Synthesizing and Characterizing Nanoenergetic Materials Formed with Supercritical Fluids

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• We would like to thank Dr. Ruth Doherty and Mr. Dan Remmers for their help with sensitivity testing of the energetic materials.

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Advantages of Supercritical Fluid for Processing of Energetic Materials

- Supercritical fluids have liquid-like densities and exhibit large changes in density near their critical point.
- Solubility is a function of density in supercritical fluids.
- **Large changes in solubility from small changes in pressure allows for a high degree of supersaturation.**
- Gas-like diffusivities allow for solvent to diffuse from the solute quickly during precipitation, reducing solvent inclusions.
- Properties give supercritical fluids unique advantages for recrystallization purposes.
Objectives for Supercritical Fluid Processing of Energetic Materials

The specific objectives are:

- Create nano-sized particles of energetic materials through supercritical fluid aided recrystallization
  - Investigate how different pre-expansion pressures and temperatures can affect particle size and morphology in the RESS process.
  - Characterize the recrystallized particles in terms of material properties and their sensitivity to unwanted initiation.
- Coat nano-sized particles by recrystallizing an energetic solute onto an insoluble particle
  - Prove that this can be accomplished through a modified RESS process called the Rapid Expansion of a Supercritical Solution with a Nonsolute (RESS-N) process developed by Mishima et al. (2001).
  - Characterize coated particles in terms of coating quality and size through electron microscopy and spectroscopy.
Nano-sized Energetic Particles
Produced by RESS
Recrystallization
Motivation and Background for RESS Recrystallization

- The reduction of oxidizer particle size in solid propellants has shown to decrease the propellant sensitivity for hot-spot initiation by mechanical forces (van der Steen, 1995, Armstrong, 2005).
- This reduced sensitivity is attractive for the development of insensitive munitions (IM) solid propellants. IM characteristics are desirable due to their safe storage and handling which allows them to be used in more applications.
- Liquid solvent recrystallization often generates non-uniform supersaturations and liquid solvent inclusions can be found in precipitated crystals. The high degree of supersaturation required to generate nano-sized particles are not possible with liquid solvent recrystallization.
- Physical grinding or milling to achieve nano-sized particles is:
  - Challenging to create and to control desirable size distribution
  - Dangerous due to the energy applied to fragment crystals of reactive material
**Principles of RESS Process**

- **RESS** stands for the **Rapid Expansion of a Supercritical Solution**, utilized initially by Coffey and Krukonis in 1989 for making nano-sized particles in the pharmaceutical field.
- In this process, a fluid is heated and compressed beyond its critical point, the solvent then dissolves a solute to form a supercritical solution.
- Supercritical solution is rapidly expanded to promote a high degree of supersaturation to form nano-sized particles.
The PSU RESS system was established during the MURI project. It is a custom designed and constructed facility with strict control for safety operation for experiments with energetic materials at elevated pressures.

- Operators are protected from ultra-high pressure section by reinforced wall.
- LABVIEW® program allows remote operation of the experiment
• Previously reported RESS systems do not operate at greater pre-expansion pressures than 34.5 MPa (~5,000 psi).
• Higher pre-expansion pressure could improve solubility and thus supersaturation, producing smaller particles than previously observed.
• Pre-expansion pressures were investigated at much higher levels than conventional RESS systems up to 121 MPa (~17,500 psi).
• Different pre-expansion temperatures and nozzle sizes have been used to investigate the effect of these operating parameters on final particle size.
Micron-Sized RDX Particles

- Field Emission Scanning Electron Microscopy (FE-SEM) image of (Class I, Type II) military grade RDX shows relatively large and imperfect crystals.
- This type of RDX can have high HMX contamination (6 wt%).
- Inclusions, cracks, and sharp edges can be seen which all make the material more sensitive to accidental initiation.
• Produced RDX particles were round and narrow in size distribution.
• Primary particles were approximately 100 nm in diameter and smaller.
• Product of fast precipitation and uniform supersaturation.
• Generally, higher pre-expansion pressures produce narrower size distribution and shift distribution curves to the left.
• Pre-expansion pressures above 86.2 MPa did not show a large improvement in size distribution.
Again, higher pre-expansion pressures yielded narrower size distributions with the peak shifted to the left.

Pre-expansion pressures higher than 86.2 MPa do not seem to show significant improvement.
Median Particle Size for RDX RESS Experiments (100 μm nozzle)

- Error bars are the FWHM deviations in the size distributions for each test.
- All median particle sizes are less than 100 nm.
- Size distributions were found to follow a lognormal distribution.
• Trends leading to smaller particles for higher pre-expansion pressures are easier to observe than those for the 100 μm nozzle.
• Higher pre-expansion pressure seems to produce a minimum particle size at pressures above 100 MPa, as can be seen from these figures.
RESS synthesized RDX has the same X-ray diffraction pattern as $\alpha$-RDX crystalline particles. RESS process also purifies RDX with respect to HMX (from liquid chromatography tests).

<table>
<thead>
<tr>
<th>RDX Sample</th>
<th>HMX mass fraction (%)</th>
<th>RDX mass fraction (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Military Grade (Class I Type II)</td>
<td>5.71</td>
<td>94.29</td>
</tr>
<tr>
<td>Recrystallized</td>
<td>0.86</td>
<td>99.14</td>
</tr>
<tr>
<td>RESS Synthesized</td>
<td>0.32</td>
<td>99.68</td>
</tr>
</tbody>
</table>
Sensitivity Test Results for RESS Synthesized RDX

<table>
<thead>
<tr>
<th>Sensitivity Test</th>
<th>Military Grade RDX</th>
<th>RESS Synthesized RDX</th>
</tr>
</thead>
<tbody>
<tr>
<td>Impact sensitivity $H_{50}$ (cm)</td>
<td>17</td>
<td>44</td>
</tr>
<tr>
<td>ABL Friction (psig)</td>
<td>135</td>
<td>100</td>
</tr>
<tr>
<td>NSWC ESD (joules)</td>
<td>0.165</td>
<td>0.165</td>
</tr>
</tbody>
</table>

- Sensitivity testing for RESS synthesized RDX was performed at the Naval Surface Warfare Center Indian Head Division (NSWC-IHD) in collaboration with Dr. Ruth Doherty and Mr. Dan Remmers.
- Sponsorship of this testing for NSWC’s work was provided by Dr. Cliff Bedford of the Office of Naval Research (ONR).
- RESS synthesized nano-sized RDX is indeed significantly (44 cm vs. 17 cm) less sensitive to impact than standard military grade RDX as hypothesized.
Bis(2,2,2-trinitroethyl)-3,6-diaminotetrazine or BTAT is a newly synthesized energetic material containing less carbon than RDX.

BTAT particles were provided by Professor Thomas Klapötke of Ludwig Maximilians University of Munich in Germany.

FE-SEM images of BTAT crystals showed that they were plate like in morphology.

The original shapes of the particles result in interparticle friction if particles are impacted, increasing sensitivity to initiation.

Particles that are plate like are hard to process in propellants and/or explosives (Doherty, 2008).
• BTAT particles were recrystallized in acetone and processed through PSU’s RESS facility.
• RESS conditions were $P_0=69$ MPa and $T_0=65^\circ$ C.
• BTAT particles did not crystallize into plate-like particles, more rounded particles were observed.
• Results are encouraging for the possibility to change particle morphology through the RESS process.
• Agglomeration could be avoided through an alternate expansion environment.
It is beneficial to operate a RESS system at a higher pre-expansion pressure than 34.5 MPa (highest pressure most systems go to) as smaller sized particles with a narrower distribution can be produced. Benefits of higher pre-expansion pressure is more apparent with narrower particle size distributions than decreasing the median particle sizes.

Maximum suggested pre-expansion pressure is approximately 100 MPa (14,500 psi) as there was limited benefit beyond this pressure from the present test results.

Particle size distributions are narrower and average particle sizes are smaller for 150 μm nozzle diameter. Explanations include higher mass flows leading to a more dilute supercritical solution which could decrease interactions (like coagulation) between particles and a wider free jet that could interact with the expansion tube and the walls of the collection vessel.
Coating of Nano-sized Aluminum Particles with RDX by Supercritical Fluid Precipitation
Motivation for Coating Nano-sized Aluminum

- Coating RDX on nano-sized aluminum has many potential benefits:
  - Help improve performance by placing RDX and aluminum in intimate contact with each other to achieve faster reaction (van der Heijden et al., 2004) as well as limiting the growth of Al$_2$O$_3$.
  - Intimate contact between RDX coating and other ingredients helps propellant processing.
  - RDX coating could prevent nano-sized aluminum particles from developing a further oxide coating.
Dubois et al. (2007) used a polymer coating to protect nano-sized aluminum particles from developing a growing oxide layer.

Glebov et al. (2006) used supercritical fluids to dissolve polymers and create a supercritical solution. The polymer was then precipitated over the nano-sized aluminum particles in a batch process.

Mishima et al. (2001) coated insoluble proteins with a protective polymer by suspending the proteins in a supercritical solution and flowing the solution through a capillary nozzle. This process was termed the Rapid Expansion of a Supercritical Solution with a Nonsolvent (RESS-N).
Rapid Expansion of a Supercritical Solution with a Nonsolute (RESS-N) Process

- RESS-N process allows for the coating of nano-sized materials in a continuous manner.
- Rapid expansion of a supercritical solution produces a tremendous change in dissolution power of the parent fluid and causes high degrees of supersaturation.
- High degree of supersaturation causes a large number of nucleation sites to form, nucleation sites form by a foreign substrate and coat the substrate by heterogeneous nucleation.

Supercritical Fluid (SCF) Controlled at Selected T, P, and Amount of Solute (RDX)

Nano-sized aluminum suspended into supercritical solution

RDX coating through heterogeneous nucleation during nozzle expansion

Solvent  Solute
Advantages of RESS-N System

- RESS-N process is a continuous process that can produce higher yields than batch coating methods.
- Chemical process of nucleation could provide uniform and consistent coatings.
- Moderate operating temperature that is below the decomposition temperature of almost all energetic materials.
- ALEX® particles are small enough to flow through a nozzle while maintaining a sufficient pre-expansion pressure (34.5 MPa) so that a large degree of supersaturation will occur from the expansion without nozzle clogging.
- Shear flow and pressure gradients from expanding jet could disperse ALEX® agglomerates when high degrees of supersaturation occur, breaking them up for coating purposes.
ALEX® particles seeded in supercritical solution act as nucleation sites. Rapid expansion of the supercritical solution of RDX and CO₂ can disperse ALEX® particles and induce a high degree of supersaturation.
Smaller agglomerates and more individual ALEX® particles were observed when ALEX® was seeded in neat supercritical CO₂ and expanded. High shear forces from fast fluid can cause agglomerates to break apart.

FE-SEM mounting stub was placed directly downstream of the discharging nozzle and then ALEX® particles were impinged on its surface to examine their dispersion.

This is an added benefit as rapid expansion of the supercritical fluid promotes insoluble particle breakup and high degrees of supersaturation simultaneously.

Similar results were witnessed by previous researchers with alumina particles (Yang and Ozisik, 2008) at the Rensselaer Polytechnic Institute.
Particle Entrainment Vessel

- Pressurization fluidizes ALEX® particles and allows them to be entrained by a supercritical solution.
- Seeded particles serve as nucleation sites as they flow through the nozzle.
Air actuated needle valve allows ALEX® particles to remain isolated from the pressurized CO₂ until a supercritical solution is present.
FE-SEM Results from Initial Particle Entrainment Vessel

- Initial particle entrainment vessel introduced ALEX® at a high flow rate compared with the low flow rate of RDX resulting in thin coating thickness.
- Tests were conducted at 4,000 psi upstream operating pressure and a temperature ranged from 50 to 70°C utilizing a 300 μm micro-orifice.
- Coatings ranged in degree from image inspection and coated particles tended to bridge together.
- Coatings tend to be very thin and may not cover all particles.
Tests were conducted at 4,000 psi upstream operating pressure and a temperature ranged from 50 to 70°C utilizing a 300 μm micro-orifice.

Coated particles have a different morphology (distinguishable crystal faces, less round, and different aspect ratios) than RESS synthesized RDX or the original ALEX® particles.

Particles were larger than RDX produced in RESS system.

Suspended ALEX® particles clearly affected RDX precipitation.
Sample Deformation Under Electron Beam

- Some particles decompose under the strong electron beam while others reveal spherical particles underneath after the beam exposure.
- Revealed spherical particles have the same size and shape as ALEX® particles. This verifies that the ALEX® particles are coated.
Summary of RESS-N Results

• Fairly consistent coating results were observed across broad samples with little foreign contamination.

• Collected samples had a noticeably different morphology than ALEX® or RESS synthesized RDX.

• Prolonged electron beam exposure shows the existence of ALEX® particles inside the collected sample.

• RESS-N process could be beneficial for encapsulating nano-sized aluminum in RDX or another propellant ingredient.
NEEM MURI

Overall Summary of Progress

• The ultra-high pressure rapid expansion of a supercritical solution (RESS) system has been developed and tested successfully for producing nano-sized RDX crystalline particles (~90 to 330 nm) through remote control operation.

• A series of ultra-high pressure tests have been conducted to investigate the effect of pre-expansion temperature and pressure levels as well as nozzle orifice diameter on final particle sizes of RDX.

• The RESS synthesized RDX was characterized for its material properties and sensitivity showing improved quality in both.

• A RESS-N system has been developed and utilized to coat nano-sized aluminum particles by heterogeneous nucleation.

• The collected particles from the RESS-N process were examined to determine the presence of a coating and the quality of the coating.
Potential Future Work

• Further understanding and expansion of the RESS process:
  – Spectroscopic solubility measurements for energetic materials dissolved in supercritical CO$_2$ at elevated pressures.
  – Better understanding of how expansion environments affect particle formation from changing expansion conditions (e.g. different expansion chamber pressures and discharging into water and surfactant solutions).
  – Consideration of producing various nano-sized energetic materials such as diaminoazotetrazine N-oxides (DAATO$_{3.5}$), triaminoguanidinium salts (TAGDNAT, TAGDNATO), N-Guanylurea-Dinitramide (Fox-12), and Ammonium Dinitramide (ADN) by using the RESS process.
  – Effect of co-solvents on final produced particles’ sizes, yield, and morphology.

• Extending the work on the RESS-N process which includes:
  – Applying a CO$_2$ soluble surfactant to reduce agglomeration of ALEX® particles to supply more surface area for coating with RDX.
  – Burning a propellant embedded with RDX-coated ALEX® particles in a strand burner and comparing the burning behavior to propellants containing both uncoated ALEX® particles and micron-sized nitramine particles.
Thank you very much for your attention

Any questions?