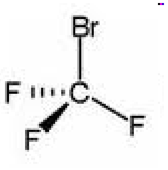
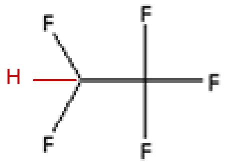
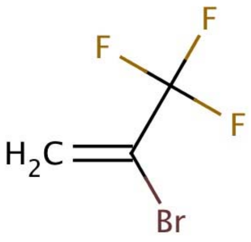
Aerosol Can Explosion Test (caution: graphic material)

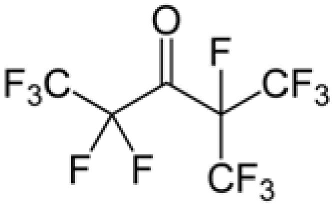
Problem: want to eliminate Halon 1301 from use in aircraft cargo bays

1. Halon 1301 (CF_3Br) => high ODP, high GWP.





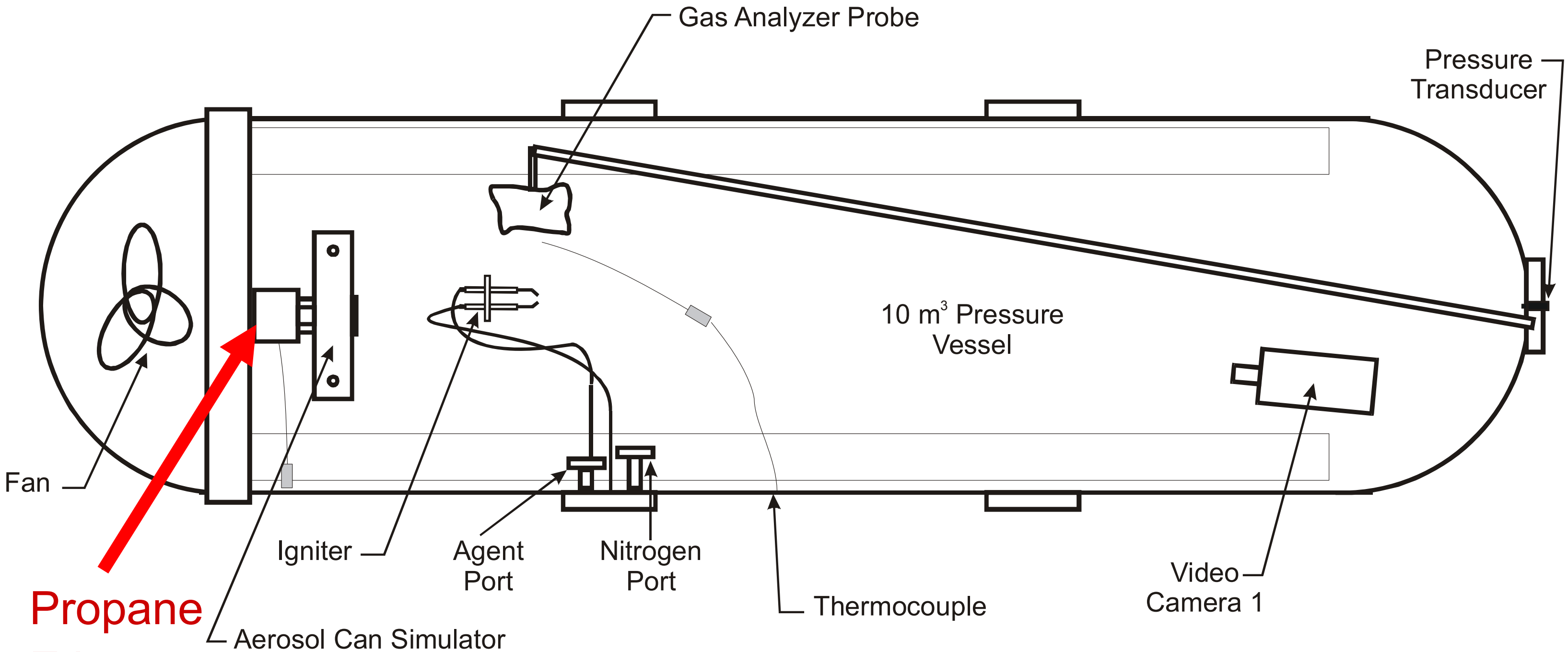




Compound	Atmospheric Lifetime (yrs)	ODP	GWP_{100}
Halon 1301 (CF_3Br)	65	12	6,900
HFC-125 (CF_3CF_2H)	29	0	3,400
2-BTP (CH_2CBrCF_3)	0.008	0	N/A
FK-5-1-12 ($CF_3CF_2C(O)CF(CF_3)_2$)	0.014	0	1

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.



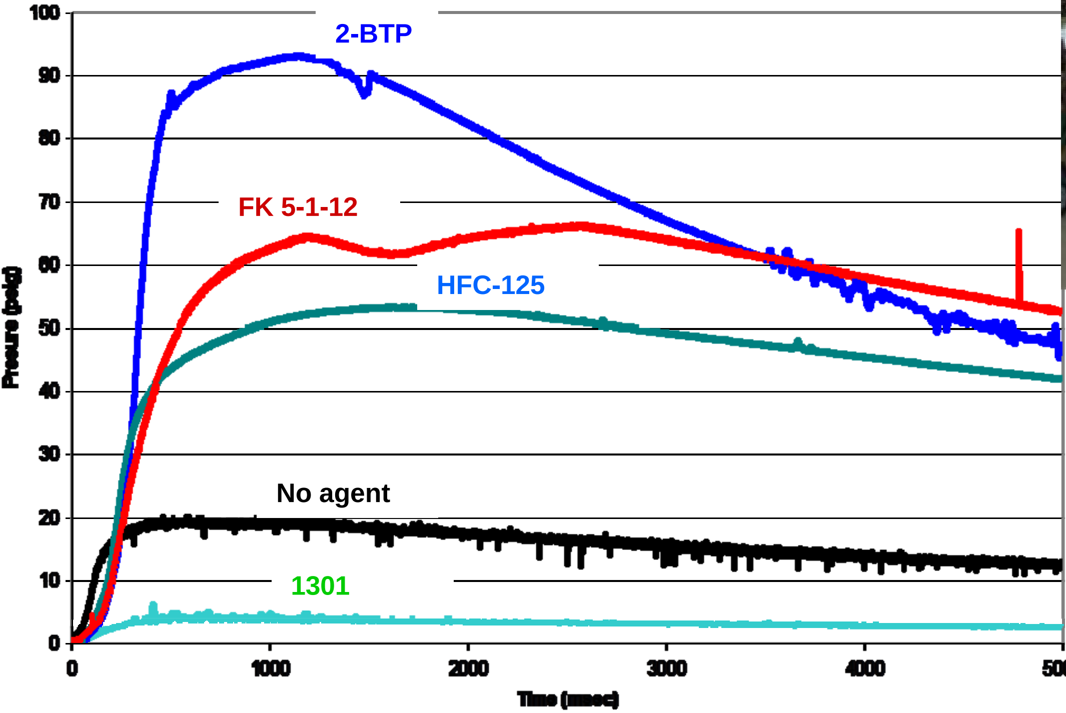
Propane
Ethanol
Water

FAA Aerosol Can Simulator

Goals

Understand the overpressure phenomena in the FAA Aerosol Can Test

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



FAA Aerosol Can Simulator

Understanding Combustion Promotion by Halogenated Fire Suppressants

INTERNATIONAL AIRCRAFT SYSTEMS FIRE PROTECTION WORKING GROUP MEETING

May 11-12, 2011

Greg Linteris, *NIST Fire Research*
Jeff Manion / Wing Tsang / Don Burgess, *NIST Chemical Kinetics*
Harsha Chelliah, *Univ. of Virginia*
Vish Katta, *Innovative Scientific Solutions, Inc.*
Fumi Takahashi, *Case Western Reserve Univ.*
Oliver Meier, *The Boeing Company*

University of Virginia
ENGINEERING

ISSI
Innovative Scientific
Solutions Incorporated

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National Institute of Standards and Technology
Building and Fire Research Laboratory

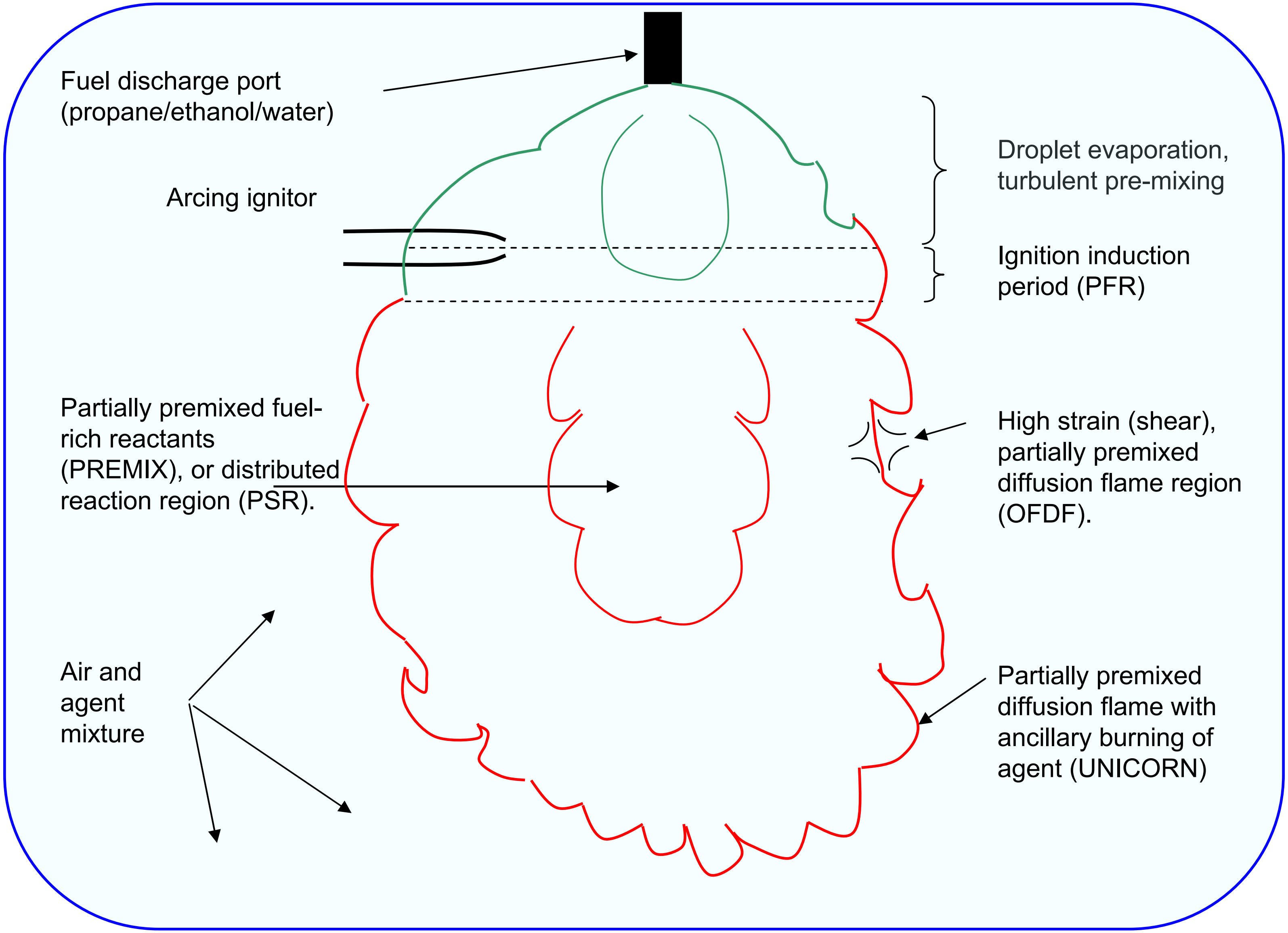
Acknowledgements

Wing Tsang, Don Burgess,	NIST
John Reinhardt, Dave Blake	FAA Technical Center
Med Colket, Ken Smith,	UTRC

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

Droplet evaporation, turbulent pre-mixing

Ignition induction period (PFR)

Partially premixed fuel-rich reactants (PREMIX), or distributed reaction region (PSR).

High strain (shear), partially premixed diffusion flame region (OFDF).

Air and agent mixture

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: Previous findings

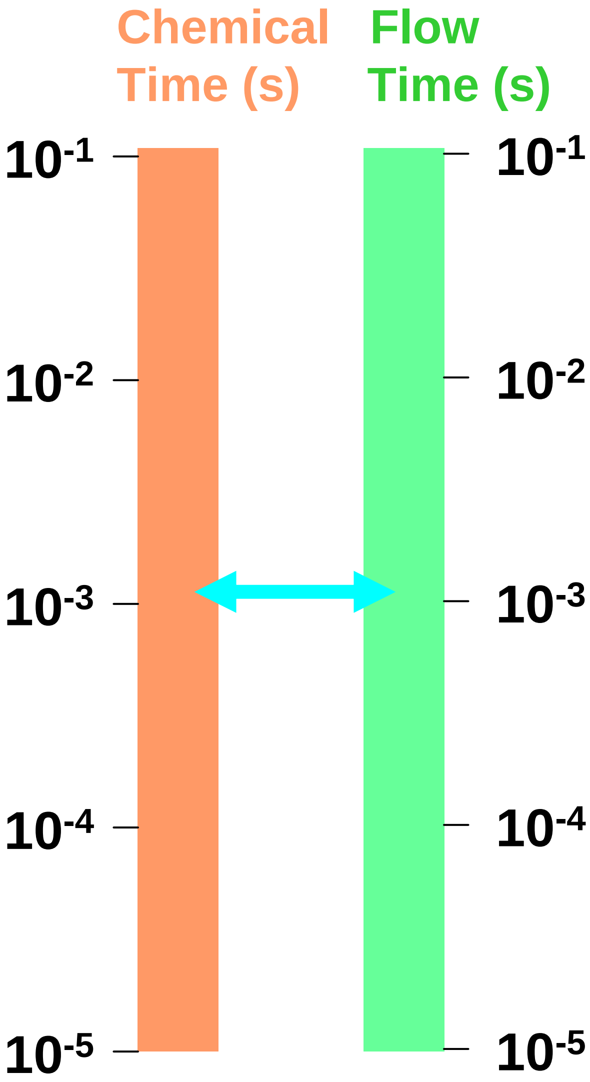
~ Of the 65 relevant papers collected and assimilated, these are highlights (in which enhanced combustion has been discussed):

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 delay	None
Ikeda and Mackie	ethane	C3HF7	Shock tube	Shorter ignition delay	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

Flame Extinction

Flames go out when:

$\tau_{chem} > \tau_{flow}$



Flame Extinction

The flow-field influences the extinction process:

$$D \equiv \tau_r / \tau_c$$

Chemical Time:

$$\tau_c \equiv \rho / w = \rho \, c_F^{-n} c_O^{-m} A^{-1} \exp(E / RT).$$

Flow Time:

$$\tau_r = \ell / v$$

Flame Extinction

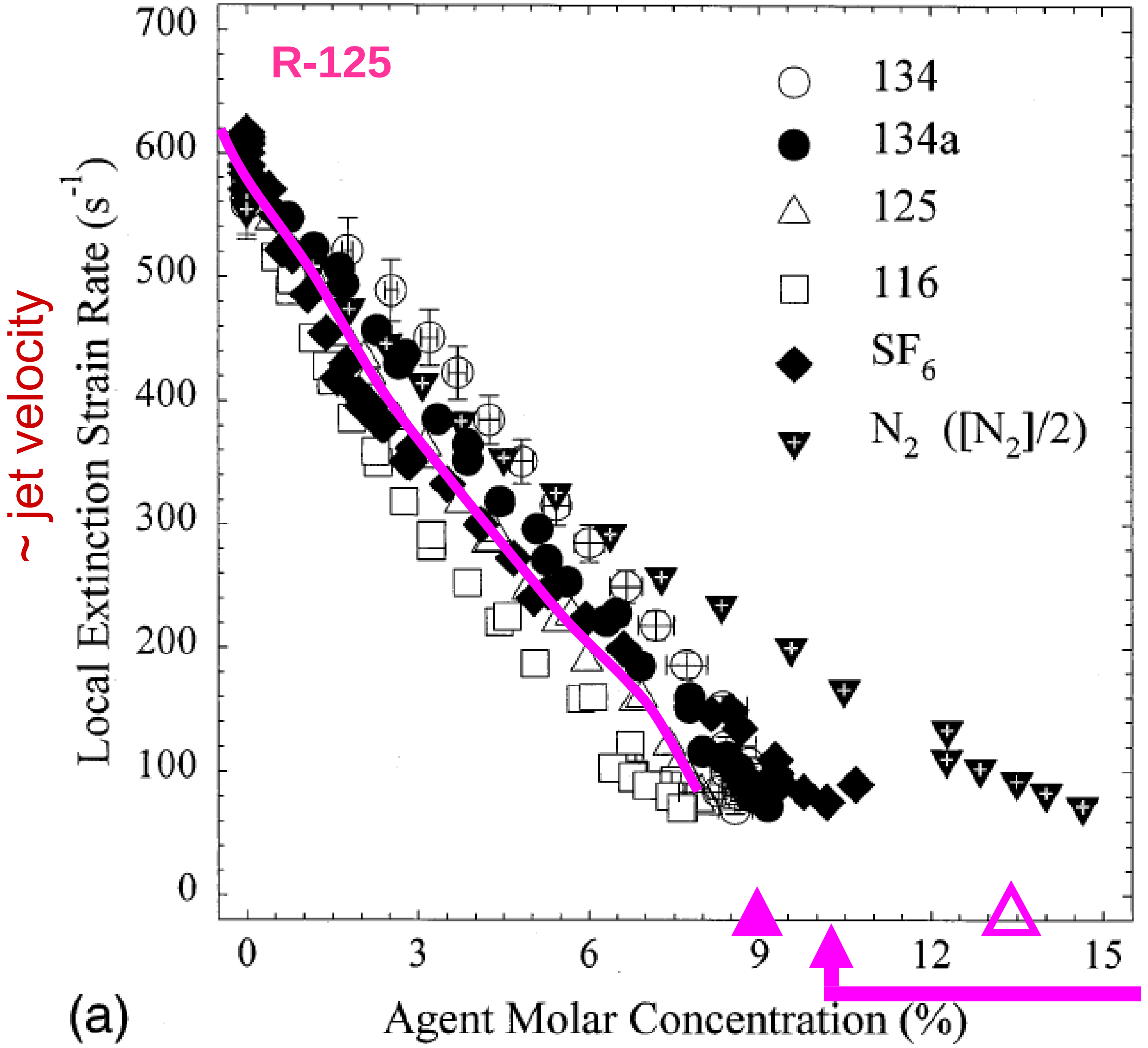
A measure of the overall chemical reaction rate can be obtained with:

Perfectly-Stirred Reactor (PSR) Calculations
Diffusion Flame Calculations (Counterflow)
Premixed Flame Calculations

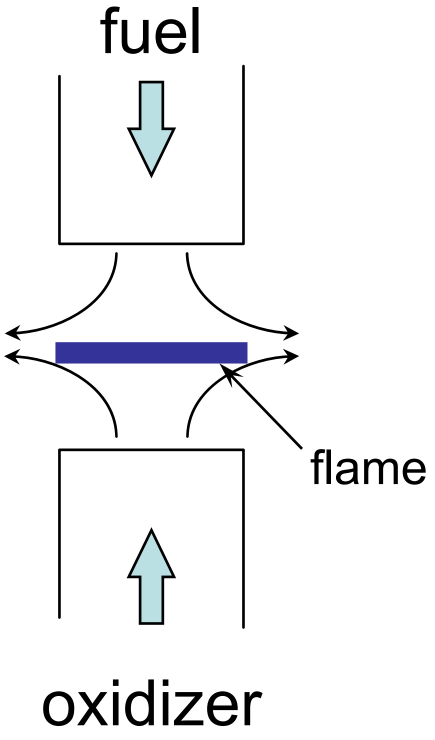
=> Concentrate on R-125

=> 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

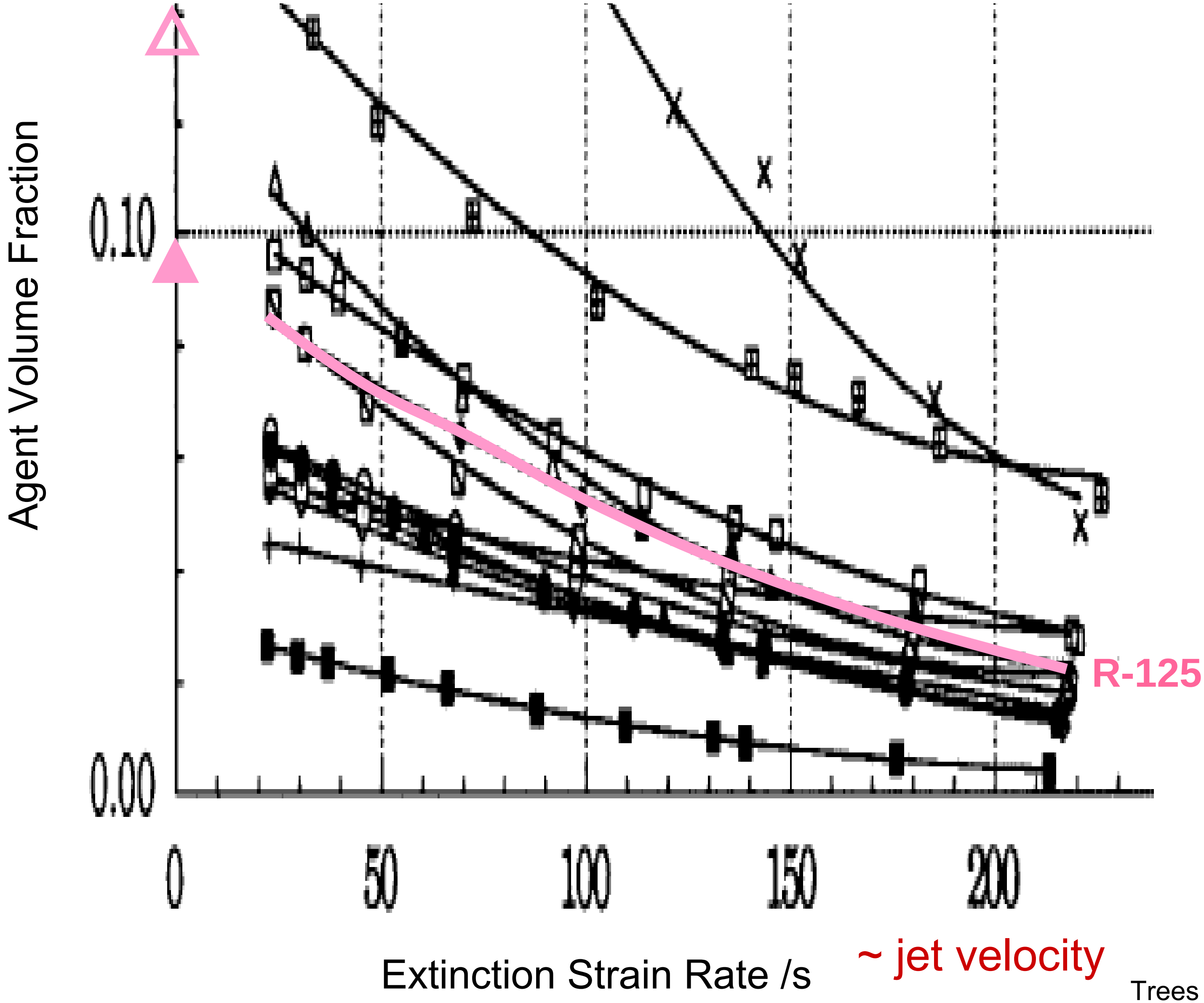


Cup burner



"Suppression of Nonpremixed Flames by Fluorinated Ethanes and Propanes," E. J. P. Zegers, et al. CNF 121:471-487 (2000)

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



~ jet velocity

Trees et al. NIST SP-861

Background:

Flame Extinction

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

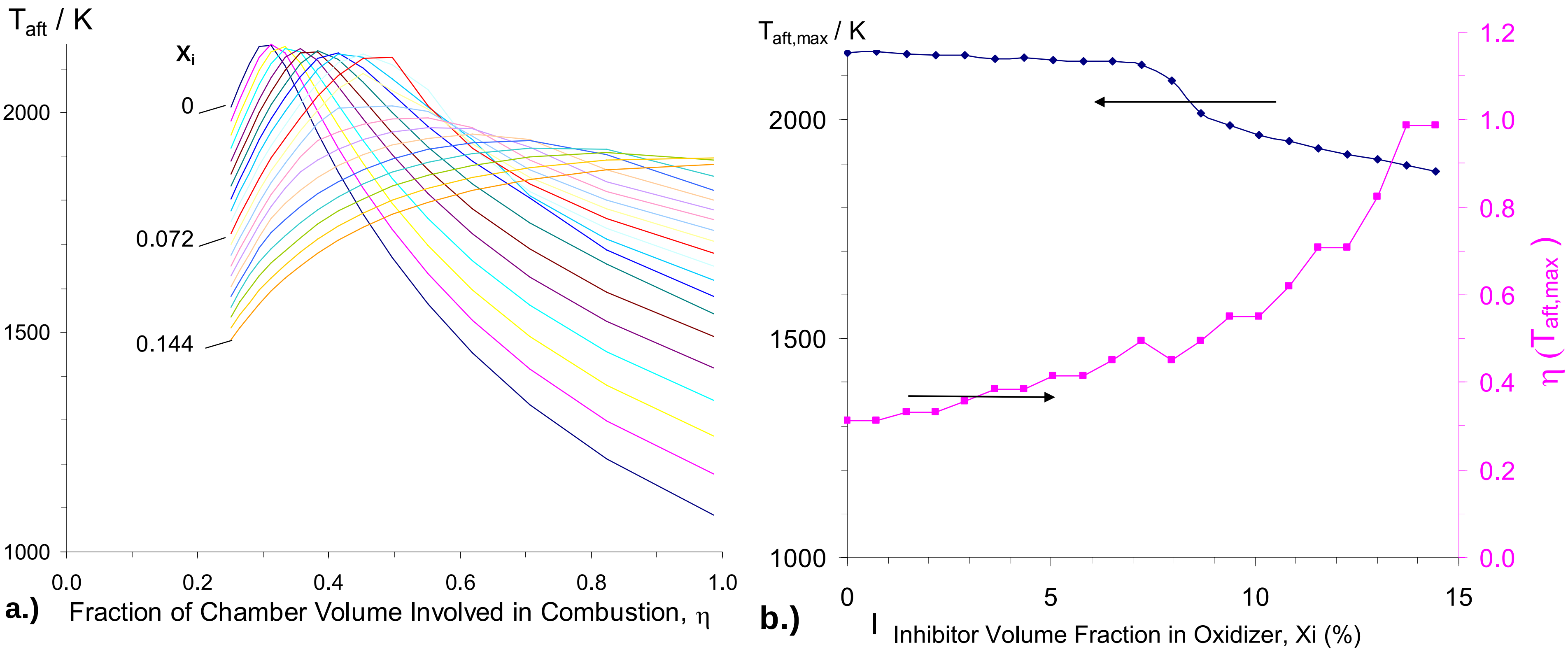
- the fuel reaction chemistry
- agent reaction chemistry
- mixing
- flame characteristics.

Thermodynamic Equilibrium Calculations

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

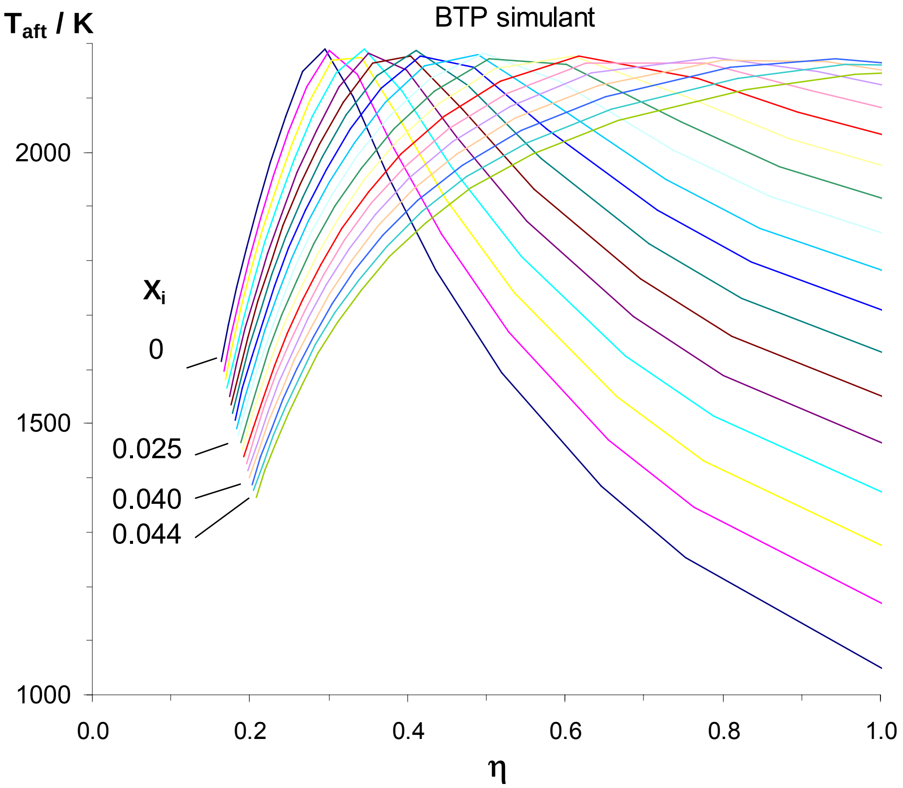
To do an equilibrium calculation, one must know the initial reactant mix (fuel, air, agent, water vapor, etc.). We don’t really know them for the ACT, so keep them all as variables, and find the equilibrium conditions for a wide range of initial mixtures.

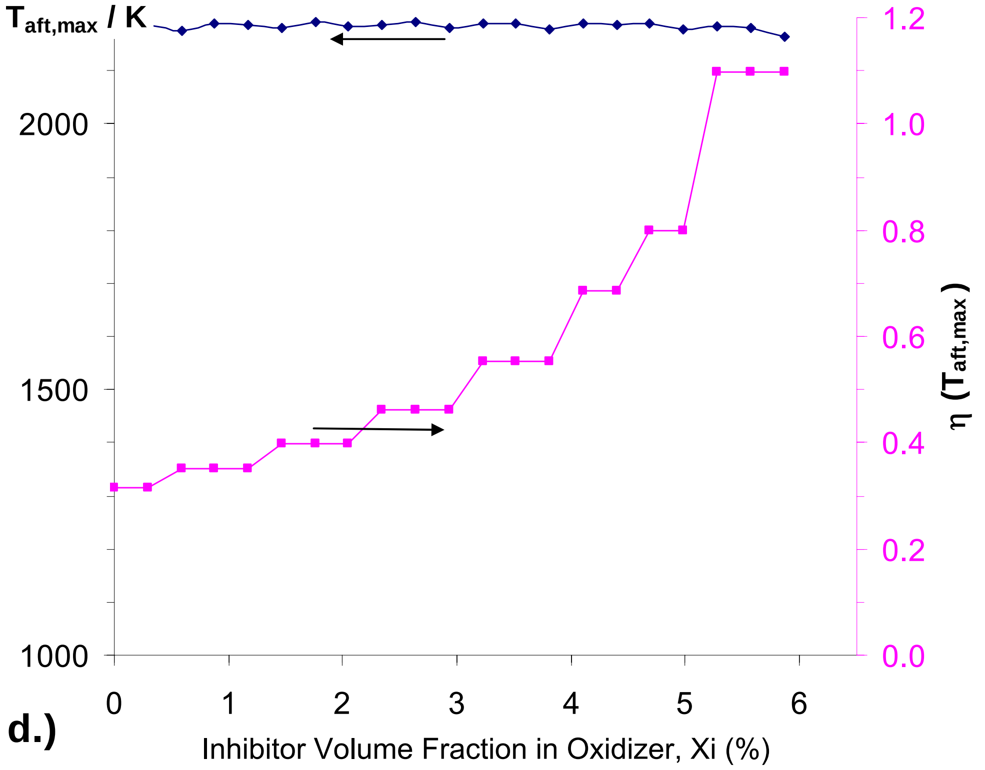
HFC-125: Adiabatic Flame Temperature (T_{aft})



- T_{aft} is high for all η.
- Change in behavior at [X]/[H]=1 (about 7.5 % HFC-125, red curve above).
- With large amounts of agent, a wide range of η gives nearly equivalent T_{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., η=1).

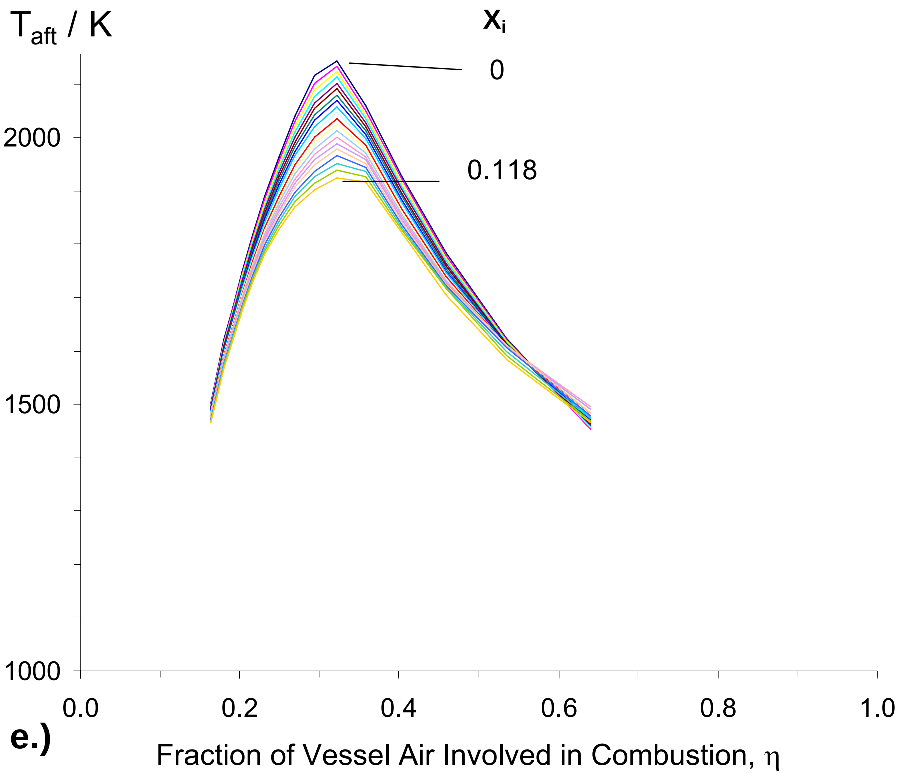
2-BTP: Adiabatic Flame Temperature (T_{aft})

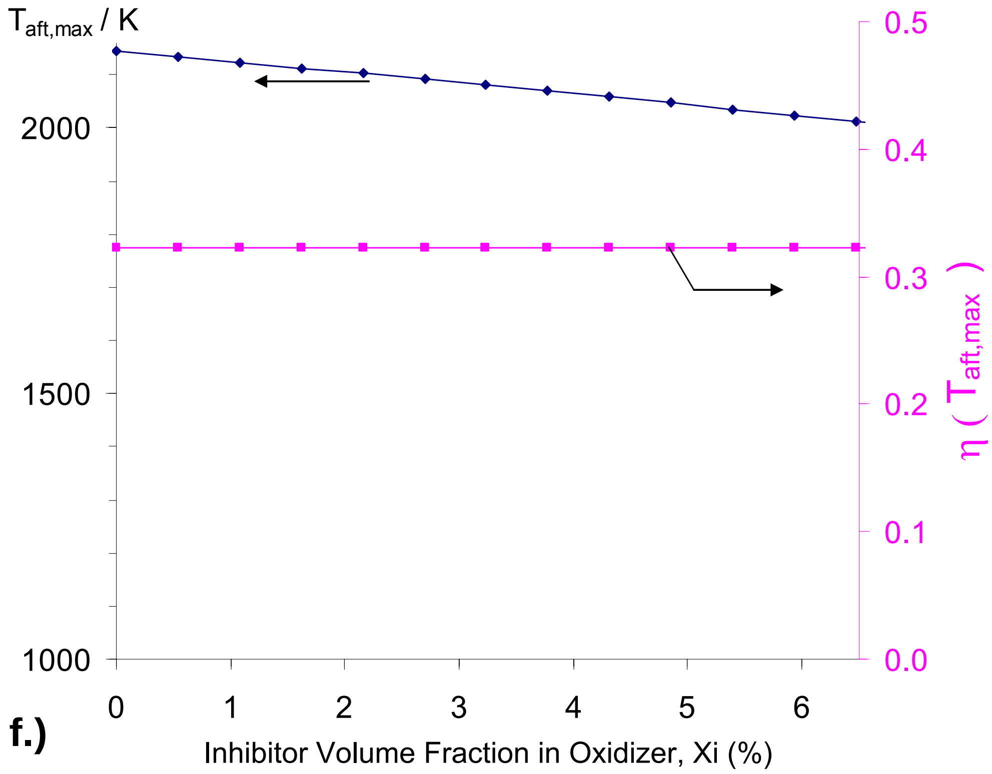




- T_{aft} is high for all η.
- most of the plot is below [X]/[H]=1 (about 6 % 2-BTP), so can't see change at [X]/[H]=1 .
- With large amounts of agent, a wide range of η gives equivalent T_{aft}.
- As agent is added, more and more chamber volume is necessary to achieve stoichiometric combustion.
- Where flame goes out (X_i=6 %), all the chamber volume is involved in combustion (i.e., η=1).

Halon 1301: Adiabatic Flame Temperature (T_{aft})





- T_{aft} is high for all η., but decreases somewhat as agent is added.
- most of the plot is below [X]/[H]=1 (about 11 % CF_3Br), 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? => $CF_3Br + 2H_2O = 3HF + HBr + CO_2$,

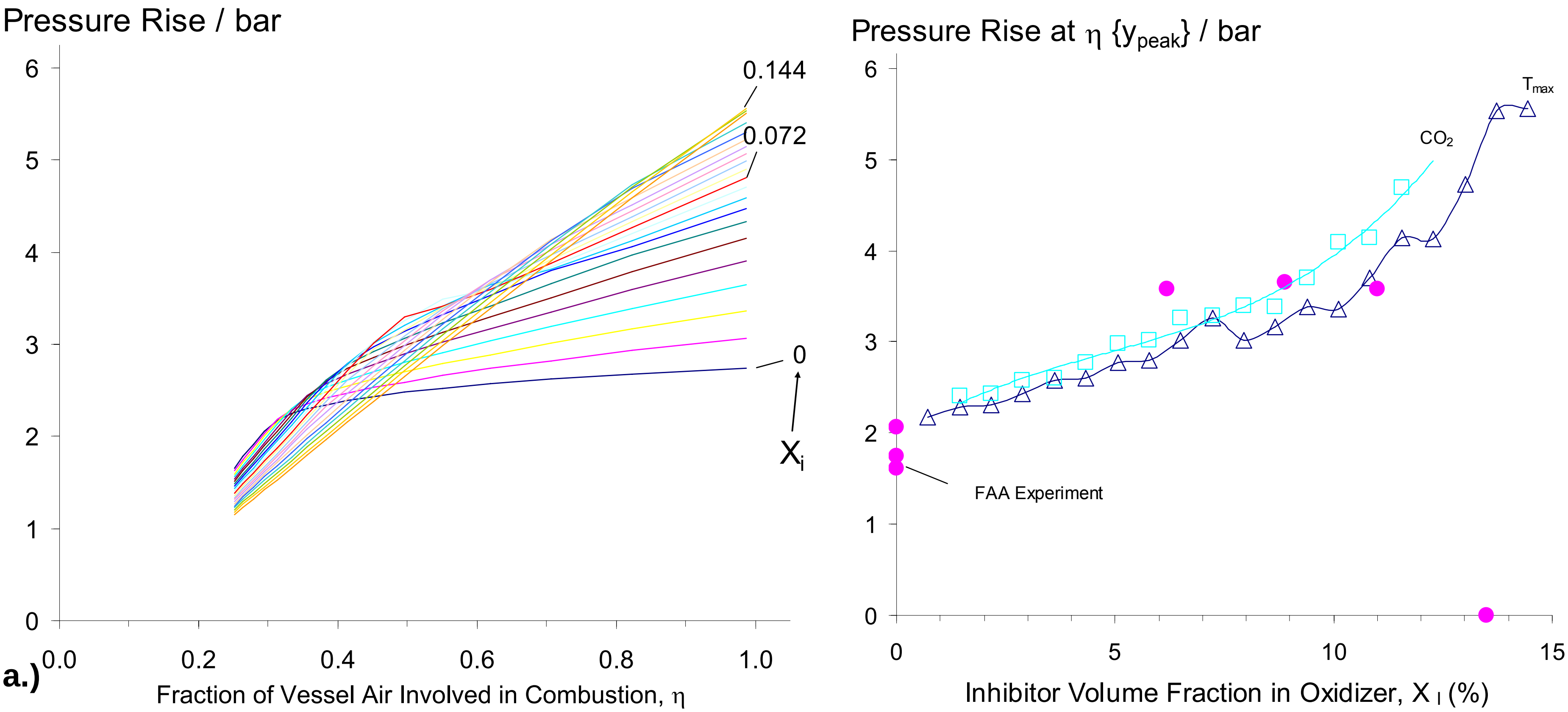
-i.e., there's always enough H and O in the system to oxidize the CF_3Br without more air!

- The T_{aft} is very sensitive to η.

Thermodynamic Equilibrium Calculations

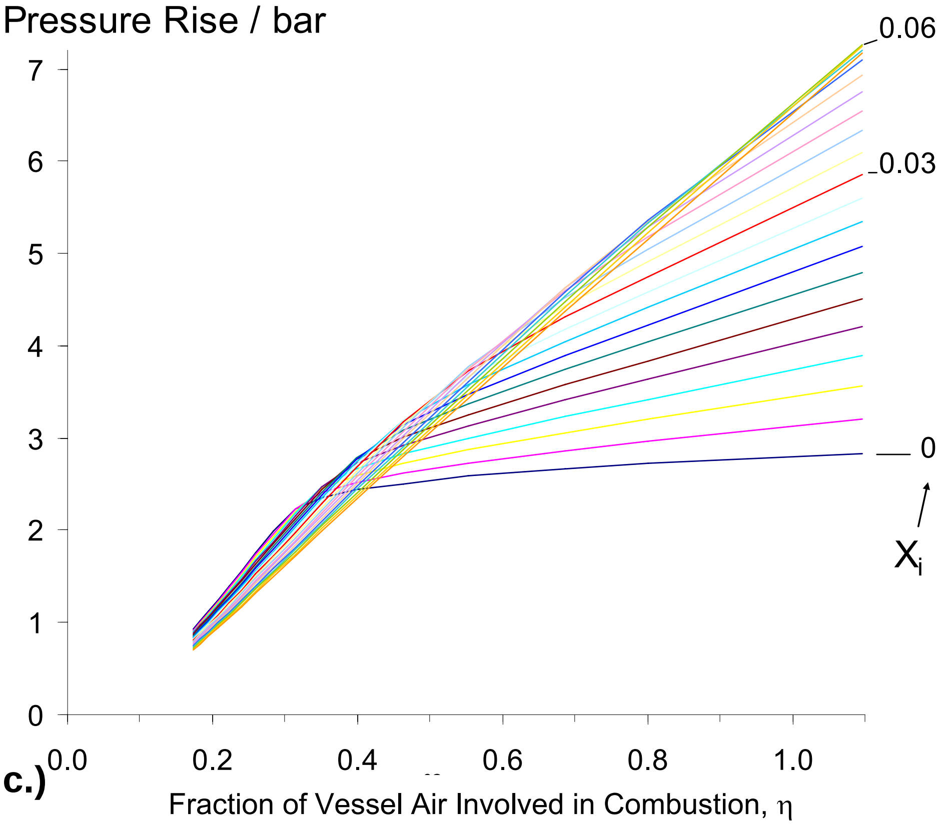
What do they tell us about the maximum pressure rise?

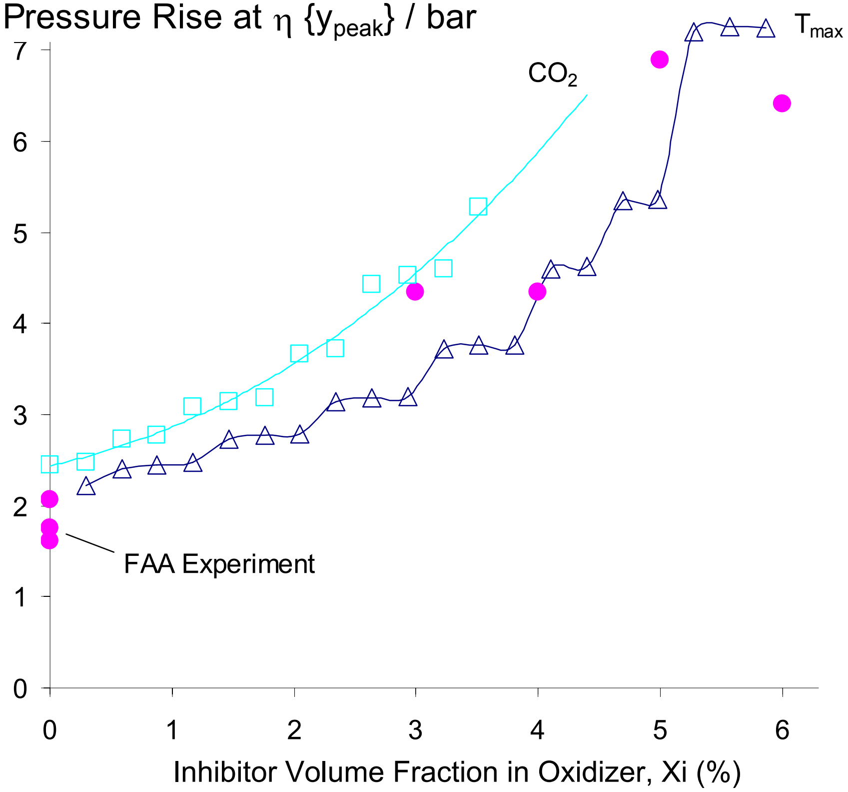
HFC-125: Predicted Pressure Rise



- The higher η, the greater ΔP (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 ΔP.
- Equilibrium thermodynamics predicts the final pressure quite well.
- Why does the agent not reduce the extent of reaction?

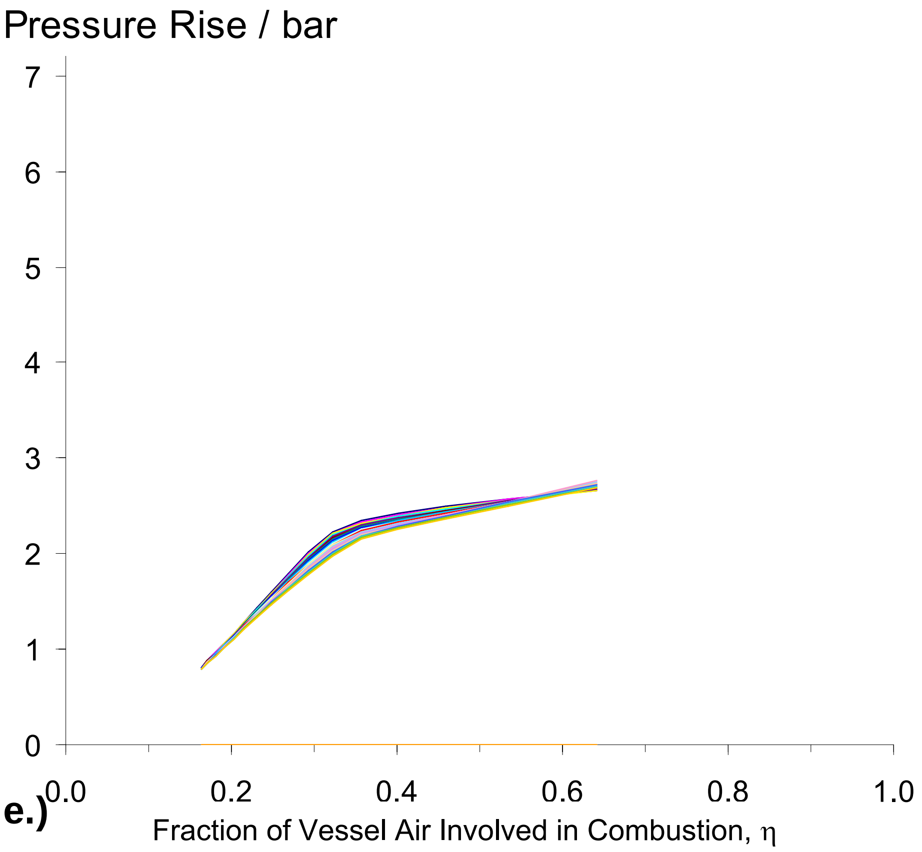
2-BTP: Predicted Pressure Rise



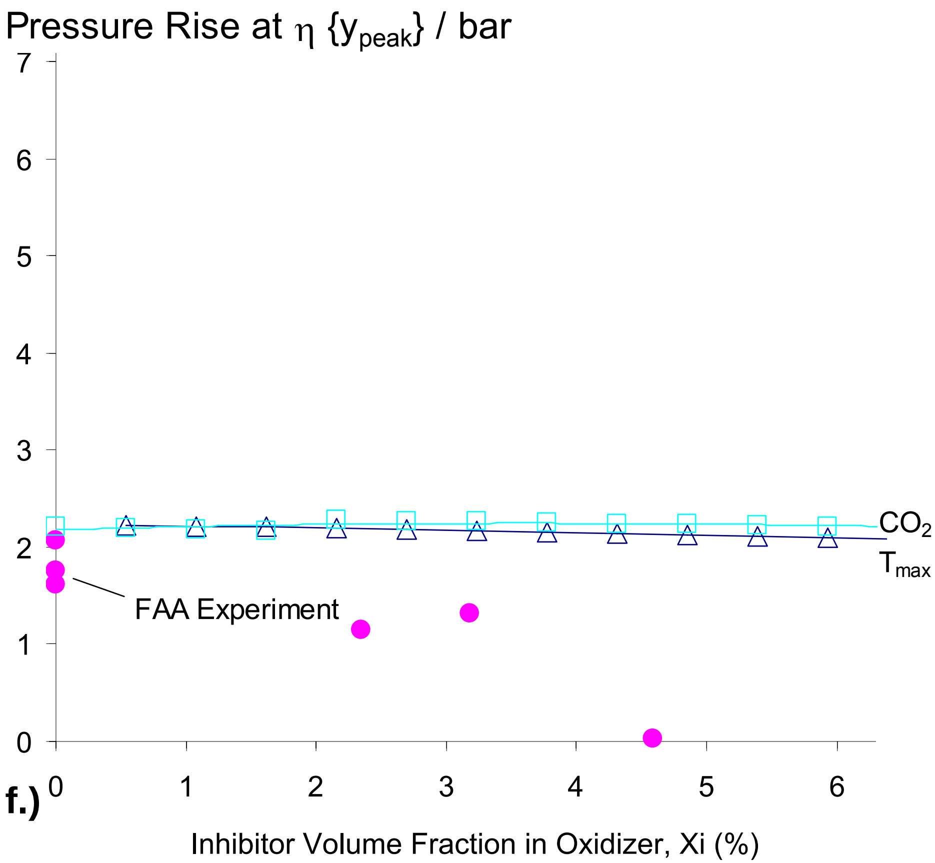


- Same basic behavior as R-125, but greater ΔP.
- The actual fraction of chamber volume (oxidizer) which can react has a large influence on ΔP.
- Equilibrium thermodynamics predicts the final pressure quite well.
- Why does the agent not reduce the extent of reaction?

Halon 1301: Predicted Pressure Rise



e.)



f.)

- Higher η has very little effect on ΔP.

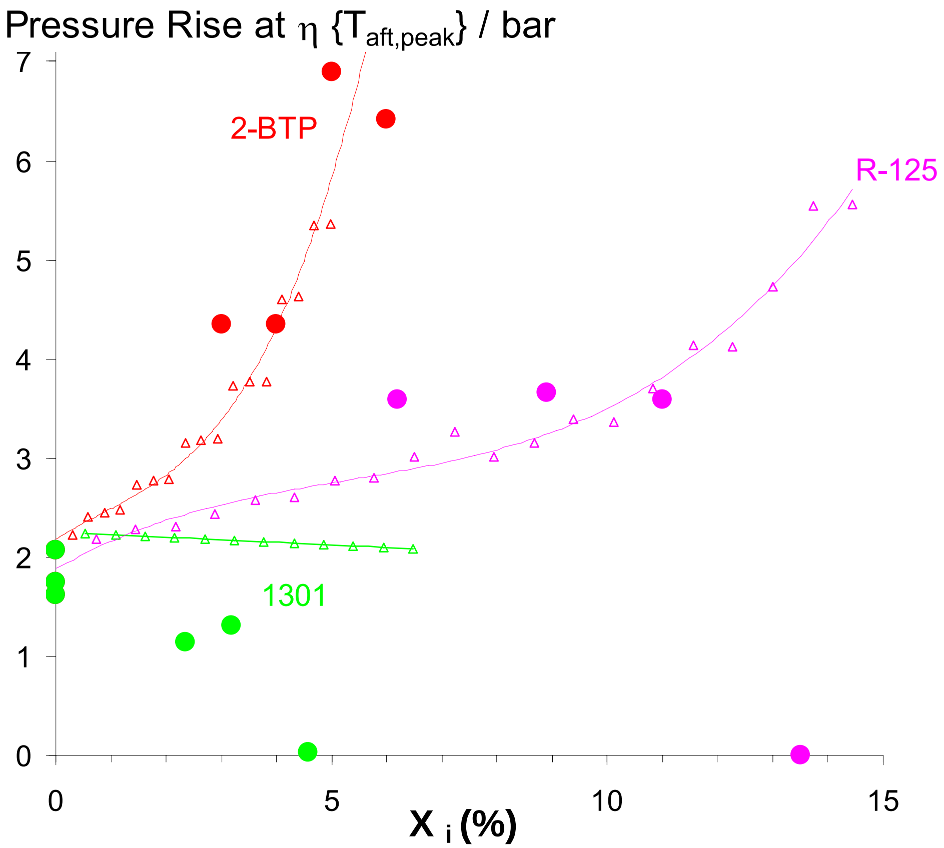
- At η of peak T_{aft}, or CO_2, the ΔP is constant! => can't use pressure rise to determine η.

- Actual ΔP 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)?

=> MUST LOOK AT THE KINETICS TO FIND OUT!

Halon 1301: Predicted Pressure Rise

Thermodynamic Equilibrium Calculations



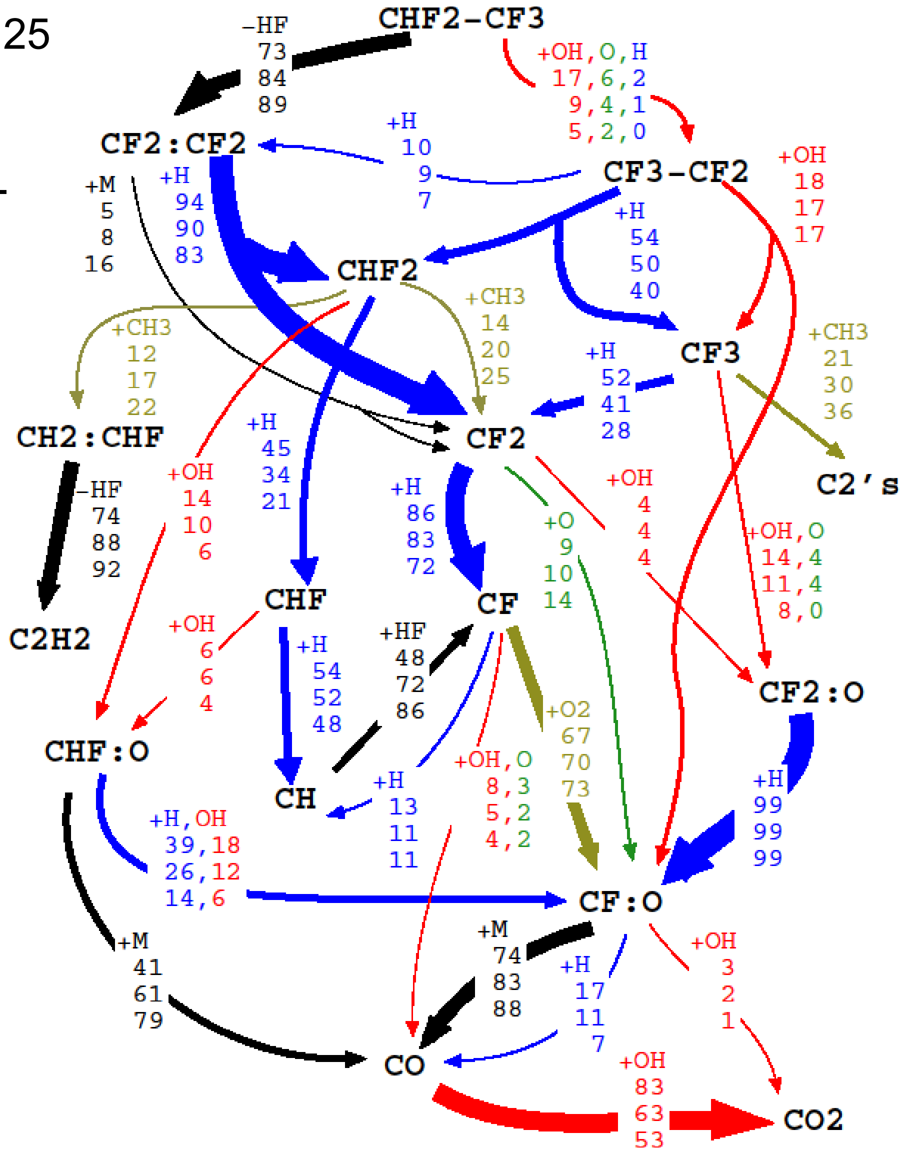
- As X_i of agent goes up, ΔP can increase for R-125 and 2-BTP, but not for 1301.

=> 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:

	Species	Reactions
C_4 hydrocarbon mechanism from Wang	111	784
Ethanol mechanism of Dryer	5	36
HFC mechanism from NIST[1,2]	51	600
CF_3Br mechanism of Babushok (NIST)[2]	10	122
	--------	--------
	177	1494

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

[2] Validation: CH_4-air and CH_3OH systems (with CHF_3 , $C_2H_2F_4$, C_2HF_5, CF_3Br, C_3HF_7):

- premixed flame speed,
- species profiles in low-pressure premixed flames,
- extinction strain rate for counterflow diffusion flames,
- cup-burner extinction.

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 => CSTL.

-But! For now, use a 2-BTP simulant:

1 mole CF_3Br,

1 mole C_2H_2,

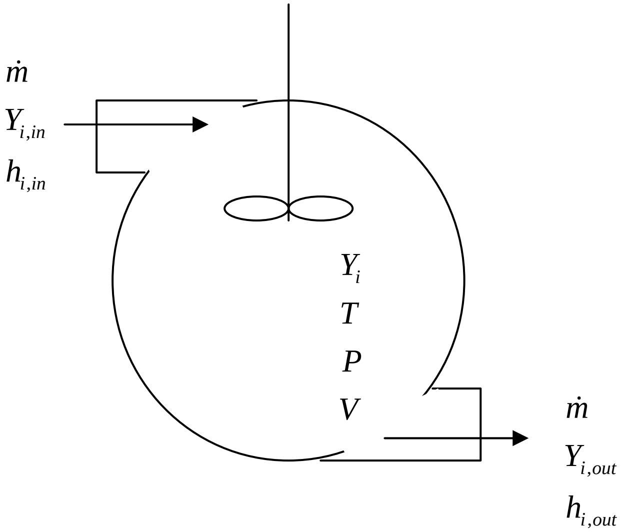
3 moles N_2

(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.

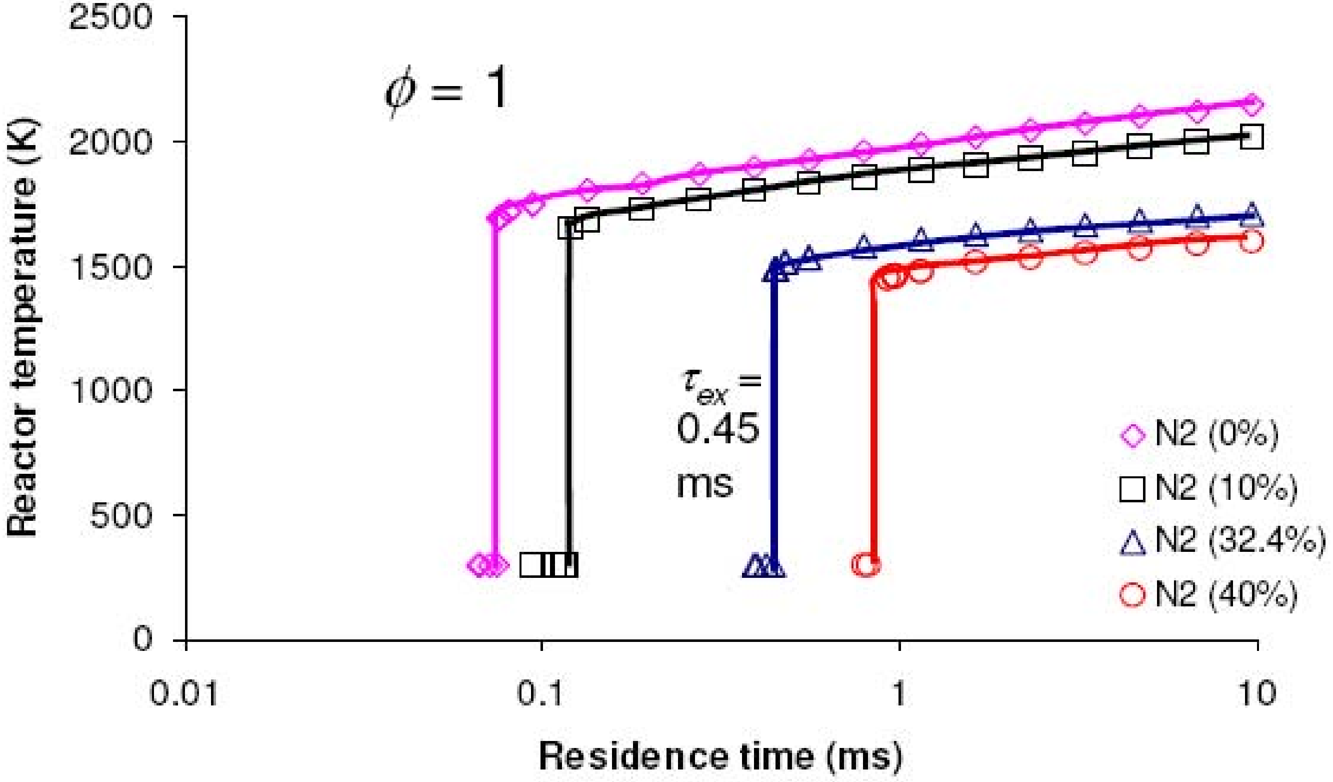
- Performed for R-125, 1301, and 1301 with N_2.



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.

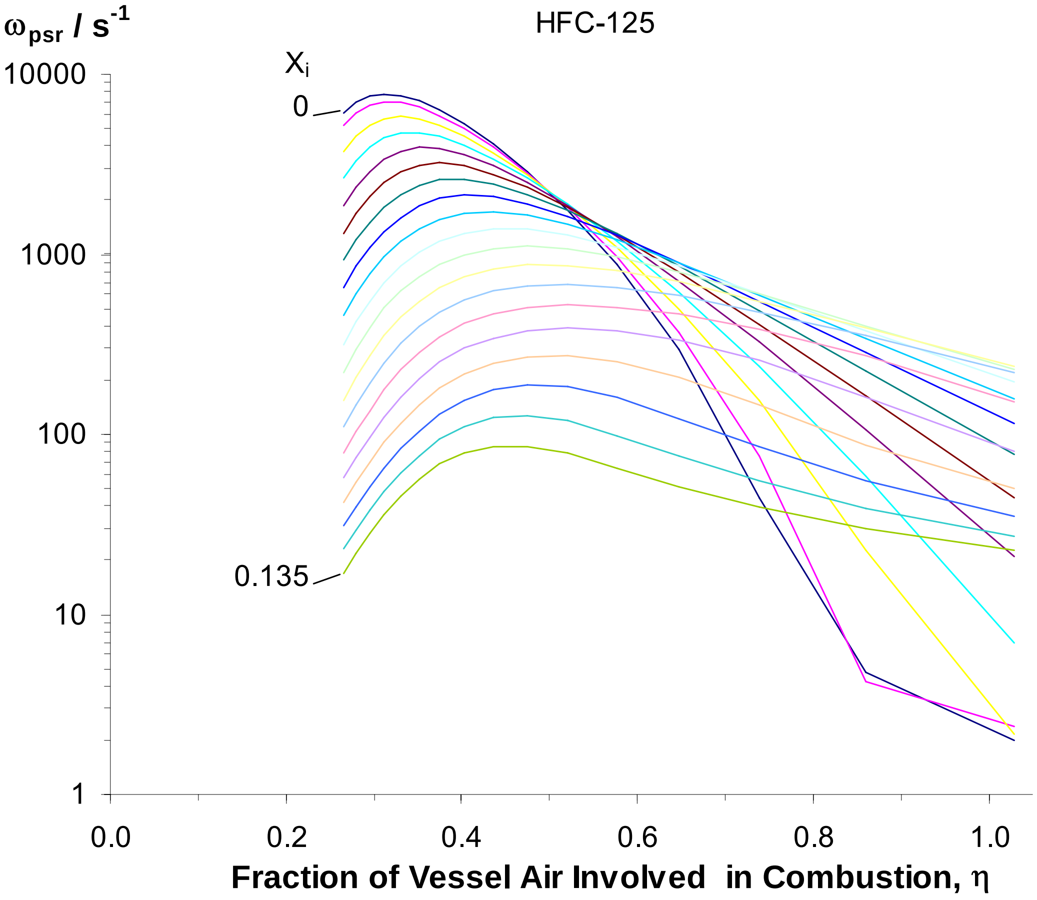
Calculation method



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

From Colket and co-workers, 2010

Overall Chemical Rate with R-125

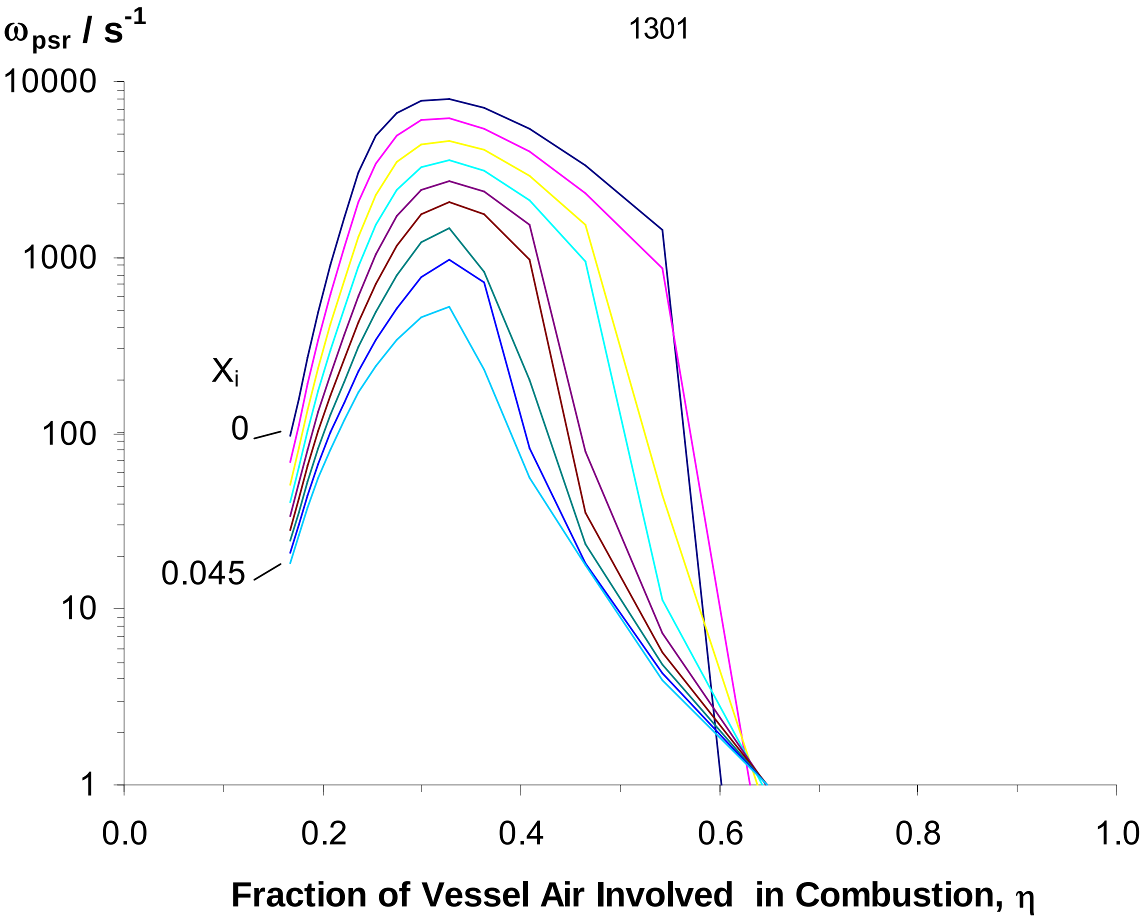


- Adding R-125 lowers ω_{chem} for rich mixtures (low η), but raises (then lowers) it for lean mixtures (high η).

–η has a big effect on overall chemical rate at low X_i, less effect at high X_i (follows temperature results).

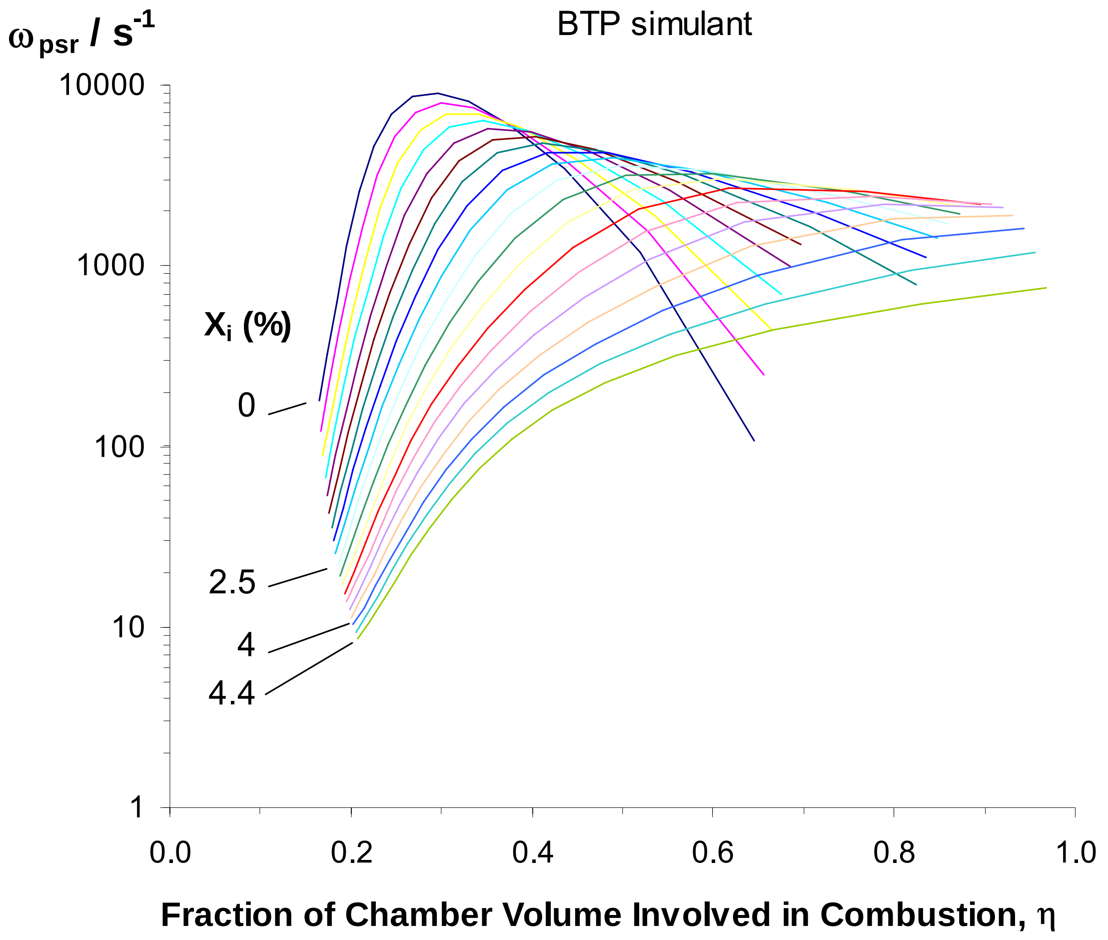
- i.e., for higher X_i, these curves flatten (ω_{chem} is insensitive to η for $\eta > 0.4$).

Overall Chemical Rate with 1301



- Adding 1301 <u>always</u> lowers ω_{chem} (for all η)
- ω_{chem} falls off very steeply with η (for all X_{inh}; follows temperature results).

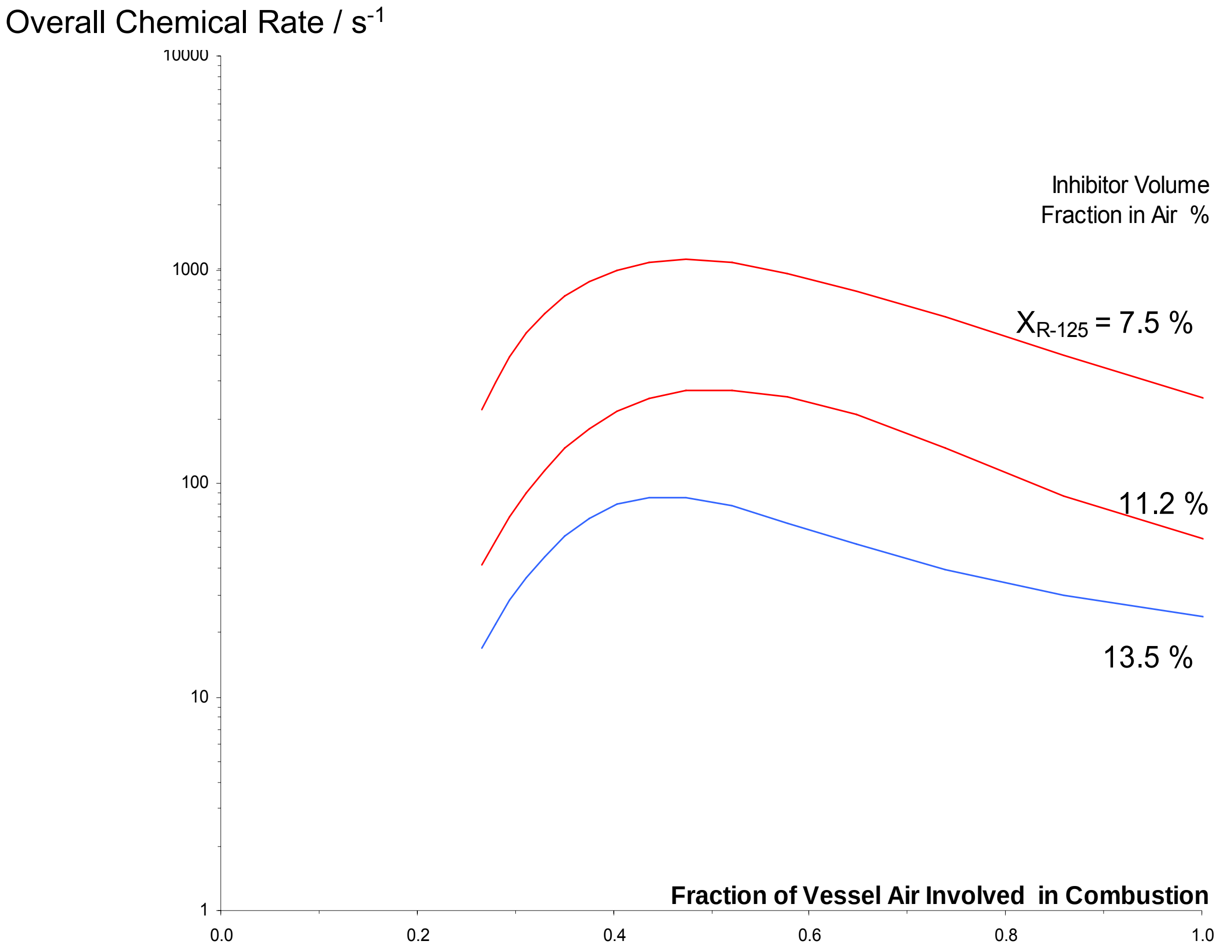
Perfectly-Stirred Reactor (PSR) Overall Chemical Rate with 2-BTP simulant



- Adding 2-BTP simulant lowers or raises ω_{chem} (depending upon η)
- variation of ω_{chem} with η is mild at high X_{inh}, but strong without agent.

Perfectly-Stirred Reactor (PSR) Calculations

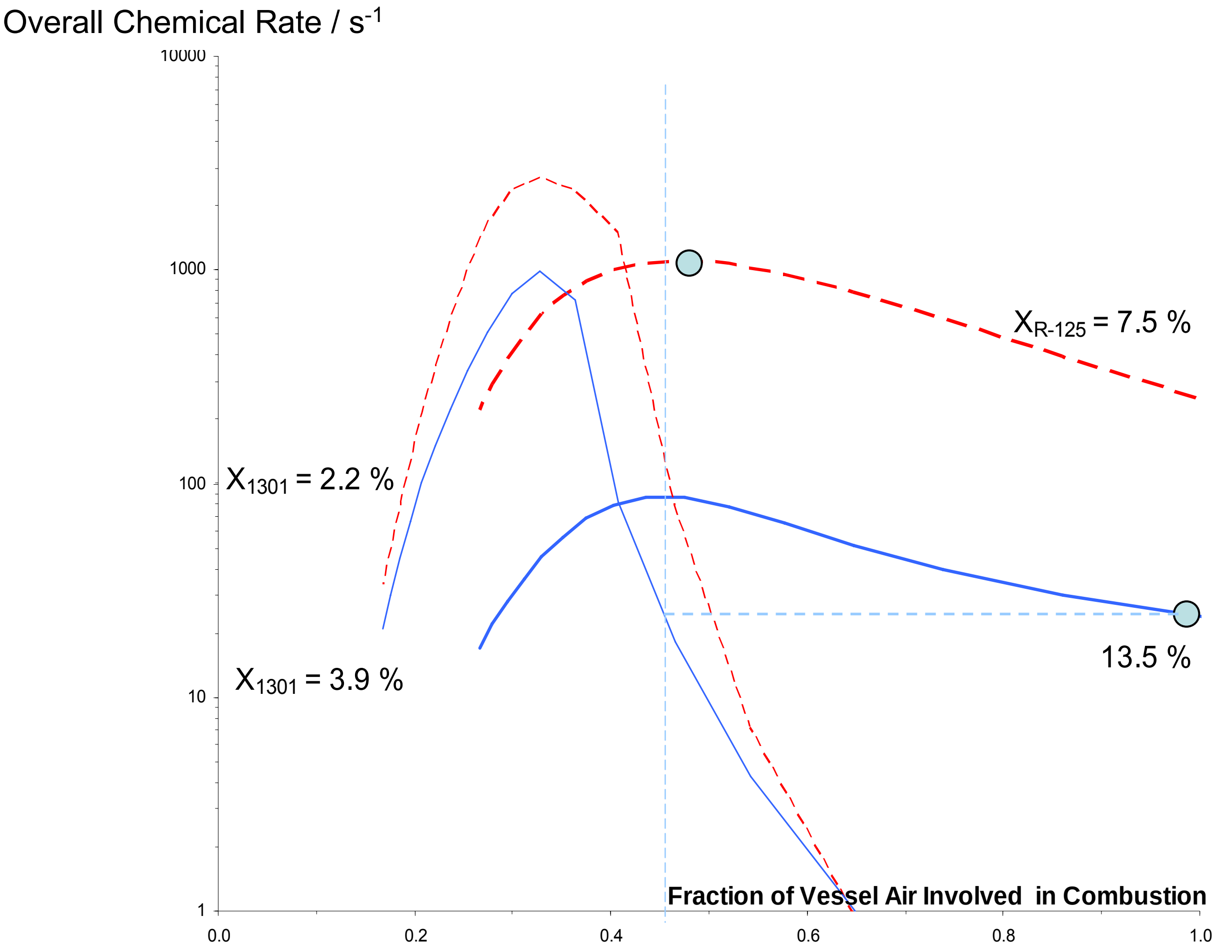
R-125 vs. 1301



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

Perfectly-Stirred Reactor (PSR) Calculations

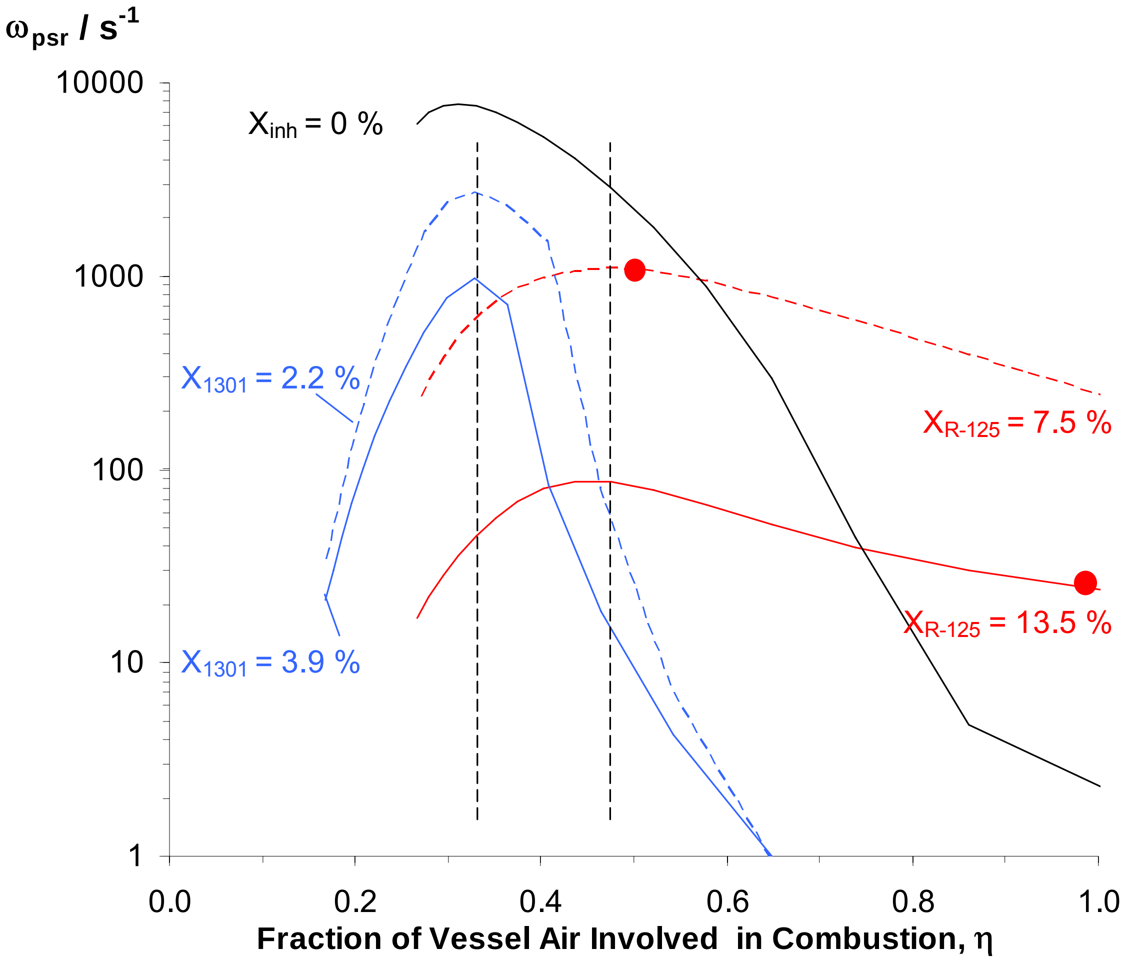
R-125 vs. 1301



- For R-125, we can use pressure rise data with equilibrium calculations to estimate η.
- For 1301, <u>can't use pressure rise</u>, so we don't really know η.

Perfectly-Stirred Reactor (PSR) Calculations

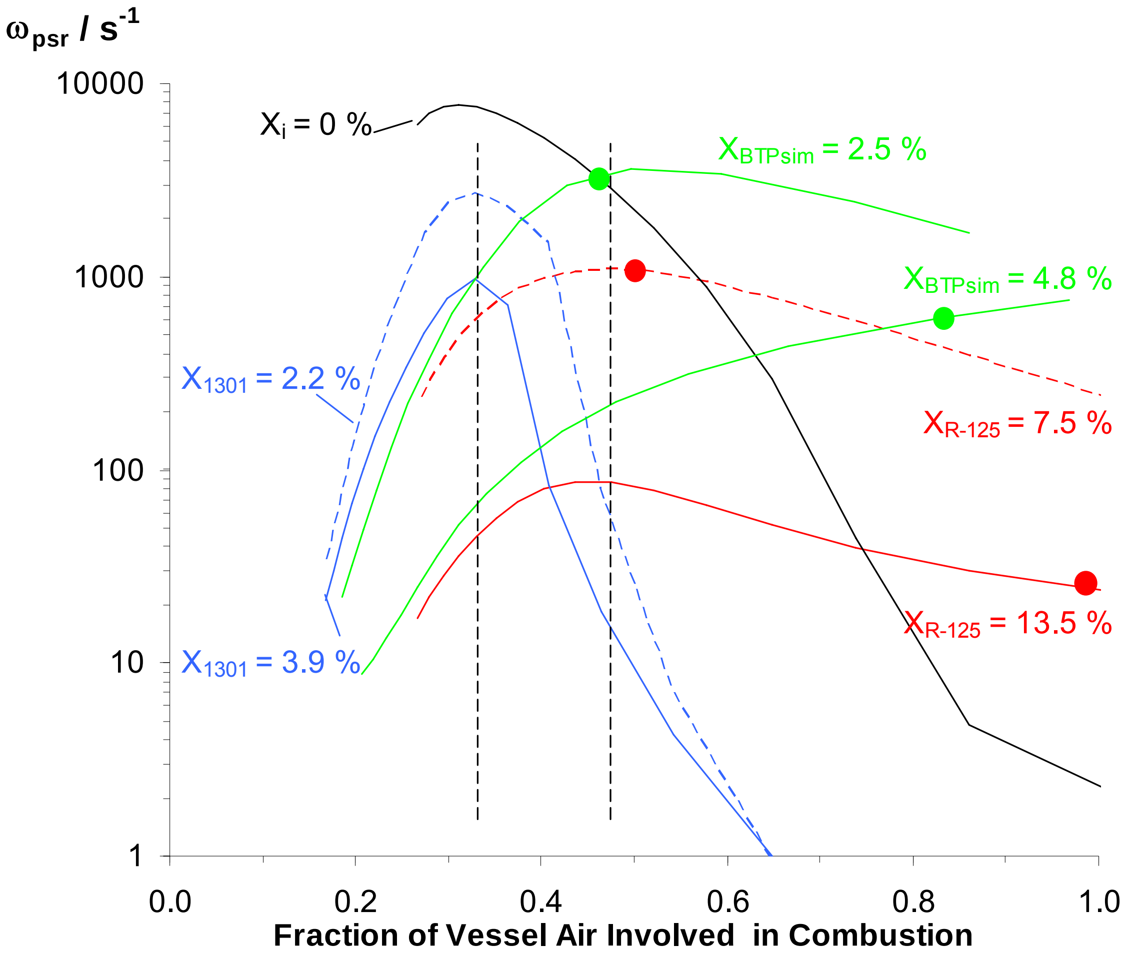
R-125, 2-BTP$_{sim}$, and 1301



- For R-125, we can use pressure rise data with equilibrium calculations to estimate η (solid dots).
- For 1301, can't use pressure rise, so we don't really know η. =>BUT for 1301 ω_{chem} is very sensitive to η.

Perfectly-Stirred Reactor (PSR) Calculations

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

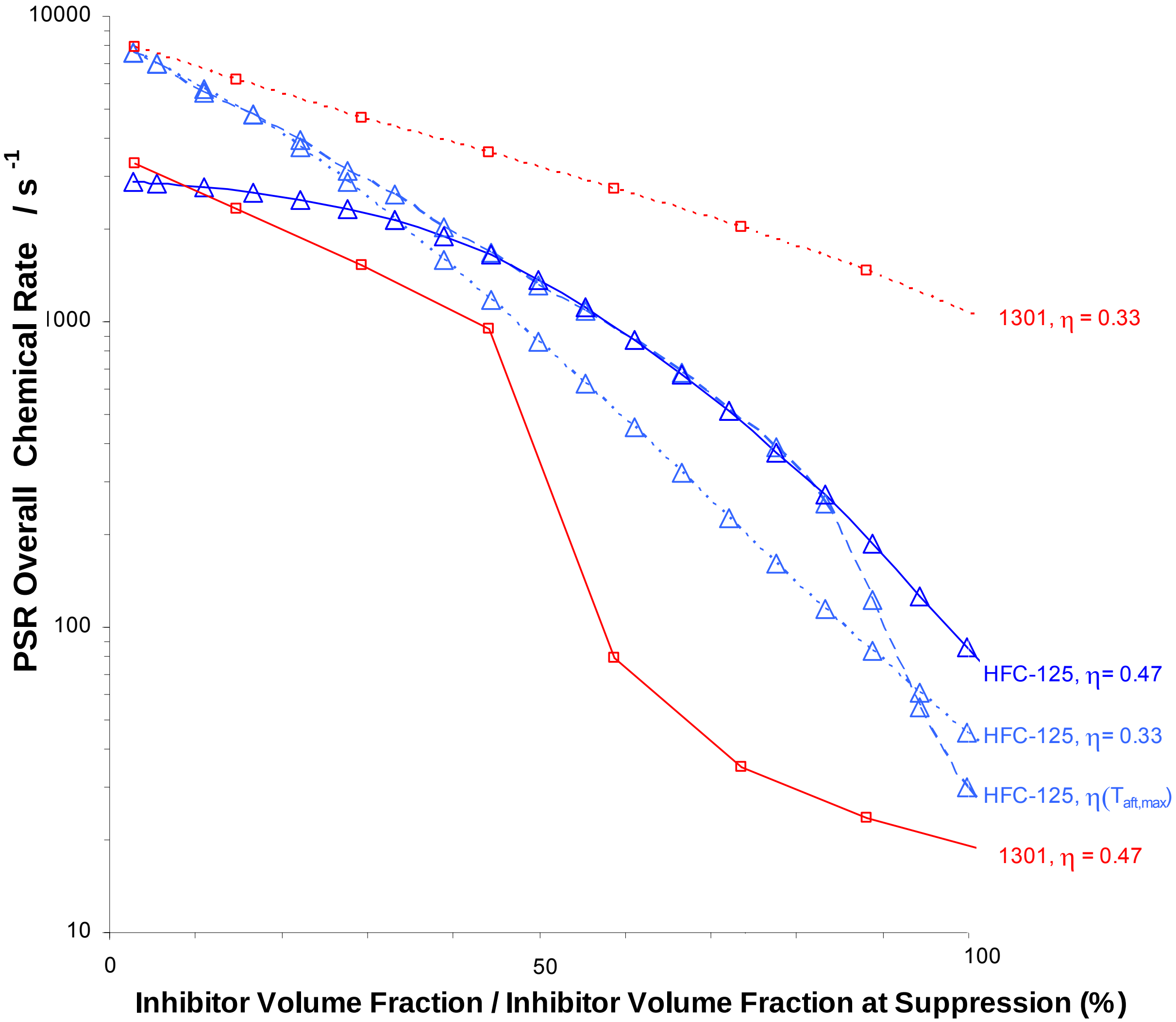


- For R-125, or 2-BTP simulant, we can use pressure rise data with equilibrium calculations to estimate η(solid dots).

- For 1301, can't use pressure rise, so we don't really know η. =>BUT for 1301 ω_{chem} is very sensitive to η.

Perfectly-Stirred Reactor (PSR) Calculations

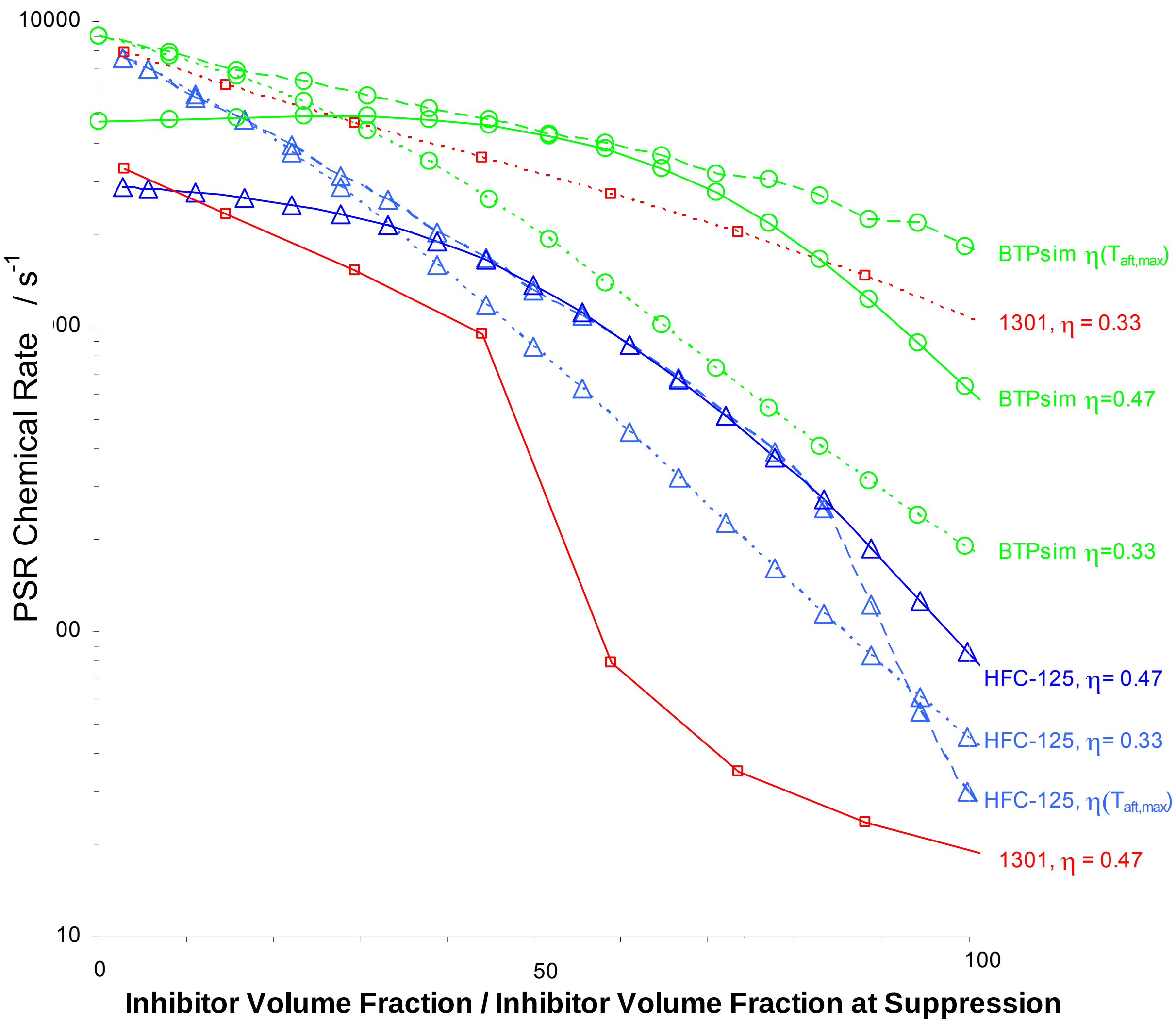
R-125 vs. 1301



1. More agent generally reduces *wpsr* , for all assumed values of η.
2. For the case η=0.47, there is little change in *wpsr* for the curve for HFC-125 up to 30 %.
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 η=0.33, η=0.47, or η(*Taft*|peak).
4. The effectiveness of the agent CF_3Br is very sensitive to the value of η.
5. For CF_3Br to be more effective than HFC-125, η must be greater than about 0.4.

Perfectly-Stirred Reactor (PSR) Calculations

R-125 vs. 1301



1. More agent generally reduces *wpsr* , for all assumed values of η.
2. For the case η=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 η=0.33, η=0.47, or η(*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, η must be greater than about 0.4.

Current Understanding

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_3Br does inhibit the flame, as expected.

4. The amount of chamber volume involved in the combustion, η, appears to be a key parameter controlling the kinetic behavior (i.e., the kinetic inhibition by CF_3Br is very sensitive to η, but R-125 is not).

5. Simulations with 2-BTPsimulant imply that the fuel portion of the 2-BTP molecule causes it to be much less effective than CF_3Br.

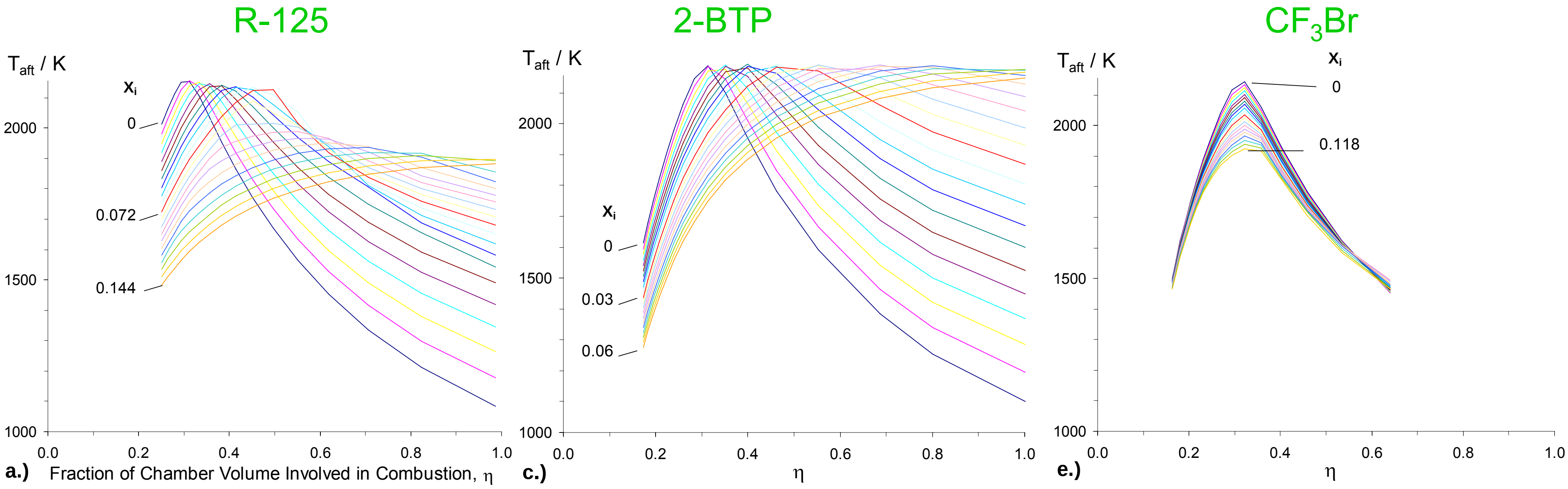
Equilibrium Calculations Indicate:

=> With R-125 or 2-BTP:

- the peak T_{aft} does not drop much with added agent.
- more agent requires higher η.
- at high X_i, T_{aft} is nearly the same regardless of the equivalence ratio.

=> With CF_3Br,

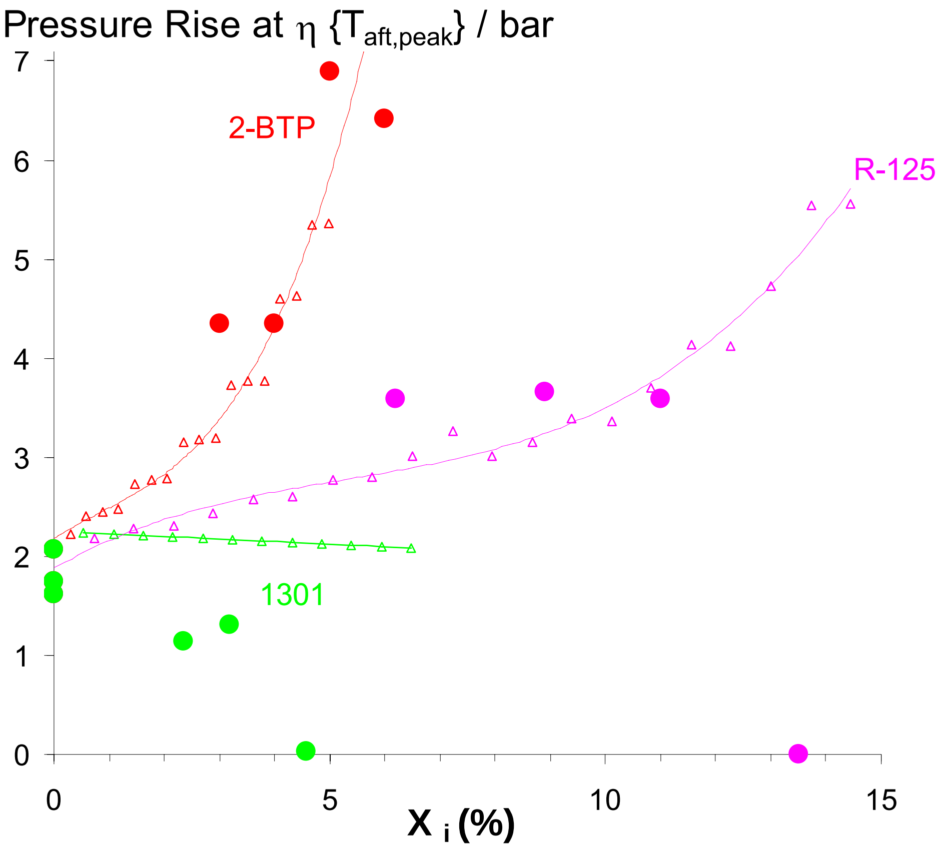
- T_{aft} drops off away from stoichiometric.
- η is not changed with added agent.



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).

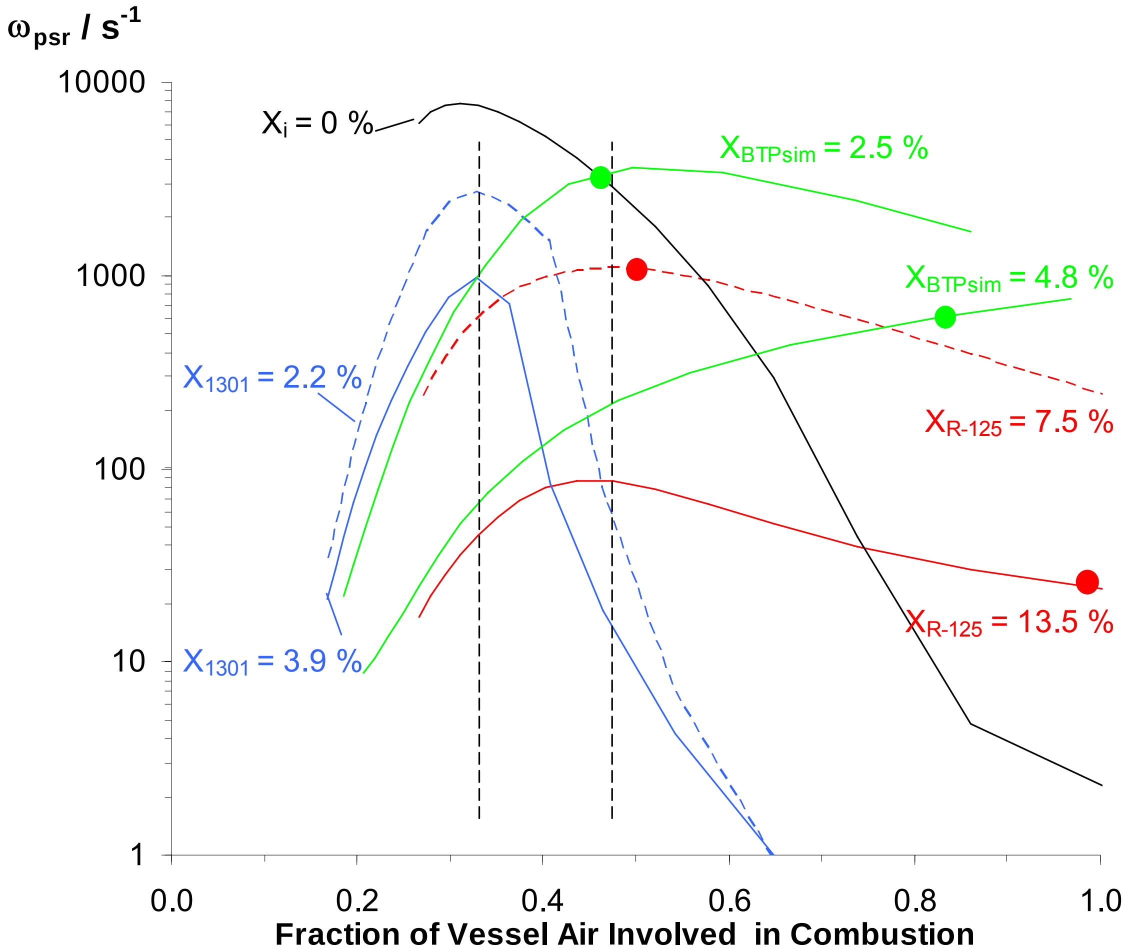
=> With CF_3Br, adding agent will never increase the pressure rise, even without kinetic inhibition.



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_3Br, 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?

Other Ongoing Work

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., η, pressure effects), and the mechanisms.
   - explore range of conditions for which inhibition/enhancement occurs
   - rapidly screen new agents.

New Constant-Volume Combustion Device*

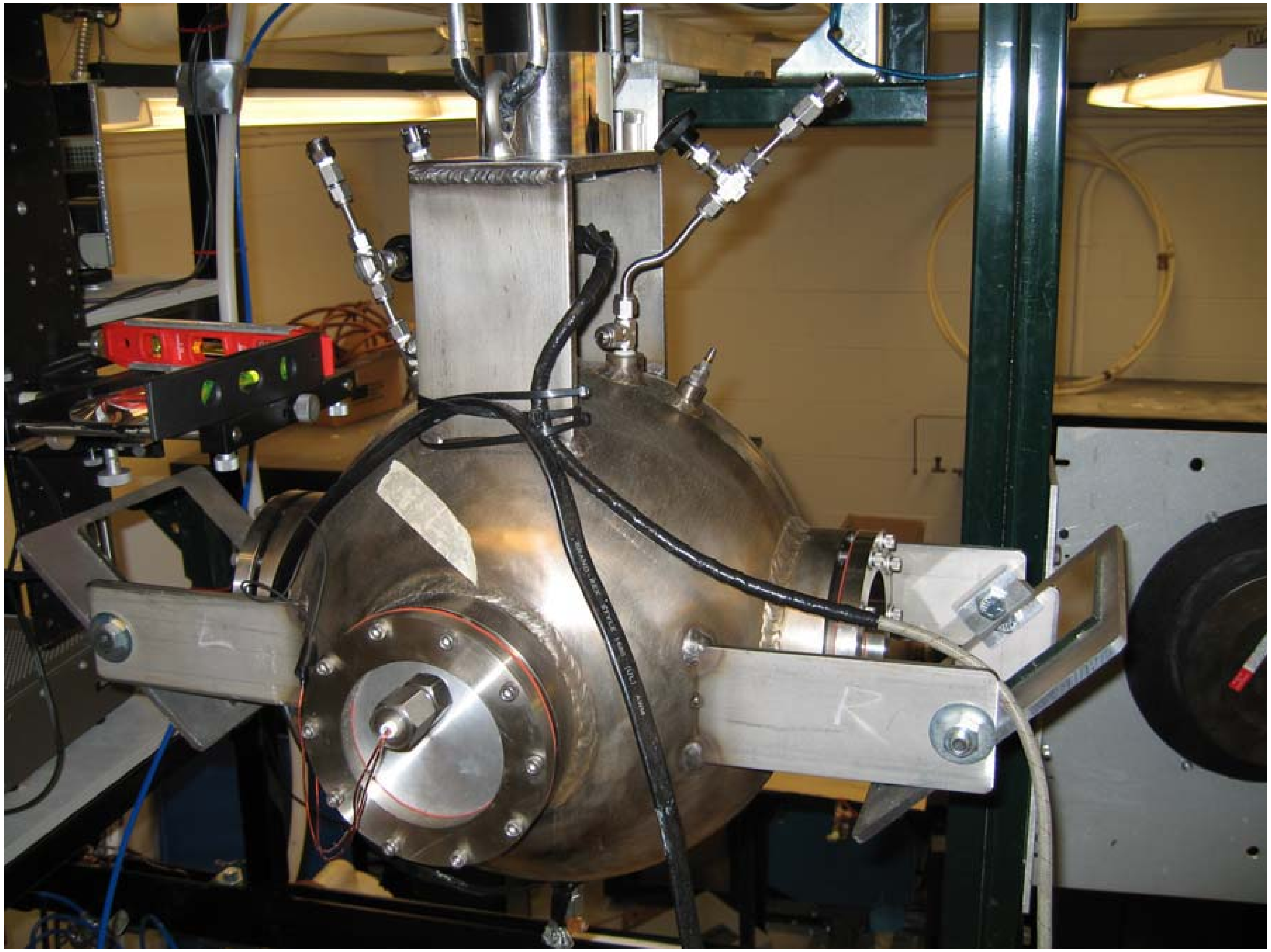


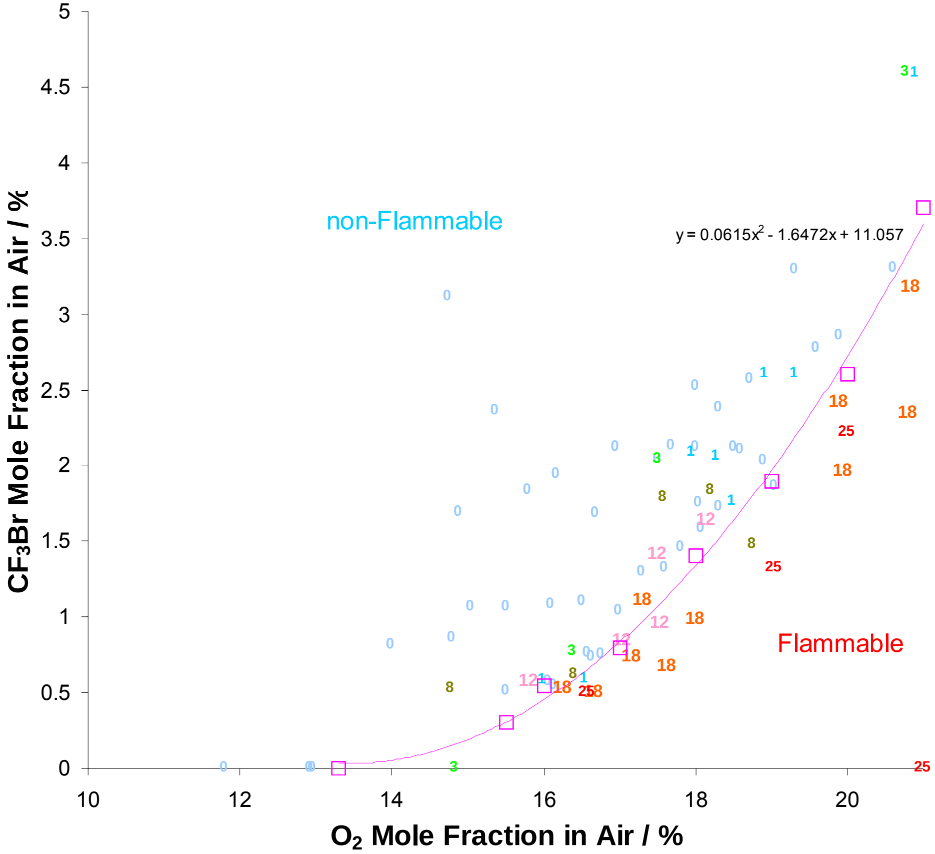
*Photo Courtesy of Prof. Li, Purdue

Questions ?

Extra Material

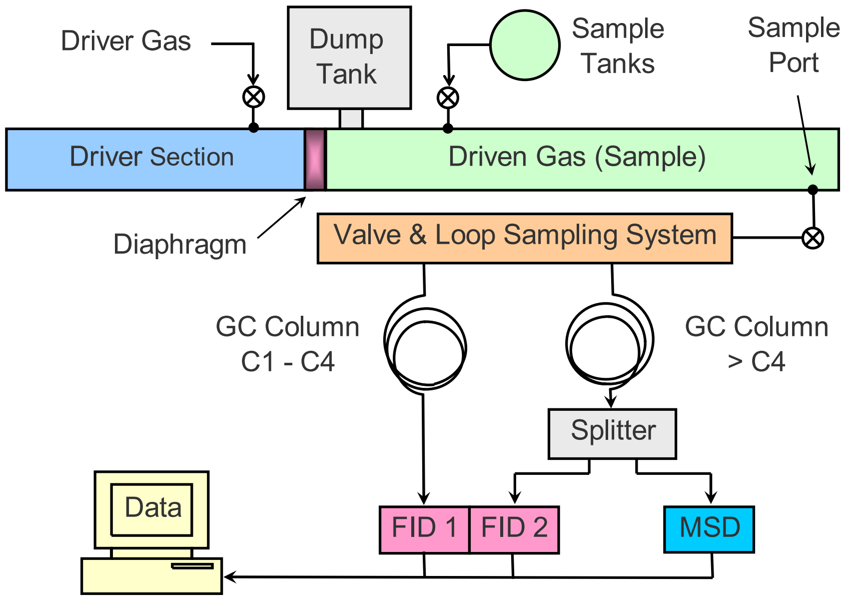
Perfectly-Stirred Reactor (PSR) Calculations

1301 with N_2



Kinetic Mechanism Development : Measurements of 2-BTP Decomposition

Single Pulse Shock Tube



Characteristics:

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

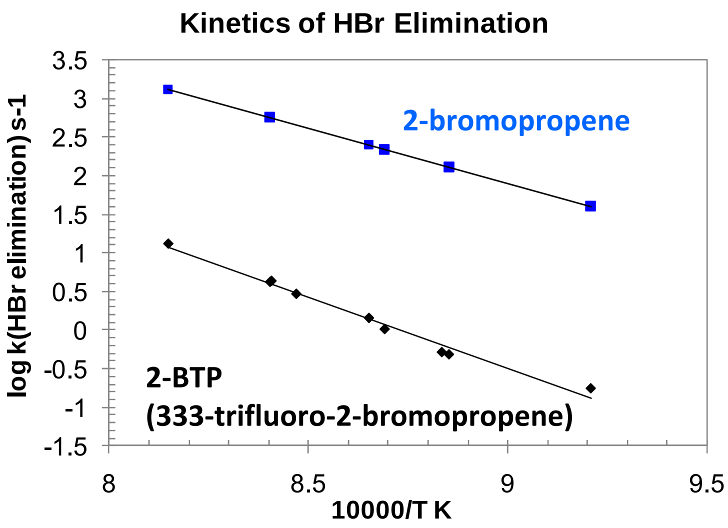
Advantages of Shock Tube for Gas Kinetic Studies:

- *Essentially a pulse heater, τ = (500 ± 50) μs*
- *No surface induced chemistry (diffusion slow compared with τ)*
- *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):

H + 2-BTP $\rightarrow$ ***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.