Flame Kinetics and Transport of Alkanes and Aromatic Mixtures

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The Basic Research Manager of the Air Force Research Laboratory

Questions to address

1. Do the MURI surrogate fuel models work for flame extinction?
2. How to address the issue of kinetic and transport interaction between aromatics and alkanes in flames?
3. How to isolate kinetic, fuel heating value, and transport effects from the global flame experiments and obtain a general correlation?
4. Can we build the missing kinetic building block of the 2nd generation jet fuel surrogate?

   n-dodecane, i-octane, n-propyl-benzene

   1,3,5 trimethyl–benzene?
5. Can we collaboratively validate this mechanism (experiments)?

Research Thrust

- **Develop and validate MURI surrogate fuel formulations of Jet fuels**

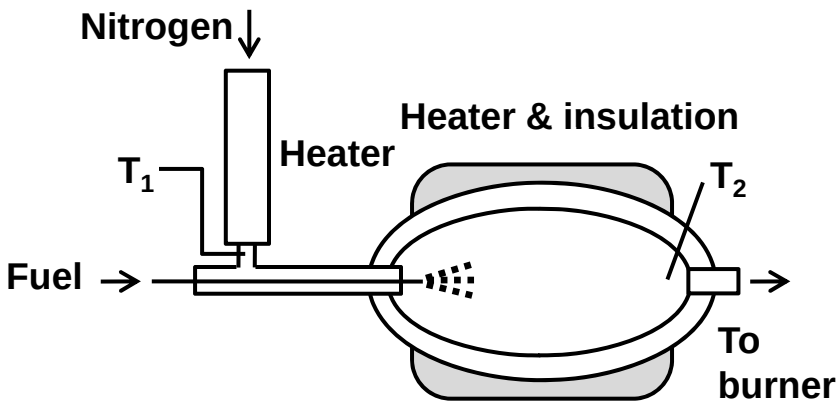
  H/C ratio, DCN, TSI, and MW

- **Understand Kinetics and Transport Interaction between alkanes and aromatics in Flames**
- **Develop a comprehensive correlation of flame extinction and extract chemistry information**
- **Develop a kinetic oxidation mechanism for 135 trimethyl benzene**
- **Develop a high pressure spherical bomb for flame measurement of liquid fuels**

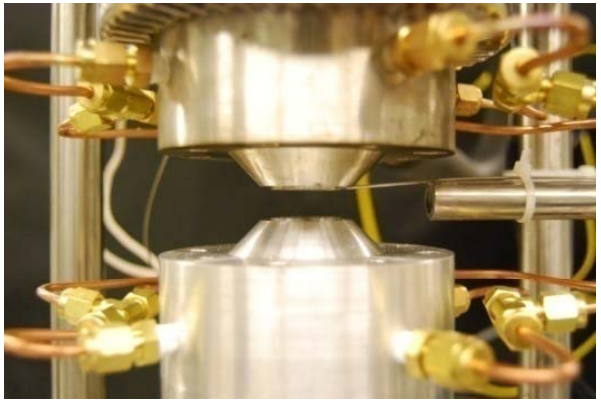
1. Flame validation of the 2nd surrogate fuel formulation of Jet fuels

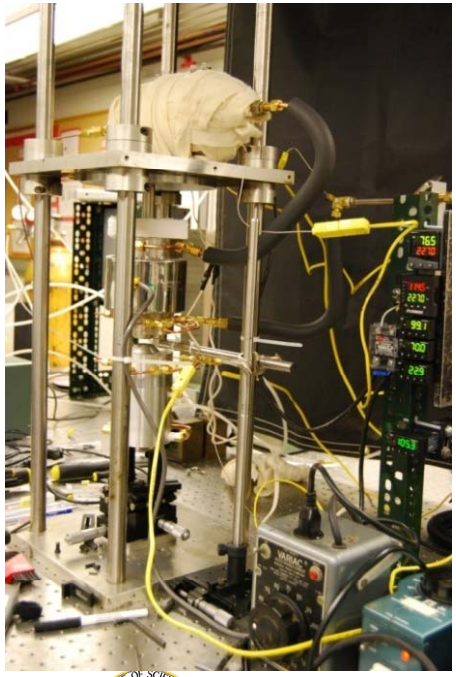
Diffusion Flame Experimental Setup

- **Extinction limits and OH measurements**
  - **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

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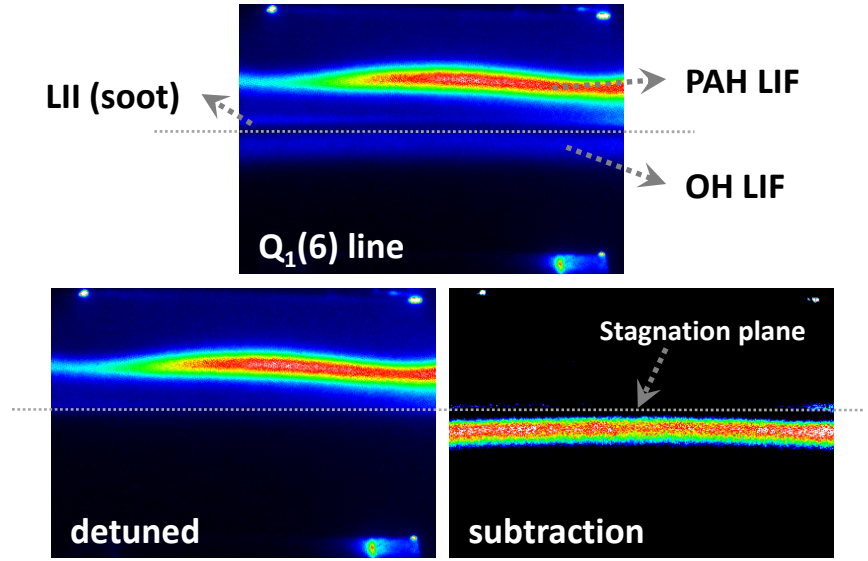
- **PLIF: Q1(6) transition (282.93 nm), linear regime, beam height 80 mm**
  Quenching, Soot, PAH corrections

Schematic photo for Rayleigh scattering and PLIF



nPB diffusion flames

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Surrogate Model Flame Validation on Jet POSF 4658

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•1st 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

•2nd 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				

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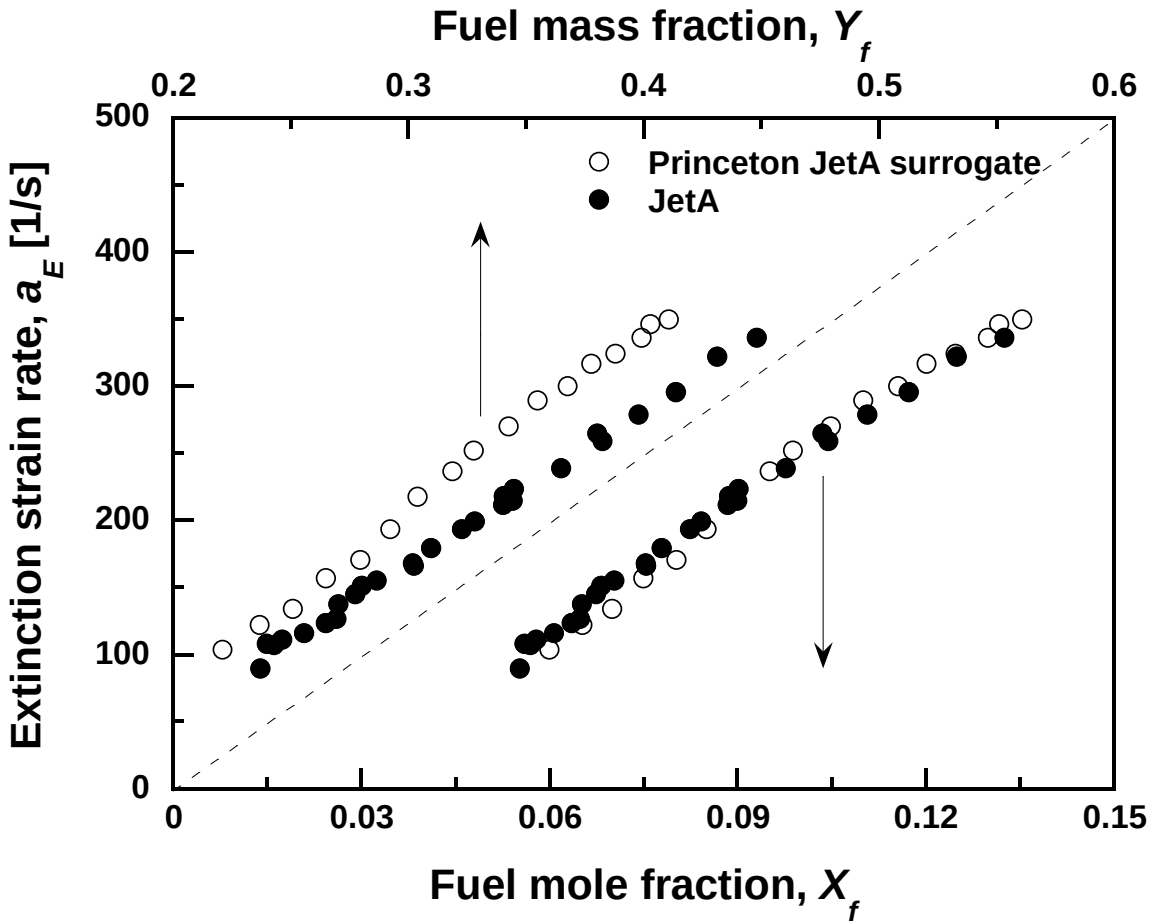
Validation: Extinction of Diffusion Flames
POSF 4658 vs. 1st generation surrogate



Problem:

Mass fraction does not match!

Validation: Extinction of Diffusion Flames

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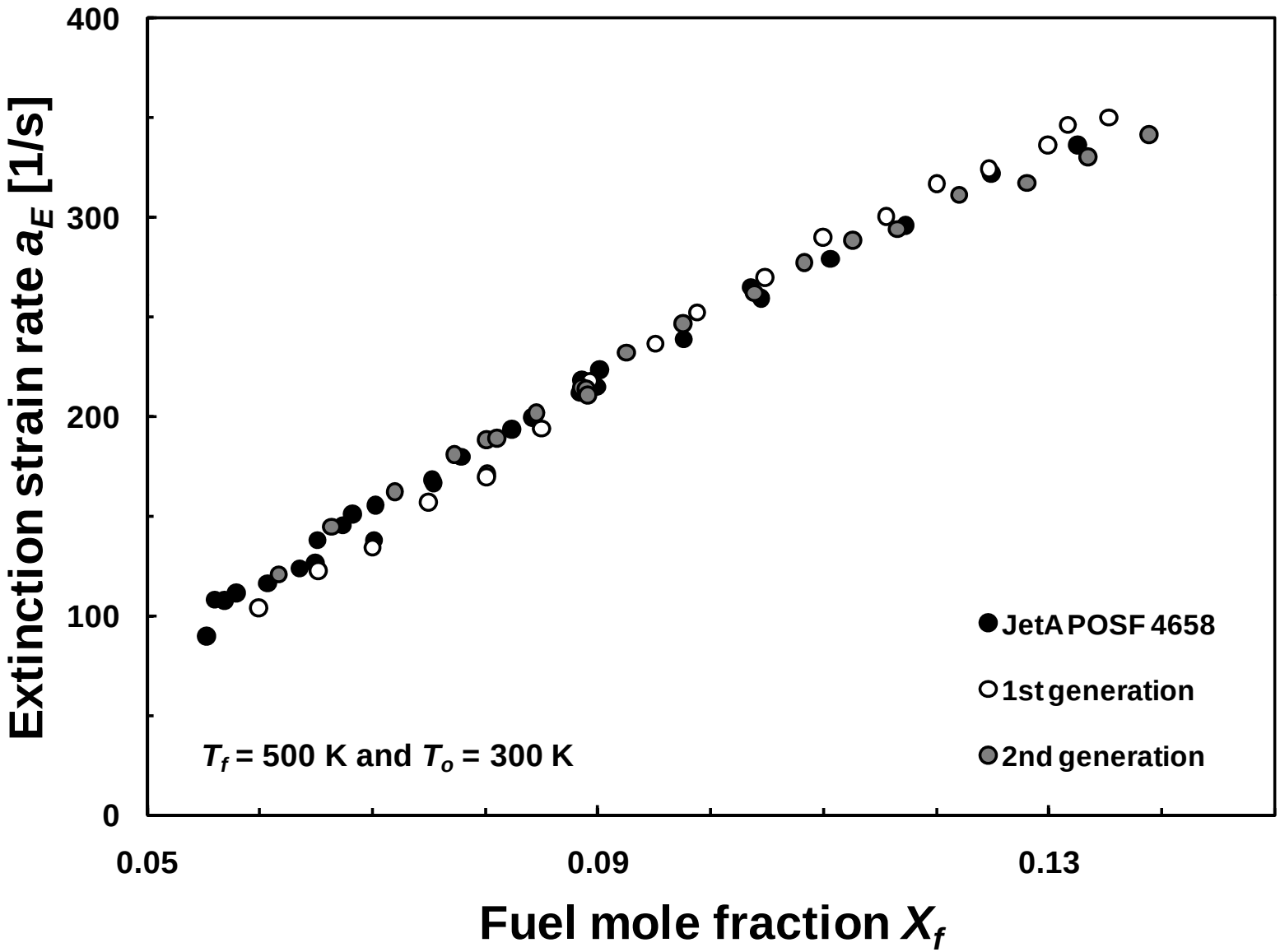
POSF 4658 vs. 1st and 2nd generation surrogates



Validation: Extinction of Diffusion Flames
POSF 4658 vs. 1st and 2nd generation surrogates

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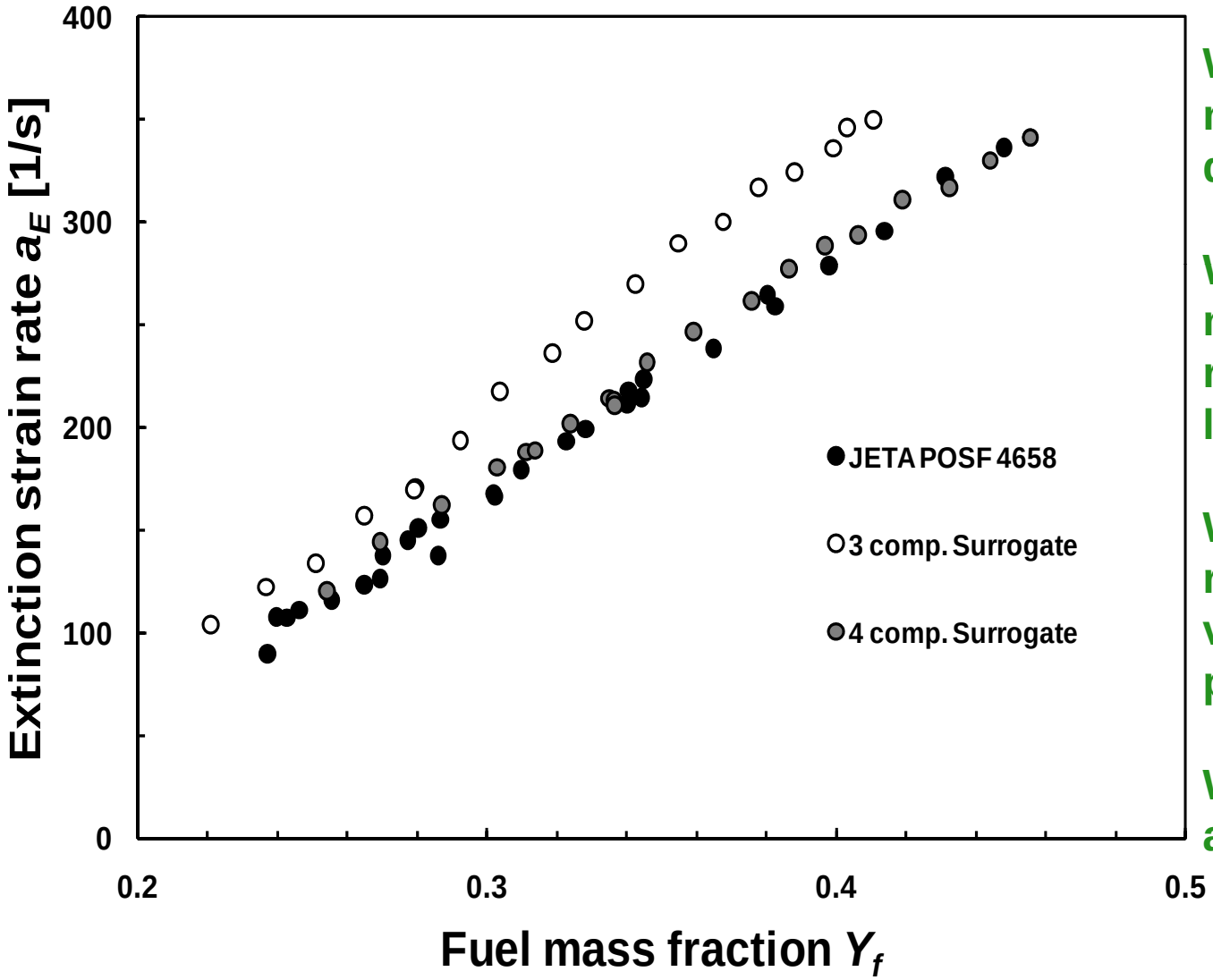


Why is the mean molecular weight a big deal?

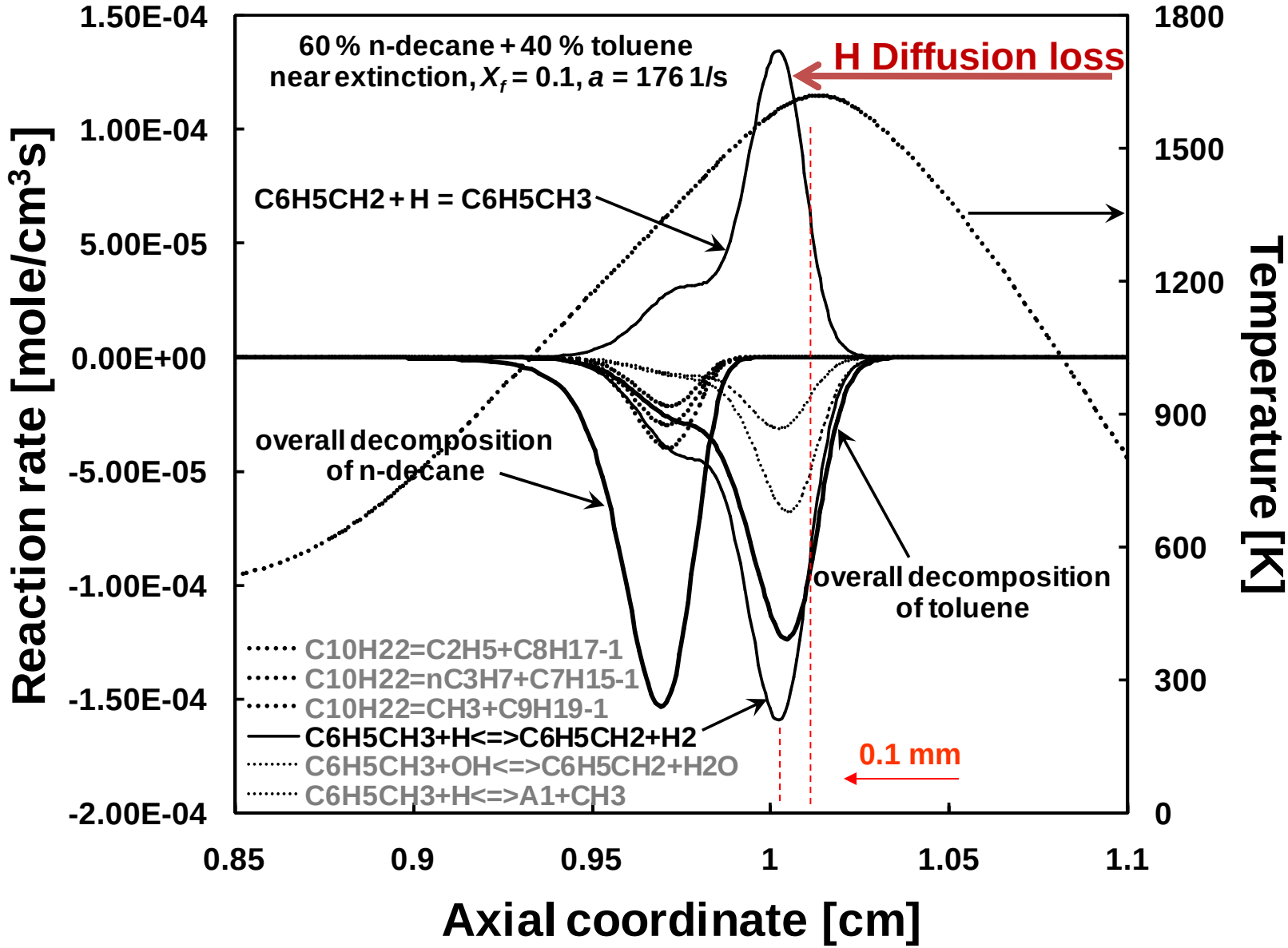
Why can such a simple mixture model mimic a real fuel extinction limit so well?

Where does the H/C ratio and fuel heating value contribute to the problem?

What is the role of aromatics?

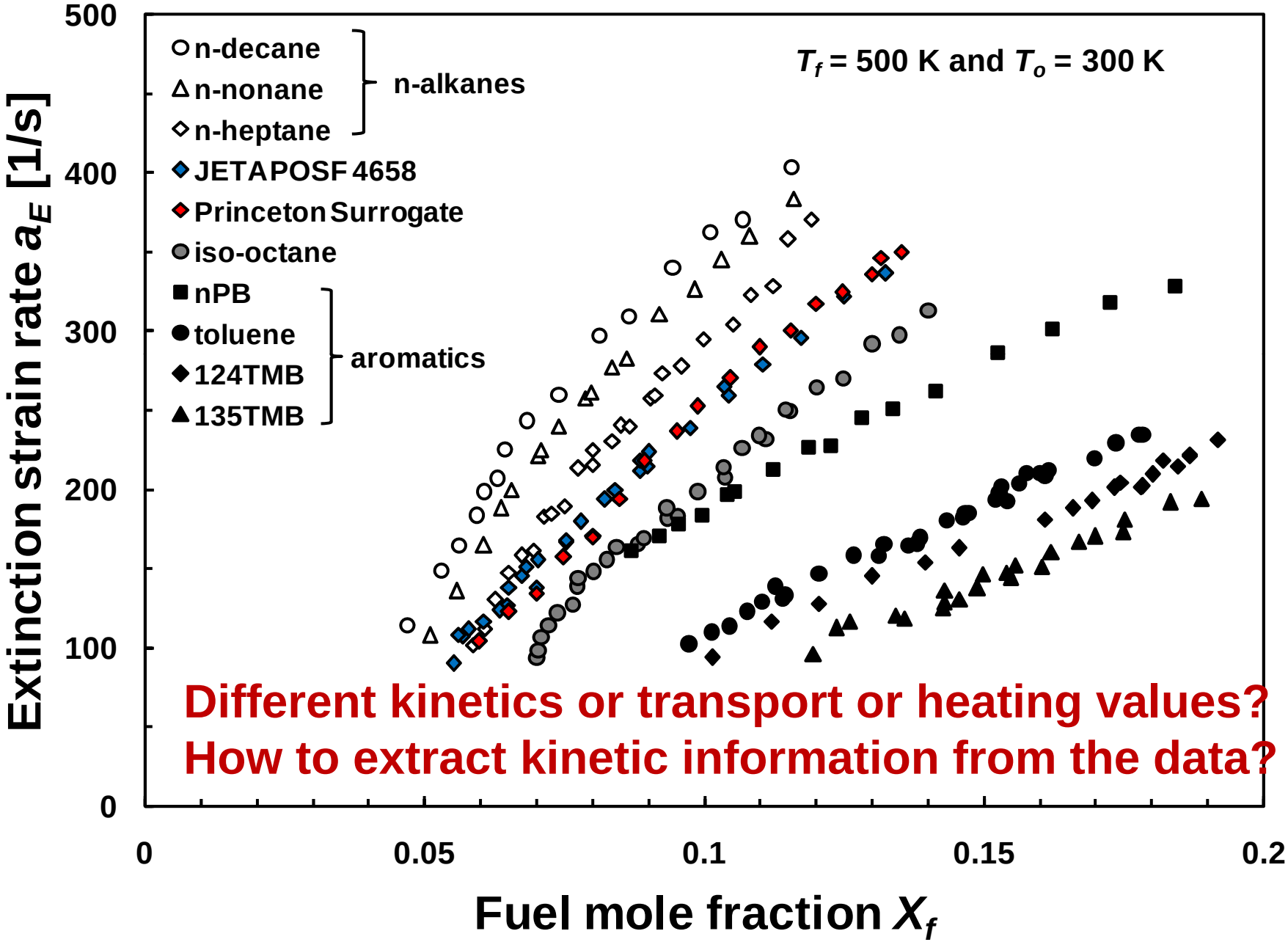
2. Kinetic and transport interaction between aromatics and alkanes in flames?

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



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

Extinction limit: Alkanes, Iso-alkanes, aromatics



Different kinetics or transport or heating values?
How to extract kinetic information from the data?

A generic correlation for extinction limit: Chemistry and Transport

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Theory of counterflow flame extinction

Extinction Damkohler number

$$\frac{1}{Da_E} = \left[\frac{2}{e} \frac{\tilde{Y}_{O,\infty}}{\tilde{Y}_{F,-\infty}^{\ 2}} Le_F^3 P(\eta_F, Le_F, Le_O) L(\eta_F, Le_F) \right] \left[\frac{1}{\tilde{T}_f - \tilde{T}_{-\infty}} \left(\frac{\tilde{T}_f^{\ 2}}{\tilde{T}_a} \right)^3 \exp\left(-\frac{\tilde{T}_a}{\tilde{T}_f} \right) \right]$$

Extinction Strain Rate (fuel diluted by nitrogen)

$$a_e \propto \frac{1}{\sqrt{M_F / \overline{M}}} \frac{Y_{F,-\infty} Q_F}{C_p (T_f - T_{-\infty})} * R_i$$

Transport

Heat release/heat loss

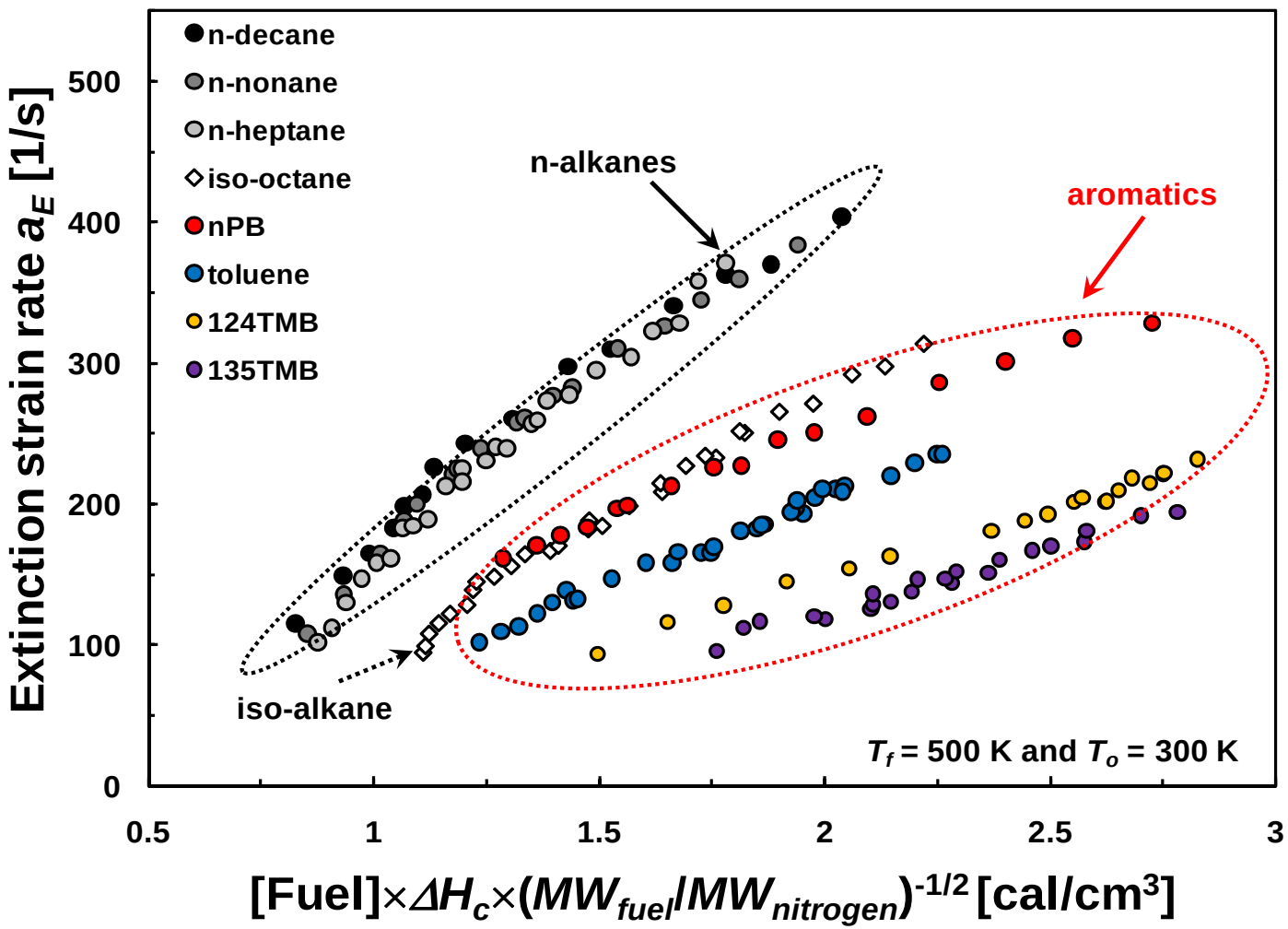
Fuel chemistry/reactivity
Radical production rate

(Won et al. 2011, C&F)

By introducing a new concept:

Transport-Weighted Enthalpy:

$$[\text{fuel}] \times \Delta H_c \times (MW_{fuel}/MW_{nitrogen})^{-1/2}$$



Introducing: Radical Index

- **Heat release and OH production/consumption pathways**
  - $H + O_2 = OH + O$, $CO + OH = CO_2 + H$ and $H_2 + OH = H_2O + H$
  - Occur mainly in the core reaction zone
- **Quasi-steady-state approximation of OH**
- **OH formation rate, $\zeta_{OH} = [OH]_{max} \times \delta_{OH} \times a$**
- **Radical Index = $\zeta_{OH}^{fuel} / \zeta_{OH}^{n\text{-}alkane}$**
  - at either maximum or *Da* >= 2

Fuel	Radical index
n-alkanes	1.0
iso-octane	0.70
Toluene	0.56
nPB	0.67
124TMB	0.44
135TMB	0.36

A General Correlation for Extinction vs. Radical Index

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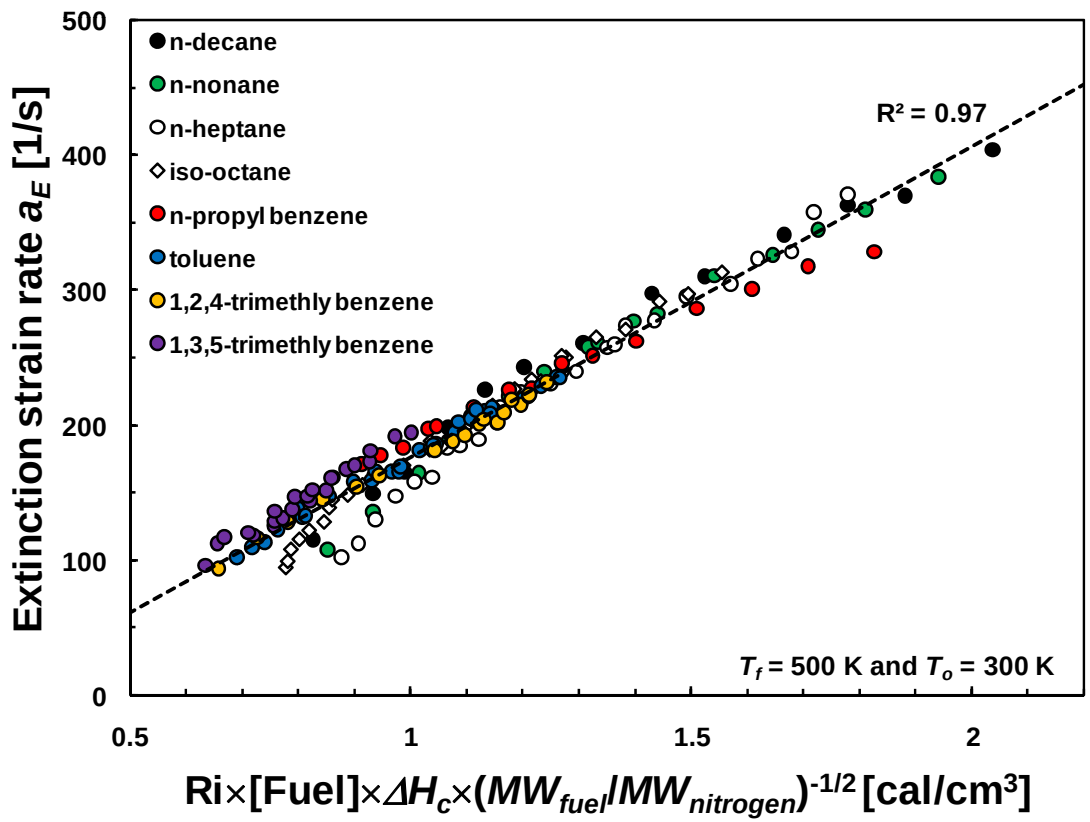
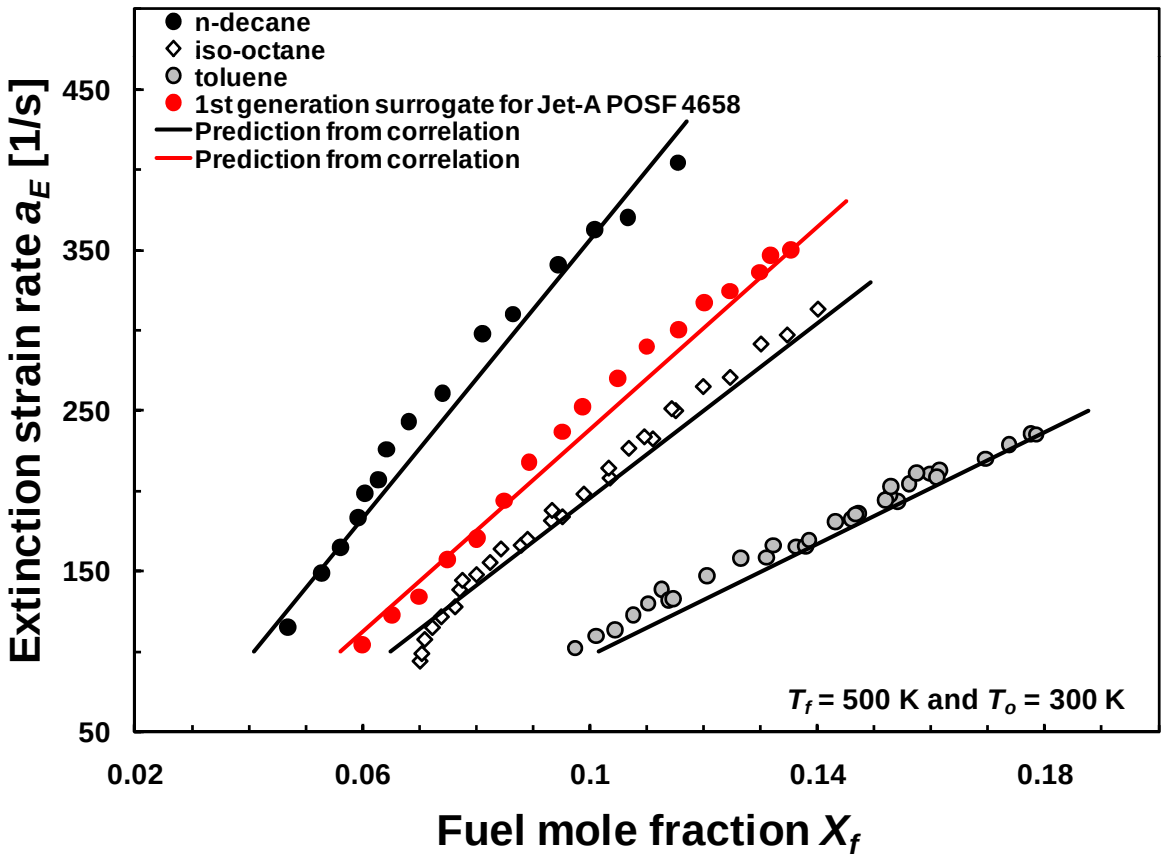
- Extinction limits are proportional to
  - ***Transport-Weighted Enthalpy, TWE***
  - ***Radical Index, Ri*** (population rate of OH)



Radical Index to predict extinction limit

- 1st generation surrogate mixtures
  - nC10/iC8/toluene
  - $Ri_{1st\ gen.} = \Sigma X_i \times Ri_i = 0.79$



Radical Index to predict extinction limit

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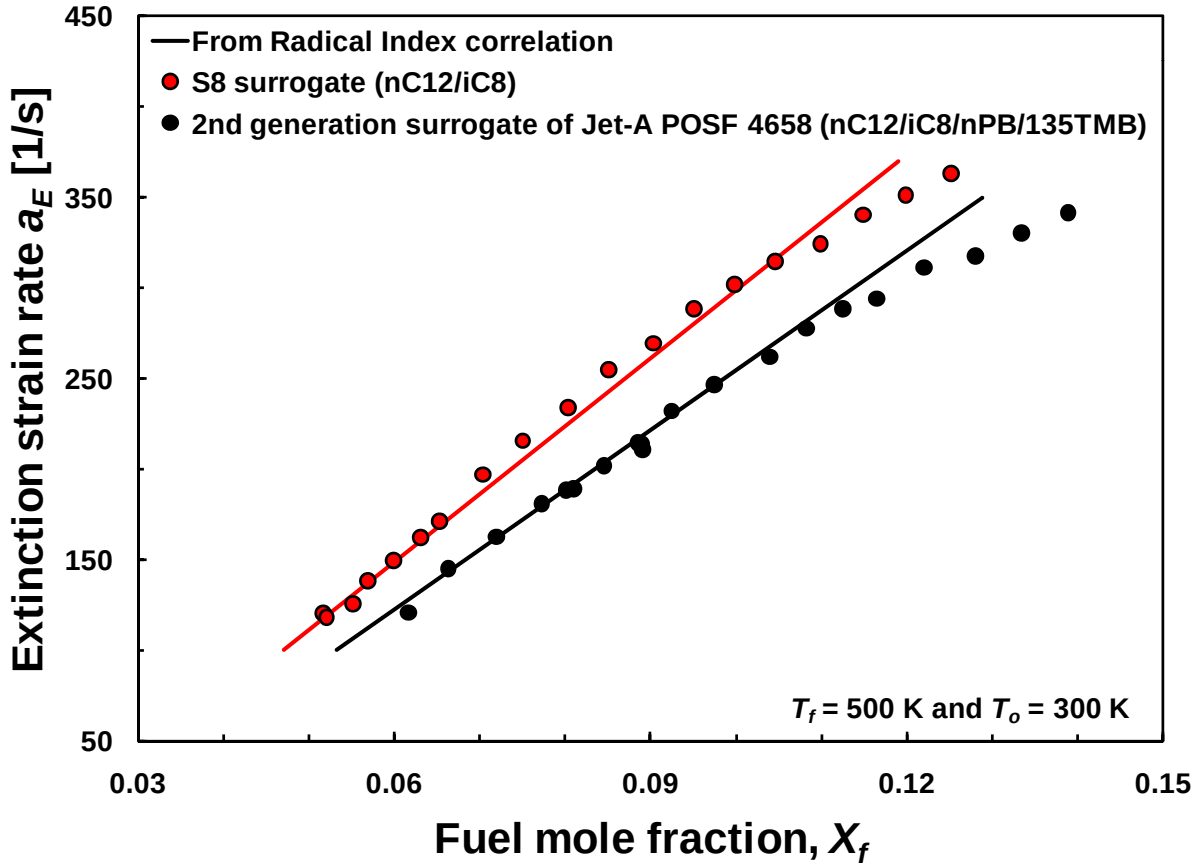
- **2nd generation surrogate**
  - nC12/iC8/nPB/135TMB, **$Ri_{2nd\ gen}$ = 0.80 ($Ri_{1st\ gen}$ = 0.79)**
- **S8 surrogate** (nC12/iC8), **$Ri_{S8\ sur}$ = 0.86**



3. Kinetic Model Development for 135 trimethyl benzene: Ignition & flames

- **Second generation surrogate model (4 components)**
- *n*-dodecane
- *iso*-octane
- *N*-propyl benzene
- 1,3,5 trimethyl benzene

Lack of a kinetic mechanism!

1,3,5 trimethyl benzene Model Development

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1,3,5-TriMethylBenzene subset

A similar oxidation pathway to the one of toluene was adopted

m-Xylene Submodel
Battin-Leclerc et al. 2006
and Gail and Dagaut et al., 2008

Kinetic parameters modified and adopted from similar reactions in toluene subset

TOLUENE Submodel
Metcalfe , Dooley, and Dryer, 2011

H_2/O_2 subset proposed by Burke et al. adopted

Thermodynamic parameters of di- and tri-methyl related species re-estimated

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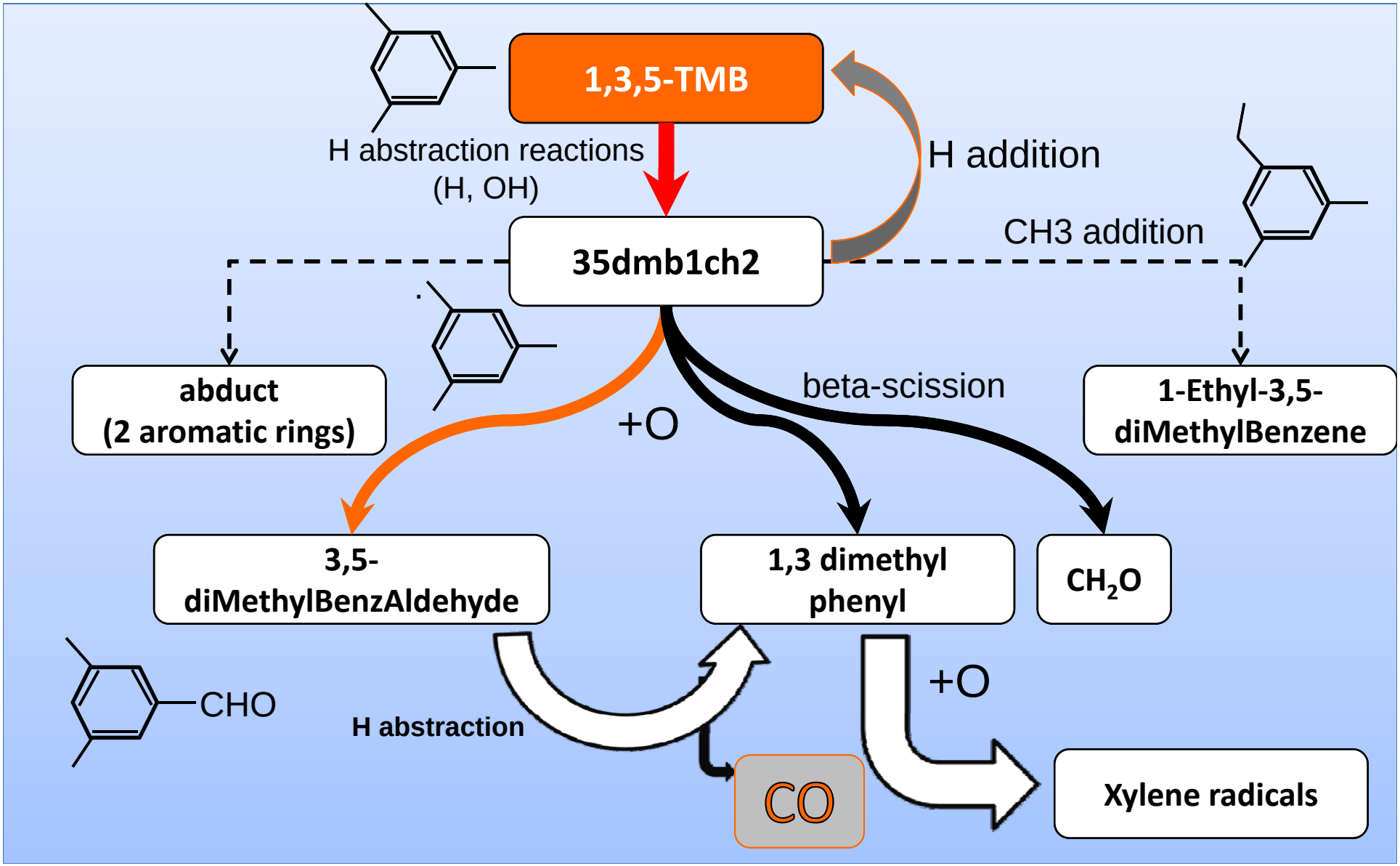
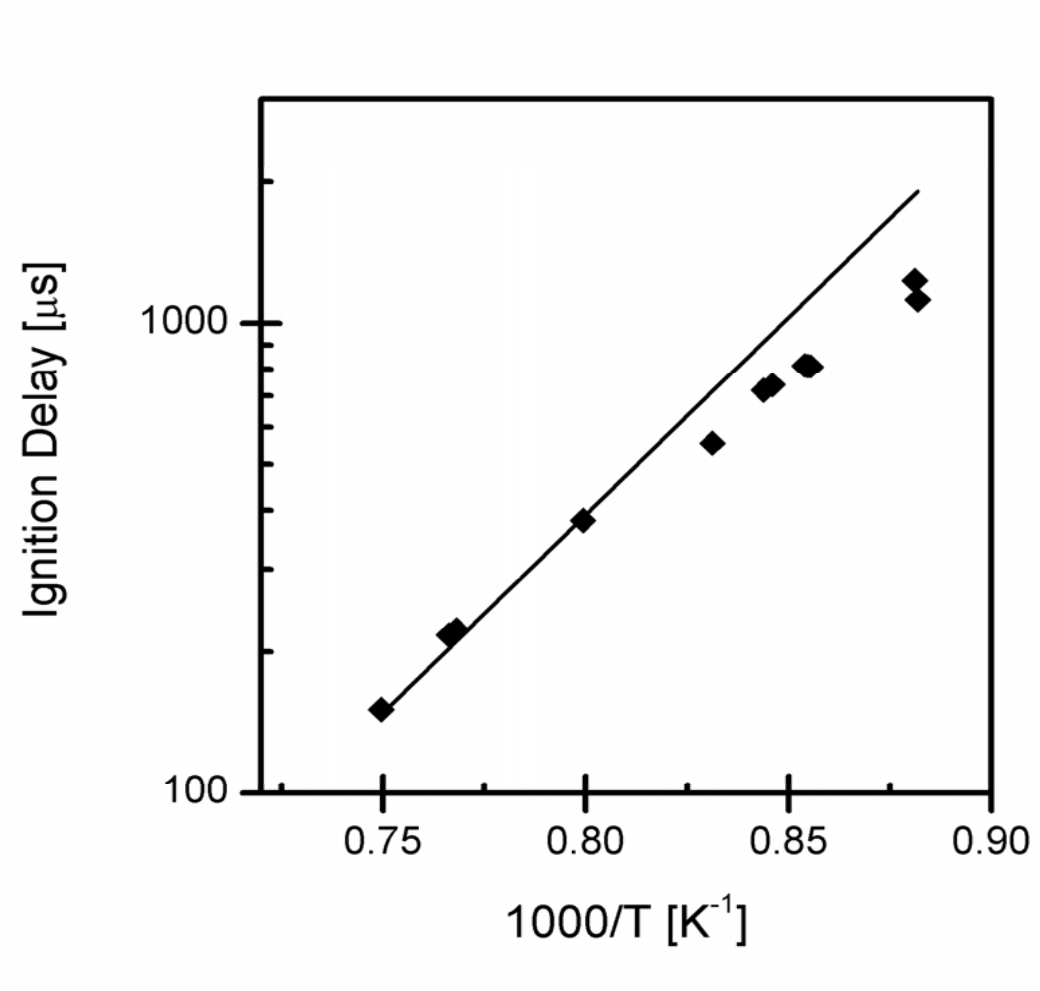
Oxidation of 135-TMB in flame configurations



Validation of 135TMB Model: Ignition

Shock Tube Ignition delay for stoichiometric 135TMB/air mixture at 20.6 atm

Oehlsclaeger et al. 2011



Validation of 135TMB Model: extinction and flow reactor

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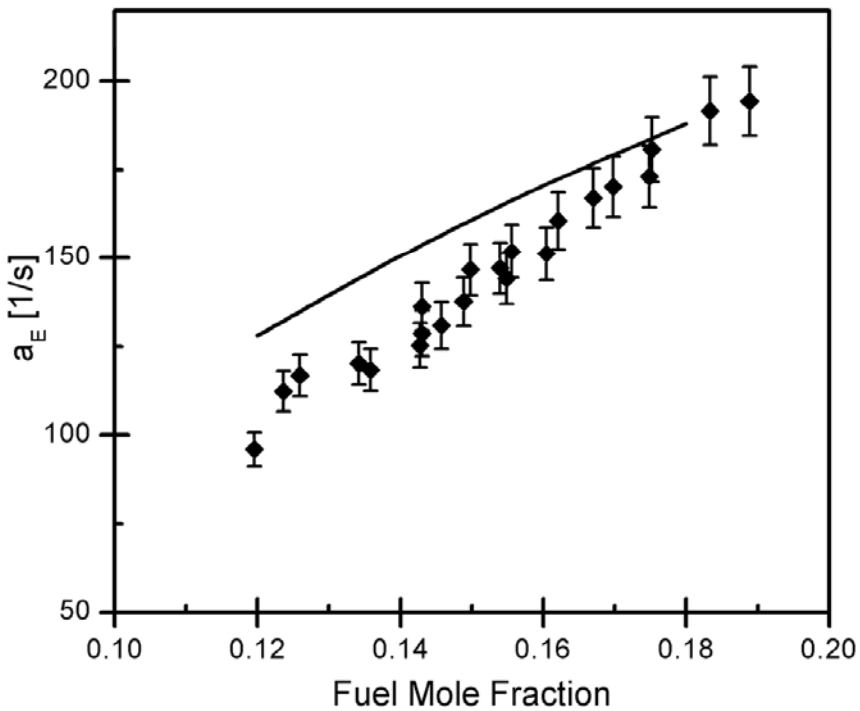
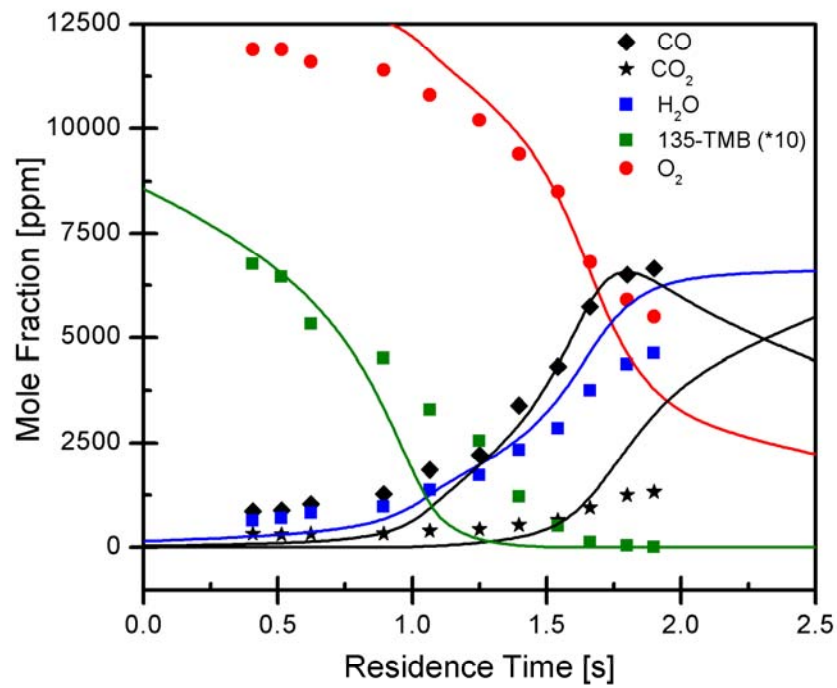
- Diffusion flame extinction at 1 atm, T_f = 500 K, T_o = 300 K
- Flow reactor oxidation at 12.5 atm, 930 K, 1111 ppm 135TMB, 13300 ppm O_2





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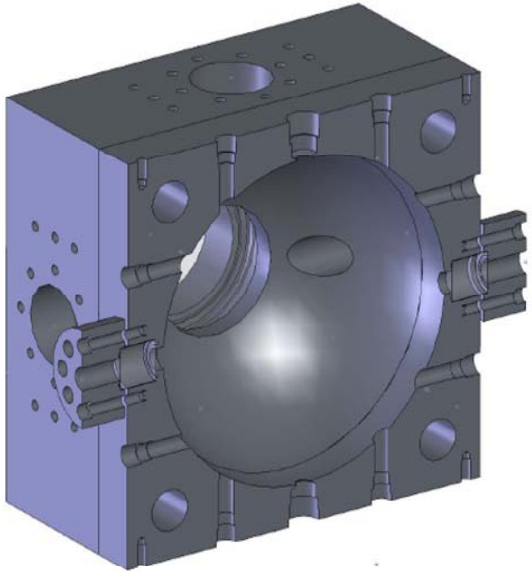
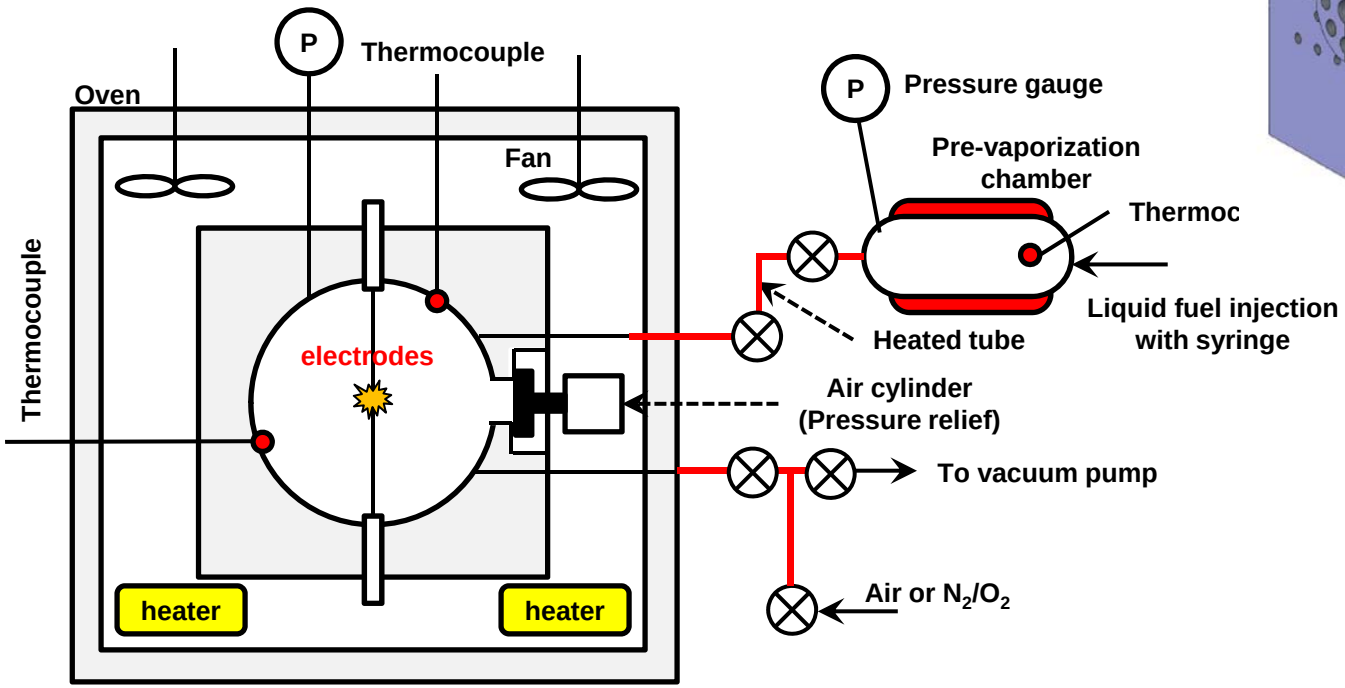
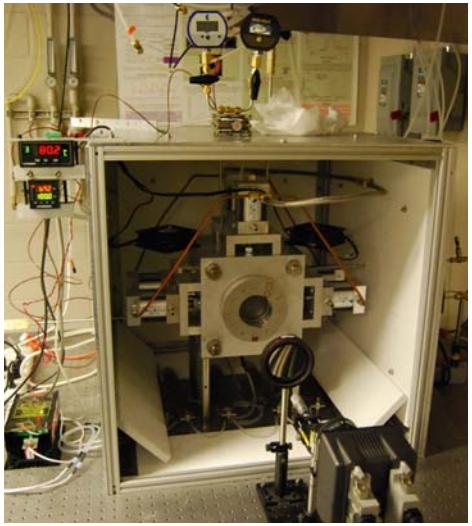
4. Measurements of Flame Speed of surrogate fuels

Development of "Spherical" Bomb for liquid fuels

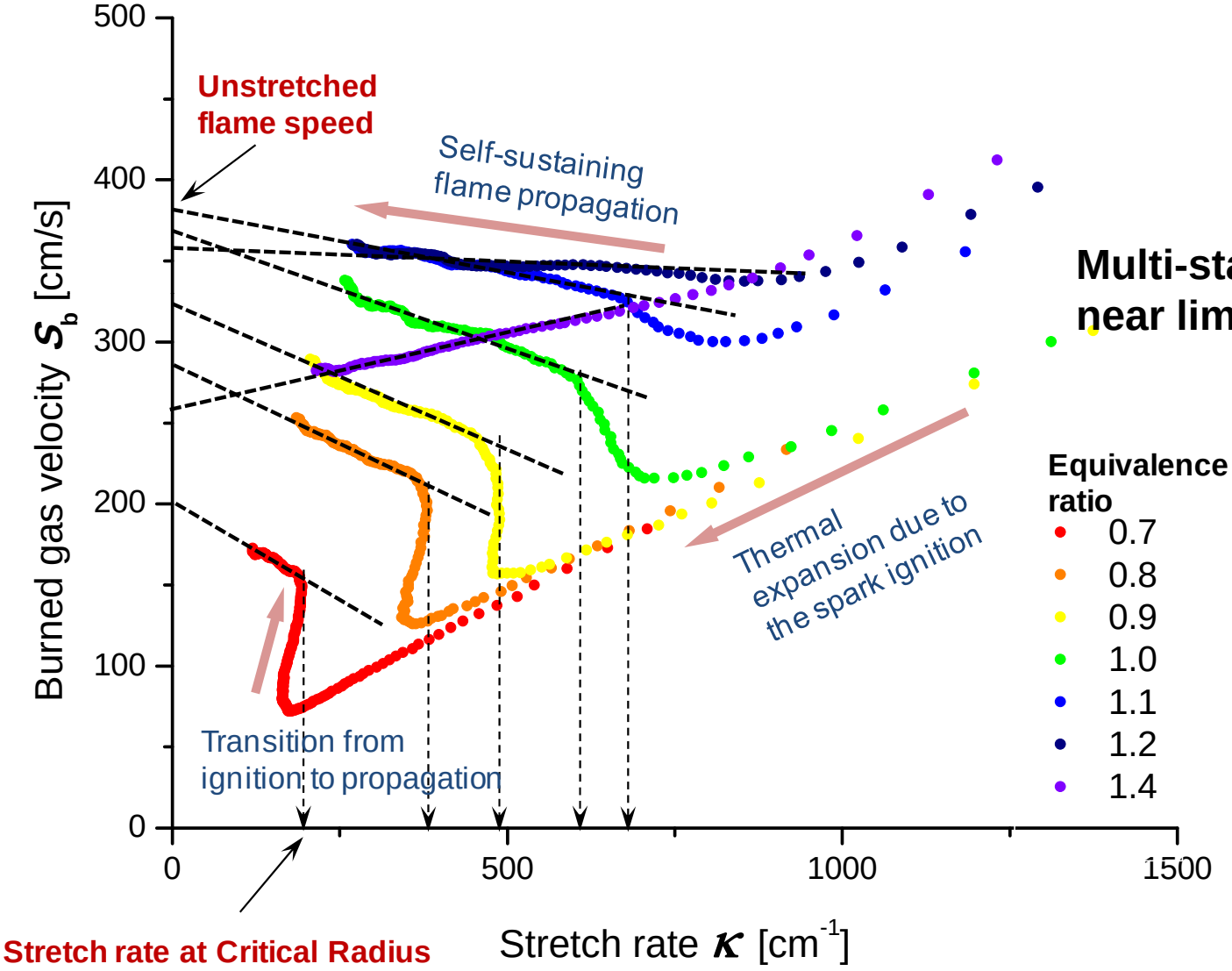






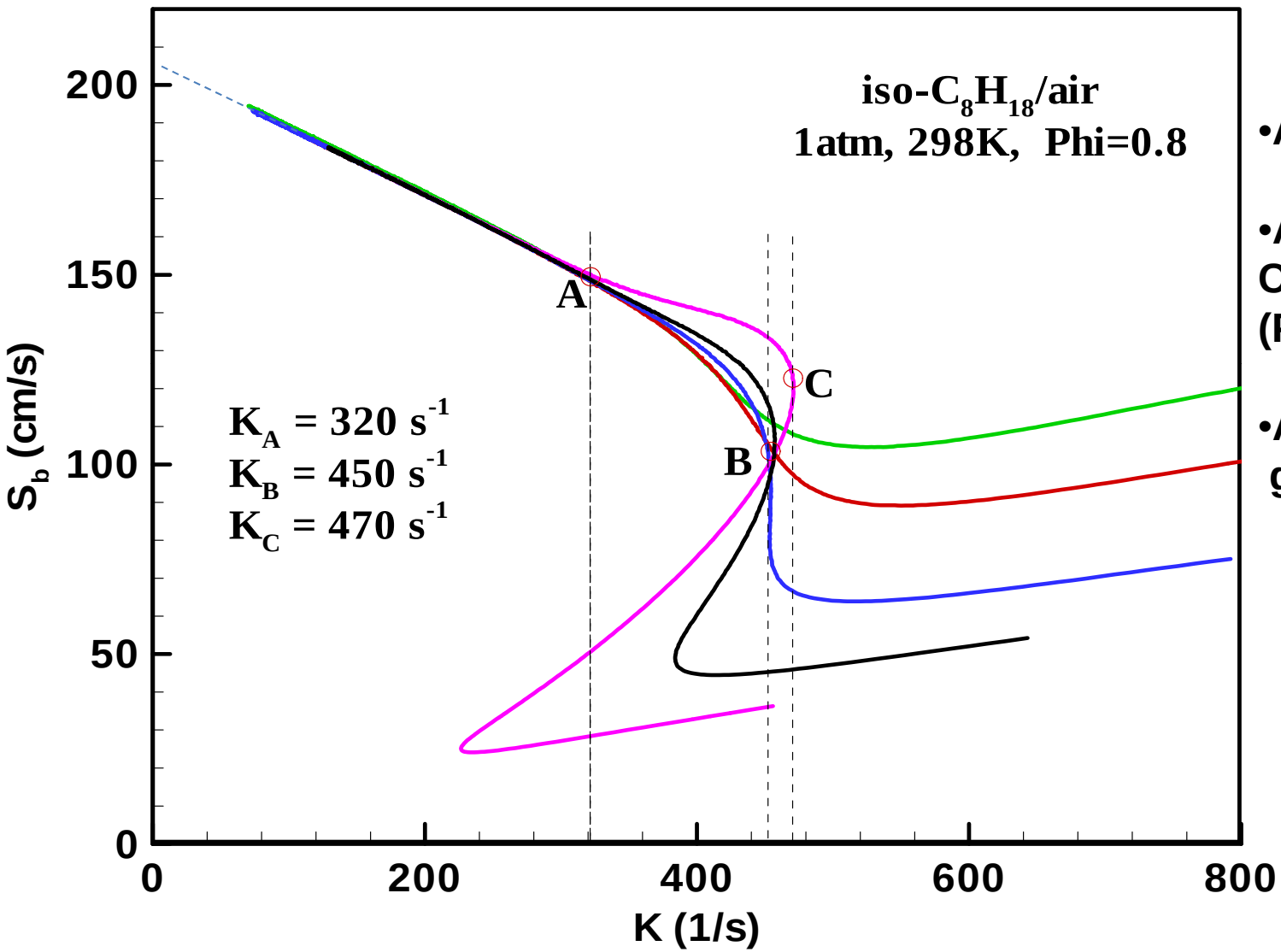
Transient Flame Trajectories and speeds

– JetA POSF 4658, n-decane, iso-octane, and 135TMB



Multi-stage flames at near limit conditions

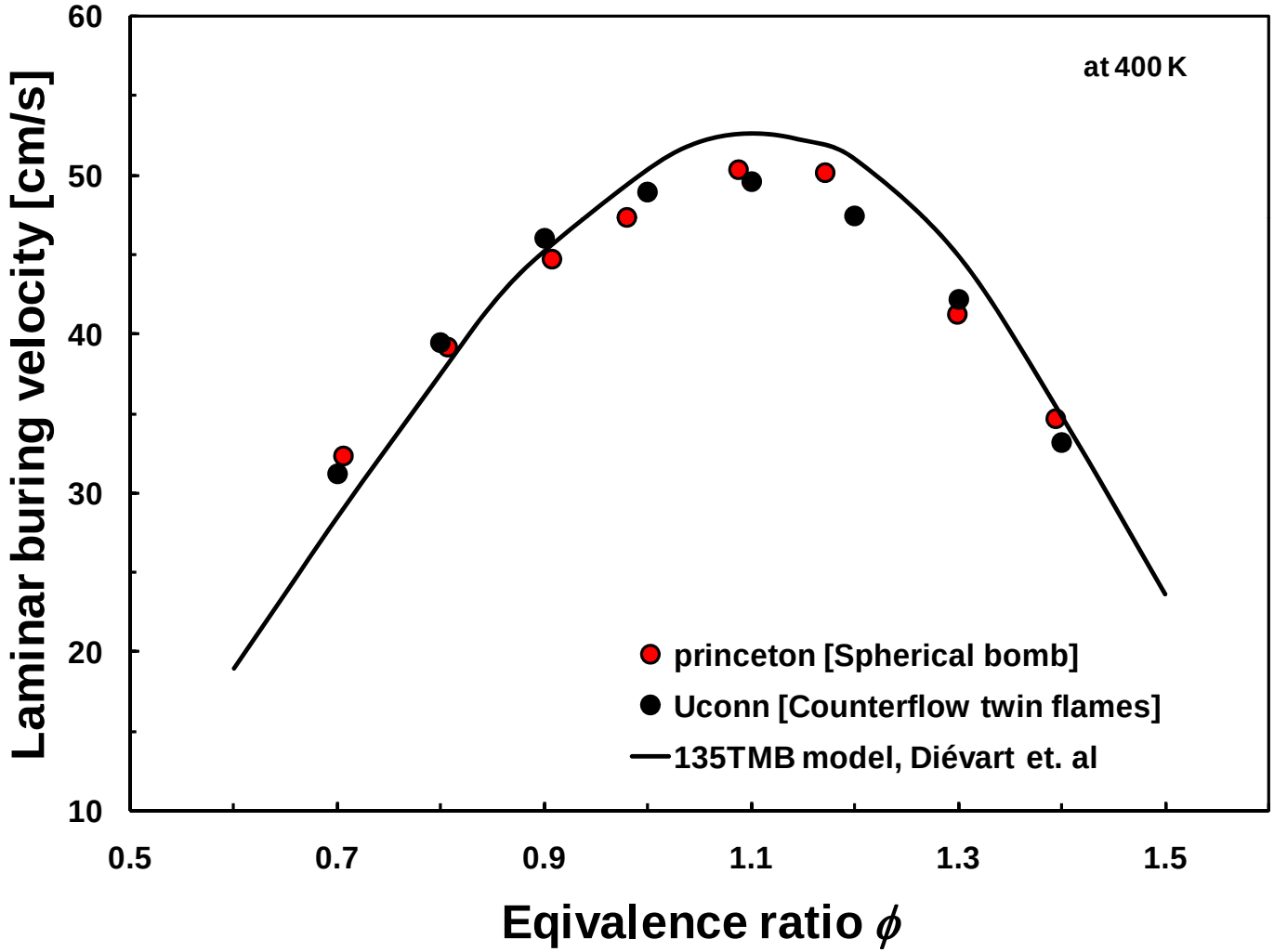
Numerical modeling



- ASURF code
- Adaptive Chemistry (PFA method)
- Adaptive grids

Validation of 135TMB Model: Flame speed

– Laminar flame speed at 1 atm, 400 K



Conclusion

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1. The 1st and 2nd generation surrogate fuel models for jet A were validated against extinction limits.
2. Aromatics play an important role in affecting flame extinction via kinetic and transport coupling.
3. A comprehensive correlation for diffusion flame extinction limits of alkanes, isoalkane, aromatics, and real fuel was obtained by using Transport weighted enthalpy and radical index.
4. Chemical kinetic model for 135TMB has been developed and validated through collaborative MURI team/RPI work. The surrogate model building blocks were completed.
5. A nearly constant pressure spherical bomb was developed to measure liquid fuel burning velocity and transient flame regimes at elevated pressures.

Acknowledgements

- MURI Surrogate fuel project monitored by Dr. Julian Tishkoff
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