Influence of Flame Characteristics on Gas-Phase Fire Retardant Effectiveness

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Outline:

Part I: Super-effective agents in co-flow diffusion flames

Background
- flame types
- iron inhibition
- particles

Phosphorus
- status

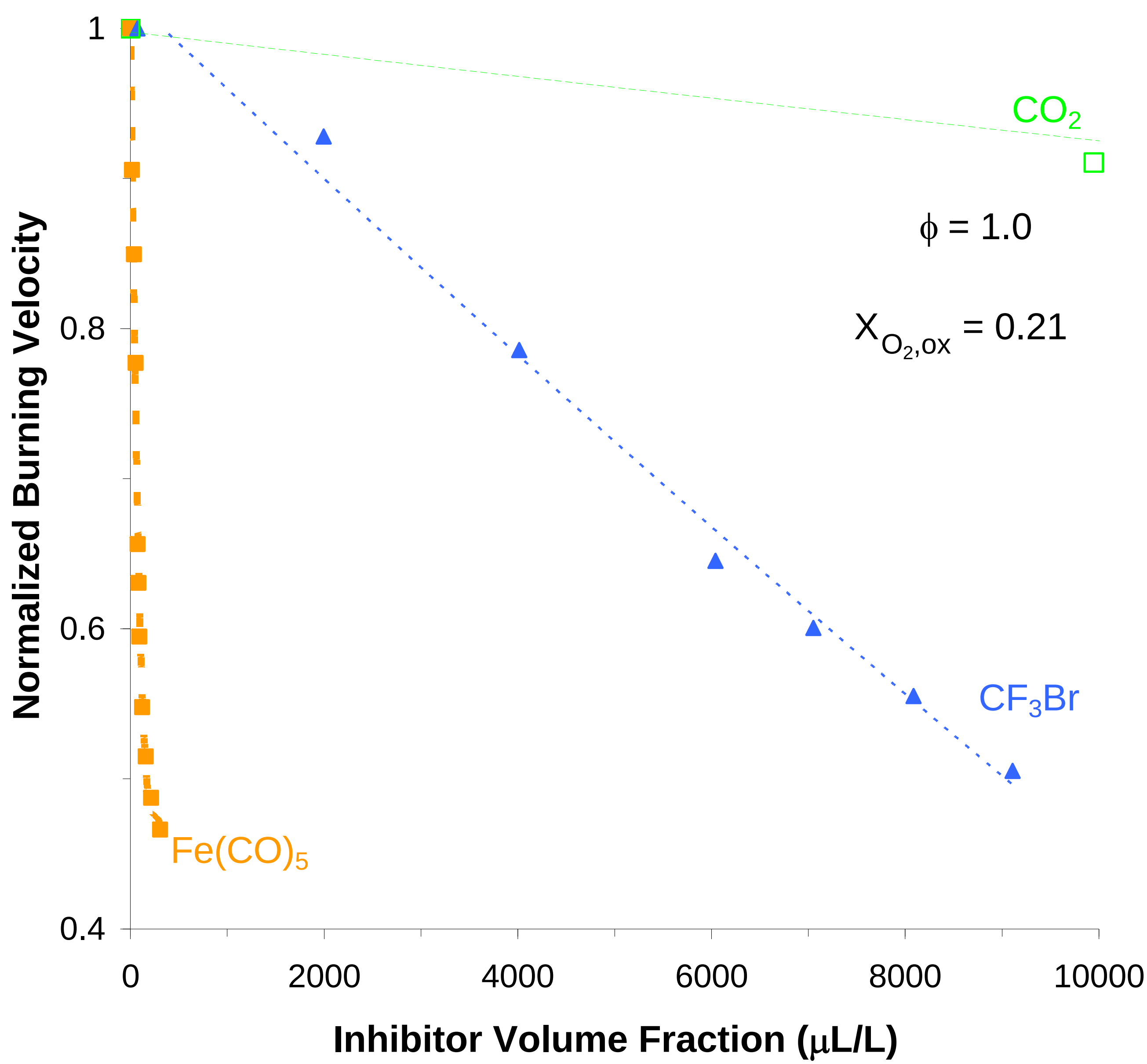
Part II: Flame Properties Affecting Inhibition Effectiveness

Flame Base Characteristics

Random Thoughts

Closing Thoughts

Gas-phase chemical inhibitor effectiveness varies dramatically.



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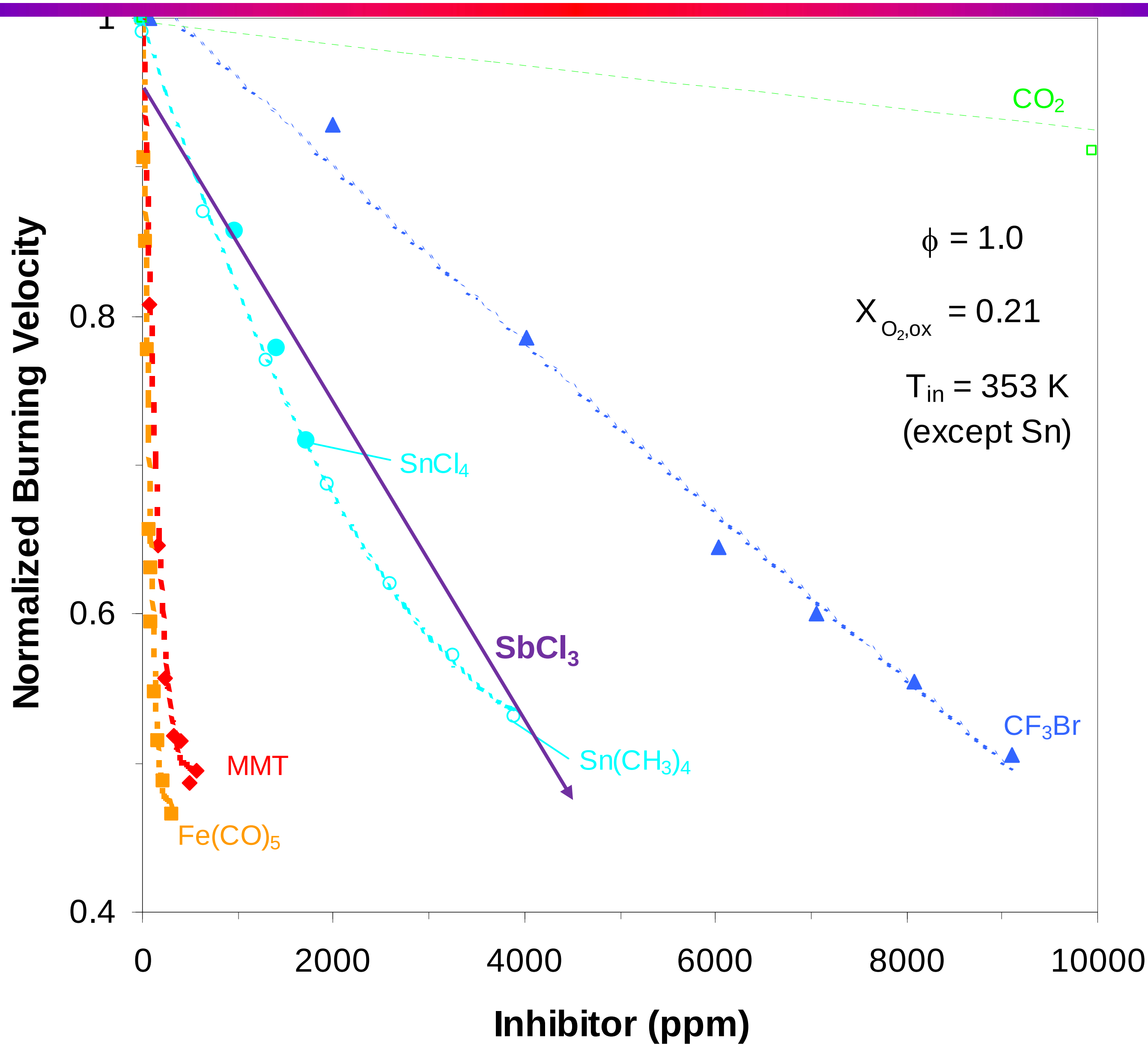

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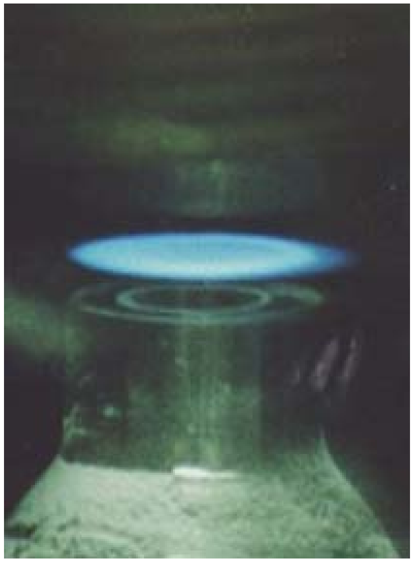
	Premixed flame	*Diffusion flame (Couterflow)*	*Diffusion flame (Coflow)*
			

Effectiveness relative to CO_2:

Fe(CO)5 :	**540**	**100**	**0**
DMMP :	**141**	**17**	**2**
CF_3Br :	**8**	**5**	**7**

Why?

How do we study flame inhibitors?

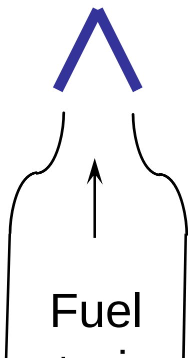
Too difficult to extract fundamental information:
- => can't include detailed chemistry
- => grid resolution is coarse
- => turbulence too complex

Pool Fire (from: http://www.me.uwaterloo.ca/~eweckman/fire/firehome.htm

Two basic types of flames :

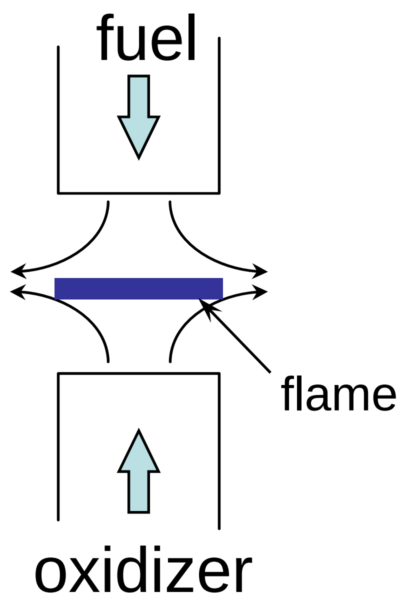
Premixed Flames

Nozzle Burner

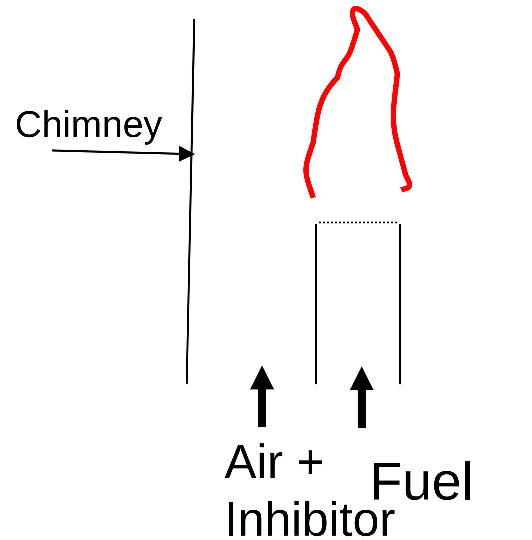


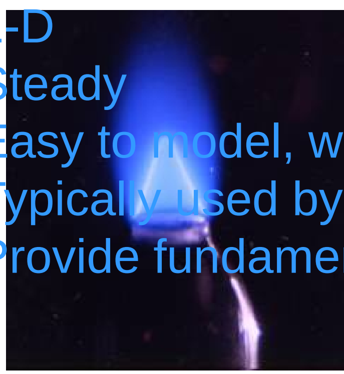
Diffusion Flames

Counter-flow



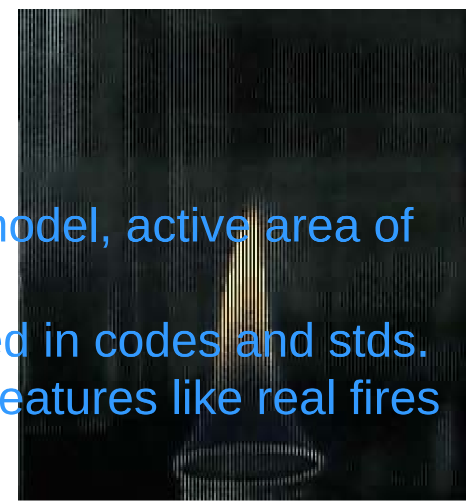
Co-flow





1-D
Steady
Easy to model, well developed theory
Typically used by researchers
Provide fundamental reaction rate data

2-D
Unsteady
Harder to model, active area of research
Widely used in codes and stds.
Has many features like real fires



Approach

1. Experiments:
    - all three fundamental flames,
    - over wide range of controlling parameters.

2. Detailed numerical simulation
    - with detailed kinetic mechanisms.

3. At NIST, we
    - build gas-phase kinetic models,
    - use other people's flame codes

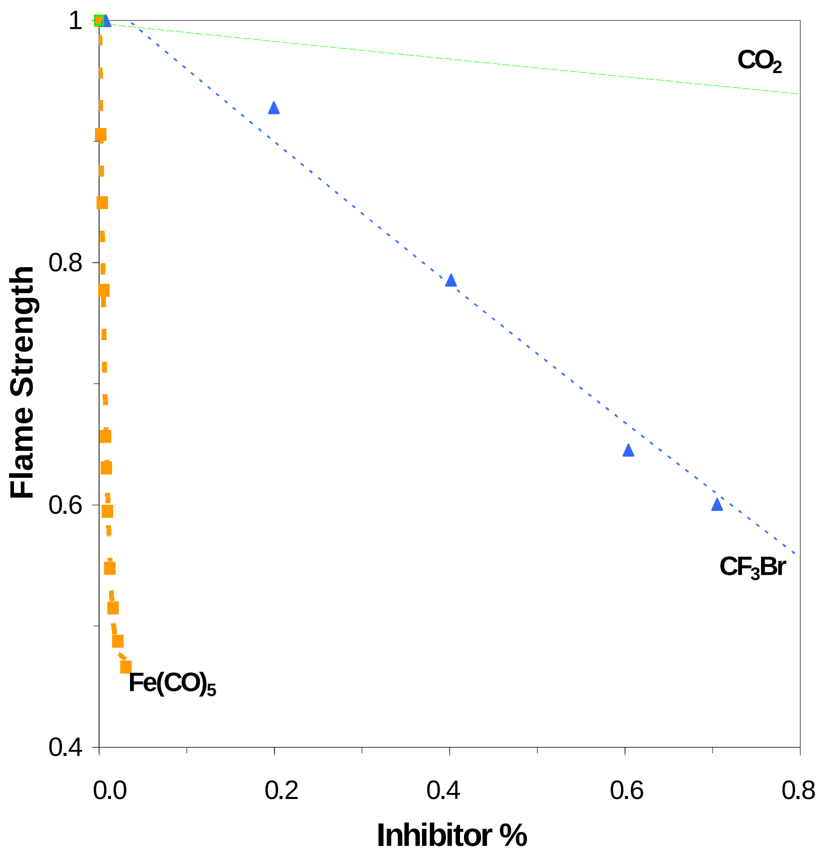
Goals:

1. Understand interaction of inhibitors with flame structure.

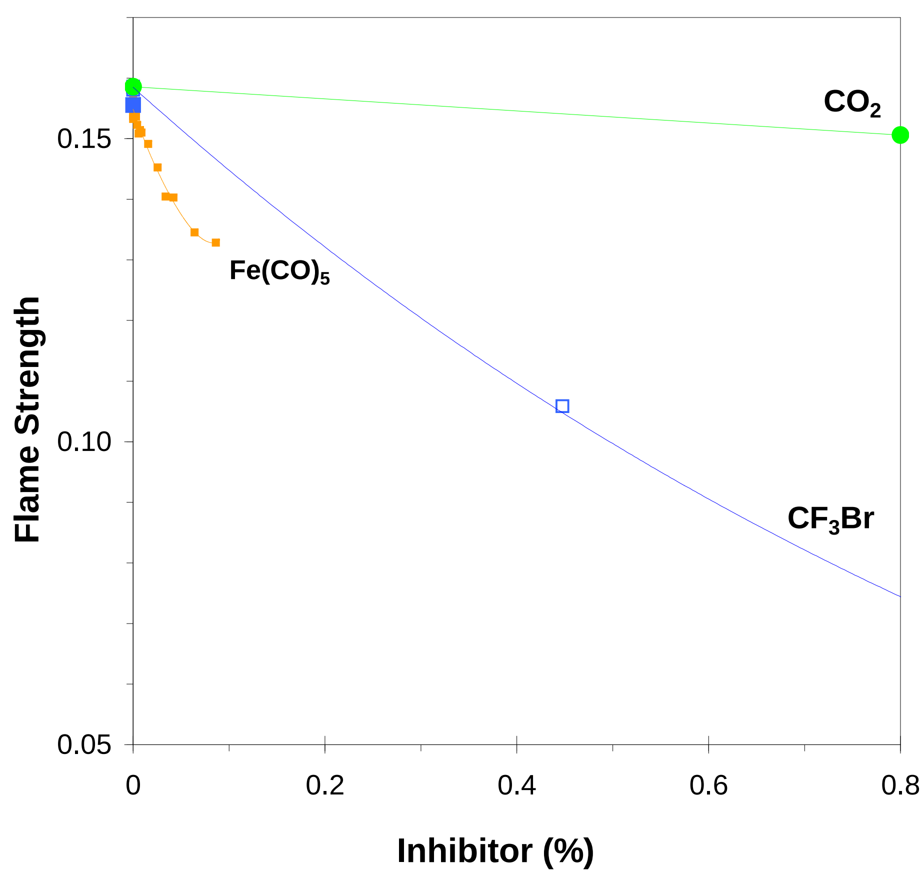
2. Eventually model:
    - standard tests,
    - full-scale fires.

Iron is super-effective relative to CF_3Br in some flames, but in others, it's relatively ineffective. Why?

Premixed flame



Cup-burner flame



Use detailed modeling of the cup-burner flame to find out why.

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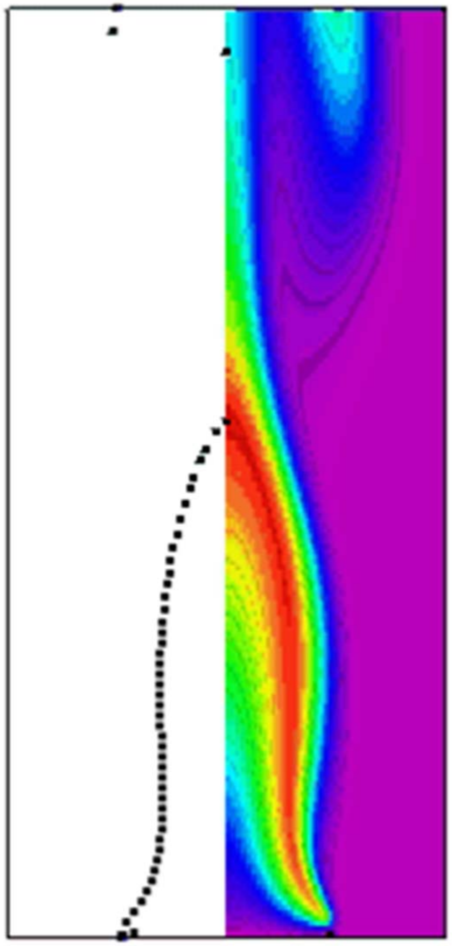
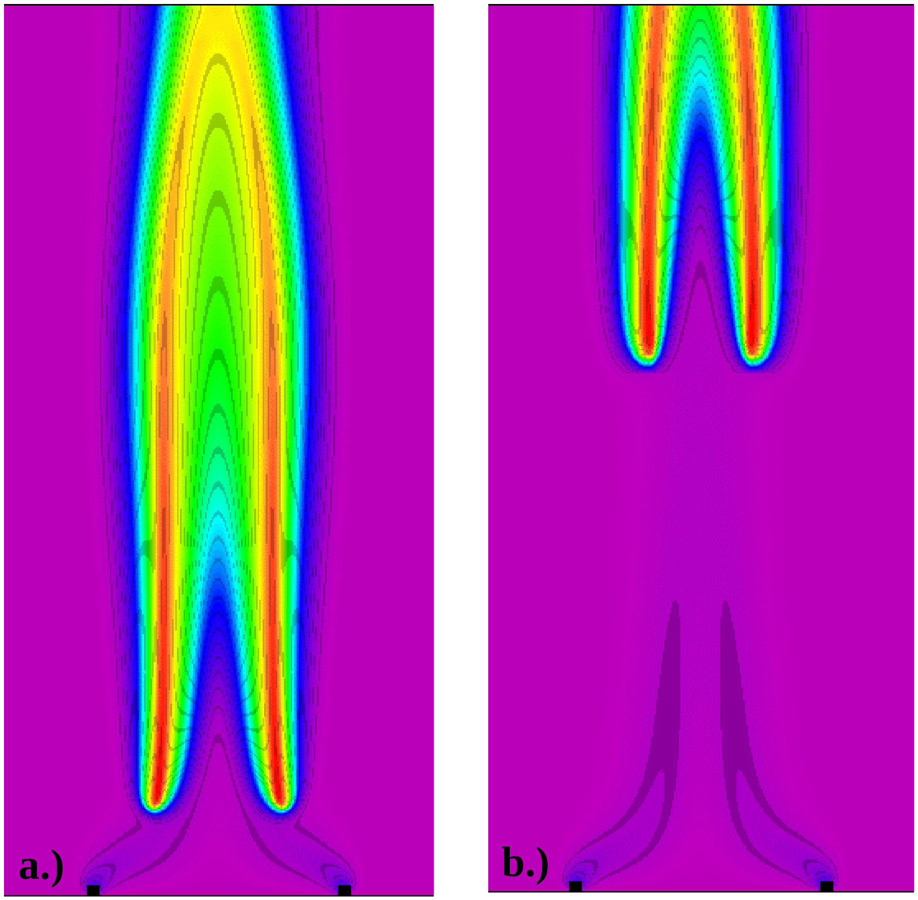
Direct Numerical Simulations for Cup-Burner Flames

- **Time-dependent 2D governing equations**
  - ⇒ mass, momentum, species, energy conservation, & state equations, including a body-force term
  - ⇒ optically thin-media radiative heat losses from CO_2, H_2O, CH_4,and CO
- **Variable thermochemical/transport properties**
  - ⇒ h_i from polynomial curve-fits
  - ⇒ μ, λ, and D from molecular dynamics and mixture rules
- **Detailed reaction mechanism** (GRI-Mech v1.2)
  - ⇒ 31 species/346 reactions for CH_4-O_2 combustion + inert (He, Ar)
  - ⇒ 82 species/1520 reactions for CH_4-O_2 – F system

Calculated temperature contours for one oscillation cycle



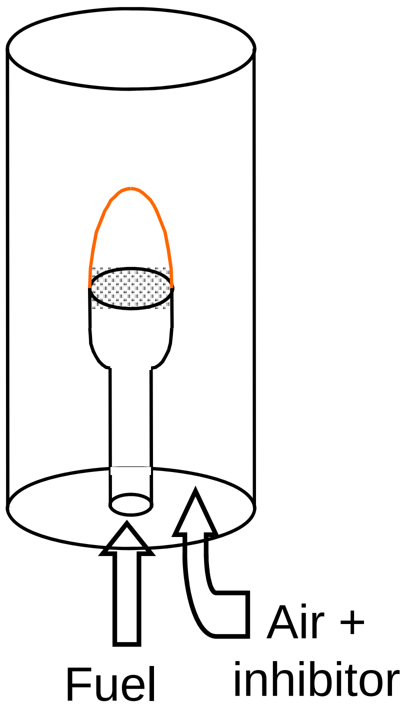
Adding slightly more agent causes flame to liftoff

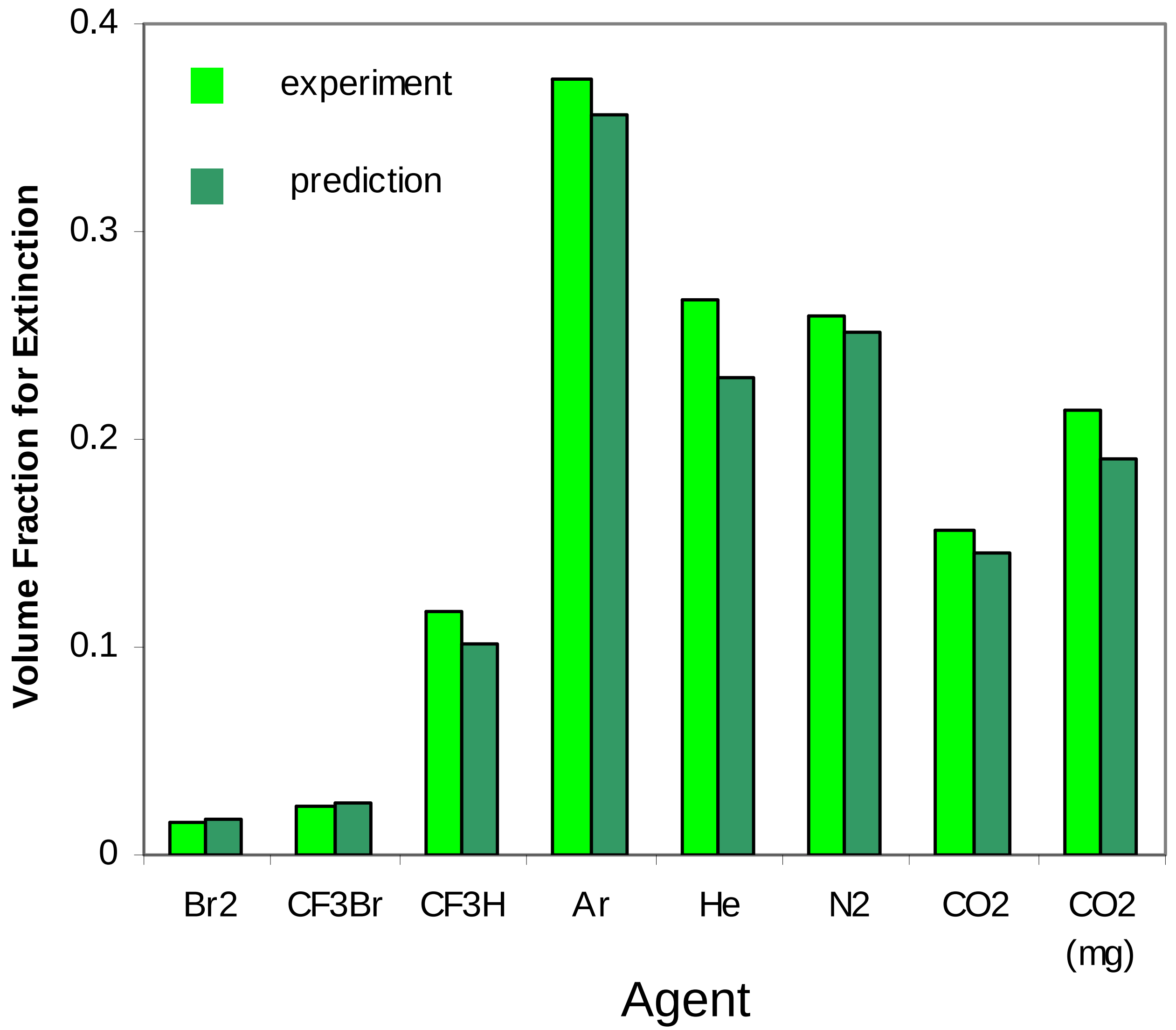


CH4-air flame,

$X_i < X_i|_{critical}$ $X_i > X_i|_{critical}$

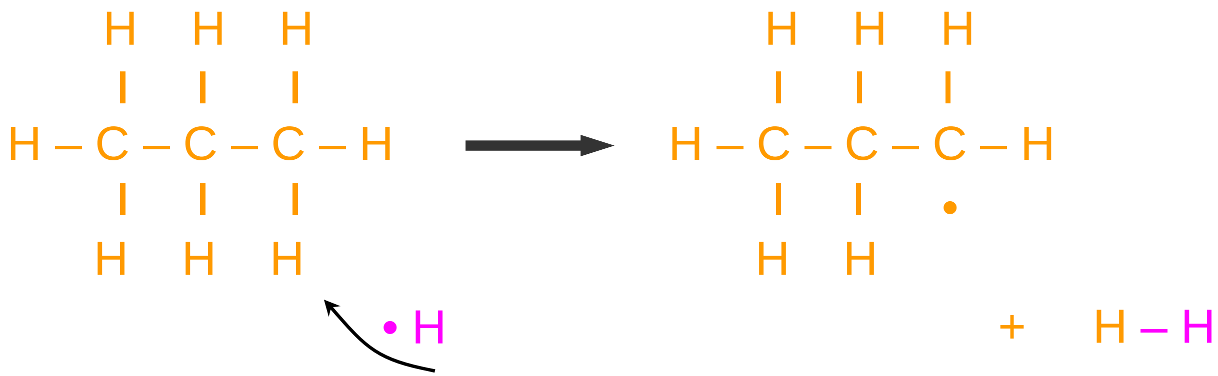
Can predict critical volume fraction of agent for blow-off well.





Review: Radical reactions dominate combustion

- radical attack dominates fuel decomposition



- radical chain branching creates the radicals

$$\dot{H} + O_2 \Rightarrow \dot{O}H + \dot{O}$$

- because of chain branching, often have super-equilibrium of radicals

- CO consumption:

$$CO + \dot{O}H \Rightarrow CO_2 + \dot{H}$$

How does iron inhibit flames?

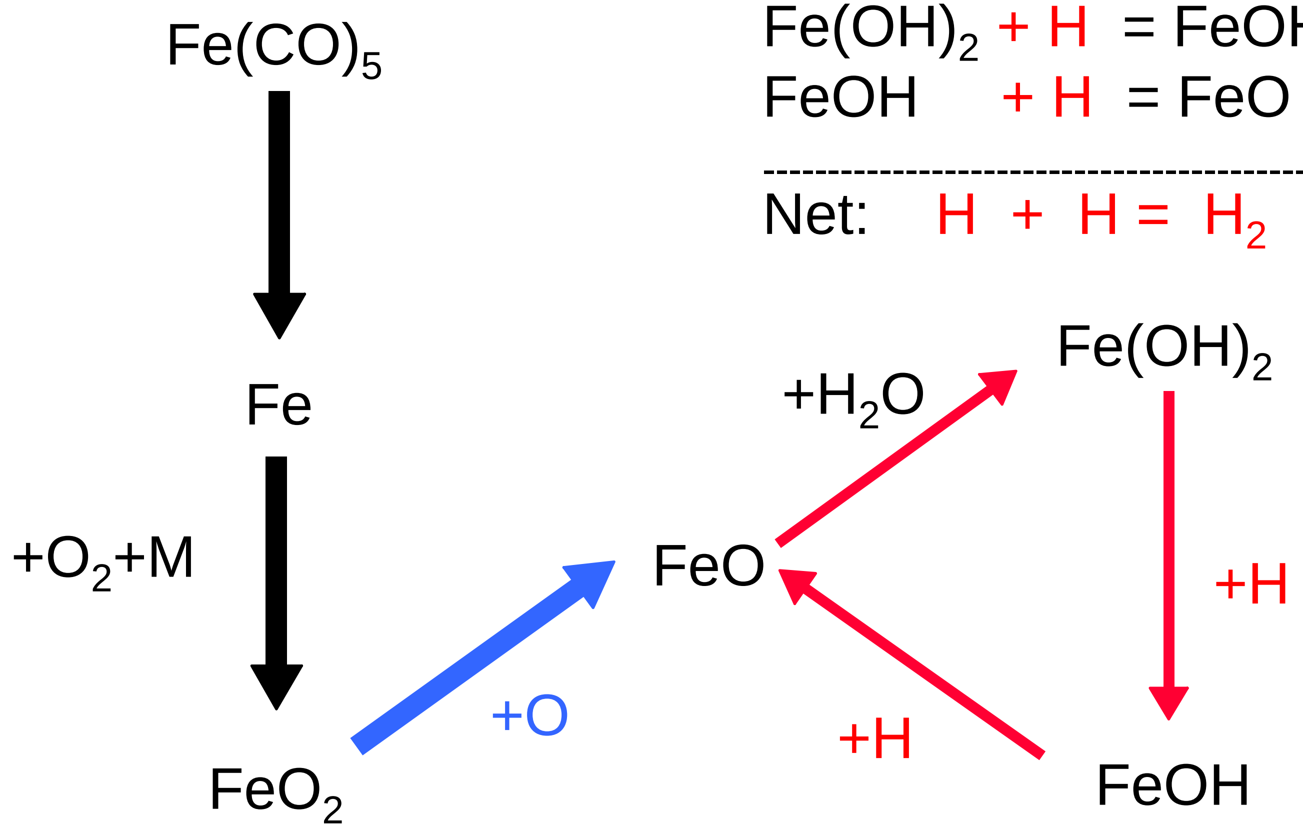
=> Gas-phase iron species recombine radicals.

$FeO \quad + H2O = Fe(OH)_2$

$Fe(OH)_2 + H \ = FeOH$

$FeOH \quad + H \ = FeO$

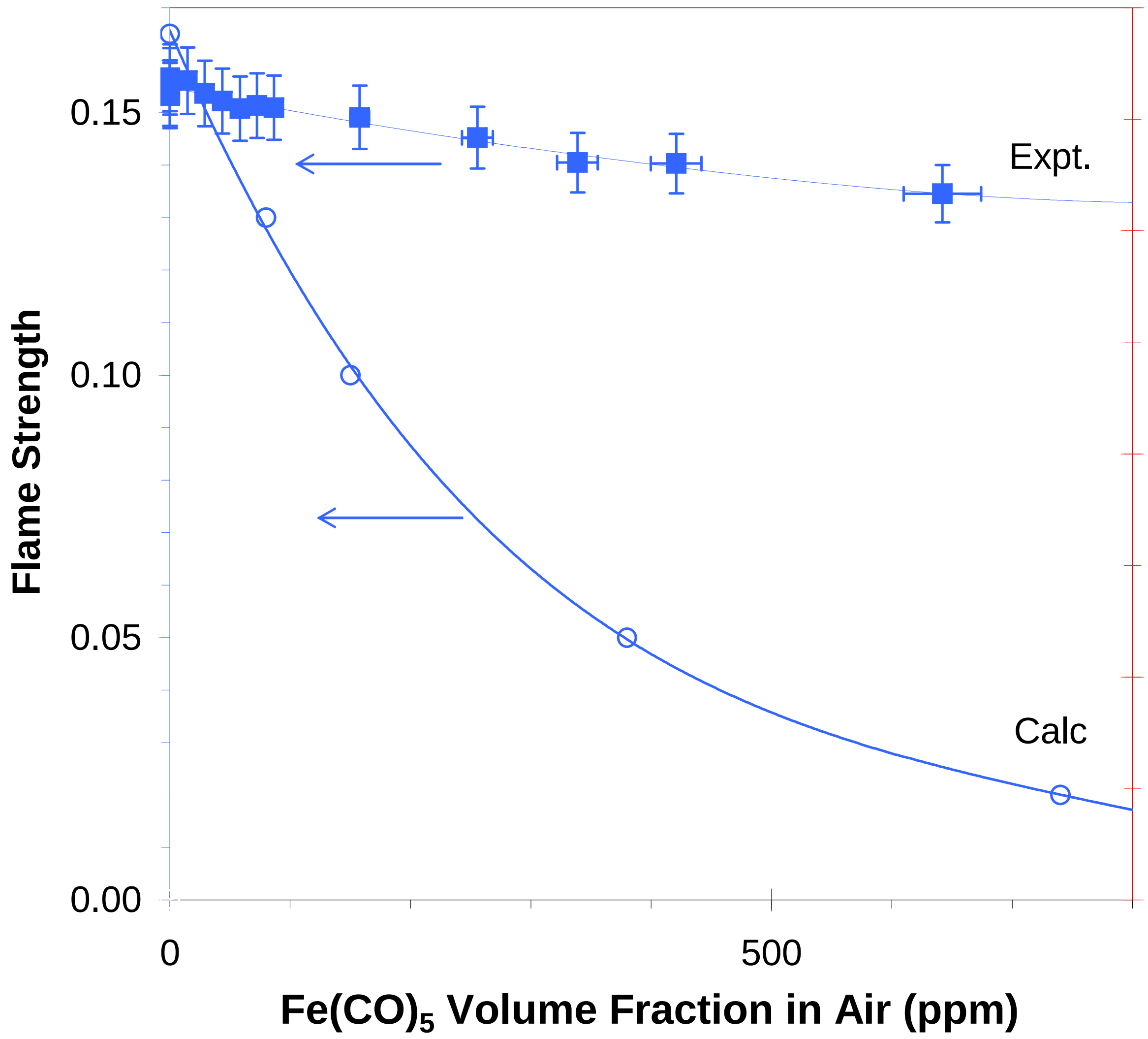
Net: $H + H = H_2$



Catalytic cycle

Predicted and measured inhibition don't agree.

=> This was a surprise. It was expected to work.



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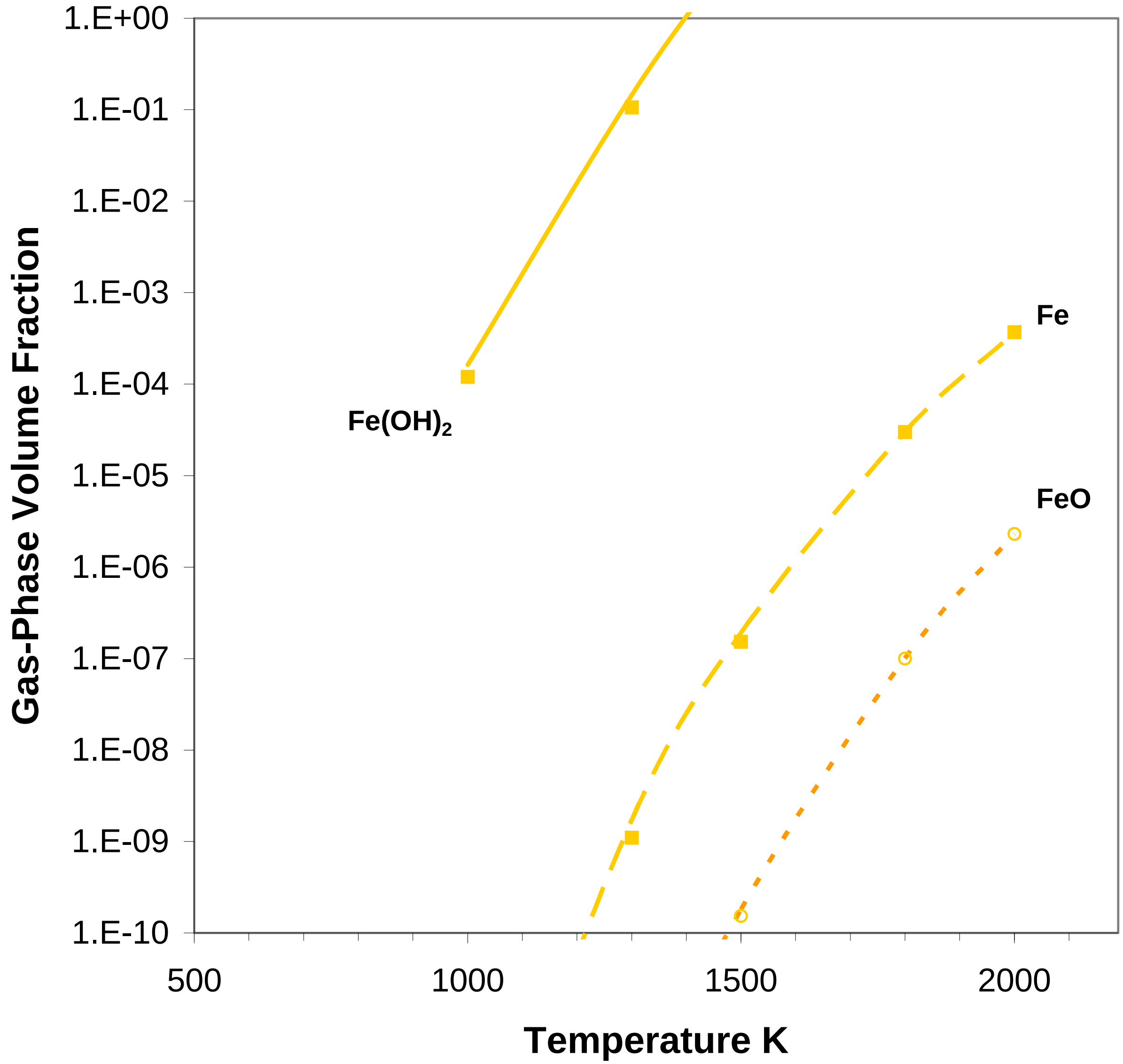
Iron species vapor pressures are strong f(T).

=> potential for condensation.



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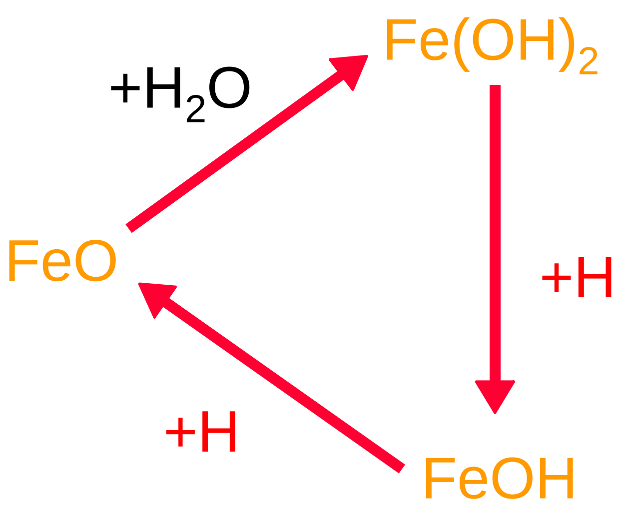
Use model to determine flame structure. Check for super-saturation of Fe compounds:

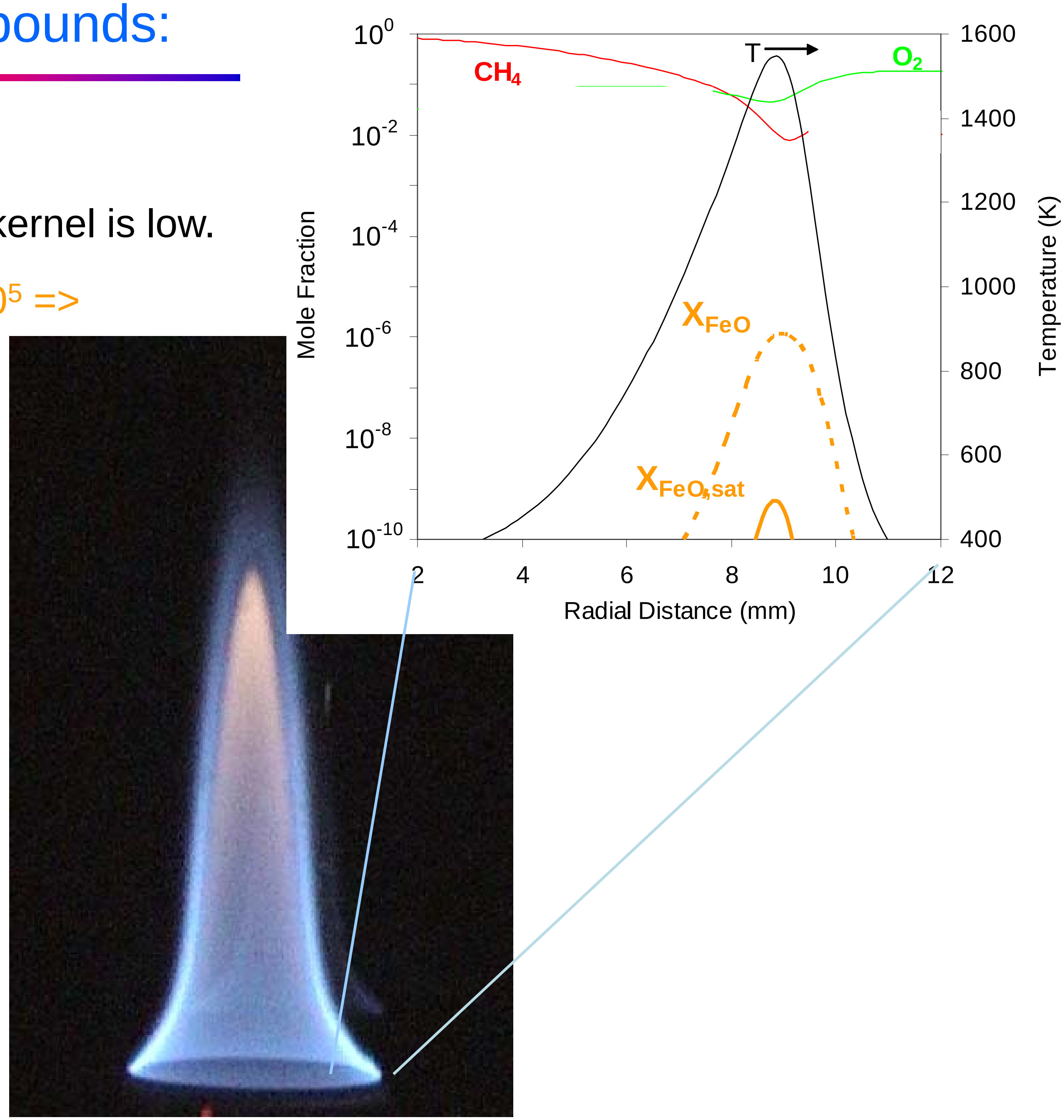
=> Temperature at reaction kernel is low.

=> $[FeO]/[FeO]_{sat} = 10^3$ to 10^5 =>
condensation is likely

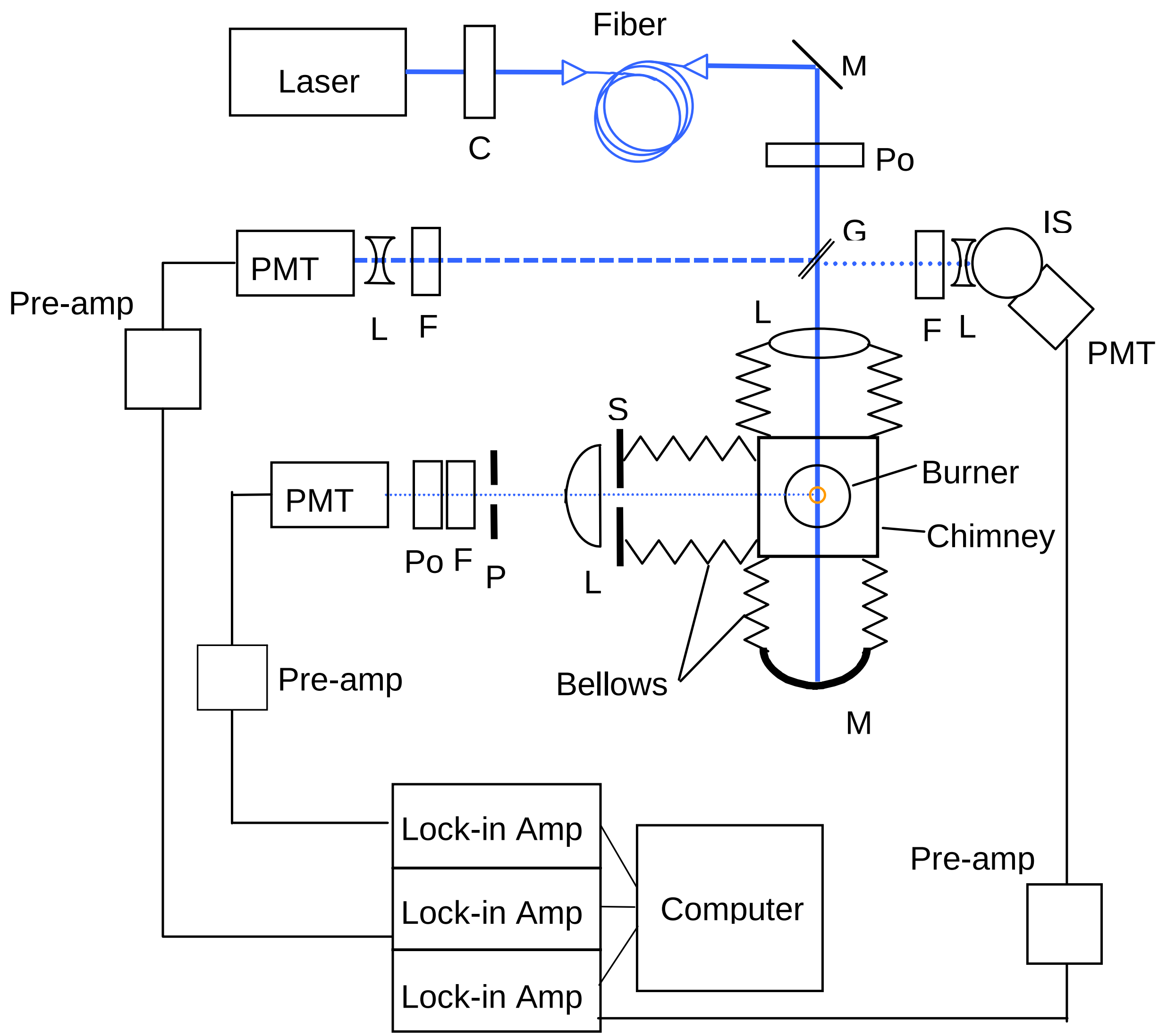
=> Particles:
sink for active Fe species



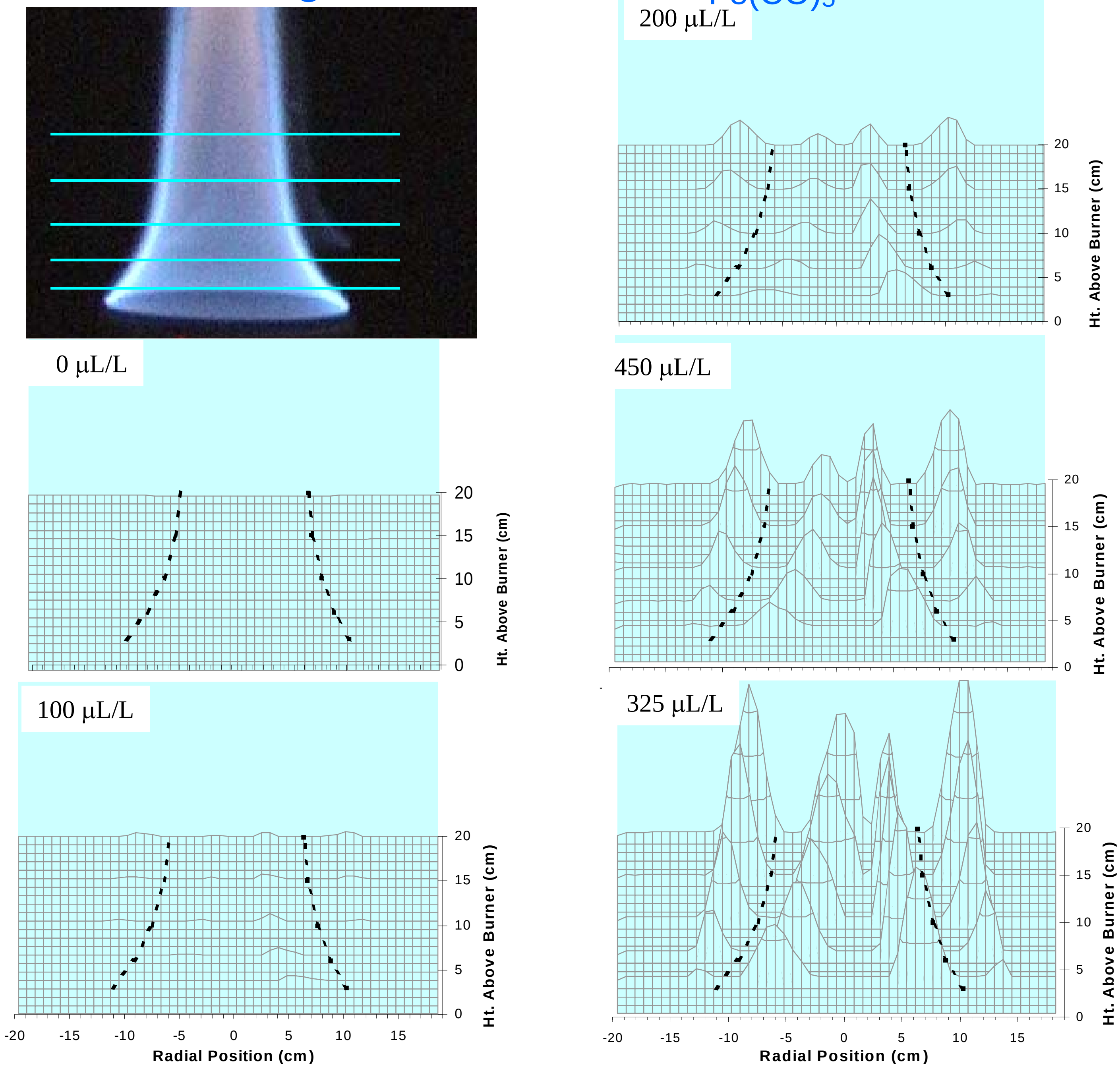
Catalytic cycle



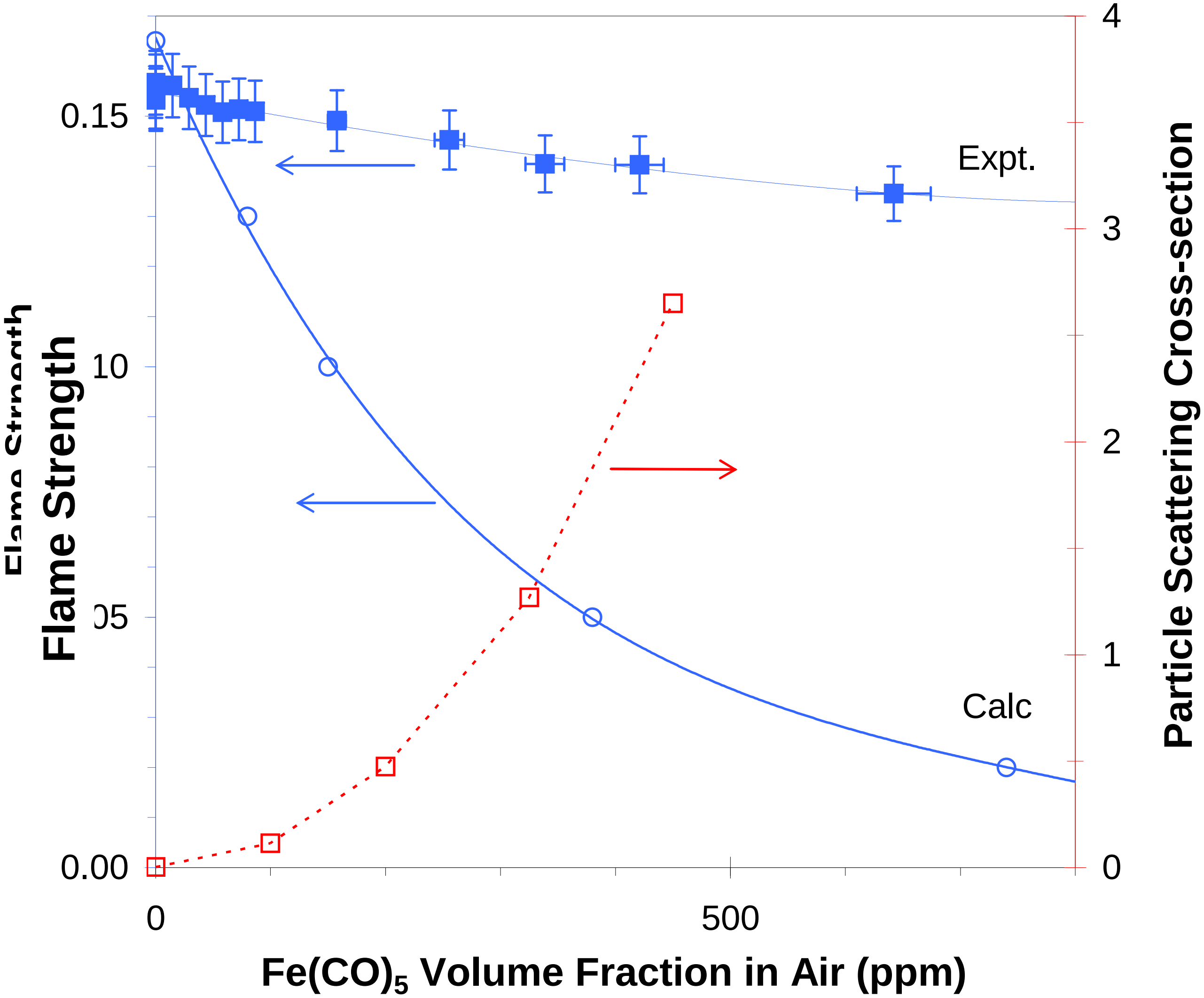
Check for particles with laser scattering system



Particle scattering increases with $X_{Fe(CO)_5}$ in air stream.



Scattering from particles is correlated with low effectiveness



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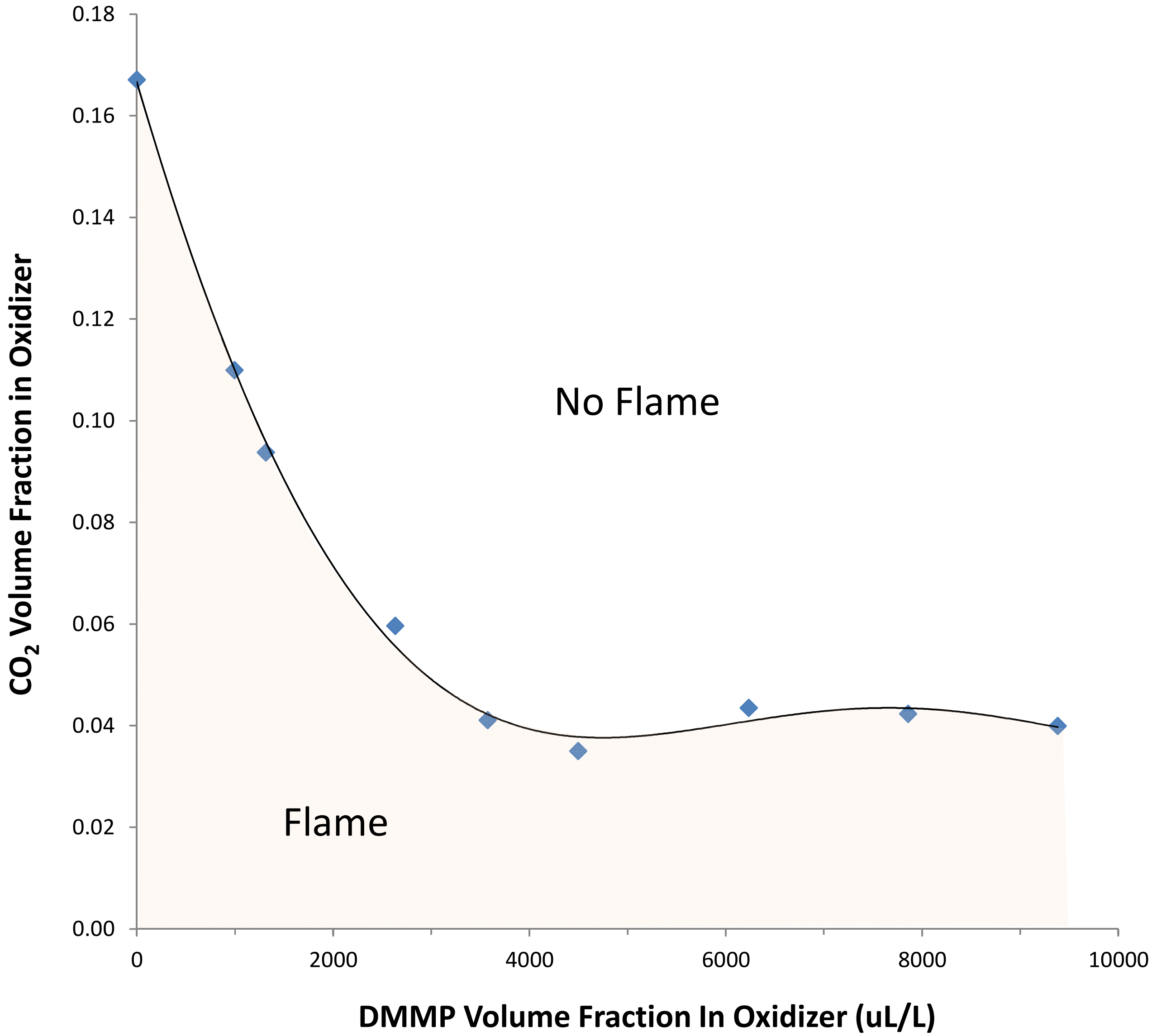
Conclusions (for iron in cup-burner flames):

Iron as a fire suppressant?

1. Much less effective than expected.
2. Gas-phase catalytic reactions => lower the radical concentrations. But…
3. Particles are a sink for the active species.
4. Lower temperature in the stabilization region leads to more particle formation.

What about DMMP?

Cup Burner Extinction with DMMP and CO_2 , (methane-air, 70°C)



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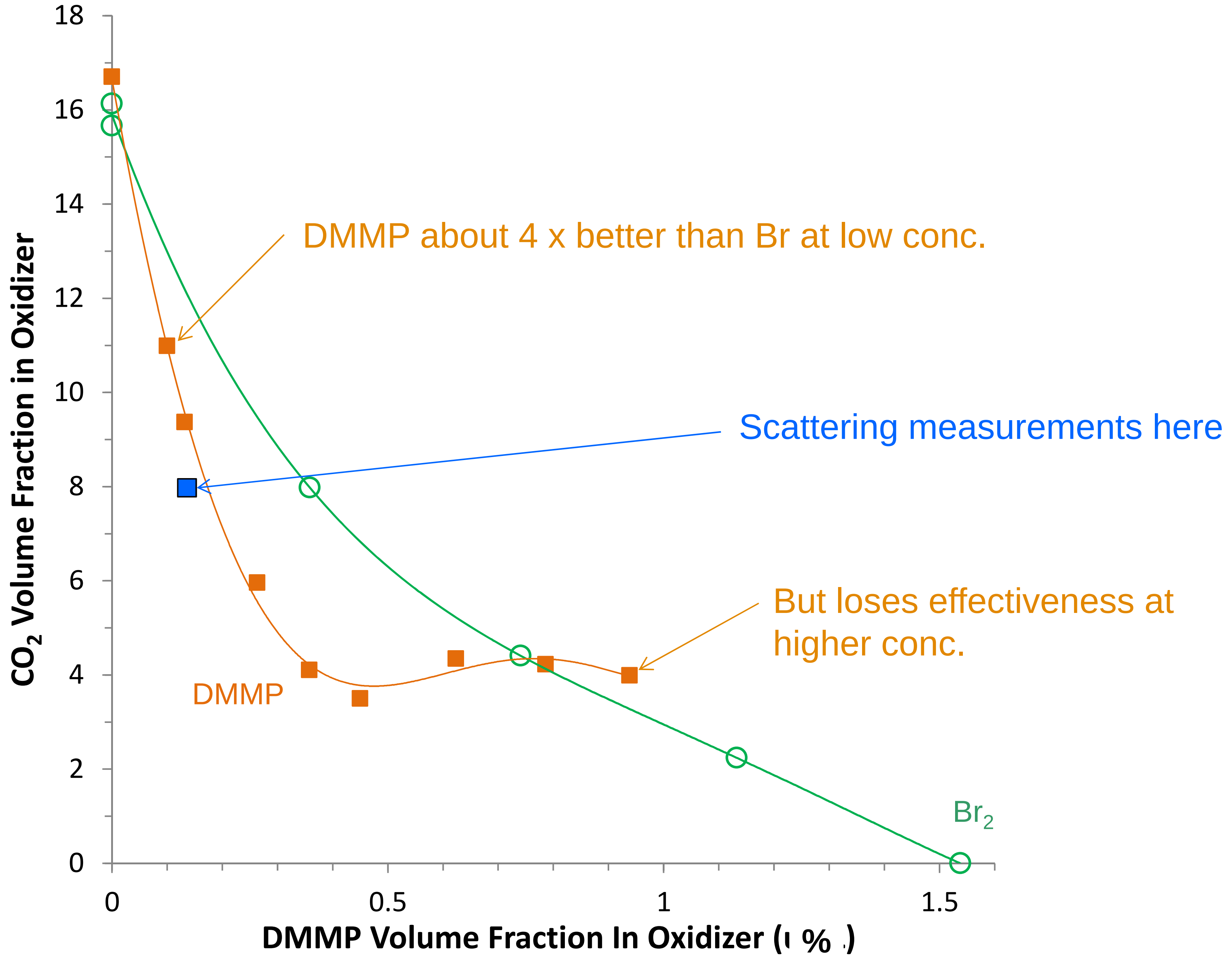
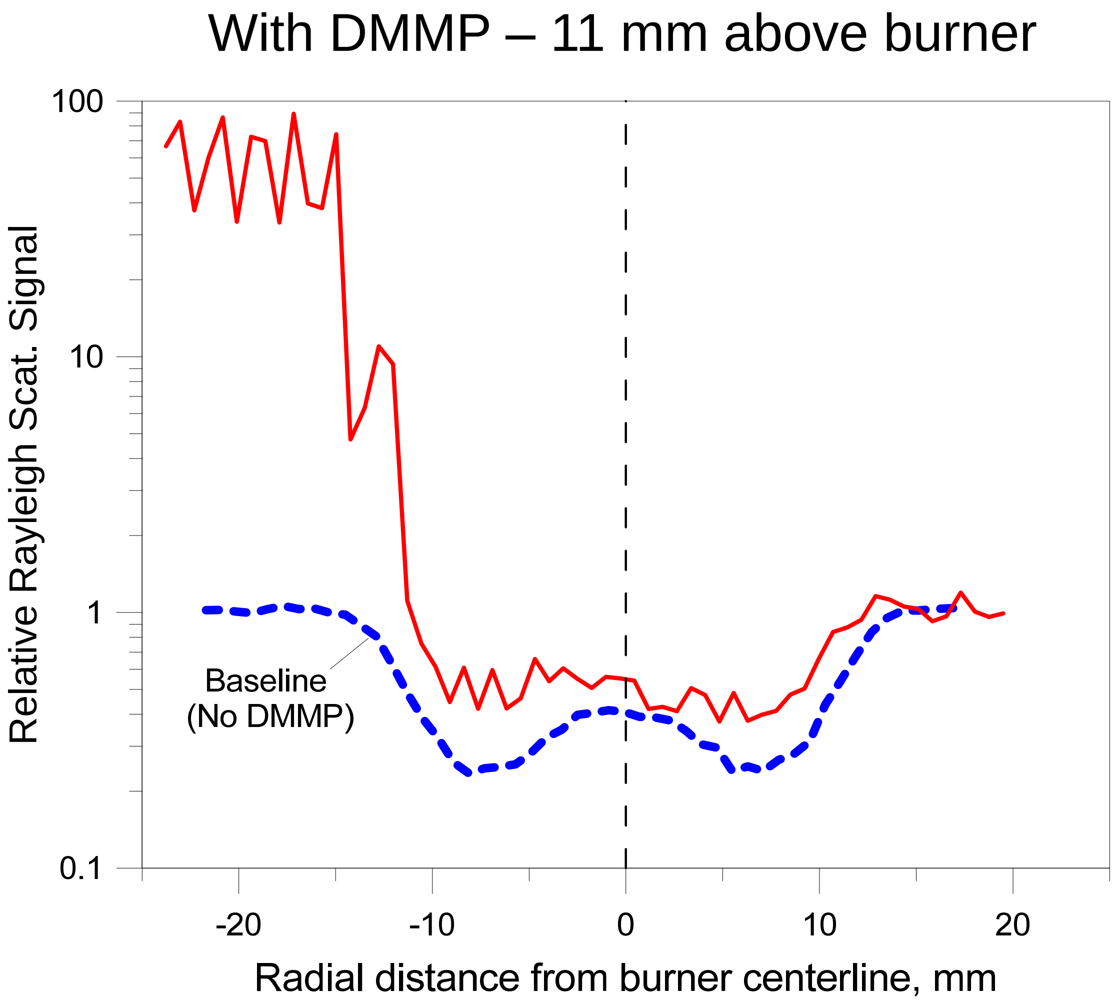
Phosphorus vs. Bromine in Cup Burner



Rayleigh scattering in flame with added DMMP in air (1000 ppm)



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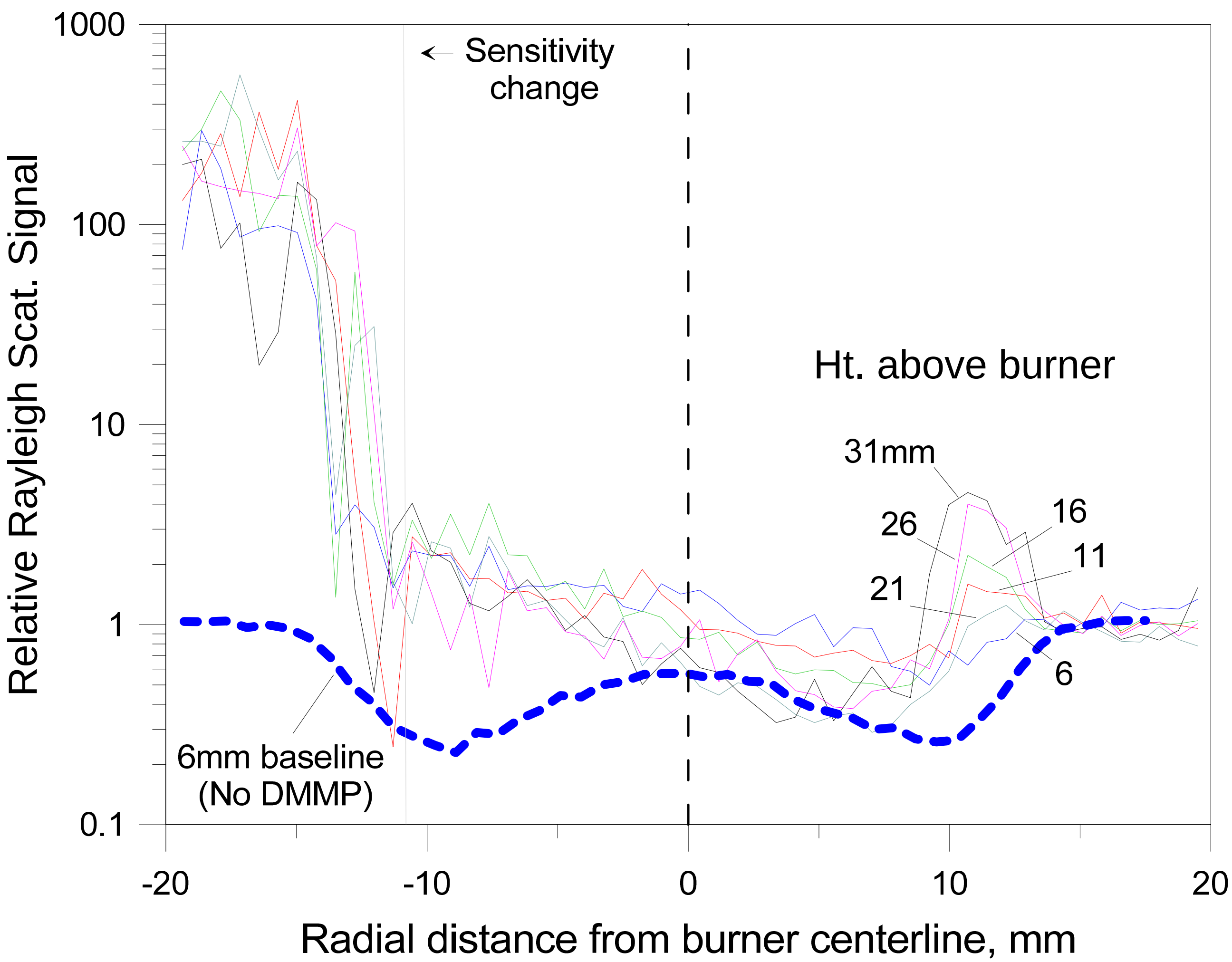

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Current Status

1. DMMP added to cup-burner flames does lose its effectiveness dramatically.

2. Particles do form – but loss of effectiveness
   could also be due to the HC component.

3. Further experiments and modeling should determine why.

Part II

=> Influence of cup-burner flame properties on inhibitor effectiveness.

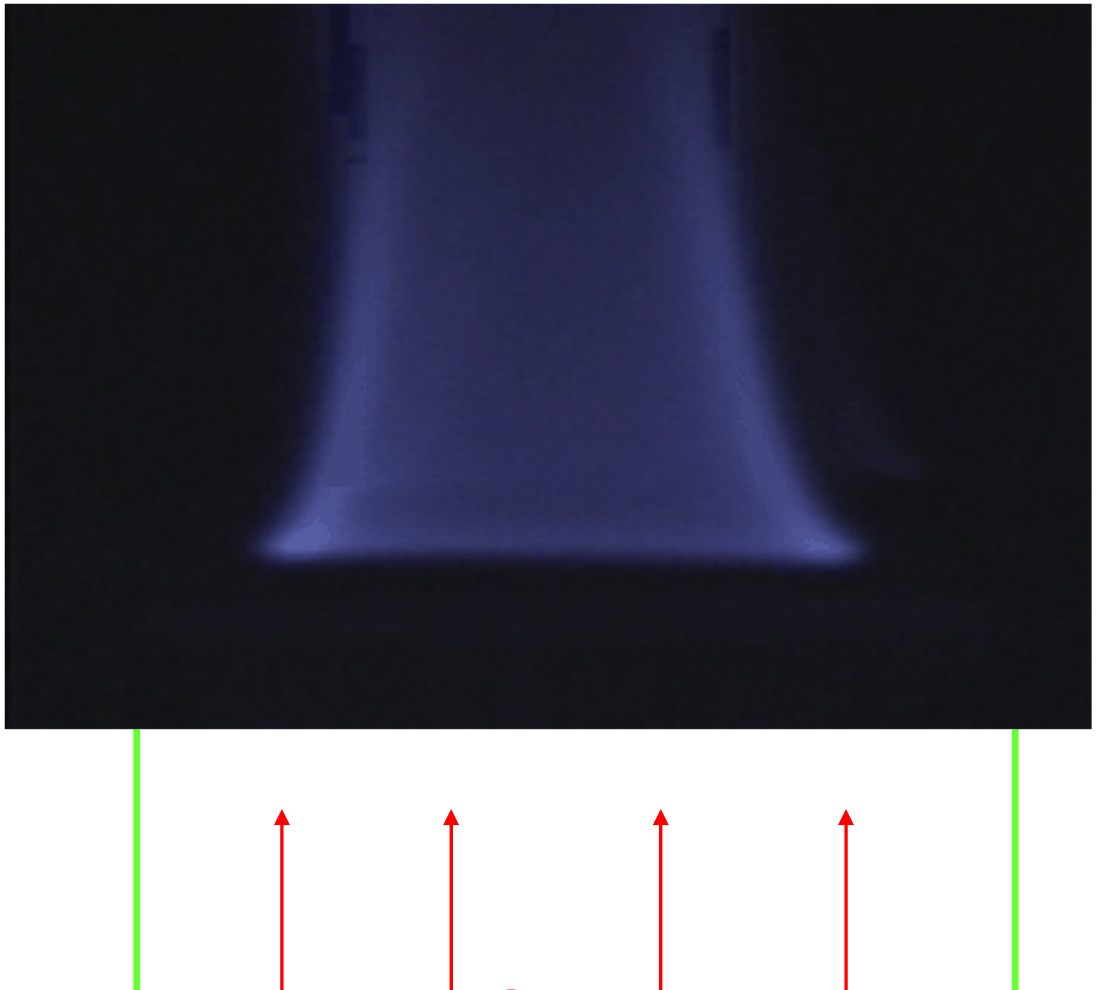
Flame is stabilized at the base, where:

- Temperature is lower.

- Mixing is good, so reactants tend to be premixed (due to flame lifting at edge, and entrainment).

- Flame oscillates, making the flame easier to extinguish.

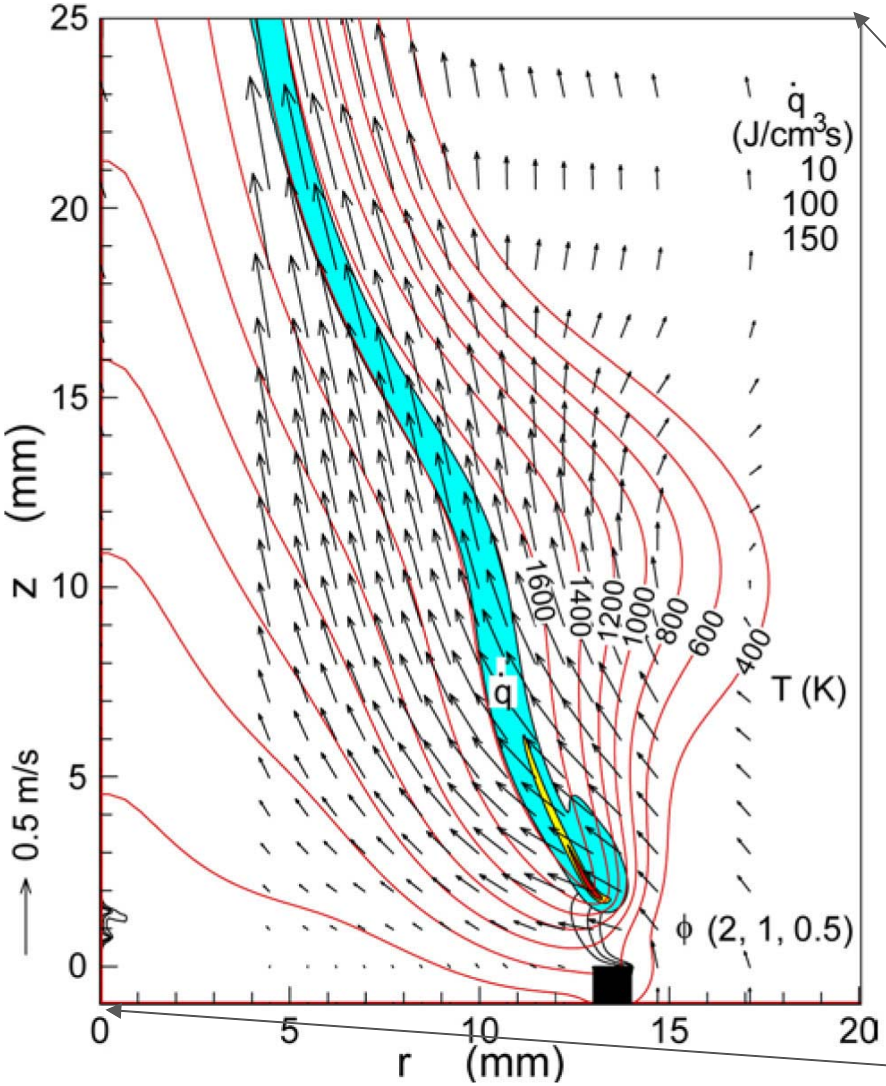
Flame Flicker: makes flame easier to extinguish



CH_4

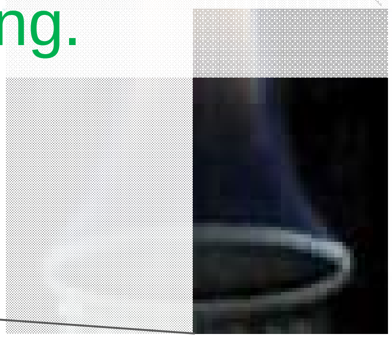
84.1% Air + 15.9% CO_2

Flame Structure (Showing Flicker) t=0.00 s



Flame flicker:

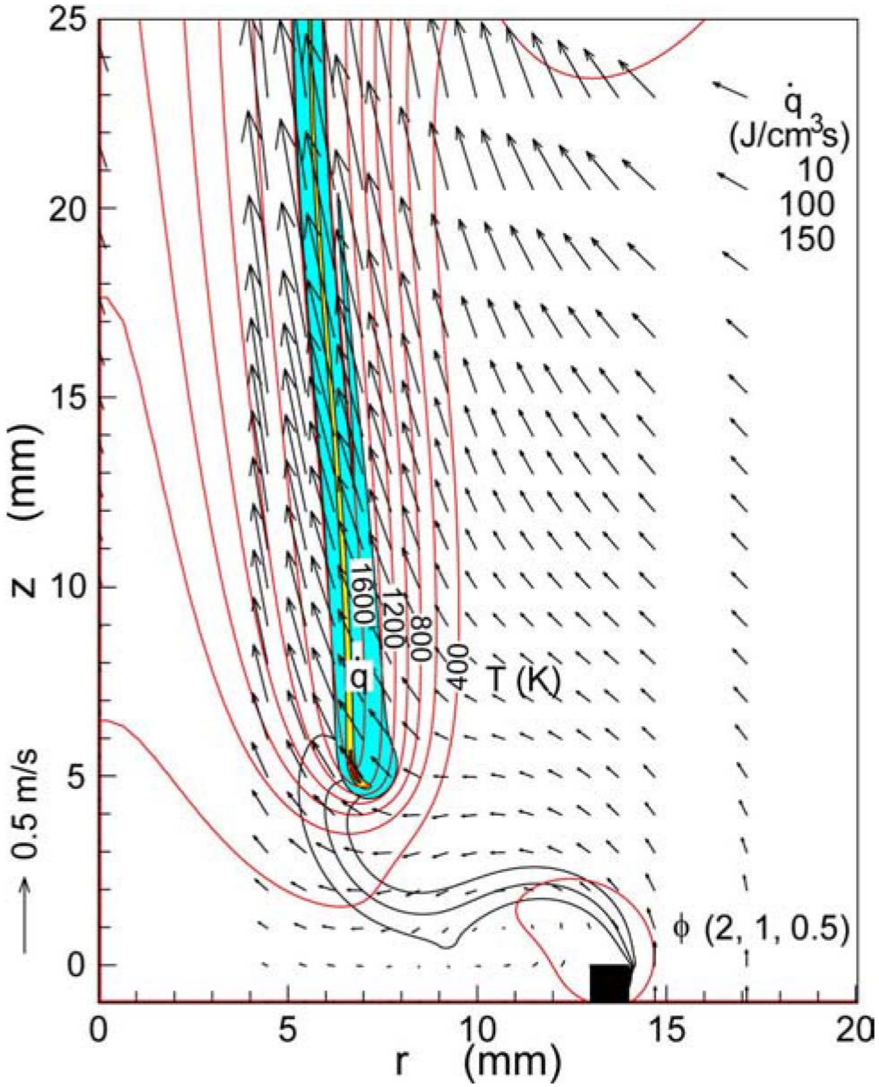
1. Makes flame easier to extinguish.
2. Without flicker, need 30% more agent for extinguishment.
3. Some agents enhance flicker, some retard it.
4. Changes with agent loading.



t = 0 s

U_{CH4}= 0.92 cm/s, U_{ox}= 10.7 cm/s, X_{CO2} = 0.14

Flame Structure (Showing Flicker) t=0.08 s



t = 0.08 s

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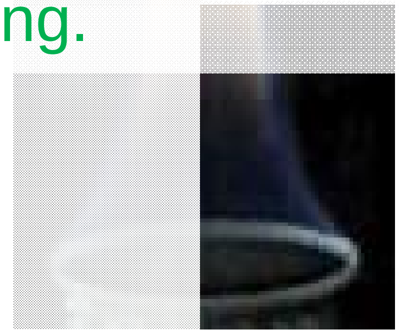
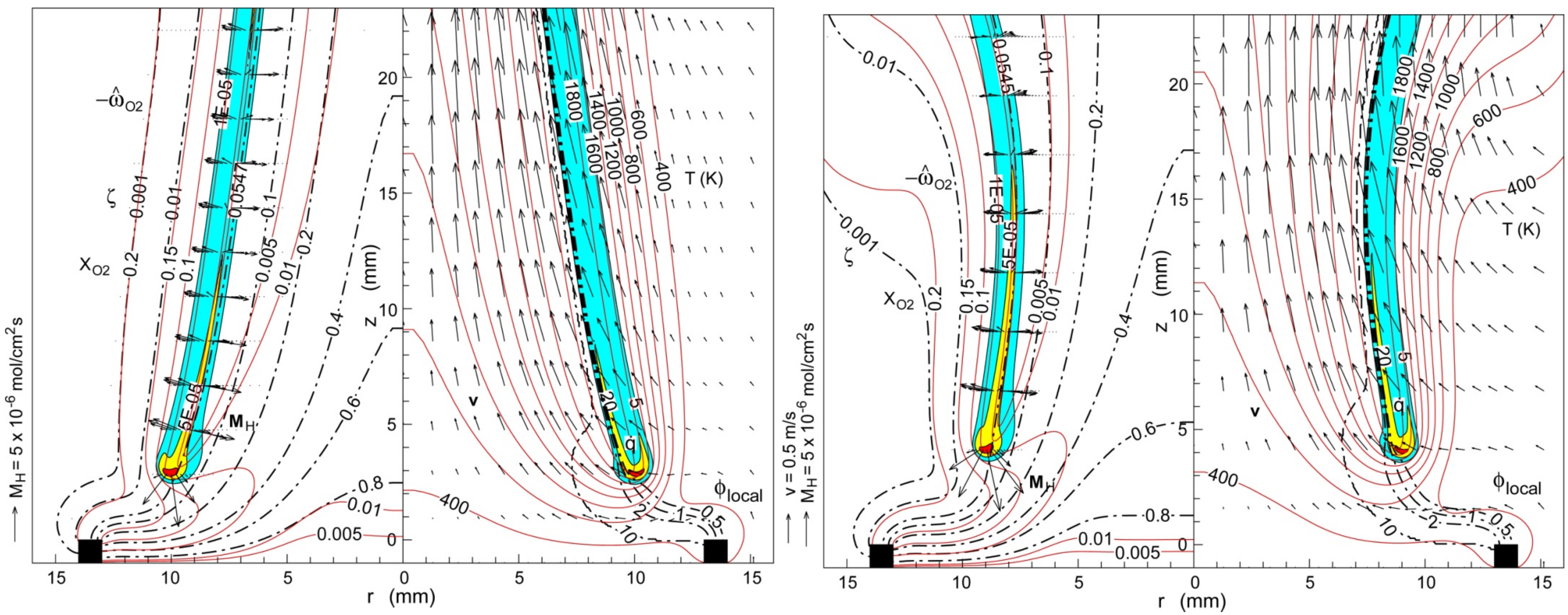


U_{CH4}= 0.92 cm/s, U_{ox}= 10.7 cm/s, X_{CO2} = 0.14

Flame lift-off

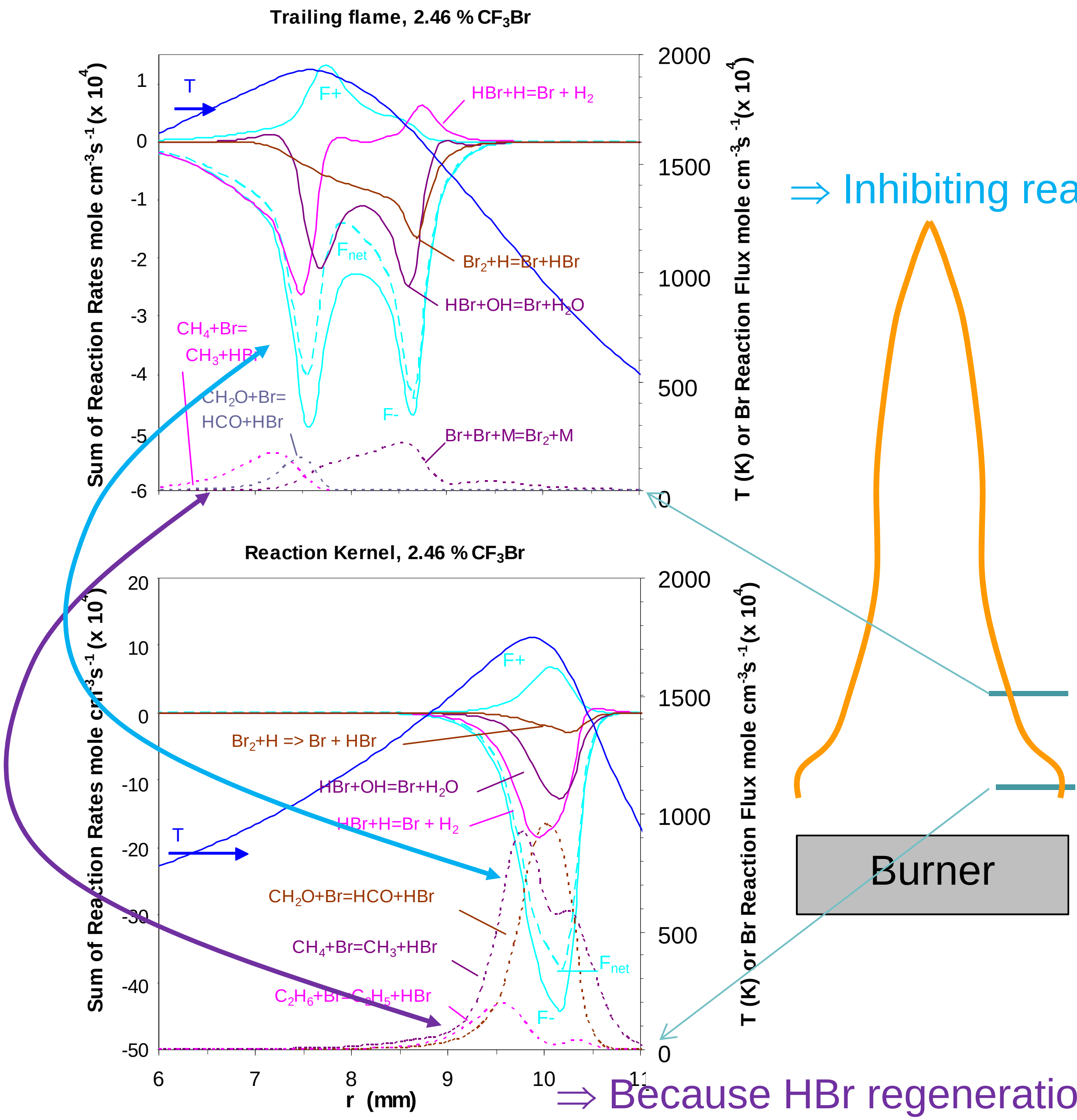
Ch$_4$ – Air + 2.46% CF_3Br CH$_4$ - Air + 1.66 % Br_2



$\Rightarrow$ Base is:

- lower temperature (1400 K) as compared to higher up in the flame (1850 K).
- Lifted, more premixed, with
  + more radical super equilibrium,
  + better inhibition at base, so blows off there first
  + different chemsitry, due to different reactants: e.g., better regeneration of HBr

Influence of Flame Base on Inhibition Chemistry



⇒ Inhibiting reactions 10x higher in base

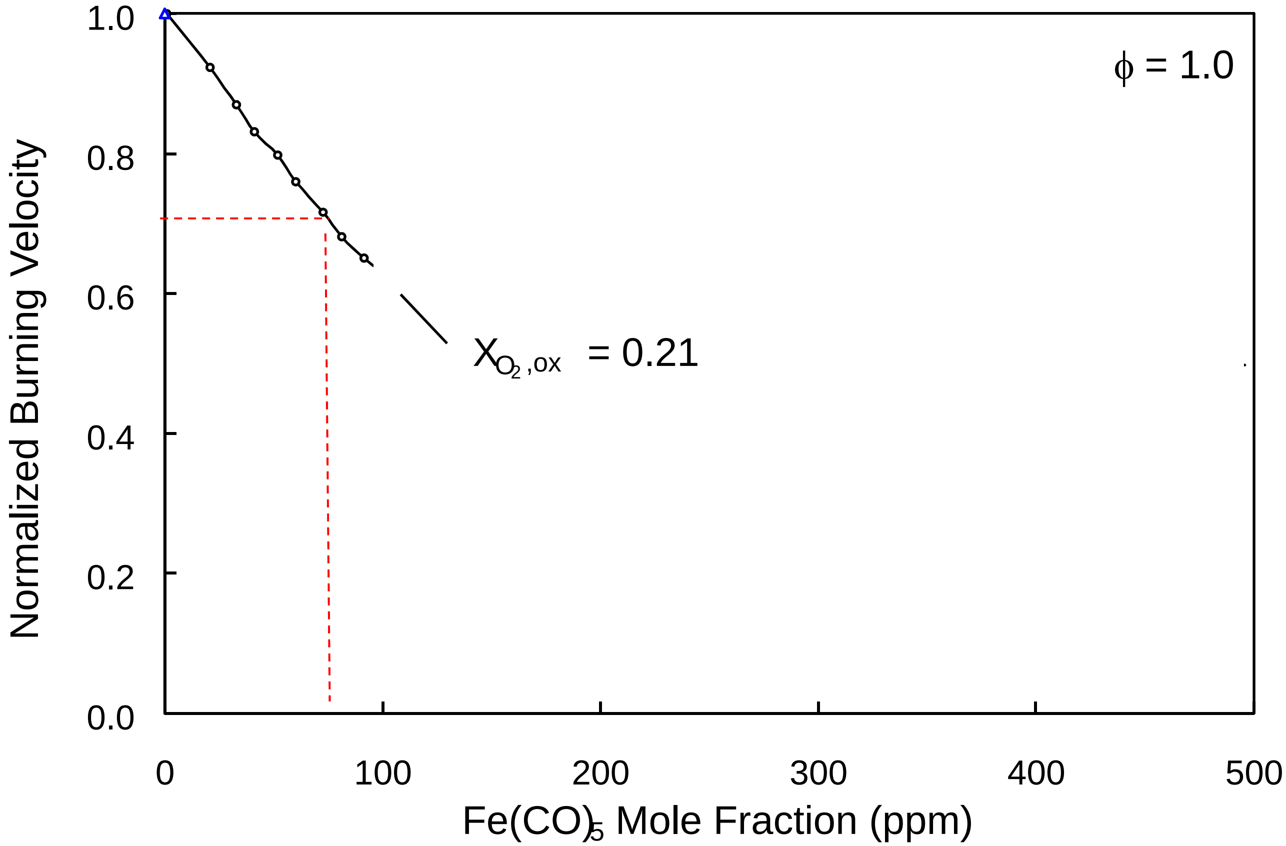
⇒ Because HBr regeneration steps are higher in base

Other Flame Properties Influencing Inhibitor Effectiveness

(Random thoughts)

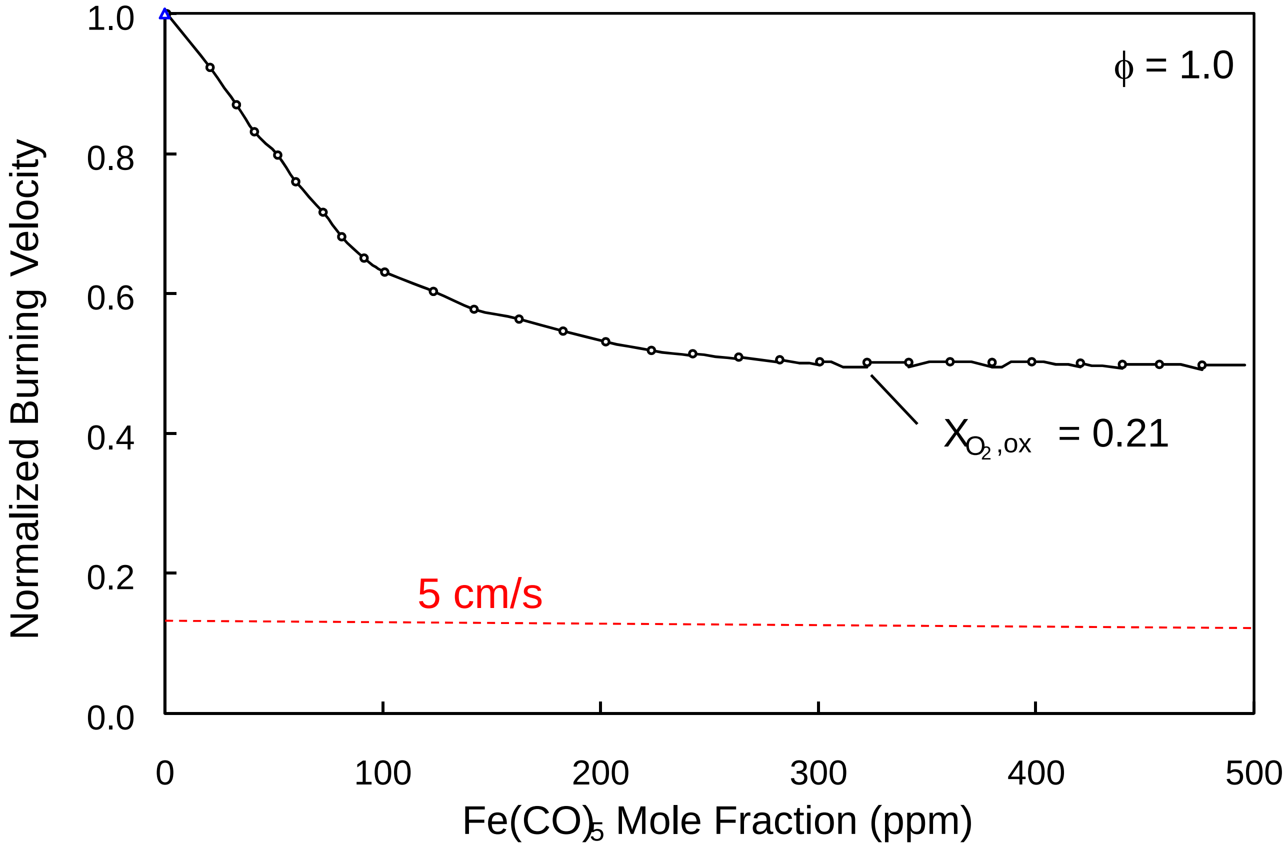
Different flame metrics influence effectiveness:

=> X_a for 30% reduction in flame speed would imply high effectiveness,



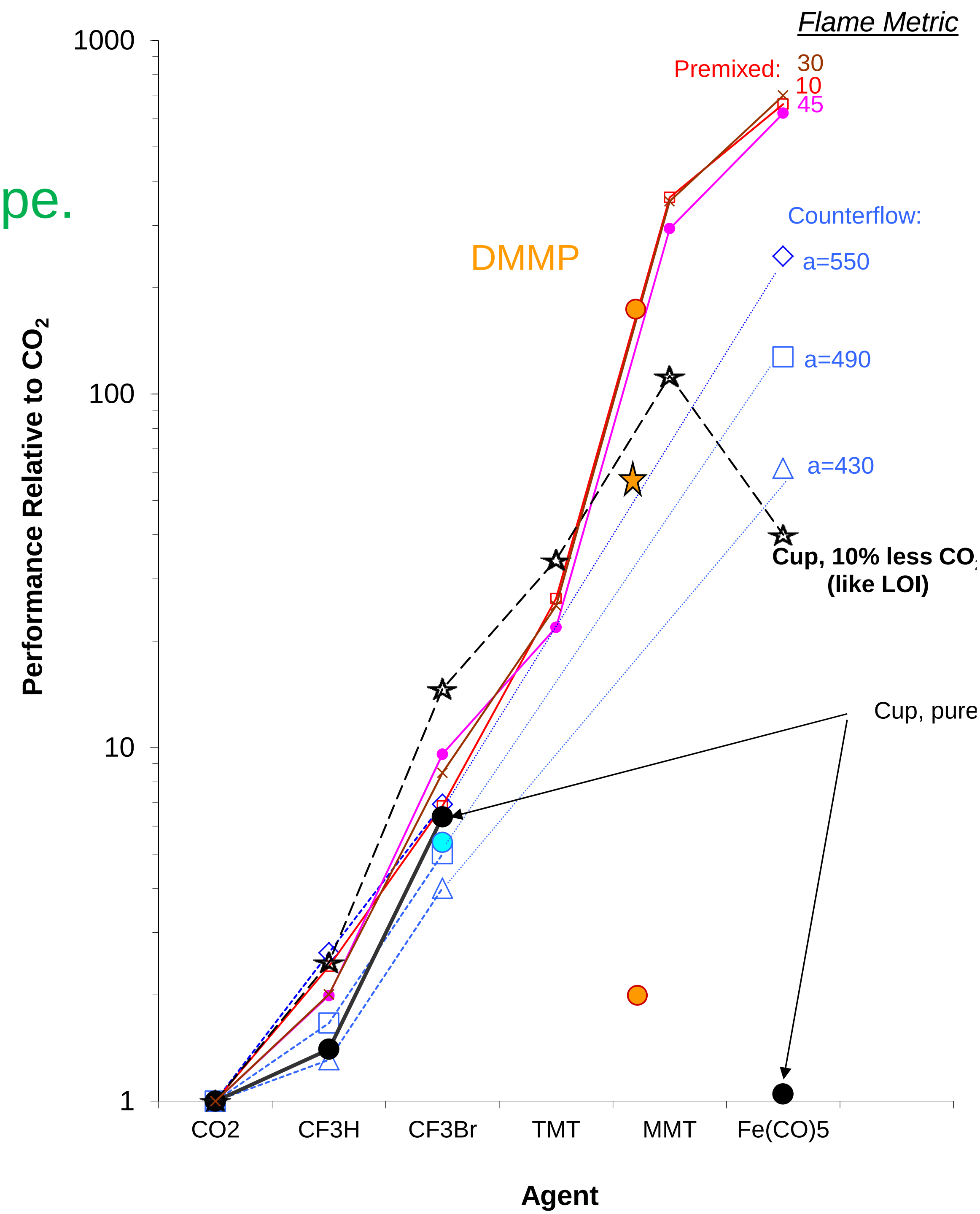
=> but, X_a for 5 cm/s flame speed would imply low effectiveness,

Different behavior sometimes shows up at higher concentrations.



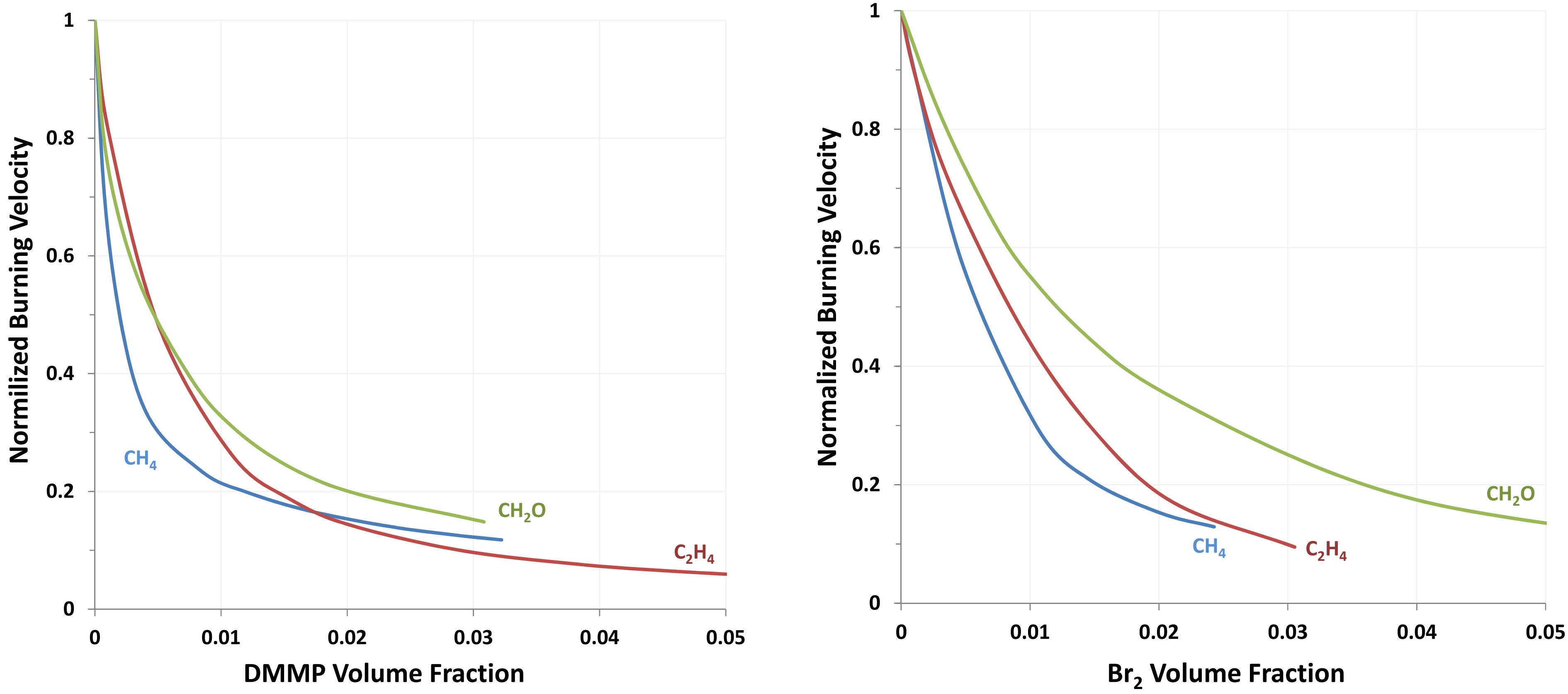
Agent Effectiveness:

=>can vary with flame type.



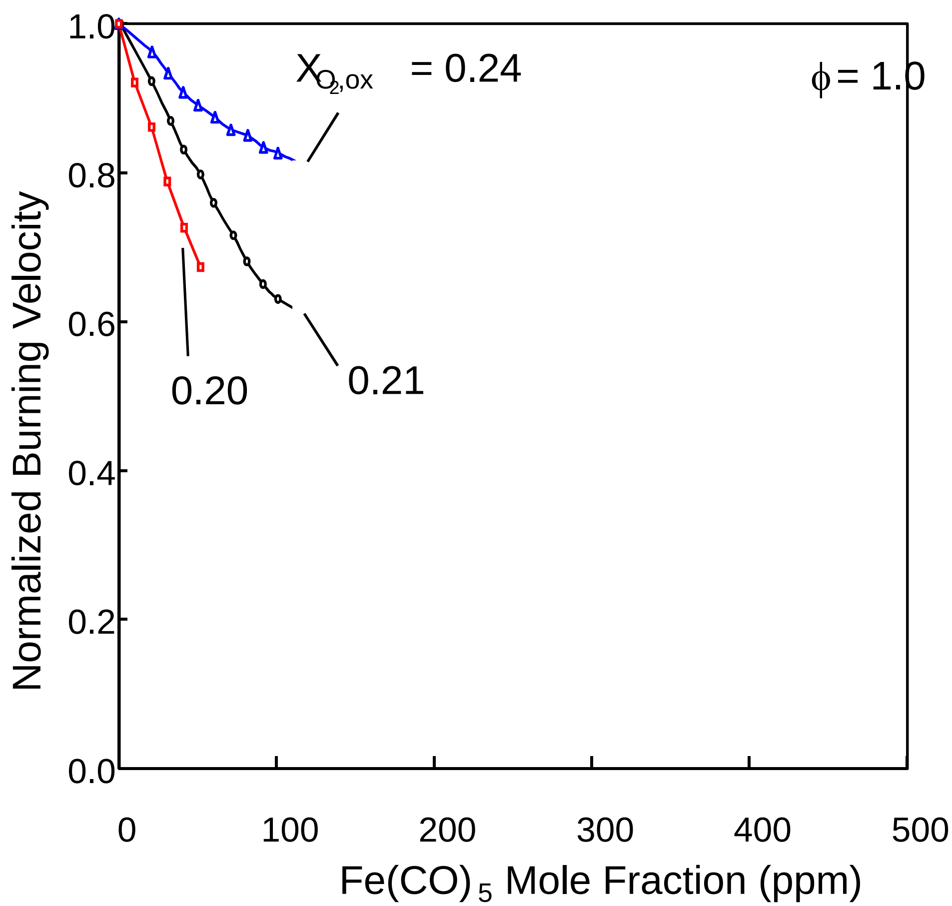
Fuel Type Can Influence Inhibitor Effectiveness

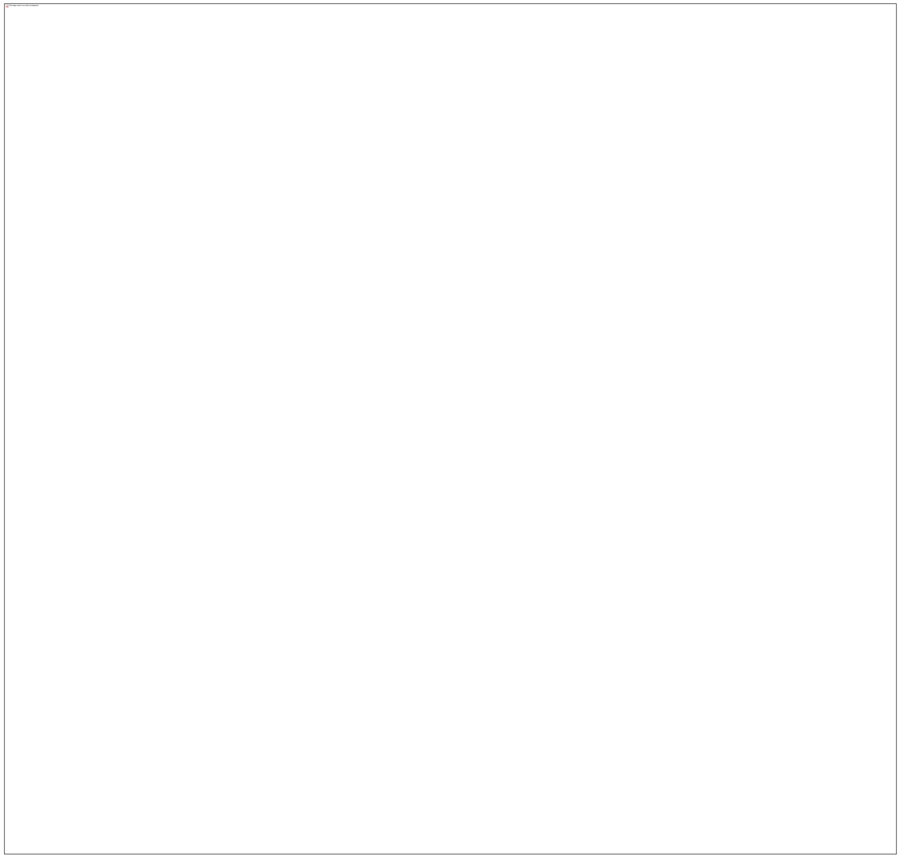
⇒ In premixed flame,
Br_2 affected more than DMMP by fuel type (for CH_4, C_2H_4, CH_2O)



Flame Temperature Affects Inhibition Efficiency

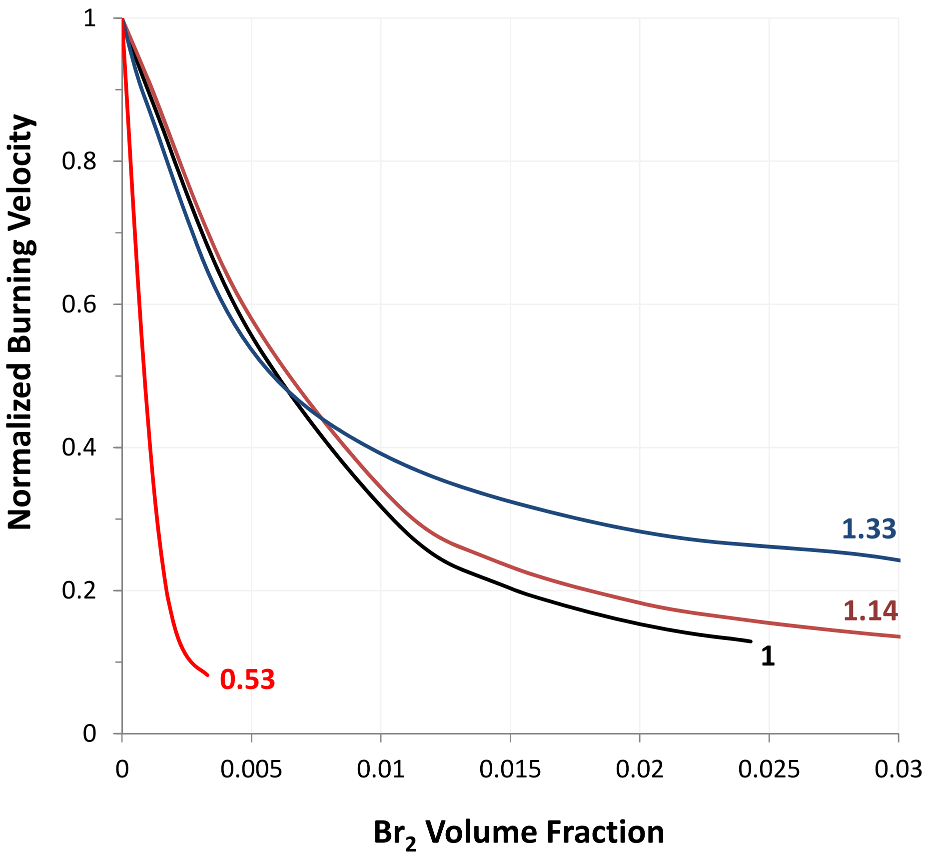
=> Cooler flames are inhibited more (for either Fe or DMMP).

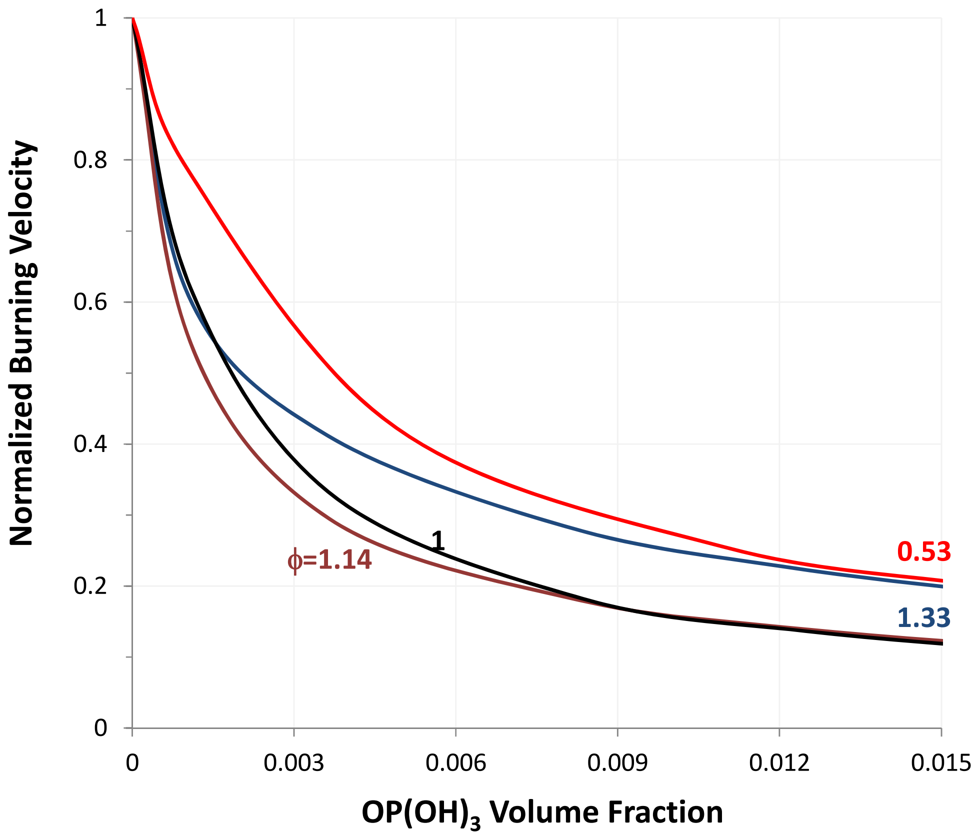




Stoichiometry Affects Inhibitor Efficiency

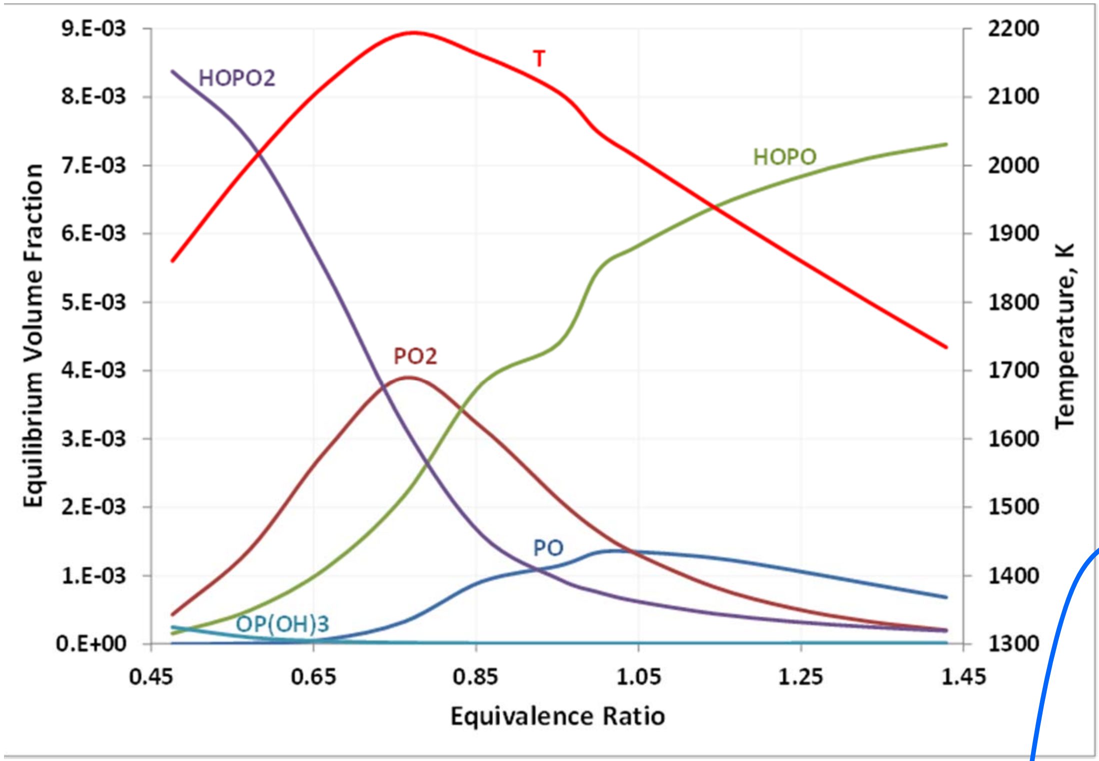
=>lean flame inhibited much more for Br_2 than for H_3PO_4.



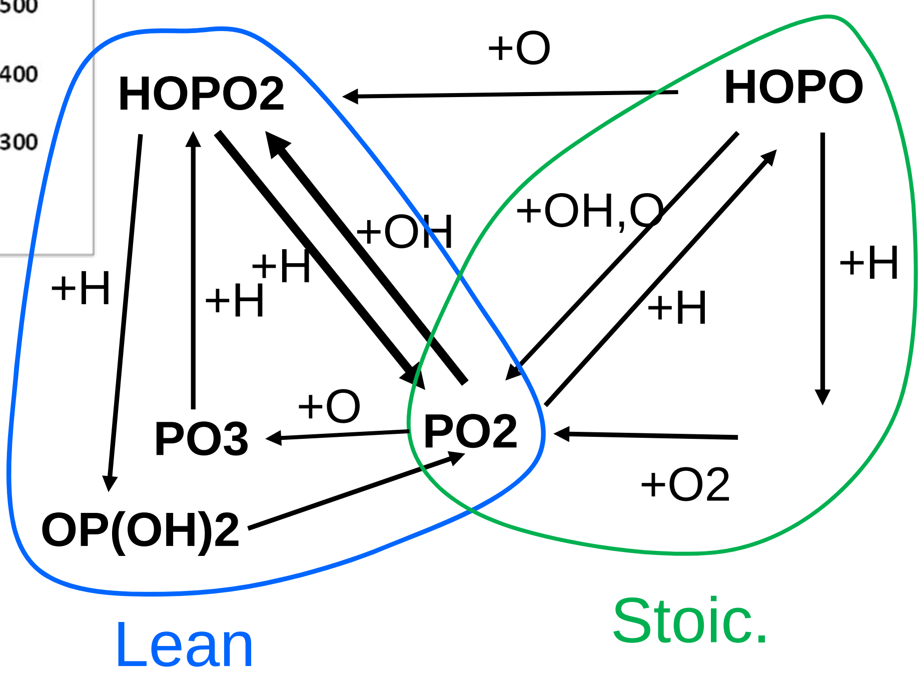


Stoichiometry Affects Inhibitor Efficiency

=>can be explained by thermodynamics



P catalytic inhibition cycle



Bottom Line:

1. Characteristics of flame system affect efficiency of chemical inhibition (via flicker, heat losses/stand-off, stabilization mechanisms, mixing conditions, etc.), BUT

2. Inhibitors can influence the physical properties of the flame itself (where and how the flame stabilizes, temperature, flow field, etc.) and hence the inhibition.

3. Most of the physical properties of the flames over polymers which can affect chemical inhibition have not been studied (even more so if a condensed-phase FR is also working).

Future Work:

1. Have excellent tools for understanding gas-phase action of fire retardants.

2. Use detailed modeling to understand:
   a. Why DMMP did not work well in cup burner.
   b. Why antimony / bromine systems does work well
      - Sb? Br? Why no condensation?

3. Study flames with polymers with FRs.

4. Use numerical code to model burning cylinder (simulating UL-94)

4. Systems of interest?

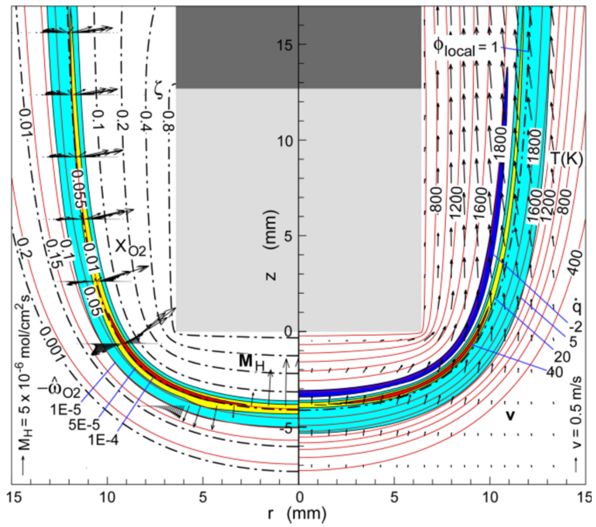
Numerical simulations to understand UL-94

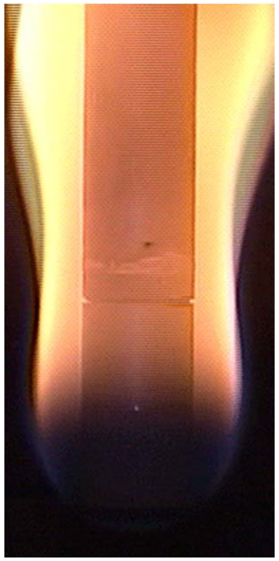
- Porous cylinder flames
  - Resemble solid burning (e.g., UL 94)
  - Perform time-dependent axisymmetric computation with full chemistry/transport for:

  - DMMP added to fuel
  - Br_2 added to fuel

PMMA in air

18% CO_2





CH_4 in air

15% CO_2

Questions?