**Goals**

Understand the overpressure phenomena in the FAA Aerosol Can Test

1. Why is the overpressure occurring with the added suppressants?
2. What can be done about it?

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**Approach**

Physics in FAA test is too complicated to examine with detailed kinetics, so simplify.

- Fuel discharge port (propane/ethanol/water)
- Arcing ignitor
- Partially premixed fuel-rich reactants (PREMIX), or distributed reaction region (PSR)
- High strain (shear), partially premixed diffusion flame region (OFDF)
- Partially premixed diffusion flame with ancillary burning of agent (UNICORN)

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**Progress**

Background
- Thermodynamic Equilibrium Calculations
- Kinetic Mechanism Development
- Measurement of 2-BTP Decomposition

Perfectly-Stirred Reactor (PSR) Calculations
- Diffusion Flame Calculations (Cup Burner)
- Homogeneous Auto-Ignition (PFR) Calculations
- Diffusion Flame Calculations (Counterflow)
- Premixed Flame Calculations (PREMIX)
Background:

~ 65 relevant papers collected and assimilated.

Highlights:

<table>
<thead>
<tr>
<th>Researchers</th>
<th>Fuel</th>
<th>Agents</th>
<th>Experiment</th>
<th>Phenomena</th>
<th>Explanation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Grosshandler and</td>
<td>Propane, ethylene</td>
<td>CF3I, CF3Br, HFCs</td>
<td>Detonation -</td>
<td>Higher Ma, flame speed,</td>
<td>None</td>
</tr>
<tr>
<td>Gmurczyk</td>
<td></td>
<td></td>
<td>Deflagration Tube</td>
<td>pressure ratio</td>
<td></td>
</tr>
<tr>
<td>Shebeko et al.</td>
<td>methane, hydrogen</td>
<td>C2H5F, C4F10</td>
<td>Deflagration</td>
<td>Higher pressure rise</td>
<td>Added heat release from agent</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>and dP/dt</td>
<td></td>
</tr>
<tr>
<td>Moriwaki et al.</td>
<td>methane, ethane</td>
<td>CH3O, CH3I, CH3, Br</td>
<td>Shock tube</td>
<td>Shorter ignition delay</td>
<td>None</td>
</tr>
<tr>
<td>Ikeda and Mackie</td>
<td>ethane</td>
<td>C3HF7</td>
<td>Shock tube</td>
<td>Shorter ignition delay</td>
<td>None</td>
</tr>
<tr>
<td>Manhimey et al.</td>
<td>heptane</td>
<td>water mist</td>
<td>Heptane pool</td>
<td>Higher heat release</td>
<td>Enhanced fluid-dynamic mixing</td>
</tr>
<tr>
<td>Hamins et al.</td>
<td>hydrocarbons</td>
<td>HFCs, water mist, N2, powders</td>
<td>Full-scale test</td>
<td>Higher pressure, visual flames</td>
<td>Enhanced fluid-dynamic mixing</td>
</tr>
<tr>
<td>Holmstedt et al.</td>
<td>propane</td>
<td>C3HF7, C2H2F4, CF3Br</td>
<td>Diffusion flame</td>
<td>Higher heat release</td>
<td>None</td>
</tr>
<tr>
<td>Katta et al.</td>
<td>methane</td>
<td>CF3H</td>
<td>Cup burner</td>
<td>Higher heat release</td>
<td>Agent reaction</td>
</tr>
<tr>
<td>Ural</td>
<td>none</td>
<td>C3HF7, C2H2F4, CH3F2</td>
<td>Flammability</td>
<td>Visual observation</td>
<td>Heat loss/gain</td>
</tr>
</tbody>
</table>

The flow-field influences the extinction process:

\[ D \equiv \frac{\tau_r}{\tau_c} \]

Chemical Time:

\[ \tau_c \equiv \frac{\rho}{w} = \rho c_F c_O \exp\left(\frac{E}{RT}\right) \]

Flow Time:

\[ \tau_r = \frac{\ell}{v} \]

A measure of the overall chemical reaction rate can be obtained with:

- Perfectly-Stirred Reactor (PSR) Calculations
- Diffusion Flame Calculations (Counterflow)
- Premixed Flame Calculations
Background: Flame Extinction, Propane-Air with R-125, Counterflow

![Graph showing Local Extinction Strain Rate vs. Agent Molar Concentration](image1)


R-125

trees et al. NIST SP-861

Background: Flame Extinction, Heptane-Air with R-125, Counterflow

![Graph showing Agent Volume Fraction vs. Extinction Strain Rate](image2)

To understand why R-125 does not extinguish the FAA ACT, we must understand:

- the fuel reaction chemistry
- agent reaction chemistry
- mixing
- flame characteristics.

Background: Flame Extinction

Thermodynamic Equilibrium Calculations

What do equilibrium calculations tell us about the general behavior of the system?

To do an equilibrium calculation, one must know the initial reactant mix (fuel, air, agent, water vapor, etc.). We don’t really know them for the ACT, so keep them all as variables, and find the equilibrium conditions for a wide range of initial mixtures.
HFC-125: Adiabatic Flame Temperature ($T_{\text{ad}}$)

- $T_{\text{ad}}$ is high for all $\eta$.
- Change in behavior at $[X]/[H]=1$ (about 7.5 % HFC-125, red curve above).
- With large amounts of agent, a wide range of $\eta$ gives nearly equivalent $T_{\text{ad}}$.
- As agent is added, more and more chamber volume is necessary to achieve stoichiometric combustion.
- Where flame goes out ($X_i=13.5$ %), all the chamber volume is involved in combustion (i.e., $\eta=1$).

Thermodynamic Equilibrium Calculations

Halon 1301: Adiabatic Flame Temperature ($T_{\text{ad}}$)

- $T_{\text{ad}}$ is high for all $\eta$, but decreases somewhat as agent is added.
- most of the plot is below $[X]/[H]=1$ (about 11 % CF$_3$Br), so can’t see change at $[X]/[H]=1$.
- The amount of chamber volume for peak $T_{\text{ad}}$ does not change with $X_i$.
- Why? => $\text{CF}_3\text{Br} + 2\text{H}_2\text{O} = 3\text{HF} + \text{HBr} + \text{CO}_2$.
- i.e., there’s always enough H and O in the system to oxidize the CF$_3$Br without more air!
- The $T_{\text{ad}}$ is very sensitive to $\eta$.

Thermodynamic Equilibrium Calculations

What do they tell us about the maximum pressure rise?
- Higher $\eta$ has very little effect on $\Delta P$.
- At $\eta$ of peak $T_{\text{post}}$ or CO$_2$, the $\Delta P$ is constant! => can't use pressure rise to determine $\eta$.
- Actual $\Delta P$ is always less than predicted. This due to a chemical kinetic effect, but is it from Br or from reduced temperature (i.e., from mixing-induced dilution)?

=> MUST LOOK AT THE KINETICS TO FIND OUT!
Kinetic Mechanism Development

**CH4-air premixed flame, 0, 4, and 6 % R-125**

Currently developing these charts for HFC-125 with propane and ACT.

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**Aersol Can Test Mechanism:**

<table>
<thead>
<tr>
<th>Species</th>
<th>Reactions</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_4$ hydrocarbon mechanism from Wang</td>
<td>111 784</td>
</tr>
<tr>
<td>Ethanol mechanism of Dryer</td>
<td>5 36</td>
</tr>
<tr>
<td>HFC mechanism from NIST1,2</td>
<td>51 600</td>
</tr>
<tr>
<td>$CF_2Br$ mechanism of Babushok (NIST)2</td>
<td>10 122</td>
</tr>
<tr>
<td>Updated rates from more recent literature, additional rates of fuel radical reaction with R-125.</td>
<td>177 1494</td>
</tr>
<tr>
<td>2 Validation: CH4-air and CH3OH systems (with CHF3, C2H2F4, C2HF5, CF3Br, C3HF7): - premixed flame speed, - species profiles in low-pressure premixed flames, - extinction strain rate for counterflow diffusion flames, - cup-burner extinction.</td>
<td></td>
</tr>
</tbody>
</table>

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Kinetic Mechanism Development: Measurements of 2-BTP Decomposition

- Can’t do calculations yet for 2-BTP because there’s no mechanism for its initial decomposition.
- Once we have its decomposition to HFC and HBrC fragments, it will feed into the overall NIST HFC mechanism.
- So, we must first estimate/measure/calculate its decomposition.

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**Single Pulse Shock Tube**

**Characteristics:**
- System heated to 100 °C
- $\tau = (500 \pm 50)$ μs (monitored with pressure transducers)
- Typical shock conditions: 2-6 bar, 900 – 1250 K

**Advantages of Shock Tube for Gas Kinetic Studies:**
- Essentially a pulse heater, $\tau = (500 \pm 50)$ μs
- No surface induced chemistry (diffusion slow compared with $\tau$)
- Use of dilute conditions, radical chain inhibitors, sensitive GC/MS analysis
  → isolation of initial processes, observation of multiple channels
Studies of 2-BTP Decomposition

Unimolecular (initial studies):
- HBr elimination from 2-BTP ca. 100x slower than unfluorinated analog
- Initial kinetic studies show some interference from radical induced decomposition (work in progress)
- Slow rate suggests importance of radical processes in practical systems

Bimolecular decomposition induced by reactive radicals (e.g. H atoms):

- \( \text{H} + 2\text{-BTP} \rightarrow \text{Products} \)
- Initial studies show products indicating displacement and abstraction of Br as major channels.
- But - product spectrum more complex than expected with some as yet unidentified species.
- Work in progress to determine mechanism and kinetics.

Perfectly-Stirred Reactor (PSR) Calculations

Calculation method

1. We want a measure of \( \tau_{\text{chem}} \)
2. At the blow-out condition, \( \tau_{\text{chem}} = \tau_{\text{flow}} \)
3. To find the blow-out condition, calculate \( T_{\text{PSR}} \) at decreasing values of the residence time, \( \tau_{\text{flow}} \), until the time is too short for reaction to occur (\( T_{\text{PSR}} \) drops to inlet temperature (blow-out)).

Perfectly-Stirred Reactor (PSR) Calculations

- Used to estimate the overall chemical reaction rate.
- Performed for R-125, 1301, and 1301 with N\(_2\).

Assumptions:
- specified premixed inlet conditions.
- adiabatic (no heat losses), no species reaction at the walls.
- perfectly stirred (outlet conditions are the same as the reactor conditions).
- steady-state operation.

Perfectly-Stirred Reactor (PSR) Overall Chemical Rate with R-125

- Adding R-125 lowers \( \omega_{\text{chem}} \) for rich mixtures (low \( \eta \)), but raises (then lowers) it for lean mixtures (high \( \eta \)).
- \( \eta \) has a big effect on overall chemical rate at low \( X_i \), less effect at high \( X_i \) (follows temperature results).
- i.e., for higher \( X_i \), these curves flatten (\( \omega_{\text{chem}} \) is insensitive to \( \eta \) for \( \eta > 0.4 \)).
- Adding 1301 always lowers $\omega_{\text{chem}}$ (for all $\eta$).
- $\omega_{\text{chem}}$ falls off very steeply with $\eta$ (follows temperature results).

- Top two curves do not put the flame out; bottom one does.

- For R-125, we can use pressure rise data with equilibrium calculations to estimate $\eta$.
- For 1301, can't use pressure rise, so we don't really know $\eta$.
Current Understanding

Equilibrium and PSR Calculations Indicate:

- In the FAA ACT with R-125 or 2-BTP, to achieve the observed pressure rise, a large fraction of the chamber volume (with the agent) must be involved in the combustion.
- Thus, the agents are not inert, but rather, act like poorly-burning fuels.
- Unlike in other flames, very little kinetic inhibition is occurring with R-125 and 2-BTP; whereas, CF₃Br does inhibit the flame, as expected.
- The amount of chamber volume involved in the combustion, $\eta$, appears to be a key parameter controlling the behavior (i.e., the kinetic inhibition by CF₃Br is very sensitive to $\eta$, but R-125 is not).
- Simulations with 2-BTP should be able to tell us why 2-BTP, which has a Br, does not inhibit the flame (but is expected to).

Perfectly-Stirred Reactor (PSR) Calculations

- Assuming a constant $n_{\text{chem}}$ for extinction (reasonable first cut) implies $\eta$ increases as $X_{O_2}$ decreases.

**UNICORN Simulations**

- **UNsteady Ignition and Combustion with ReactioNs**
- Time-dependent, asymmetric reacting flows are simulated by solving full Navier-Stokes equations.
- Momentum Equations — QUICKEST Scheme (3rd order accurate in time, 4th order accurate in space)
- Pressure Field — Direct solution of Poisson Equations
- Species and Enthalpy — Hybrid scheme of Upwind and Central Differencing
- Turbulence — $k$-$\varepsilon$ model
- Radiation — Optically thin-media assumption
- Soot — Detailed kinetics for gas phase and a two-equation model for solid phase
- Detailed Chemistry Models.
Calculated temperature contours for one oscillation cycle

Agent leaks into the fuel region at the base

Diffusion Flame Calculations (Cup Burner): Oscillation of base is captured

Lift-off of base is captured

Methane in Air

Methane in 66%Air + 34%N2
Diffusion Flame Calculations (Cup Burner): Goals

Cup burner calculations can tell us:

1. What is the inerting concentration for ACT fuel, and why?
2. What is happening to the flame chemistry as \( X_i \) increases, for 1301 or R-125?
3. How does agent react in a partially-premixed environment?

Diffusion Flame Calculations (Cup Burner): Results

- Graphs showing the maximum temperature and minimum temperature as functions of agent volume fraction for different fuels and agents.

Fuel: Propane
Agent: Halon 1301

Fuel: ACT fuel
Agent: HFC-125
Diffusion Flame Calculations (Cup Burner) Results

**Table 2: Minimum Extinguishing Concentration (MEC) and Inerting Concentration**

<table>
<thead>
<tr>
<th>Fuel</th>
<th>Hydrogen</th>
<th>Propane</th>
<th>Ethanol</th>
<th>ACT fuel</th>
<th>Extinguishing Concentration</th>
<th>Inerting Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Actuator</td>
<td>Halon</td>
<td>HFC-125</td>
<td>Halon</td>
<td>HFC-125</td>
<td>Halon</td>
<td>Halon</td>
</tr>
<tr>
<td>Sheinson et al. (1989)</td>
<td>3.1</td>
<td>8.8</td>
<td></td>
<td></td>
<td>3.0</td>
<td>10.3</td>
</tr>
<tr>
<td>Hamins et al. (1994)</td>
<td>3.1</td>
<td>8.7</td>
<td>3.9</td>
<td>10.3</td>
<td>4.3</td>
<td>10.2</td>
</tr>
<tr>
<td>Saito et al. (1996)</td>
<td>3.4</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Moore et al. (1997)</td>
<td>2.9</td>
<td>9.4</td>
<td>2.8</td>
<td>3.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mean</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Measured Inerting Concentrations**

- Moore et al. (1995)       | 6.2
- Kondo et al. (2009)      | 14.8
- Mean                     | 6.2

**Calculated MECs**

- This study (1g)    | 2.86  | 8.6
- This study (0g)    | 2.59  | 15.1

% by volume:

- 1% by volume.
- 1% by volume.

- 1% by volume.

- 1% by volume.

**Why do 0-g calculations?**

- 0-g cup-burner extinguishment correlates with inerting concentration.

Diffusion Flame Calculations (Counterflow) Status

- 2-D, time-dependent calculations completed for:
  - Propane-air-HFC-125
  - Propane-air-1301
  - ACTfuel-air-HFC-125
  - ACTfuel-air-1301

- 1-D, steady calculations completed for:
  - Propane-air
  - ACTfuel-air

**Status**

- fuel
- flame
- oxidizer
**Diffusion Flame Calculations (Counterflow)**

Propane with R-125

- Experimental and simulated (UNICORN) extinction conditions in the counterflow diffusion flame (propane) agree well.
- This gives us confidence in the mechanism, and the numerical simulations, so they can be used to understand the overpressure causes.

**Premixed Flame Calculations (Counterflow)**

- Specified premixed inlet composition, $T_{ini}$, and fixed $P$.
- Adiabatic (no heat losses), no species reaction at the walls.
- Homogeneous mixture (no transport).
- Time-varying behavior.
Homogeneous Auto-Ignition Calculations

ACT Fuel Only

1. Literature reviewed.
2. Thermodynamic data obtained.
3. Kinetic mechanism for R-125 assembled, tested, updated.
4. Thermodynamic data for 2-BTP
5. IR emission data for HF, and COF$_2$
6. Wrote pre- and post-processors for all the numerical codes.
7. Initial shock-tube results for 2-BTP decomposition obtained.
8. Calculations (finished or in progress) for R-125:
   - Equilibrium
   - PSR
   - Ignition
   - Counterflow burner
   - Cup burner
   - Premixed
9. FAA ACT data obtained and compared with above.
10. New test chamber
    - specified, drawn, in machine shop
    - sensors ordered and/or obtained
    - Image analysis program written

Future Plans

1. Perform further analysis of simulations in progress to understand reasons for lack of kinetic inhibition with R-125.
   - Perform 2-D, axi-symmetric, unsteady simulations for a turbulent fuel jet to understand the effects of mixing on the extinction.
   - Repeat existing calculations at higher pressure.
2. Perform large-scale tests in cooperation with the FAA Technical Center to test our understanding.
3. 2-BTP:
   - measure and estimate decomposition rate
   - develop kinetic mechanism
   - perform calculations
   - analyze results to understand lack of kinetic effect with 2-BTP
4. Develop a new laboratory-scale experiment to:
   - validate our understanding (e.g., $\eta$, pressure effects), and the mechanisms.
   - explore range of conditions for which inhibition/enhancement occurs
   - rapidly screen new agents.
5. A Ph.D. student, and a Prof. at U. Maryland have applied for a NIST/ARRA Fellowship to work on this problem.
Key Questions Still to Answer

1. Is the amount of involved oxidizer the key feature?
2. Does the agent reaction rate affect the strain conditions in the FAA ACT?
3. Why are the kinetics with R-125 not slower (i.e., slow enough for extinguishment)?
4. Does Br help slow the kinetics with 2-BTP?
5. Is the overpressure due to a pressure enhancement of the agent flammability?
6. Is the inerting concentration required for suppression?
7. Is there any way around the undesired results?
Katta, V.R. et al. "Effects of halon replacements on burning characteristics of test fuels." to be presented at the 49th Aerospace meeting in Orlando, 4-7 January 2011.