Correlation between molecular structure and global combustion properties for surrogate fuel modeling:

Extinction Limit, Radical Index, and Flame Speed

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Introduction: Surrogate Fuel Model Development

- **Synthetic fuels have to be used by blending with jet fuel:**
  - normal, branched, and cyclo alkanes, and aromatics

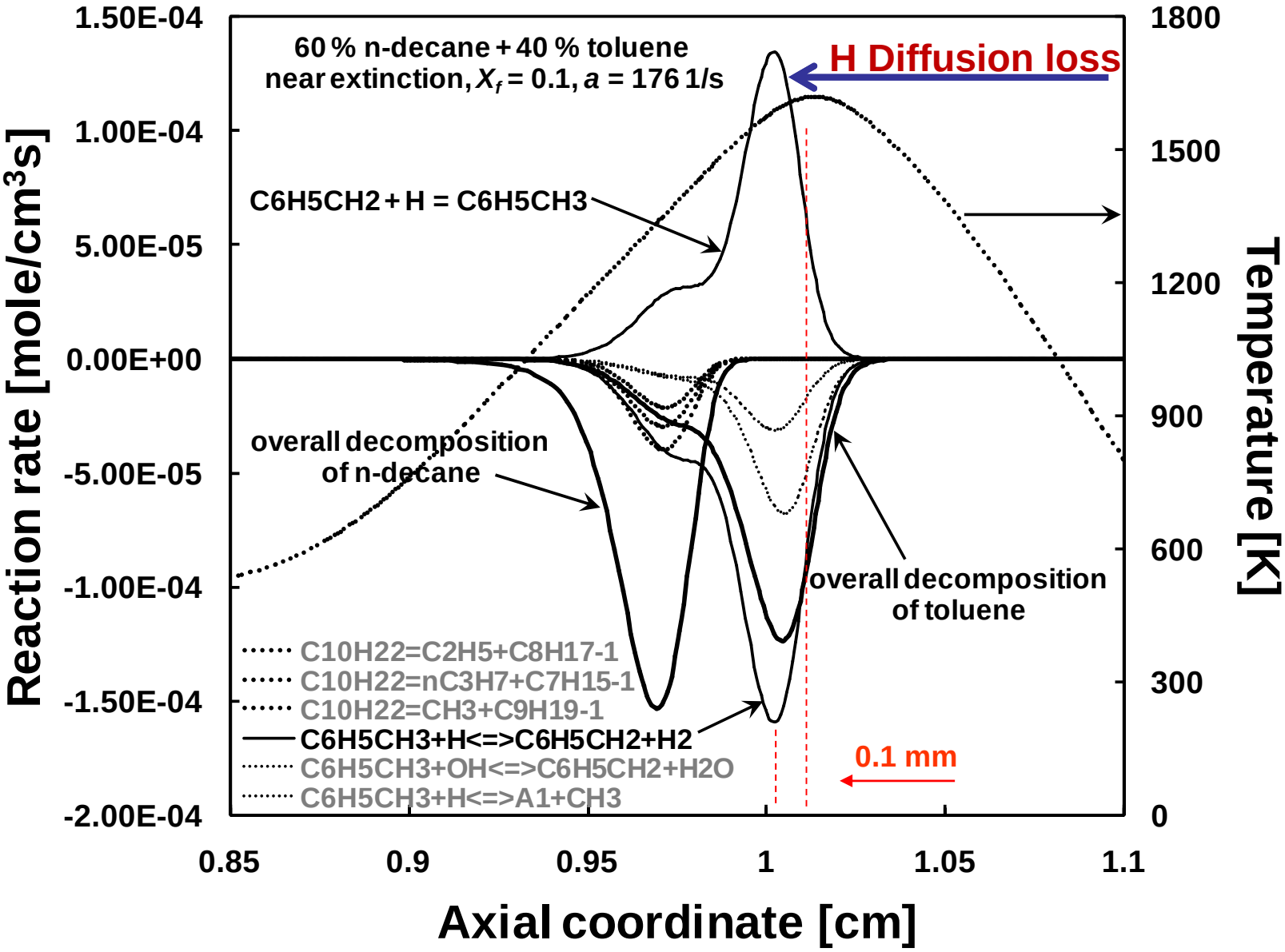
- **MURI team selected surrogate jet fuel components**
  - n-decane, methyl-cyclohexane, n-propyl- and trimethyl- benzenes, toluene…

- **Goals:**
  - **Identify an aromatic fuel candidate for surrogate component**
  - **Obtain fundamental flame data**
  - **Identify the correlation between fuels with different molecular structures and global burning properties for surrogate fuel model construction**

Previous work and findings

- **Strong kinetic coupling between n-decane and toluene.**
- **Diffusion flame extinction of n-decane/toluene is governed by the peak OH radical concentration.**
- **Fuel chemistry and transport affect diffusion flame extinction limit.**
- **A multi-timescale (MTS) and multi-generation path flux analysis model reduction method were developed.**

Example: Complexity in Flame Chemistry: Kinetic coupling between n-decane and toluene in flames



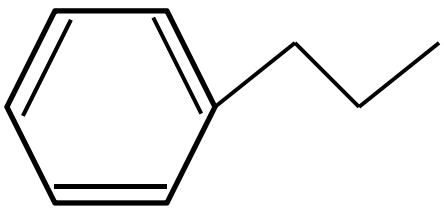
Won, Sun, Dooley, Dryer, and Ju, CF 2010

The questions to answer:

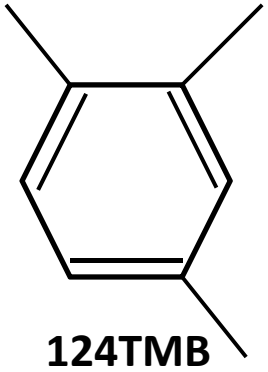
- **Will n-propyl- and trimethyl- benzenes with same H/C & molecule weight and similar "T_{ad}" have different extinction limits?**
- **Will the MURI generic rule for surrogate fuel model really work for both flames and ignition?**
- **How do we create a correlation between global flame properties and fuel chemical and transport properties?**
- **What are the uncertainties in experimental measurements of global flame properties?**
- **How does the PFA model reduction approach work for surrogate fuel mixtures?**

1. Experimental Studies of Molecule Structure of Aromatics on Diffusion Flame Extinction Limits

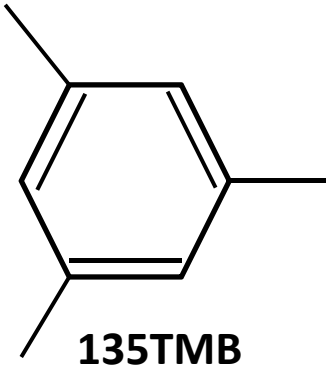
- **Four aromatics**
  - Toluene,
  - n-propylbenzene, 124- and 135- trimethylbenzenes
    - Same H/C ratio, molecular weight (C_9H_{12}), flame temperature



nPB

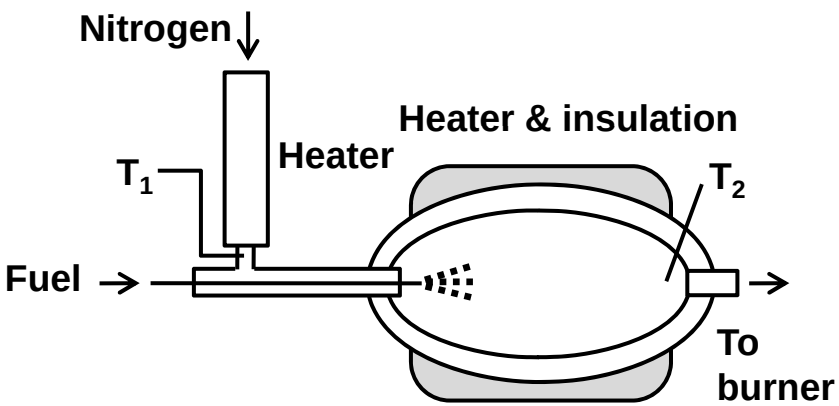


124TMB

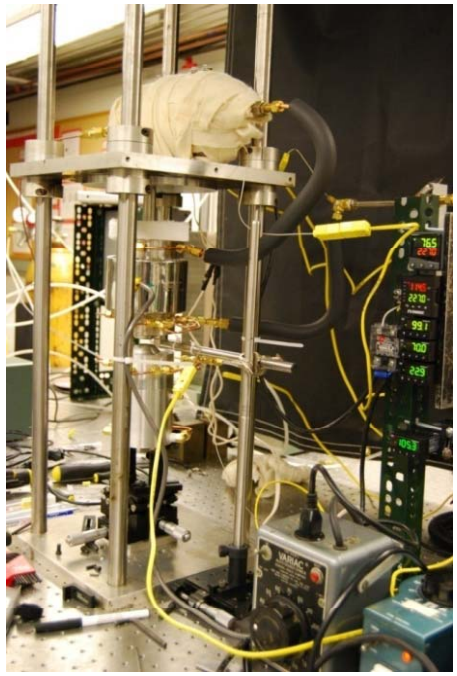


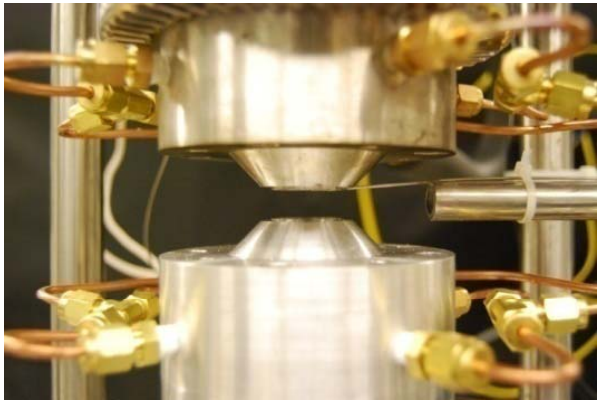
135TMB

- **Experimental setup: extinction limits**
  - Using FTIR measurements to check thermal decomposition and concentration variation: Concentration fluctuation < 1%
  - OH radical measurement: Q1(6) excitation ~ 282.93 nm



Schematics of evaporation system

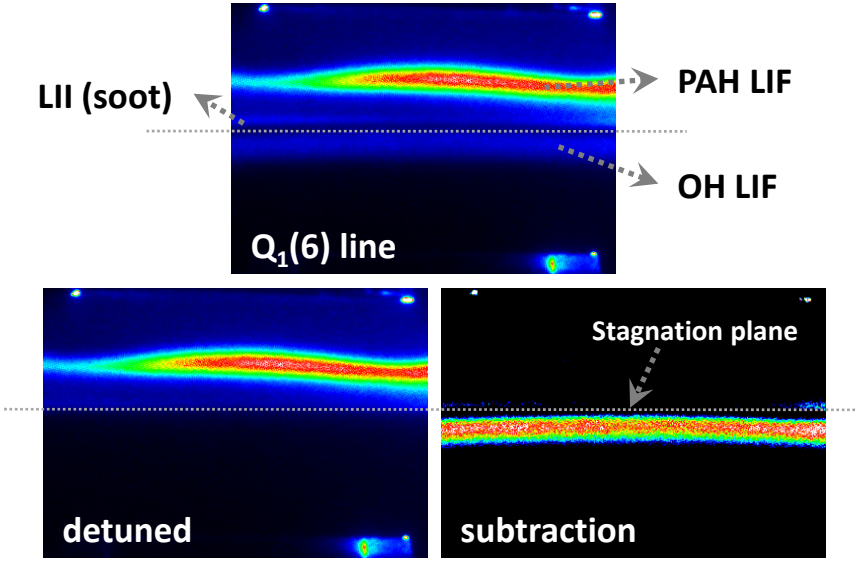




Experimental Measurements of OH Concentration
by using laser induced fluorescence

- Nd:YAG Laser : Quanta-Ray (532 nm), Cobra-stretch dye laser
- ICCD Camera : PIMAX-Gen II (Princeton Instrument)
- **PLIF: Q1(6) transition (282.93 nm), linear regime, beam height 80 mm**
  Quenching, Soot, PAH corrections

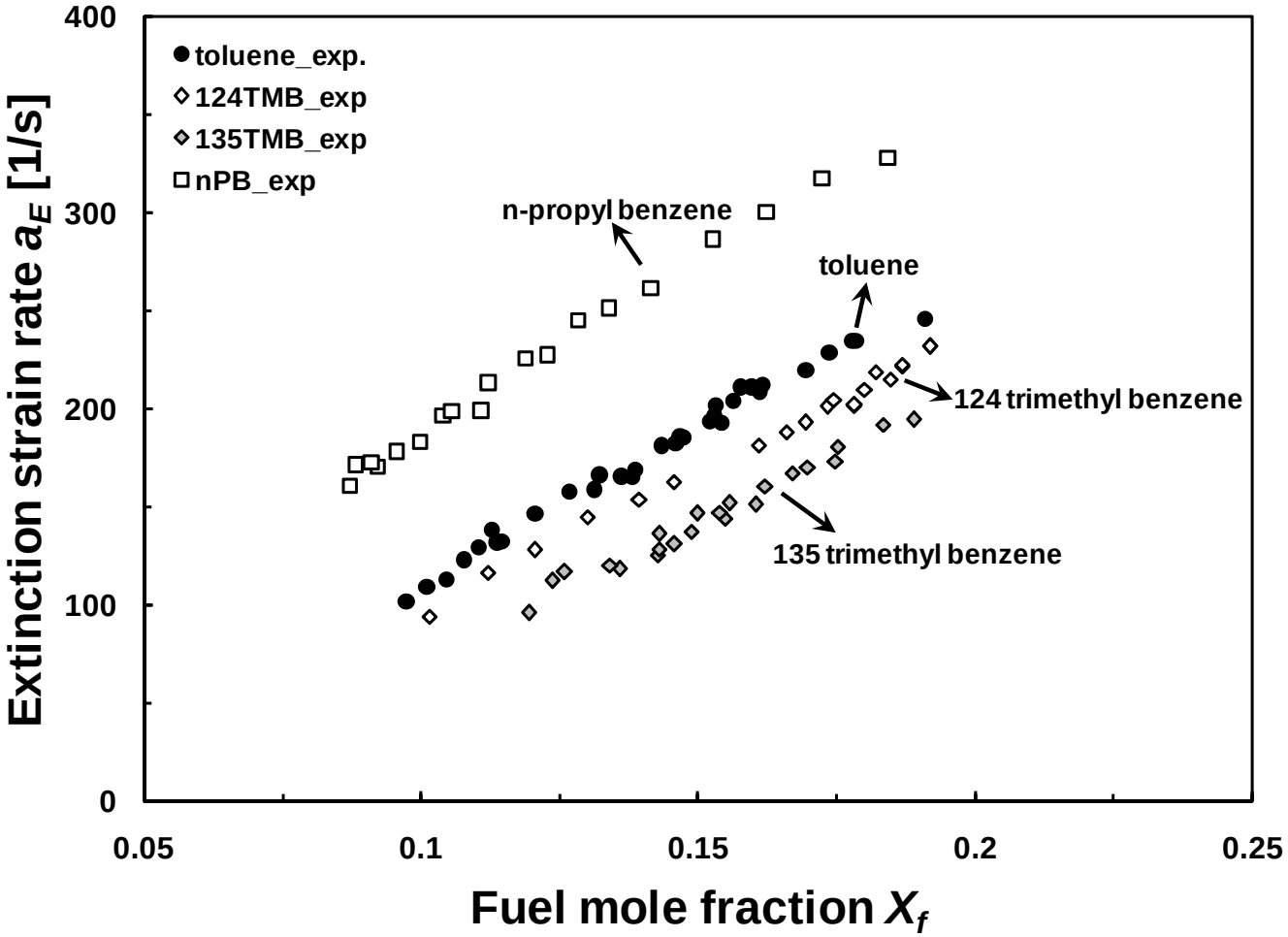
Schematic photo for Rayleigh scattering and PLIF



nPB diffusion flames

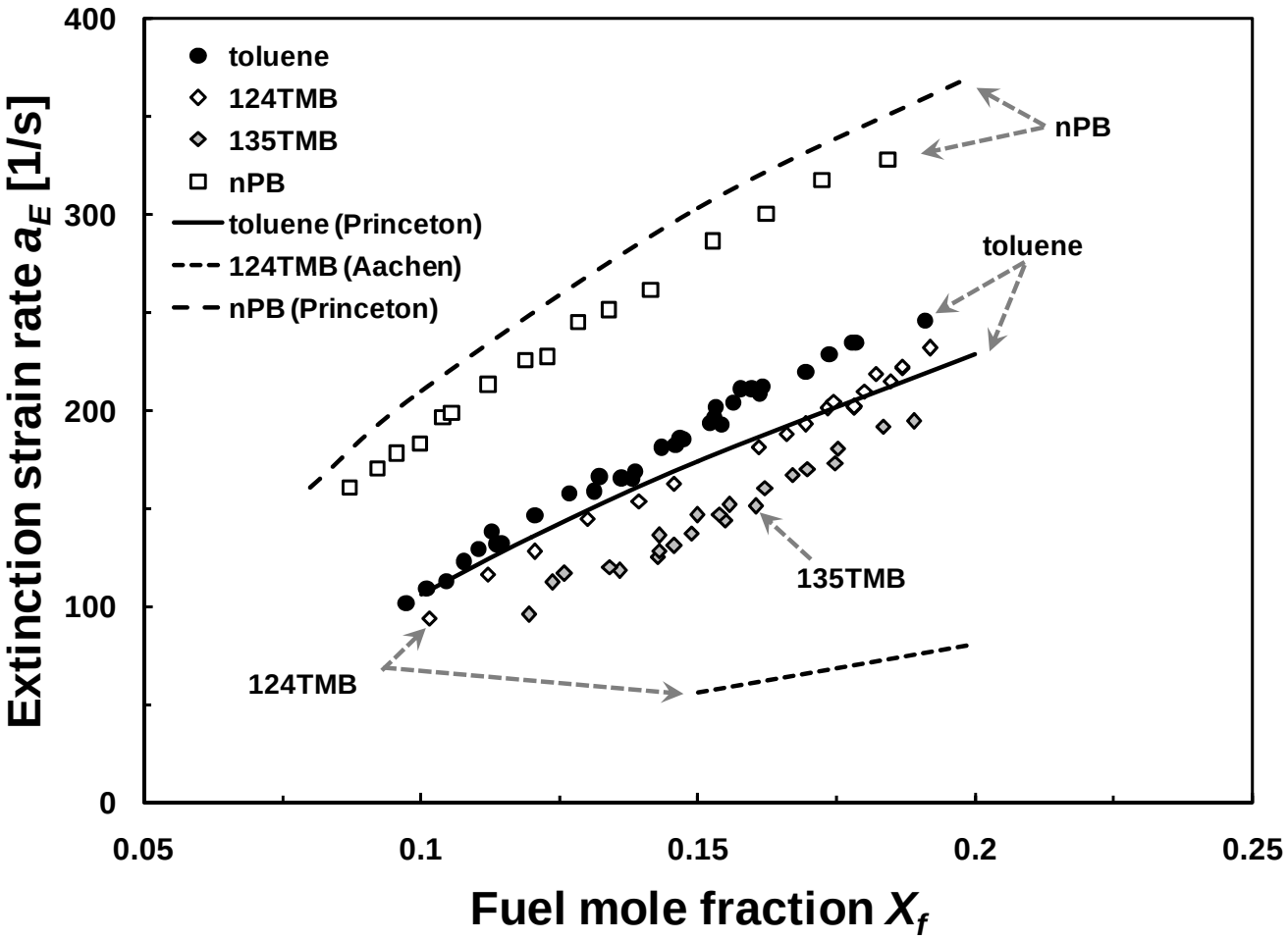
Extinction Limit Comparison

- Extinction limits vary significantly according to fuel structure
  - nPB > toluene > 124TMB > 135TMB
  - **Kinetic effects from the specific fuel chemistry!**

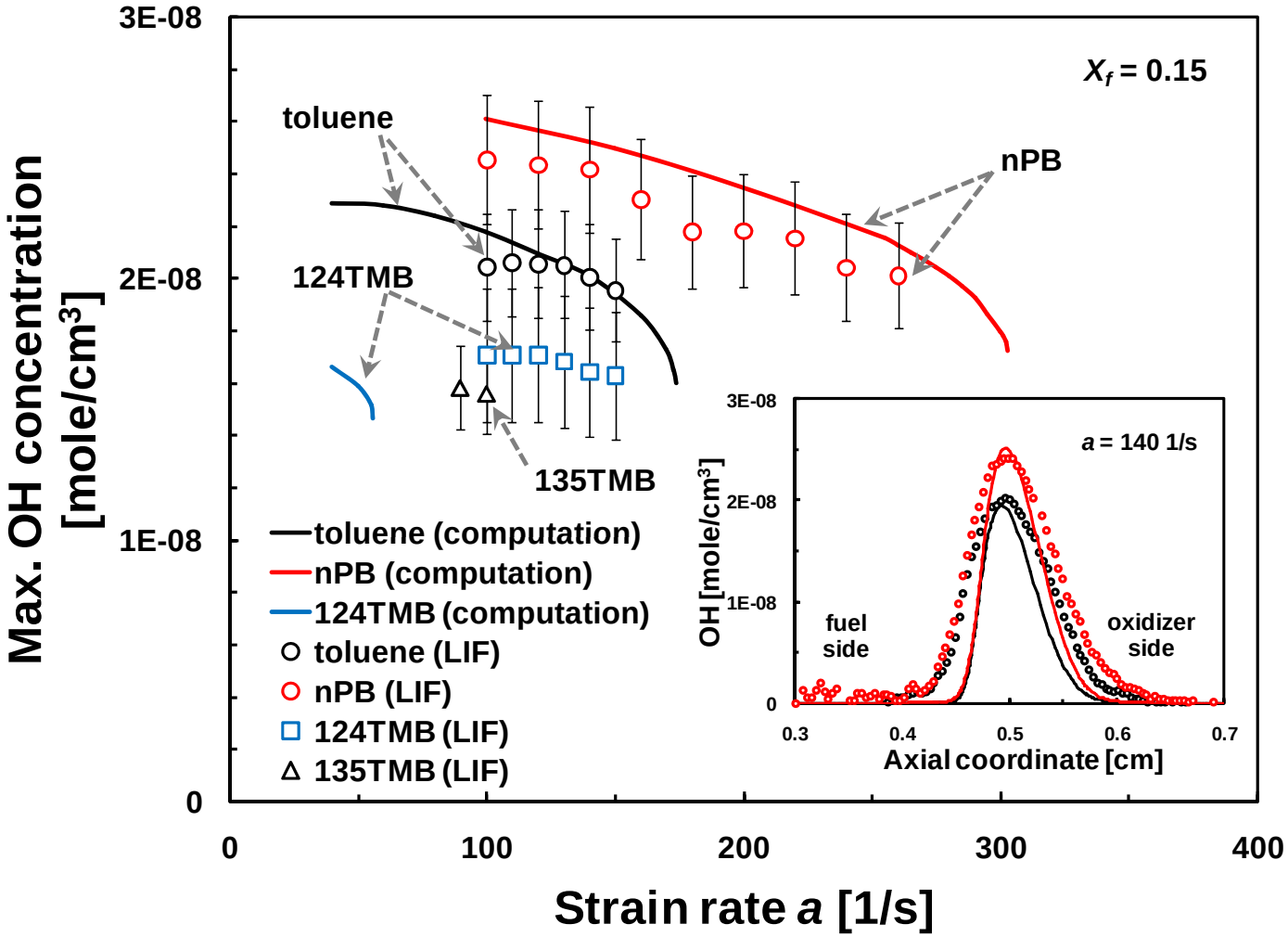


Measurements and Prediction Comparison

- Poor agreement with TMBs, why? Transport or kinetics



OH concentrations and comparisons



- $[OH]_{max}$ proportional to the extinction strain rates
- $[OH]_{max}$: nPB > toluene > 124TMB > 135TMB

2. Surrogate Model Flame Validation on Jet POSF 4658

•**First generation surrogate model (3 components)**

Surrogate Fuel: Mole Fraction			DCN	H/C	MW / g mol^{-1}	TSI
Jet-A POSF 4658			47.1	1.957	142.01	21.4
***n*-decane**	***iso*-octane**	**Toluene**				
0.4267	0.3302	0.2431	47.1	2.01	120.7	14.1

Mechanism compilation: *n*-decane/*iso*-octane/toluene

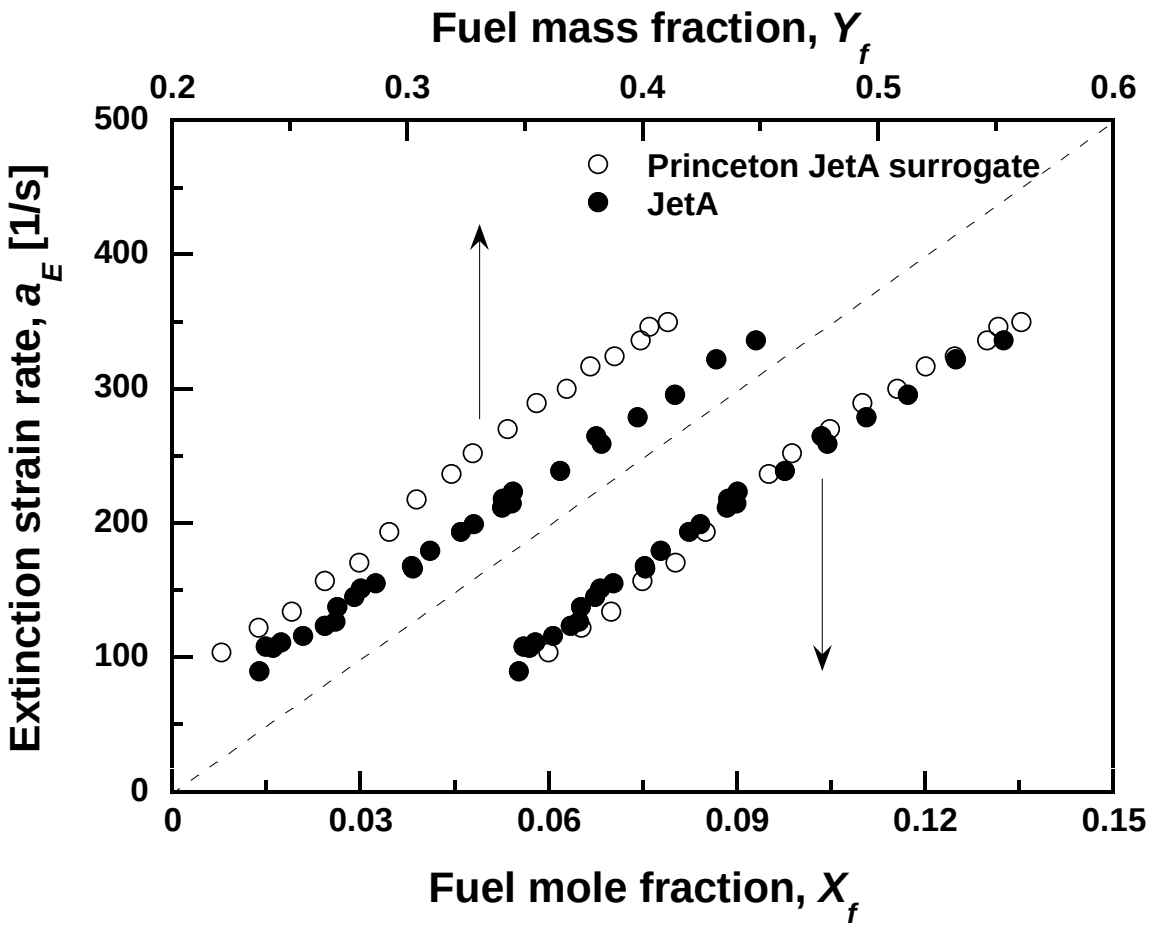
- *n*-decane => Westbrook et al. (LLNL) 2008.
- *iso*-octane => Mehl et al. (LLNL revision of Curran et al.) 2010.
- Toluene => Princeton, (Metcalfe, Dooley and Dryer) 2010.
- C_0-C_4 assembled and tested at Princeton

•**Second generation surrogate model (4 components)**

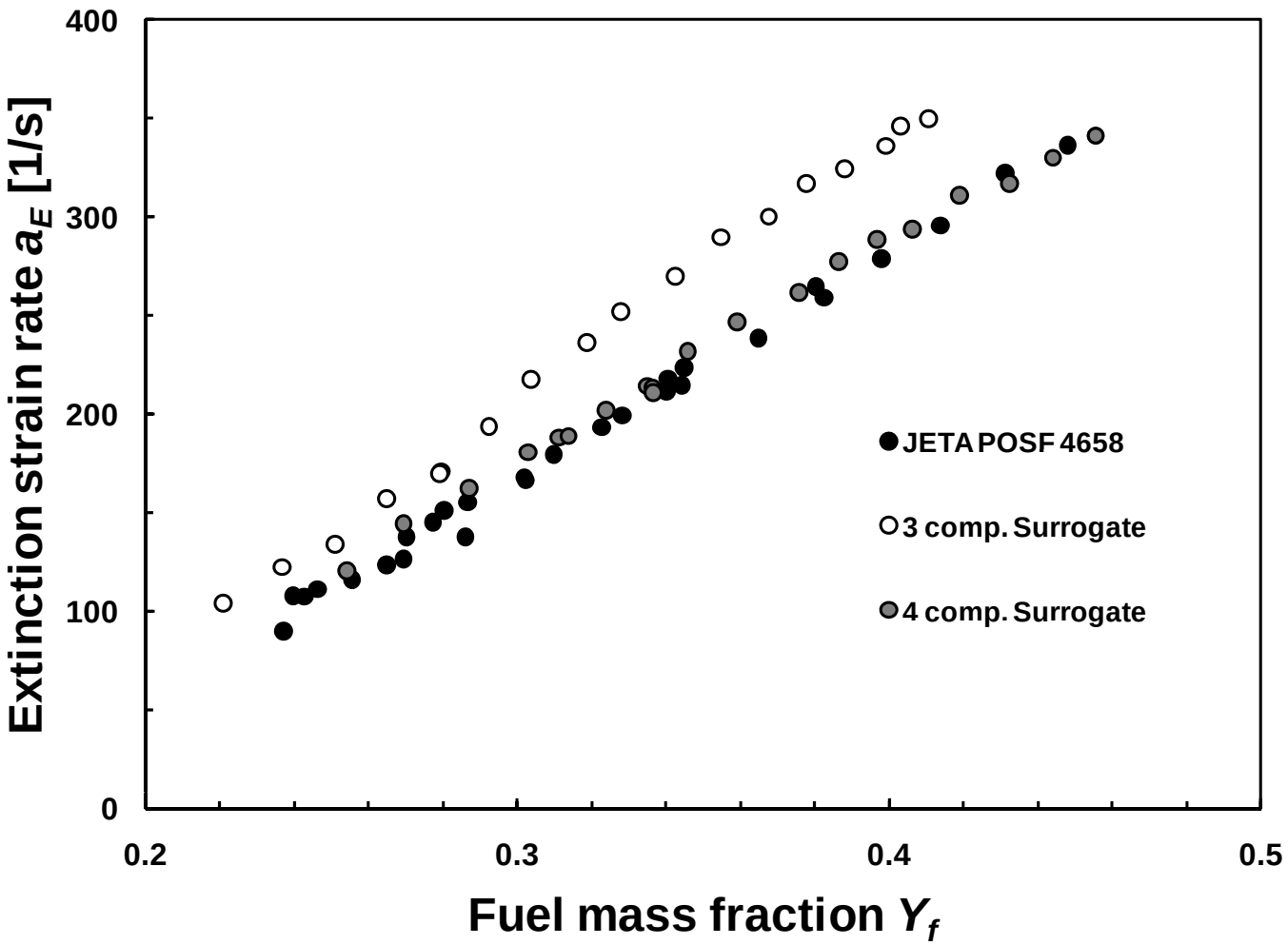
•*n*-dodecane/*iso*-octane/ propyl benzene / 1.3.5 trimethyl benzene

Mole Fraction					DCN	H/C	MW / g mol^{-1}	TSI
Jet-A POSF 4658					47.1	1.957	142.01	21.4
1st Generation surrogate	*n*-decane	*iso*-octane	Toluene		47.1	2.01	120.7	14.1
	0.427	0.33	0.243					
2nd Generation surrogate	*n*-dodecane	*iso*-octane	Mesitylene	n-propyl benzene	48.5	1.95	138.7	20.4
	0.40	029	0.07	0.23				

Validation: Extinction of Diffusion Flames
POSF 4658 vs. first generation surrogate

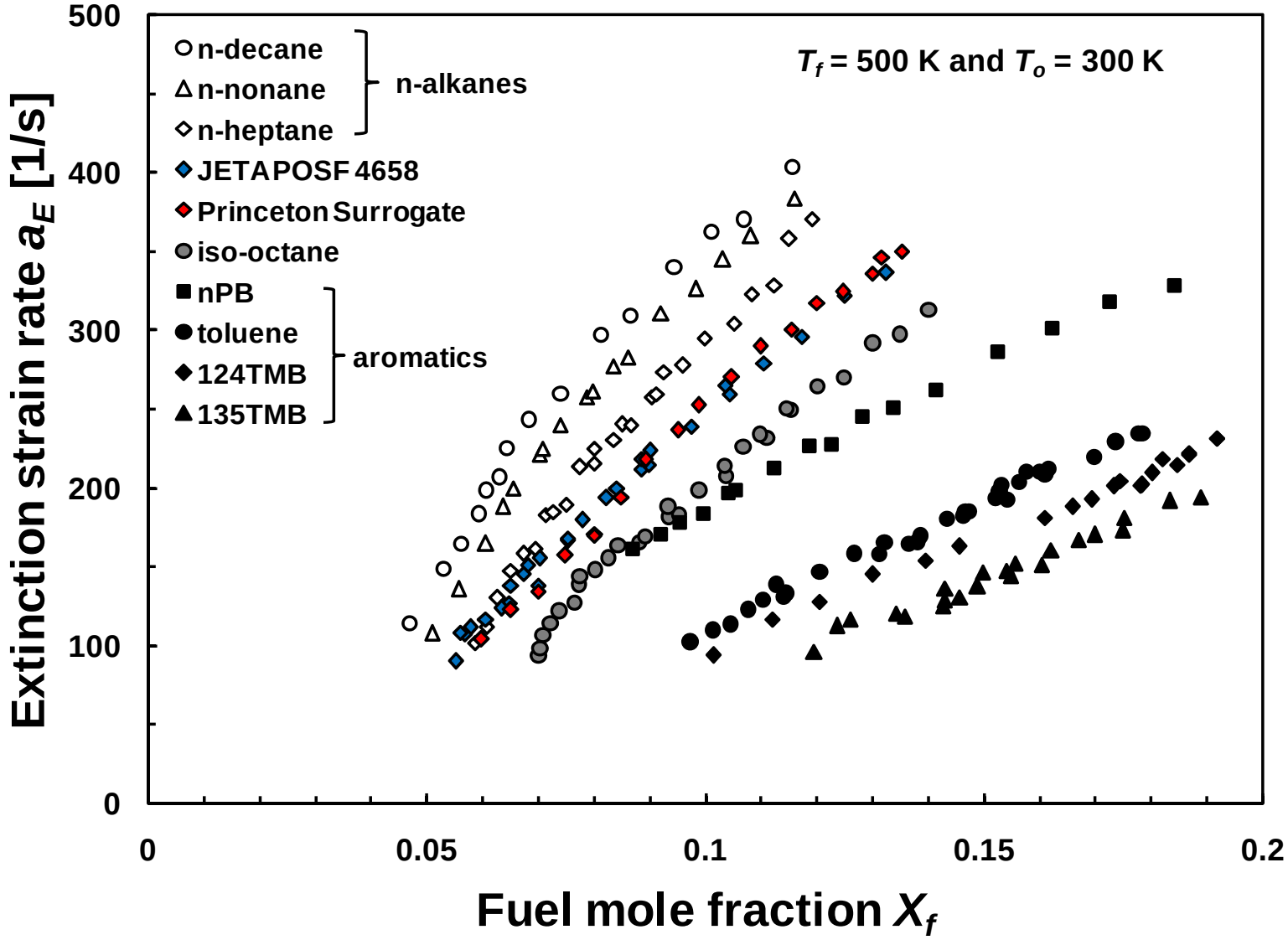


Validation: Extinction of Diffusion Flames
POSF 4658 vs. second generation surrogate

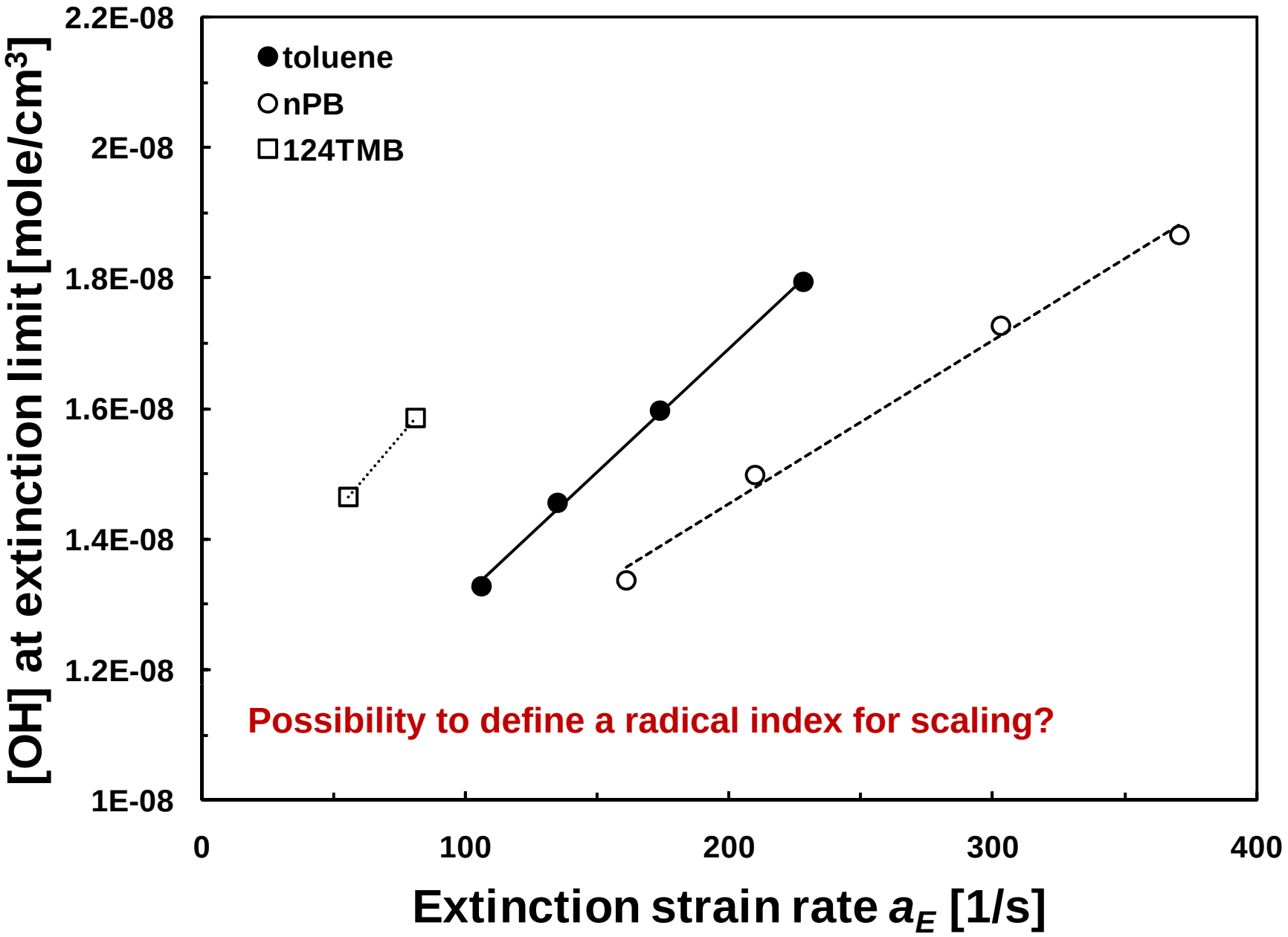


Why?

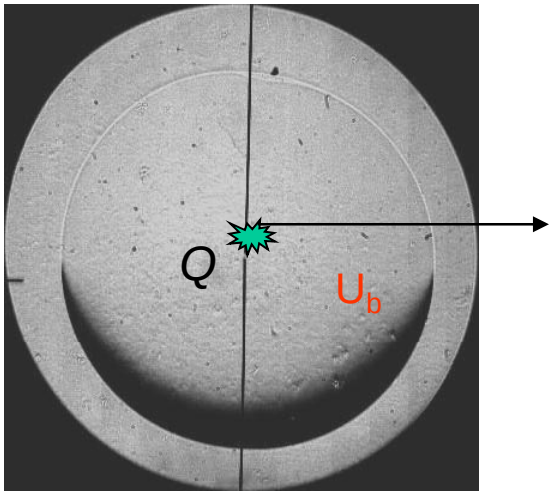
3. Correlations for extinction limit: radical Index

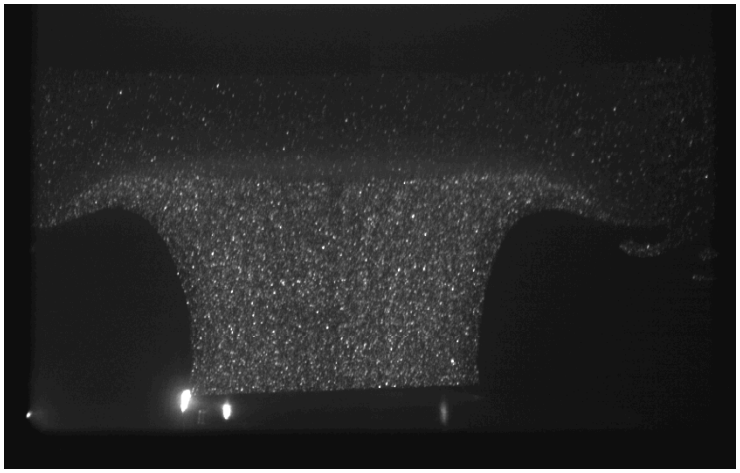


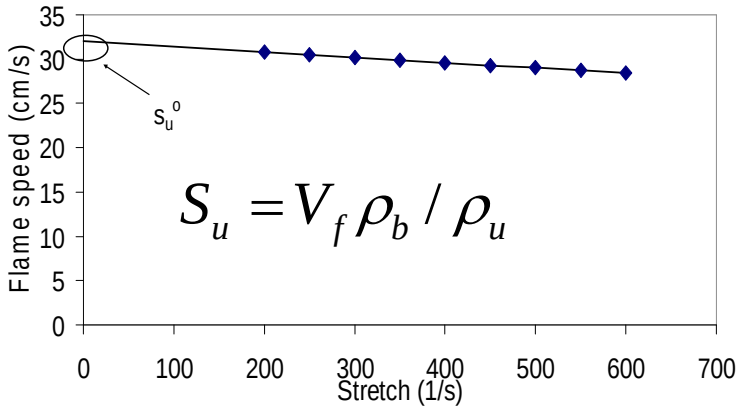
The role of radicals?

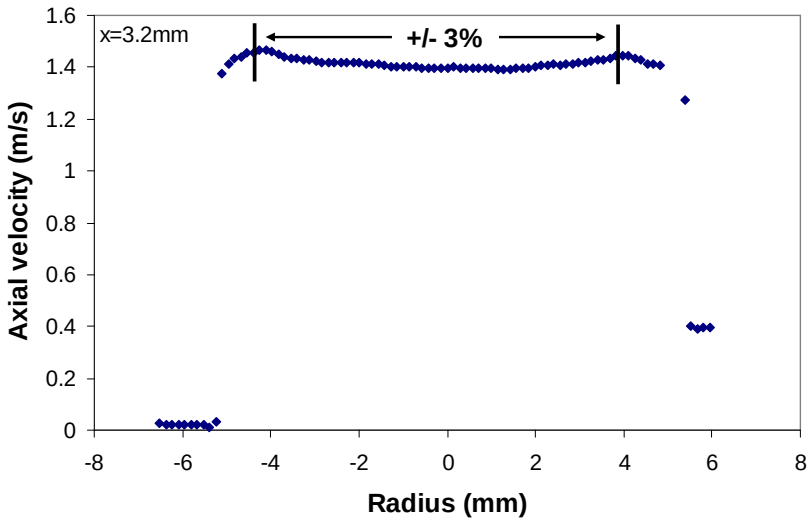


4. Uncertainty in flame speed measurements:
Spherical flames vs. Counterflow flames





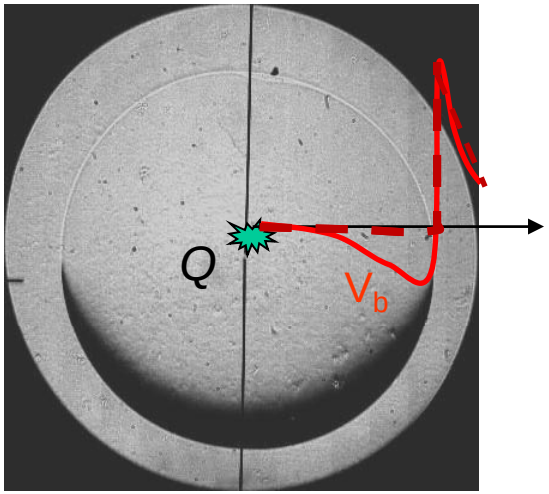


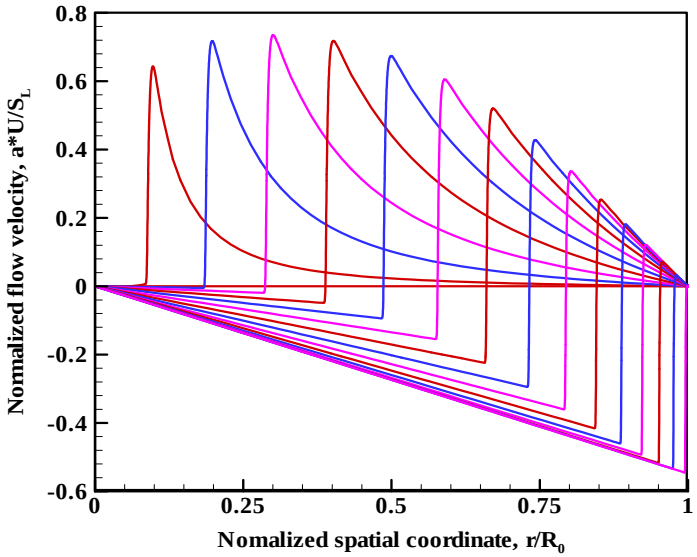


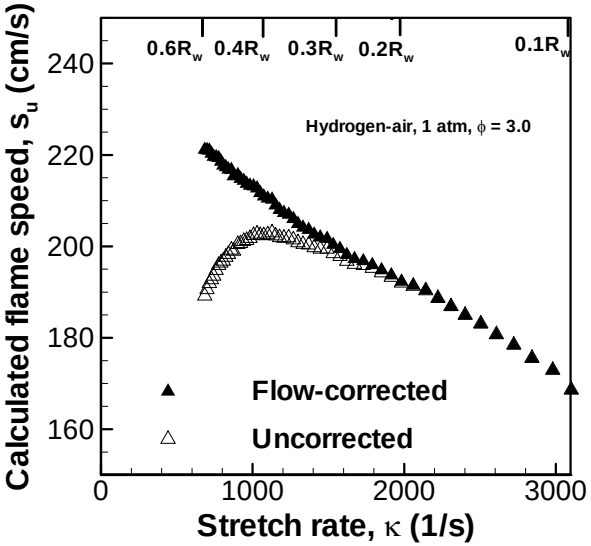
Good experiments?

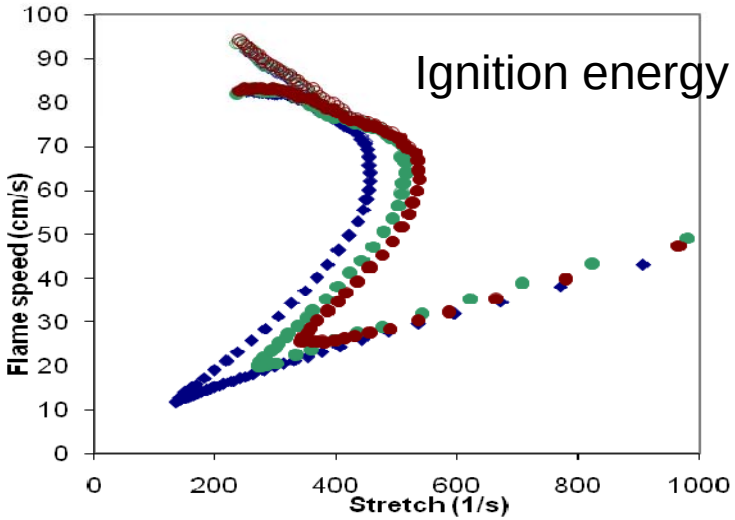
4. Uncertainty in flame speed measurements:

Spherical flames: Effect of flow compression, ignition, and stretch





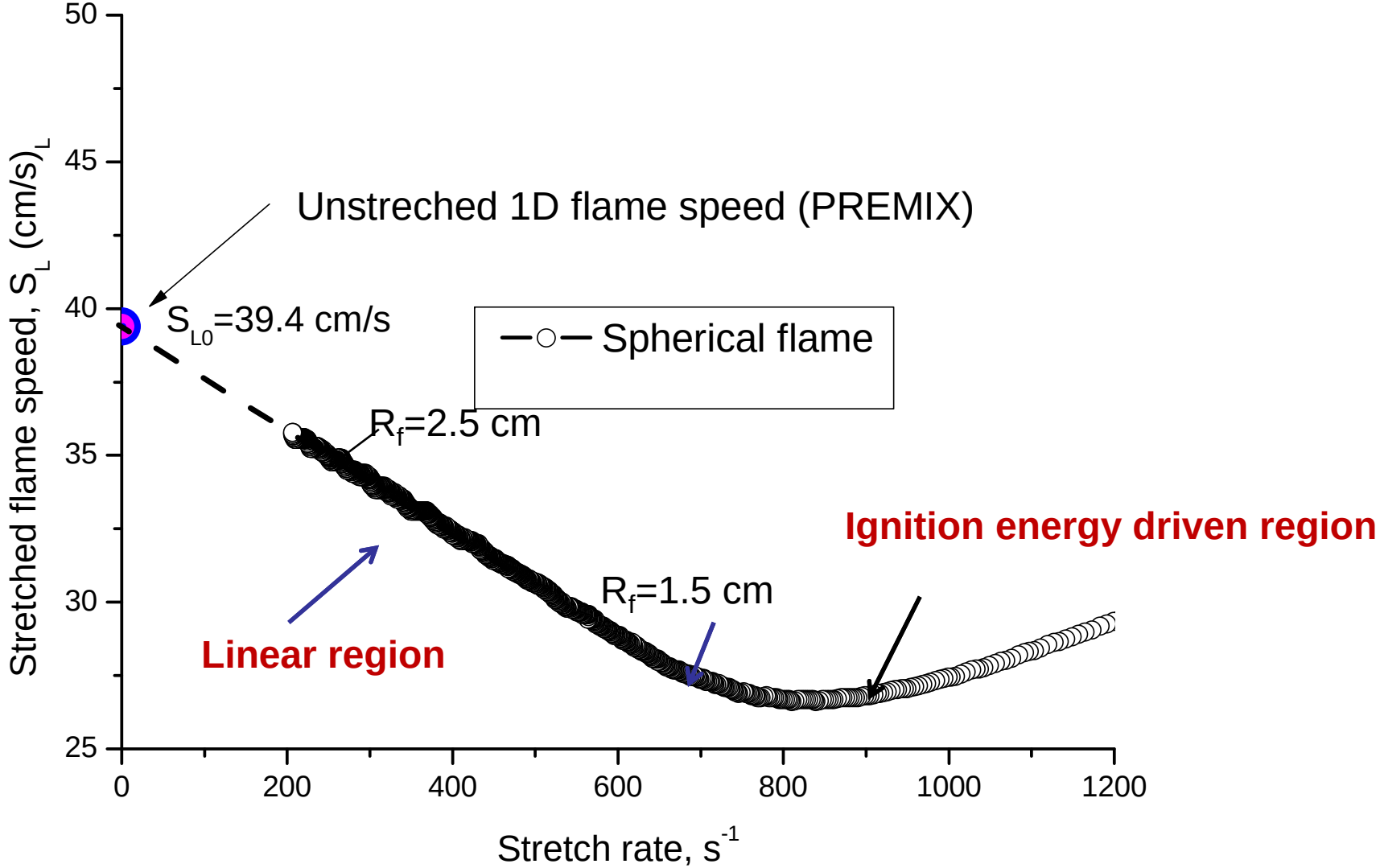




$$S_u = (V_f - V_b)\rho_{b,u} / \rho_u * (\rho_{b,u} / \rho_b)$$

Uncertainty in flame speed measurements: n-heptane/air

Spherical flame: flame speed extraction



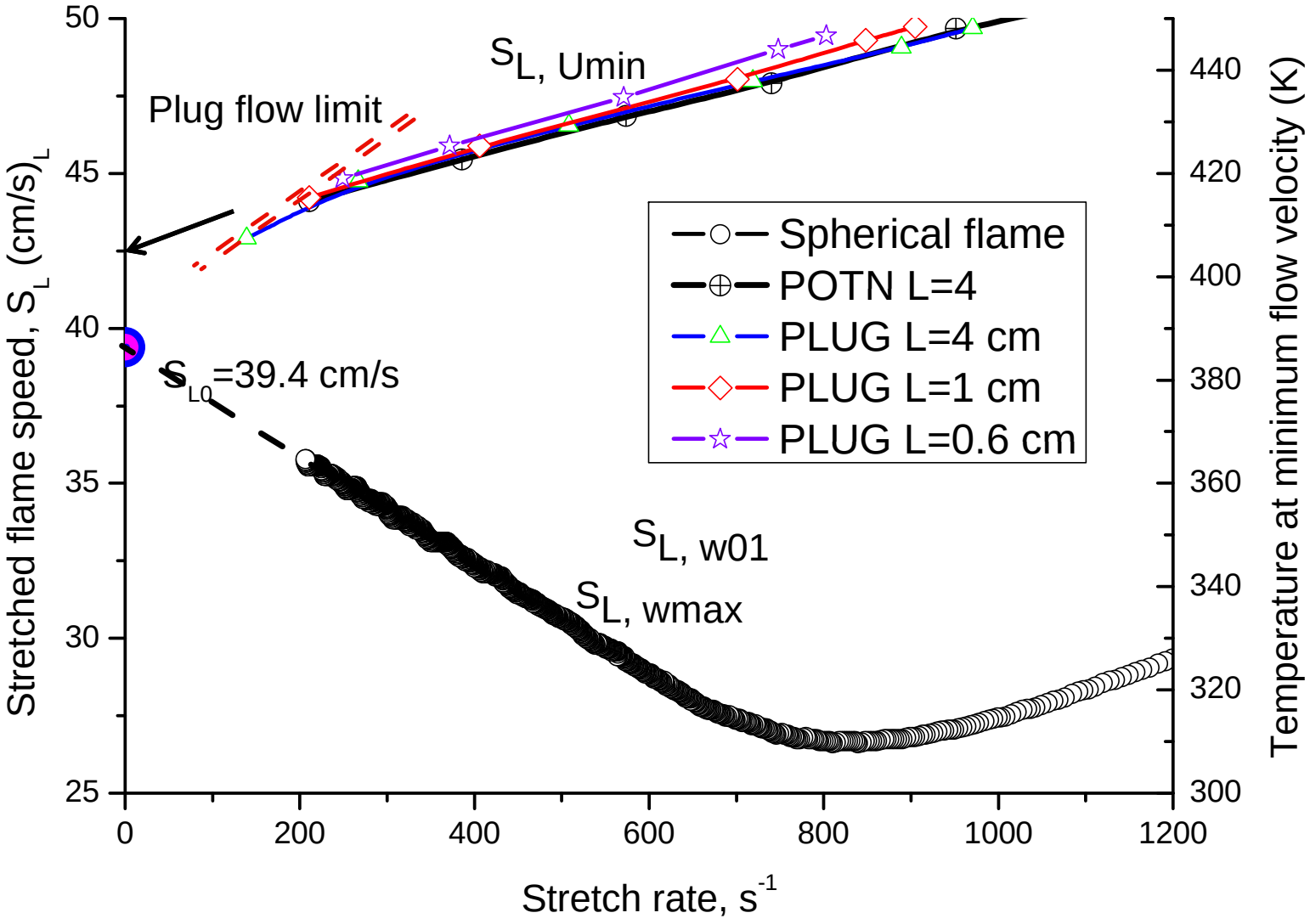
Spherical flame modeling: Multi-generation PFA + MTS + A-SURF1D

(Sun, Gou, Chen, and Ju, CF, 2010)

engine/princeton.edu/downloads

Uncertainty in flame speed measurements: n-heptane/air

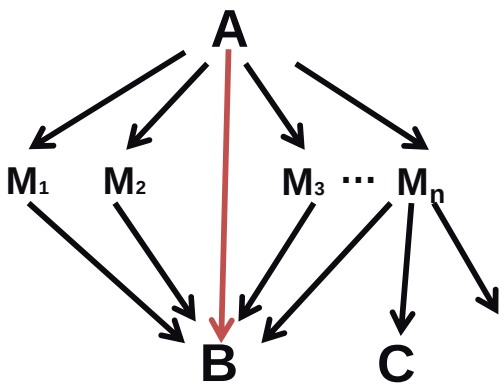
Counterflow flames: flame speed definition and burner separation distance



5. Model reduction for surrogate fuel mixtures using multi-generation PFA method

Challenges:

- **Multiple fuel components and surrogate targets: 3-5 fuels**
- **Unstable flame regimes for large molecule fuels**



Objectives:

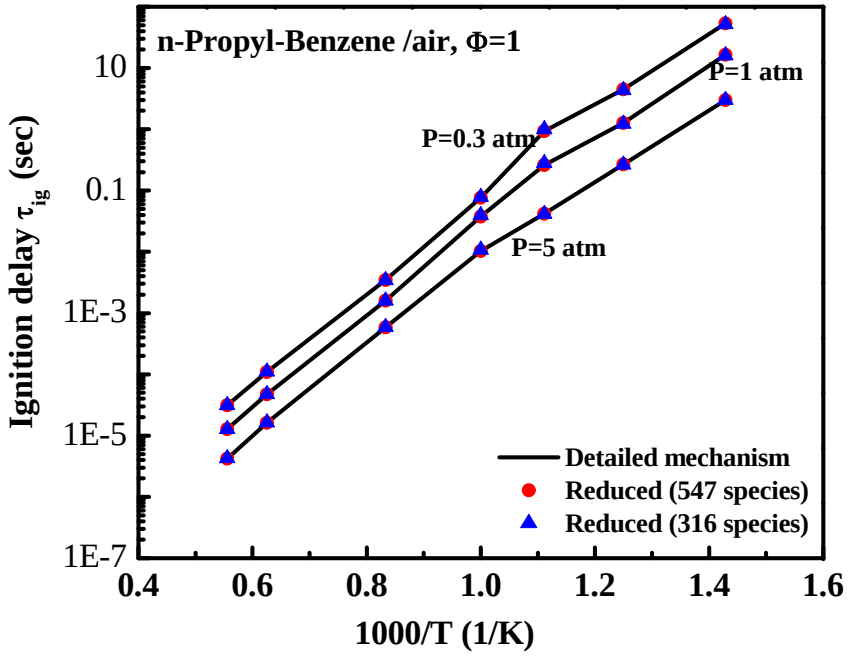
Examine the potential of the multi-generation Path flux analysis (PFA) method for jet fuel surrogates

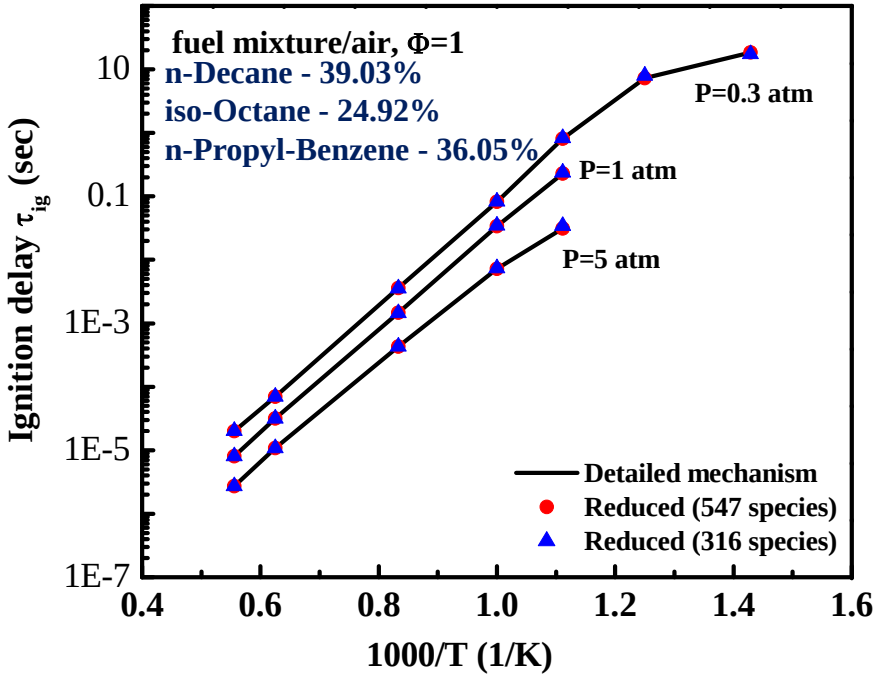
Chem-RC (PFA) download site:
http://engine.princeton.edu

Target models: CSE Kerosene and MURI Surrogates

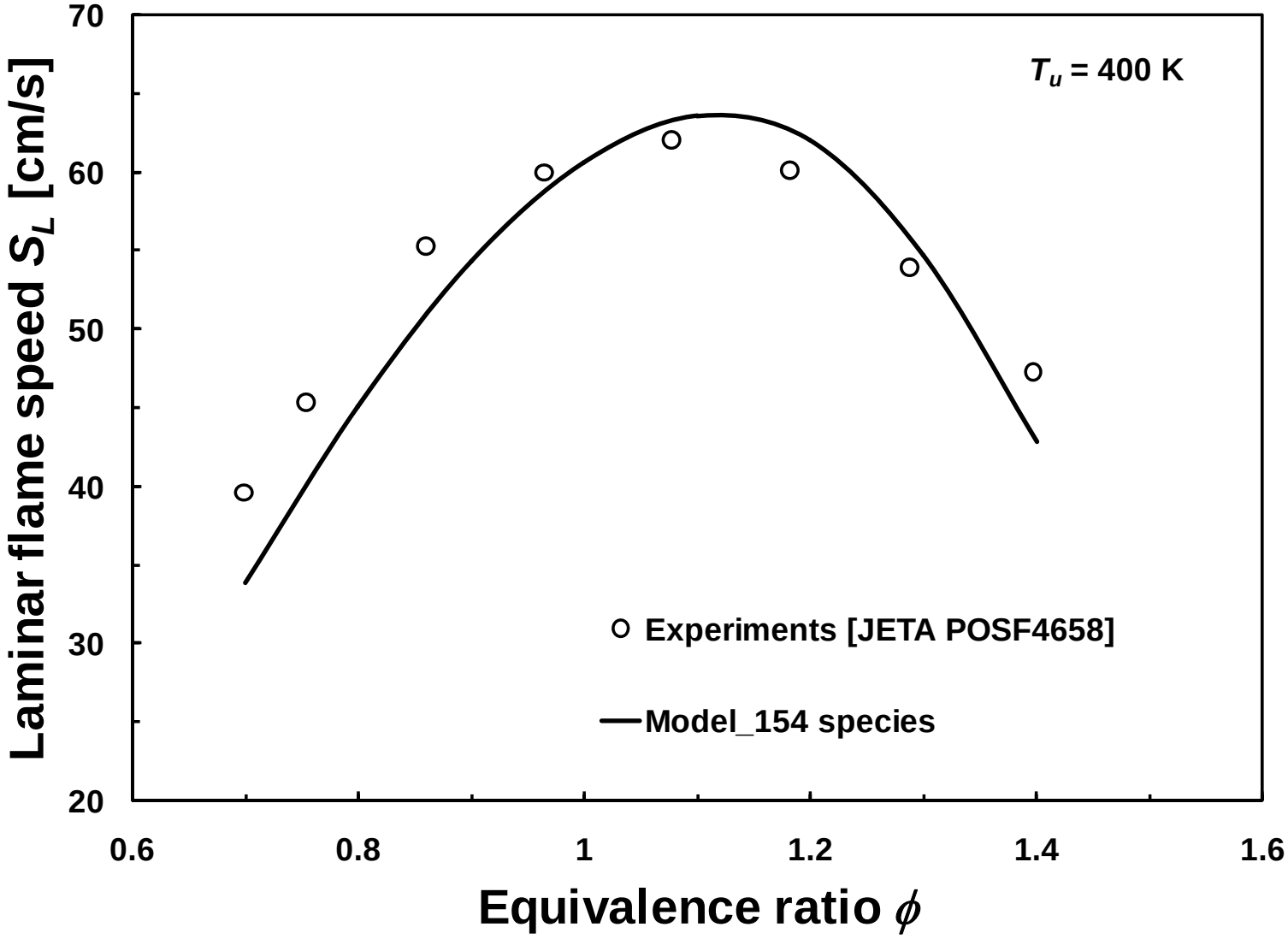
- **(n-Decane, iso-Octane, n-Propyl-Benzene) > 1000 species**
- **(MURI first generation surrogate model) >1000 species**

Validation of Kerosene surrogate fuels





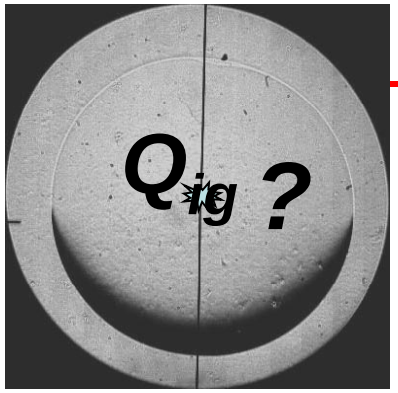
Validation of MURI first generation surrogate



Conclusion

- **Trimethyl benzenes and n-propyl-benzene have the same H/C ratio and molecular weight but different extinction limits.**
- **Extinction limits are proportional to the maximum OH concentrations, and strongly affected by transport and fuel heating value.**
- **A linear correlation between extinction limit and radical index, heating value, and molecular weight was proposed and validated for fuels with different molecular structures.**
- **Measurements of intermediate species and radicals in flames are important to provide additional constraints for kinetic mechanisms.**
- **The first generation jet surrogate model works well in reproducing extinction limit of real fuel in molar correlation, and the second generation surrogate works well for both molar and mass correlations.**
- **Uncertainty in flame property measurements remains to be a challenging issue and needs to be addressed in a unified way.**
- **The multi-generation path flux method for model reduction were tested for a kerosene surrogate with multi-component fuel mixtures, and integrated to multi-timescale method with adaptive mechanisms.**

Thanks Dr. Tishkoff for
the MURI research grant



A flame evolution theory

Assumptions:

Constant density
One-step chemistry
Center energy deposition

Theory: **Chen and Ju, 2007**

$$T_f \cdot \frac{R^{-2}e^{-UR}}{\int_R^\infty \tau^{-2}e^{-U\tau}d\tau} - \mathbf{Q_{ig}} \cdot R^{-2}e^{-UR} = \frac{1}{Le}\frac{R^{-2}e^{-ULeR}}{\int_R^\infty \tau^{-2}e^{-ULe\tau}d\tau} = \exp\left[\frac{Z}{2}\frac{T_f - 1}{\sigma + (1-\sigma)T_f}\right]$$

Large flame

Nonlinear Model: $(U + \frac{2}{R})\ln(U + \frac{2}{R}) = \frac{Z}{2}\cdot\frac{2}{R}(\frac{1}{Le} - 1) - \frac{2}{R}(\frac{1}{Le} - 1)$

Small velocity derivation

Not included in **Sivashinsky, 1979**

Linear Model: $S_u / S_u^0 = 1 - Ma \cdot Ka$

Sivashinsky, 1979