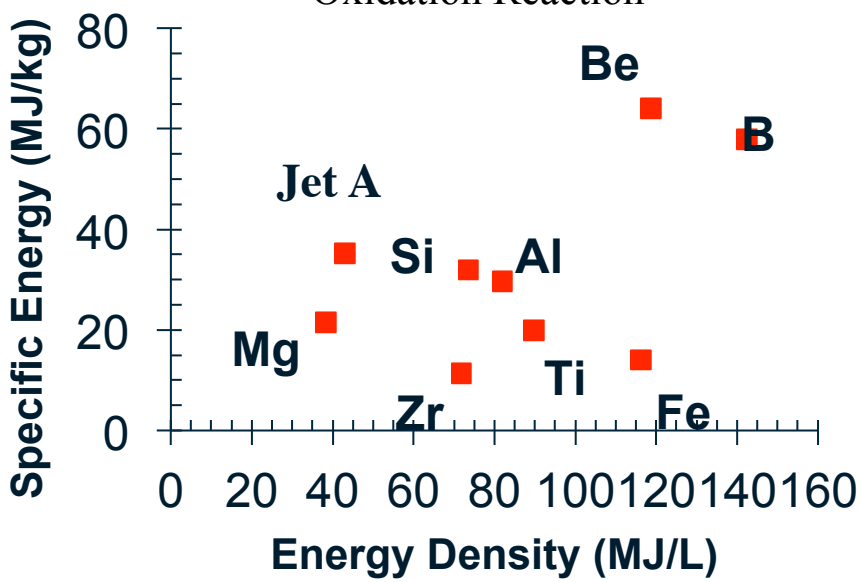
Nano-Fuel → Liquid Hydrocarbon Fuel + Metallic Nano-particle

Metals – Energy Carriers
Oxidation Reaction



Potential Benefits

- Enhance Energy Density
- Enhance Burn Rates
- Reduce Ignition Delay
- Reduce Green-house gas emissions
- Enhance thermal Conductivity-Cooling
- Reduce Electrical Resistivity-Static Dissipater

Old Concept – Failed because of large metallic particles – incomplete particle combustion & rapid particle separation from fuel.

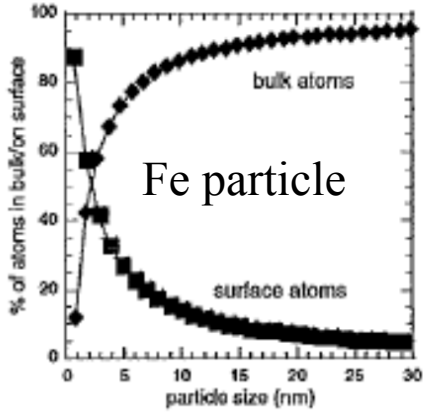
Nano-particle Advantage:

- Enhance fuel-to-oxidizer contact.
- Reduces the diffusion distance for rapid oxidation.

Nano-Particles

Metallic nano-powders are commercially available:

- Particles are passivated to reduce fire/explosion potential.
- Nano-powders are agglomerated and difficult to disperse into stable suspensions.



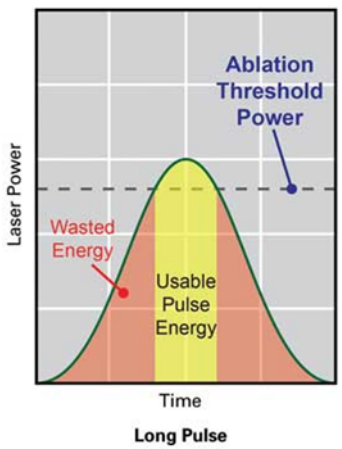
Inactive surface oxide layer decreases energy density

<u>Approach</u> – In-situ synthesis of metallic nano-particles in the fuel by laser ablation.
Stable suspensions of metallic nano-particles have been reported.
Potential to engineer the particle surface chemistry by process control.

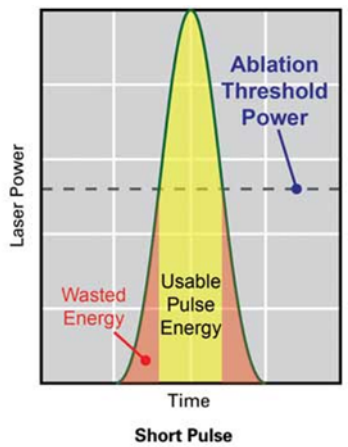
Laser Ablation

- All materials have an ablation threshold (minimum peak intensity for remove material).
- Pulse lasers deliver high power densities – 10^8 to 10^{13} W/cm^2

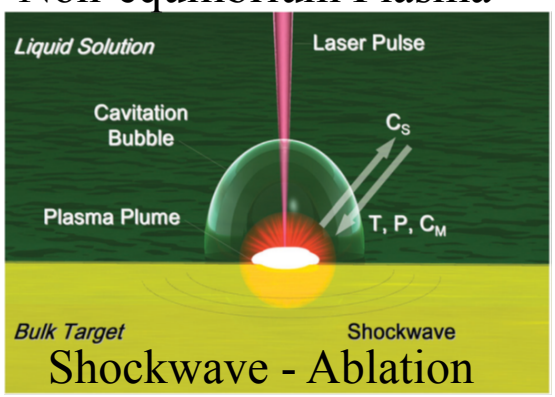
Pulse $\geq 10^{-9}$ s



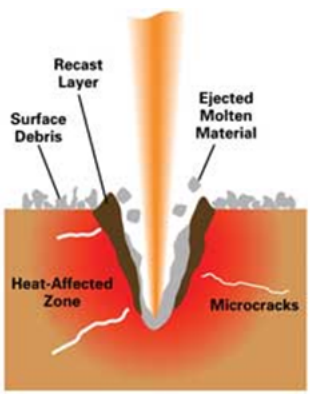
Pulse $\leq 10^{-12}$ s

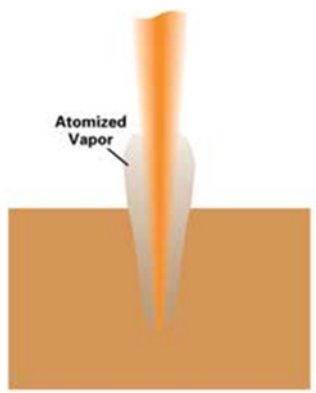


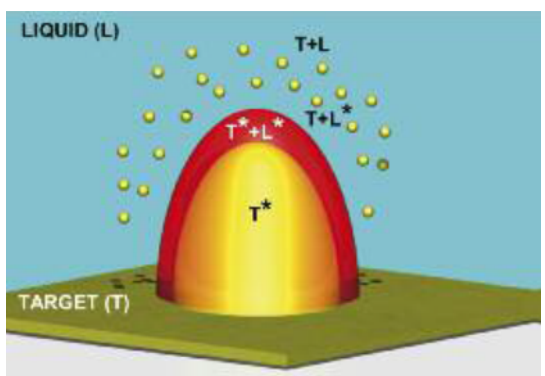
Non-equilibrium Plasma



- Temp. ~ 10^4 K
- Pressure >1 GPa
- Rapid cooling
- Metastable Phases







<u>NP Formation</u>

- Nucleation/Growth
- Molten Droplet

Reaction with Fuel

Laser Ablation

Experimental

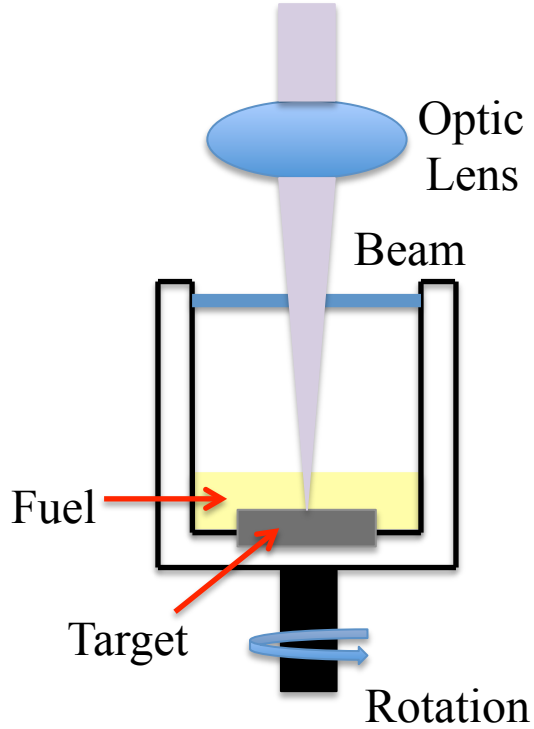
Laser – Excimer

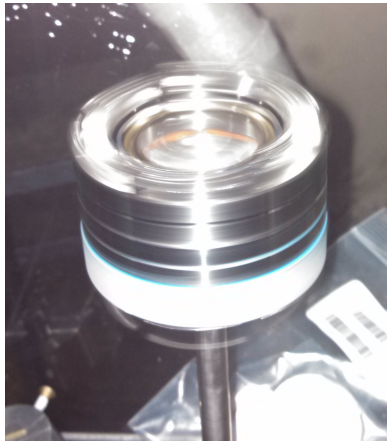
- Wavelength – 248/351 nm
- Energy – 1.2/0.4 J
- Pulse Frequency – 1-50 Hz
- Pulse Width – 20 ns

Fuels – Butanol, Kerosene

Process Parameters

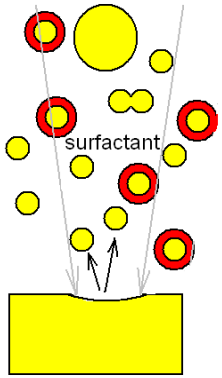
- Wavelength
- Energy Density(J/cm^2)
- Pulse Frequency
- Surfactants
- Fuel Depth above Target
- Rotation Speed





Surface Chemistry

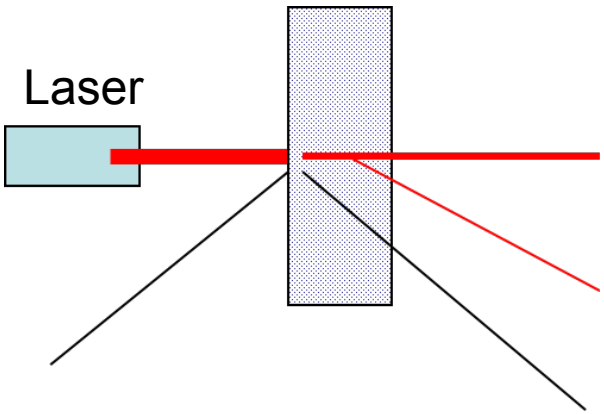
- Cathodic surfactant- CTAB-$(C_{16}H_{33})N(CH_3)_3Br$
- Anionic surfactant-SDS-$CH_3(CH_2)_{11}OSO_3Na$
- Non-ionic surfactant- Span 80-$C_{24}H_{44}O_6$
- Poly Acrylic Acid- PAA-$(C_3H_4O_2)_n$



Particle Size Analysis

A) Electron Microscopy – Direct Measurement
B) Dynamic Light Scattering – Indirect Measurement

Dynamic Light Scattering

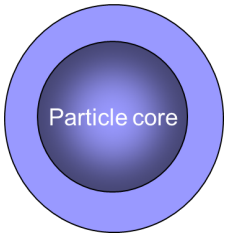


Particle size information is obtained from intensity of the scattering pattern at various angles.

DLS measures Brownian motion and relates this to the size of the particles.

Stoke-Einstein $$d = \frac{k_B T}{6\pi\eta D}$$

The diffusion coefficient(D) will depend not only on the size of the particle core, but also on any surface structure, as well as the concentration and type of ions in the medium.



Hydrodynamic Diameter

Laser Parameters

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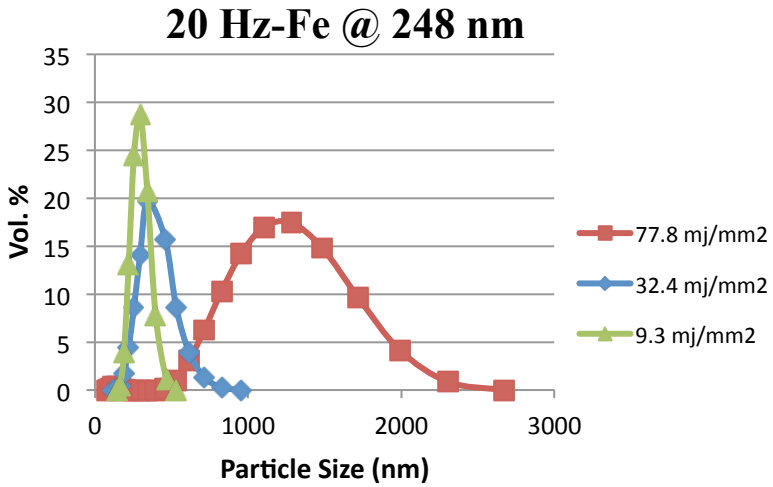

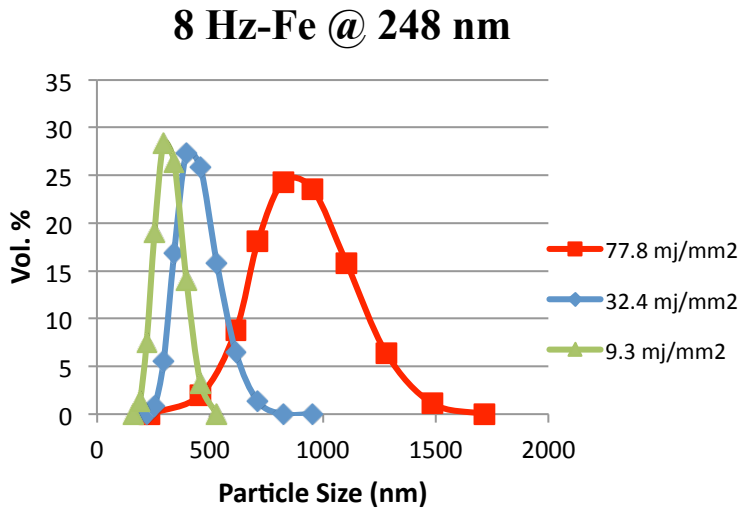

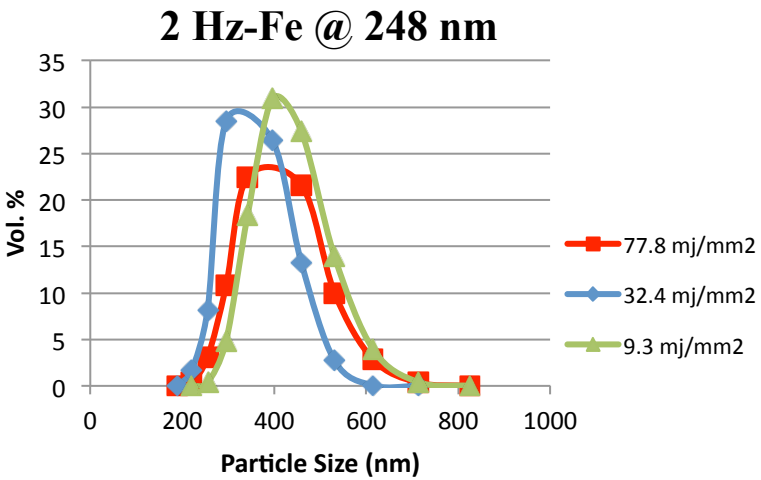

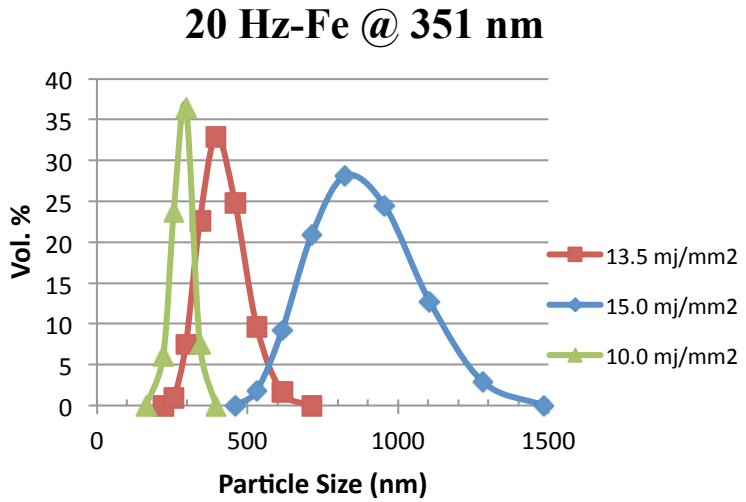

Fe Particle Size

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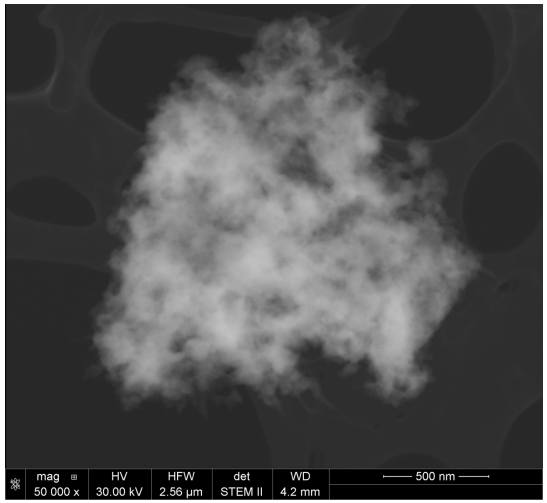
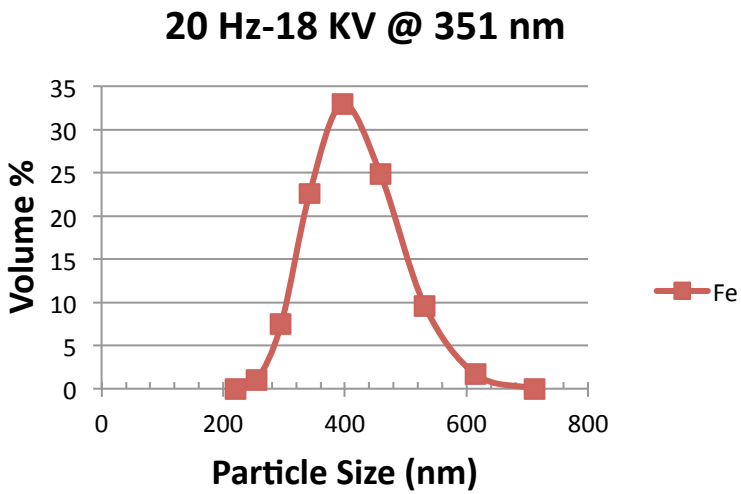
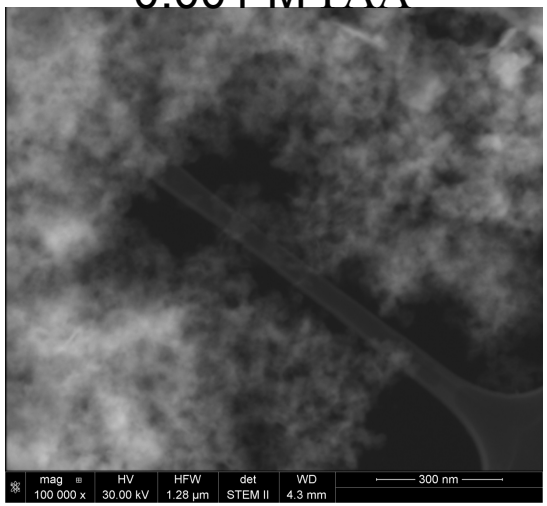
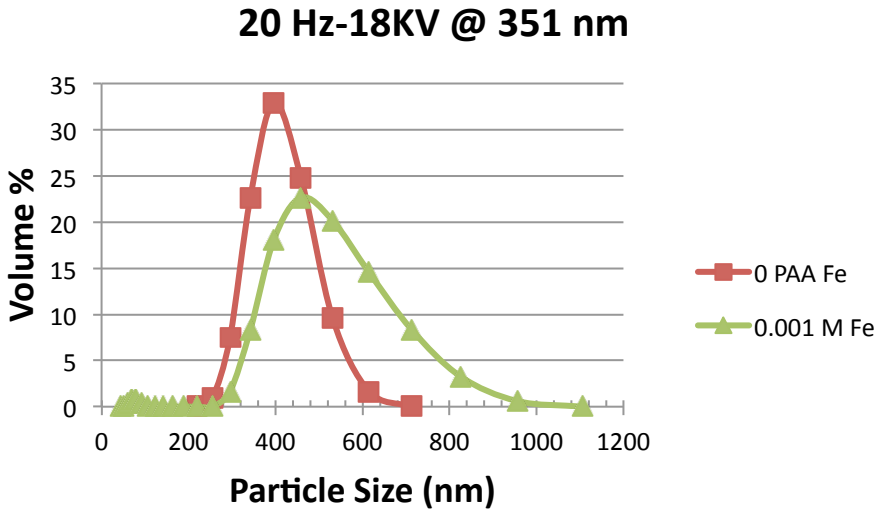
No Surfactant





0.001 M PAA





Al Particle Size

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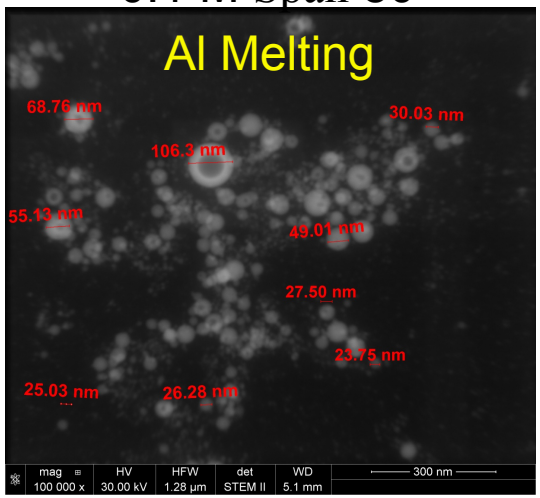
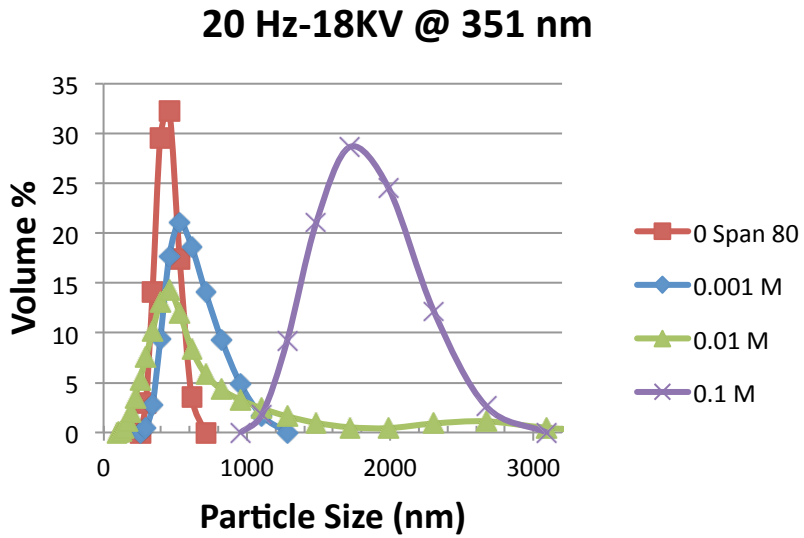
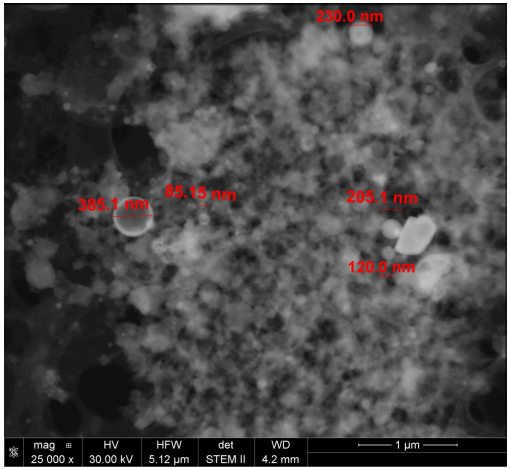
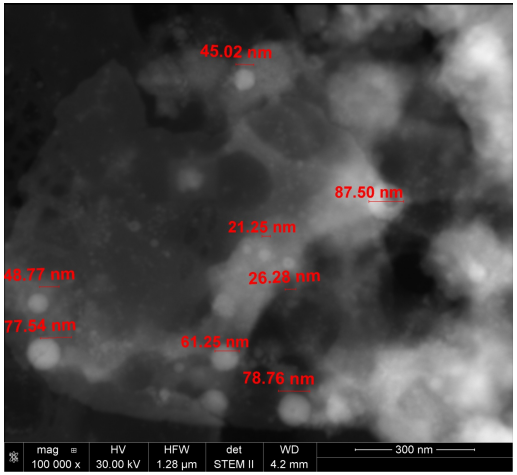
0.1 M Span 80

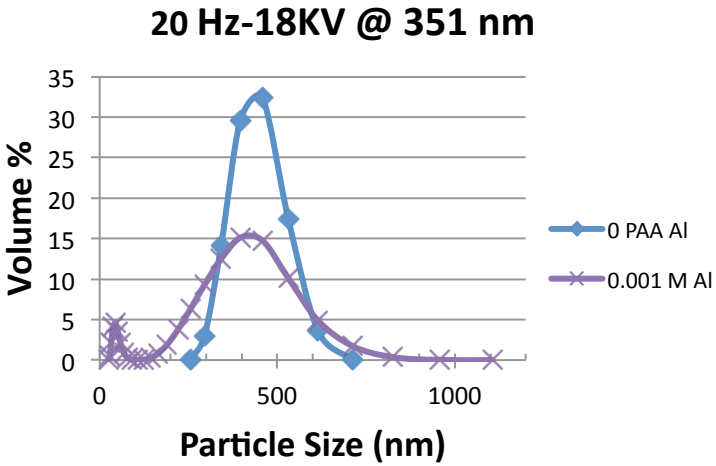




0.001 M PAA







Aluminum

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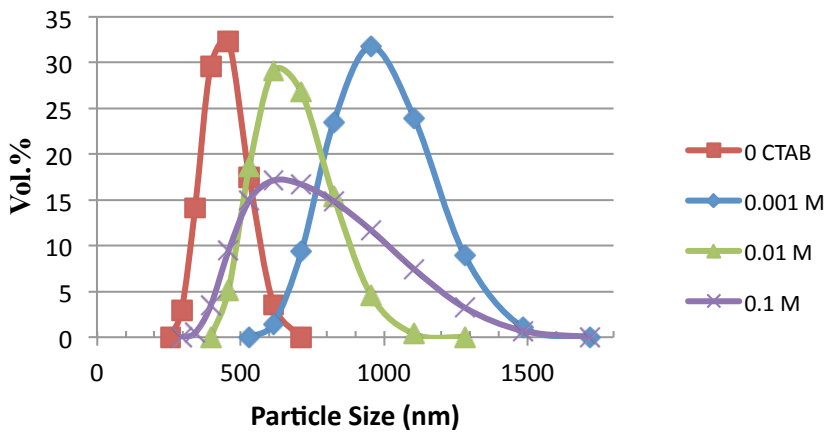
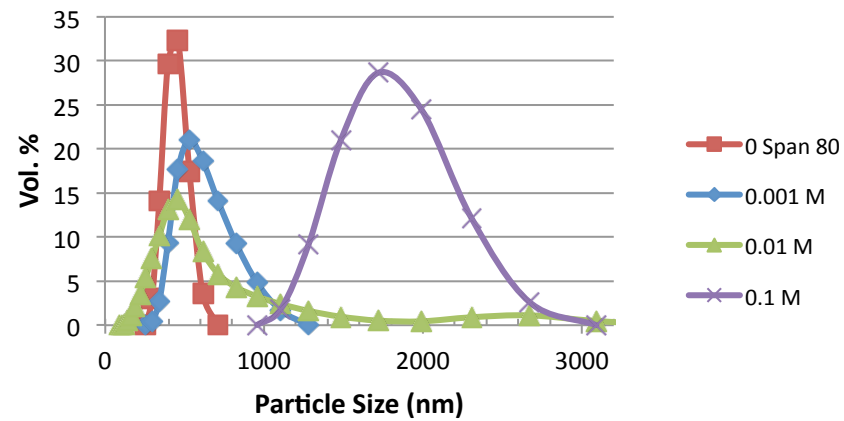
20 Hz-Al-18KV @ 351 nm

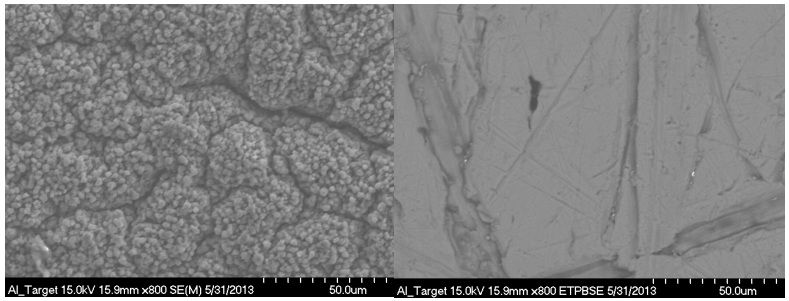


20 Hz-Al-18KV @ 351 nm

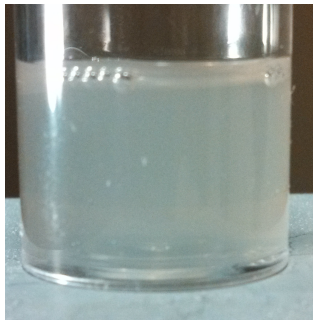


<u>Ablation Rate</u> – 1 mg/hr – 0.001 M SDS

Target Surface



Ablated Non-Ablated



Al/butanol suspension destabilizes after 3-4 wks

<u>Electrical Resistivity</u>

Butanol – 1.6 x 10^7 W-cm

0.02 v% - 1.0 x 10^6 W-cm – No Surfactant

Iron

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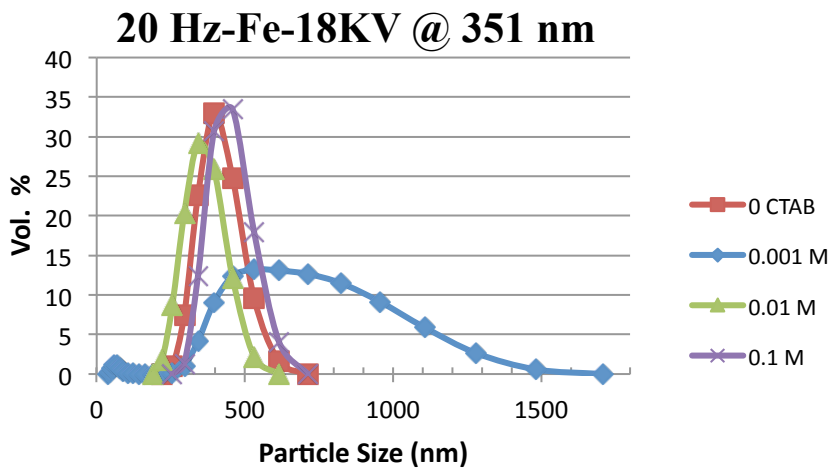
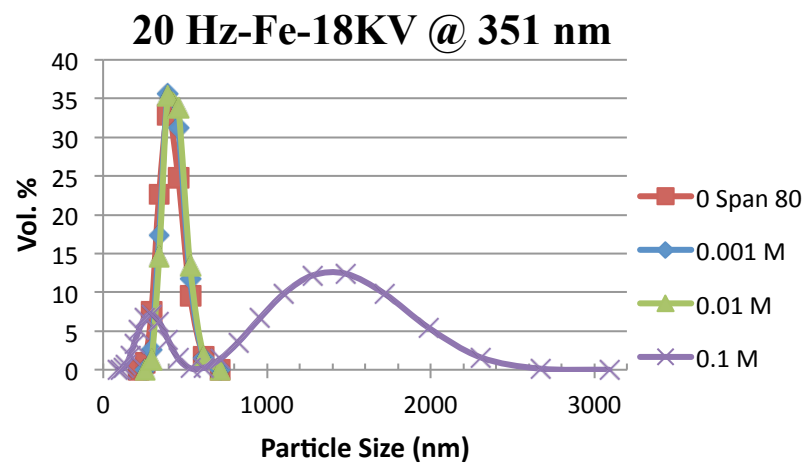
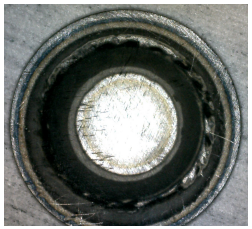
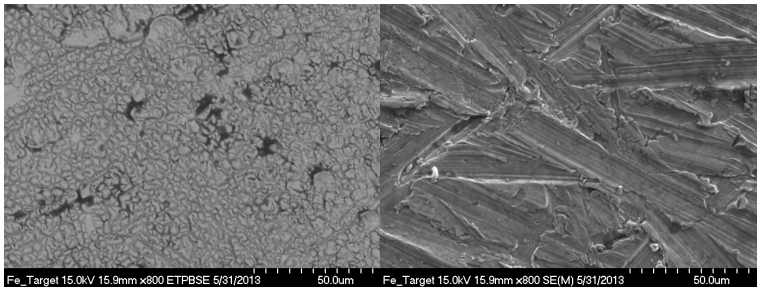






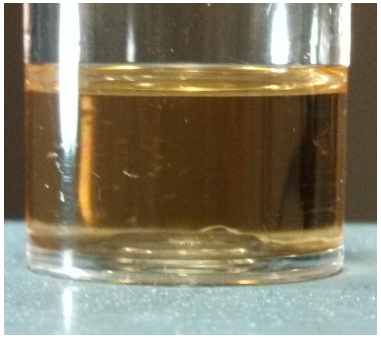
Target wt. loss erratic
Carbon deposition - coking

Target Surface



Ablated

Non-Ablated



Stable Fe/butanol suspensions – 8 mos

Electrical Resistivity

Butanol – 1.6 x 10^7 Ω-cm

0.02 v% - 1.8 x 10^6 Ω-cm – No Surfactant

Boron

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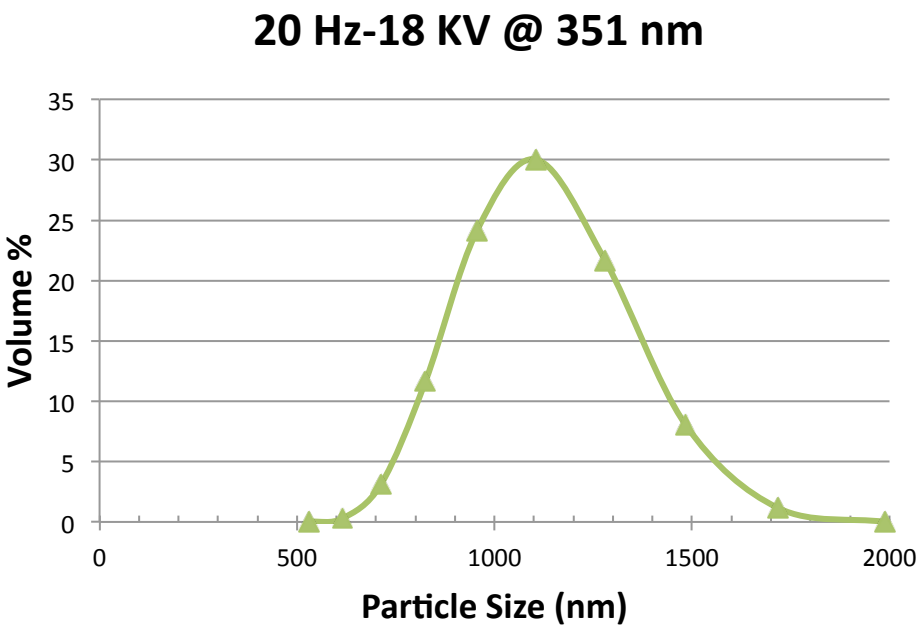
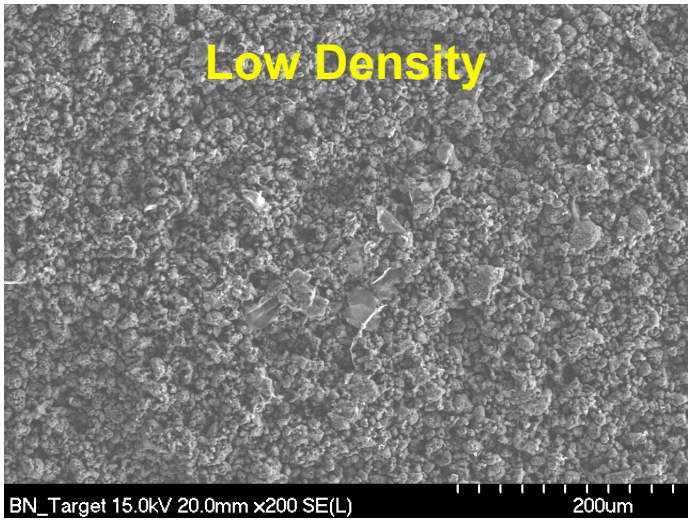


Target Surface



Ablation Rate – 40 mg/hr – Shockwave Ablation

Suspension Stability – rapid sedimentation

Combustion Experiments

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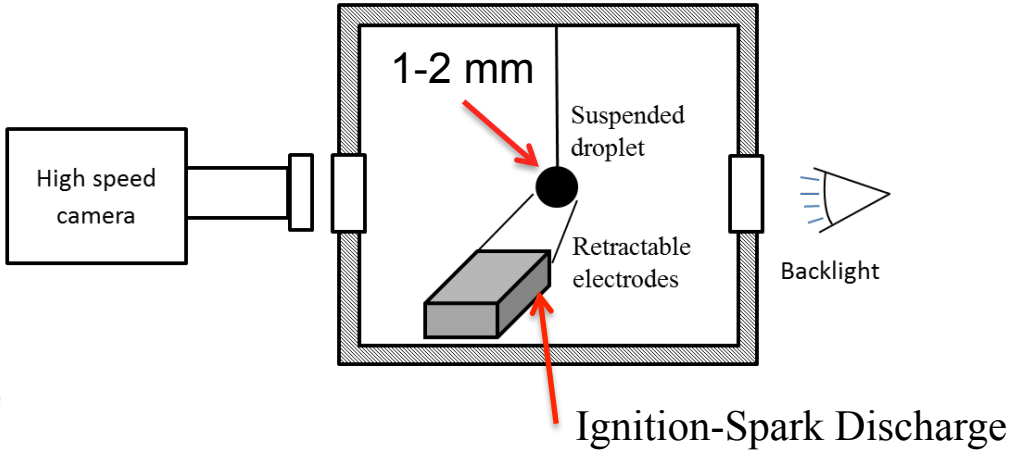
Suspended Droplet Ignition

- Burning rate
- Burning behavior
- Mode of combustion

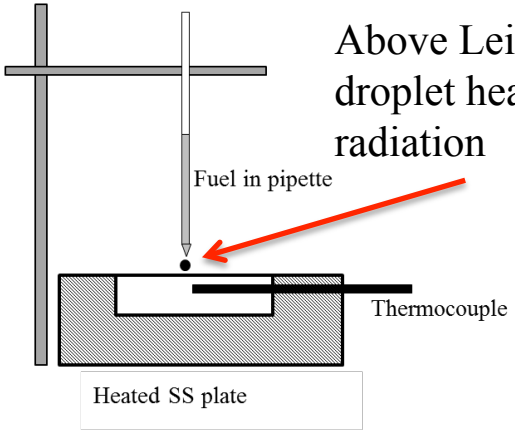


Hot Plate Droplet Ignition

- Minimum Ignition temperature

Energy Density Measurement

- Calorimetry



Above Leidenfrost temperature, droplet heated by convection and radiation

800 °C Capability

Nano-Fuel Preparation - Baseline

1. Commercial Powders
   - Al – 40 nm
   - Fe – 70 nm
2. 0.5 Wt. % Span 80
3. Butanol

Fe suspensions – rapid sedimentation

Burning Behavior
Butanol

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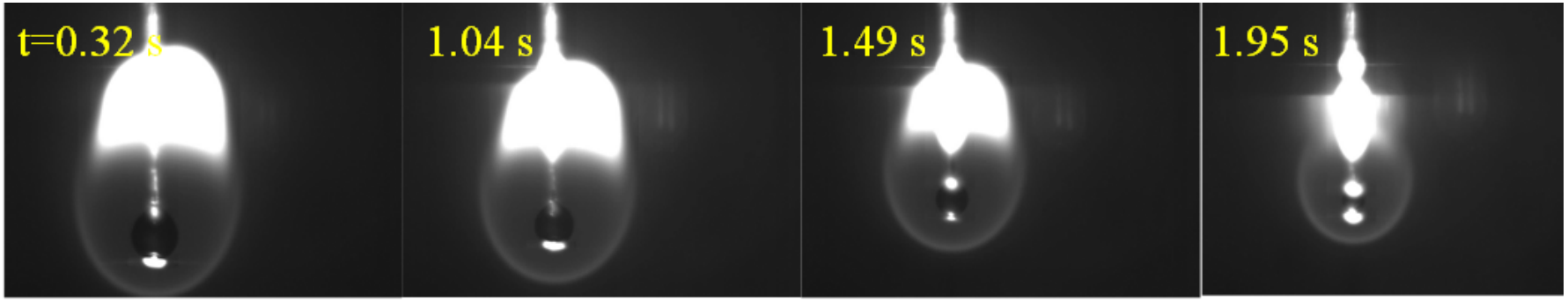

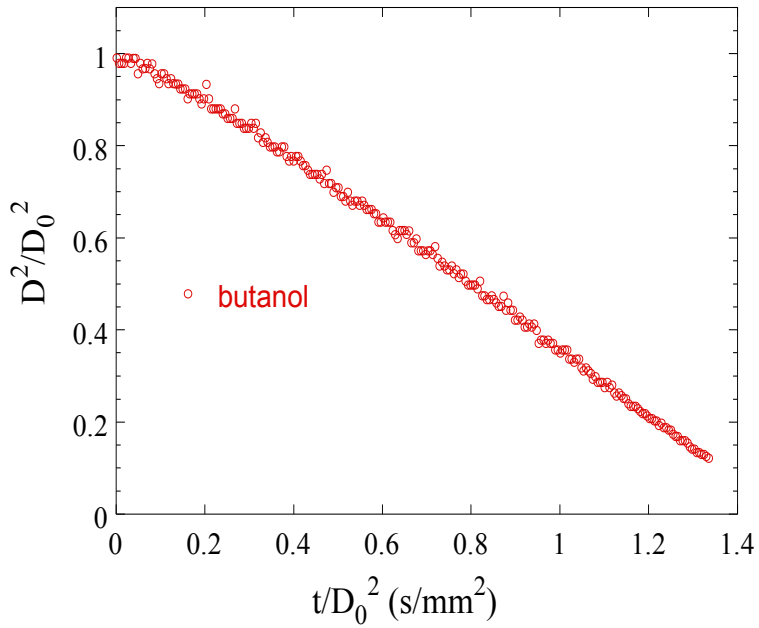

Follows D^2 Law

Burning Behavior
Butanol + 0.02 v% Al
(laser ablated)

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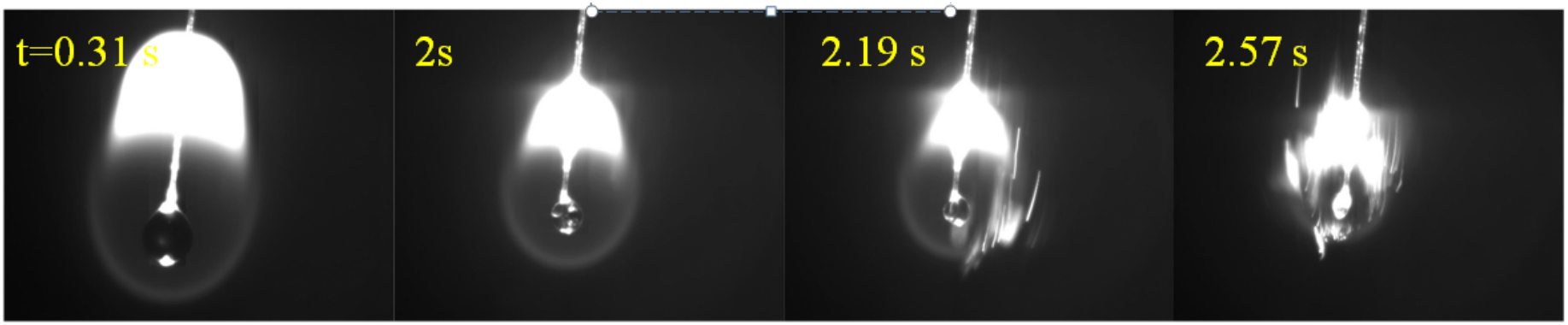
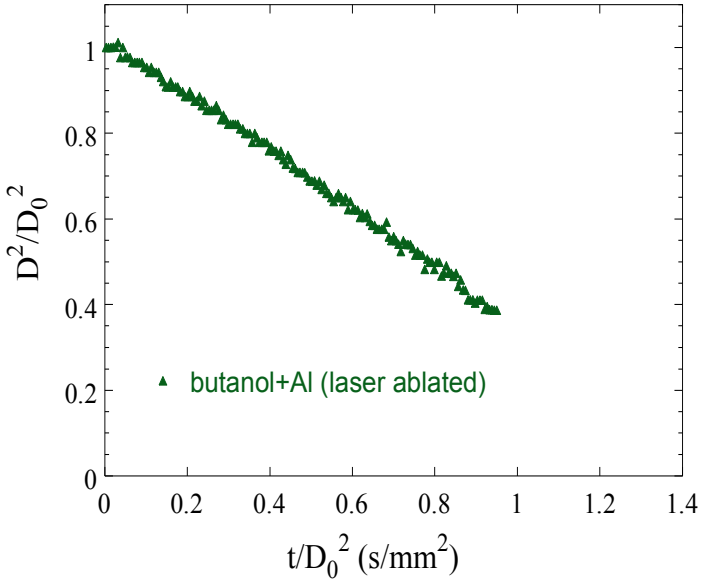


Steady Flame | Steady Flame | Particle Streaks | Intense Disruption



- Particles burn simultaneously with butanol

Burning Behavior

Butanol + 1 v% Al + 0.5 w% Span 80

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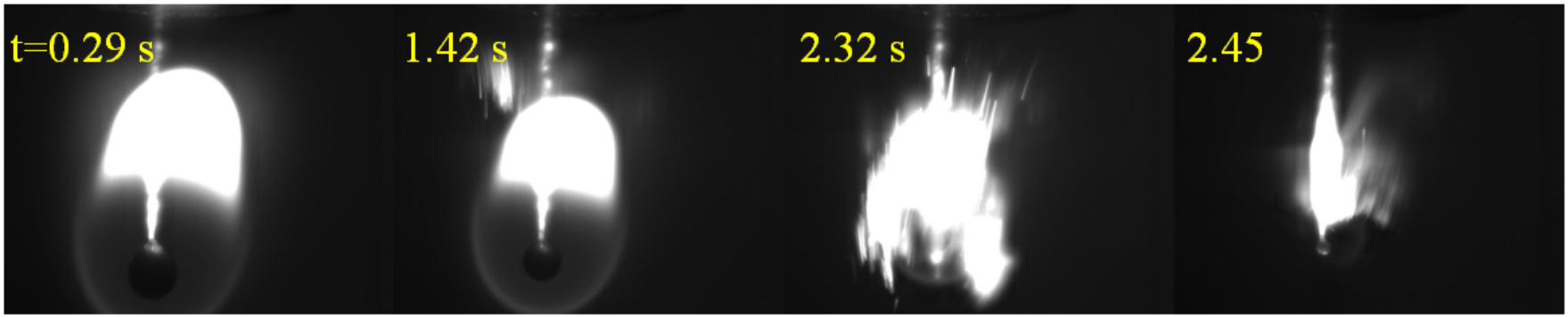
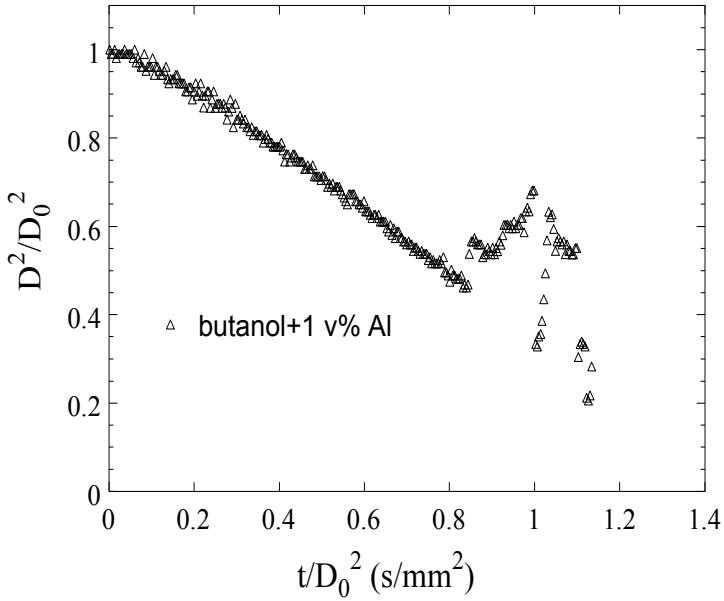


Steady Flame | Particle Streaks | Intense Disruption | Clear Bead Near End



- Strong disruption
- Droplet expands and contracts
- Particles burn simultaneously with butanol leaving bead without residue
- Simultaneous burning – increased rate of energy release, better combustion

Burning Behavior

Butanol + 2.5 v% Al + 0.5 w% Span 80

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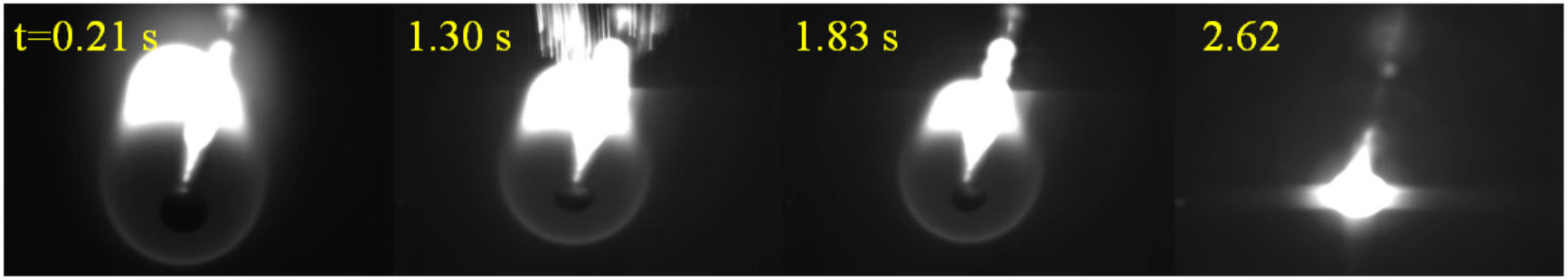
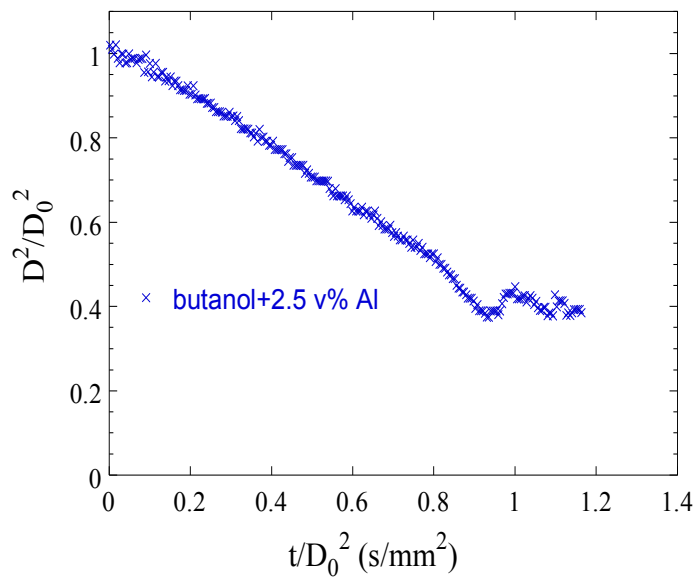


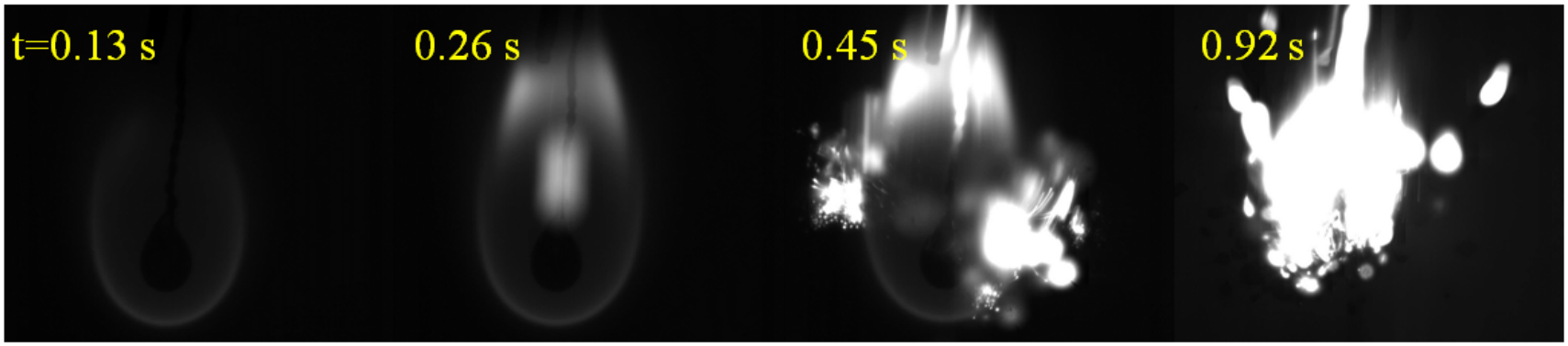
Steady Flame | Particle Streaks | Steady Flame | Al Burning on Bead



- Al burns on bead as agglomerate after butanol combustion

Burning Behavior

Butanol + 5 v% Fe + 0.5 w% Span 80



Steady Flame | Particle Streaks | Intense Disruption | Near End

- Particle streaks and disruption start early
- Particles burn simultaneously with butanol leaving bead without residue
- Decreased soot luminosity

Ignition/Calorimetry

Minimum Ignition Temperature-Droplets

- Butanol (690 ^{o}C)
- Butanol + 2.5 v% Al (660 ^{o}C)

Lower temperatures – No droplet burning

- Al agglomerate left after butanol evaporation burnt even at temperature as low as 370 ^{o}C

Calorimetry Results

- Butanol – 29.89 MJ/L
- Butanol+ 1 v% Al – 30.33 MJ/L
- Butanol + 2.5 v% Al – 31.24 MJ/L

Phase II

1. Increase Ablation Rate – g/hr scale
   a) Pico-second laser – 1064, 532 & 355 nm
   b) New Cell Design – liquid flow – cavitation bubbles
   c) Organic-metallic chemistry – ferrocene - $[(Fe(C_5H_5)_2]$
2. Suspension Stability - >6 mos
3. Nano-particle Characterization – chemical & physical properties
4. Combustion
   a) Smaller droplet size – 50-200 μm
   b) Combustion in radiative environment
   c) Evaporation rate
   d) Burning rate
   e) Burning behavior
   f) Completeness of metal combustion