NANOTECHNOLOGY AND GELLED CRYOGENIC FUELS

Presentation to
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NASA Nano / Bio Initiative

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Nanoparticulates for Gelled
and Metallized Gelled Propellants

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Turbomachinery and Propulsion Systems Division

O2 / RP-1 /Aluminum combustion –
Aerogel and nanoparticulate metals
 can gel the fuel, making it denser, more
energetic, and safer

The Benefits of Nanogellant Gelled Cryogenic Propellants and Nanoparticulates

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- **Nanogellant Gelled Propellants**
  - Increased safety
  - Increased fuel density
  - Reduced leakage
  - Reduced slosh
  - Reduced cryogenic boiloff
  - Potential reduction in specific fuel consumption
  - Potential increases in engine thrust

- **Nanoparticulate Metallized Gelled Propellants**
  - All of the above and
  - Large increases in fuel density
  - Larger potential reductions in specific fuel consumption
  - Larger potential increases in engine thrust
Nanogellant and Nanoparticulates

**What are nanogellant and nanoparticulate fuels?**

- Nanogellants are gellants that have a nanometer scale structure, which have enormously high surface area per gram
  - Gelled fuel reduce leakage and increase safety
- Nanoparticulates are metal particles that are 20 nanometers in diameter, much smaller than traditional 7 micron particles used for metal additives
  - Smaller particles allow for more efficient combustion and lower specific fuel consumption
Why are Gelled Cryogenic Fuels revolutionary?

– Gelled cryogenic fuels reduce leakage and increase safety

– Gelled cryogenic fuels are critical for increasing operability of cryogens for aerospace vehicles

– Nanogellant for gelled cryogens has a surface area of nearly 1000 m²/g, leading to cryogenic fuels gelled with 1-7 weight % gellant, 25 to 50% less mass than traditional gellant material

• Synergy

– Gelled and metallized gelled propellants have been an area of considerable interest in the rocket propulsion and explosives
Propellant Technologies: Teams

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- **National team**
  - NASA MSFC (large scale rocket engine testing)
  - NASA GRC (gelled and metallized gelled propellants, small scale engine tests)

- **NASA partners and contacts**
  - U.S. Army Picatinny Arsenal (potential collaboration in nanoparticles)
  - USAF Research Laboratory (hydrocarbons)
  - U.S. Army Aviation and Missile Command (metallized gelled propellants)
  - U.S. Naval Surface Warfare Center, Indian Head (nanoparticle aluminum, explosives)
  - Technanogy (nanometer aluminum particles)
  - Small Business Innovation Research (Argonide, Orbitec, etc.)
  - Many other industry, Government, and university partners
Metallized Gelled Propulsion

<table>
<thead>
<tr>
<th>Oxidizer</th>
<th>Fuel</th>
<th>Metal</th>
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<tbody>
<tr>
<td>O₂</td>
<td>H₂</td>
<td>Al</td>
</tr>
<tr>
<td>O₂</td>
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<td>Al</td>
</tr>
<tr>
<td>NTO</td>
<td>MMH</td>
<td>Al</td>
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</tbody>
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- Metal additives are suspended in gelled fuel and they undergo combustion with oxidizer
Metallized Gelled Propellants: Increasing Rocket Specific Impulse for Mars Missions

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- Mars missions using metallized gelled O2/H2/Al have an Isp of 475 to 480 seconds.
- O2/H2 without gellants or metal particles has an Isp of 470 seconds
- Rocket specific impulse (Isp) increased for several reasons:
  - Adding metal shifts O/F ratio from 6.0 to 1.6 (with 60 wt% Al), reducing the molecular weight of the rocket exhaust
  - Reducing the molecular weight increases engine Isp
  - Adding metal actually decreases the combustion temperature by 500 K
  - The added metal weight percent (wt%) is 60 to 70 % of the total H2/Aluminum fuel mass
  - Adding 60 wt% Aluminum increases engine Isp by 5 seconds
  - Adding 70 wt% Aluminum increases engine Isp by 10 seconds
  - O/F change increases Mars vehicle volume by only 1.1 % over the O2/H2 case
- References:
Metallized Gelled Propellants: How Gellants Work

• Gellants create a cross-linked structure in the liquid fuel, much like a long chain polymer
• The gelled liquid fuel is gelled with a small amount of gellant
  – RP-1: 0.9 wt% nanogellant
  – Liquid hydrogen: 7 to 8 wt% nanogellant
• The resulting gelled liquid is thixotropic (shear thinning), and its viscosity is 5 to 10 times that of the liquid alone
• The viscosity drops to the liquid viscosity when the fuel flows
• Metal particles, if small enough (nanometer sized), can act as a self gellant, reducing or eliminating the need for a separate gellant
Mars Missions:
Space Exploration Initiative (SEI)
and Metallized Gelled Propellants

- Mars missions using
  - O2 /H2
  - Metallized gelled propellants: O2 /H2 /Al
- 20 to 33% higher payload to Mars surface for each flight
Mars Missions: Space Exploration Initiative (SEI) and Metallized Gelled Propellants

- Mars missions using
  - O2/H2
  - Metallized gelled propellants: O2/H2/Al
- 20% more payload to Mars surface for each flight, with metallized gelled H2/Aluminum
- Significant launch vehicle savings with O2/H2/Al propellants
- 16 STS-C launches saved over 5 Mars missions
- Faster payload delivery schedule, and billions saved

Metallized Gelled Propellants: Mars Evolution-Class Missions: SEI, 1990

Payload mass delivered to Mars surface (1000's kg)

STS-C launches (68,000 kg)
O$_2$/RP-1/Aluminum Liquid Rocket Booster for Space Shuttle (Future STS)

- Payload increases of 14% possible with 55-wt% RP-1/Al (56,600 lbm)
- Small 1-ft diameter increase lifts payload to 70,000 lbm
- O$_2$/RP-1: 324 s Isp O/F = 2.7
- O$_2$/RP-1/Al: 317 s Isp O/F = 1.1
Nanogellant Gelled Propellants: Past Work

- Worked with TRW (1989-1996) developing nanoparticulate gellants
- Nanogellants are hydrocarbon alkoxide materials, created with a supercritical processing method
  - Nanogellant for gelled cryogens has a surface area of nearly 1000 m²/g, leading to cryogenic fuels gelled with 0.9 to 7 to 8 weight % gellant,
  - 25 to 50% less mass than traditional gellant material
- Liquid hexane, RP-1, propane (cryogenic), etc. gelled with less than 0.9 wt% of nanogellant
- Liquid hydrogen gelled with 7 to 8 weight % nanogellant (NAS3-25793, 1994 and NAS3-26714, 1996)
- Extensive data base on gelled propellants at NASA Glenn
- Joint NASA /TRW work in nanogellants being reinvigorated
Model GEL Structure

Gel Merit Figures
- Pore volume $= \frac{V_{GEL} \cdot V_{SKEL}}{W_{SKEL}}$
- Yield strength
- Shear thinning
- Energy density
Transmission Electron Microscopy (TEM) photo of nanogellant
TRW aerogel type nanogellant,
Circa 1990
Dynamic Gas Condensation Is Used At LANL To Fabricate MIC Reactants

- Ultra fine particles (~20 nm)
- Uniform size distribution
- Size easily controlled
- Amenable to continuous production (currently ~25g/hr)
- Process self-purifies source metal

LANL Al Powder
Russian Al Powder (“ALEX”)
Japanese Al Powder

Materials Science and Technology
LANL Al Powders Have A Smaller Mean Size And A Narrower Size Distribution Than Commercial Powders

\[ P(d) = \exp \left[ \frac{(\ln(d) - \ln(D))^2}{2(\ln(s))^2} \right] \]

- log-normal distribution function fits measured data well
- \( D \) = peak position
- \( s \) fixes distribution width

Materials Science and Technology
LANL UFG ALUMINUM PARTICLES ARE SINGLE CRYSTALS WITH NEGLIGIBLE STRUCTURAL DEFECT DENSITY

GAS-CONDENSED Al PARTICLE  Al (III) LATTICE FRINGES

1. interior aluminum is crystalline
2. no structural defects apparent
3. 2.5 nm thick Al₂O₃ passivation layer

Materials Science and Technology
SEM of LANL UFG ALUMINUM PARTICLES
Nanoparticle and Nanogellant Fuels: Small Business Innovation Research (SBIR)

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- **Argonide (Sanford, FL)**
  - Title: Metastable electroexploded nanophase aluminum based gels as a component of propulsion fuels
  - SBIR Phase II completed - 2001
  - Alex and other metals produced by the electroexplosion of metal wire are metastable, producing additional energy and burning rate
  - Discovered reduction of ignition delay with gelled Oxygen /RP-1/ Aluminum fuels

- **Orbitec (Madison, WI)**
  - Title: Gelled LH2 /UFAL /LOX propellant system
  - SBIR Phase I underway - 2001
  - Uses ultra-fine aluminum powder (UFAL) to develop a gelled LH2 fuel and LOX propellant system.
  - This innovation will increase the performance, density, and combustion efficiency of LH2/Al/LOX for use in rockets and combined-cycle vehicles
Propellant Technologies – Applications and Fuels

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- Nanogelled Cryogenic Propellants with Nanoparticulate Additives
  - Revolutionary Aeropropulsion vehicles
  - Next generation aerospace vehicles
  - Many others

- Planned fuels:
  - Liquid methane
  - Liquid propane
  - Liquid nitrogen
  - RP-1
  - Jet A
  - JP-8
  - Liquid hydrogen (last to be addressed in testing)
Approach

First year goals:

- Determine the location for Nanogellant Production
  - Produce nanogellant
  - Characterize the nanogellant production uniformity
  - Determine the effects of storage (shelf life) of the nanogellant

- Determine the location for Nanoparticulate Production
  - Produce nanoparticles
  - Characterize the particle size and uniformity

- Determine the location for the multi-fuel test area

- Ambient temperature check out
  - Produce gelled aviation fuel (high H/C ratio fuel)
  - Produce an aviation fuel doped with nanoparticulates
  - Produce a gelled aviation fuel doped with nanoparticulates
  - Determine the characteristics of the gelled-doped aviation fuel
Approach

Second year and third year goals

- Liquid nitrogen (LN2) check out
  - Produce gelled LN2 using nanogellants
  - Produce a mixture of LN2 and nanoparticles
  - Produce doped-gelled LN2
  - Determine characteristics of the doped-gelled LN2

- Determine cryogenic fuels of interest (potential fuel include but are not limited to liquid propane, liquid methane, and liquid hydrogen)

- Fuel 1 to N testing
  - Produce gelled Fuel 1 to N using nanogellants
  - Produce a mixture of Fuel 1 to N and nanoparticles
  - Produce doped-gelled Fuel 1 to N
  - Determine characteristics of the doped-gelled Fuel 1 to N
  - Optimize production process if necessary to obtain desired results
Approach

**Fourth and fifth year goals**

- Build up combustion test area
- Produce sufficient quantities of gelled-doped fuel in production area to support combustion tests
- Develop diagnostic techniques
  - Measure uniformity of nanogellant/nanoparticulate dispersion in fuel
  - Effect of nanoparticulates on rotating machinery
  - Combustion process
  - Emissions
- Perform initial combustion tests
- Optimize fuel formulation and repeat combustion tests
Gelled and Metallized Gelled Propellants

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Fuels and Space Propellants Web Site
http://www.grc.nasa.gov/WWW/TU/launch/foctopsb.htm
Gelled Hydrogen Propellants

Past Results

• First gelled cryogen (nitrogen) was formulated circa 1960
• Evaporation (boiloff) of gelled hydrogen
  – reduced by factor of 2 to 3 (NAS3-4186, 1966)
  – reduced by factor 25 to 50 % (NAS3-2568, 1964)
• variations due to tank geometries, heat leaks
  – both used silica gellants, at high weight percentages (36 weight %)
• Work with Lockheed (LMSC) and MSFC, with frozen ethane (NAS8-20342, 1968)
• Later work used frozen ethane or methane gellant, at 4 to 10 weight % (Aerojet, SNP-1, 1970)
• Work with TRW using nanoparticulate gellants, at 7 to 8 weight % (NAS3-25793, 1994 and NAS3-26714, 1996)
• Extensive data base on gelled propellants at NASA Lewis
Metallized Gelled Propellants

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• Goal
  – Determine combustion and heat transfer characteristics of metallized
gelled RP-1 /Al propellants in a rocket engine
  – Evaluate fuels including traditional RP-1 and metallized gelled RP-1 /Al
with 0-, 5-, and 55-wt % loadings of aluminum, with gaseous oxygen as the
oxidizer
• Hardware
  – Experiments conducted with a 40-lbf thrust engine composed of a modular
injector, igniter, chamber, and nozzle
  – 31 cooling channels for chamber calorimeter measurements, with
temperature and pressure sensors
• Results
  – Gelled fuel coating, composed of unburned gelled fuel and partially
combusted RP-1, formed in the 0-, 5- and 55-wt % engines
  – Coating caused a decrease in calorimeter engine heat flux in the last half of
the chamber for 0- and 5-wt % RP-1 /Al propellants
Metallized Gelled Propellants

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5 wt% RP1-Al rocket engine test firing at the GRC.

Three-dimensional roller-coaster plot of metallized gelled propellant heat flux: 5-wt % RP-1/Al.
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- **Gelled propellants**
  - Increased safety
  - Increased fuel density
  - Reduced leakage
  - Reduced slosh
  - Reduced cryogenic boiloff
  - Increases in engine specific impulse (in some cases)

- **Metallized Gelled Propellants**
  - All of the above and
  - Large increases in fuel density
  - Large increases in engine specific impulse (in some cases)
Nanotechnology is applied to rocket and aerospace propellants

- Gellants
  - for hydrocarbons
  - for liquid cryogenic fuels (hydrogen, methane, propane)
  - Nanoparticulate materials used for gellants (hydrocarbon alkoxides)
  - Gellants increase fuel safety, density, and energy
  - Gellants reduce fuel slosh, and reduce the vehicle dry mass with higher fuel density

- Nanophase aluminum particles added to rocket and aerospace fuels
  - Metallized gelled propellants
    - RP-1 /Aluminum
    - Hydrogen / Aluminum
    - Others (MMH / Aluminum, etc.)

- Adding metal particles can increase engine exhaust velocity and fuel density
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• Gelled Propellants
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  – Reduced slosh
  – Reduced cryogenic boiloff
  – Reduction in engine specific fuel consumption (in some cases)
  – Increases in engine specific impulse (in some cases)

• Metallized Gelled Propellants
  – All of the above and
  – Larger increases in fuel density
  – Larger reductions in engine specific fuel consumption (in some cases)
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