RA3-FA2: High Temperature Properties and Chemistry of Agents and Simulants

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Problems and Challenges


Events Range Over Many Orders of Magnitude in Time & Space

R. Sinha, CRAFT Tech report prepared for DTRA.
Scientific Drivers

**Scientific Drivers:**
- Identify intermediate and final decomposition products and reaction rates at high temperatures and under fast heating rates
- Understand & control reaction chemistry for various conditions of C-WMD operations

**Thrust 1: AGENT/SIMULANT**
- **PYROLYSIS**
  - Speciation; phosphorus chemistry; kinetics
- **OXIDATION**
  - Speciation; hydrocarbon chemistry; ignition delay time/flame speed
- **GAS/LIQUID DROPLETS INTERACTIONS**
  - Hot/burning agent/simulant; interaction of reaction products; evaporation

**Thrust 2: AGENT/SIMULANT + RM/EM**
- **REACTIVE MATERIALS (RM)**
  - Composition; size; size distribution
- **THERMAL EFFECTS**
  - Temperature; burning duration; heating rate
- **CHEMICAL EFFECTS**
  - Composition; chemical additive; catalysis

**Thrust 3: AGENT/SIMULANT + RM/EM + TURBULENCE/ DUST**
- **INTERACTION WITH TURBULENT MIXING**
  - Particle size distribution; configuration; thermal gradients
- **CONTROL ON CHEMICAL TIMESCALE**
  - Composition; additives to enhance or inhibit reactivity; catalysts
- **OTHER EFFECTS**
  - Interactions with concrete; dust; heat sinks

**Diagnostics and Modeling/Simulation**
### Investigators and Collaborators

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<th>Name</th>
<th>Position</th>
<th>Institution</th>
<th>Workforce</th>
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Long-term Goals and Strategies

• Long-term Goal
  • Identify, understand, and control decomposition reactions and kinetics of agents and simulants under counter-WMD conditions.

• Strategies
  • Complementary experimental and computational investigations of the fundamental chemical reactions and kinetics.
  • Develop and implement novel experimental techniques and new computational models and tools.
  • Characterize agents/simulants under relevant conditions.
  • Biweekly meetings to coordinate experimental and computational approaches to achieve a coherent overall approach.
IPP Goals and Strategies

• IPP Goals
  • Identify a canonical model.
  • Generate initial results to validate the selected approaches.
  • Institute and solidify collaborations between PIs and other collaborators.

• Strategies
  • Initial weekly meetings of the FA PIs and their teams.
  • In coordination with DTRA, develop a comprehensive roadmap for the required experimental and computational research.
  • Implement research activities and generate initial results.
  • Meet biweekly to provide updates and discuss progress and problems, and to ensure the validity of the selected approaches.
What is Revolutionary and/or Unique About this Research

- Experimentalists, modelers, and DTRA addressing existing challenges in a coherent and well-coordinated manner.
- New capabilities for more realistic and better-controlled counter-WMD conditions while using improved diagnostics for in-situ monitoring.
- Leverage dual-phase combustion to tune thermal and chemical kill.
- Broadband QCL-based sources for time-resolved chemistry/physics.
What is Revolutionary and/or Unique About this Research

- Heterogeneous shock tube to quantify kinetics of particle-based agent decomposition.
- Optical tweezers to study individual simulant droplets.
- Flow/flame burner to study new RMs.
- Combine new experimental capabilities with detailed CFD models.
- Use predictions of chemical processes under relevant conditions.
- Use inverse UQ modeling to assess accuracy of predictions.
Defeat of Agents/Simulants

Physics and Chemistry of interest:
- Droplet breakup
- Droplet evaporation
- Chemical reactions & kinetics
- Turbulent transport

Additional Dimensions:
- Pressure
- Chemistry
- Catalysis
- Photo
- T-dependent property parameters

Multi-dimensional problem
UIUC heterogeneous shock tube allows explicit kinetics investigations of agent surrogate decomposition with or without particulates.

- Collaborations with Phillips at UA using QCL diagnostics for direct detection of surrogates and primary decomposition products
- Collaboration with JHU and NJIT to test particulates for agent defeat efficiency.
Explosion tests with surrogate can be conducted up to 5 gram scale, with or without added particulates

- QCL measurements by Phillips at UA are the primary diagnostic
  - Allows detection of surrogate and primary decomposition products
- Particles injected as clouds or dispersed by HE charge.
Fast dispersive Infrared spectrometer coupled with small explosion chamber allows for exploration of 8-12 micron region during agent surrogate/fireball interaction

- Sub-ms duration of each scan; 5 ms between scans
- Bright carbon-arc & f/2 spectrometer allow high SNR
- Can test various surrogates in 1-2 g HE fireballs
Advanced Laser Diagnostic

• Simultaneously measure simulants and decomposition products via broadband, tunable infrared laser absorption spectroscopy

• Identify time-resolved mixing ratios and temperatures via broadband, swept-wavelength external cavity quantum cascade lasers (ECQCLs)

• Develop QCL-based frequency comb sources for higher speed measurements

• Support experiments throughout MSEE team by bringing custom instrumentation to PI laboratories
  • Shock-tube measurements (Glumac)
  • Small-scale explosive tests (Glumac)
  • Burner/flame/flash/laser heating experiments (Phillips, Eilers)
  • Flow reactors (Dreizin)

• Improve spectral modeling and analysis for high-temperature, inhomogeneous media (Sinha)
High-speed spectroscopy of explosive detonations

- Collaboration with Nick Glumac, UIUC
- MWIR ECQCL swept from 2050-2300 cm\(^{-1}\) at 100 Hz rate
  - 1 spectrum each 10 ms, continuous
  - Faster rates up to ~ 1 kHz possible
- Simultaneous absorption/emission measurement
- Spectral fitting to determine CO, CO\(_2\), H\(_2\)O, N\(_2\)O and temperature

LWIR swept-ECQCL prior results

- Collaboration with Nick Glumac, UIUC
- LWIR (8-12 µm) “fingerprint” region valuable for trace species measurements
- Time-resolved measurements critical for reactive/transient species

### Detection of transient NH$_3$

**PBXN-5**

- 10-110 ms
- 100-200 ms
- 1-2 s
- 10-11 s

**Measurement of ethene and propene from decomposition**

Broadband, time-resolved infrared absorption spectroscopy enables study of chemistry over wide range of time-scales and temperature regimes
Multi-functional Flow system with Flame Burner

Dreizin, NJIT

Characterizing prompt defeat of CWA

Study effect of:
- Elevated temperature
- RM combustion products
- Mixing conditions/turbulence
Explore additional parameter space

- Recovering kinetics of CWA defeat at different temperatures and exposure times
  - Modifying kinetics by Glaude et al., Eilers et al.

- Interacting with CRAFT Tech for guidance/interpretation of experiments
  - Effects of turbulence, aerosol concentration

- Kinetics of metal-oxide assisted prompt CWA decomposition
  - Varied RM compositions

Characteristic temperatures and exposure time achievable in experiments on thermal decomposition of DIMP

![Graph showing characteristic temperatures and exposure times for different methods of CWA decomposition.](image)

- Pyroprobe, Yuan et al., 2019
- Tubular flow reactor, Zegers and Fisher, 1998
- Shock tube, Neupane et al., 2018
- Calculation using kinetics by Glaude et al., 2002
- Data missing

- Laser heating, Thompson et al., 2019
- Data missing

- 99.999% reduction
- 99.99% reduction
- 99.9% reduction
- 99% reduction
- 90% reduction

1000/T, K^{-1}

Time, s
Collaborative efforts

• Combustion of RM: diagnostics and cross-reference:
  • Glumac, Phillips, Eilers

• RM samples
  • Weihs, Zachariah, Groven

• Combustion of RMs with chemicidal products/Prompt defeat mechanisms
  • Sinha, Menon
On-Going DTRA Basic Research Activities

Metal-Based Reactive Materials for Rapid Destruction of Chemical Weapon Agents (Dreizin/NJIT):
Modeling activities (Year 1):

- CWAS + RM kinetic model development:
  - Retrieve/assemble components for preliminary model: DIMP kinetics
  - Systematically develop kinetic models for CWAS inactivation via thermal, catalytic and kinetic mechanisms (mechanistic description)

- Test planning support and model validation:
  - Perform scope-out parametric studies: 3-D CFD and 1-D reactor networks
  - Provide detailed temperature/flow distributions from refined calculations
  - Validate kinetic models and explore scaling effects

3-D CFD Representation of NJIT Flow Reactor

Air + DIMP

Air (+ Hot Products + RM)

Reduced Kinetic Model: 19 species in 34 reactions

1-D Reactor Network Representation

UCF Kinetic Model v2.0: 131 species in 1350 reactions
DIMP Kinetic Model Reduction: Pyrolysis and Oxidation

- **Basic Research**: Very large detailed kinetic models (LLNL, UCF v1.1, UCF v2.0): 100s species in 1000s reactions
- **Computationally-tractable CFD**: 20-30 species desirable
- **Systematic kinetic model reduction**:
  - Sensitivity analysis
  - Element flux analysis
  - QSSA-based reduction
- **MSEE Shock Tube/Explosive/Reactor Data**
  - Collaborate: Glumac, Phillips, Eilers & Dreizin

Combined P, C, H and O Element Flux

Reduction of UCF DIMP Model v1.1

Coarse-Grain Reduction

Fine-Grain Reduction
IPP and Beyond

Sinha, CRAFT Tech

Path: Develop tabulated chemistry for AD CFD simulations:

- Computationally-tractable with limited number of scalars: Higher-fidelity kinetic models without aggressive reduction (Collaborate with Menon)
- Turbulence-chemistry interactions and finite-rate chemistry effects
- Combustion of RMs with chemicidal products/Prompt defeat mechanisms (Collaborate with Dreizin)

AD problem: Major challenges:

- Highly compressible environment (to date only pressure fluctuations)
- Three-stream reacting formulation (to date only 3rd stream as diluent)
- Multi-phase implementation for RM (to date only droplet evaporation)
- Multiple combustion regimes (to date non-premixed/partially premixed)

Agent Defeat Problem

CRAFT Tech Multi-Time Scale Flamelet Progress Variable Approach for Gas Turbine Combustors

UDF Call

Primary Flame Look-Up

\( Y_{p,1} \) primary progress variable
\( Y_{p,NO}, Y_{p,N} \) secondary NO, progress variable

\( \Phi(Z, T, Y_{p,1}) \)

Table Look-Up

\( \Psi(P, T, Z, Y_{p,1}, Y_{p,NO}, Y_{p,N}) \)

\( N + NO = N_2 + O \)
\( N + O_2 = NO + O \)
\( N + OH = NO + H \)
\( N + N + M = N_2 + M \)
Simulant – Kinetics and Turbulence Assessment

Menon, GIT

- Kinetics – Shock tube studies with iUQ:
  - DIMP: Earlier (AIAA-2020-1237) reduced 278 species & 1250 reactions to 73 species & 275 reactions for IUQ studies
  - Further kinetics reduction based on data and reduction methods (CRAFT)
  - Shock tube data for V & V needed
- Turbulence – Re-Shocked RMI studies
  - Simulant curtain with and w/o metal oxide particles.
  - Turbulent mixing with and w/o combustion planned later

Planned: Schematics of re-shocked RMI
Pyroprobe with kinetic FTIR

Propene + IMP

MOPO + 2-Propanol ?
(not observed)

MPA + Propene

MOPO + 2-Propanol + Propene

Propene

10 deg/s; 1,000 °C
~1,800 deg/s; 500 °C
Thermodynamic reaction

Ethylene at 1200 °C, 5 s

~1,800 deg/s; 1,000 °C
~18,000 deg/s; 1,000 °C
Kinetic reaction
Characterization of individual simulant droplets

Physics and Chemistry of interest:
• Droplet breakup
• Droplet evaporation
• Chemical reactions & kinetics
• Turbulent transport

Optical Tweezers

Contact-free trapping, micro-manipulation, and characterization

Cavity-enhanced droplet spectroscopy (Whispering gallery modes) via SRS:
• Droplet size (evaporation)
• Composition
• Temperature

http://www.journalnano.org/?p=98
Optical tweezers with laser heating

Eilers, WSU

Options:
- FTIR, MS
- Multiple traps (SLM): simulant droplet and RM particle.
- SLM & mirror: double beams & macro-traps.
- AOM beams: rotate particles to expose specific surfaces.
- SLM: Beam-shaping (e.g., donut to generate optical shields).
H2 Al Powders

Al-Mg-Zr Powders

~2x increase in combustion efficiency

Enhanced Ignition and Combustion

Vary vapor phase elements (Al, Mg, Ca, Zn) and condensed phase elements (Zr, Ti, Hf, B)
Producing and Characterizing Nano-oxides

Weihs, JHU

Al & Mg oxidation in vapor

Zr-Al-Mg-N-O liquid

N then O when Al, Mg vapor slows

Zr nitridation in liquid

Alumina Soot

~ 100 µm

2 µm

TEM Analysis of Nano-oxides

Al₂O₃

MgO

0.1 µm
Plans for Collaborative Exchanges

RA2-FA2 Material Development
DFT Calculations

Flow reactor
Dreizin

Optical Tweezers/Laser / Pyroprobe
Eilers

Fast Infrared Diagnostics
Phillips

Continuum
Menon

Cold plasma
Weihs

Shock tube / Blast chamber
Glumac

RA2-FA3 Turbulent Environments

Continuum
Sinha

GCAP: NAWCWD China Lake
- Clare Dennis
- Nathaniel Davis

GCAP: CCDC ARL
- Jennifer Gottfried

GCAP: NSWC Indian Head
- Demitrios Stamatis
- Michael Soo
Collaborative Exchanges w/ CCRI

CCRI Modeling
UQ (Shields)
Machine Learning (Mueller, Barnes)

Optical Tweezers/Laser / Pyroprobe
Eilers

Flow reactor
Dreizin

Fast Infrared Diagnostics
Phillips

Cold plasma
Weihs

Shock tube / Blast chamber
Glumac

Continuum
Menon

Continuum
Sinha

CCRI Data Management (Elbert)

CCRI Diagnostics
Compressed Sensing (Foster)
In-situ visualization (Hufnagel)