Exothermic Reaction of Fire Suppressants: An Update

INTERNATIONAL AIRCRAFT SYSTEMS FIRE PROTECTION WORKING GROUP MEETING

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This presentation is a summary of the work presented in the following publications:

1. Linteris, G.T., Takahashi, F., Katta, V.R., Chelliah, H.K., Meier, O. "Thermodynamic analysis of suppressant-enhanced overpressure in the FAA Aerosol Can Simulator," accepted for publication in *Fire Safety Science: Proceedings of the Tenth International Symposium,* International Association for Fire Safety Science (IAFSS), Boston, MA, 2011.

2. Linteris, G.T., Takahashi, F., Katta, V.R., Chelliah, H.K., Meier, O., "Stirred Reactor Calculations to Understand Unwanted Combustion Enhancement by Potential halon Replacements," *Combustion and Flame*, **159**:1016-1025, 2012.

3. Linteris, G.T., Babushok, V.I., Sunderland, P.B., Takahashi, F., Katta, V.R.,Meier, O., "Unwanted Combustion Enhancement by $C_6F_{12}O$ Fire Suppressant," accepted for publication in *Proceedings of the Combustion Institute*, July 2012.

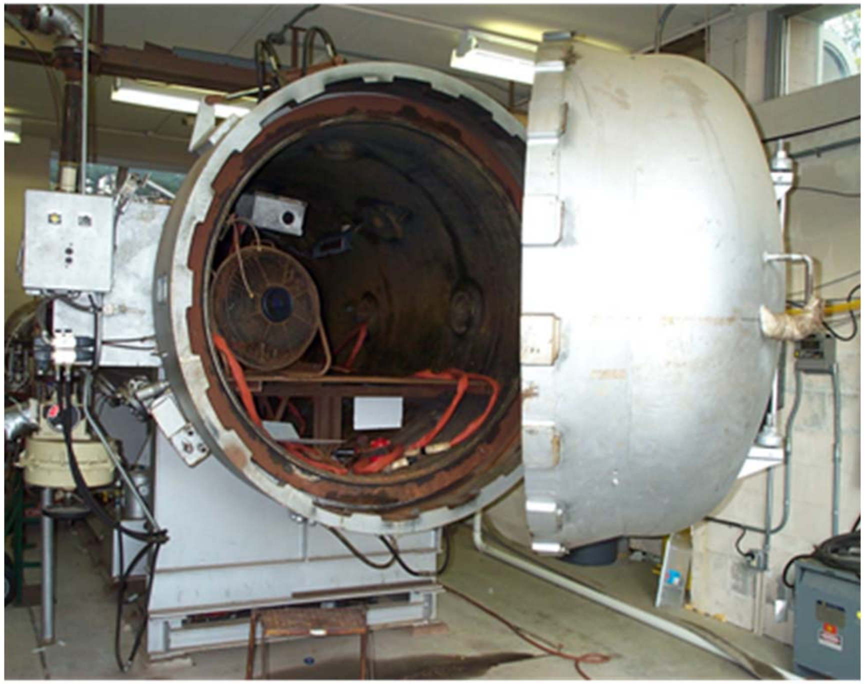
4. Takahashi, F., Katta, V.R., Linteris, G.T., Meier, O., "Cup-burner Flame Structure and Extinguishment by CF_3Br and C_2HF_5 in Microgravity," accepted for publication in *Proceedings of the Combustion Institute*, July 2012.

5. Babushok, V.I., Linteris, G.T., Meier, O., "Combustion Properties of Halogenated Fire Suppressants," accepted for publication in *Combustion and Flame*, 159, 3569–3575, 2012.

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).

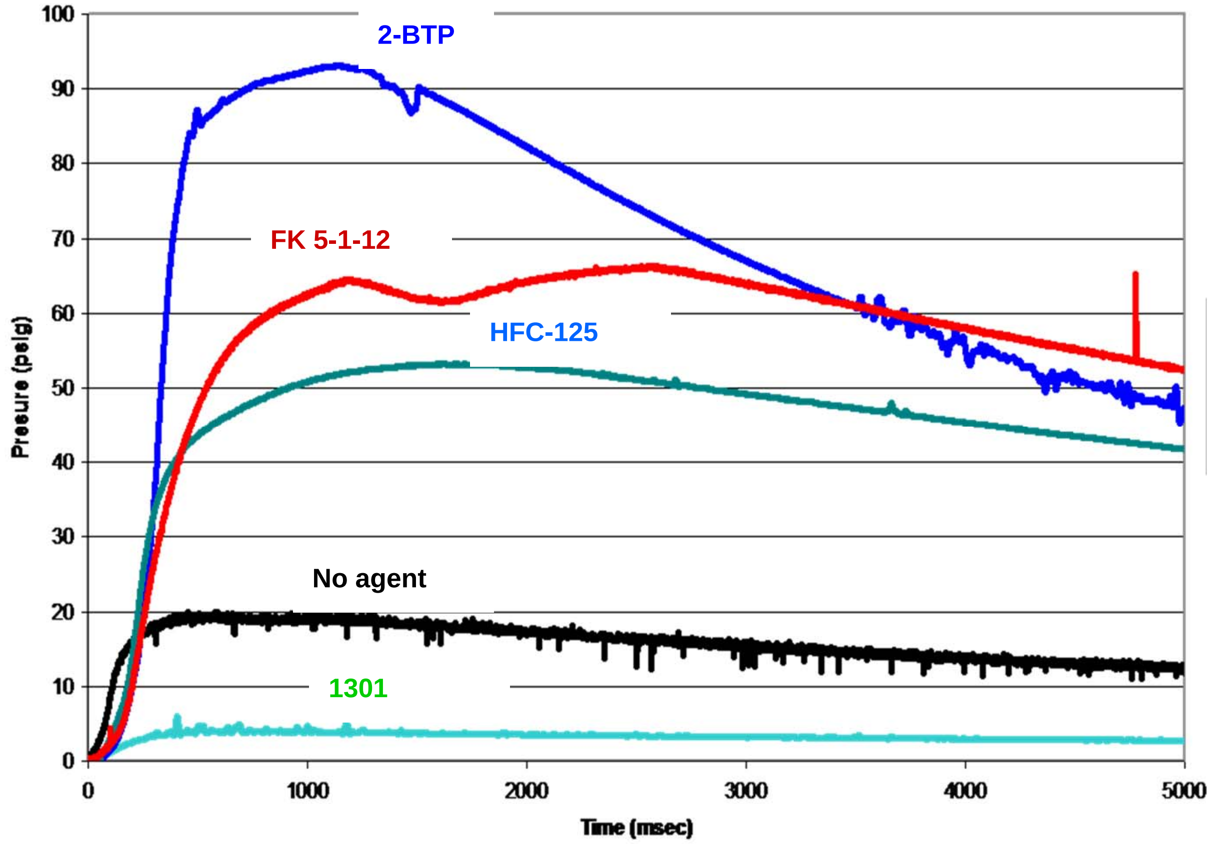


FAA Aerosol Can Simulator

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?



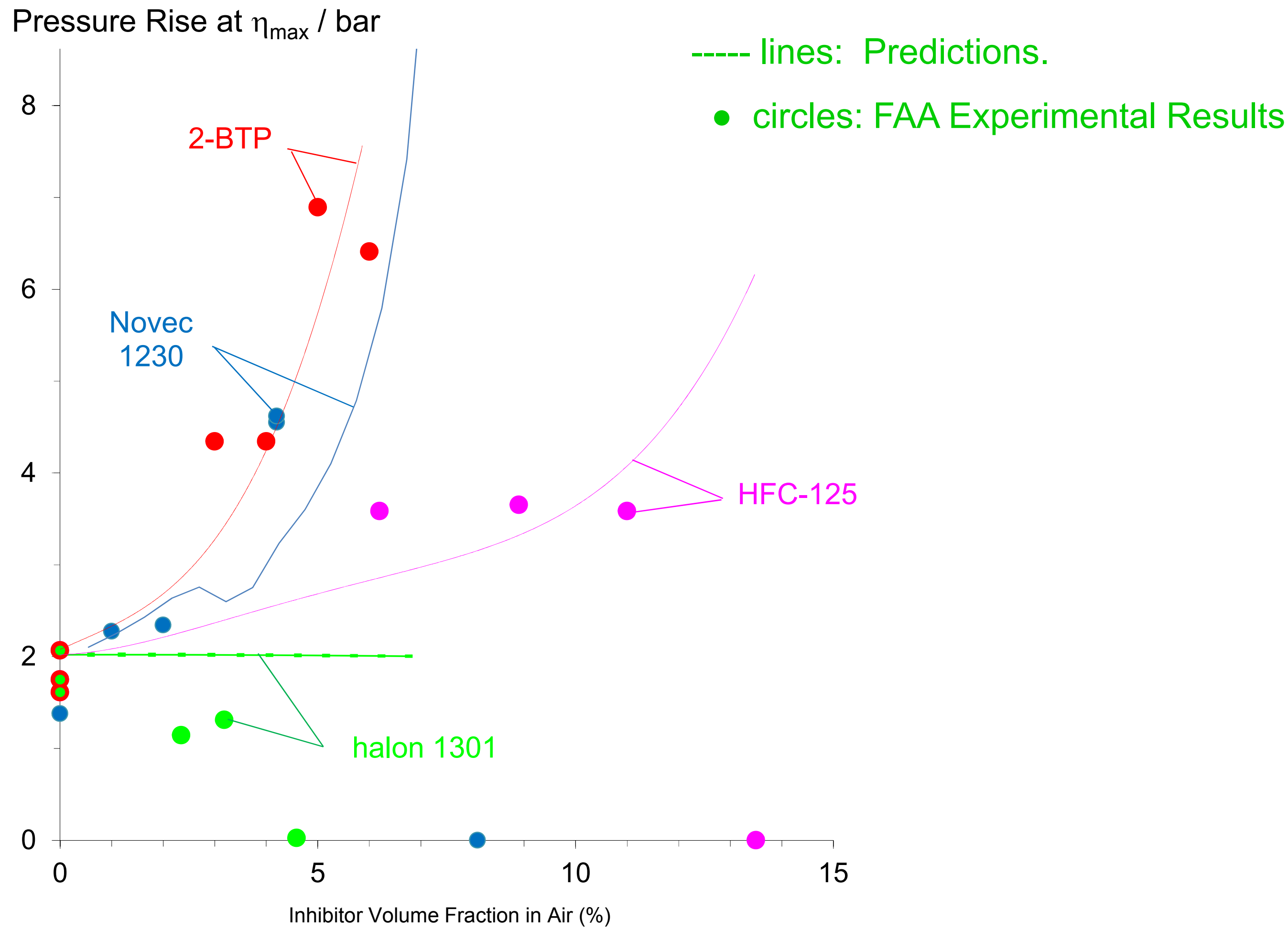
From: Reinhardt, J. "Aircraft Cargo MPS Test of FK-5-1-12," International Aircraft Systems Fire Protection Working Group Meeting October 25-26, 2006, slide 19.

Background: Enhanced combustion in the presence of fire suppressants has been observed.

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

Researchers	Fuel	Agents	Experiment	Phenomena	Explanation
Grosshandler and Gmurczyk	Propane, ethylene	CF3I, CF3Br, HFCs	Detonation - Deflagratoin Tube	**Higher Ma, flame speed, pressure ratio**	None
Shebeko et al.	methane, hydrogen	C2HF5, C4F10	Deflagration	**Higer pressure rise and dP/dt**	Added heat release from agent
Moriwaki et al.	methane, ethane	CH3Cl, CH3I, CH3, Br	Shock tube	**Shorter ignition dela**	None
Ikeda and Mackie	ethane	C3HF7	Shock tube	**Shorter ignition dela**	None
Mawhinney et al.	heptane	water mist	Heptane pool fi	**Higher heat release**	Enhanced fluid-dynamic mixing
Hamins et al	hydrocarbons	HFCs, water mist, N2, powders	Full-scale tests	**Higher pressure, visual flames**	Enhanced fluid-dynamic mixing
Holmstedt et al.	propane	C3HF7, C2H2F4, CF3Br,	Diffusion flame	**Higher heat release**	None
Katta et al.	methane	CF3H	Cup burner	**Higher heat release**	Agent reaction
Ural	none	C3HF7, C2H2F4, CHClF2	Flammability tube/chamber	**Visual observation**	Heat loss/ gain

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



- Overpressure in FAA-ACT can be predicted reasonably well (based on equilibrium thermodynamics) .
- Implies that the agent itself is reacting.

=> But to understand differences (e.g., at inerting point, or with halon 1301), must look at kinetics.

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. <u>Competition between these effects will determine whether the net effect is to reduce or increase pressure rise in FAA-ACT.</u>

=> 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.

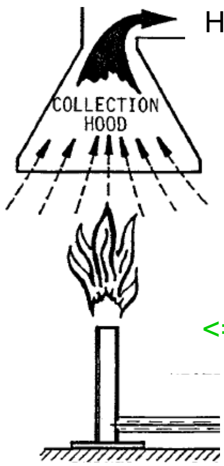
2. Do pure agents burn?
   => Premixed Flame Calculations for: pure suppressants.

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

Added HFCs to Propane-air Flame Increases Heat Release

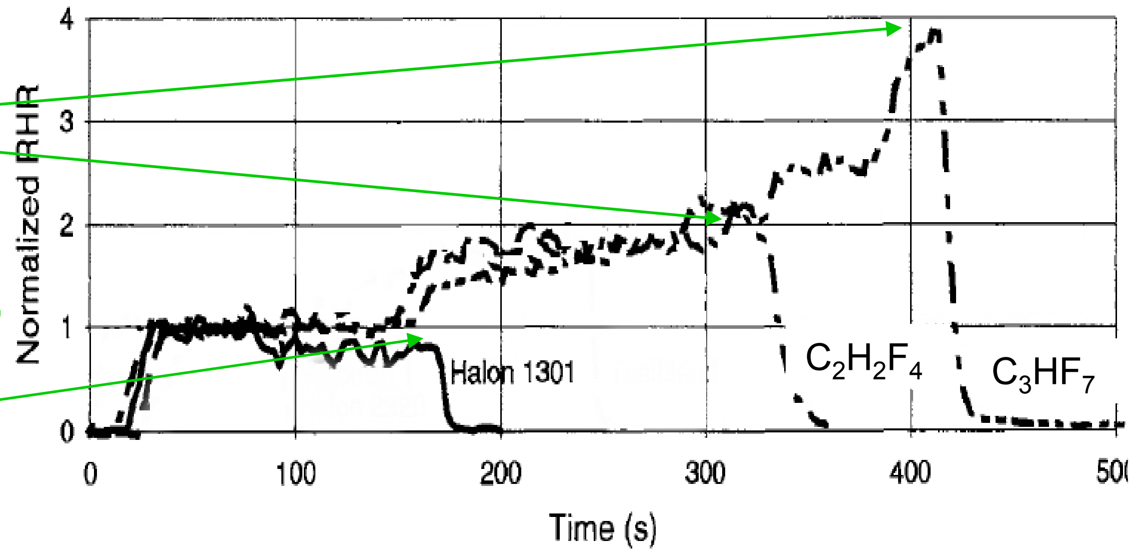


Heat Release Rate Measurement

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

<= propane

From: Holmstedt et al. 1994



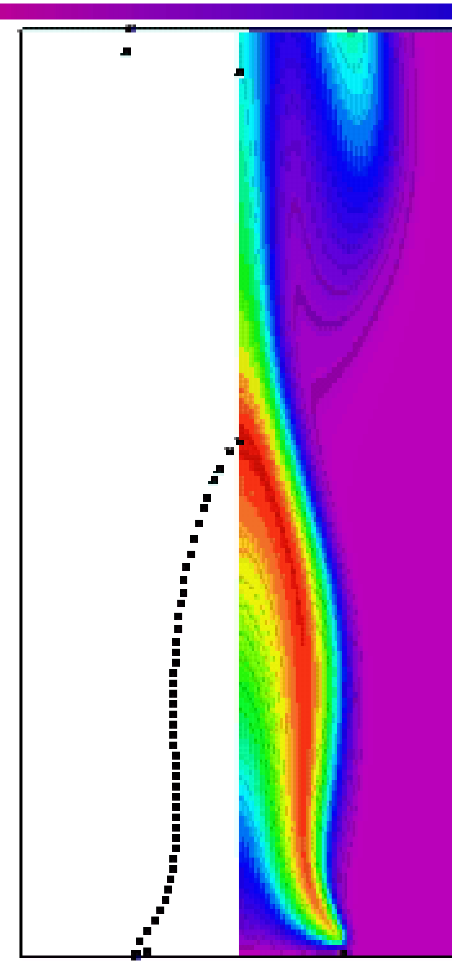
⇒ Total heat release increases (≈2 to 4 times) for $C_2H_2F_4$ (HFC-134a) or C_3HF_7, (HFC-227ea) at concentrations just below extinction,

=> but decreases for halon 1301.

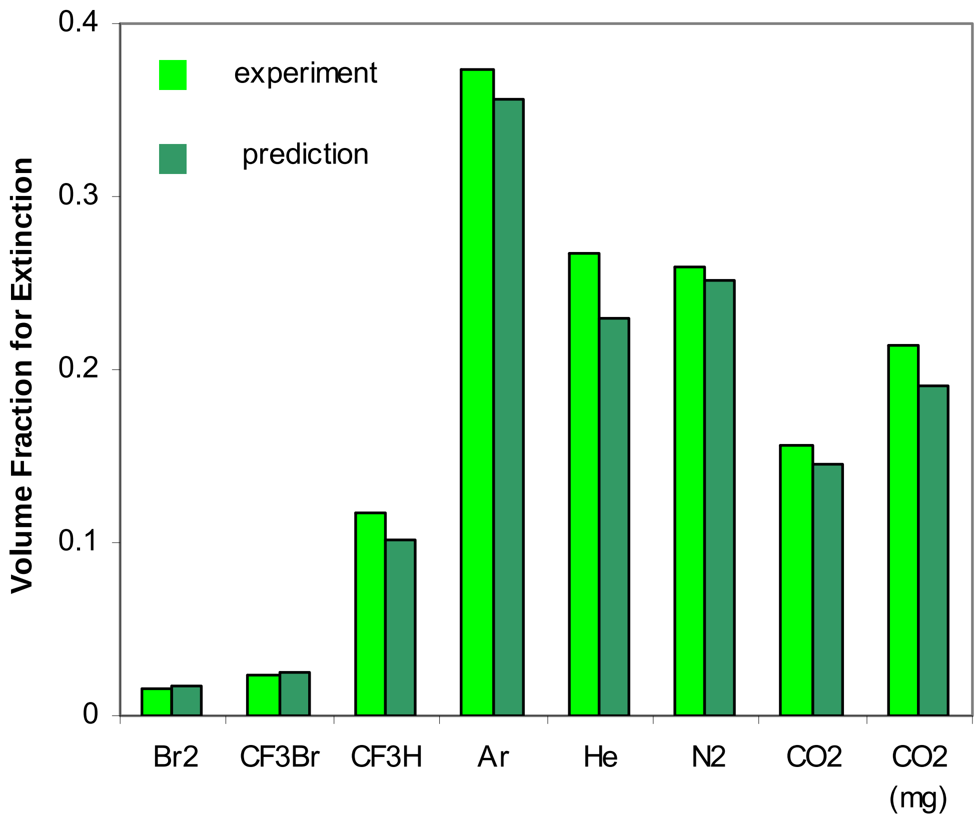
Why?

Cup Burner Flame Simulations: HFC-125 and CF_3Br

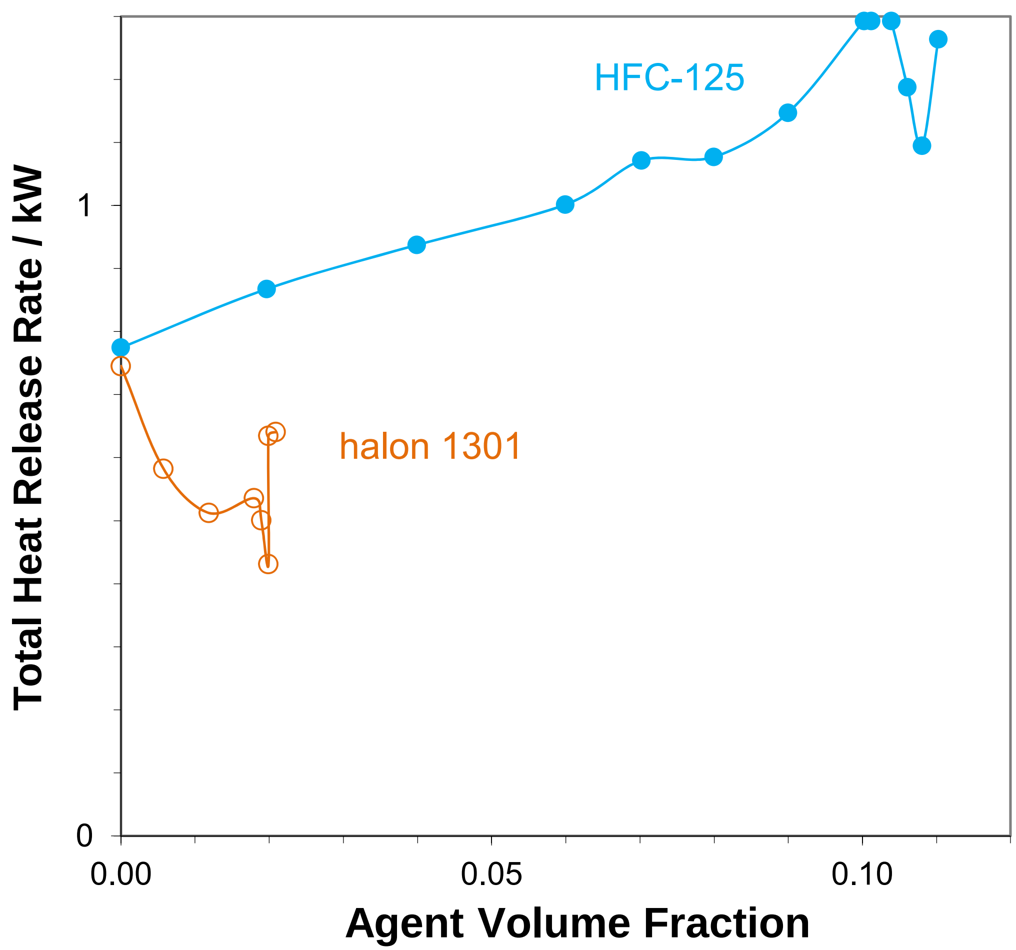
1. Detailed numerical simulation (solves Navier-Stokes equations) with full kinetics (177 species, 2986 reactions).
2. Time dependent, 2-D, axi-symmetric, full transport, gray thin-limit radiation model.



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



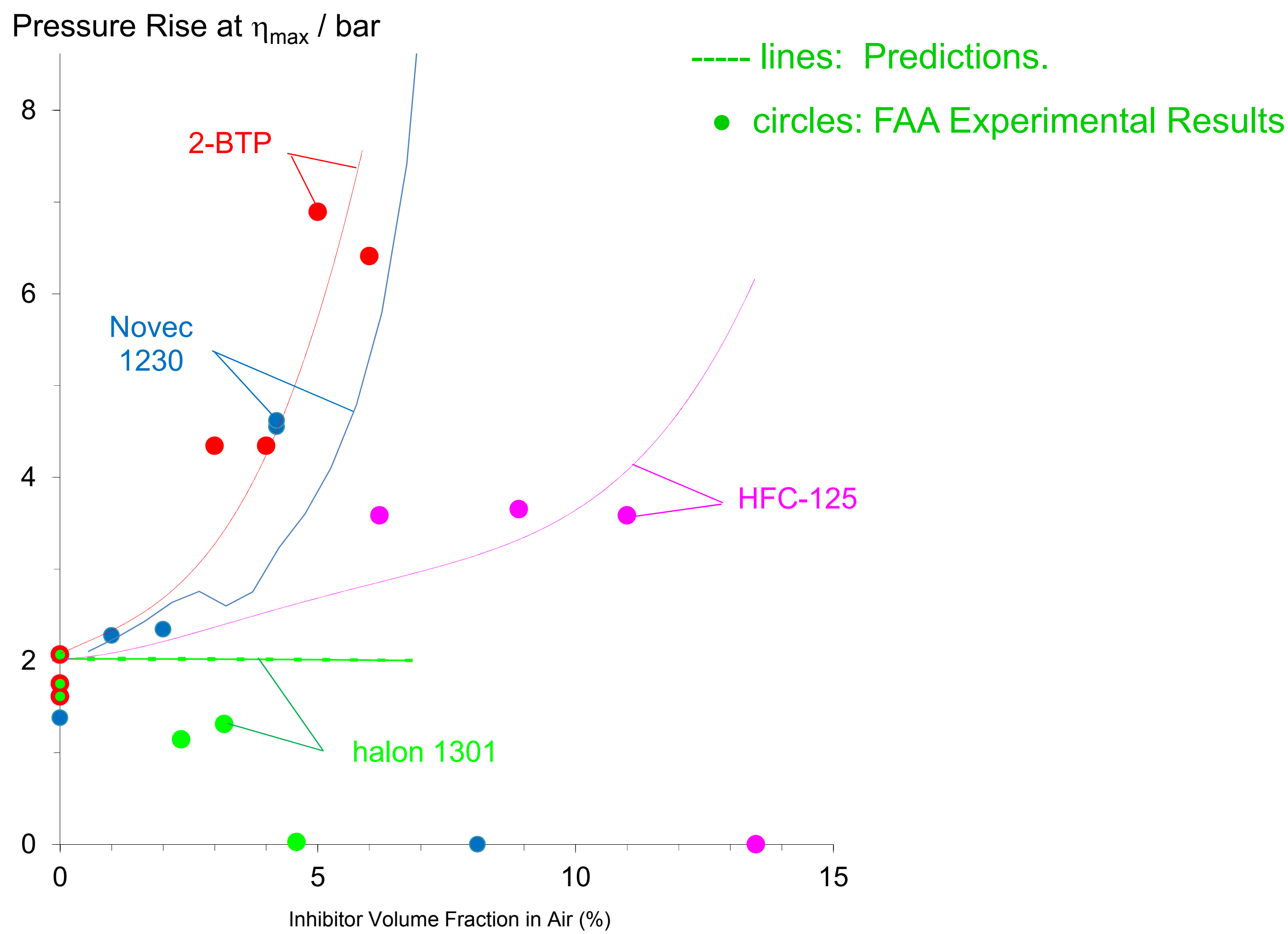
Examine heat release in flame with added C_2HF_5 and CF_3Br .



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)

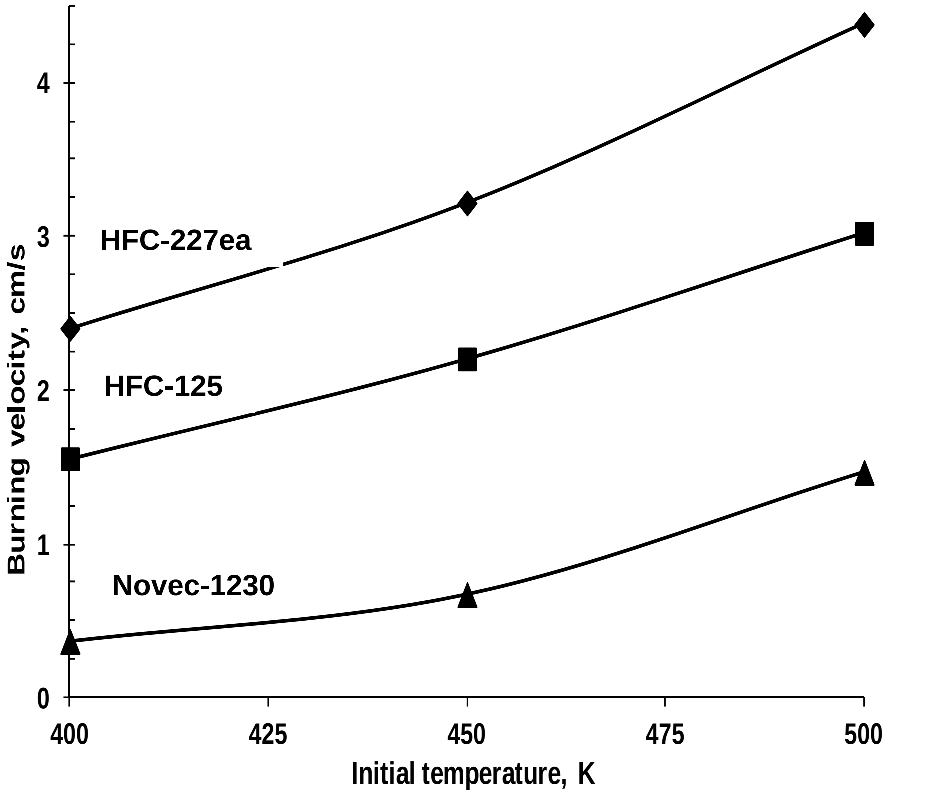
Agent	Formula	Oxidizer	Initial Temperature, K	Peak Adiabatic Flame Temperature K	Burning Velocity, cm/s
HFC-23	CF_3H	air	400	1751	0.567
HFC-125	C_2F_5H	air	400	1858	1.56
HFC-227ea	C_3F_7H	air	400	1874	2.48
Novec 1230	$C_3F_7COC_2F_5$	air	400	1864	0.367
Triodide	CF_3I	oxygen	500	1528	1.33
halon-1301	CF_3Br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

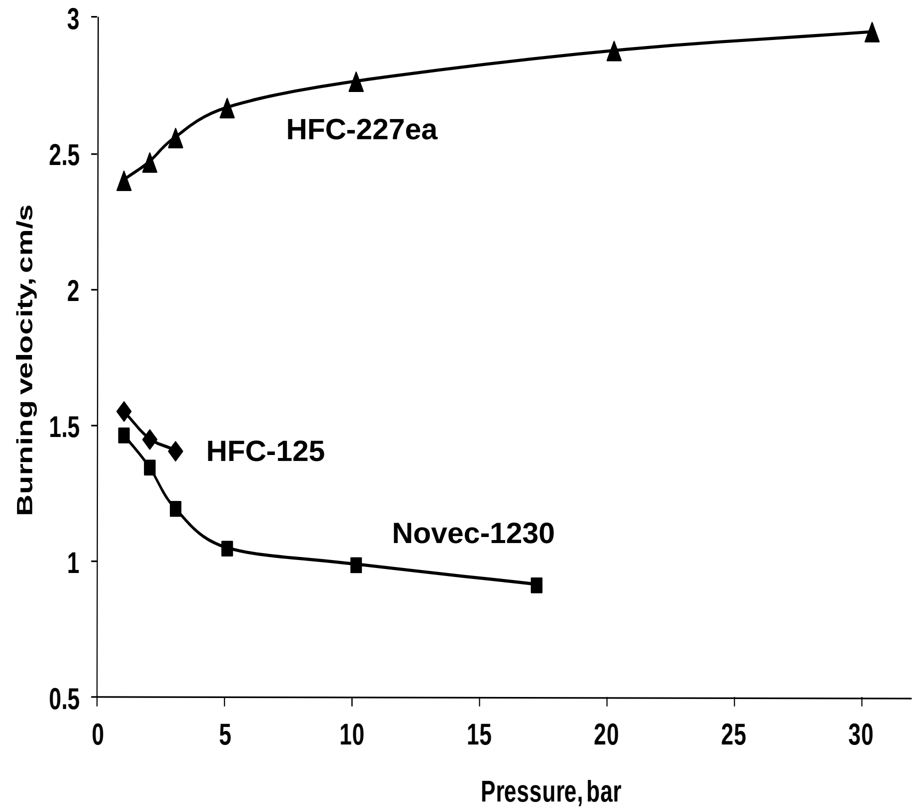
(values down to ≈1 cm/s can be measured.)

- 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.

Flames of pure suppressants with air: effect of T and P





=> Effect of initial temperature on flame speed: significant.

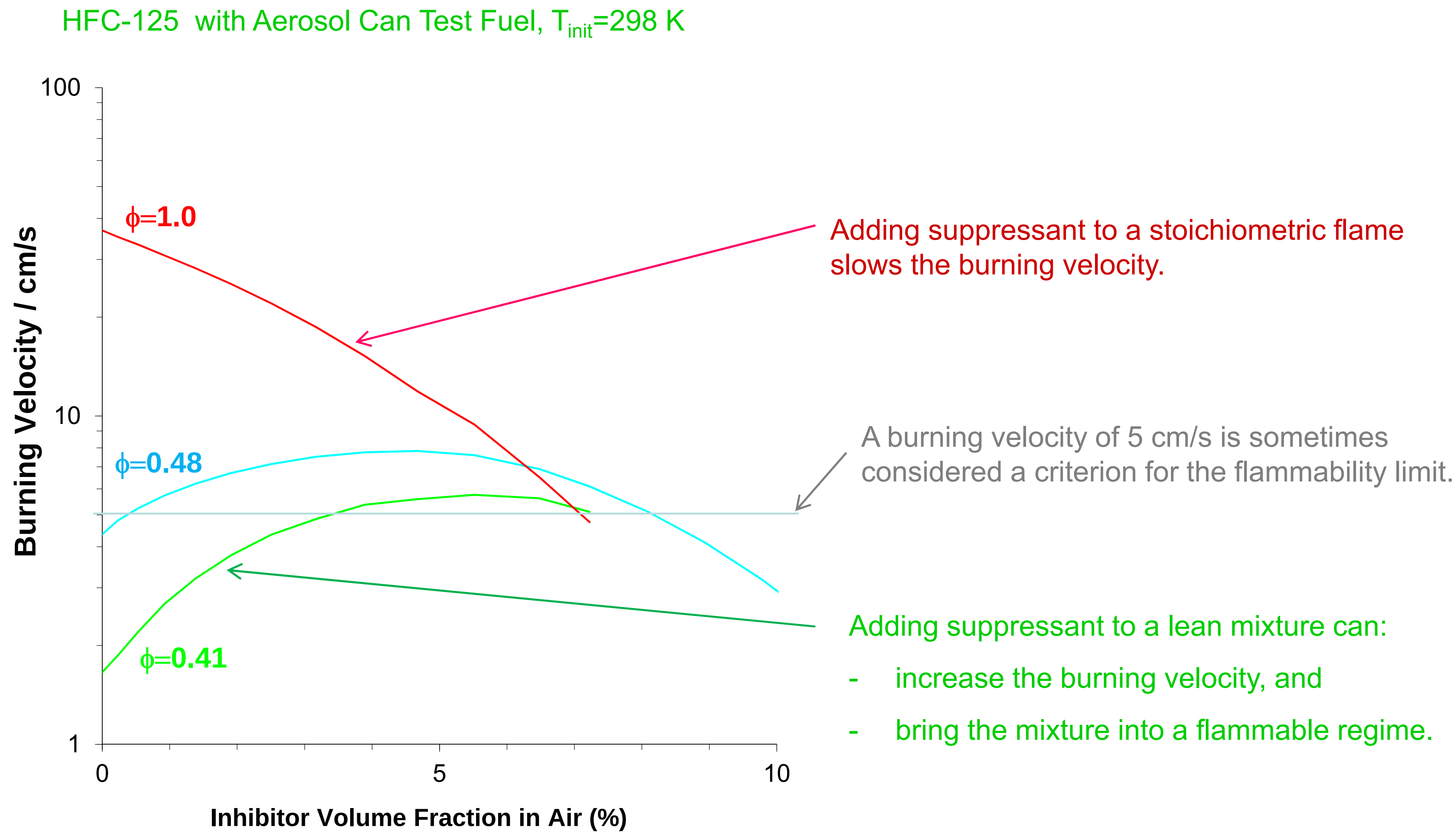
=> Compressive heating may contribute to reactivity of HFC-125 and Novec in FAA aerosol can test.

=> Effect of initial pressure on flame speed varies with agent, but is relatively low for pressures below 5 bar.

=> Pressure rise itself probably is not responsible for enhanced pressure rise with HFC-125 or Novec in ACT.

=> What about effect of agent in a lean hydrocarbon flame beyond the flammability limit?

Does adding suppressants to lean flames make them more flammable?



Conclusions

1. At sub-inerting concentrations, HFC-125, Novec, and 2-BTP all react in the FAA aerosol can test as though they were fuels; halon 1301 does also, but it: 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. Calculated burning velocities show that adding HFC-125 or Novec 1230 to a lean hydrocarbon-air system can increase the overall heat release and reactivity of the system (i.e., and bring the system from a typically non-flammable condition to a flammable one).

=> 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.

Questions To Answer:

1. What are the properties of the Aerosol Can Test and the agents that cause many clean agents to fail that test? Can anything be done about that?

2. Why are the kinetics with the agents not slower (i.e., slow enough for extinguishment in the FAA-ACT)? Would other halogenated hydrocarbons be expected to work?