Aerosol Can Explosion Test (caution: graphic material)
Problem: want to eliminate Halon 1301 from use in aircraft cargo bays

1. Halon 1301 (CF$_3$Br) => high ODP, high GWP.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Atmospheric Lifetime (yrs)</th>
<th>ODP</th>
<th>GWP$_{100}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Halon 1301 (CF$_3$Br)</td>
<td>65</td>
<td>12</td>
<td>6,900</td>
</tr>
<tr>
<td>HFC-125 (CF$_3$CF$_2$H)</td>
<td>29</td>
<td>0</td>
<td>3,400</td>
</tr>
<tr>
<td>2-BTP (CH$_2$CBrCF$_3$)</td>
<td>0.008</td>
<td>0</td>
<td>N/A</td>
</tr>
<tr>
<td>FK-5-1-12 (CF$_3$CF$_2$C(O)CF(CF$_3$)$_2$)</td>
<td>0.014</td>
<td>0</td>
<td>1</td>
</tr>
</tbody>
</table>
Problem: want to eliminate Halon 1301 from use in aircraft cargo bays

2. But in one FAA-mandated qualification test, the possible replacements make things worse.
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?
Understanding Combustion Promotion by Halogenated Fire Suppressants

INTERNATIONAL AIRCRAFT SYSTEMS FIRE PROTECTION WORKING GROUP MEETING
May 11-12, 2011

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Acknowledgements

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The work was supported by The Boeing Company.
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).
- Air and agent mixture
- Droplet evaporation, turbulent pre-mixing
- Ignition induction period (PFR)
- High strain (shear), partially premixed diffusion flame region (OFDF)
- Partially premixed diffusion flame with ancillary burning of agent (UNICORN)
Progress

Reviewed previous work

**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:

Of the 65 relevant papers collected and assimilated, these are highlights (in which enhanced combustion has been discussed):

<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 Gmurczyk</td>
<td>Propane, ethylene</td>
<td>CF3I, CF3Br, HFCs</td>
<td>Detonation -</td>
<td>Higher Ma, flame speed, pressure ratio</td>
<td>None</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Deflagration</td>
<td></td>
<td></td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>Tube</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Shebeko et al.</td>
<td>methane, hydrogen</td>
<td>C2HF5, C4F10</td>
<td>Deflagration</td>
<td>Higher pressure rise and dP/dt</td>
<td>Added heat release from agent</td>
</tr>
<tr>
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</tr>
<tr>
<td>Moriwaki et al.</td>
<td>methane, ethane</td>
<td>CH3Cl, CH3I, CH3, Br</td>
<td>Shock tube</td>
<td>Shorter ignition delay</td>
<td>None</td>
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</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>
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<td></td>
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<td></td>
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<tr>
<td>Mawhinney et al.</td>
<td>heptane</td>
<td>water mist</td>
<td>Heptane pool fi</td>
<td>Higher heat release</td>
<td>Enhanced fluid-dynamic mixing</td>
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<tr>
<td>Hamins et al</td>
<td>hydrocarbons</td>
<td>HFCs, water mist, N2, powders</td>
<td>Full-scale tests</td>
<td>Higher pressure, visual flames</td>
<td>Enhanced fluid-dynamic mixing</td>
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<td></td>
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</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>
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<td></td>
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<td></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>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ural</td>
<td>none</td>
<td>C3HF7, C2H2F4, CHClF2</td>
<td>Flammability</td>
<td>Visual observation</td>
<td>Heat loss/ gain</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>tube/chamber</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Flames go out when:

\[ \tau_{\text{chem}} > \tau_{\text{flow}} \]
The flow-field influences the extinction process:

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

**Chemical Time:**

\[
\tau_c \equiv \frac{\rho}{w} = \frac{\rho c_F^{-n} c_O^{-m} A^r}{\exp(E / RT)}
\]

**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

=> Concentrate on R-125

=> Why is it surprising that R-125 did not put out the ACT at 11.3 %
Background: Flame Extinction, Propane-Air with R-125, Counterflow

Background: Flame Extinction, Heptane-Air with R-125, Counterflow
To understand why R-125 does not extinguish the FAA ACT, we must understand:

- the fuel reaction chemistry
- agent reaction chemistry
- mixing
- flame characteristics.
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 ($T_{\text{aft}}$)

- $T_{\text{aft}}$ 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 $T_{\text{aft}}$.
- 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., $\eta=1$).
- $T_{\text{aft}}$ is high for all $\eta$.
- most of the plot is below $[X]/[H]=1$ (about 6 % 2-BTP), so can’t see change at $[X]/[H]=1$.
- With large amounts of agent, a wide range of $\eta$ gives equivalent $T_{\text{aft}}$.
- As agent is added, more and more chamber volume is necessary to achieve stoichiometric combustion.
- Where flame goes out ($X_i=6$ %), all the chamber volume is involved in combustion (i.e., $\eta=1$).
- $T_{aft}$ is high for all $\eta_i$, 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 $T_{aft}$ does not change with $X_i$.
- Why? => CF$_3$Br + 2H$_2$O = 3HF + HBr + CO$_2$ ,
- i.e., there’s always enough H and O in the system to oxidize the CF$_3$Br without more air!
- The $T_{aft}$ is very sensitive to $\eta_i$. 

Halon 1301: Adiabatic Flame Temperature ($T_{aft}$)  
Thermodynamic Equilibrium Calculations
Thermodynamic Equilibrium Calculations

What do they tell us about the maximum pressure rise?
- The higher $\eta$, the greater $\Delta P$ (more reactants, more heat release, more expansion of hot products—since the oxidizer also includes a “fuel” species).

- The actual fraction of chamber volume (oxidizer) which can react has a large influence on $\Delta P$.

- Equilibrium thermodynamics predicts the final pressure quite well.

- Why does the agent not reduce the extent of reaction?
2-BTP: Predicted Pressure Rise

Thermodynamic Equilibrium Calculations

- Same basic behavior as R-125, but greater $\Delta P$.
- The actual fraction of chamber volume (oxidizer) which can react has a large influence on $\Delta P$.
- Equilibrium thermodynamics predicts the final pressure quite well.
- Why does the agent not reduce the extent of reaction?
- Higher $\eta$ has very little effect on $\Delta P$.
- At $\eta$ of peak $T_{\text{aft}}$ 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 is due to a chemical kinetic effect, but is it from Br or from reduced temperature (i.e., from mixing-induced dilution)?

$\Rightarrow$ MUST LOOK AT THE KINETICS TO FIND OUT!
- As \( X_i \) of agent goes up, \( \Delta P \) can increase for R-125 and 2-BTP, but not for 1301.

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

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

Currently developing these charts for HFC-125 with propane and ACT.
### Aersol Can Test Mechanism:

<table>
<thead>
<tr>
<th>Species</th>
<th>Reactions</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₄ 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>CF₃Br mechanism of Babushok (NIST)²</td>
<td>10 122</td>
</tr>
</tbody>
</table>

¹ Updated rates from more recent literature, additional rates of fuel radical reaction with R-125.

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.
- 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 => CSTL.

-But! For now, use a 2-BTP simulant:
  1 mole CF$_3$Br,
  1 mole C$_2$H$_2$,
  3 moles N$_2$

  (gives the right T$_{aft}$, and has the right number of molecules).
Perfectly-Stirred Reactor (PSR) Calculations

- Used to estimate the overall chemical reaction rate.

- Performed for R-125, 1301, and 1301 with N₂.

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.
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)).

From Colket and co-workers, 2010
- 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 $\eta$ (for all $X_{\text{inh}}$; follows temperature results).
Adding 2-BTP simulant lowers or raises $\omega_{\text{chem}}$ (depending upon $\eta$).

Variation of $\omega_{\text{chem}}$ with $\eta$ is mild at high $X_{\text{inh}}$, but strong without agent.
Perfectly-Stirred Reactor (PSR) Calculations

R-125 vs. 1301

- 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 $\eta$. 

Perfectly-Stirred Reactor (PSR) Calculations

R-125 vs. 1301
- For R-125, we can use pressure rise data with equilibrium calculations to estimate $\eta$ (solid dots).

- For 1301, can't use pressure rise, so we don't really know $\eta$. =>BUT for 1301 $\omega_{\text{chem}}$ is very sensitive to $\eta$. 
- For R-125, or 2-BTP simulant, we can use pressure rise data with equilibrium calculations to estimate $\eta$ (solid dots).

- For 1301, can’t use pressure rise, so we don’t really know $\eta$. => BUT for 1301 $\omega_{\text{chem}}$ is very sensitive to $\eta$. 

**Perfectly-Stirred Reactor (PSR) Calculations**

R-125, 2-BTP$_{\text{sim}}$, and 1301

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**Diagram Description**

- $\omega_{\text{psr}} / \text{s}^{-1}$
- Fraction of Vessel Air Involved in Combustion

- $X_{1301} = 2.2\%$
- $X_{1301} = 3.9\%$
- $X_{\text{BTP}_{\text{sim}}} = 2.5\%$
- $X_{\text{BTP}_{\text{sim}}} = 4.8\%$
- $X_{\text{R-125}} = 7.5\%$
- $X_{\text{R-125}} = 13.5\%$
1. More agent generally reduces $w_{psr}$, for all assumed values of $\eta$.

2. For the case $\eta=0.47$, there is little change in $w_{psr}$ for the curve for HFC-125 up to 30%.

3. For HFC-125 (blue curves), the reduction in $w_{psr}$ with addition of agent is similar regardless of the value of $\eta$; i.e., for $\eta=0.33$, $\eta=0.47$, or $\eta(\text{Taft|peak})$.

4. The effectiveness of the agent CF$_3$Br is very sensitive to the value of $\eta$.

5. For CF$_3$Br to be more effective than HFC-125, $\eta$ must be greater than about 0.4.
1. More agent generally reduces $wpsr$, for all assumed values of $\eta$.

2. For the case $\eta=0.47$, there is little change in $wpsr$ for the curve for HFC-125 up to 30%, and for the curve for 2-BTP simulant up to 50%.

3. For HFC-125 (blue curves), the reduction in $wpsr$ with addition of agent is similar regardless of the value of $h$; i.e., for $\eta=0.33$, $\eta=0.47$, or $\eta(Taft|peak)$.

4. The 2-BTP simulant (green curves) is much less effective than HFC-125.

5. The effectiveness of the agents CF3Br and 2-BTP simulant (which differ primarily in the addition of C2H2 to CF3Br in the 2-BTP simulant) are both very sensitive to the value of $h$, but the influence is in the opposite direction: increasing $h$ reduces the effectiveness of 2-BTP simulant, but increases the effectiveness of CF3Br.

6. For CF3Br to be more effective than HFC-125, $\eta$ must be greater than about 0.4.
Equilibrium and PSR Calculations Indicate:

1. 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.

2. Thus, the agents are not inert, but rather, act like poorly-burning fuels.

3. Unlike in other flames, very little kinetic inhibition is occurring with R-125 and 2-BTP; whereas, CF$_3$Br does inhibit the flame, as expected.

4. The amount of chamber volume involved in the combustion, $\eta$, appears to be a key parameter controlling the kinetic behavior (i.e., the kinetic inhibition by CF$_3$Br is very sensitive to $\eta$, but R-125 is not).

5. Simulations with 2-BTP simulant imply that the fuel portion of the 2-BTP molecule causes it to be much less effective than CF$_3$Br.
Equilibrium Calculations Indicate:

=> With R-125 or 2-BTP:
  - the peak $T_{\text{aft}}$ does not drop much with added agent.
  - more agent requires higher $\eta$.
  - at high $X_i$, $T_{\text{aft}}$ is nearly the same regardless of the equivalence ratio.

=> With CF$_3$Br,
  - $T_{\text{aft}}$ drops off away from stoichiometric.
  - $\eta$ is not changed with added agent.
Equilibrium Calculations Indicate (pressure rise):

=> With R-125 or 2-BTP, complete reaction of the agent at the equivalence ratio giving peak $T_{aft}$ can predict the pressure rise (except at the extinction point).

=> With CF$_3$Br, adding agent will never increase the pressure rise, even without kinetic inhibition.
Perfectly-Stirred Reactor (PSR) Calculations Indicate:

=> With R-125 or 2-BTP simulant, at high $X_i$, the overall reaction rate is relatively unchanged as equivalence ratio changes.

=> With CF$_3$Br, the overall reaction rate is very sensitive to the equivalence ratio.
Key Questions Still to Answer

0. Are the results for 2-BTP itself the same as for 2-BTP simulant?
   • Is the amount of involved oxidizer the key feature?
   • Does the agent reaction rate affect the strain conditions in the FAA ACT?
   • Why are the kinetics with R-125 not slower (i.e., slow enough for extinguishment)?
   • Does Br help slow the kinetics with 2-BTP?
   • Is the overpressure due to a pressure enhancement of the agent flammability?
   • Is the inerting concentration required for suppression?
   • Is there any way around the undesired results?
1. Cup burner flame simulations.
2. Premixed flame simulations.
3. Counterflow diffusion flame simulations.
4. Homogeneous ignition simulations.
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.
New Constant-Volume Combustion Device*

*Photo Courtesy of Prof. Li, Purdue
Questions ?
Extra Material
Perfectly-Stirred Reactor (PSR) Calculations

\[ y = 0.0615x^2 - 1.6472x + 11.057 \]

Flammable

non-Flammable

O\(_2\) Mole Fraction in Air / %

CF\(_3\)Br Mole Fraction in Air / %
Kinetic Mechanism Development: Measurements of 2-BTP Decomposition
Kinetic Mechanism Development: Measurements of 2-BTP Decomposition

Single Pulse Shock Tube

**Characteristics:**
- System heated to 100 °C
- $\tau = (500 \pm 50) \mu s$ (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, $\tau = (500 \pm 50) \mu s$
- 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.