

Analysis of Suppressant-Enhanced Overpressure in the FAA Aerosol Can Simulator

INTERNATIONAL AIRCRAFT SYSTEMS FIRE PROTECTION WORKING GROUP MEETING

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Atlantic City, New Jersey, USA

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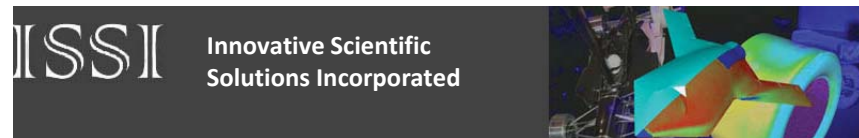
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Building and Fire Research Laboratory**



Acknowledgements

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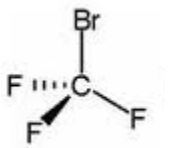
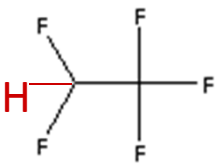
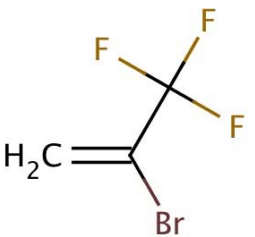
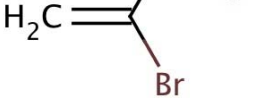
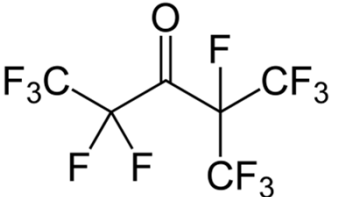
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The work was supported by The Boeing Company.

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

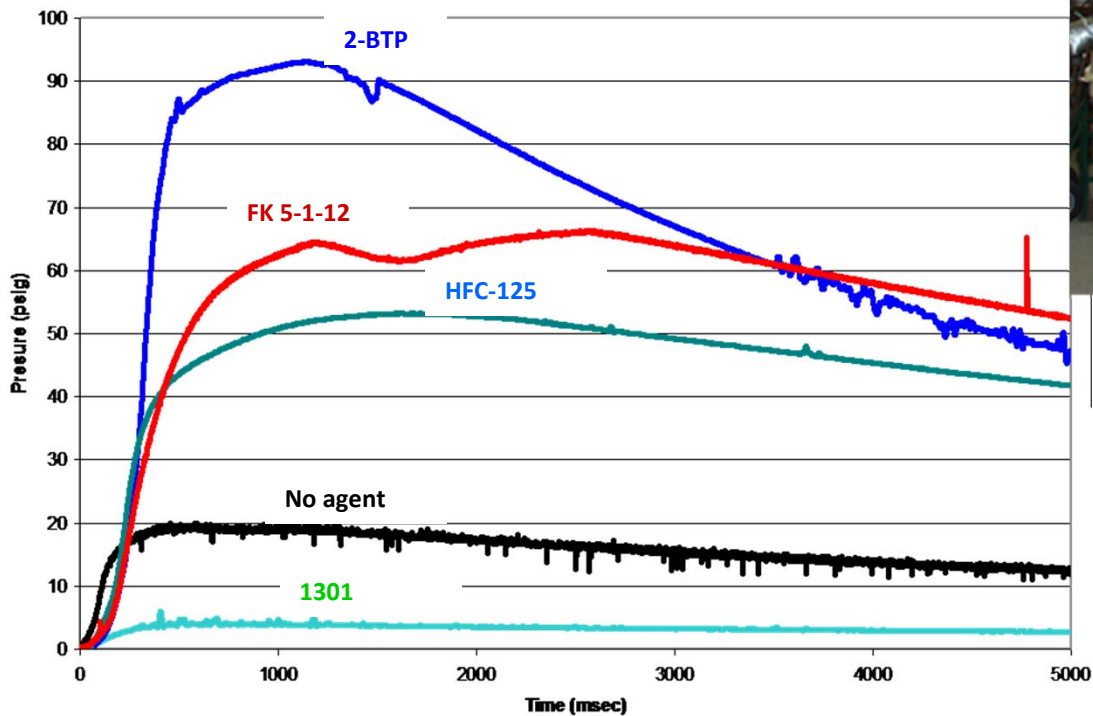
1. Halon 1301 (CF₃Br) => high ODP, high GWP.

| | Compound | Atmospheric Lifetime (yrs) | ODP | GWP ₁₀₀ |
|-------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------|----------------------------|-----|--------------------|
|  | Halon 1301 (CF ₃ Br) | 65 | 12 | 6,900 |
|  | HFC-125 (CF ₃ CF ₂ H) | 29 | 0 | 3,400 |
|  | 2-BTP (CH ₂ CBrCF ₃) | 0.008 | 0 | N/A |
|  | FK-5-1-12 (CF ₃ CF ₂ C(O)CF(CF ₃) ₂) | 0.014 | 0 | 1 |
|  | | | | |

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?



FAA Aerosol Can Test Chamber

Other Applications

1. Flammable refrigerants

a.) new, low-ODP, low-GWP, working fluids are more flammable than the fire suppressants—which themselves burn under some conditions,

b.) refrigerants may be mixed with more flammable materials (natural gas, hydrocarbons, oils, etc.).

2. Clean agent suppression of electrical fires.

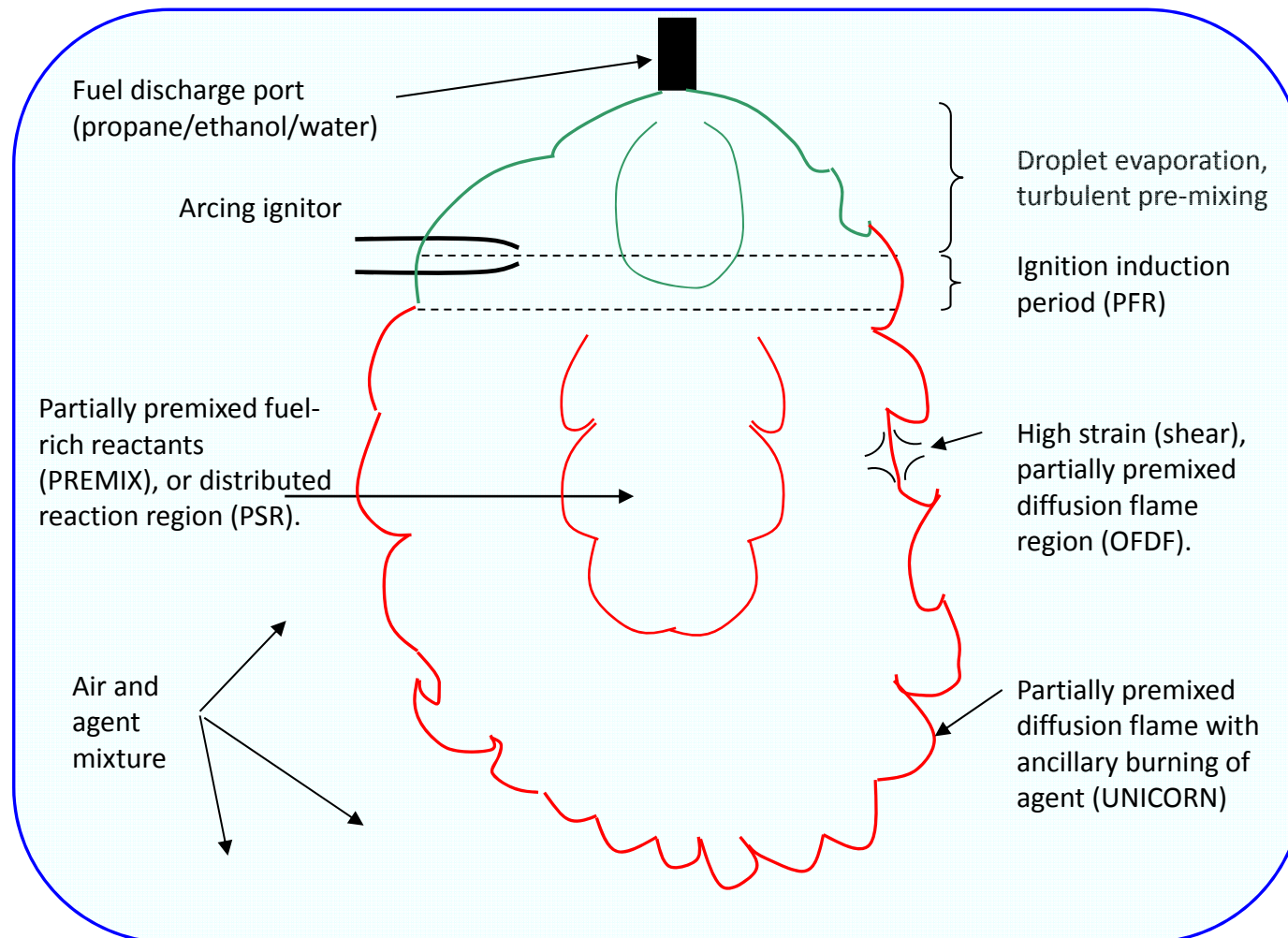
a.) added energy from an electrical source may put the fire suppressants into a regime in which they are flammable.

Approach

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

1. simplify, use flame descriptions which will be accurate in some parts of the test

2. η , X_{inh}



Progress

1. Review of previous work
2. Thermodynamic Equilibrium Calculations (HFC-125, CF_3Br , 2-BTP)
3. Perfectly-Stirred Reactor (PSR) Calculations (HFC-125, CF_3Br)
4. Novec Mechanism and Simulations
5. 2-BTP Mechanism (end)
6. Premixed Flame Calculations for HFC-125 (PREMIX)
7. Homogeneous Auto-Ignition (PFR) Calculations
8. Combustion Bomb Experiments
9. Comparison of Flammability limits and Bomb Results

- Last presentation
- This presentation

Background:

Previous findings

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

| <u>Researchers</u> | <u>Fuel</u> | <u>Agents</u> | <u>Experiment</u> | <u>Phenomena</u> | <u>Explanation</u> | | |
|---------------------------|-------------------|-------------------------------|--------------------------------|----------------------------------------|-------------------------------|--|--|
| Grosshandler and Gmurczyk | Propane, ethylene | CF3I, CF3Br, HFCs | Detonation - Deflagration Tube | Higher Ma, flame speed, pressure ratio | None | | |
| Shebeko et al. | methane, hydrogen | C2HF5, C4F10 | Deflagration | Higher 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 fire | 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 | | |

Flames go out when: $\tau_{\text{chem}} > \tau_{\text{flow}}$

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

Perfectly-Stirred Reactor (PSR) Calculations

Diffusion Flame Calculations (Counterflow)

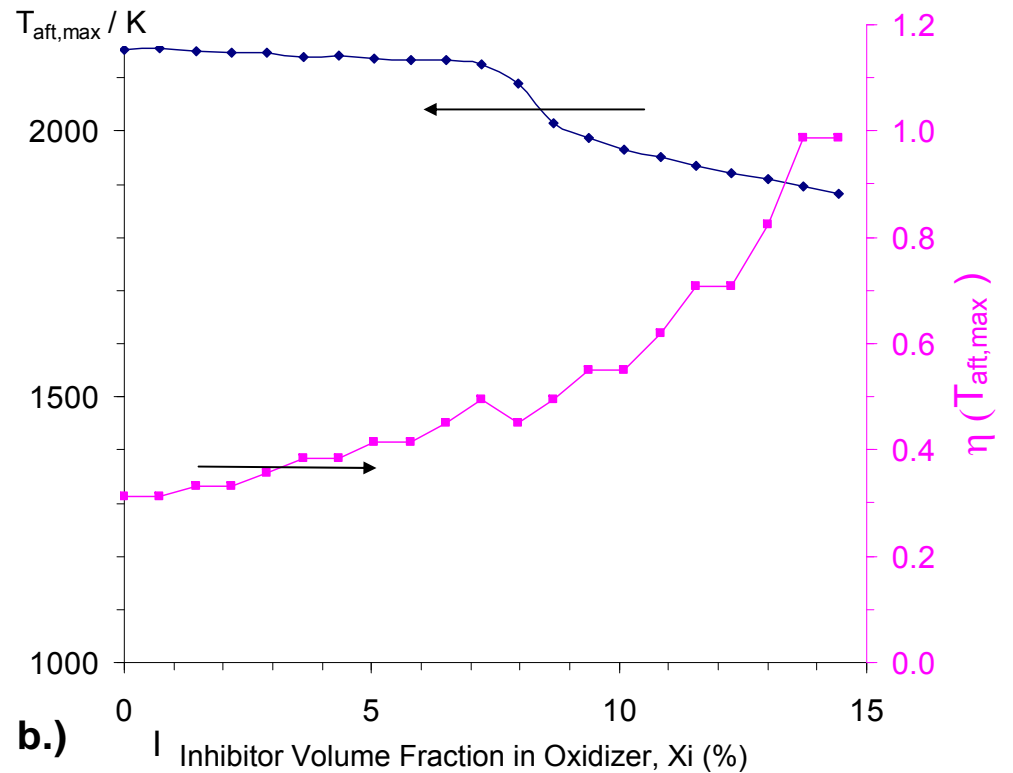
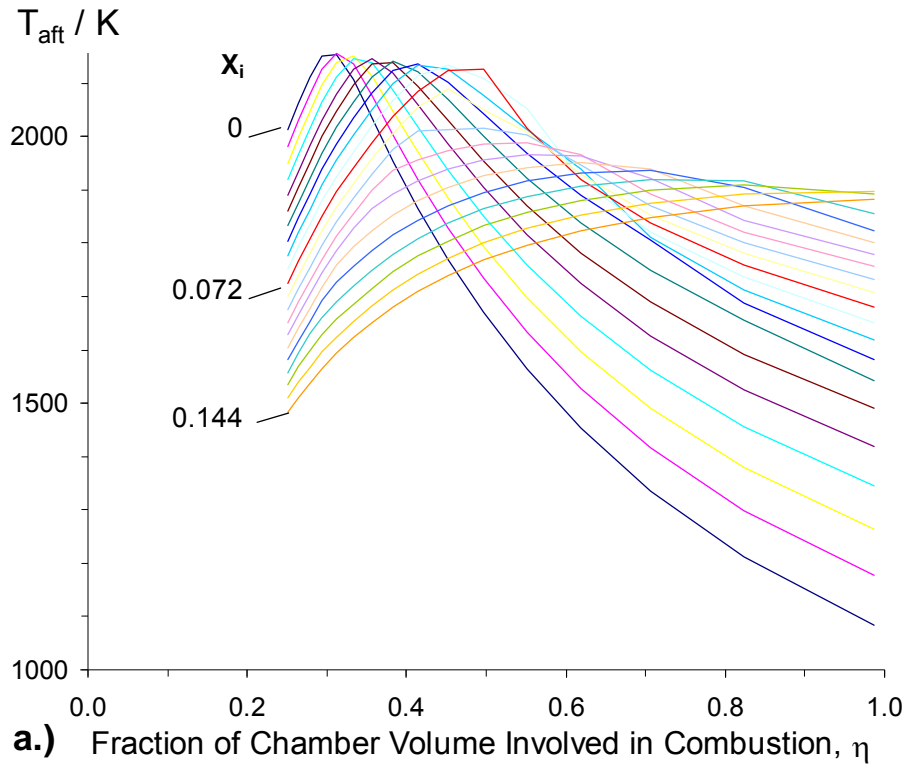
Premixed Flame Calculations

=> Examine behavior of R-125, 2-BTP, Novec 1230 and CF_3Br

⇒ Why is it surprising that R-125 enhanced combustion in the ACT at 11.3 % ?

Experimental R-125 Extinction Results:

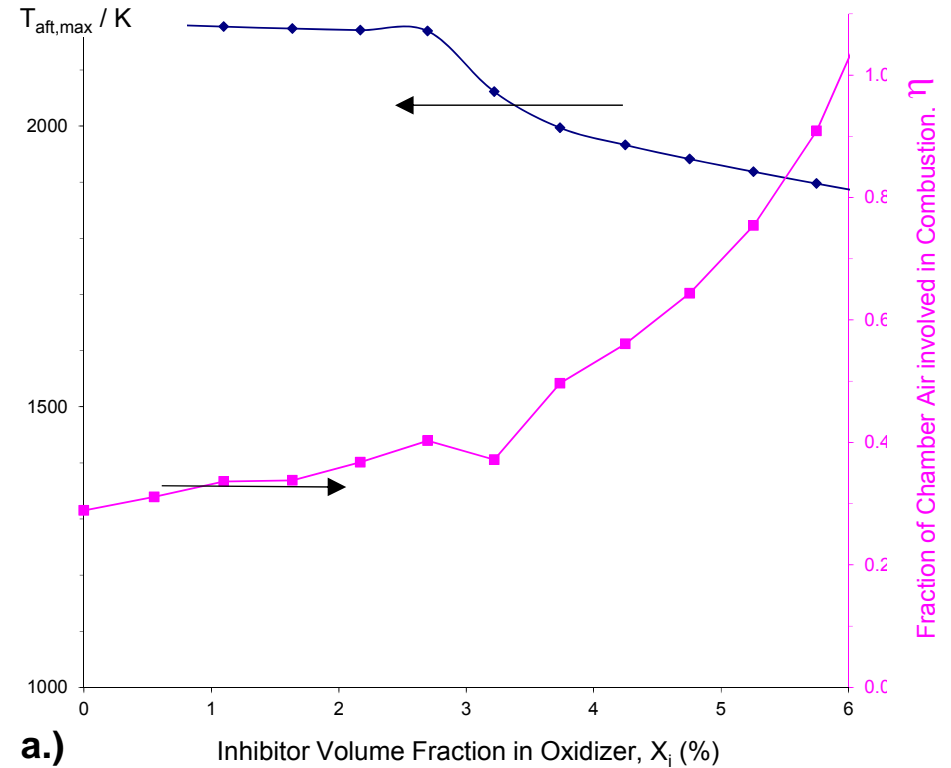
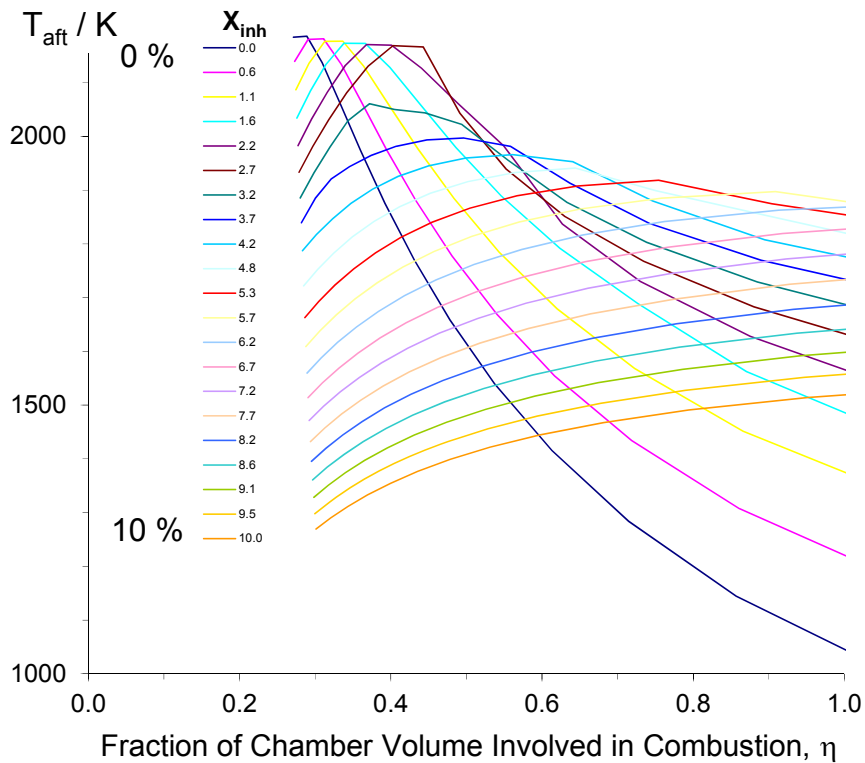
1. Methane – air cup burner: ~10.4%
2. 0 strain, heptane – air counterflow diffusion flame: ~9%
3. 0 strain, propane – air counterflow diffusion flame: ~ 9.5%



- 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.

Novec 1230: Adiabatic Flame Temperature (T_{aft})

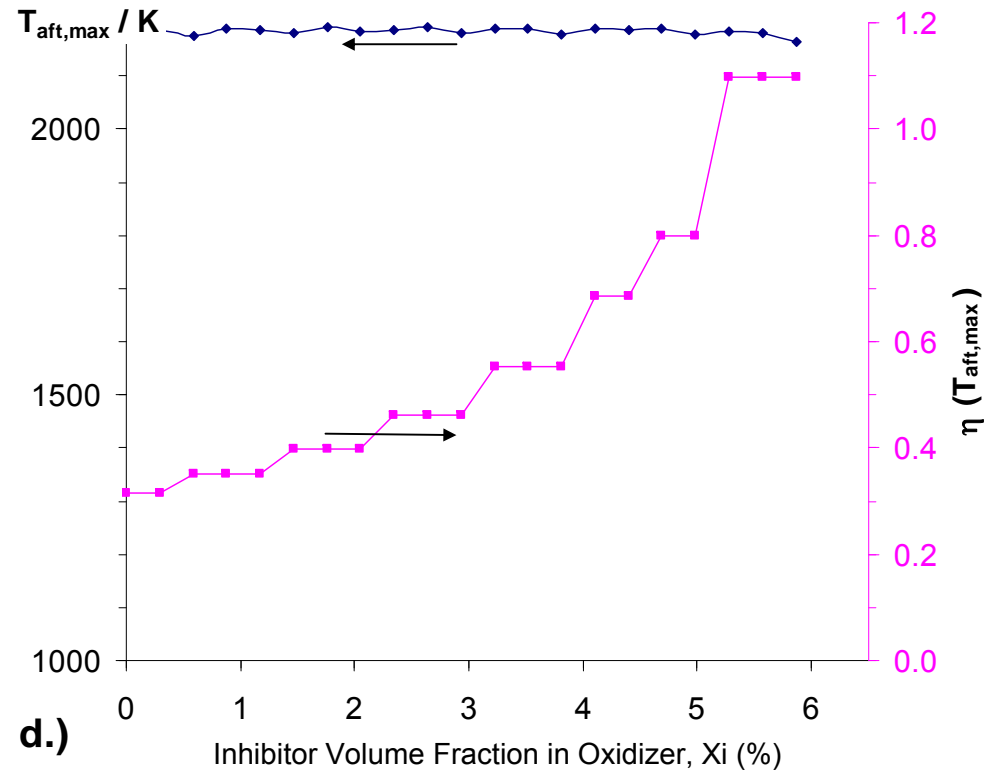
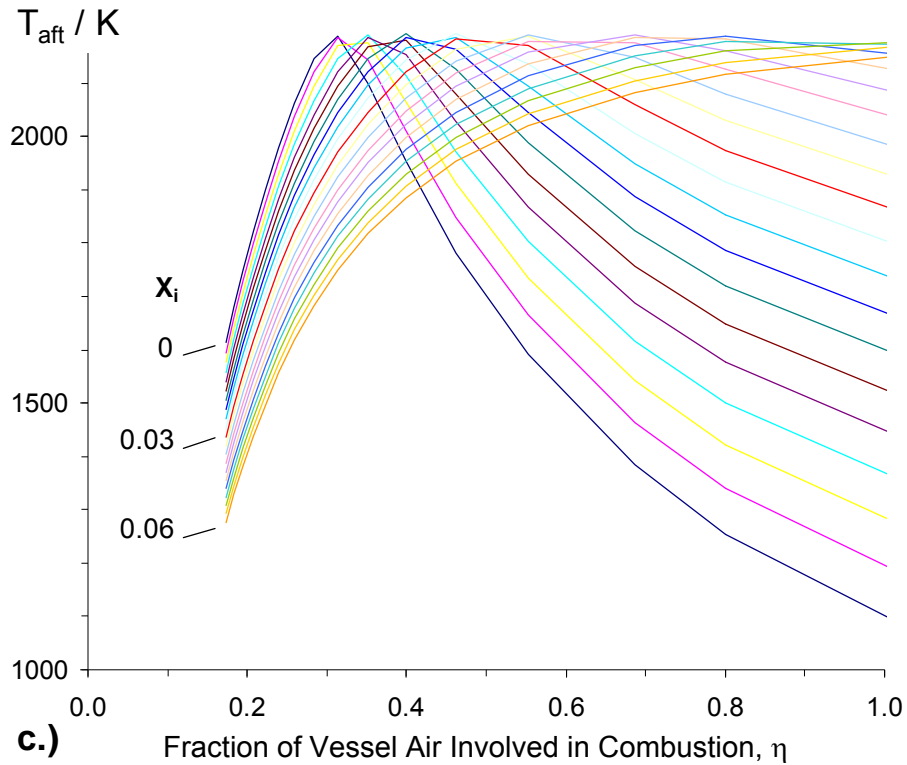
Thermodynamic Equilibrium Calculations



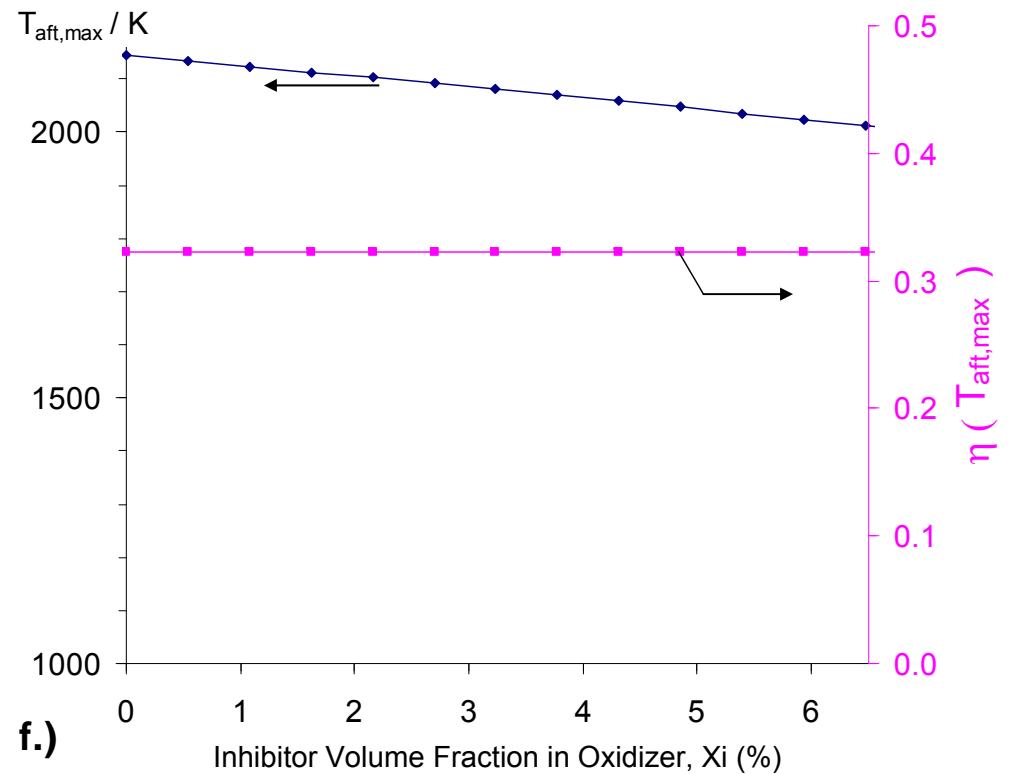
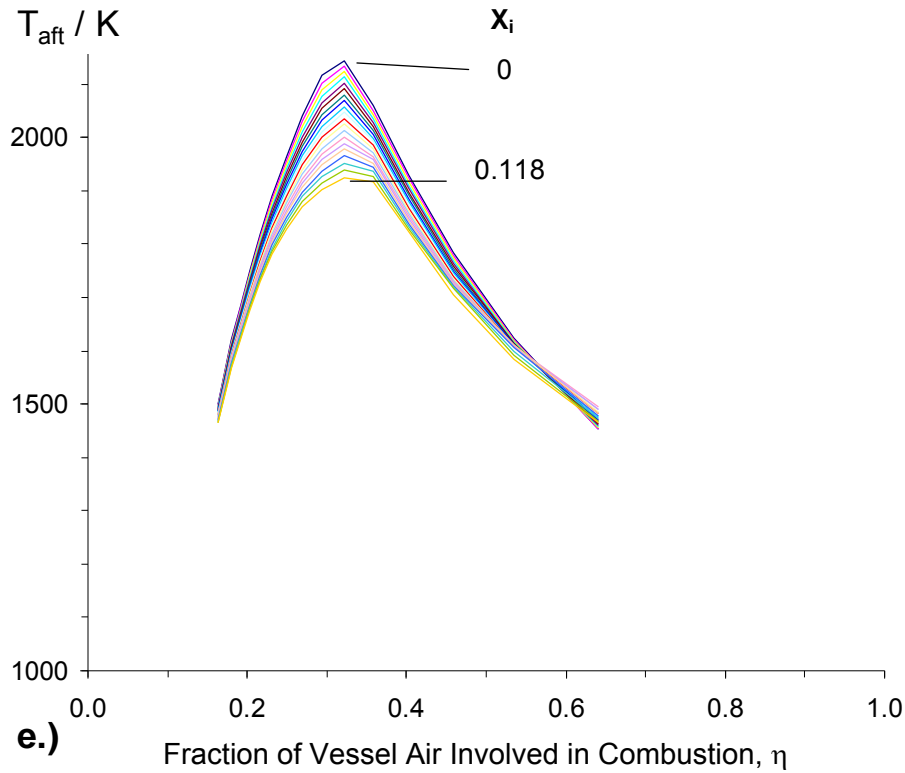
- T_{aft} is high for all η .
- Change in behavior at $[X]/[H]=1$ (about 2.7 % Novec 1230, purple curve above)
- With large amounts of agent, a wide range of η gives nearly equivalent T_{aft} .
- As agent is added, more and more chamber volume is necessary to achieve stoichiometric combustion.

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

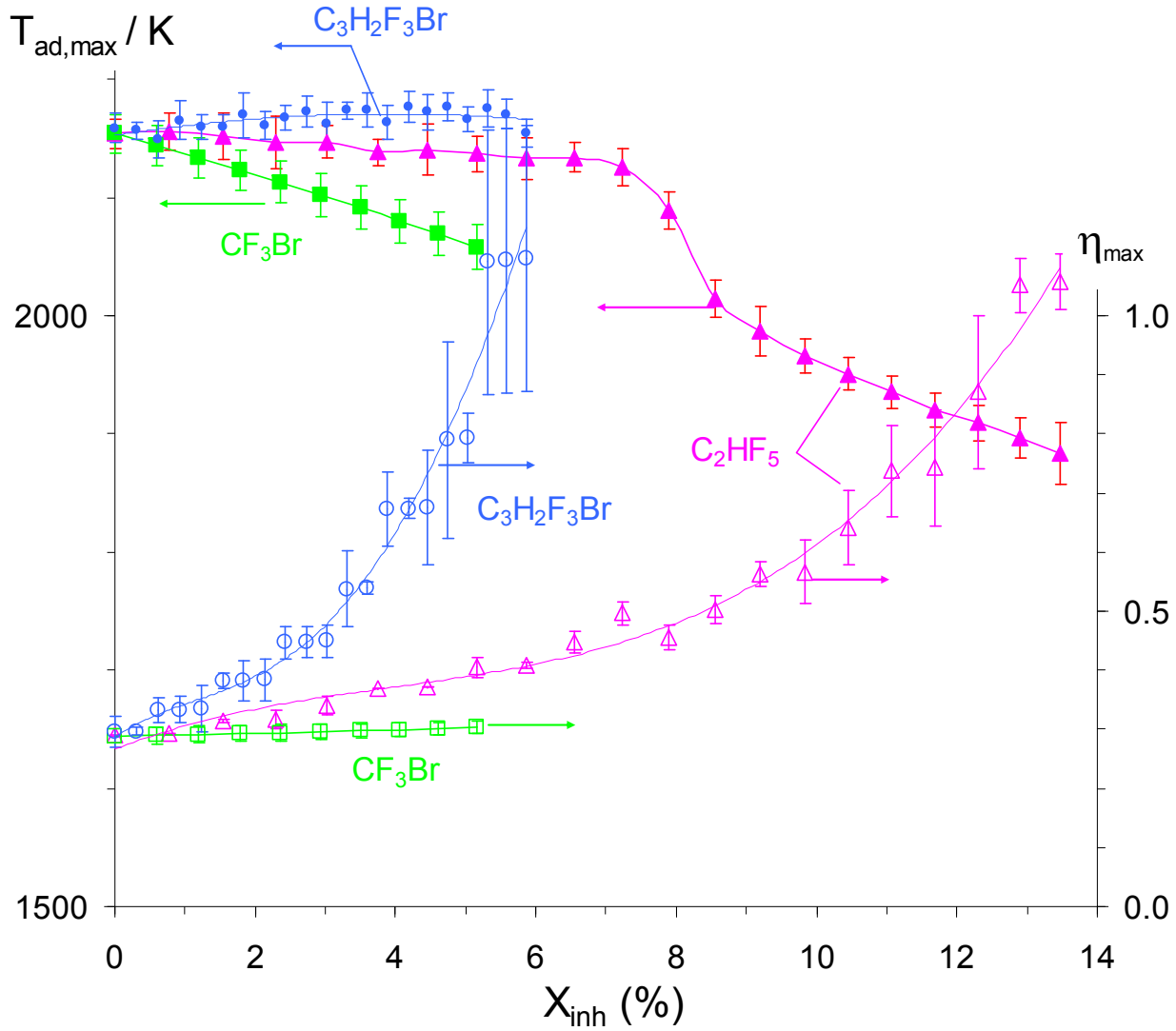
Thermodynamic Equilibrium Calculations



- 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 might extinguish ($X_i=6\%$), all the chamber volume is involved in combustion (i.e., $\eta=1$).



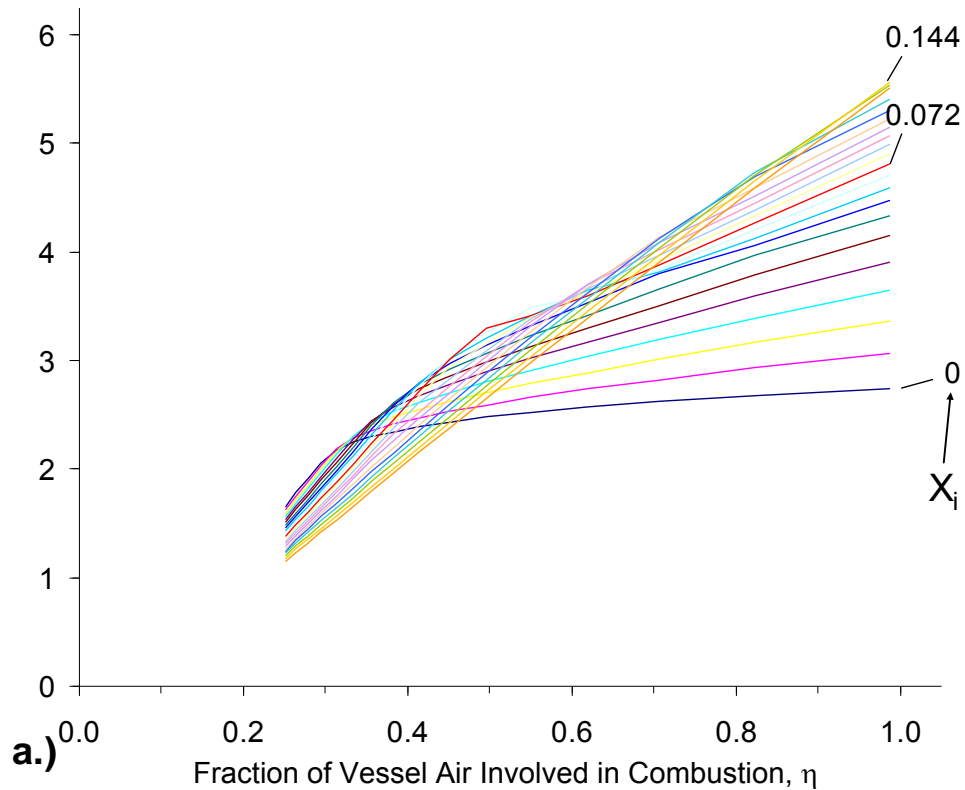
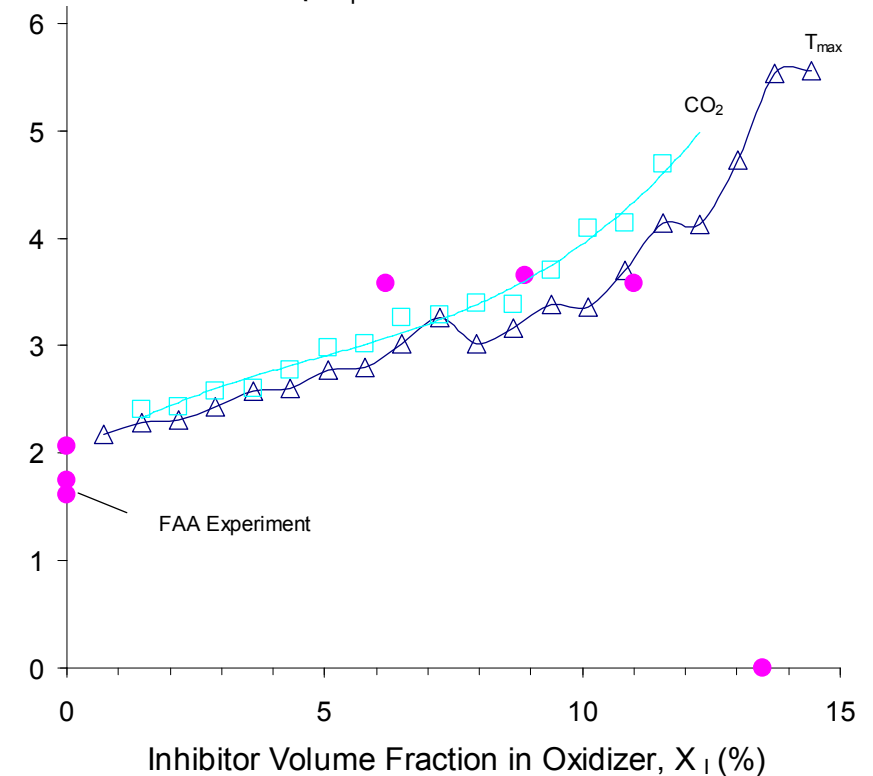
- T_{aft} is high for all η ., but **decreases** somewhat as agent is added.
- most of the plot is below $[X]/[H]=1$ (about 11 % CF_3Br), so can't see change at $[X]/[H]=1$.
- **The amount of chamber volume for peak T_{aft} does not change with X_i .**
- Why? => $CF_3Br + 2H_2O = 3HF + HBr + CO_2$,
- 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

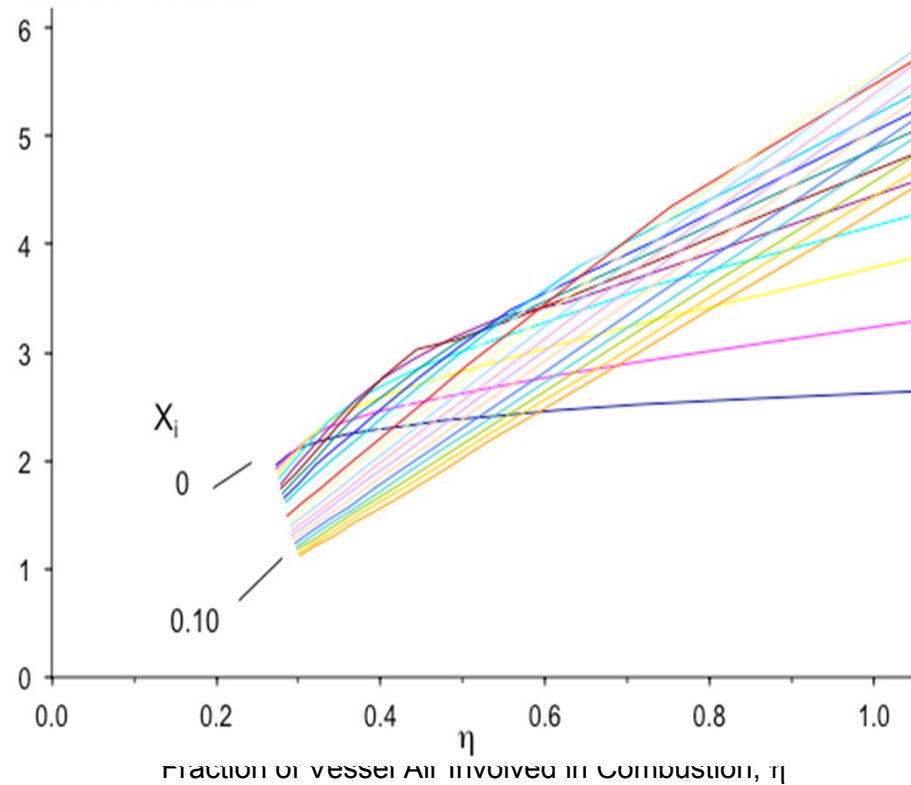
What do they tell us about the maximum pressure rise?

Pressure Rise / bar

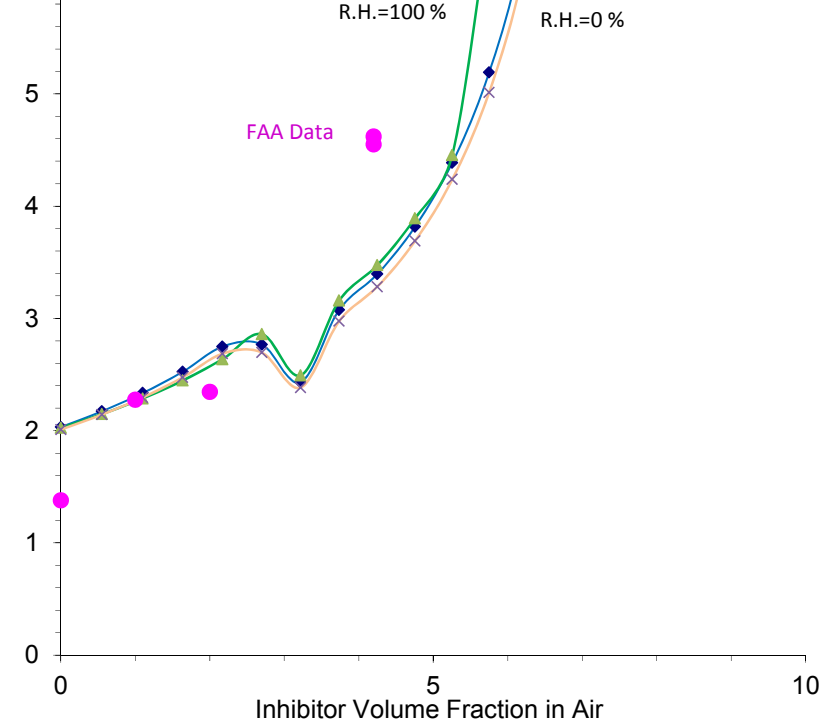
Pressure Rise at $\eta \{y_{\text{peak}}\}$ / bar

- 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?

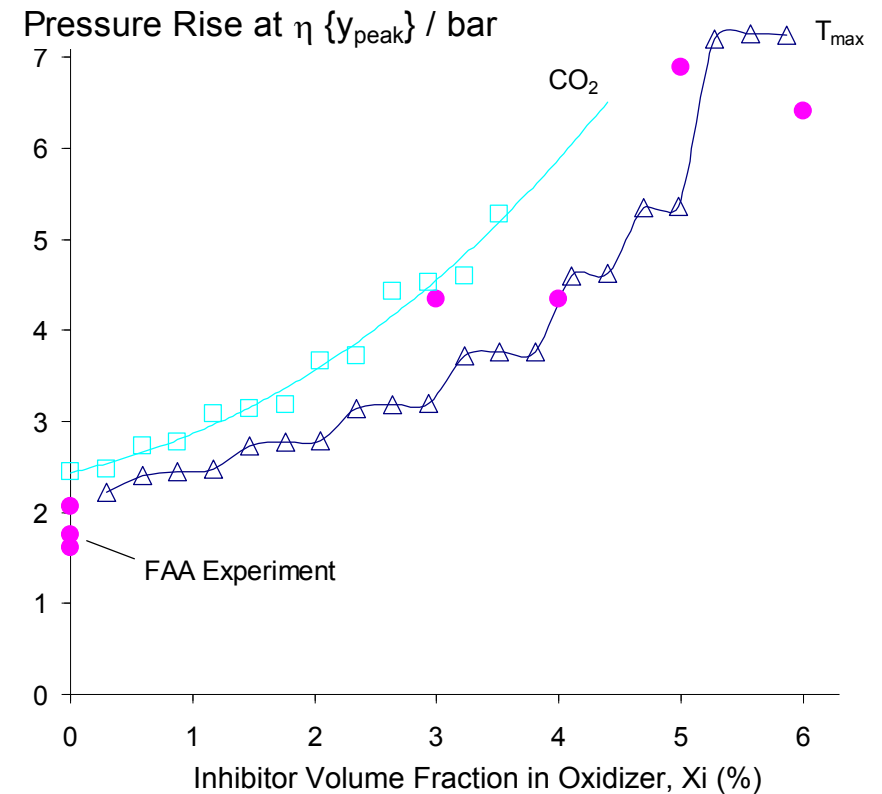
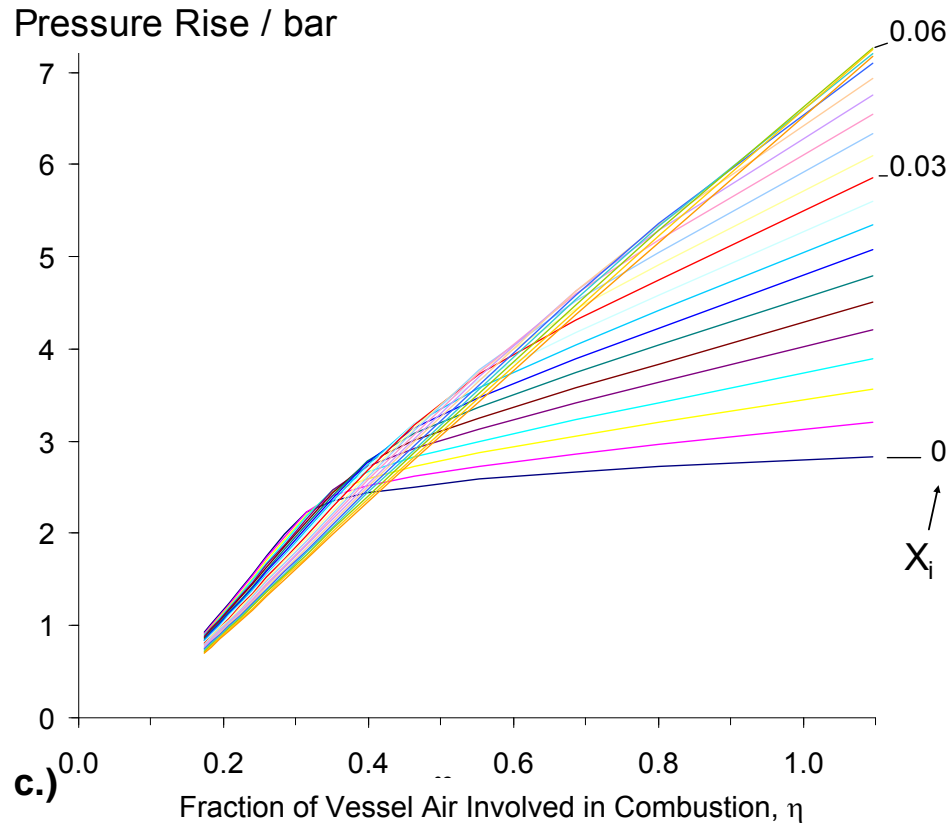
Pressure Rise / bar



P at T_{max} / bar

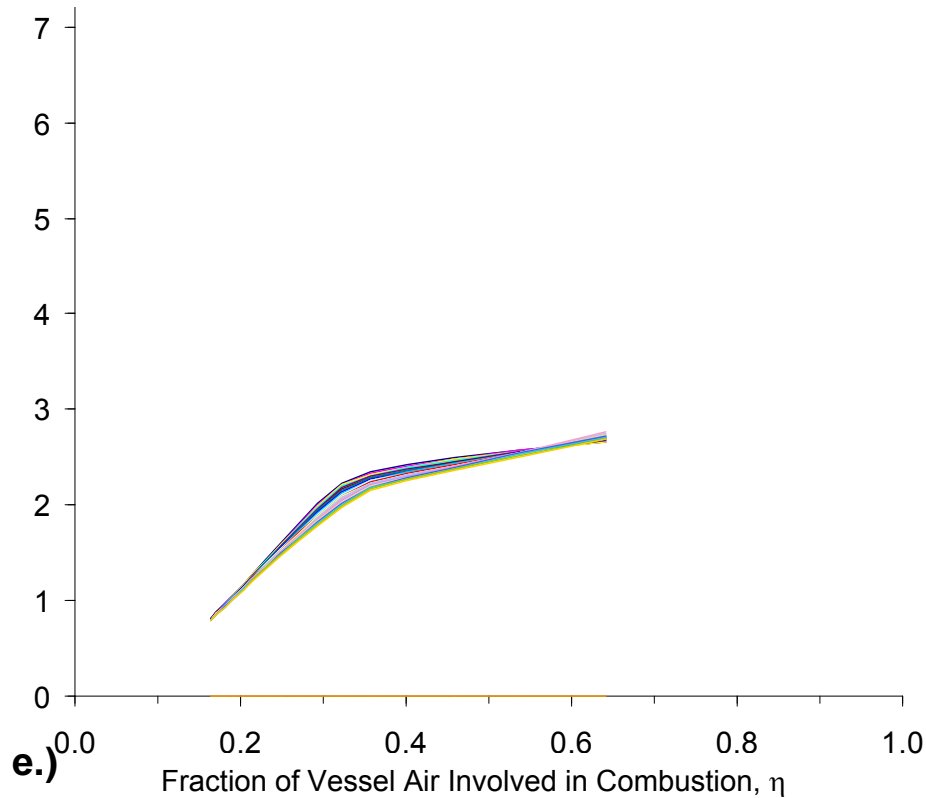


- The higher η , the greater ΔP (more reactants, more heat release, more expansion of hot products—since the oxidizer also includes a “fuel” species).
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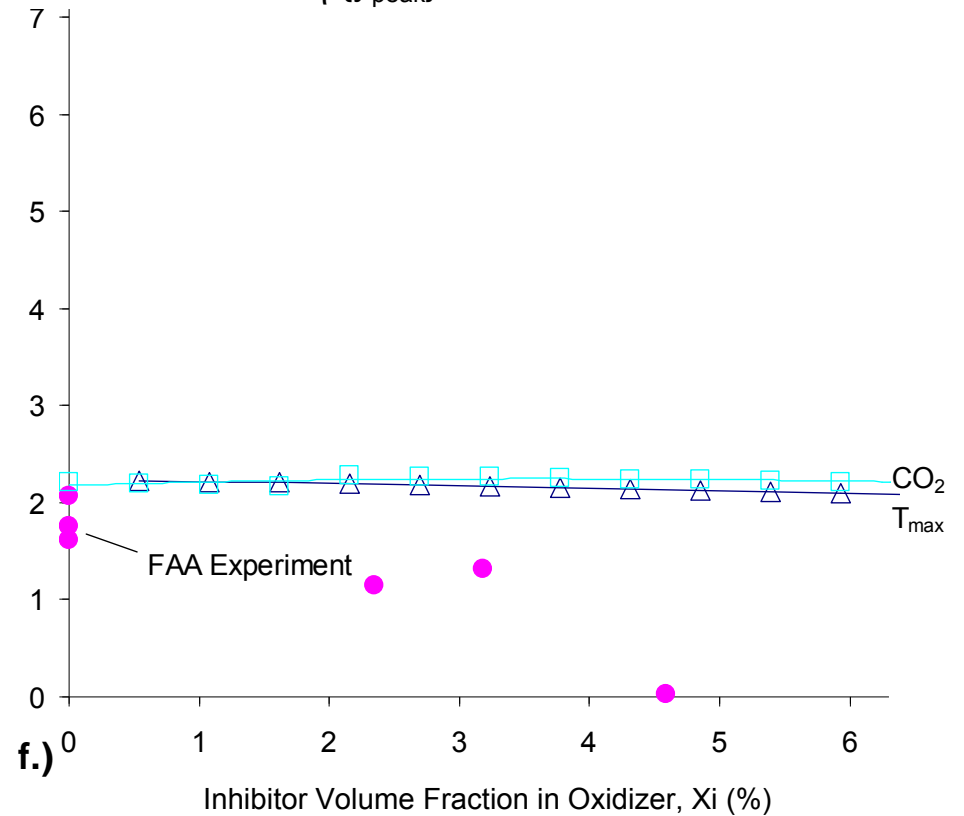


- Same basic behavior as R-125, but greater ΔP .
- The actual fraction of chamber volume (oxidizer) which can react has a large influence on ΔP .
- Equilibrium thermodynamics predicts the final pressure quite well.
- Why does the agent not reduce the extent of reaction?

Pressure Rise / bar



Pressure Rise at $\eta \{y_{peak}\}$ / bar



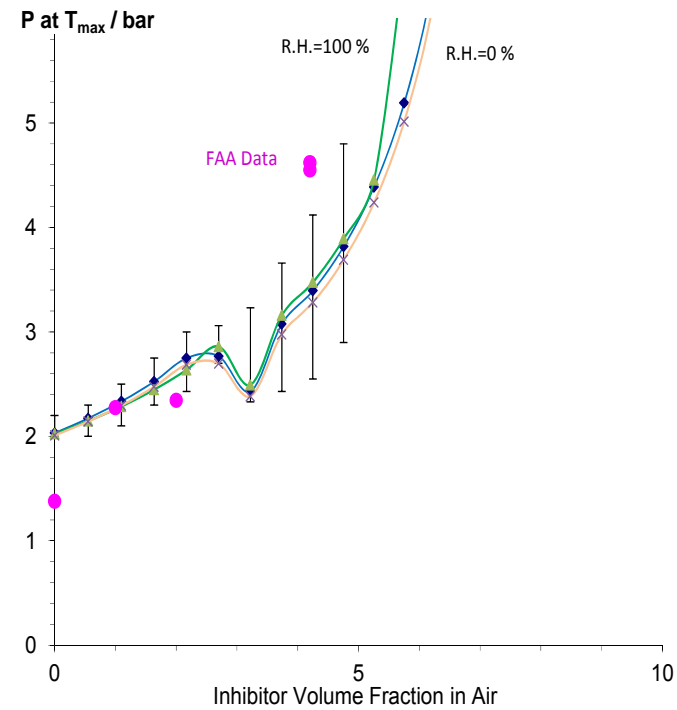
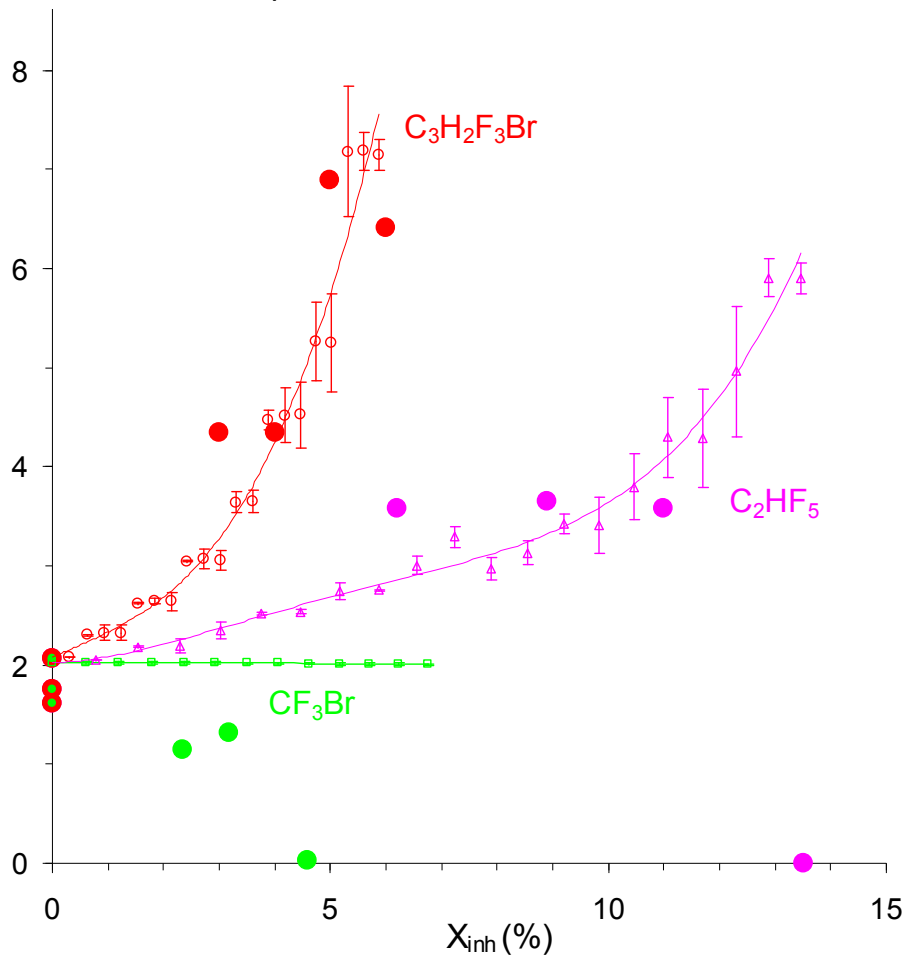
- Higher η has very little effect on ΔP .

- At η of peak T_{aft} , or CO_2 , the ΔP is constant! \Rightarrow 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)?

\Rightarrow MUST LOOK AT THE KINETICS TO FIND OUT!

Pressure Rise at η_{\max} / bar



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

- But why don't all the agents lower the reaction rate?

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

Sub MechanismC₄ hydrocarbon mechanism from WangSpecies

111

Reactions

784

Ethanol mechanism of Dryer

5

36

HFC mechanism from NIST

51

600

CF₃Br mechanism of Babushok (NIST)

10

122

177

1494

Novec 1230 mechanism (Babushok)

3

14

| Reaction |
|------------------------------------------|
| C2F5COC3F7 => C3F7+C2F5CO |
| C2F5CO = CF3-CF2+CO |
| C2F5COC3F7 + H = C2F5CHO + C3F7 |
| C2F5CHO + H = C2F5CO + H2 |
| C2F5CHO = CF3-CF2 + HCO |
| C2F5COC3F7+OH = C2F5CO+C3F7OH |
| C2F5COC3F7+O = C2F5CO+C3F7O |
| CF3+C2F5CHO = CHF3+C2F5CO |
| CH3+C2F5CHO = CH4+C2F5CO |
| CF3COF+CF3=CF3CO+CF ₄ |
| CF3COF+CF3-CF2=CF3CO+CF3-CF ₃ |
| CF3-CF3+CF3=CF4+CF3-CF ₂ |
| CF3CO+F=CF3+CF:O |
| CF3CO+F=CF4+CO |

2-BTP Mechanism Development

Jeff Manion, Don Burgess, Iftikhar A. Awan

Combustion and Kinetics Group
Chemical and Biochemical Reference Data Division
Material Measurement Laboratory
NIST

(to be discussed at the end)

2-BTP Simulant

- 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 ,

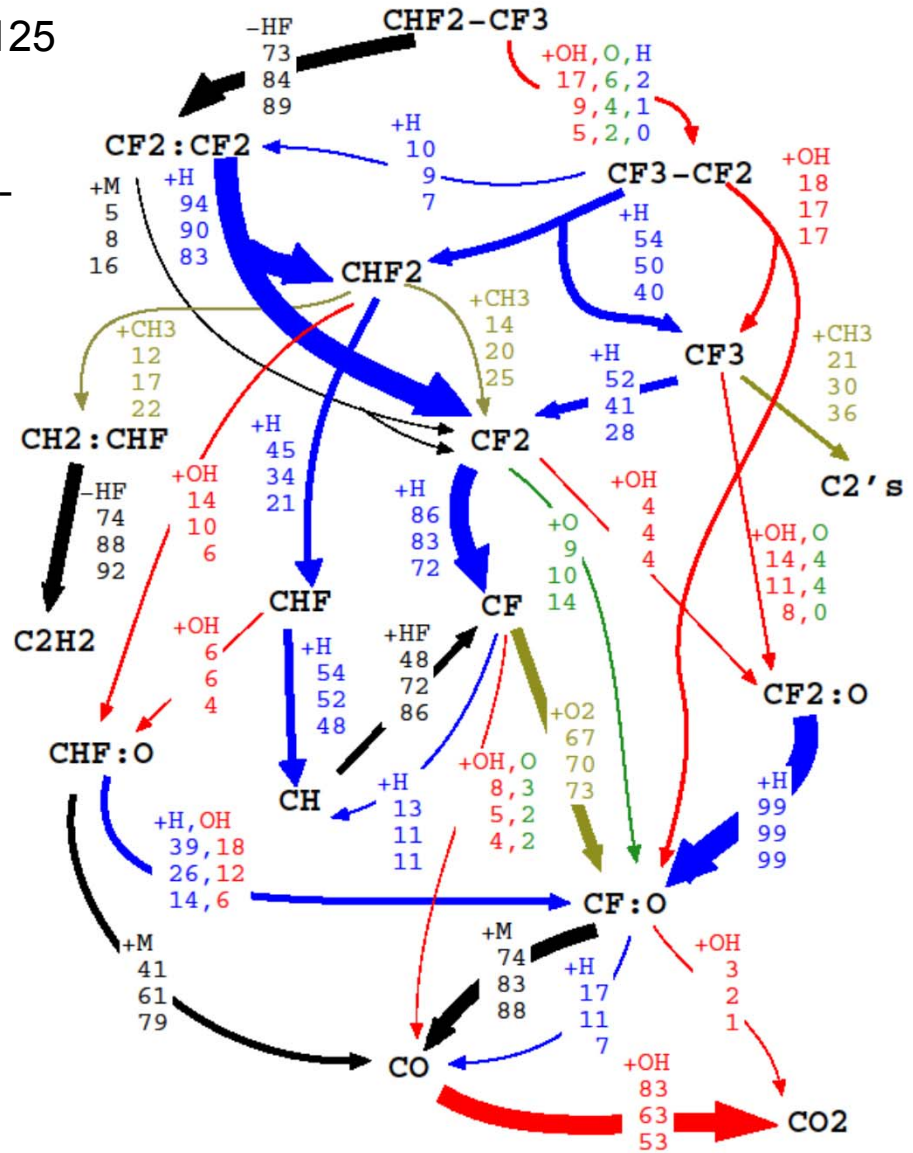
3 moles N_2

(gives the right T_{aft} , and has the right number of molecules).

Kinetic Mechanism Development

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

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



Background: Why PSR?

Perfectly-Stirred Reactor (PSR) Calculations

Overall reaction rate in a PSR has been correlated with

- flame speed [1],
- extinction of cup-burner flames [2].

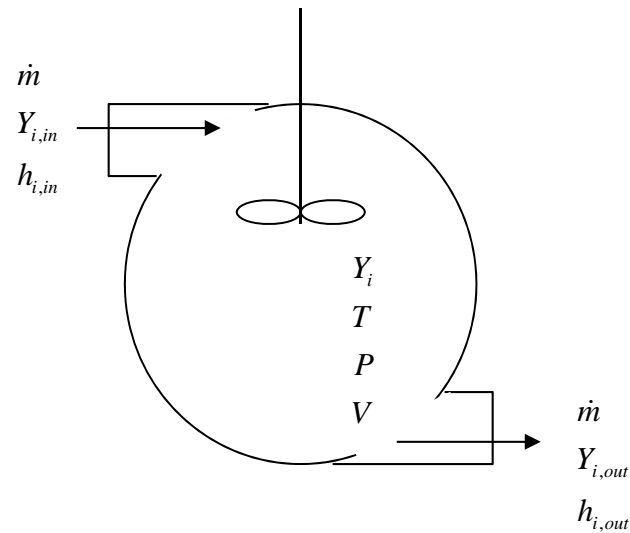
The Aerosol Can test is turbulent, 2-phase, partially premixed, so a PSR is a reasonable approximation.

[1] R.B.Barat, Chemical Engineering Science 56 (2001) 2761-2766.

[2] S.Liu, M.C.Soteriou, M.B.Colket, J.A.Senecal, Fire Safety Journal 43 (2008) 589-597.

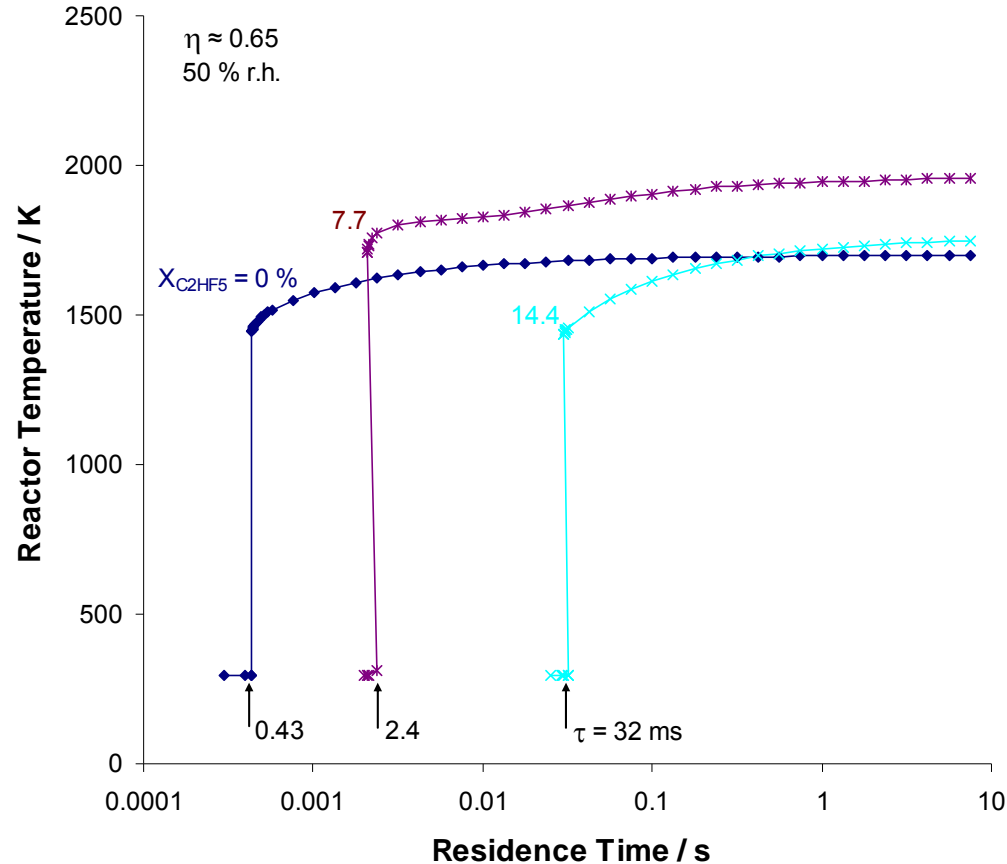
Perfectly-Stirred Reactor (PSR) Calculations

- Used to estimate the overall chemical reaction rate.
- Performed for R-125, Novec, 2-BTP simulant, and 1301.

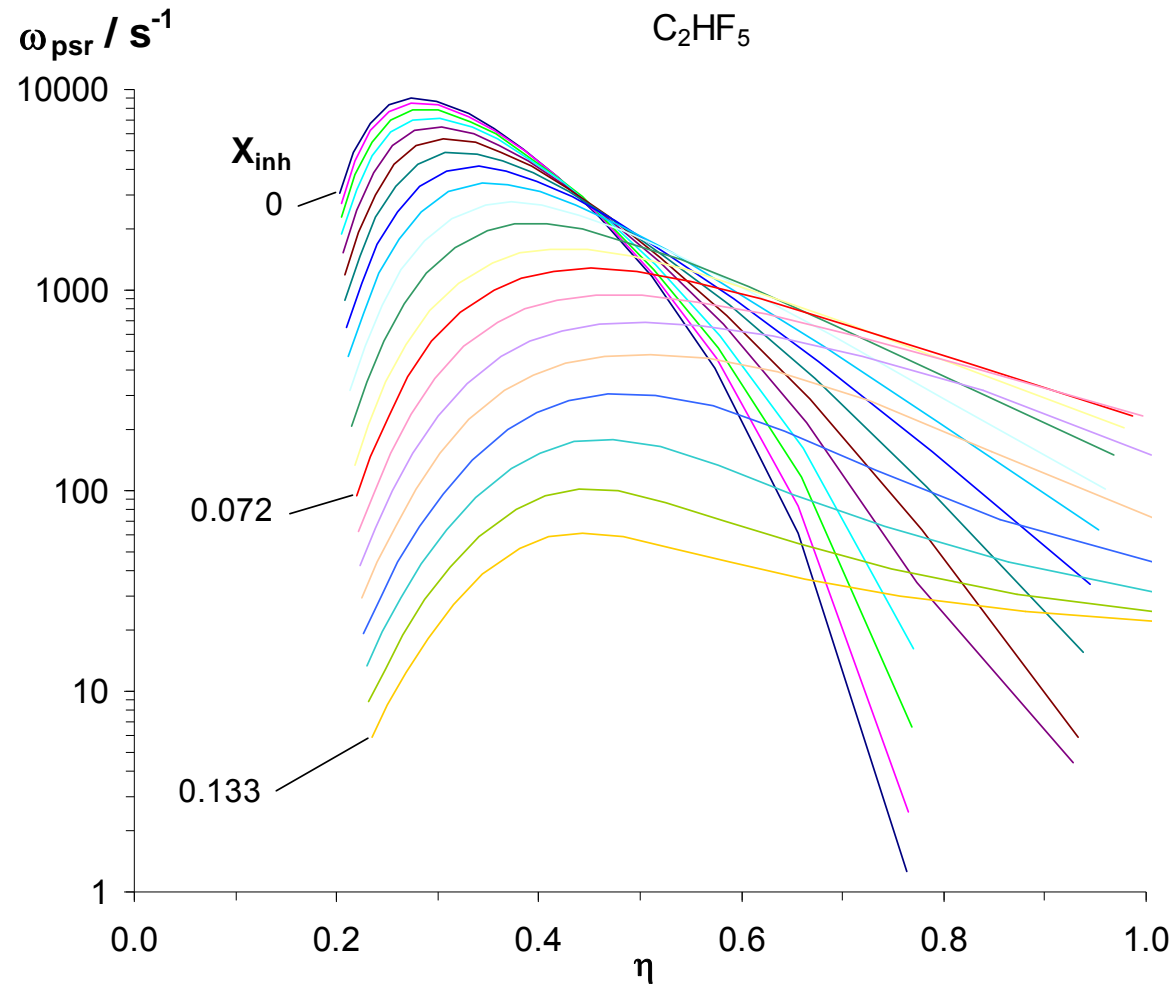


Assumptions:

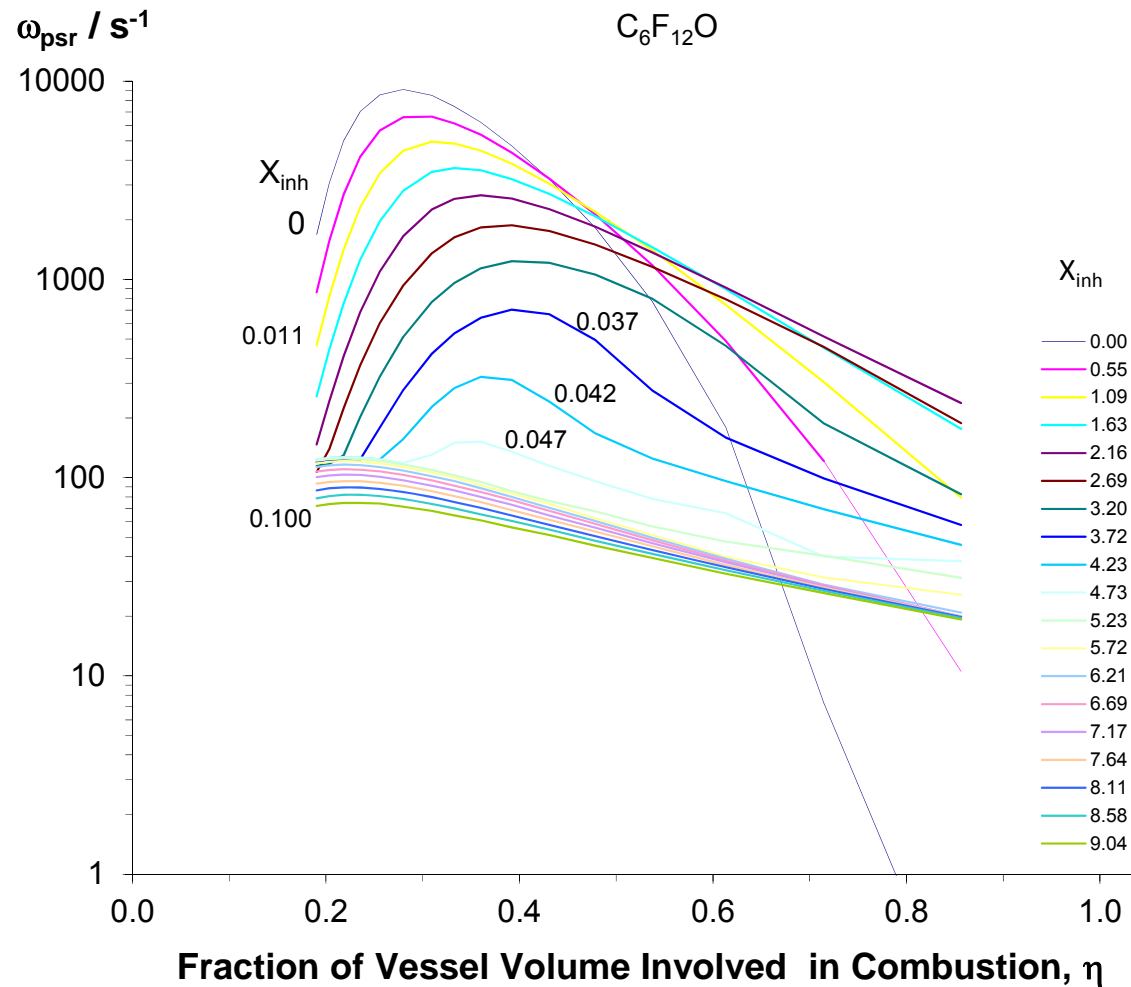
- specified premixed inlet conditions.
- adiabatic (no heat losses), no species reaction at the walls.
- perfectly stirred (outlet conditions are the same as the reactor conditions).
- steady-state operation.



1. We want a measure of τ_{chem}
2. At the blow-out condition, $\tau_{\text{chem}} = \tau_{\text{flow}}$
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 at blow-out).

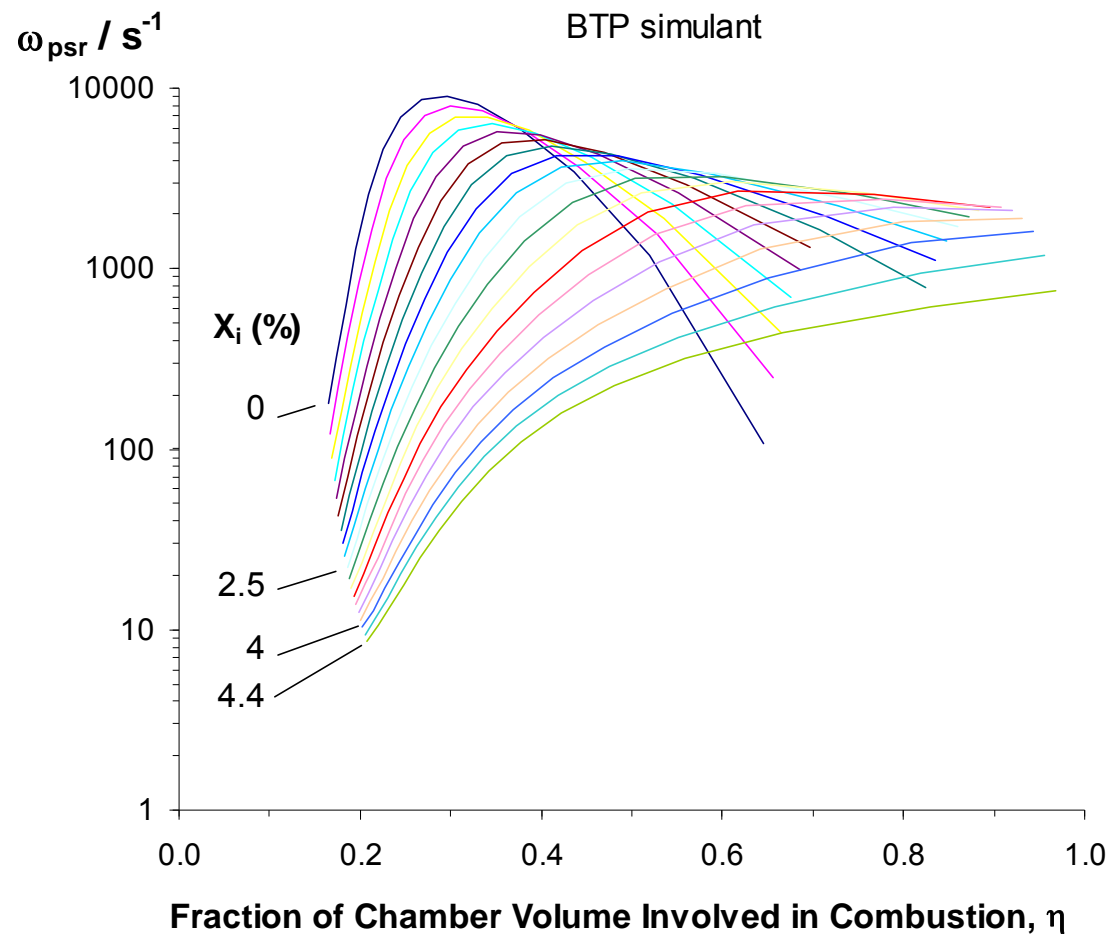


- Adding R-125 lowers ω_{chem} for rich mixtures (low η), but raises (then lowers) it for lean mixtures (high η).
- η has a big effect on overall chemical rate at low X_i , less effect at high X_i (follows temperature results).
- i.e., for higher X_i , these curves flatten (ω_{chem} is insensitive to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

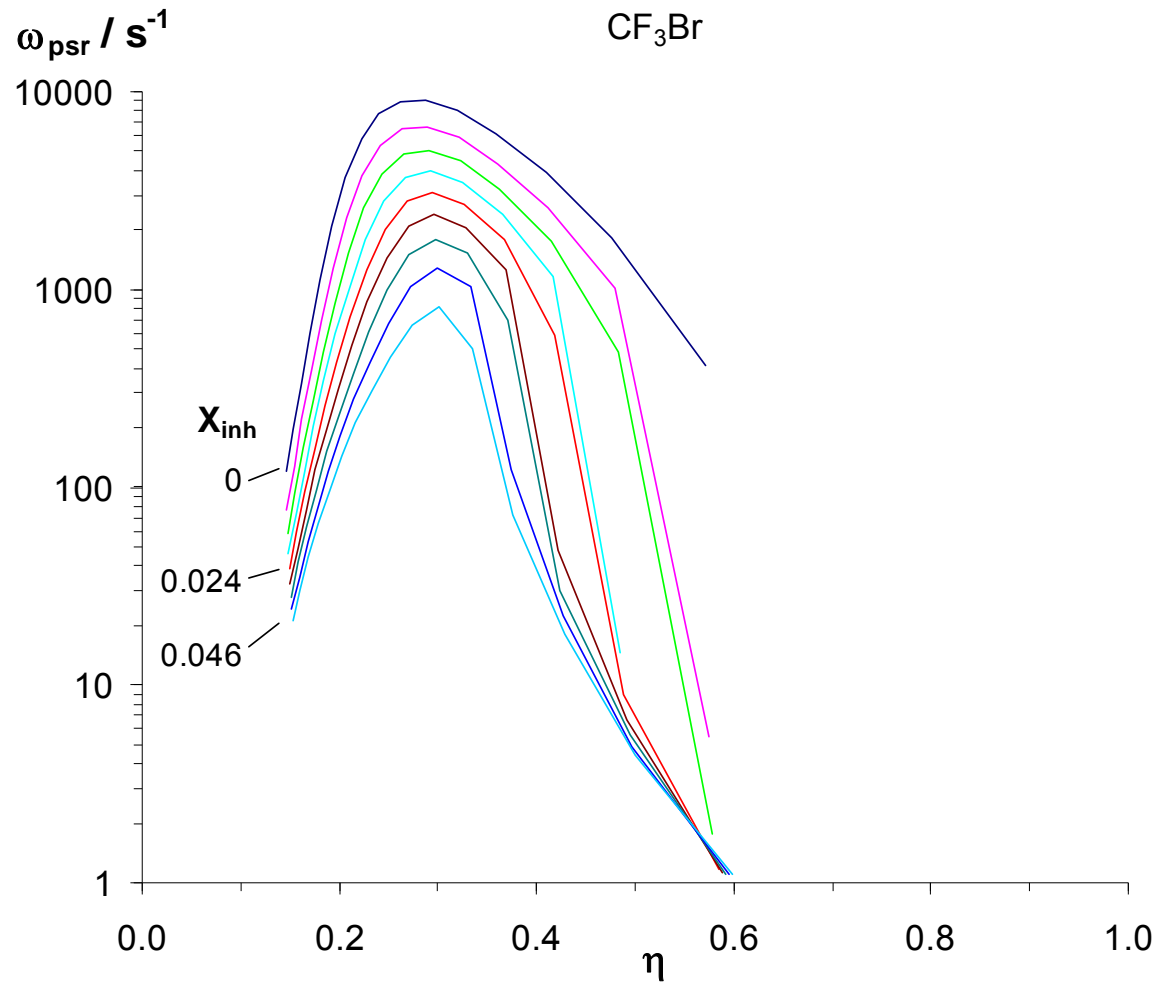


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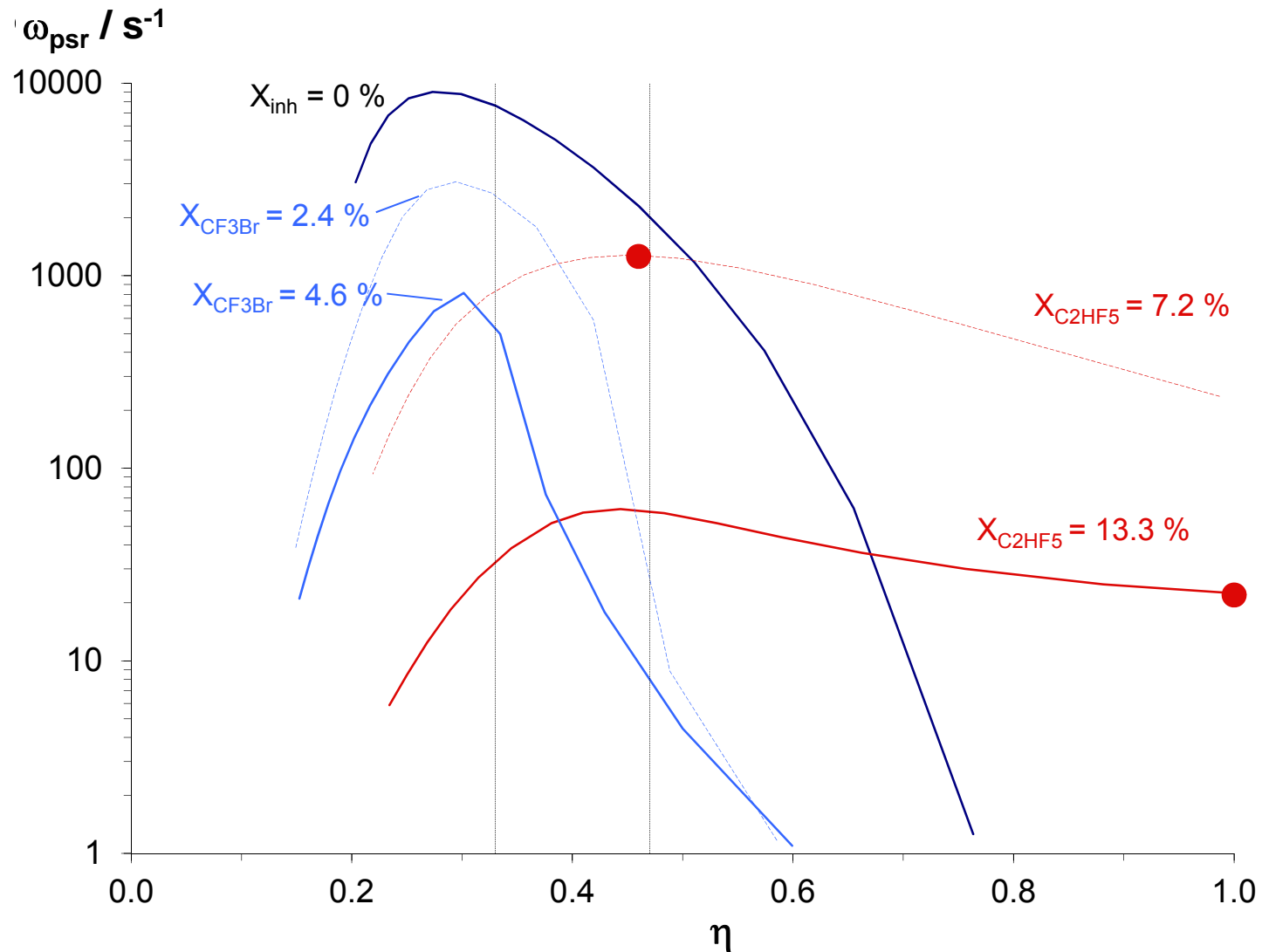
Perfectly-Stirred Reactor (PSR) Overall Chemical Rate with 2-BTP simulant



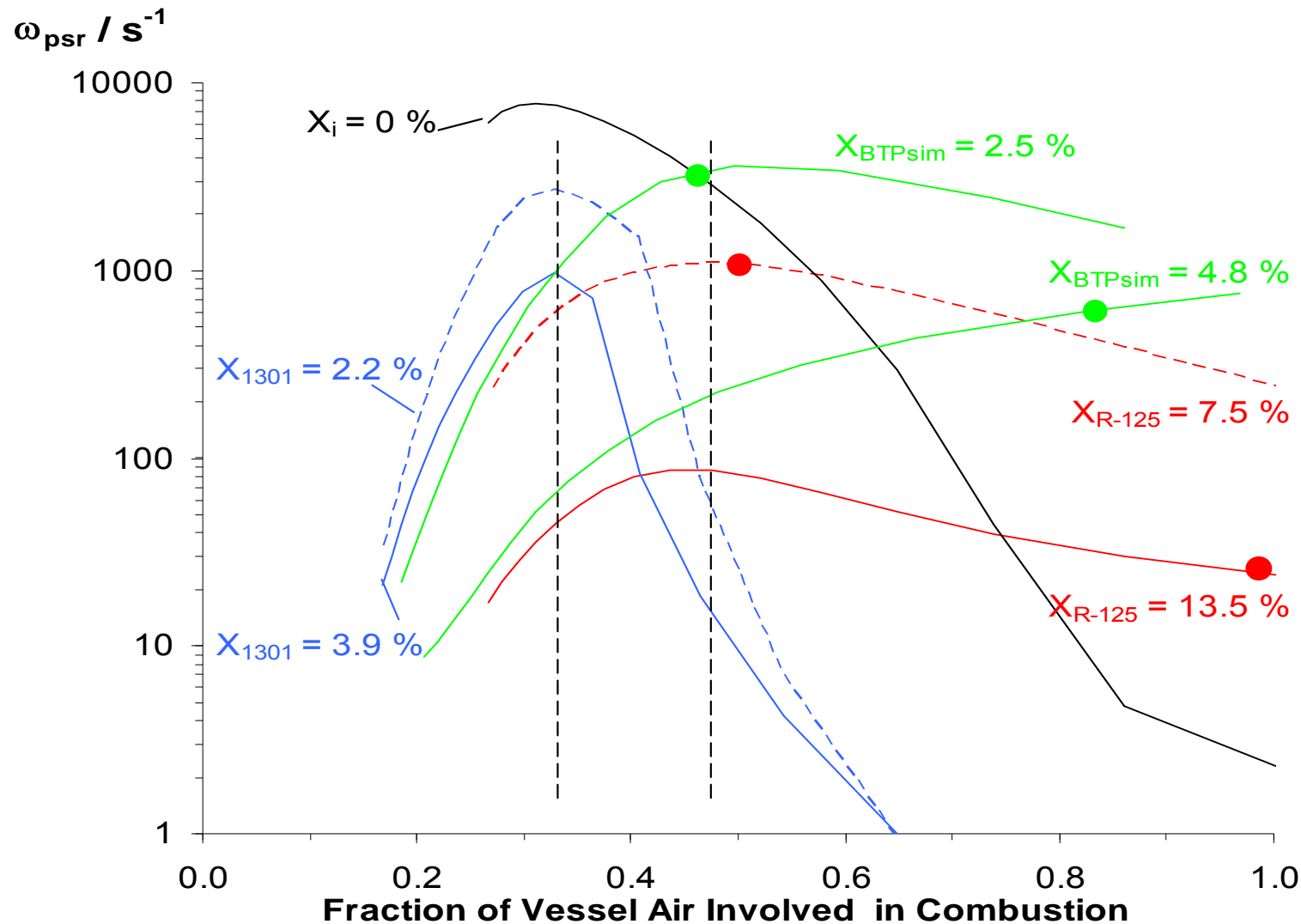
- Adding 2-BTP simulant lowers or raises ω_{chem} (depending upon η)
- variation of ω_{chem} with η is mild at high X_{inh} , but strong without agent.



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

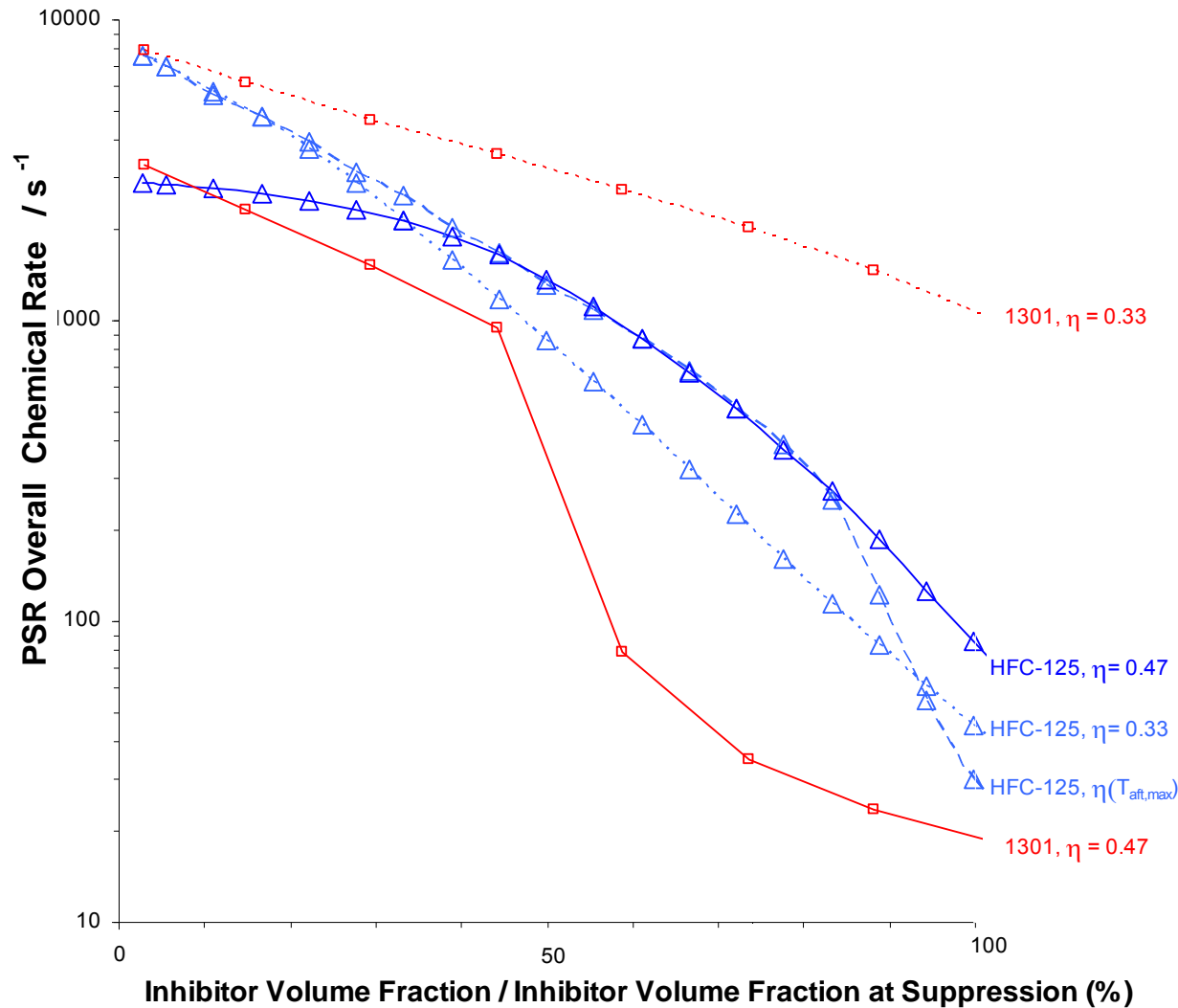


- For R-125, we can use pressure rise data with equilibrium calculations to estimate η (solid dots).
- For 1301, can't use pressure rise, so we don't really know η . => BUT for 1301 ω_{chem} is very sensitive to η .

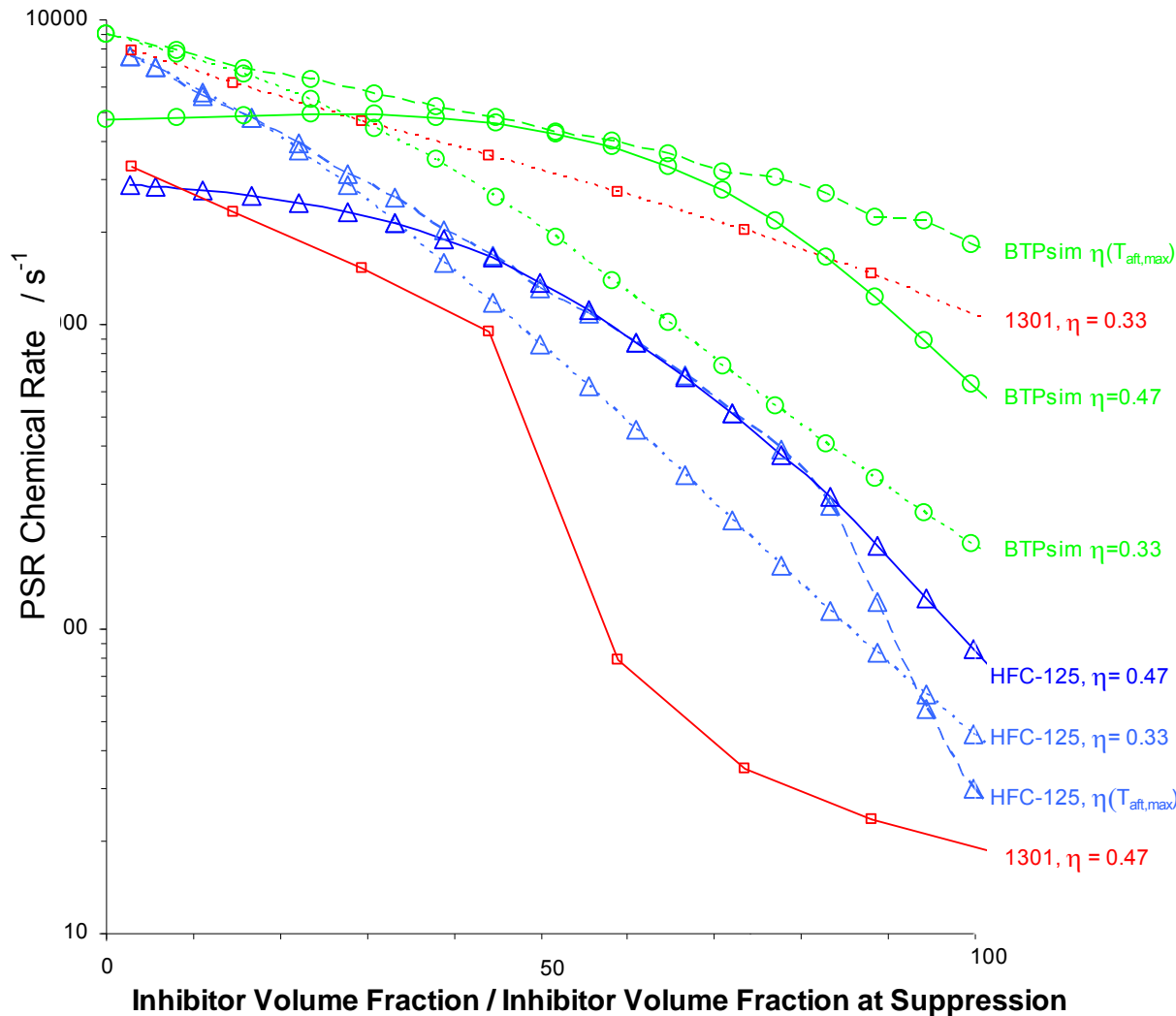


-2-BTP_{sim} simulation, we can use pressure rise data with equilibrium calculations to estimate BTP (colored dots).

- 2-BTP is less effective than either 1301, or HFC-125. Probably due to temperature sensitivity of HBR reaction.



1. More agent generally reduces reaction rate, for all assumed values of η .
2. For the case $\eta=0.47$, there is little change in reaction rate for the curve for HFC-125 up to 30 %.
3. For HFC-125 (blue curves), the reduction in reaction rate with addition of agent is similar regardless of the value of h ; i.e., for $\eta=0.33$, $\eta=0.47$, or $\eta(T_{aft,peak})$.
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.



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5. For CF_3Br to be more effective than HFC-125, η must be greater than about 0.4.
6. For $\eta=0.47$, there is little change in overall reaction rate for the curve for 2-BTP simulant up to 50 %.
7. The 2-BTP simulant (green) is much less effective than HFC-125.
8. The influence of η on the effectiveness is in the opposite direction for CF_3Br and 2-BTP simulant.

Equilibrium and PSR Calculations Indicate:

1. In the FAA ACT with R-125, Novec 1230, 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. CF_3Br will not cause a pressure rise in hydrocarbon-air systems (due to $\text{H}_2\text{O} + \text{CF}_3\text{Br}$ stoichiometry).
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 a 2-BTP simulant imply that the fuel portion of the 2-BTP molecule causes it to be much less effective than CF_3Br .

Key Questions Still to Answer

- Are the results for 2-BTP itself the same as for 2-BTP simulant?
- Does Br help slow the kinetics with 2-BTP?
- Is the amount of involved oxidizer the key feature?
- Why are the kinetics with R-125 not slower (i.e., slow enough for extinguishment)?
- Does the compression heating enhancement of the agent flammability and stop the chemical inhibition?
- Is the inerting concentration required for suppression?
- Is there any way around the undesired results?