Exothermic Reaction of Fire Suppressants: Behavior of Brominated and Chlorinated Compounds

INTERNATIONAL AIRCRAFT SYSTEMS FIRE PROTECTION WORKING GROUP MEETING

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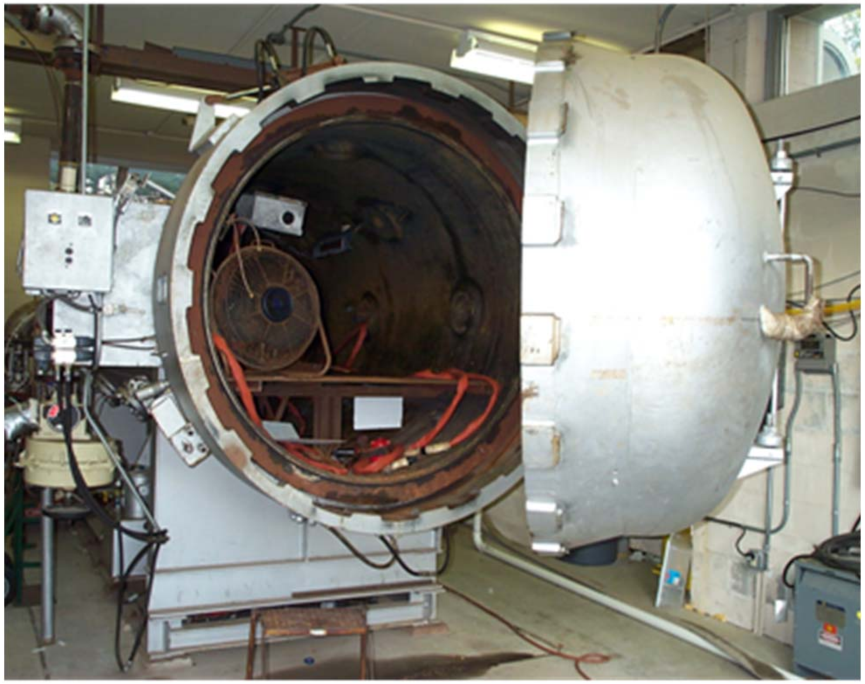
Problem: Want to eliminate halon 1301 from use in aircraft cargo bays

FAA Aerosol Can Test:

1. Sealed pressure vessel (v= 11400 L)
2. P_{init} = 1.01 mPa to 1.04 mPa
3. T_{init} = - 4 ^{o}C to 22 ^{o}C
4. Fuel: ethanol (270 g), propane (90 g), water (90 g).
5. Ignition: constant high-voltage DC arc, (max 10 kV, 20 mA).

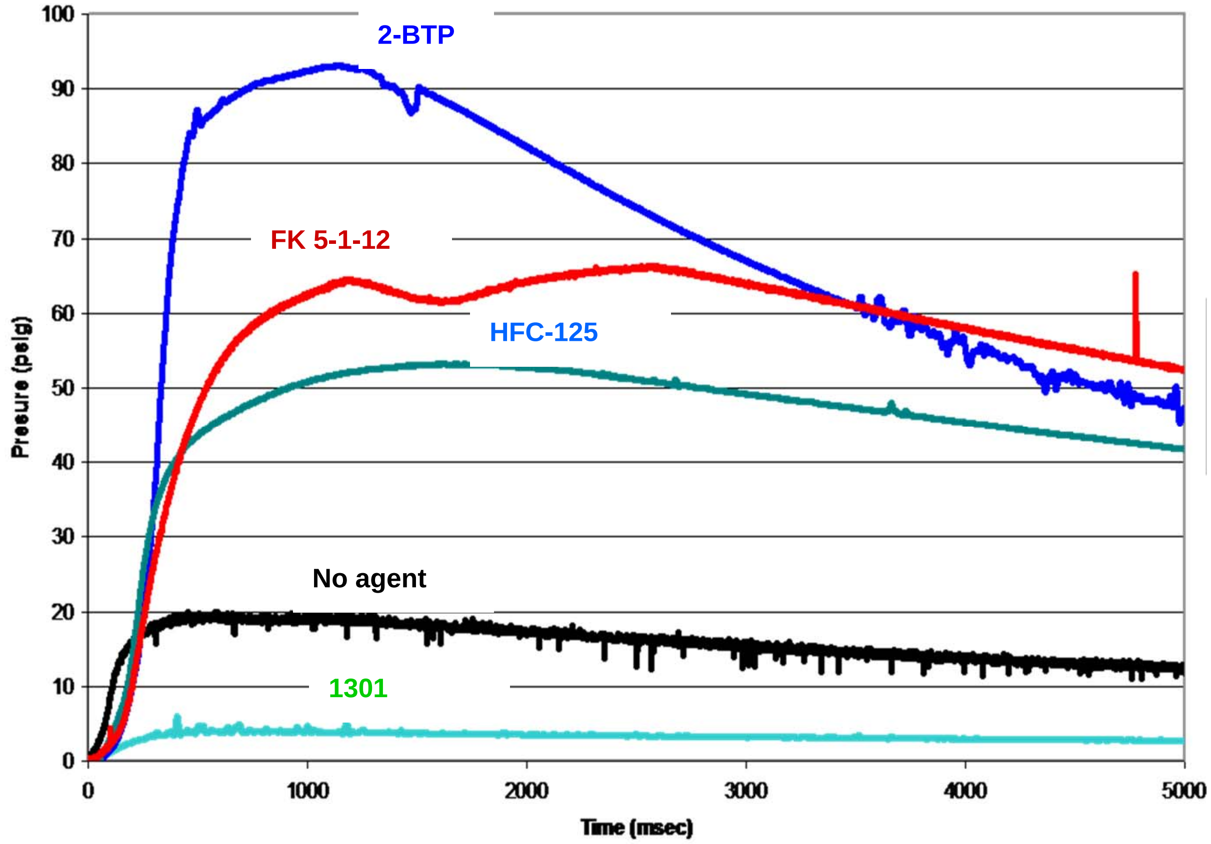


FAA Aerosol Can Simulator

Problem: Want to eliminate halon 1301 from use in aircraft cargo bays

Goal: 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?



From: Reinhardt, J. "Aircraft Cargo MPS Test of FK-5-1-12," International Aircraft Systems Fire Protection Working Group Meeting October 25-26, 2006, slide 19.

Tools

Numerical Simulations (w/ kinetic modeling):

Thermodynamic Equilibrium

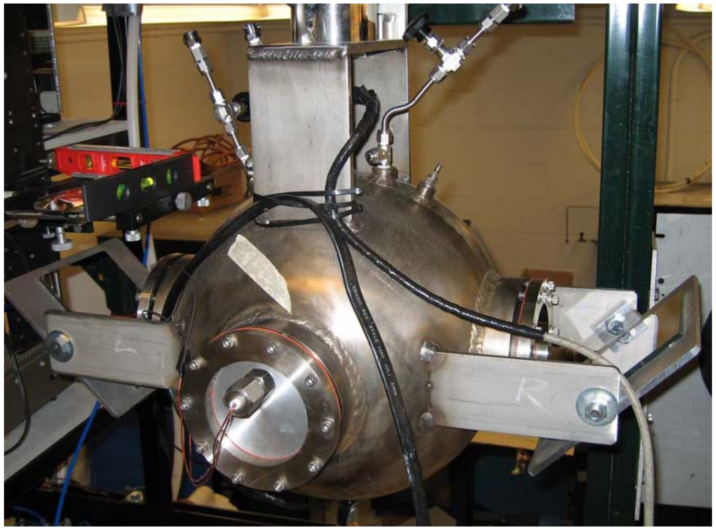
Overall Reaction Rate:
- -Stirred Reactor Blow-out
- -Burning Velocity
- -Cup Burner Extinction/Heat Release

Experiments:

Explosion Pressure

Burning Velocity (Overall Reaction Rate)

FAA Full-Scale Tests



Competing effects of suppressant:

1. Agent adds energy to the system (like a fuel) => more heat release => higher ΔP.
2. More energy may increase final T, which will raise reaction rate.
3. But, agent also adds chemical moieties which slow the kinetics (CF_3, Br, etc.).
4. To have inertion, chemistry must be slowed sufficiently
5. Competition between these effects will determine whether the net effect is to reduce or increase pressure rise in FAA-ACT.

=> To understand this competition, have to look at the detailed chemical kinetics of reaction of the different agents in combustion systems.

Examine rates of reaction using detailed kinetics.

1. Does agent reaction add energy to the flame, and where?
   => Cup-burner simulations with HFC-125 and CF_3Br in air stream.

2. Do pure agents burn?
   => Premixed Flame Calculations for: pure suppressants.

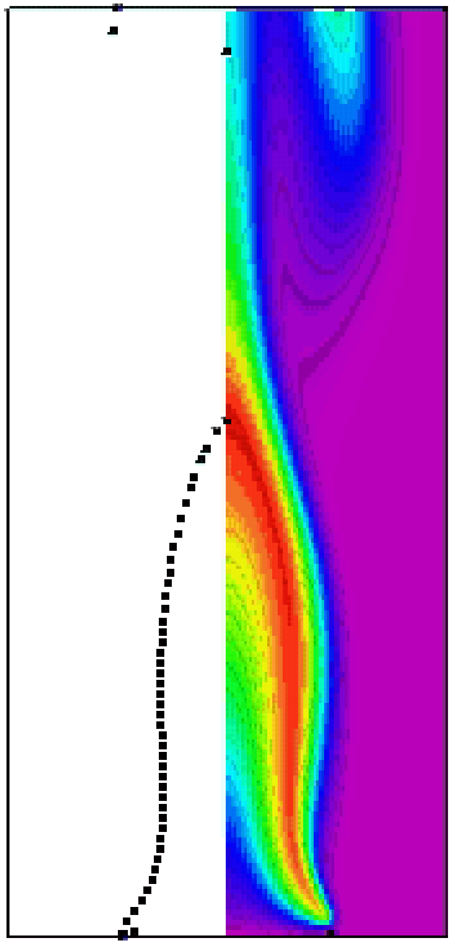
3. Can addition of fire suppressant bring a non-flammable mixture into the flammable condition?
   => Premixed Flame Calculations for: lean flames with added HFC-125 and Novec.

4. Development of laboratory-scale test methods to investigate and validate the modeling and full-scale results.

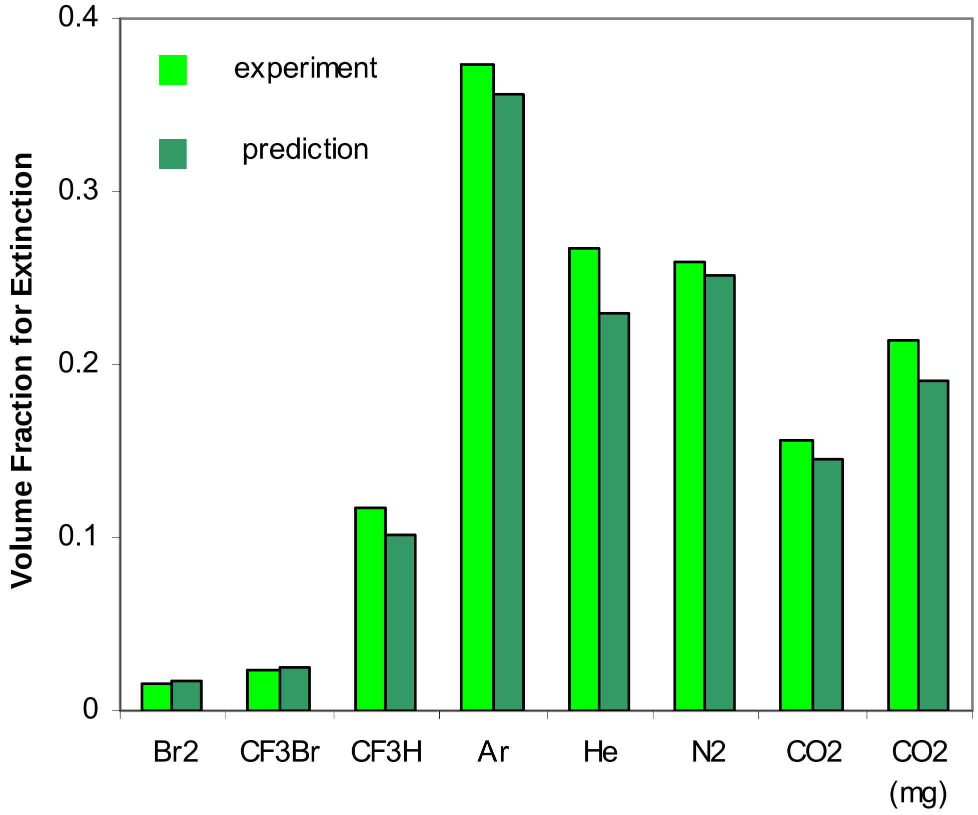
- This presentation
- Future presentations

Cup Burner Flame Simulations: HFC-125 and CF_3Br

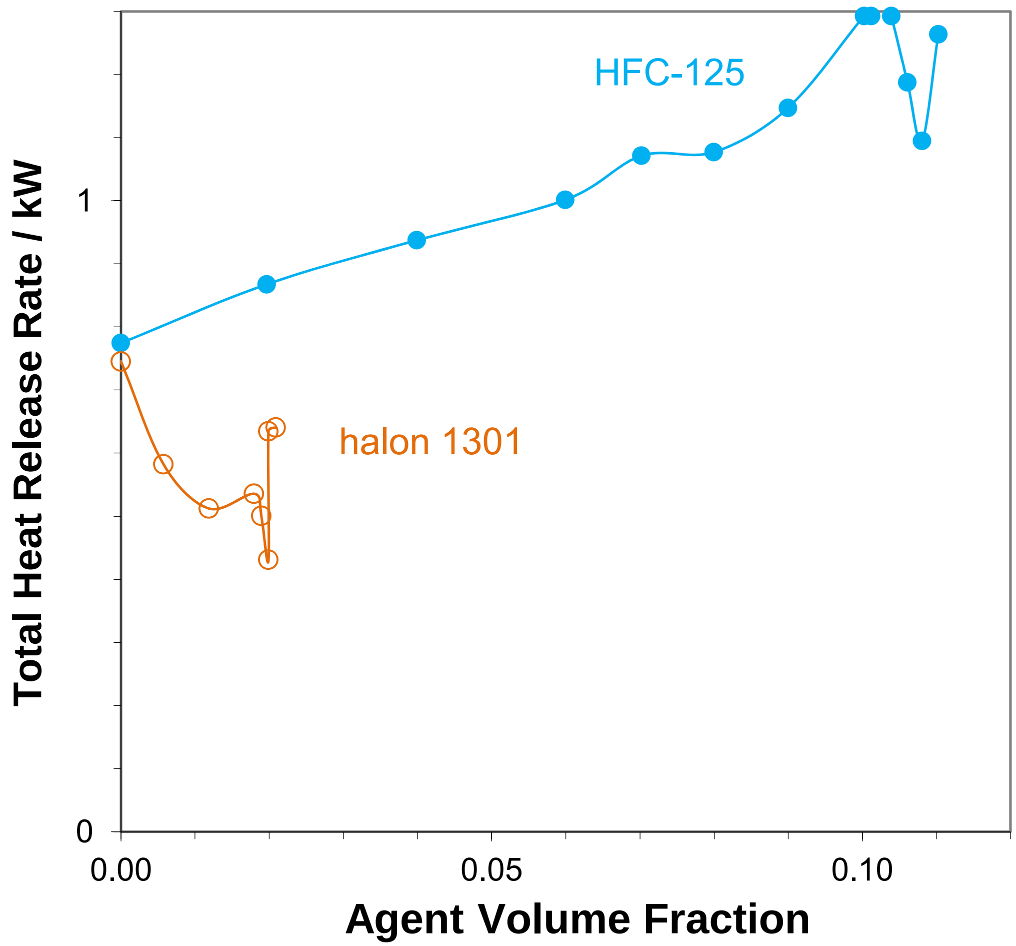
1. Detailed numerical simulation (solves Navier-Stokes equations) with full kinetics (177 species, 2986 reactions).
2. Time dependent, 2-D, axi-symmetric, full transport, gray thin-limit radiation model.



1. The model has can predict extinction of the cup burner.



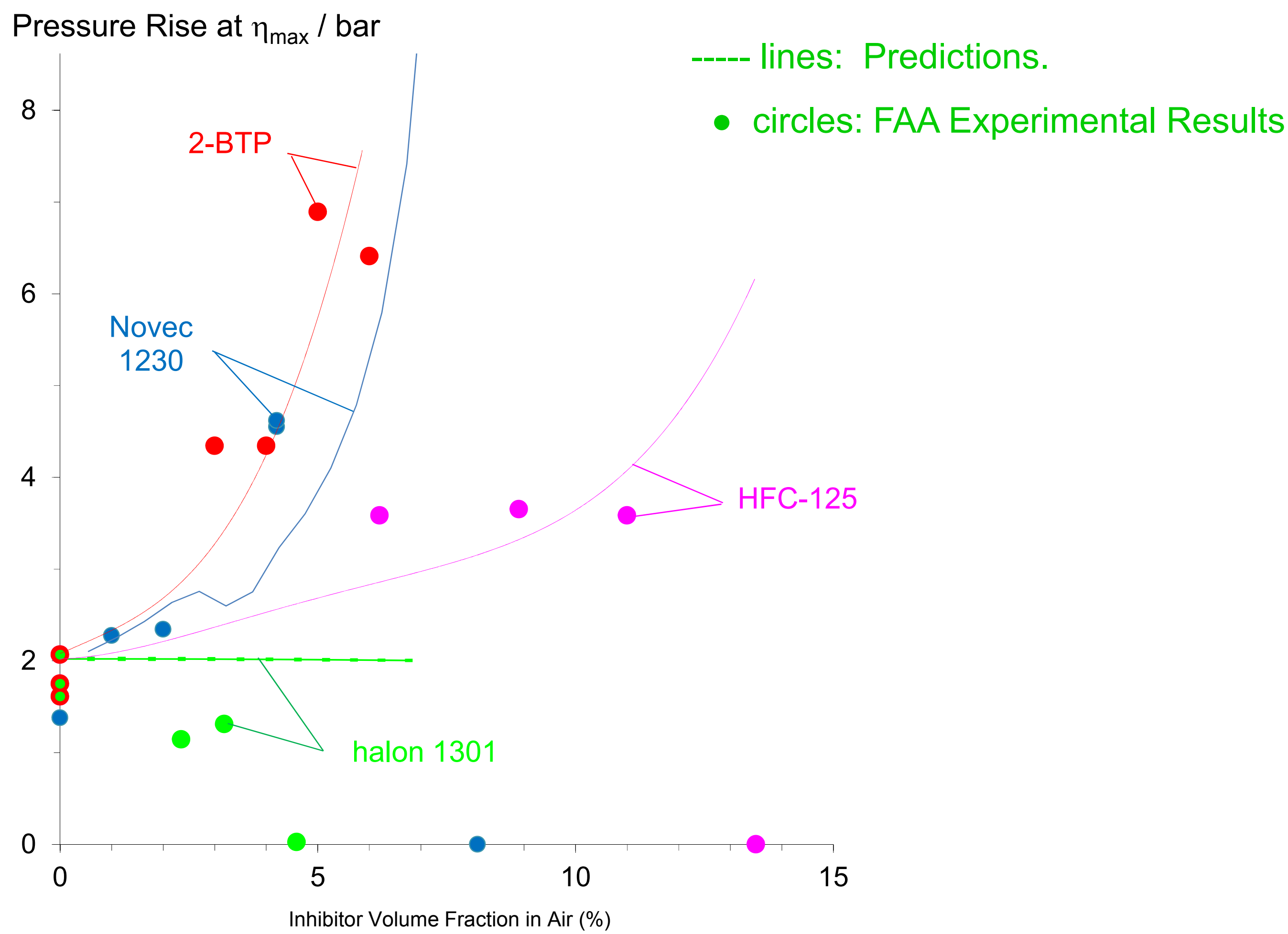
Examine heat release in μg flame with added C_2HF_5 and CF_3Br .



Near the agent concentration for extinguishment, the heat release:

- increases ≈2x with HFC-125, but
- decreases by ≈ 1/3 with CF_3Br.

Pressure Rise Prediction for All agents



- Thermodynamics determines possible pressure rise.
- Kinetics determines fraction of pressure rise achieved.

Do mixtures of the pure fire suppressants in air burn under some conditions?

=> Premixed burning velocity is a measure of overall reaction rate.

Calculated Burning velocities of fire suppressant/air stoichiometric mixtures (1 bar)

Agent	Formula	Oxidizer	Initial Temperature, K	Peak Adiabatic Flame Temperature K	Burning Velocity, cm/s
HFC-23	CF_3H	air	400	1751	0.567
HFC-125	C_2F_5H	air	400	1858	1.56
HFC-227ea	C_3F_7H	air	400	1874	2.48
Novec 1230	$C_3F_7COC_2F_5$	air	400	1864	0.367
Triodide	CF_3I	oxygen	500	1528	1.33
halon-1301	CF_3Br	oxygen	500	1485	<0.15

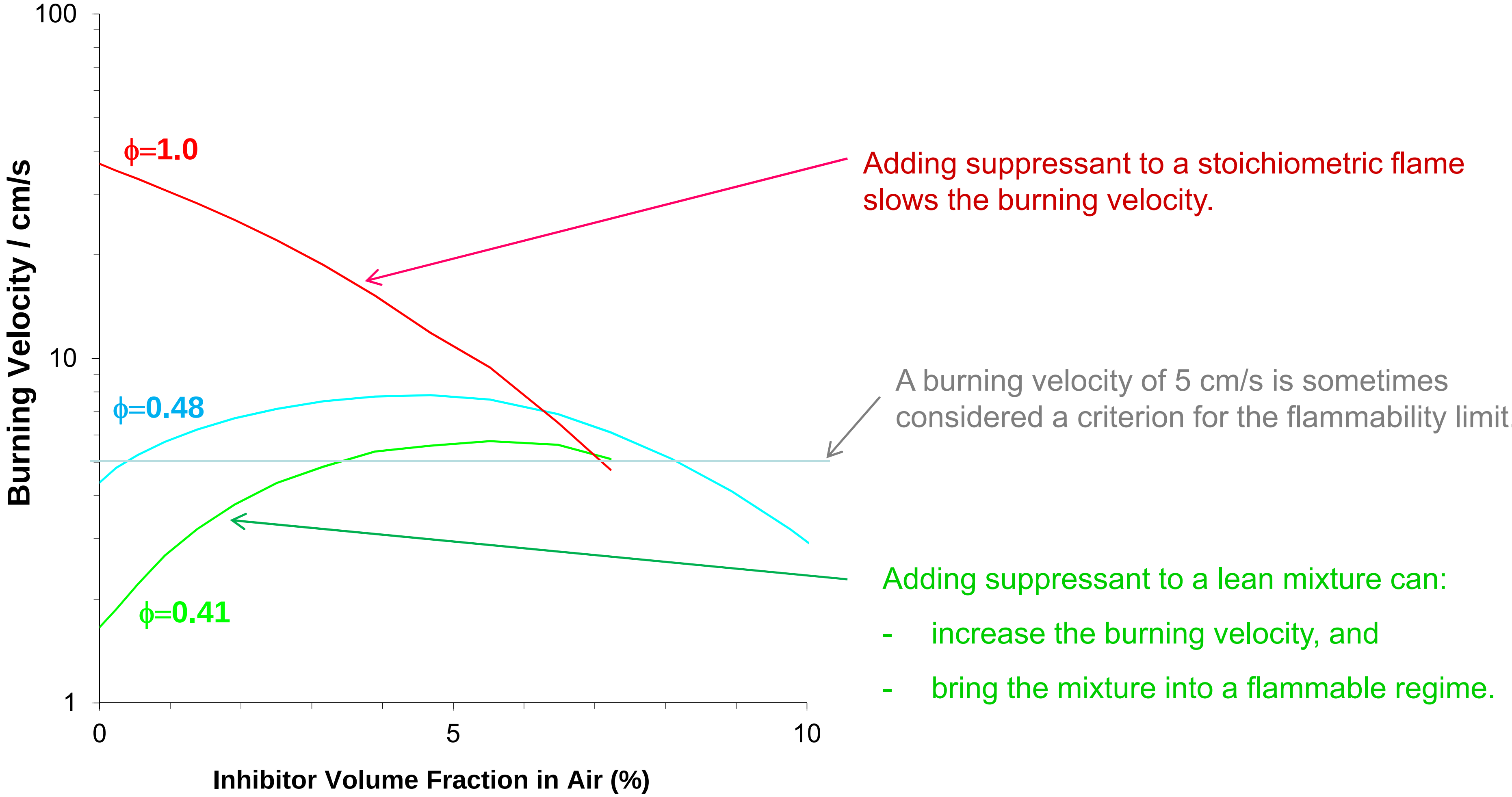
(values down to ≈1 cm/s can be measured.)

- some fire suppressants themselves may support flames (although very weak) in air at elevated temperatures.

- behavior for CF_3Br is different: flame speed is < 0.15 cm/s at 500 K with O_2 oxidizer.

Does adding <u>suppressants</u> to lean flames make them more flammable?

HFC-125 with Aerosol Can Test Fuel, T_{init}=298 K



Exothermic Reaction

1. FAA aerosol can test: at sub-inerting concentrations, HFC-125, Novec, and 2-BTP all **react exothermically**; halon 1301 does also, but: i.) does not cause a pressure increase, and ii.) lowers the overall reaction rate.
2. At slightly elevated temperatures, some fire suppressants with air may have measurable (but low) flame speeds (i.e., compressive heating in aerosol can test can enhance the agent flammability).
3. HFC-125 (and probably HFC-23, HFC-227ea, etc.) added to the air stream of a cup burner can double the heat release at sub-extinguishing concentrations; halon 1301 lowers the HRR.
4. Some agents added to lean mixtures beyond flammability limit can make the lean mixtures more flammable.

=> The possible exothermic heat release of fire suppressants is balanced against slower kinetics; these effects need to be more clearly delineated for a variety of chemical families.

Brominated Compounds

1. 2-BTP did not work in the FAA Aerosol Can Test.
2. Even for CF_3Br, adding it with a fuel-like molecule (e.g., C_2H_2) probably renders it ineffective in the FAA Aerosol Can Test. (This is based on stirred reactor simulations which showed that while CF_3Br alone reduces the overall reaction rate effectively, adding CF_3Br / C_2H_2 / inert mixtures does not reduce the overall reaction rate nearly enough to cause extinction).

⇒This implies that many molecules with CF_3 and a Br plus some hydrocarbon component may not work in the FAA-ACT.

⇒ Need to check the tradeoff between number of Br, F, and the amount of hydrocarbon character to see if it looks like other compounds can work.

Iodinated Compounds

1. We estimate that CF3I should work in the FAA Aerosol Can Test.

=> Other considerations will dictate its suitability.

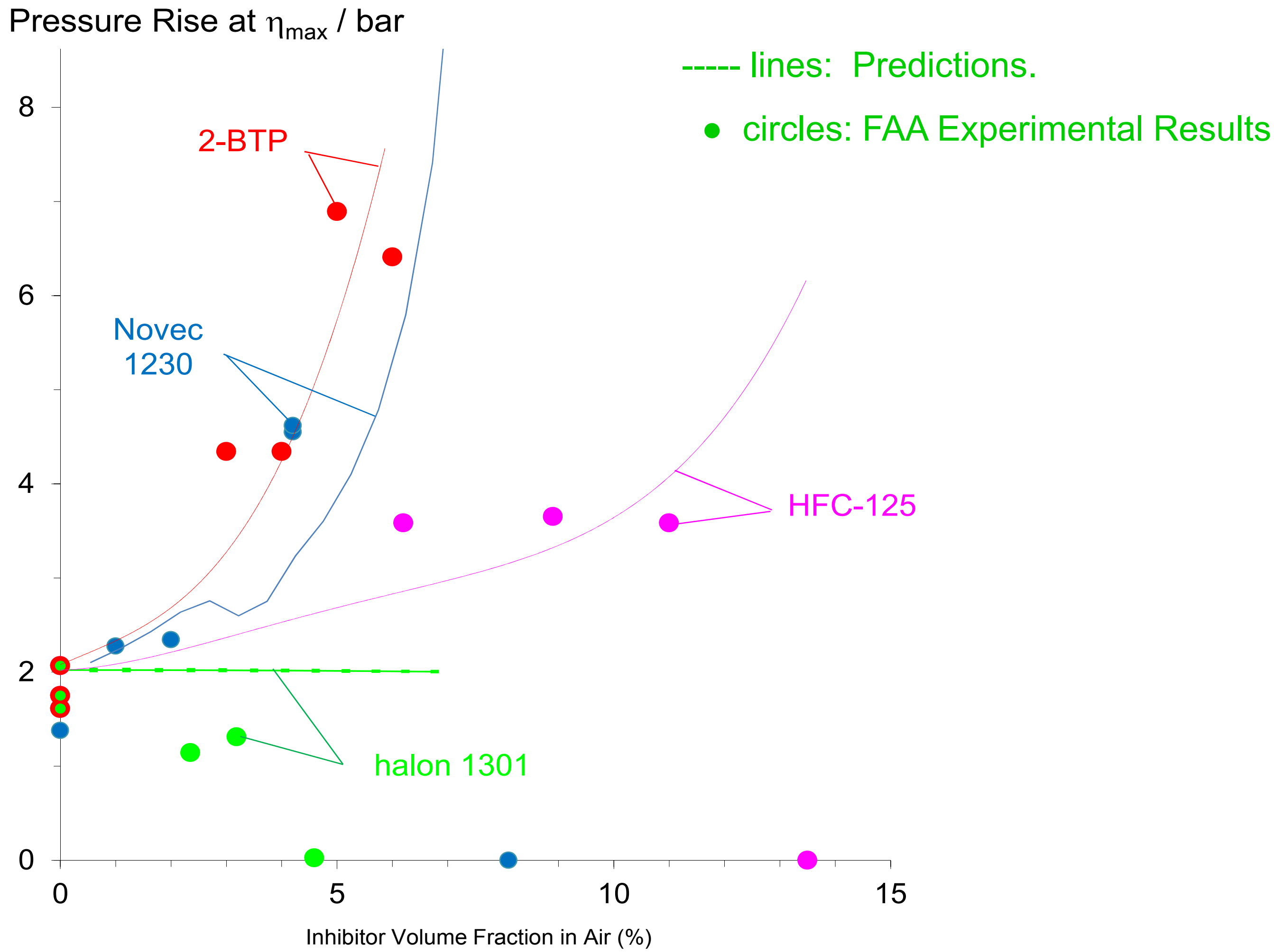
=> But, it ought to be tested (see below).

Next Steps:

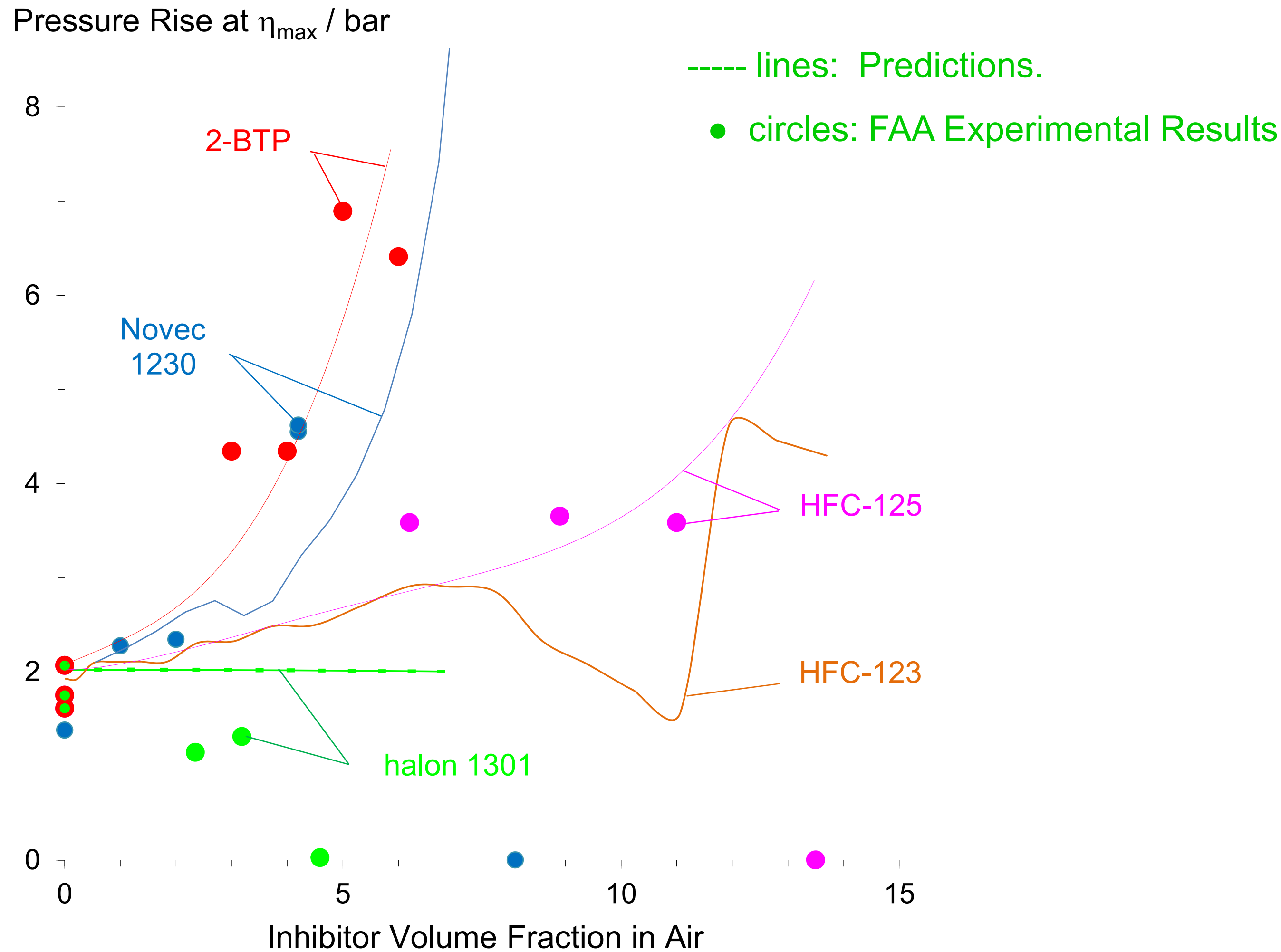
⇒ Estimate if it is affected by a hydrocarbon component in the suppressant molecule as is CF_3Br.

R-123 has chance of working in the FAA Aerosol Can Test

We can predict the pressure rise (at sub-inerting concentrations) for alternative agents

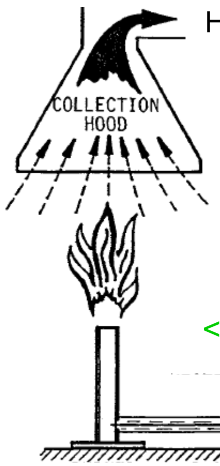


HCFC-123 is expected to give less overpressure than HFC-125 in the Aerosol Can Test



=> HCFC-123 ($C_2HCl_2F_3$) may not cause the overpressure. But to understand its potential, must look at kinetics.

HFCs added to Propane-air Flame Increases Heat Release, but HCFCs do not.

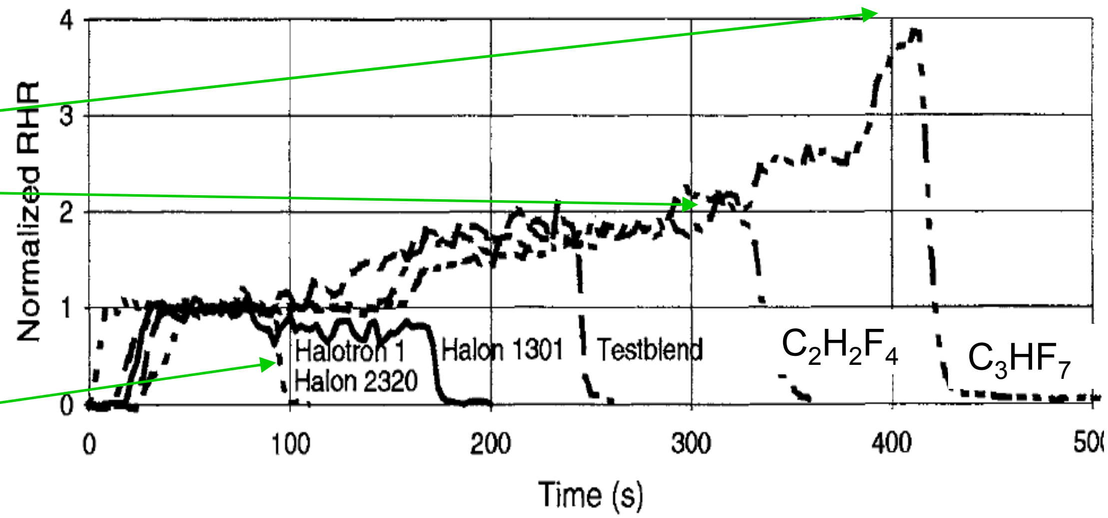


Heat Release Rate Measurement

<= air and agent input (Increase agent concentration in air linearly in time.)

<= propane

From: Holmstedt et al. 1994



⇒ Total heat release increases (≈2 to 4 times) for $C_2H_2F_4$ (HFC-134a)

or C_3HF_7, (HFC-227ea)

at concentrations just below extinction,

=> but does not increase for Halotron 1 (mostly $C_2HCl_2F_3$; i.e., R-123).

=> So this test <u>also</u> indicates that R-123 may work in FAA Aerosol Can Test.

Why might chlorinated compounds work better than fluorinated?

1. Different equilibrium products for $C_2HCl_2F_3$ (Cl and Cl_2) vs C_2HF_5 (HF and COF_2).
2. This lowers final temperature for HCFCs relative to HFCs; lower temperature means less pressure rise.
3. Stoichiometry for peak temperature occurs with much lower fraction of chamber volume, so less mass of HCFC reactants=> less pressure rise.
4. Chlorine species will slow reaction rates slightly more than fluorine species, so explosion should reach a lower fraction of the maximum pressure rise.
5. <u>Chlorine-containing HCFCs should work somewhat better than corresponding HFCs.</u>

=> To understand the potential of HCFCs, must look at the detailed chemical kinetics.

Current Status, Path Forward

1. Chlorinated hydrocarbons might not cause as much overpressure as fluorinated. e.g., HCFC-123 might not cause as high a pressure rise as does HFC-125. Hence, it may work in the FAA Aerosol Can Test.

2. If HCFC-123 is better than HFC-125, we can then look for other chlorinated hydrocarbons that have lower ODP and GWP.

To do:

1. Test HCFC-123, and CF_3I in FAA Aerosol Can Test

2. Ask agent manufacturers if they can come up with chlorinated agents that have acceptable vapor pressure, toxicity, GWP, ODP, etc.

3. Explore boundaries of CF_3Br and CF_3I effectiveness when combined with a hydrocarbon,HFC, or HCFC.

4. Continue development of laboratory-scale experiments for validating these principles (and the kinetic models upon which they are based), to serve as a screening test.