Laminar Flames and the Role of Chemistry and Transport

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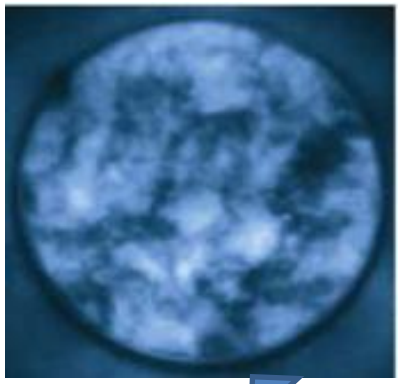
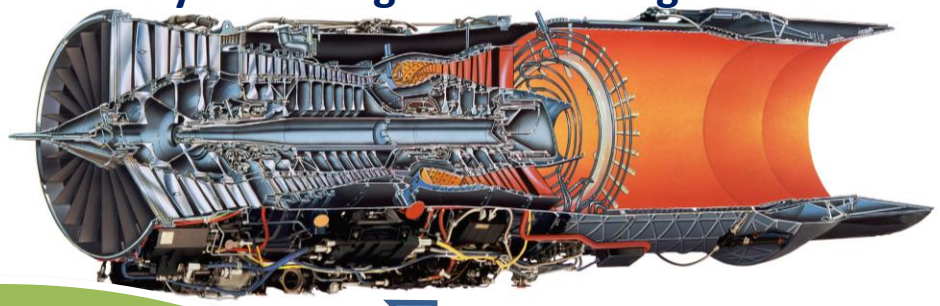
1st Flame Chemistry Workshop

Advanced Engines
require fuel flexibility and work near kinetic limit



HCCI

Synfuels in gas turbine engine

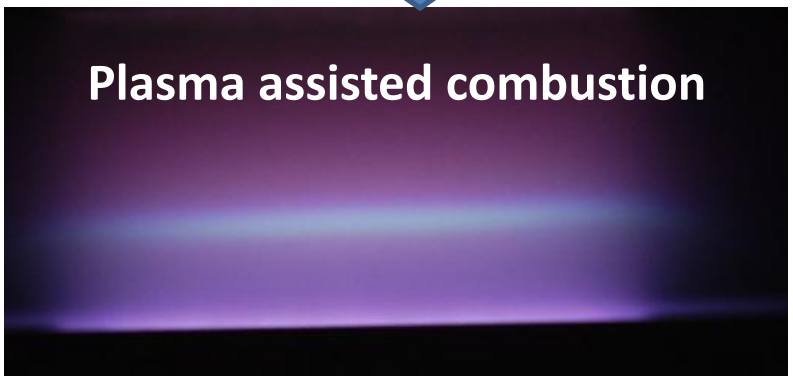


- Low temperature,
- High pressure,
- Near ign./ext . limit,
- Multiple fuels,

Kinetic limiting

"Validated"mechanisms?

- Hundreds of fuels
- Different structures elements H, C, O, N, S…)
- Thousands species
- Extreme conditions

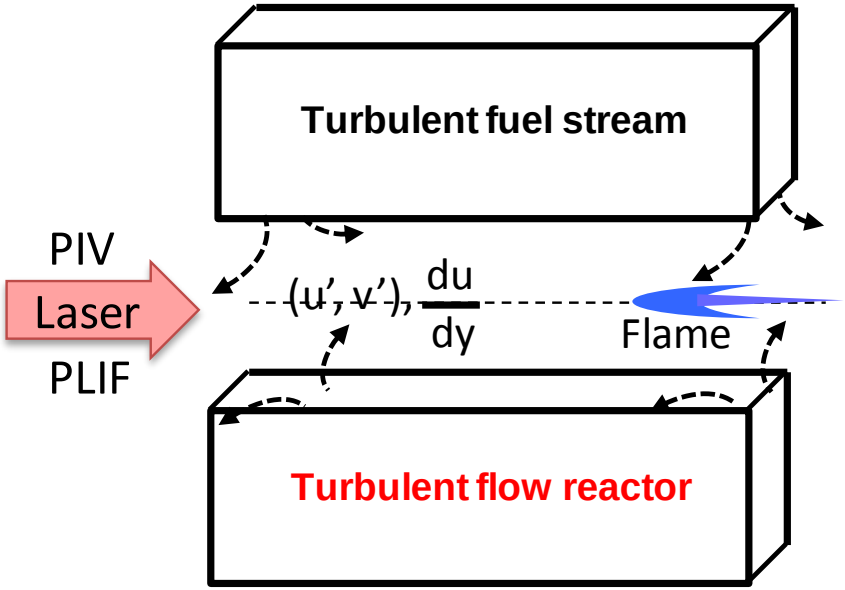


Two validation targets

- **Homogeneous ignition/reactor**
- **Inhomogeneous flames**

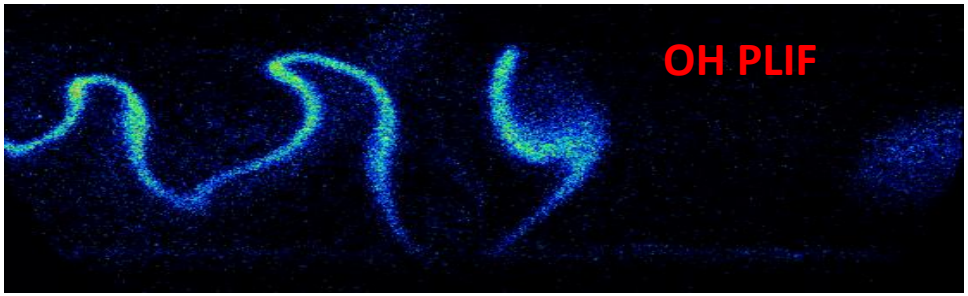
Flame regimes in combustion

How does chemistry affect flames?

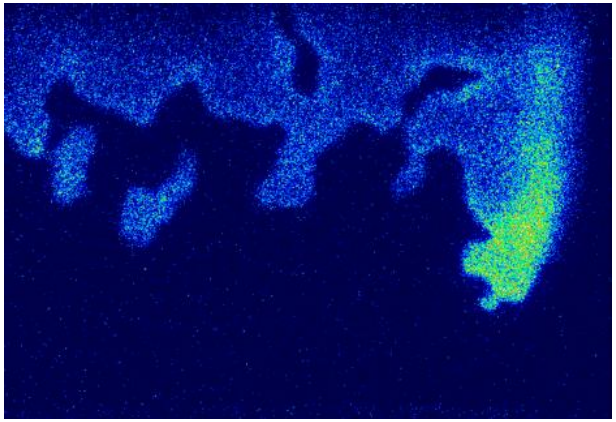


Reactive flow

- **Thin flame**
- **Thickening flame**
- **Local extinction**
- **Re-ignition**



Propagating edge flame in a mixing layer

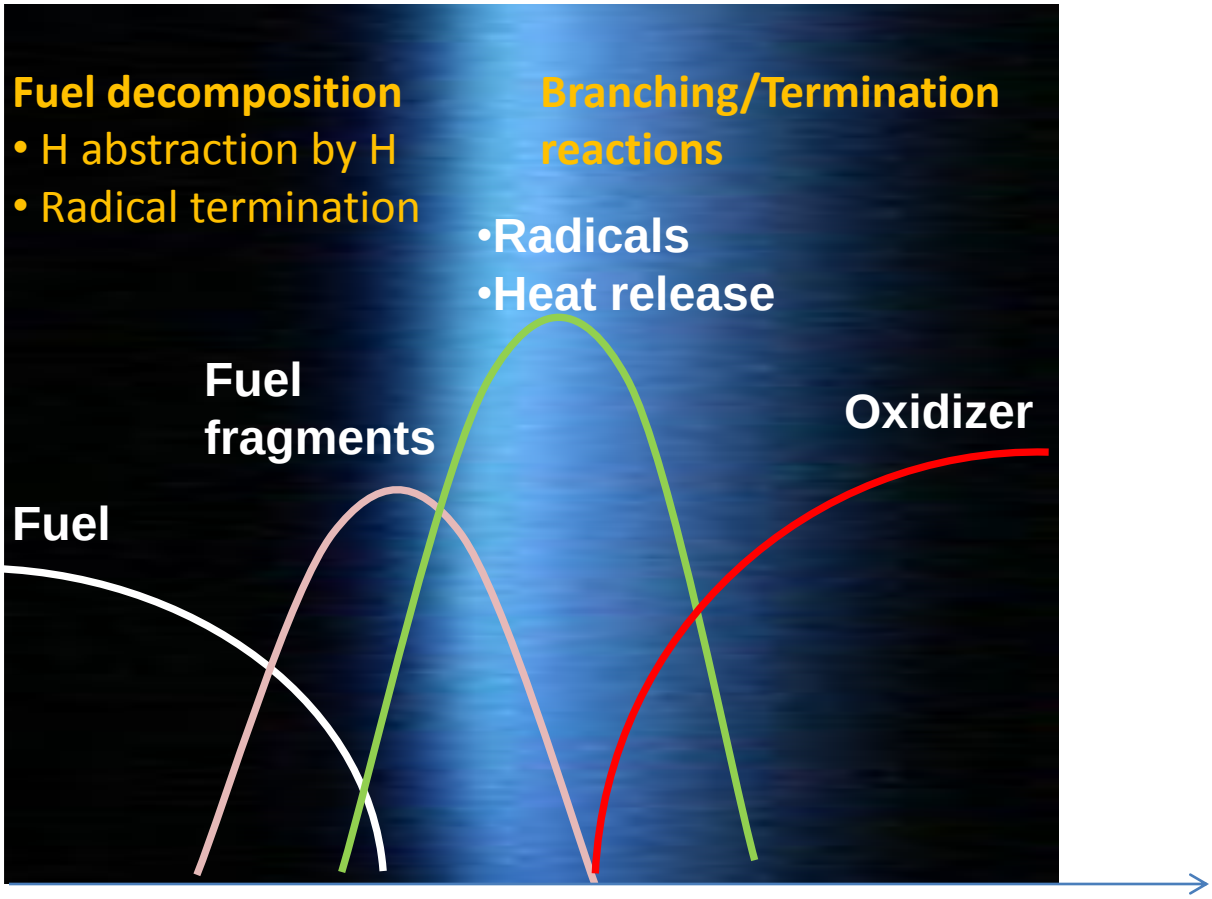


Premixed flame front

in non-uniform flow field with complex transport and chemistry coupling

Flames

➢ "Flame" is a ignition/reaction front supported by thermal and species transport



Diffusion
Fuel/Oxygen
Radicals/Fragments,
(e.g. H and C2H4)

Heat release rate
OH + CO =CO2 +H
HCO+OH= CO2+H2O

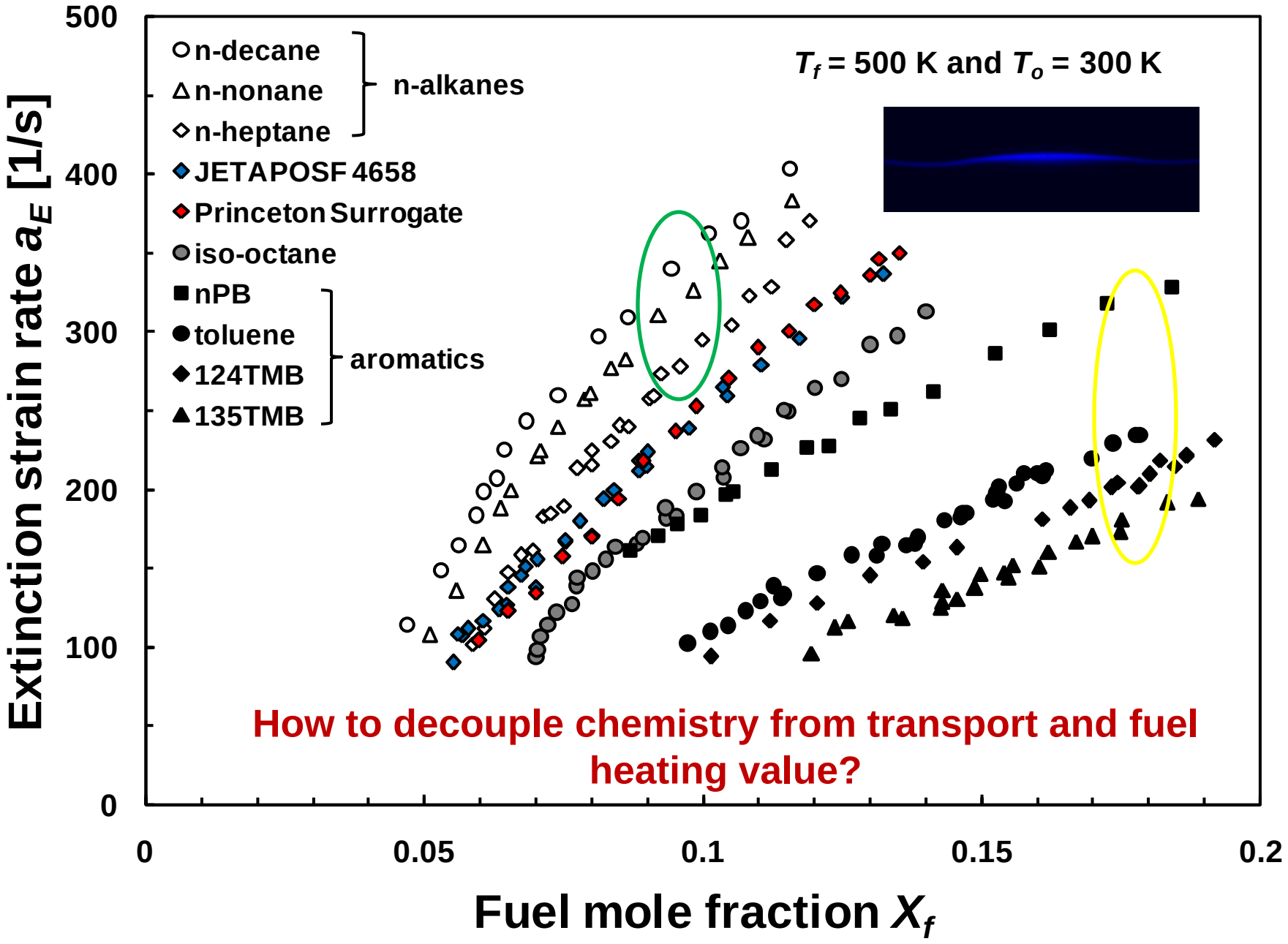
Non-uniform species/temperature distribution

1. Why is flame chemistry different from ignition?

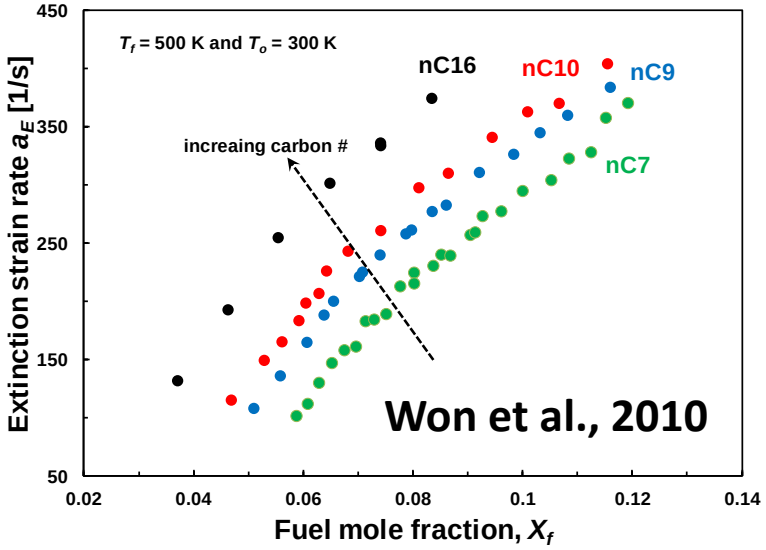
➢ **Then, what is the role of transport on kinetics?**

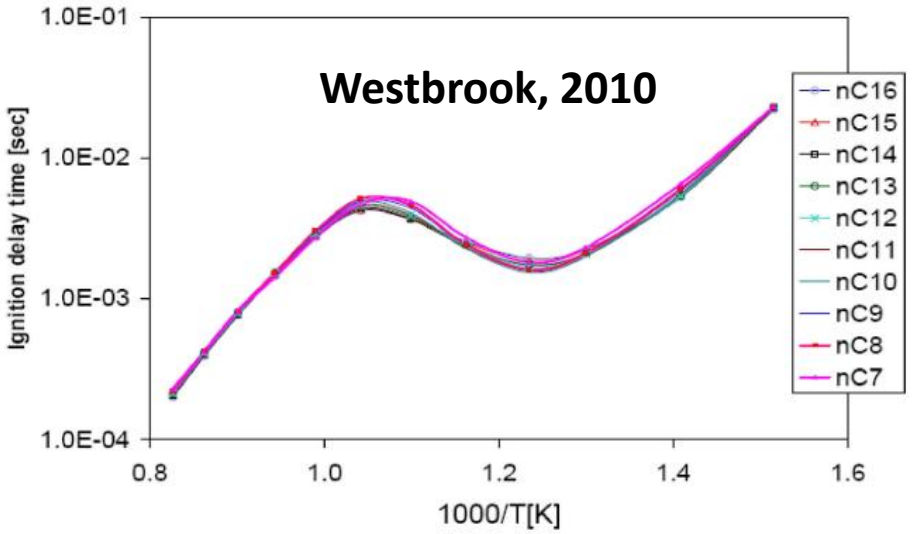
- **Is flame chemistry different from that of homogeneous ignition?**
- **How does transport and flame chemistry govern flame extinction?**
- **How does transport and flame chemistry affect unsteady flame initiation and propagation?**
- **How does low temperature chemistry change flame regimes?**

Flames: Different fuels have different extinction limits



Ignition vs. flames: n-alkanes and esters

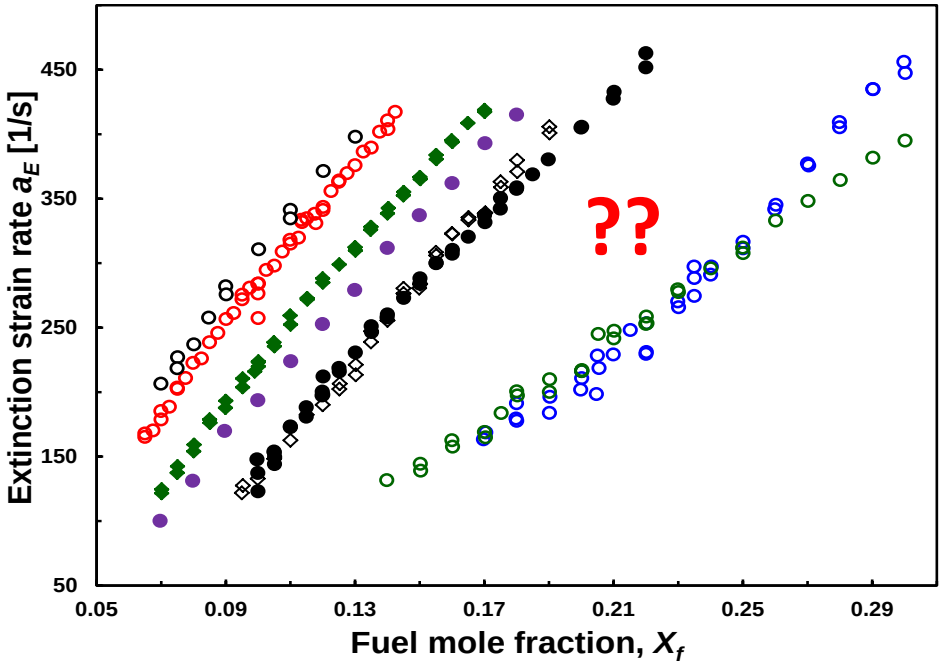




?

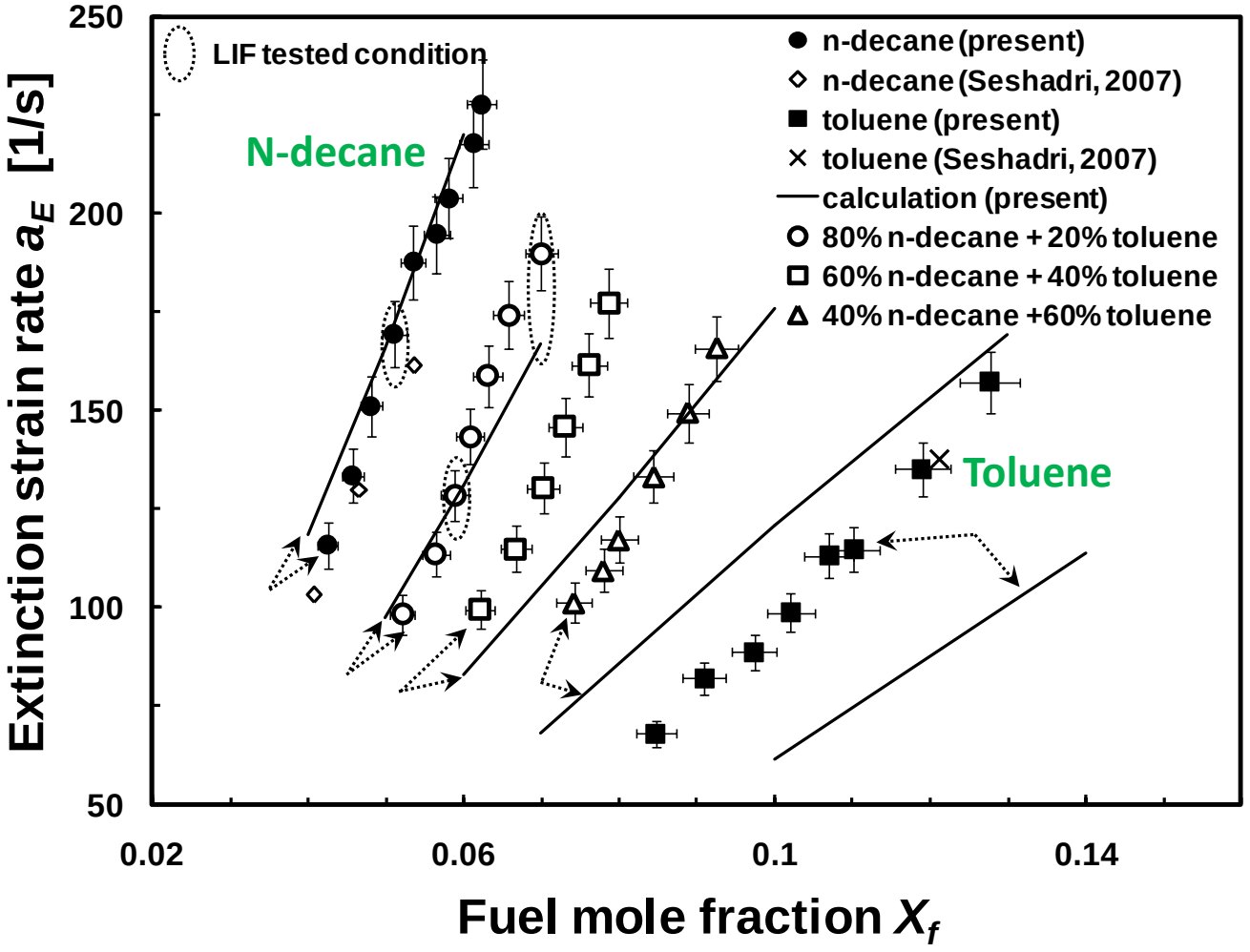
T_f = 500 K, T_{ox} = 298 K

- Methyl Formate
- Methyl Ethanoate
- Methyl Propanoate
- Methyl Butanoate
- Methyl Pentanoate
- Methyl Hexanoate
- Methyl Octanoate
- Methyl Decanoate



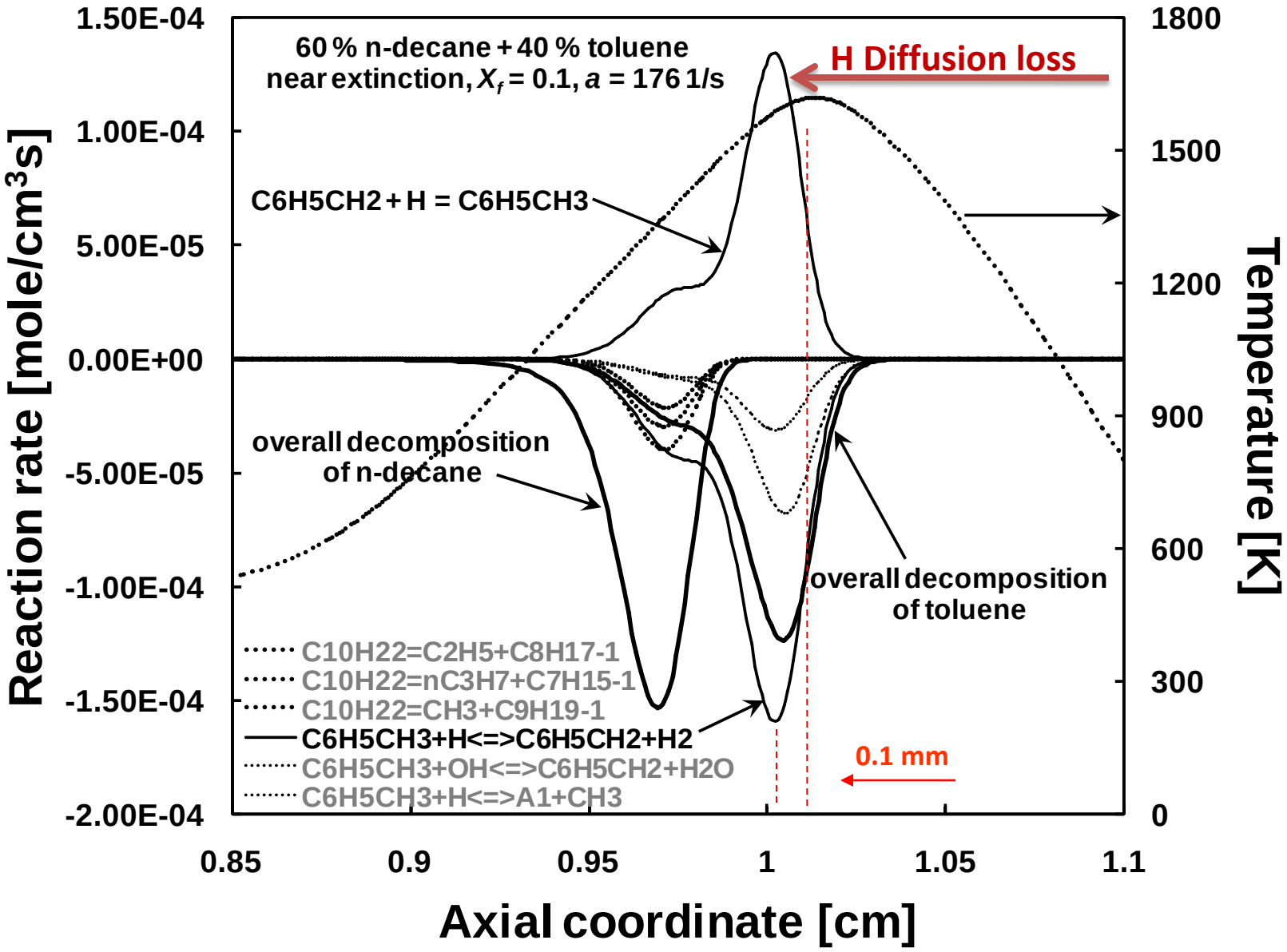
Kinetic coupling between alkanes and aromatics

Blending toluene into n-decane: Extinction Limits



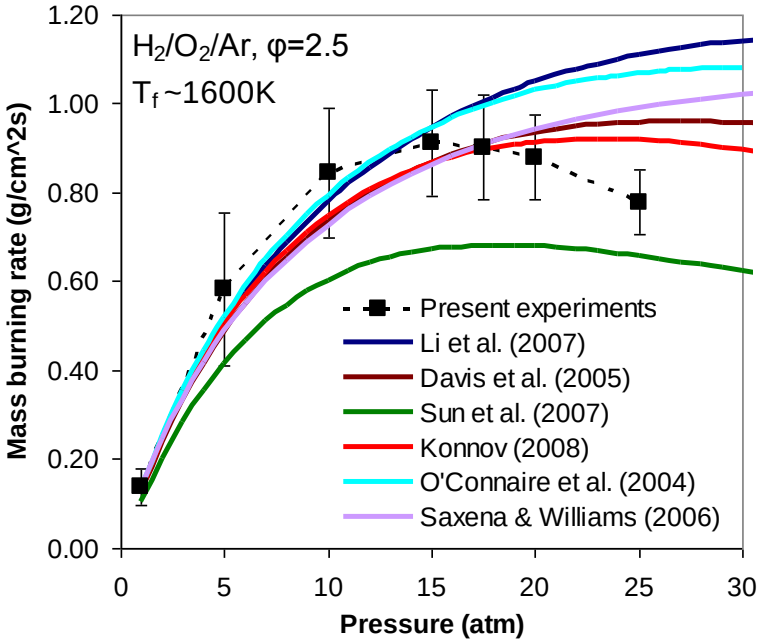
Won, Sun, Dooley, Dryer, and Ju, CF 2010

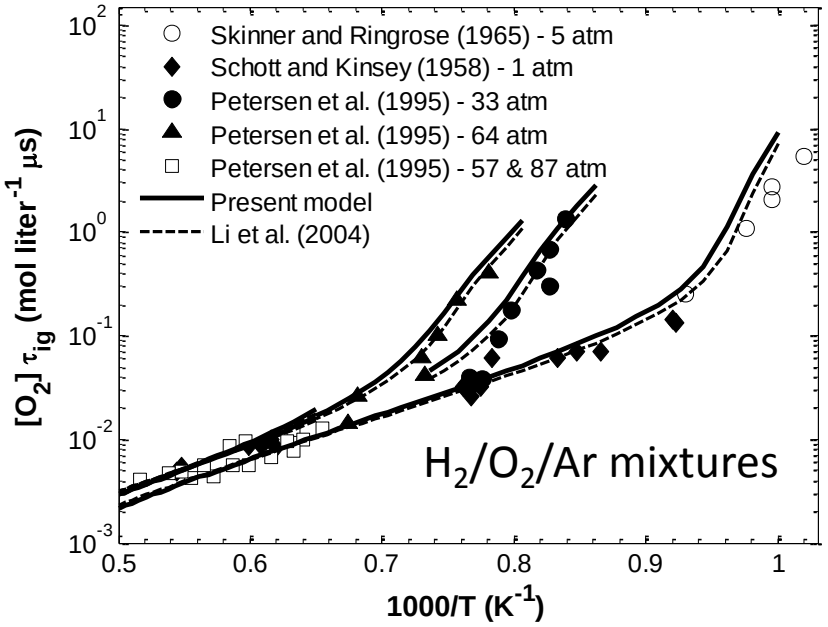
Kinetic coupling between n-decane and toluene in diffusion flames



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

High pressure hydrogen kinetics: ignition and flames





Uncertainty of HO2 related kinetics at high pressure,

- **Ignition governed more by chain initiation and branching rates**
- **Flames governed more by branching rate and heat release rate**
- **Different radical pool concentration (H, OH, …)**

Bulke, Marcos, Dryer, Ju, CF, 2010
Burke, Chaos, Ju, Dryer, Klippenstein, IJCK 2011

Difference of kinetics in homogeneous reactor and flames

Homogeneous reactor (800 K)

Fuel consumption by radicals

component	% consumed by radical reaction			
	OH	HO_2	H	O
n-decane	86%	6.0%	3.6%	2.0%
iso-octane	82%	6.5%	5.8%	2.3%
Toluene	88%		2.8%	4.5%

OH is r the most significant radical in fuel consumption

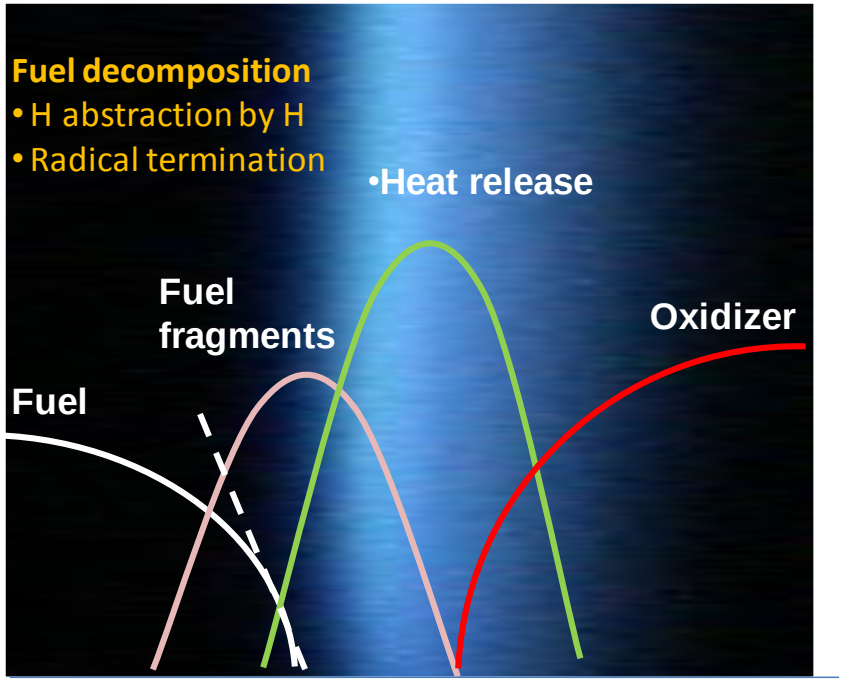
Diffusion flames (~1600K)

Fuel consumption by Radicals

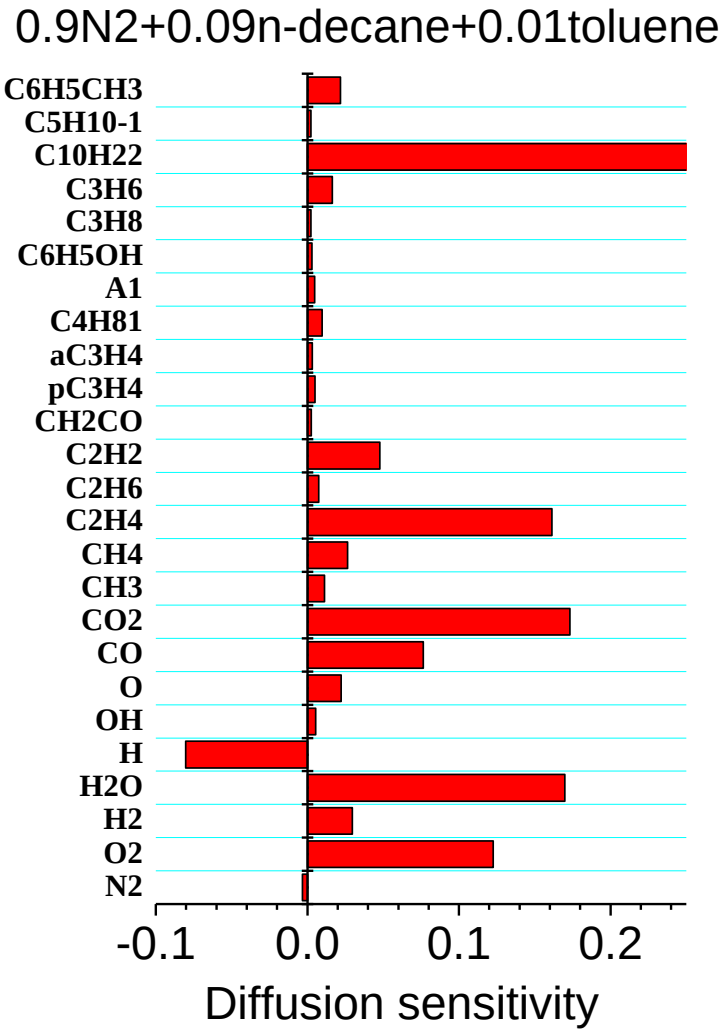
component	% by uni-molecular decomposition	% consumed by radical reaction			
		H	OH	CH_3	O
n-decane [1]	19.3%	67.2%	6.1%	5.8%	0.1%
Methylbutanoate [2]	6.6%	70.8%	10.3%	8.1%	3.7%

1. Won et al. CNF 159 (2012)
2. Dooley et al. CNF 159 (2012) 1371-1384.

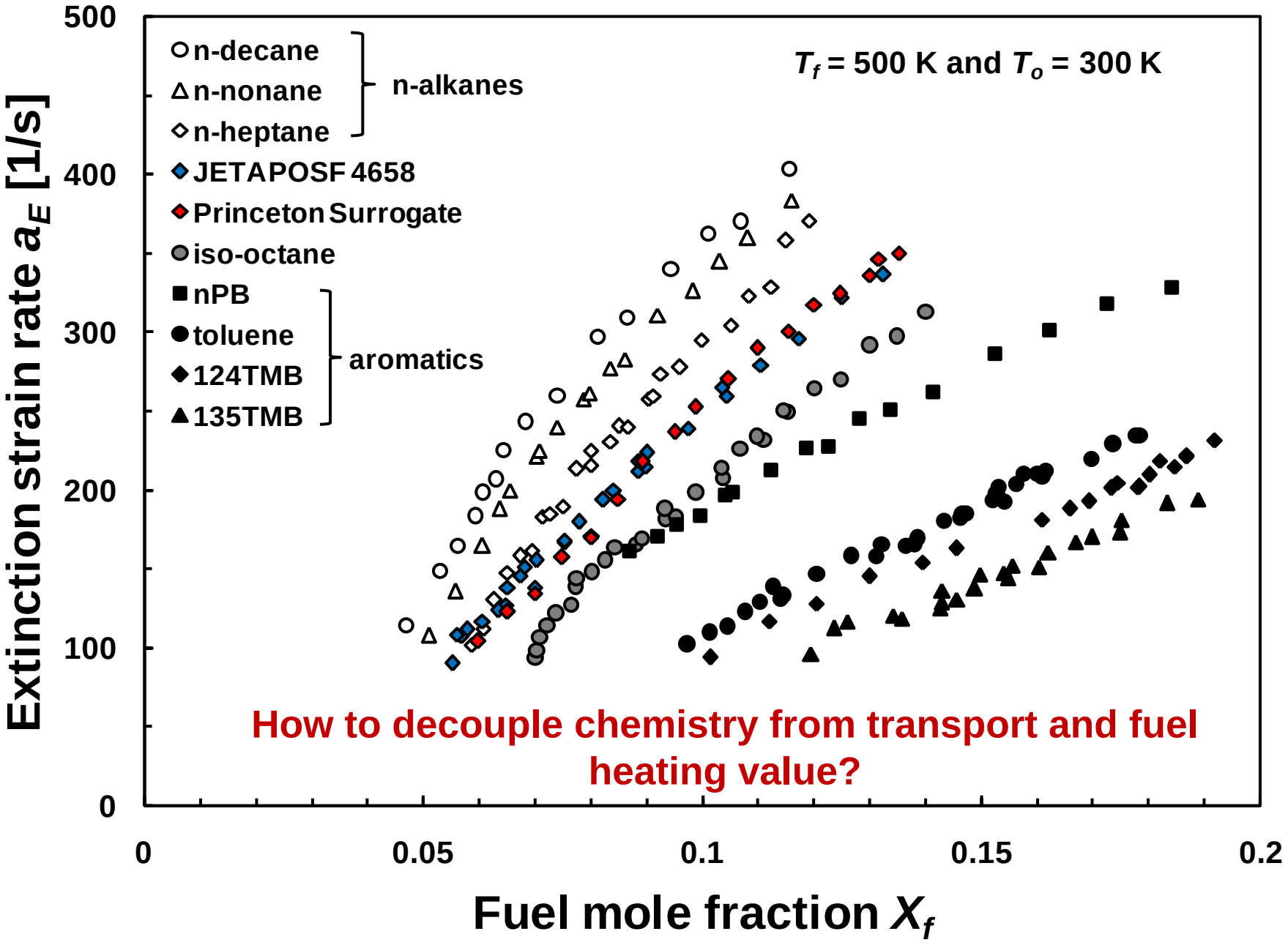
2. How does transport and flame chemistry govern diffusion flame extinction?



$$Q \sim \rho D_i \left. \frac{dY_F}{dx} \right|_{0-}^{0+} = \int_0^{\delta} \omega_i dx$$



Flames: Different fuels have different burning limits



A generic correlation for extinction limit: Transport weighted Enthalpy & radical index

Theoretical analysis of 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

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

Transport

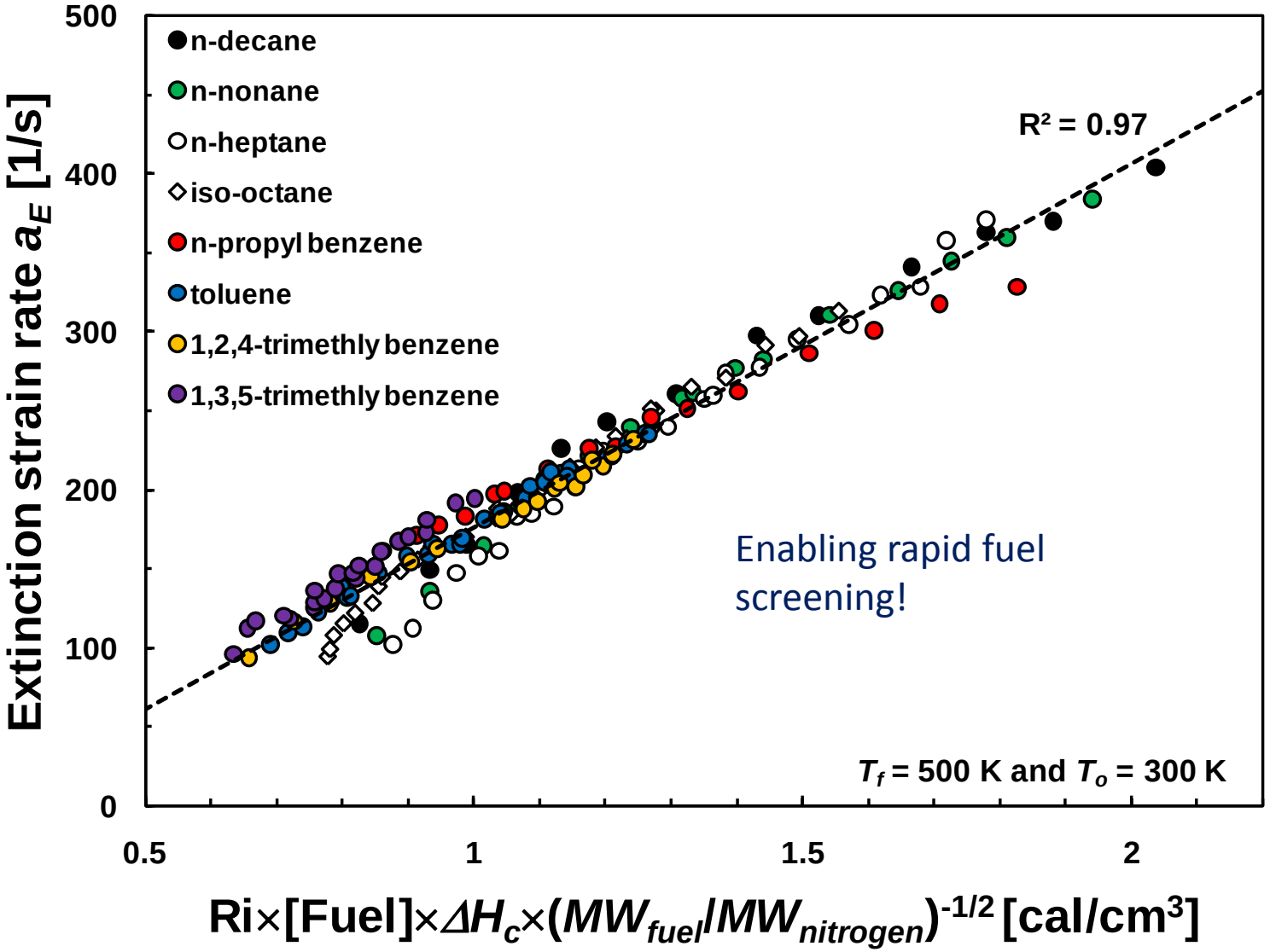
Heat release/heat loss

Fuel chemistry
Radical production rate

Transport weighted Enthalpy *Radical index

Won et al. CNF 159 (2012)

A General Correlation of Hydrocarbon Fuel Extinction vs. Transport Weighted Enthalpy (TWE) and Radical Index



TWE and radical index for predicting extinction limits and synfuel fuel ranking and screening

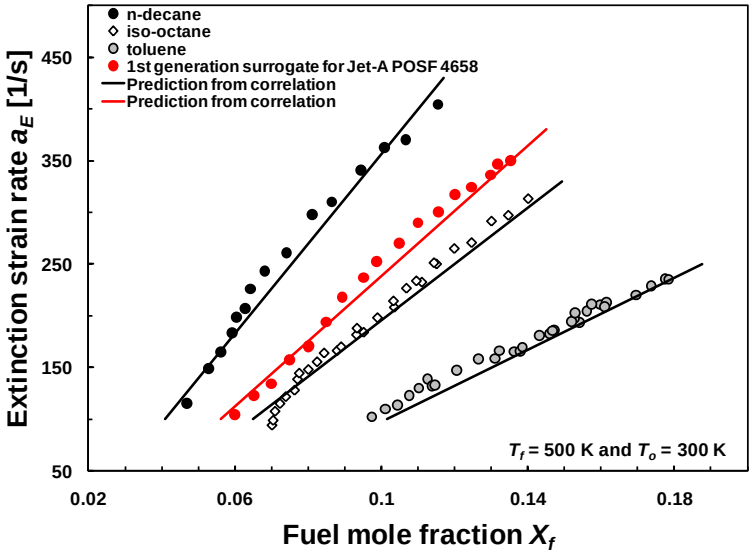
Radical Index

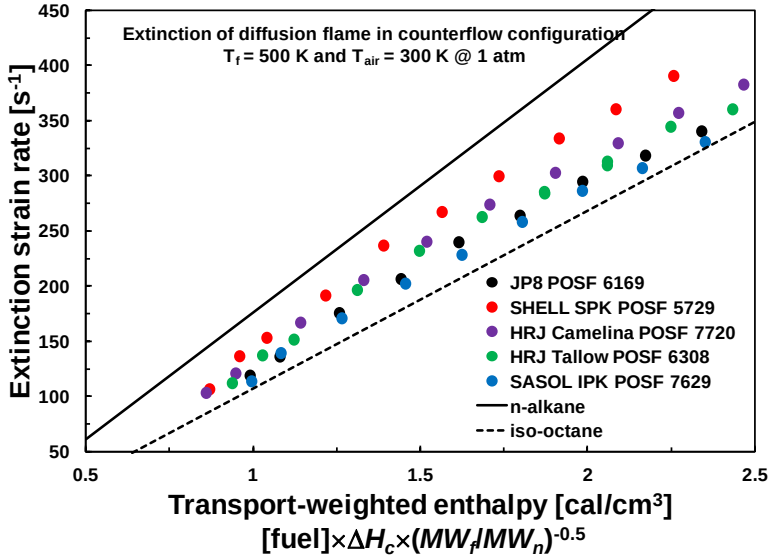
Representing radical pool
High temperature reactivity

Fuel	Radical Index
n-dodecane	1.0
iso-octane	0.7
toluene	0.56
n-propyl benzene	0.67
1,2,4-trimethylbenzene	0.44
1,3,5-trimethylbenzene	0.36
JetA POSF 4658	0.79
S8 POSF 4734	0.86
JP8 POSF 6169	0.80
HRJ Camelina POSF 7720	0.82

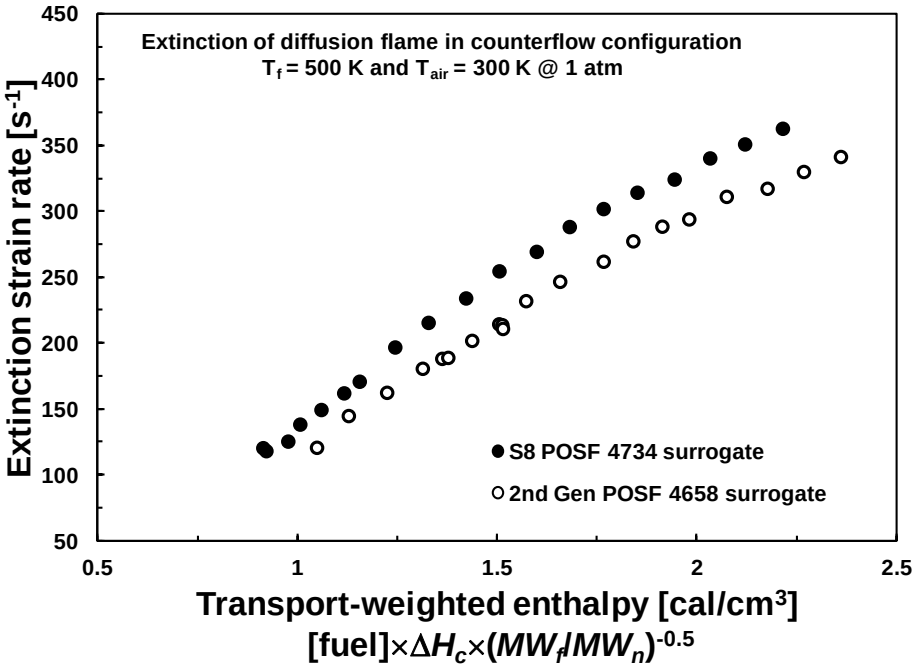
Single fuel
Real fuel

Synfuels

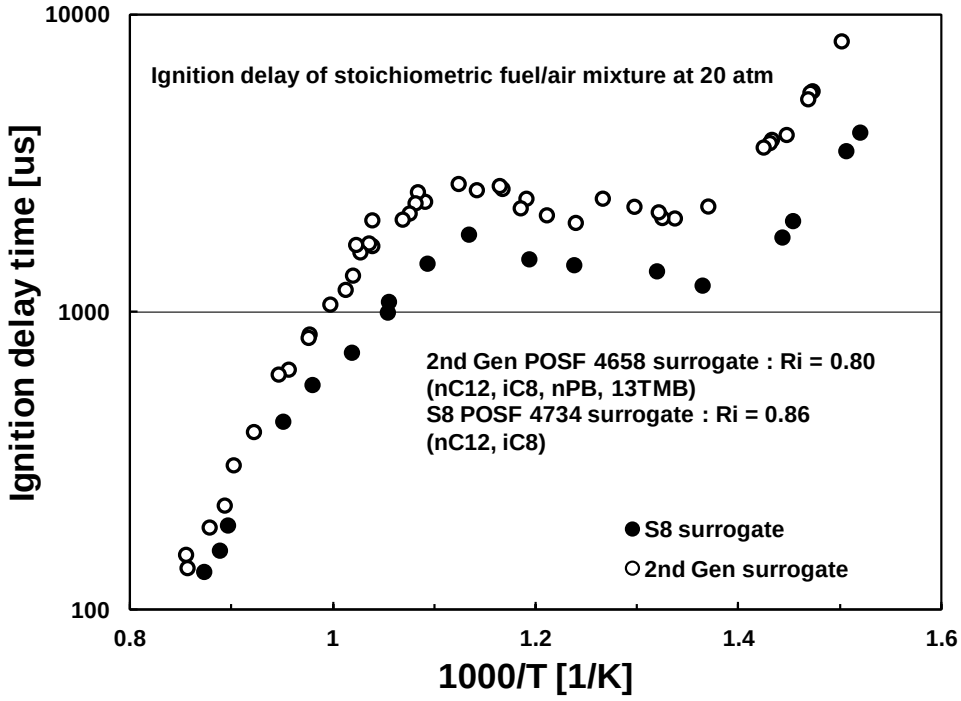




Ignition Delay vs. Radical Index (real fuel)



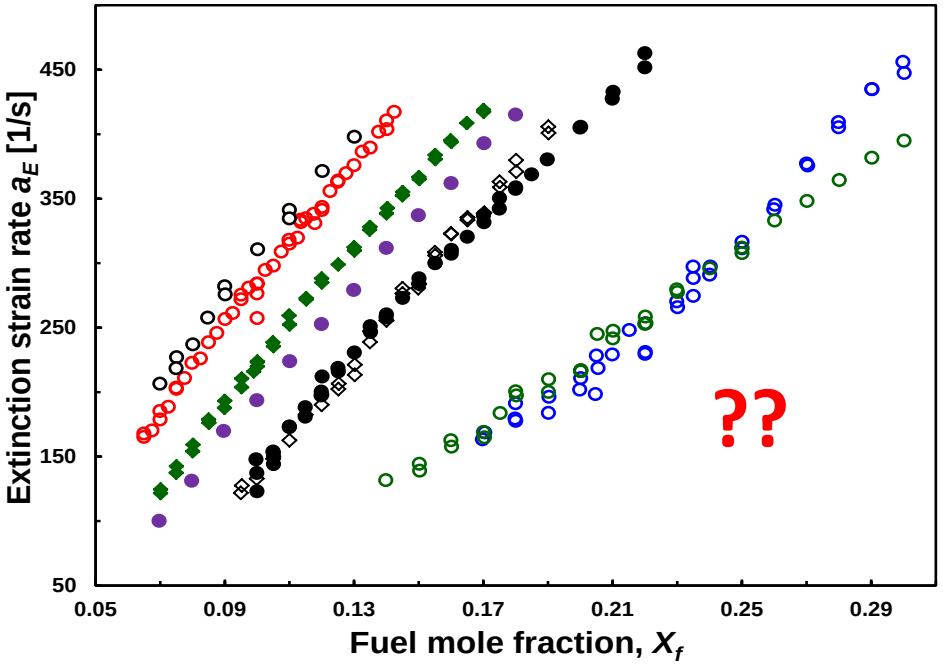
Dooley et al., CNF 159 (2012)



Consistent in high temperature reactivity

Measurements from RPI (Oehlschlaeger), Dooley et al., CNF 159 (2012), Dooley et al., CNF (2012) in press

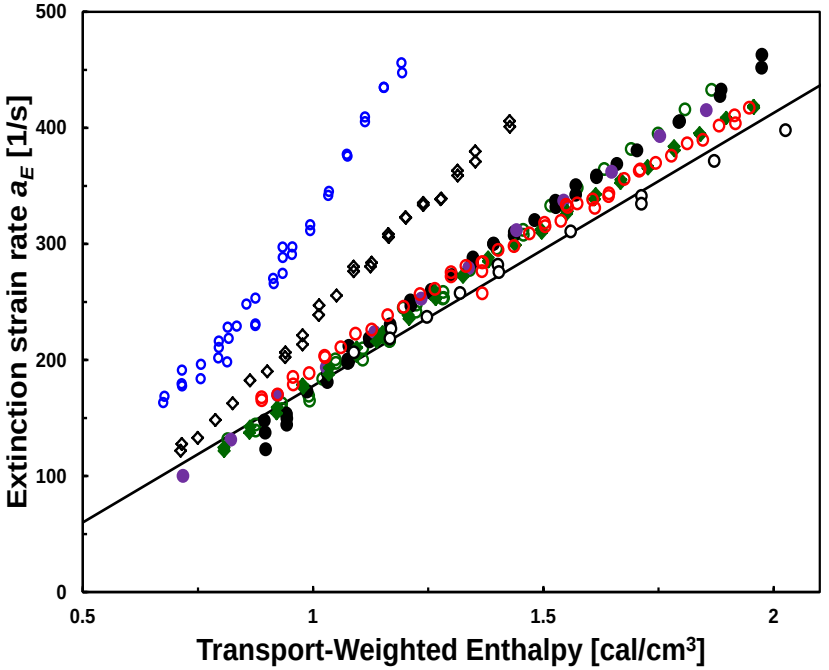
Scaling high temperature reactivity of methyl esters: Using TWE and Radical Index



T_f = 500 K, T_{ox} = 298 K

- Methyl Formate
- Methyl Ethanoate
- Methyl Propanoate
- Methyl Butanoate
- Methyl Pentanoate
- Methyl Hexanoate
- Methyl Octanoate
- Methyl Decanoate

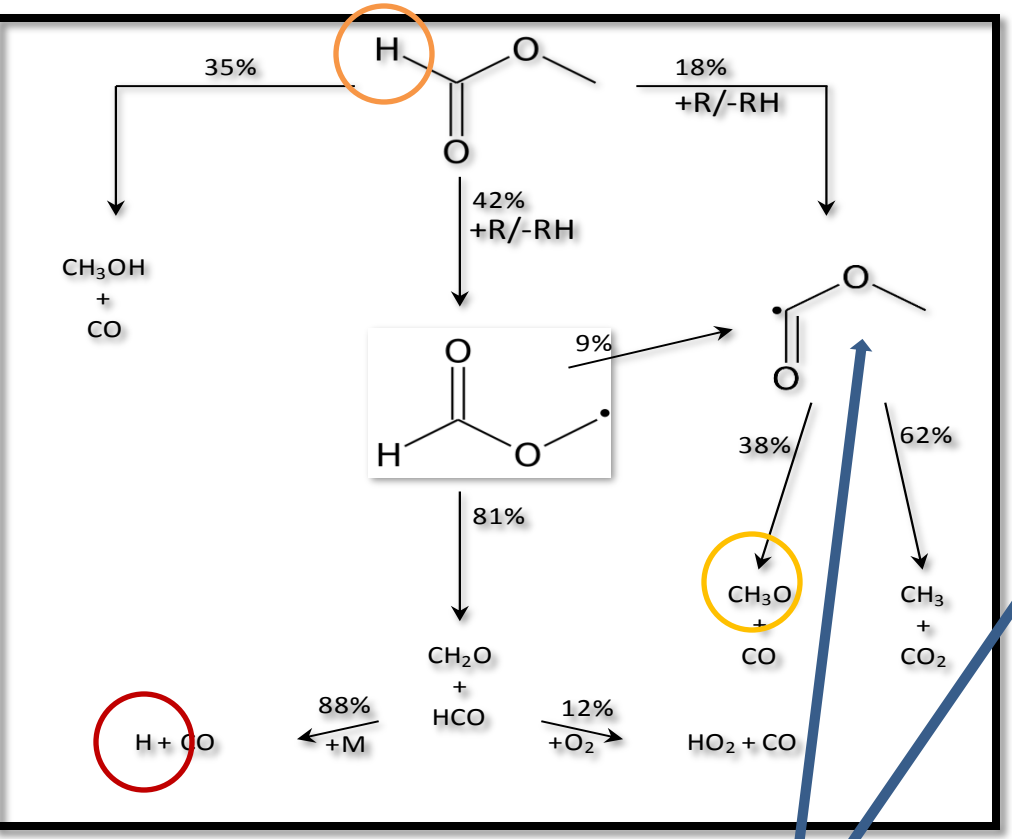
Different heating values
Transport properties



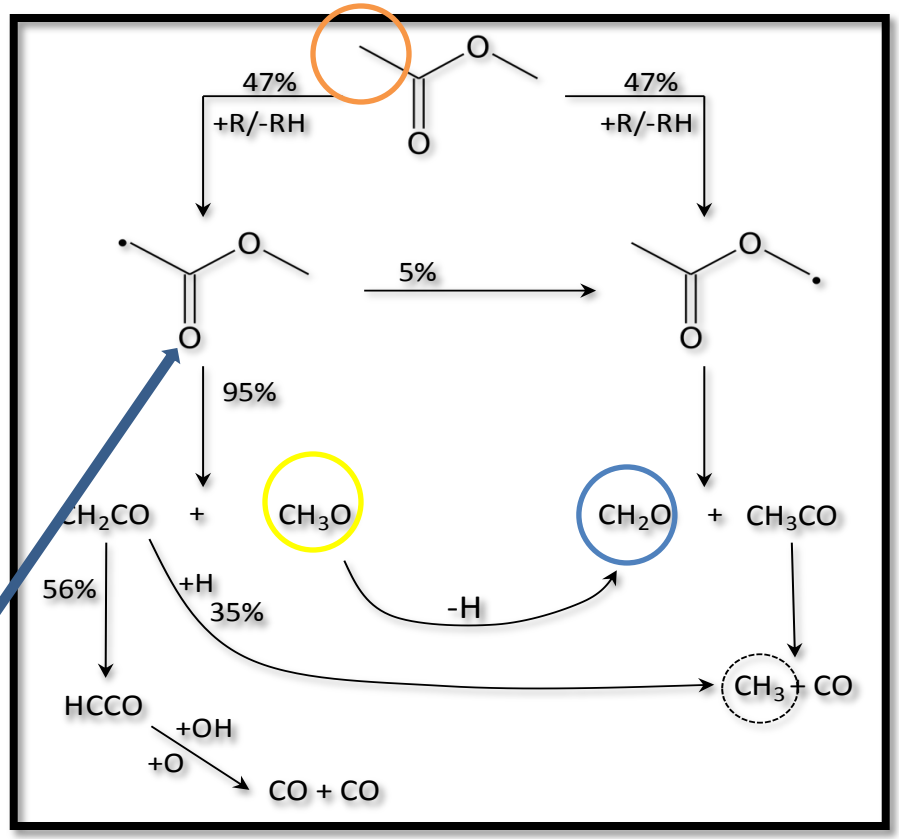
Diévart et al, 2012
to presented on Monday at 34th Symposium

Impact of alkyl chain length on methyl ester reactivity

Methyl Formate, R0C



Methyl Acetate, R1C



Higher reactivity

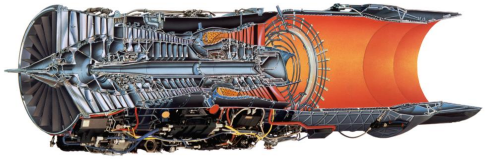
Lower reactivity

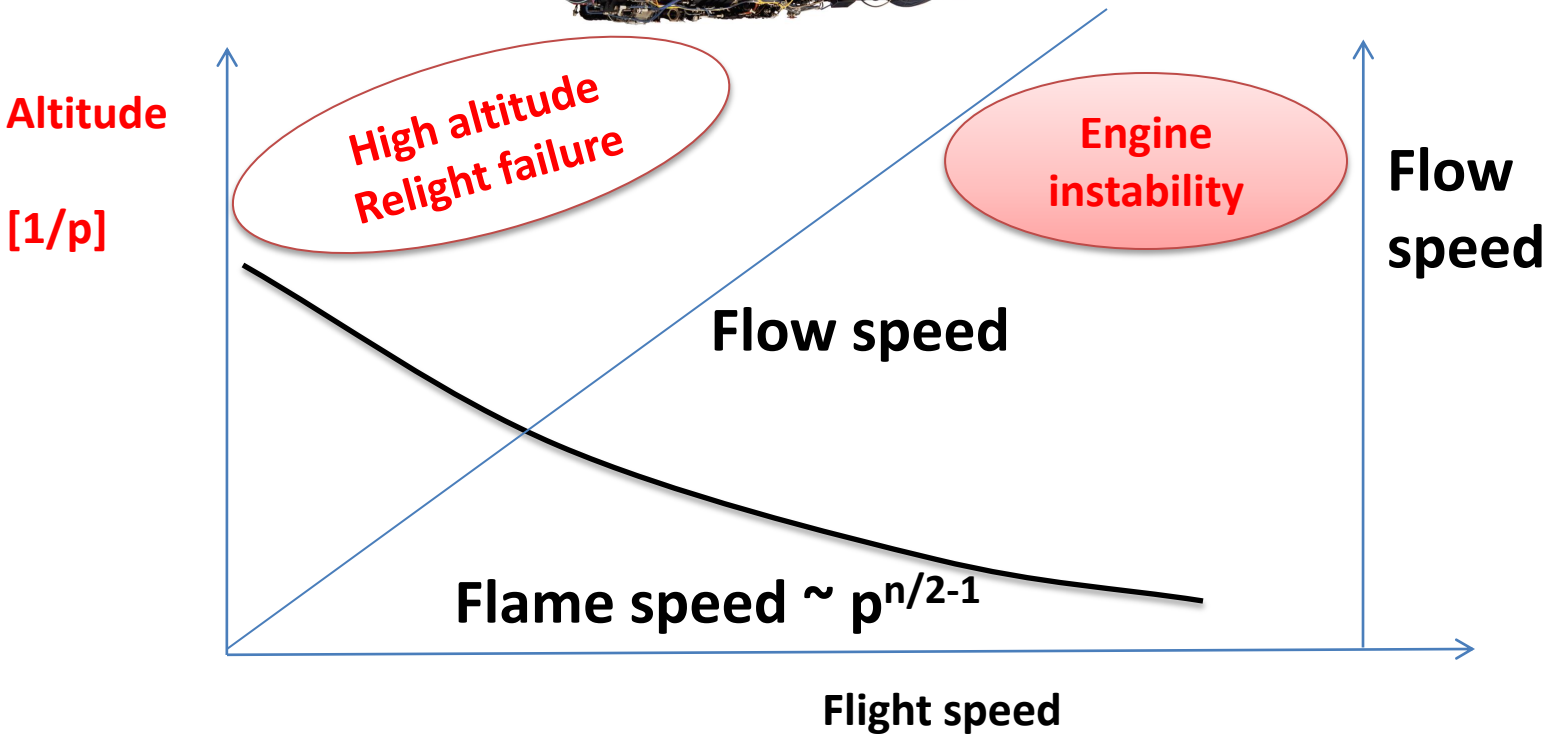
H abstraction reactions, CH3OCO and CH3OC(O)CH2 decomposition reaction rates: large discrepancies (Xueliang, 2012)

Diévart et al, 2012
to presented on Monday at 34th Symposium

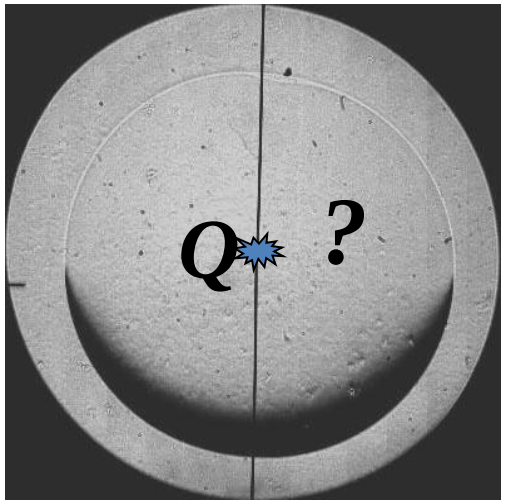
3. How does transport and flame chemistry affect flame initiation and propagation?

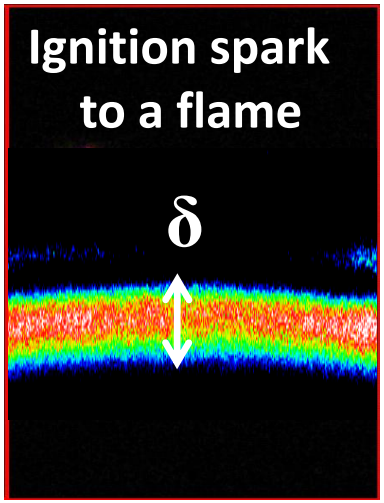
Puzzle of high altitude relight: an unresolved ignition problem or a flame problem?





Is the flame speed really a problem for relight?





- **What governs the ignition & E_{ig}?**
- **What are the chemistry and transport effects?**

$$Le = \frac{\text{Thermal diffusivity}}{\text{Mass diffusivity}} = \frac{oxygen}{Jet\ \ fuel}$$

•$E_{ig,min}$: Defined by flame thickness, δ (make a guess)?

B. Lewis and Von Elbe (1961), Ronney, 2004, Glassman (2008)

$$E_{ig} = \frac{4}{3}\pi\delta^3\rho C_p(T_{ad} - T_\infty) \propto \frac{1}{S_u{}^3} \propto \frac{1}{Le^{3/2}}$$

volume

heat capacity

Larger fuel molecules ⇔ smaller E_{ig}

•$E_{ig,min}$: Defined by stable "flame ball" size?

Zeldovich et al. (1985), Champion et al. (1986)

$$E_{ig} = \frac{4}{3}\pi R_Z{}^3\rho C_p(T_{ad} - T_\infty) \sim Le$$

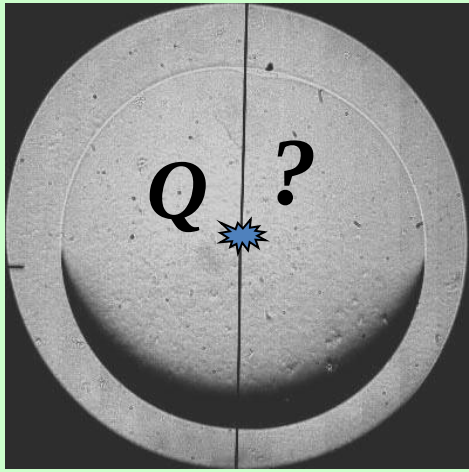
Larger fuel molecules ⇔ larger E_{ig}

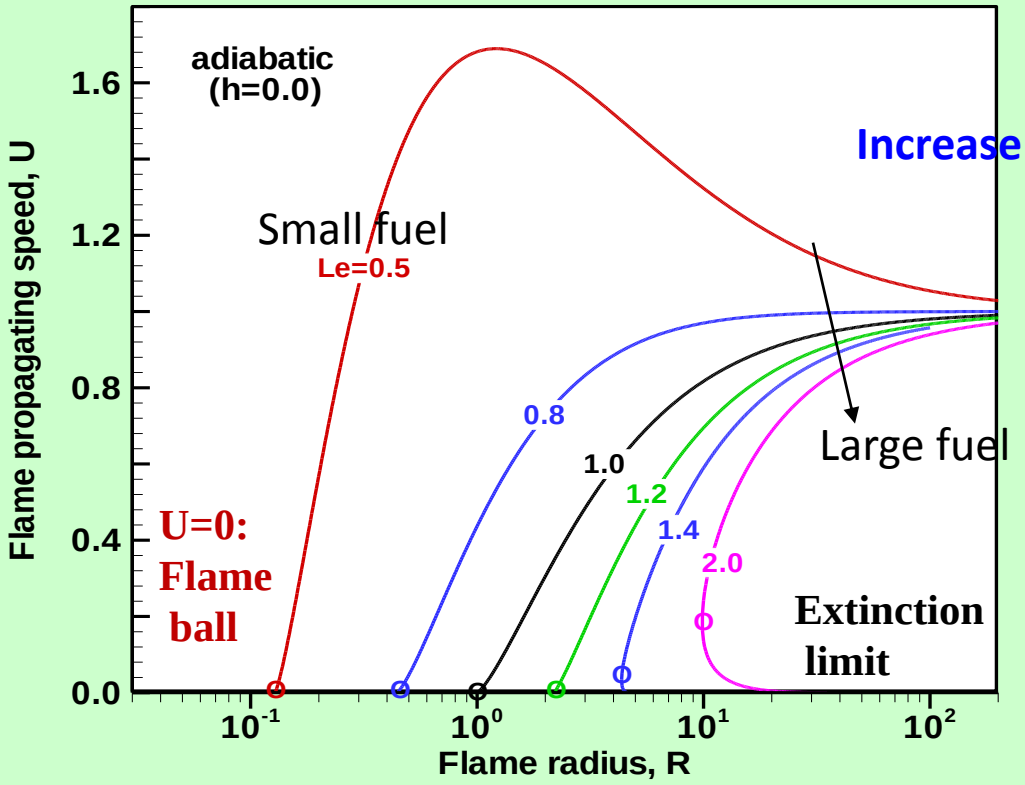
Theory: Critical Ignition Size vs. Flame Speed

Assumptions and simplification:

- **1D quasi-steady state, Constant properties**
- **One-step chemistry**
- **Center energy deposition**

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





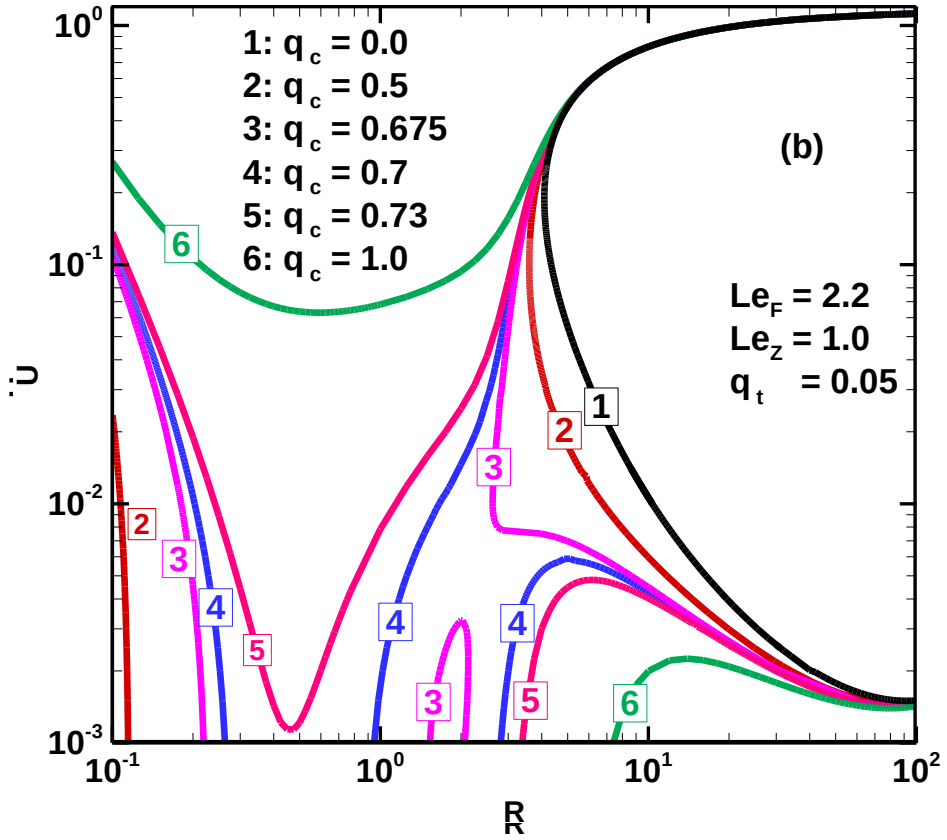
Chen & Ju, Comb. Theo. Modeling, 2007

Increase of fuel molecule size

The critical ignition size and energy is governed by two different length scales

- **Flame ball size (small Le)**
- **Extinction diameter (large Le)**

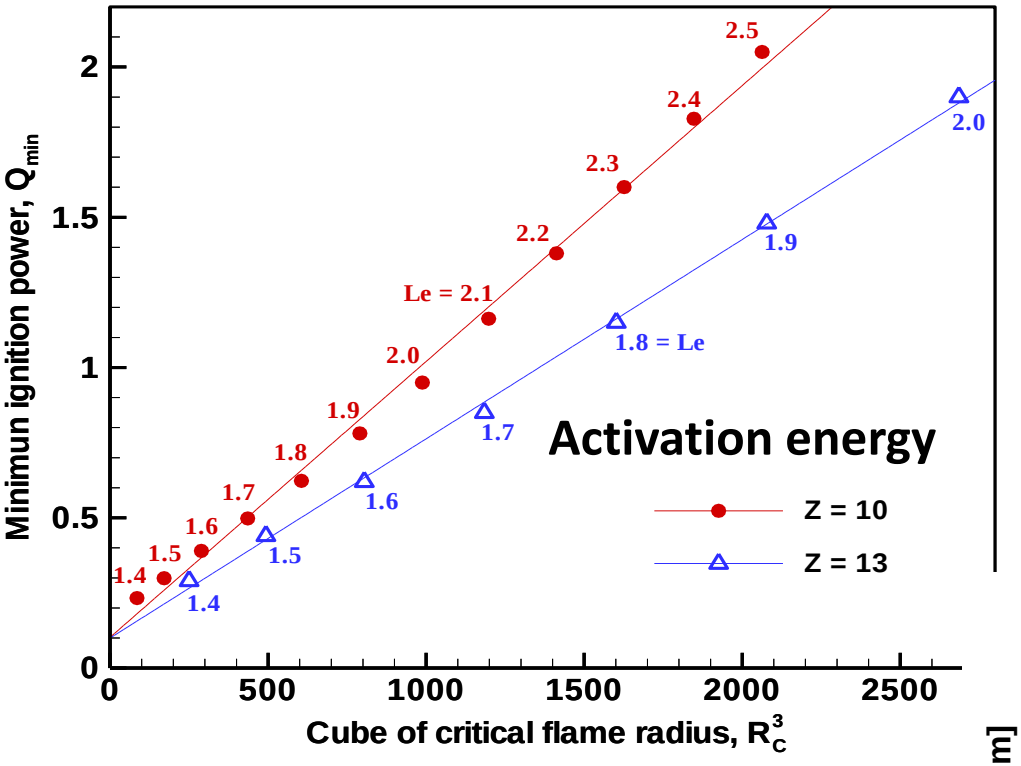
Ignition by heat and radical deposition (q_t=0.05)



Le_F = 2.2

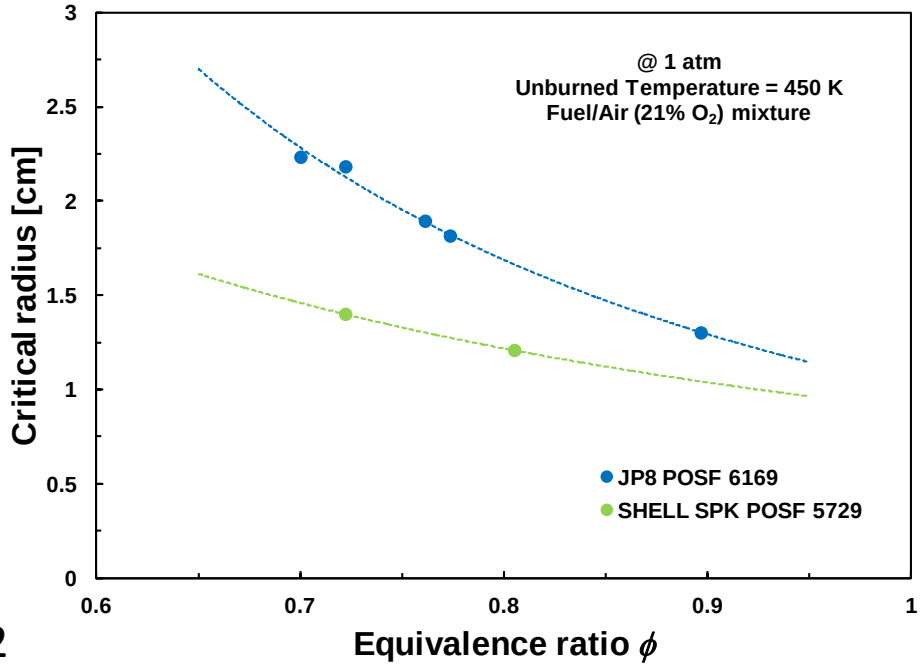
Chen et al. 2011

Ignition energy: impacts of flame chemistry and transport



Chen, Burke, Ju, Proc. Comb. Inst. Vol.33, 2010

Fuel	Mean molecular weight	Radical Index
JP8 POSF 6169	153.9	0.80
SHELL SPK POSF 5729	136.7	0.85

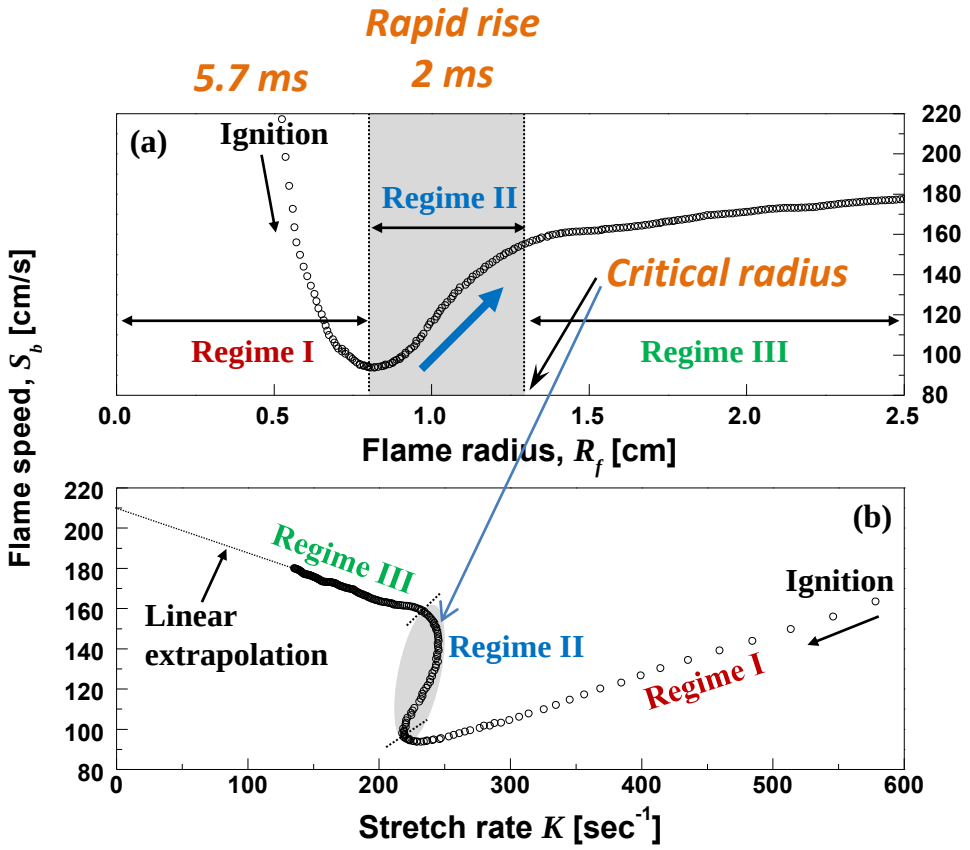


Won, Santer, Dryer, Ju, 2012

Unsteady flame initiation

Three different flame regimes (n-heptane/air)

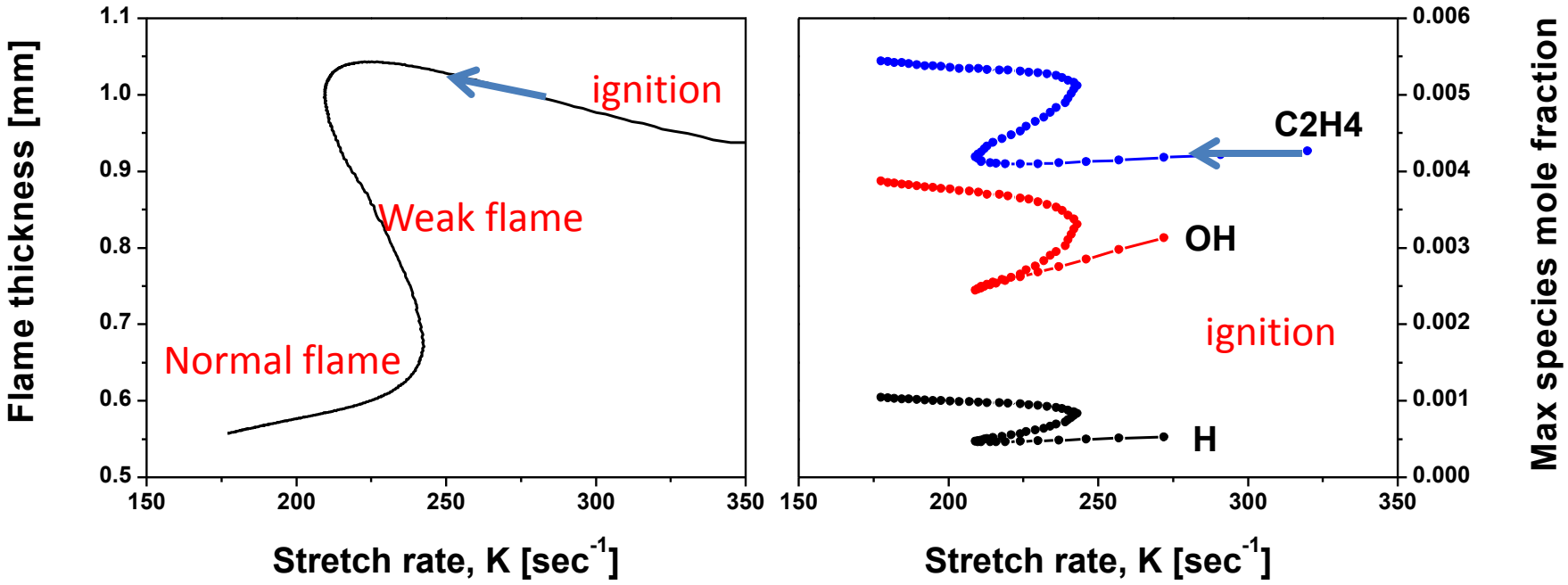
- **Regime I**
  - Spark assisted ignition kernel
- **Regime II**
  - Weak flame regime from sparked driven ignition kernel to normal flame
- **Regime III**
  - Self-sustained propagating normal flame



Kim et al, 2012, to be presented on Wednesday at 34th Symposium

Rapid change of flame structure in flame initiation process

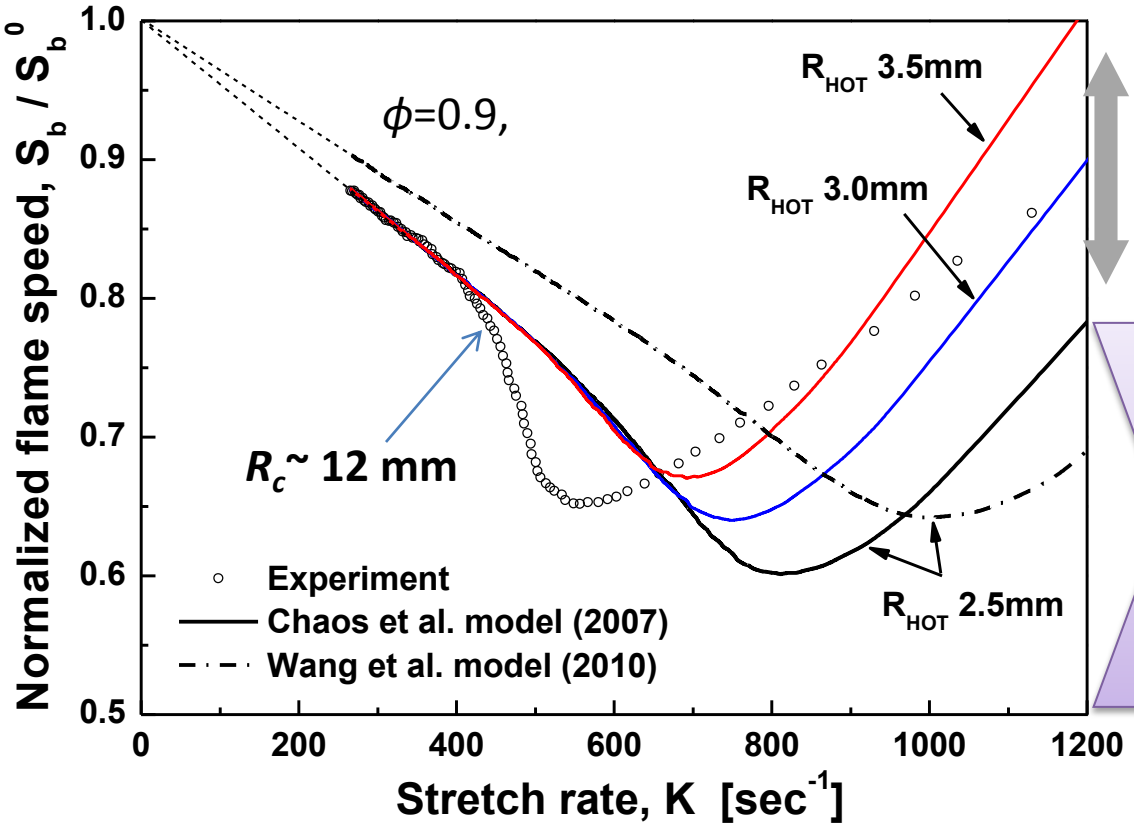
(lean n-heptane/air)



Completely different flame structures!

Kim et al, 2012, to be presented on Wednesday at 34th Symposium

Will a model for flame speed predict the unsteady flame initiation?
An example: Lean n-heptane flame initiation



Varying the Hot spot size

Accurate transient flame speed prediction

Turbulent modeling

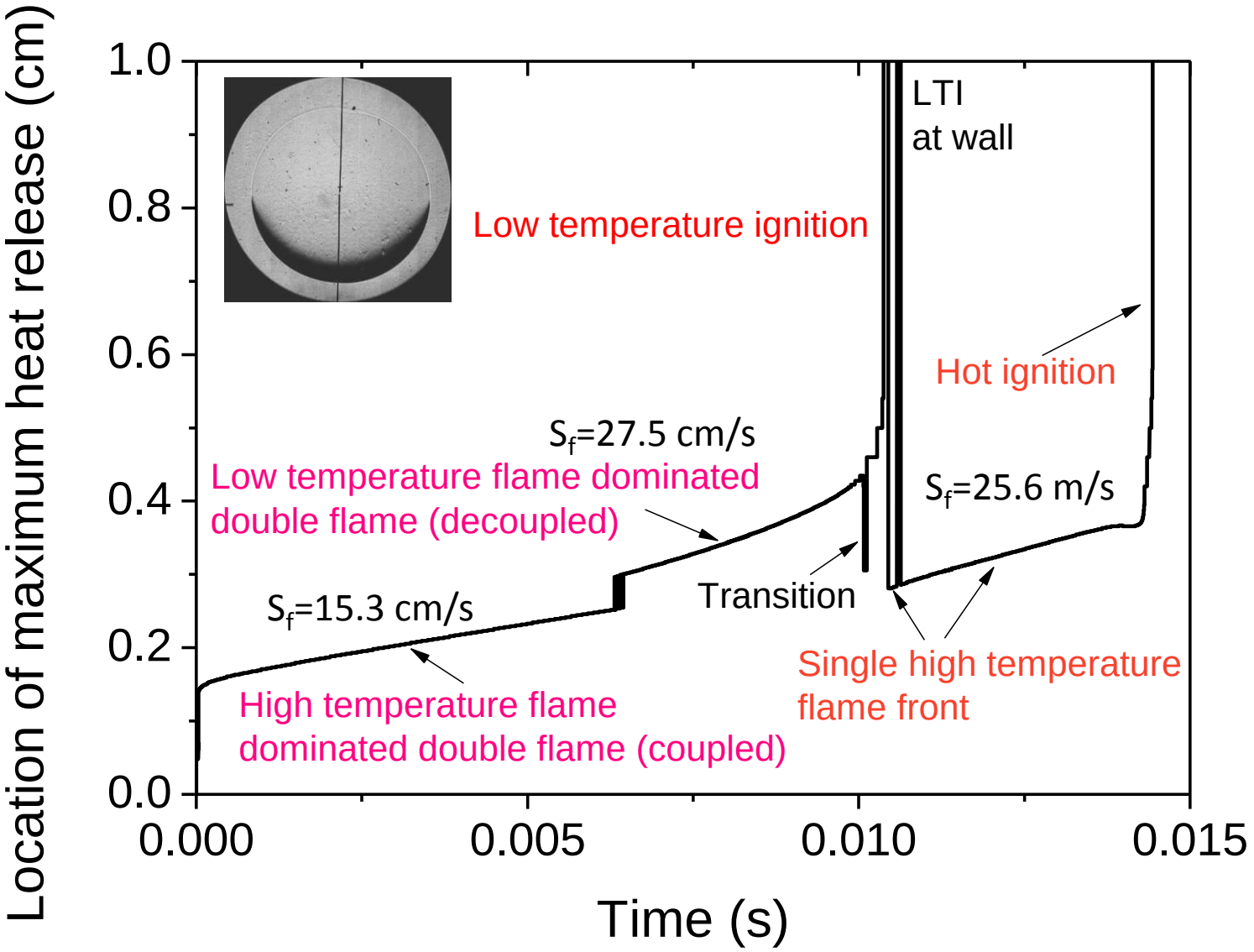
Critical flame initiation radius (R_c) >10 mm

4. How does low temperature flame chemistry affect flame initiation and propagation, and stabilization?

- **Low temperature chemistry (multi-stage ignition)**
- **Plasma assisted low temperature ignition. extinction**

Multi flame regimes in HCCI ignition n-heptane:40 atm, T=700 K

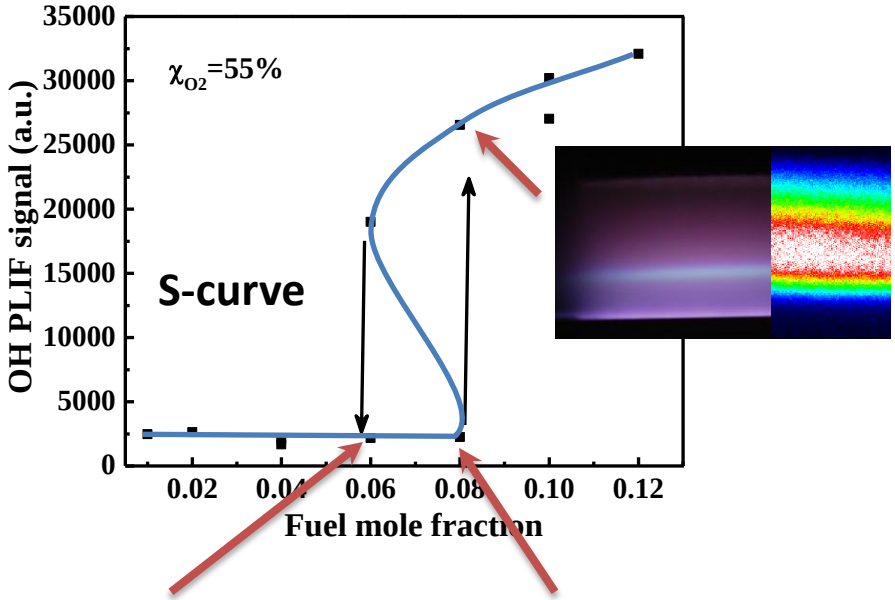
Movie

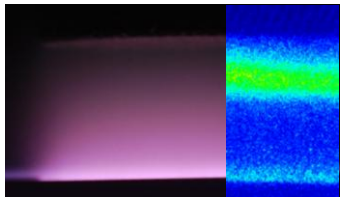


Ju et al. 33rd symposium 2011

New low temperature flame regime in Plasma assisted combustion

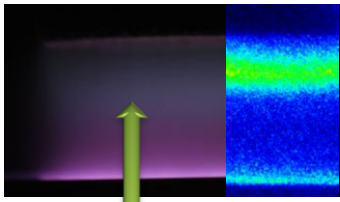
(Counterflow DME/O_2/He ignition)





Same OH LIF signal

different emissions



$CH_3O + OH \rightarrow CH_2O^* + H_2O$

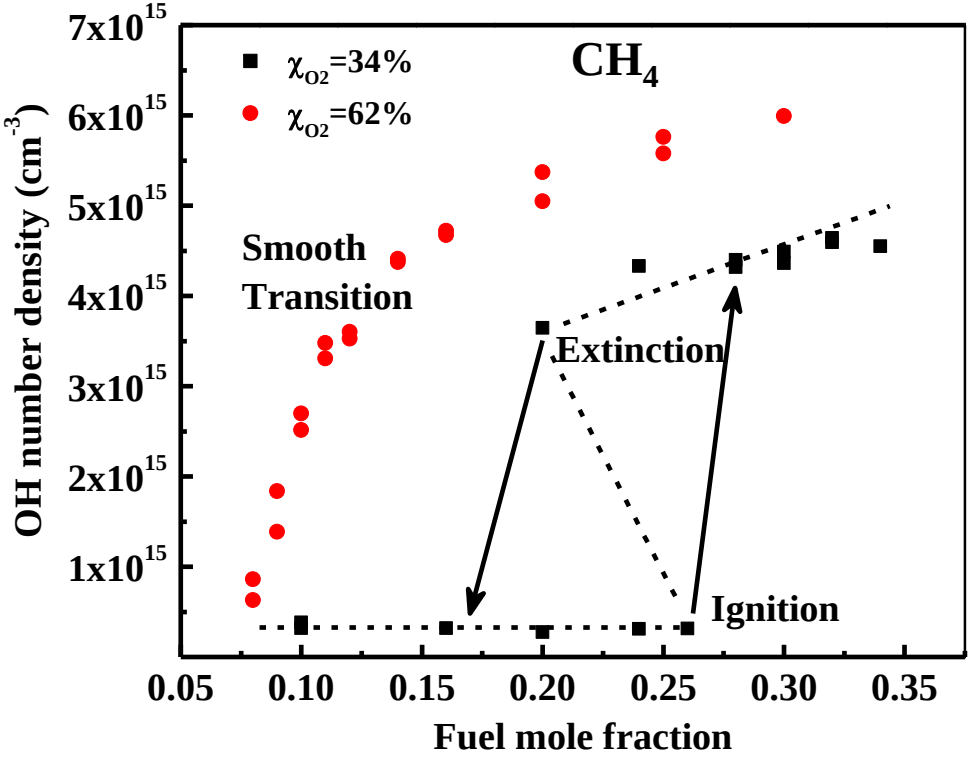
$RCH_2O + OH \rightarrow CH_2O^* + ROH$

R: organic radicals

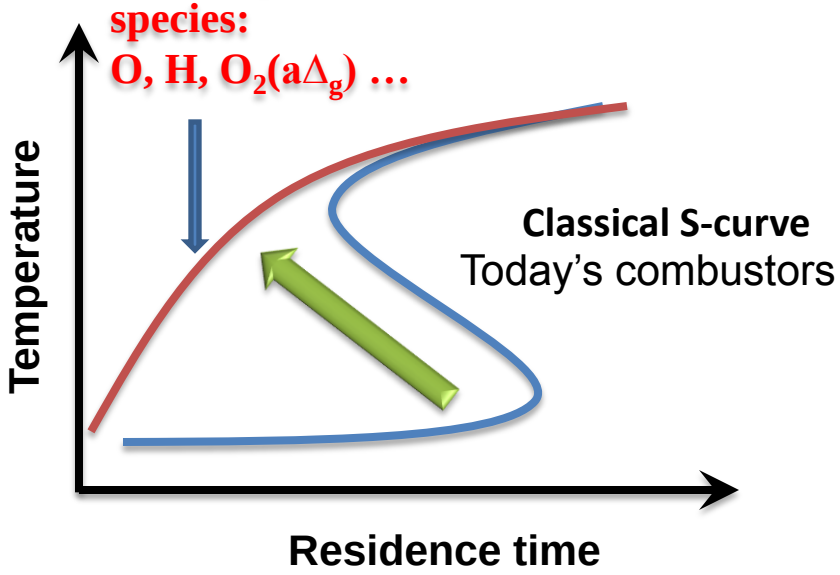
Sun et al., Friday 34th symposium on combustion, 2012

Kinetic enhancement of plasma assisted ignition: Change of S-curve

He/O_2 = 0.66:0.34 and 0.38:0.62 , P = 72 Torr, *f* = 24 kHz, a = 400 1/s



Plasma assisted LTC



Role of kinetics on PAC at low temperature?

Sun et al., 34th symposium on combustion, 2012

Conclusion

- Flames chemistry differs from homogeneous ignition in diffusion, fuel decomposition, radical pool production/consumption.
- Low temperature and unsteady combustion processes lead to new different flame regimes and structures.
- Flame initiation and extinction are strongly affected by both transport and chemical kinetics.
- Transport weight enthalpy and radical index are developed for predicting extinction limit and ranking fuel reactivity
- Large uncertainties in elementary reaction rates of kinetic mechanisms for simple fuels exist in extreme conditions.
- A validated mechanism using flame speeds fails to predict unsteady flame transition and the critical flame radius.

Welcome to
The 1st International Flame Chemistry Workshop

Sincere Thanks To:

- Invited lecture (11) speakers and Session (4+1+2) chairs
- Committee and advisory board members
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