# Kinetic effects of blended n-alkane and aromatic fuel mixtures on the extinction limits of diffusion Flames
# &
# A new dynamic multi-time scale algorithm and path flux analysis method for mechanism reduction

**Sang Hee Won, Wenting Sun, Xiaolong Gou, Yiguang Ju***

**Department of Mechanical and Aerospace Engineering**
**Princeton University**

**Sept.14-17, 2009**

# 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…

  *By matching H/C ratio, sooting index, burning rates, ignition time…*
- **Example: Gasoline Surrogate model (PRF+1)**
  - Blending of toluene to n-heptane and iso-octane to match both burning and soot formation targets
- **Challenge 1**:

  How does the kinetic coupling between aromatics and alkanes affect burning rate and extinction limit?

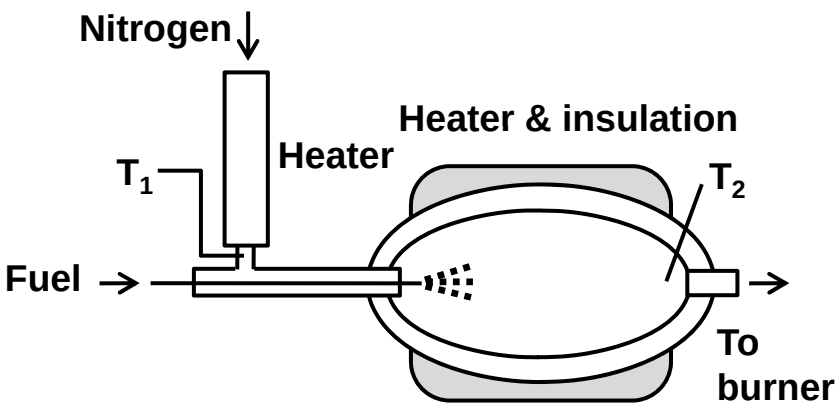
  How can we predict burning limits, flame speeds from mixing rule?
- **Challenge 2**:

  How to generate robust, efficient, & user friendly reduced kinetic models?

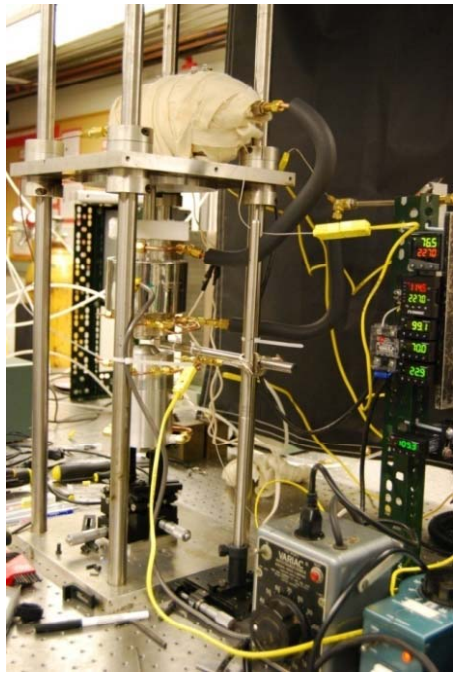
# 1. Experimental Studies of Kinetic Effects of Diffusion Flame Extinction Limits

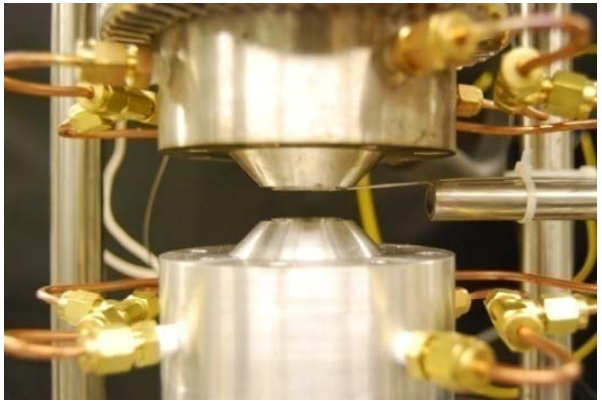
**(Fuel Vaporization and Counterflow Burner)**

- **Experimental setup of the measurements of n-decane/aromatics extinction limits**
  - Using FTIR measurements to check thermal decomposition and concentration variation: Concentration fluctuation < 1%




Schematics of evaporation system

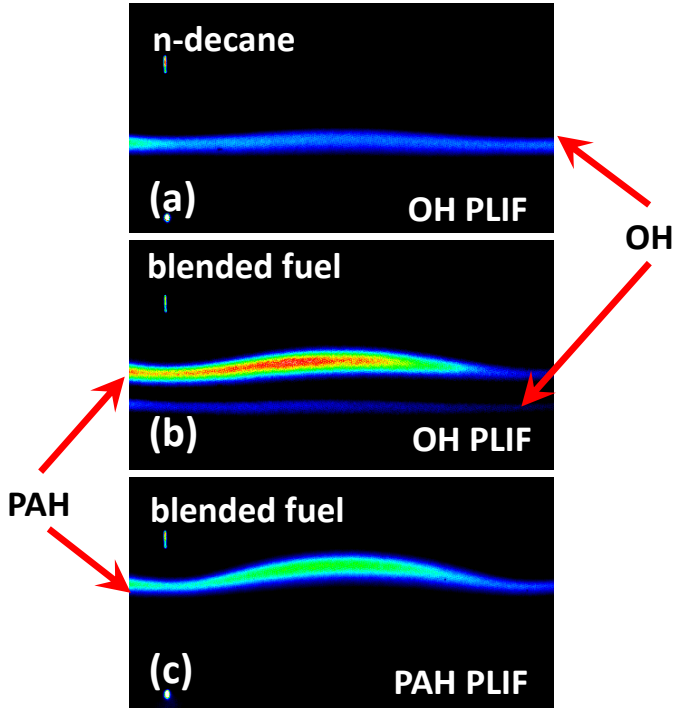




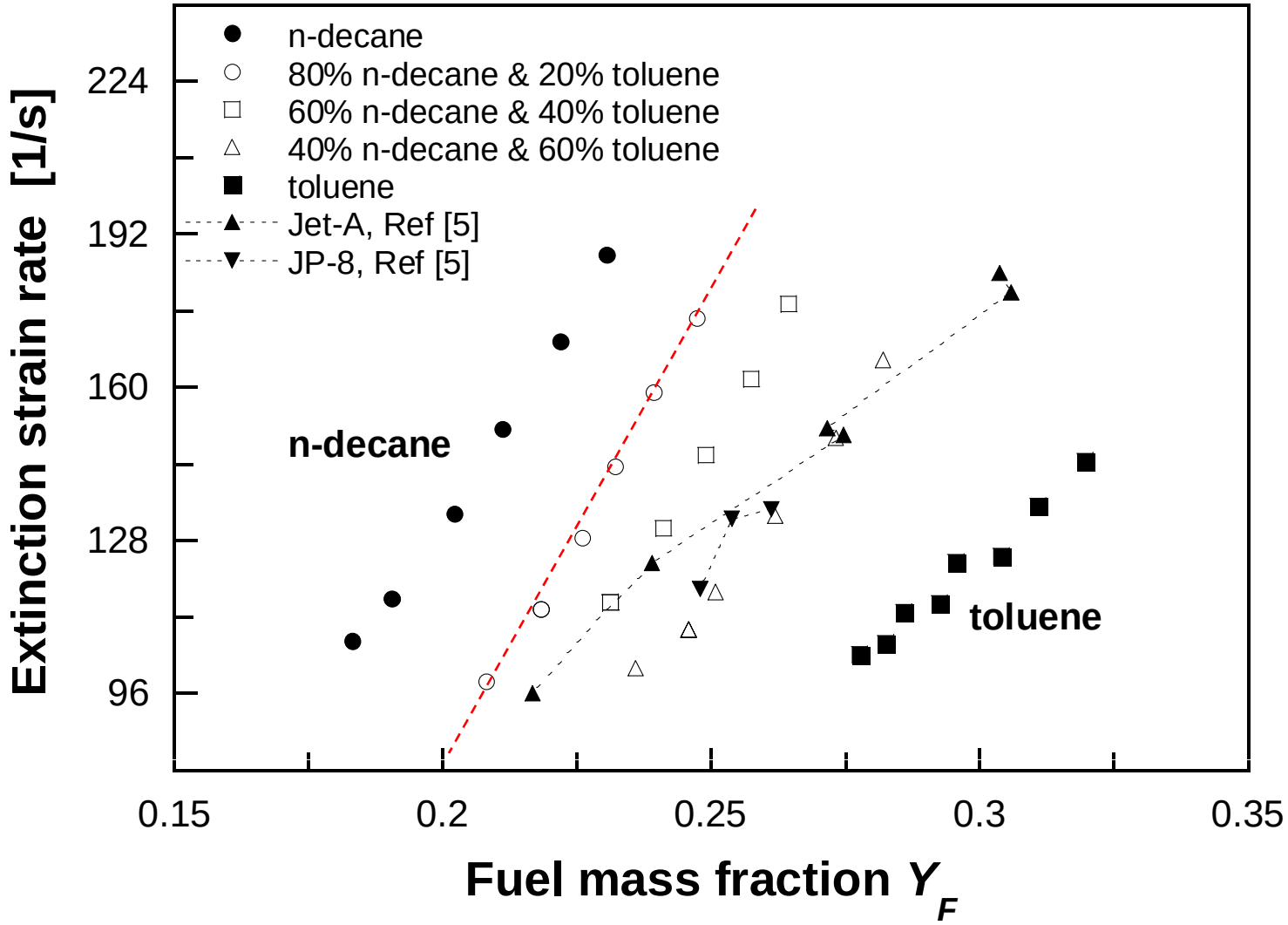
# Experimental Measurements of OH Concentration
## by using laser induced fluorescence

- 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 correction

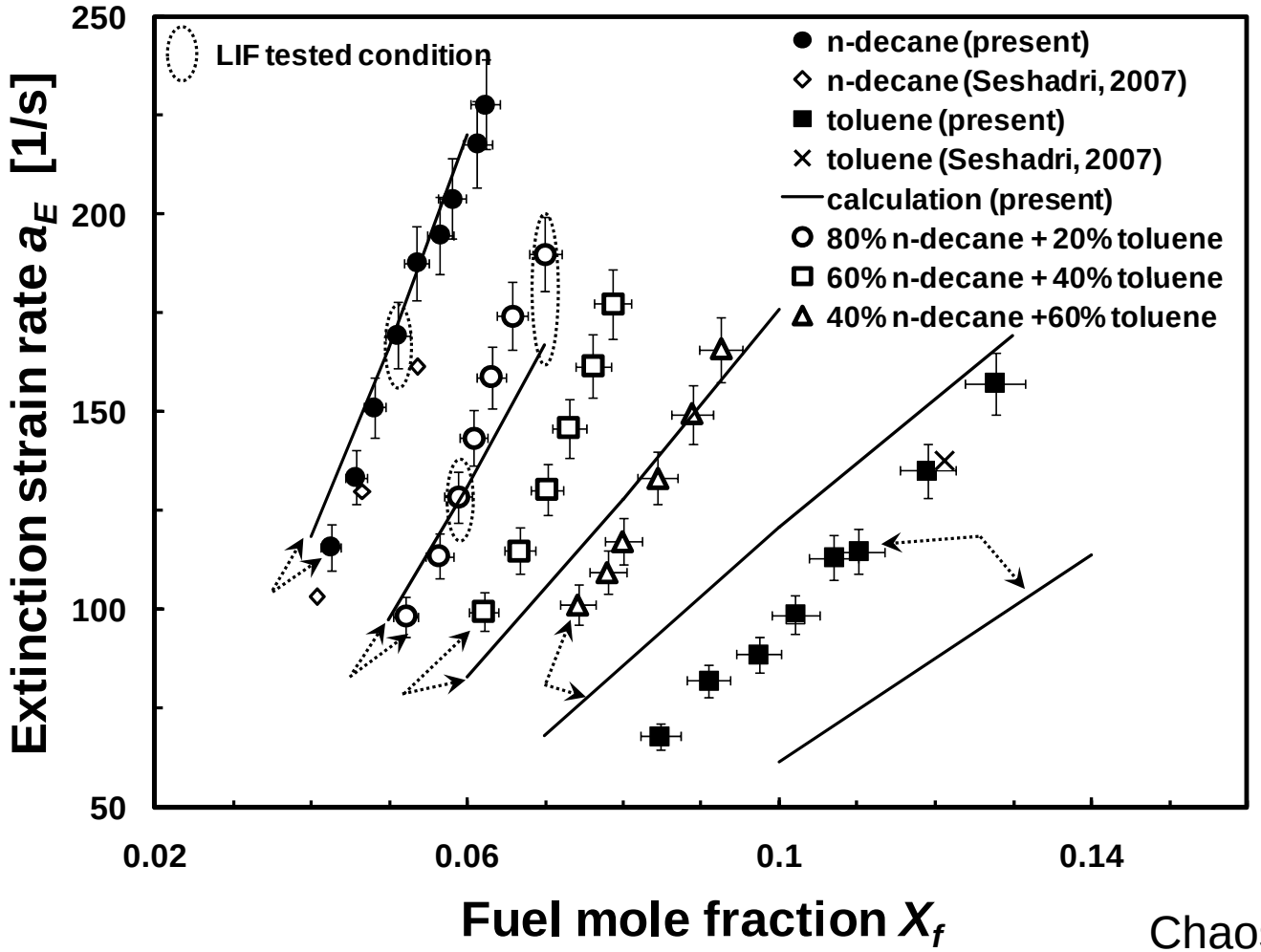
**Schematic photo for Rayleigh scattering and PLIF**



# Extinction limits of toluene blended n-decane–air Mixtures

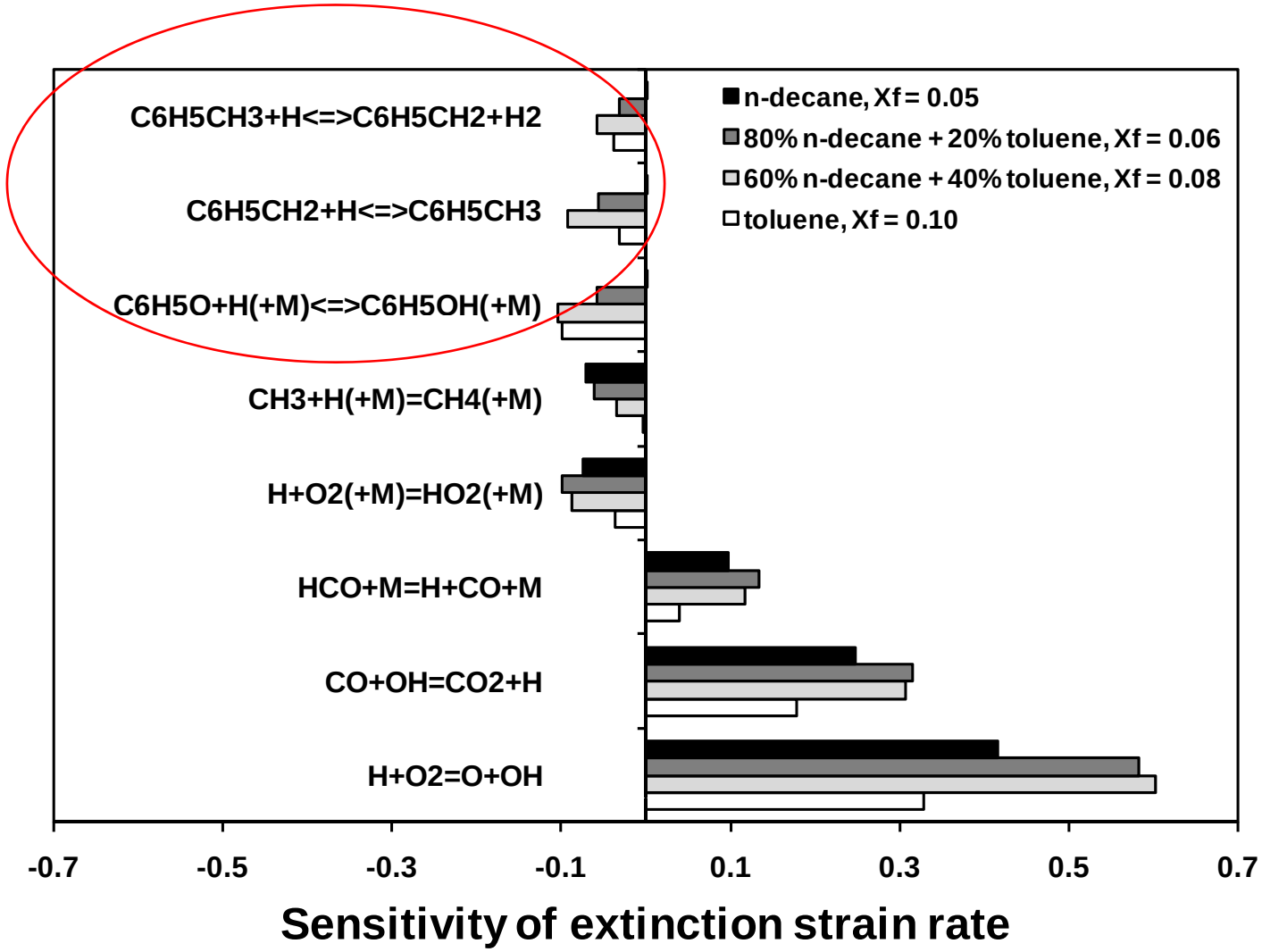


# Validation of n-decane-toluene mechanism: Extinction Limits

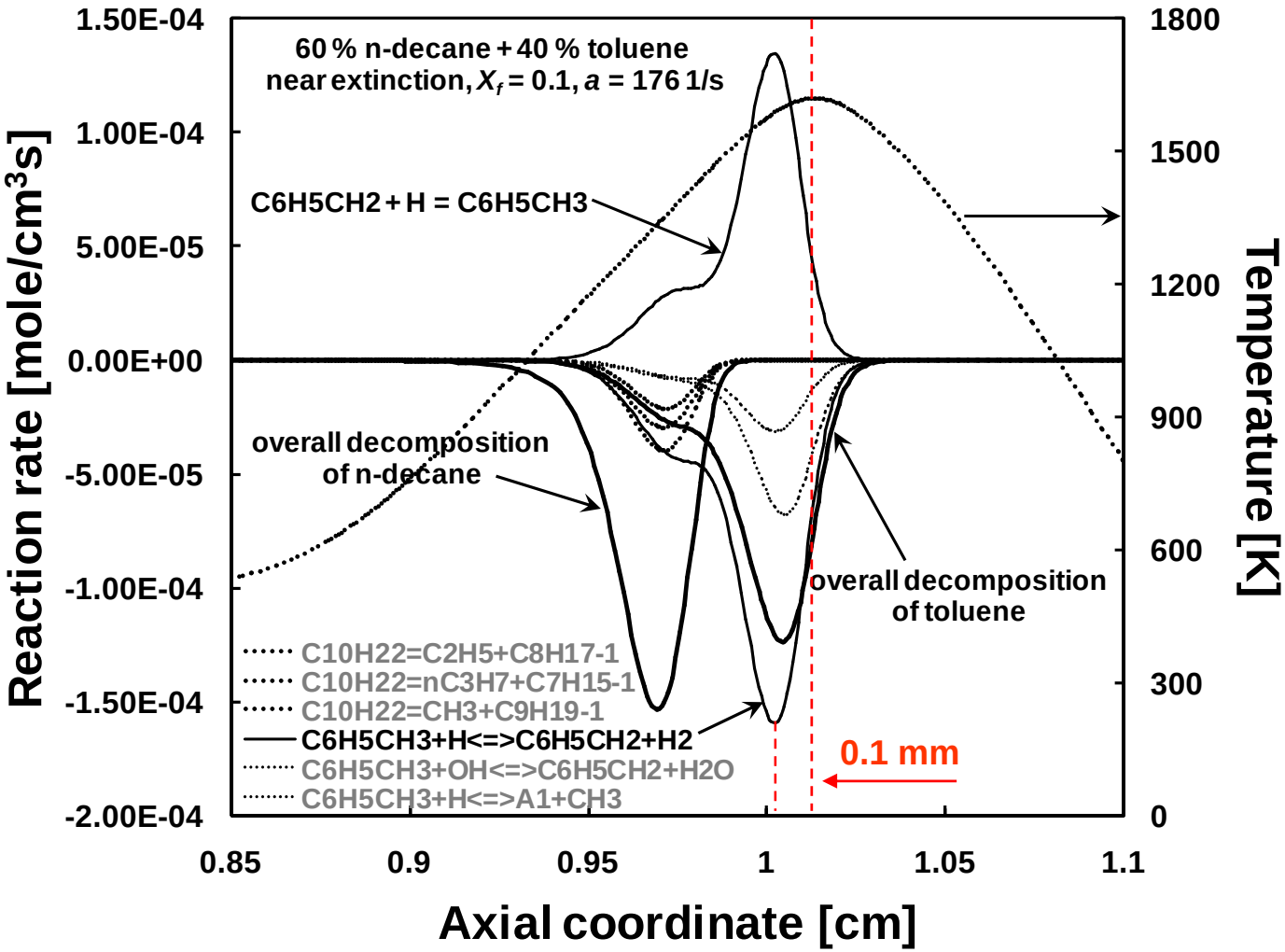



Chaos et al. 2005

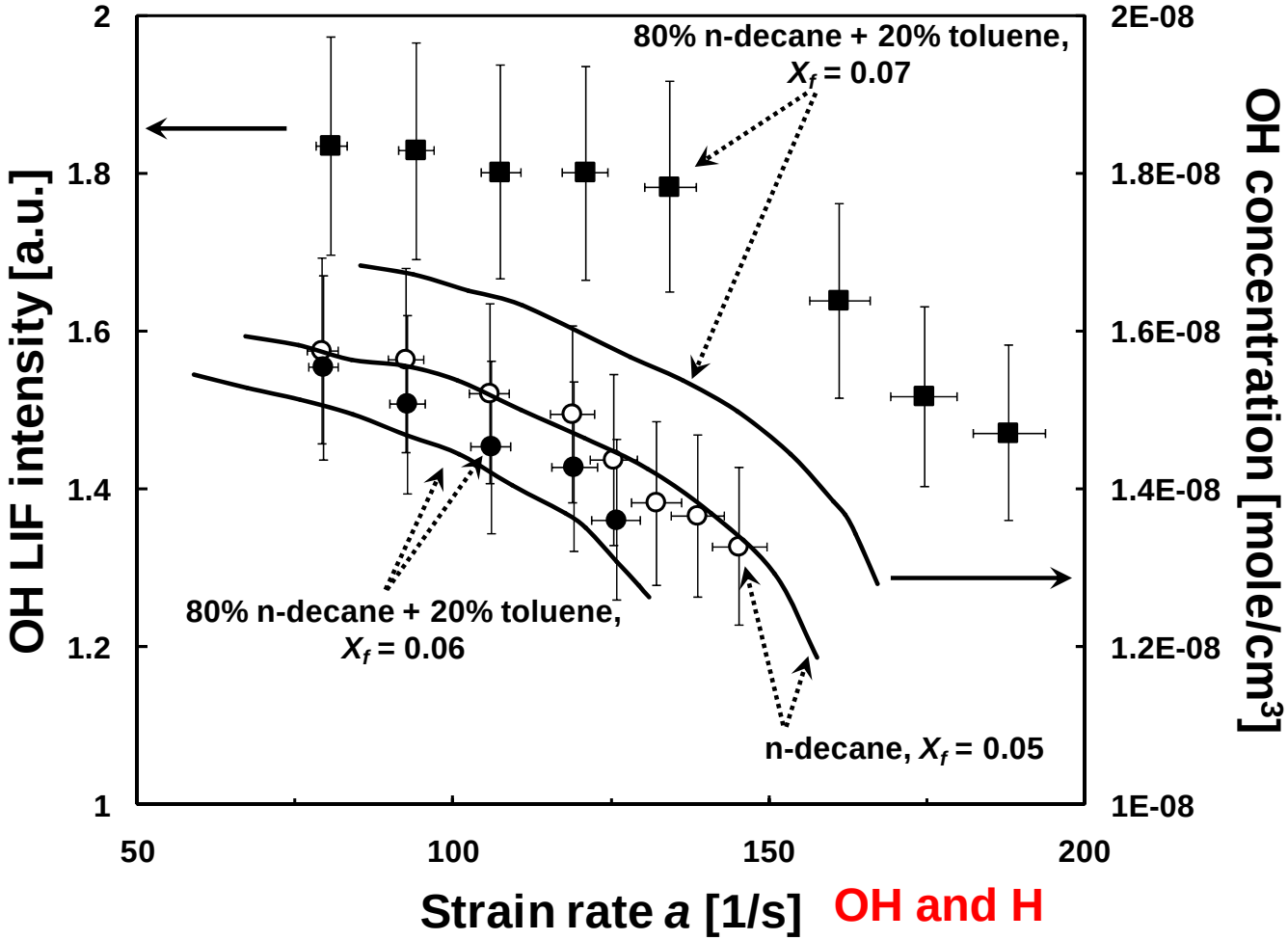
# Kinetic coupling between toluene fragment H abstraction reactions with chain-branching reactions



# Kinetic coupling between toluene fragment H abstraction reactions with chain-branching reactions

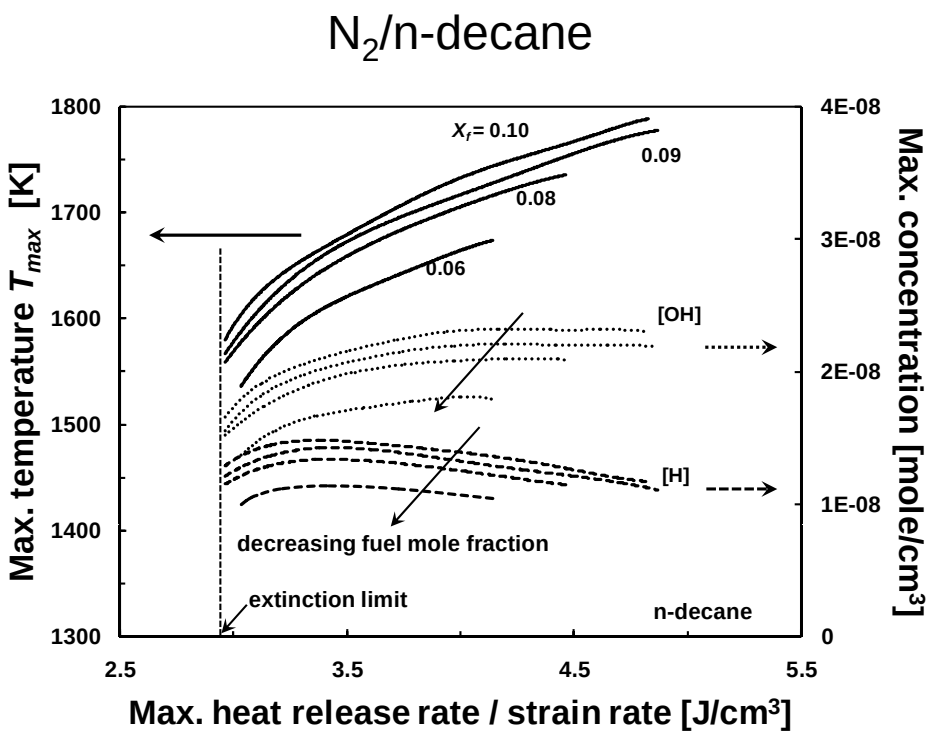


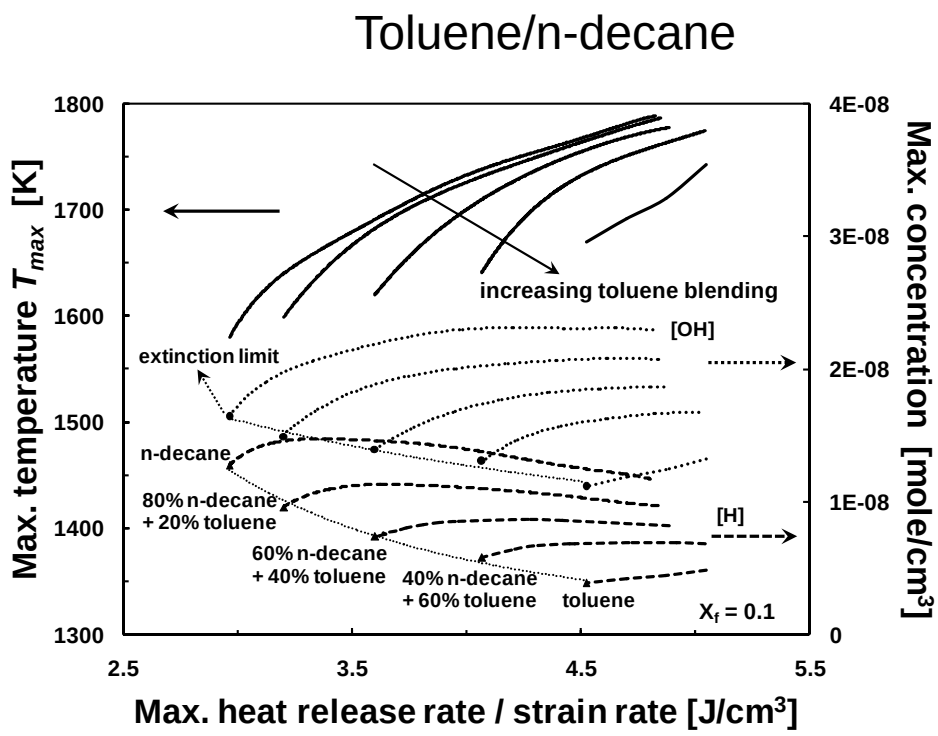
# Validation of Kinetic Mechanism (OH concentration)



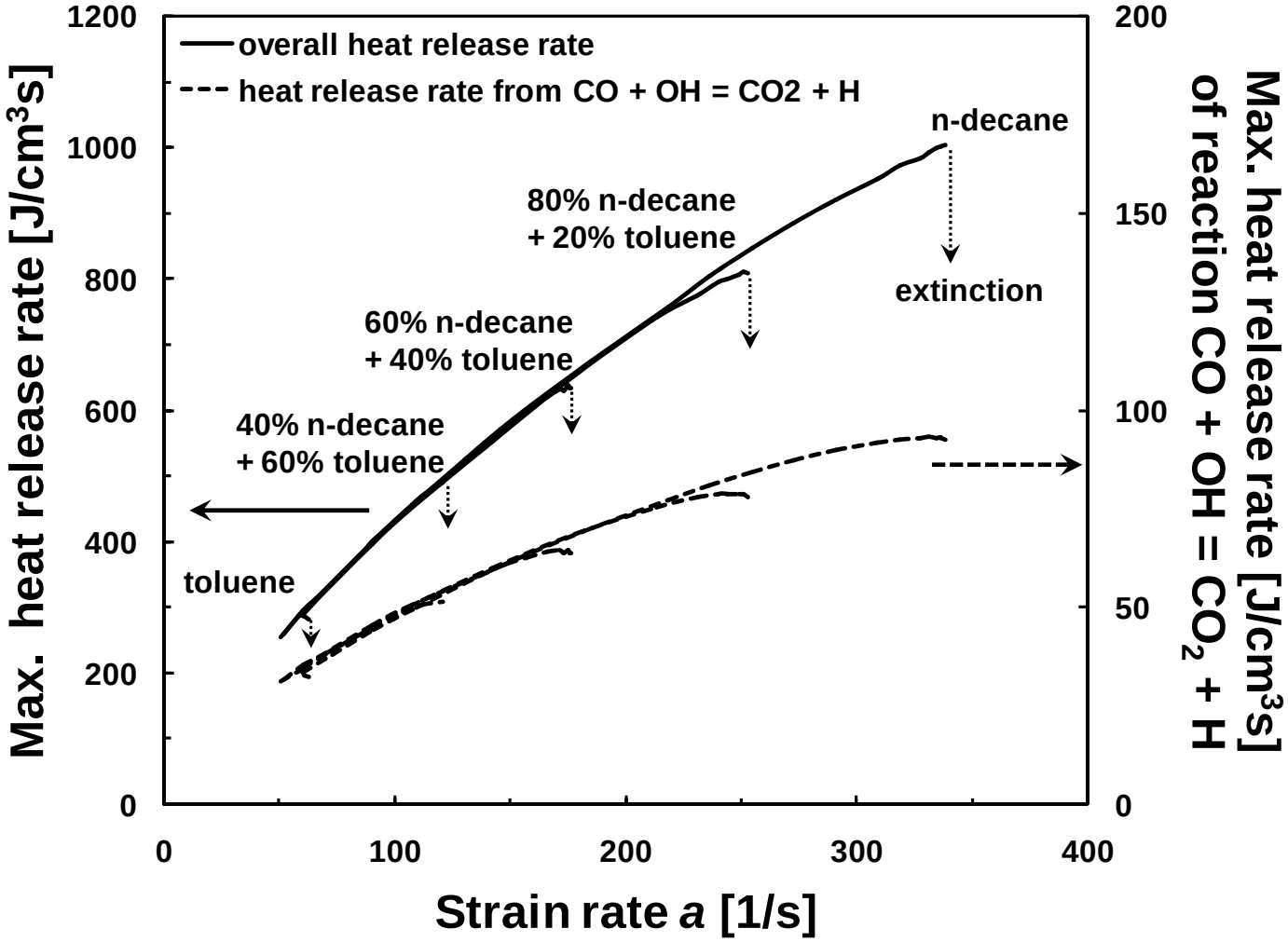

**OH and H**
**Over prediction of H abstraction?**

# Thermal and Kinetic effects on Extinction Limits



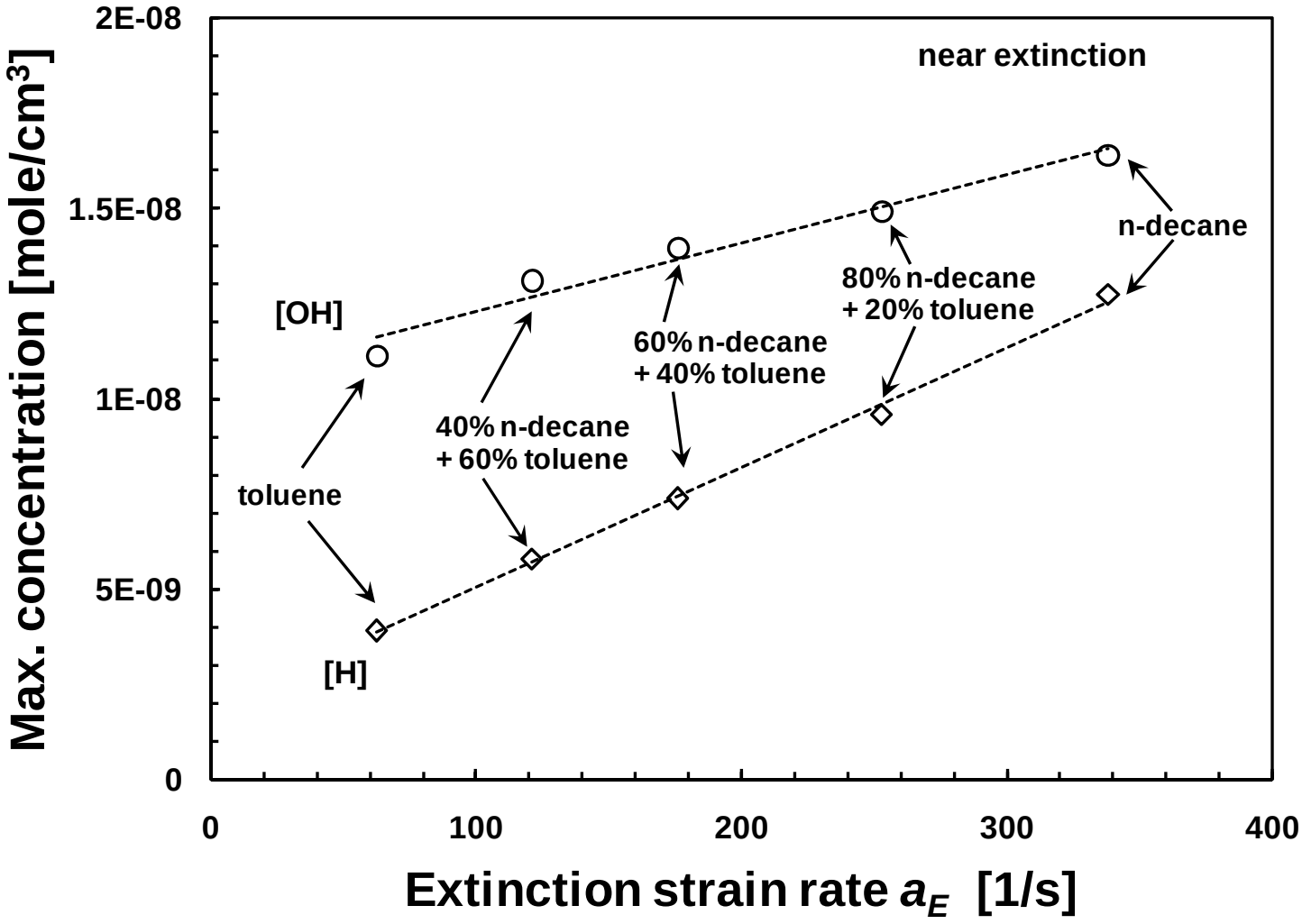



# Low dimensional correlation between strain rate and heat release

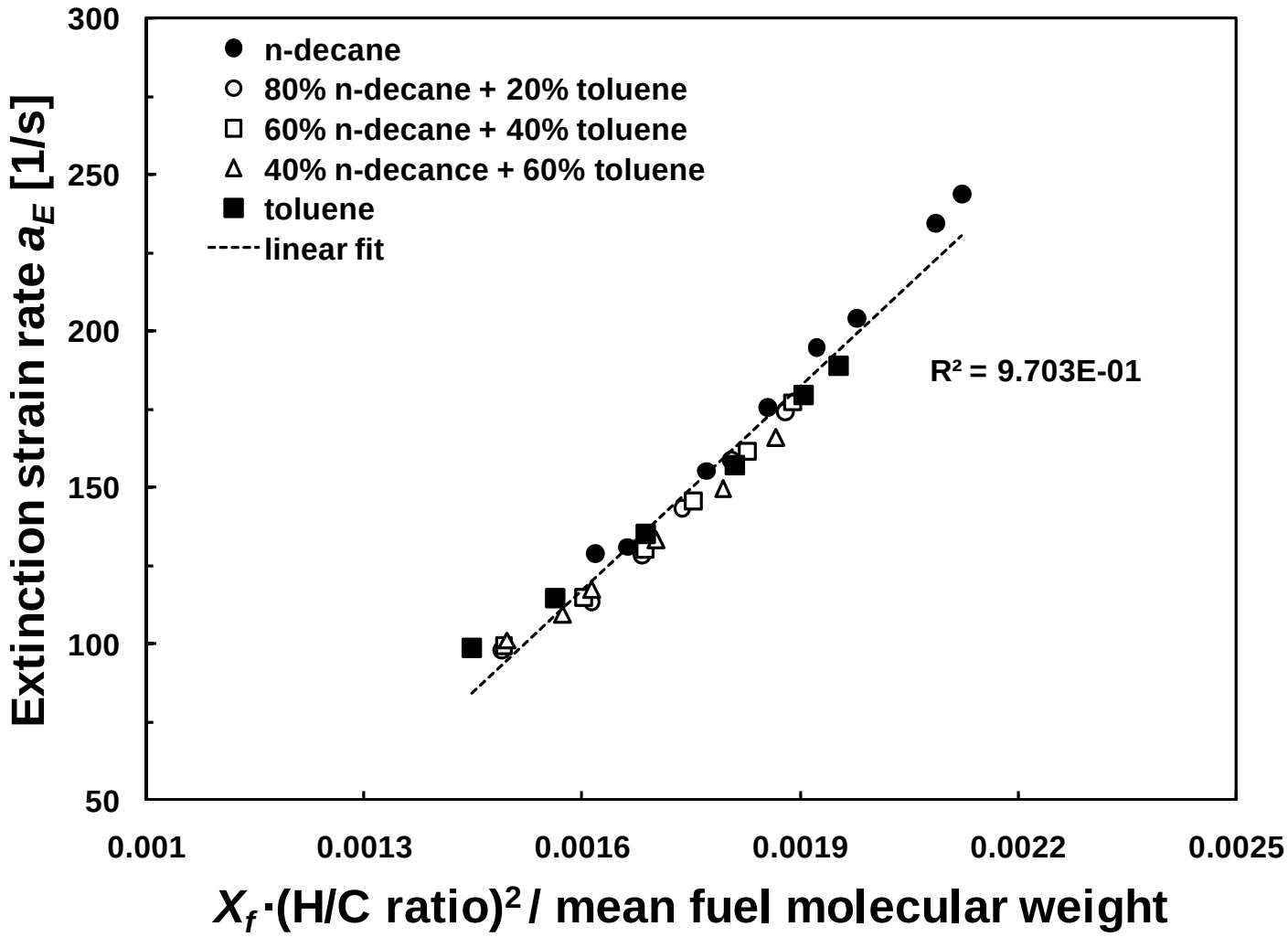



~50% heat release involves directly in OH

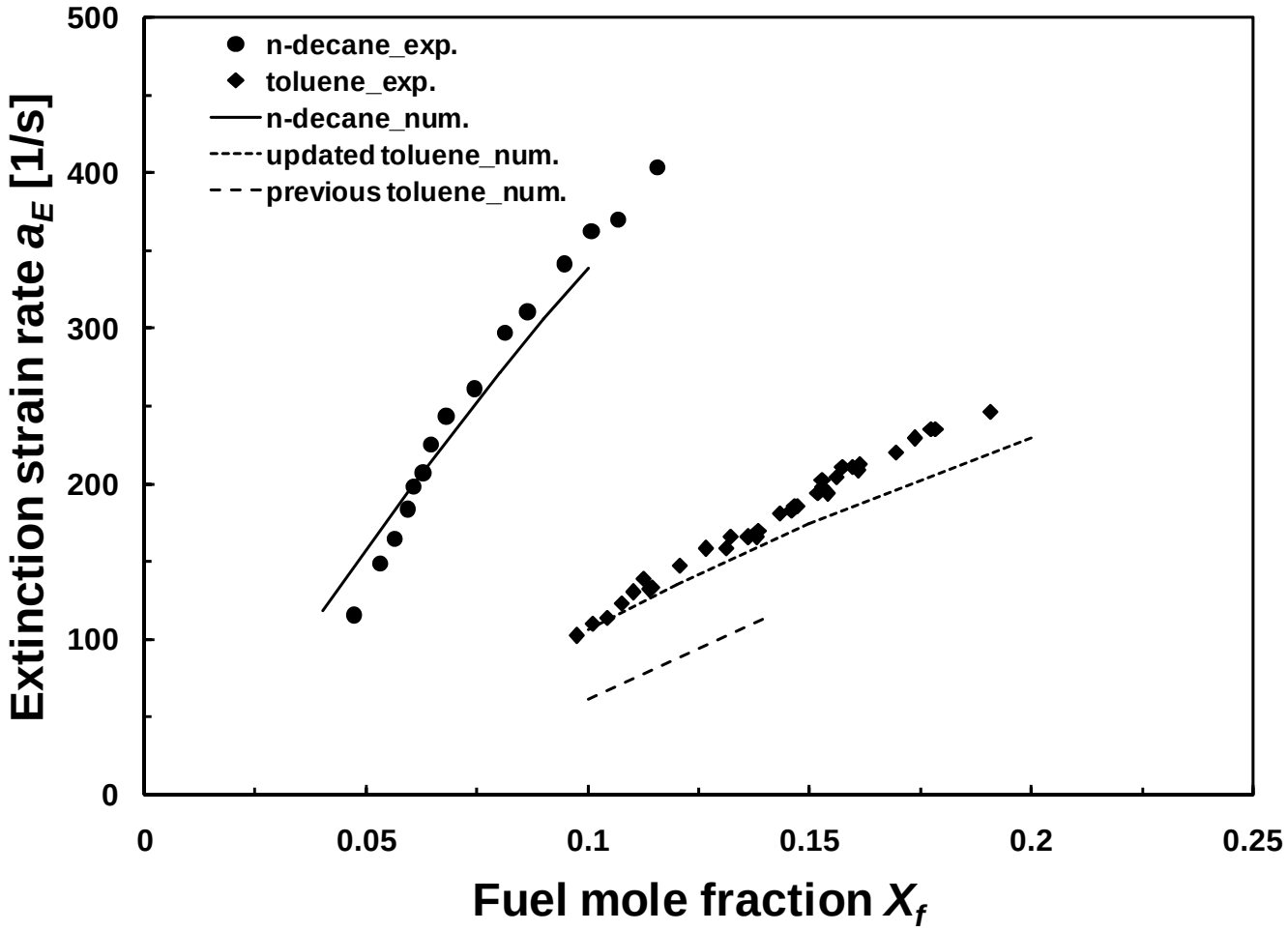
# Linear Correlations between OH concentration and extinction limit



# Linear correlation of extinction limits for toluene-n-decane mixtures



# Update of toluene kinetic mechanism



# 2. A Dynamic Multi-Time Scale (MTS) Method with Path Flux Analysis (PFA) for Mechanism Reduction

- Dynamic (Hybrid) Multi Timescale Method (MTS/HMTS)
- A Path Flux Analysis (PFA) Method for Mechanism Reduction
- Validations of MTS using ignition, steady/unsteady flames

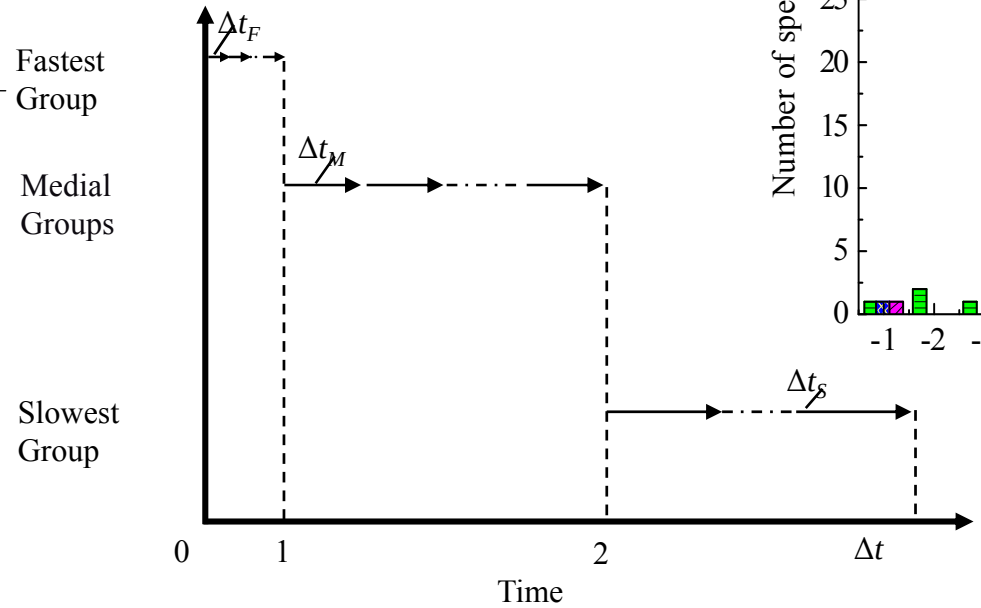
**Reduced mechanisms generated by existing approaches remain**
**•Very large**
**•Broad reaction timescale distributions and physical interests**
**•Quasi-steady assumption, ILDM only apply to limited conditions.**

**Can we develop a simple, rigorous, time accurate method?**

# Multi Timescale (MTS) Method

## The Basic Idea of Multi-Time Scale Method: timescale changes!

$$Y_k = K_k e^{-\frac{t}{\tau_k}}$$



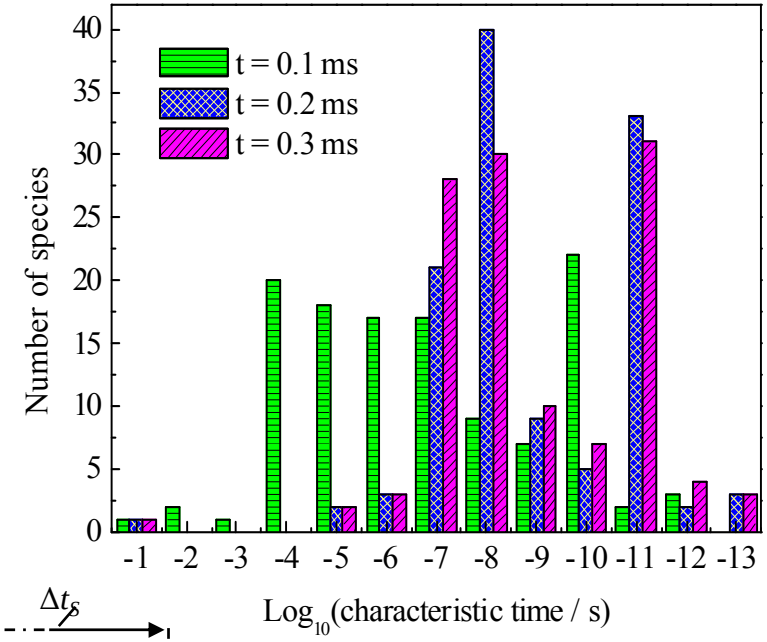
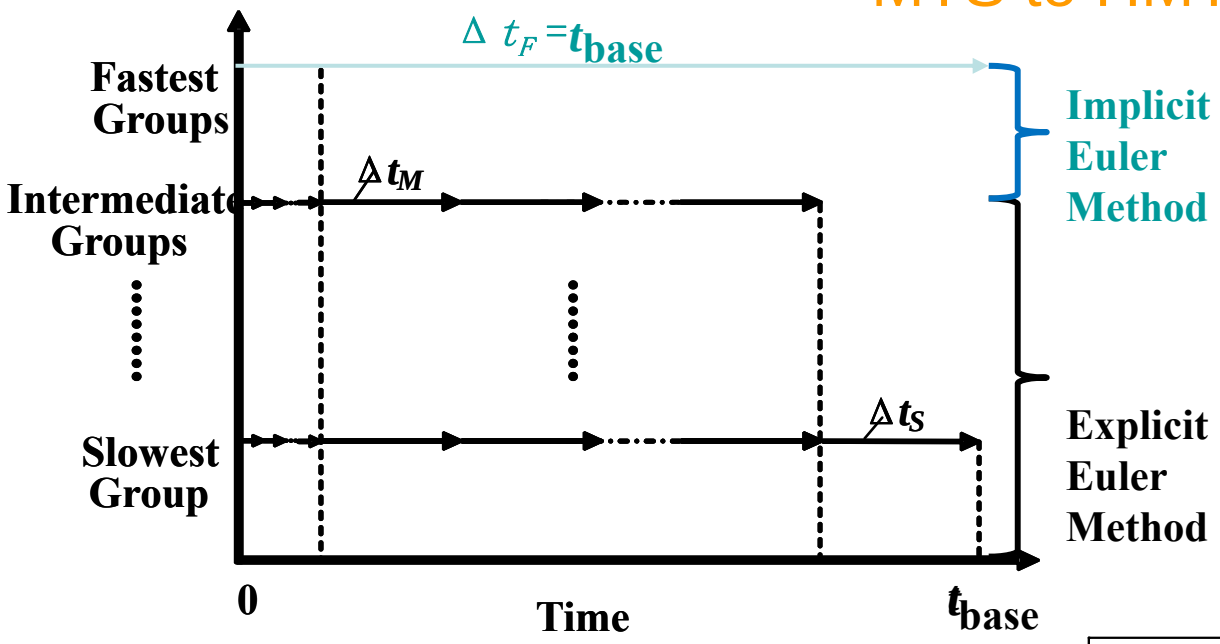



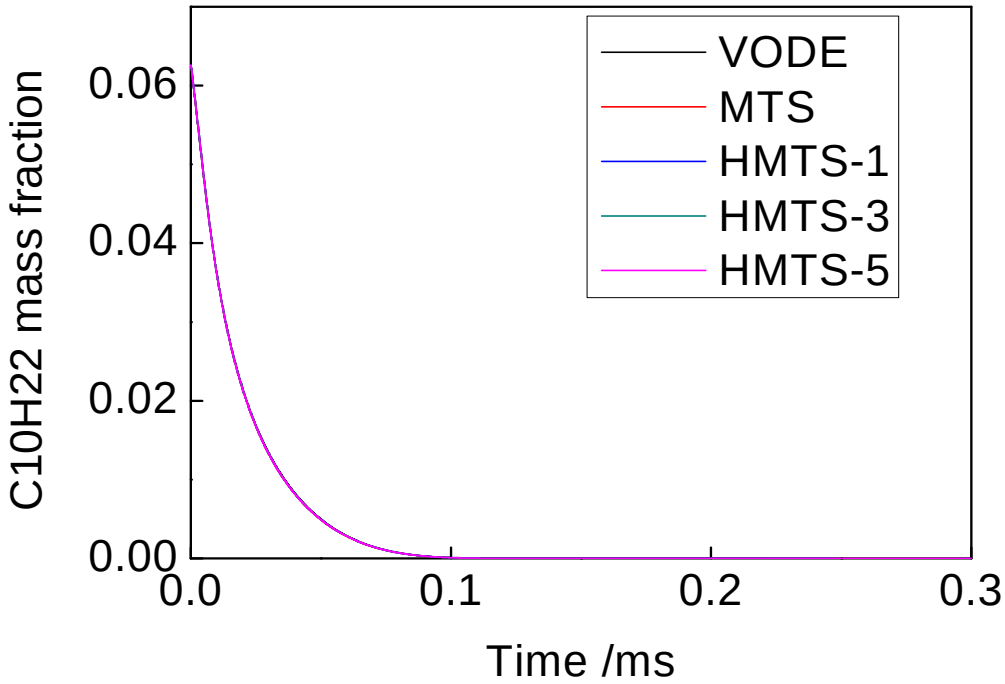

**Diagram of multi time scale scheme**

**$\Delta t_F$ is the time step of the fastest group, $\Delta t_M$ is the time step of the medial group, and $\Delta t_S$ is the time step of the slowest group**

# Hybrid Multi Timescale (HMTS) Method

## MTS to HMTS

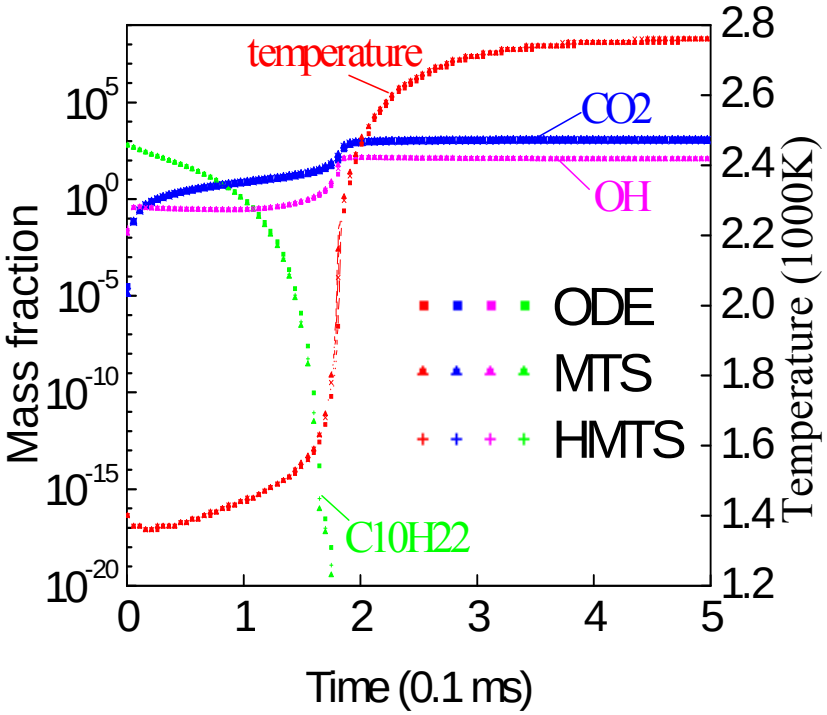


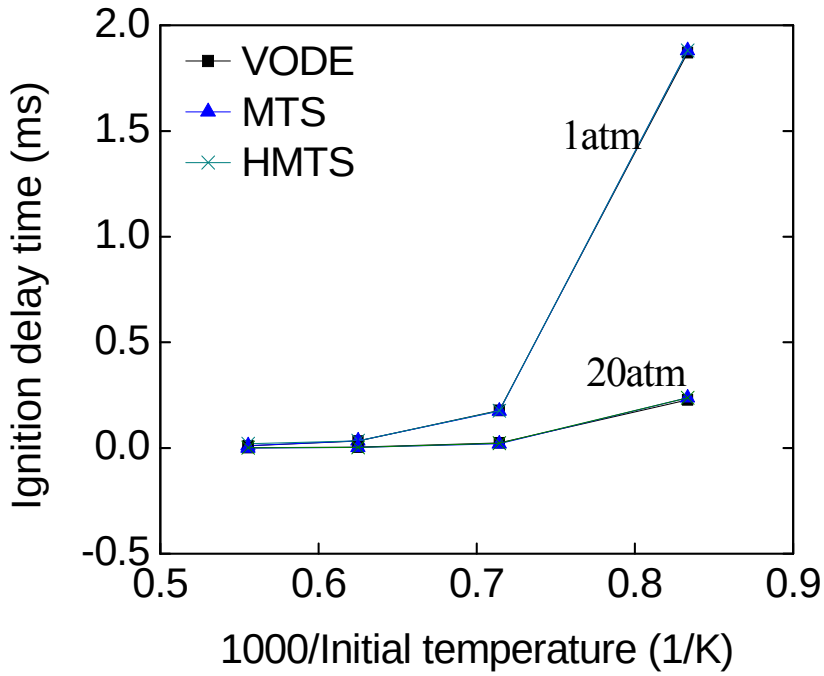



# Validation by homogeneous ignition

Ignition in homogeneous mixture

**n-decane/air** **121 species (M. Chaos, IJCK, 2007)**



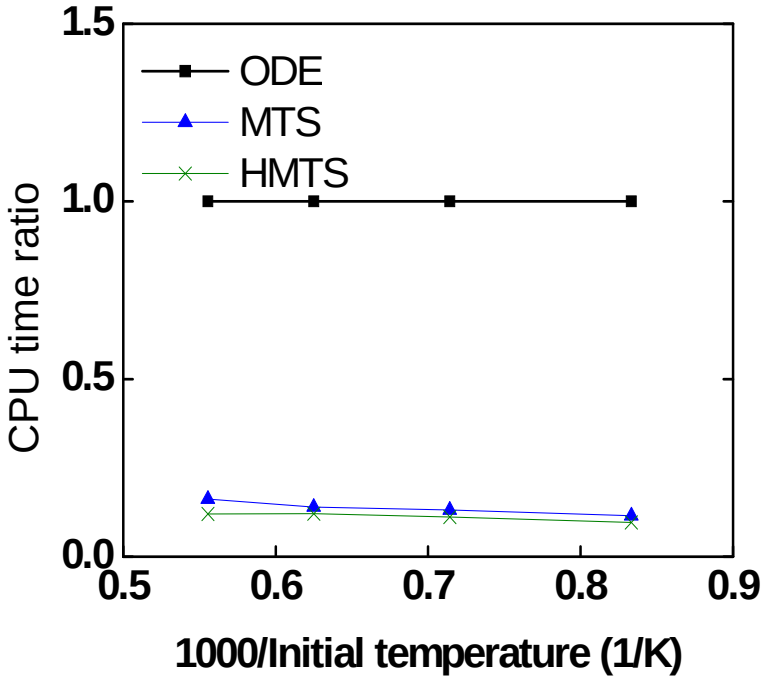




**Temperature and species profiles**

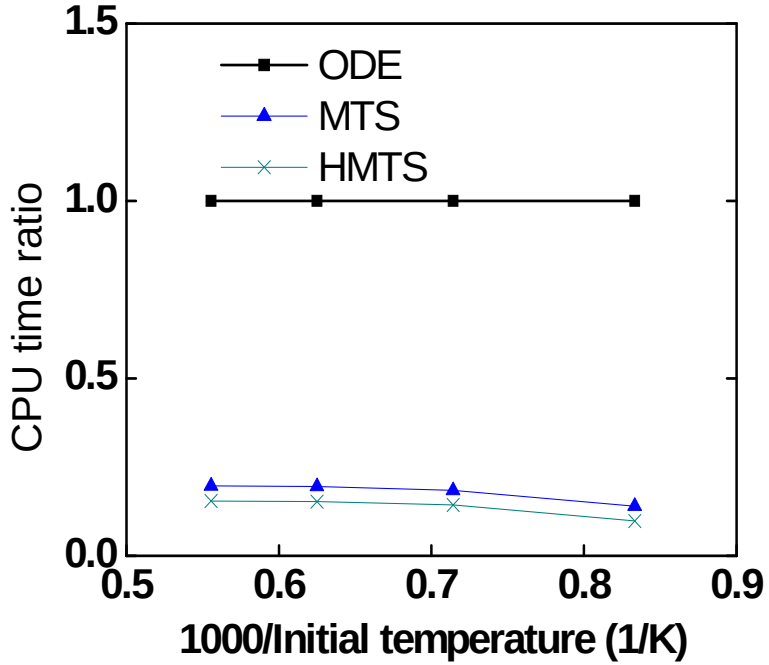
**Ignition delay time for n-decane-air**

# Computation efficiency: comparison with ODE solver

Normalized by the computation time of ODE solver




*1atm*



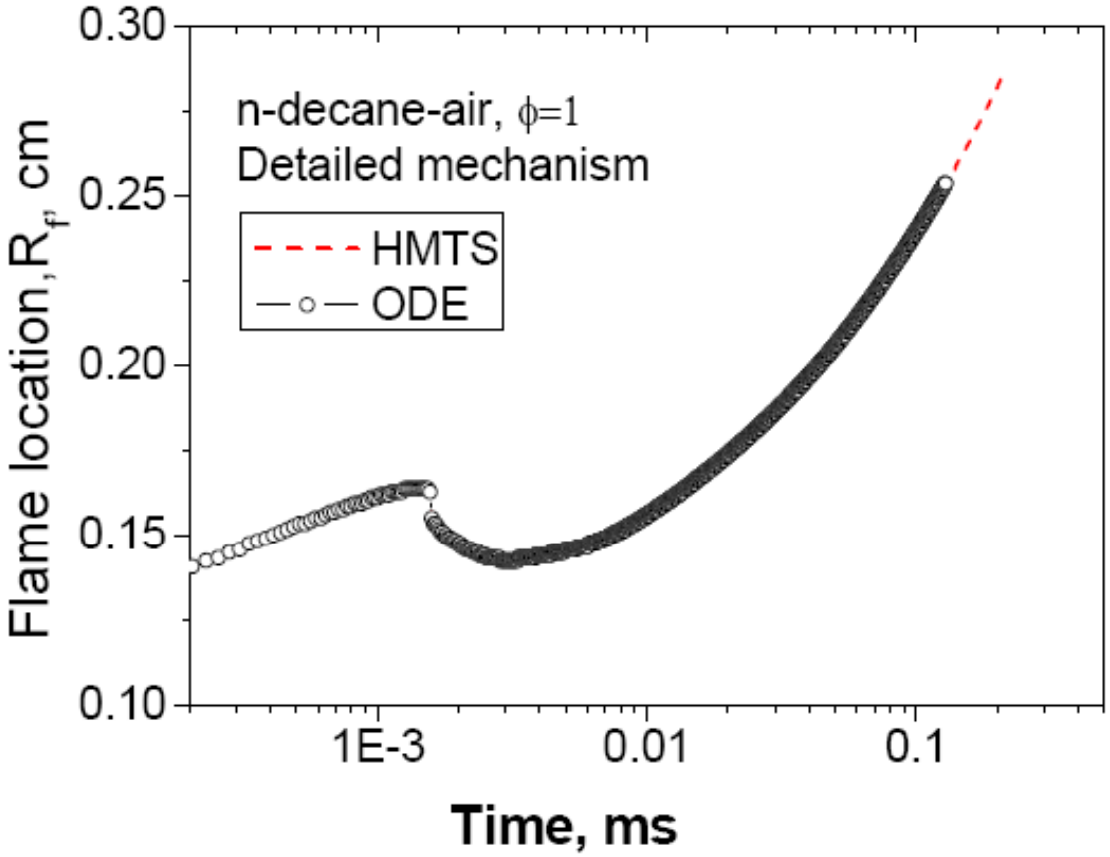

*20atm*

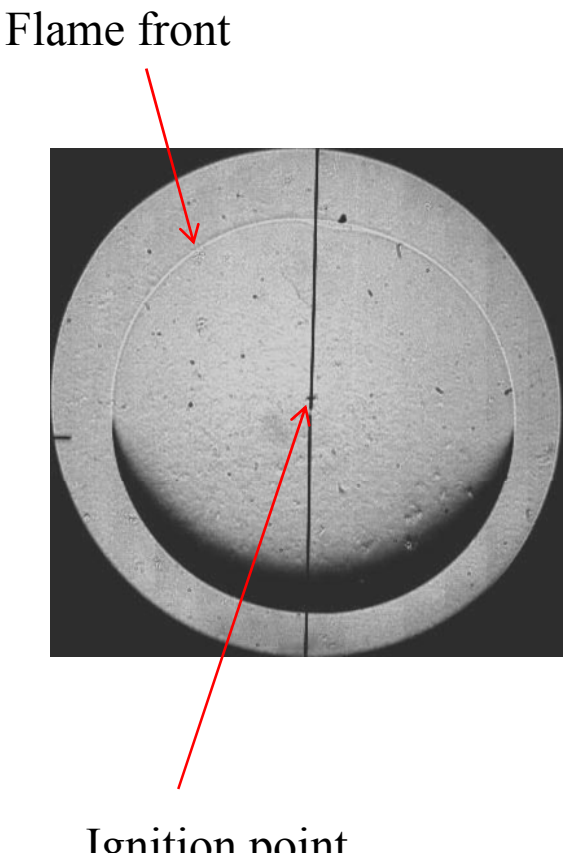
7~10 times faster

# Validation by propagation of unsteady spherical flames

## Detailed Mechanism

**Outwardly propagating spherical n-decane flames (ASURF-1D Princeton)**



# Can we further reduce the computation time?

## A Path Flux Analysis (PFA) Method for Mechanism Reduction

### Reaction path, DRG & DRGEP

- Only direct relation;
- *r* is not conservative;
- Multi-path reaction?

DRG:

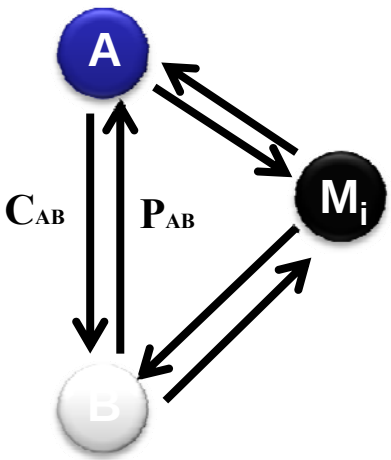
$$r_{AB} \equiv \frac{\sum_{i=1,I} \left| \nu_{A,i} \omega_i \delta_{Bi} \right|}{\sum_{i=1,I} \left| \nu_{A,i} \omega_i \right|} = \frac{P_{AB} + C_{AB}}{P_A + C_A} \qquad \delta_{B,i} = \begin{cases} 1 & \text{if the } i\text{th elementary reaction} \\ & \text{involves speceis B} \\ 0 & \text{otherwise} \end{cases}$$

DRGEP:

$$r_{AB} \equiv \frac{\left| \sum_{i=1,I} \nu_{A,i} \omega_i \delta_{Bi} \right|}{\max(P_A, C_A)} = \frac{P_{AB} - C_{AB}}{\max(P_A, C_A)}$$

$$r_{AB} \equiv \max_{all\ paths\ M_i} (r_{AM_i} \cdot r_{M_i B})$$

- Net reaction rate;
- Consider strongest indirect path
- Catalytic reactions?



# Path Flux Analysis Method

- Both forward and backward fluxes
- Both direct and indirect relations *r* are conservative
- Multi-generation fluxes
- Multi-reaction pathways

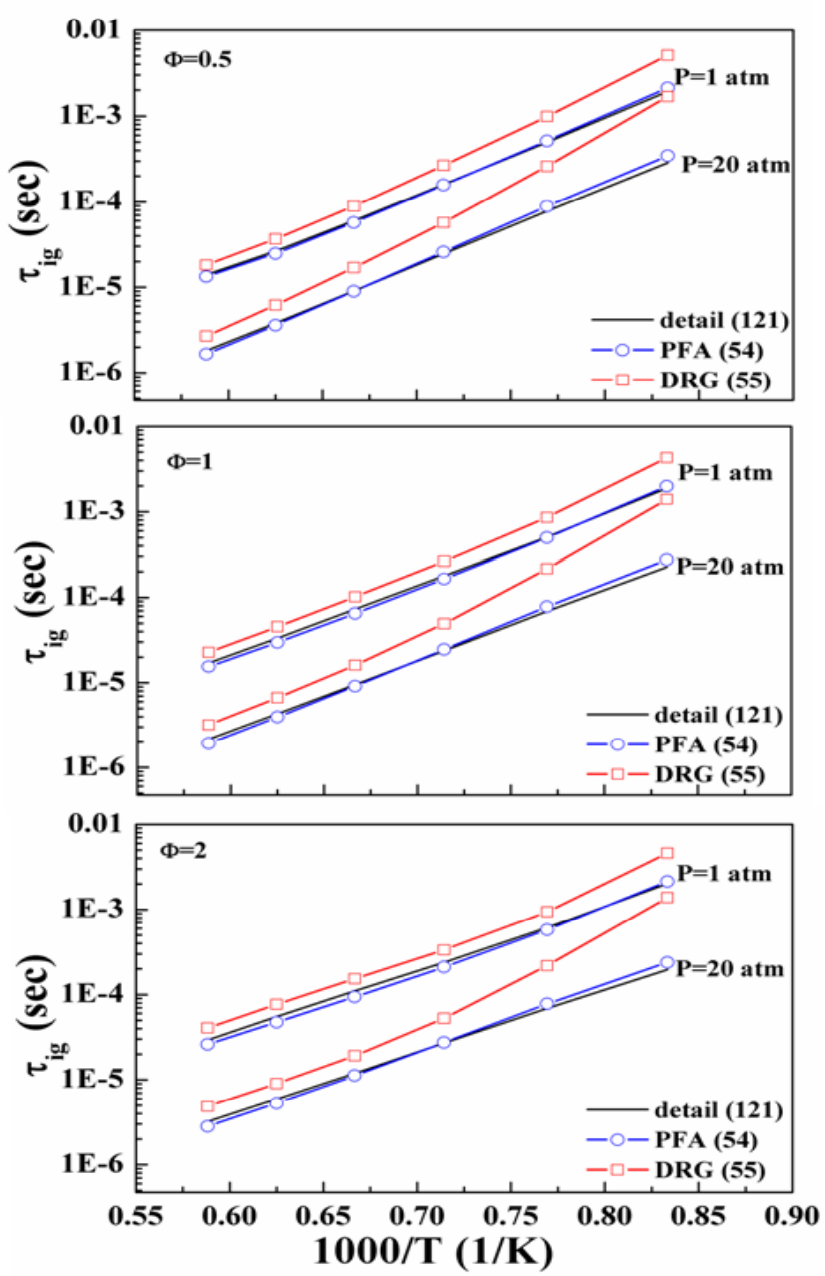
$$r_{AB}^{pro-1st} = \frac{P_{AB}}{\max(P_A, C_A)} \qquad r_{AB}^{con-1st} = \frac{C_{AB}}{\max(P_A, C_A)}$$

$$r_{AB}^{pro-2nd} = \sum_{i=1,I} [\frac{P_{AM_i}}{\max(P_A, C_A)} \times \frac{P_{M_iB}}{\max(P_{M_i}, C_{M_i})}] \qquad r_{AB}^{con-2nd} = \sum_{i=1,I} [\frac{C_{AM_i}}{\max(P_A, C_A)} \times \frac{C_{M_iB}}{\max(P_{M_i}, C_{M_i})}]$$

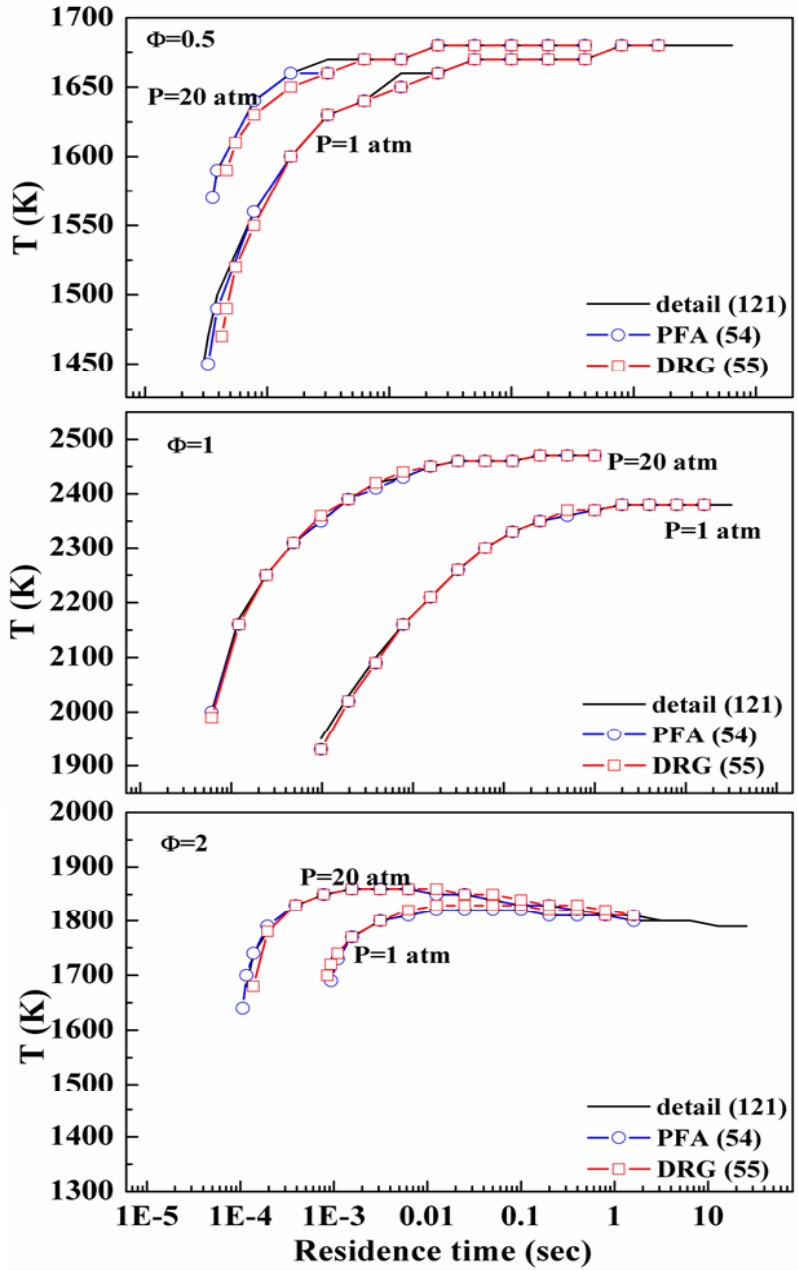
$$r_{AB} = r_{AB}^{pro-1st} + r_{AB}^{con-1st} + r_{AB}^{pro-2nd} + r_{AB}^{con-2nd}$$

# Validation by n-decane homogeneous ignition

**Ignition delay times**

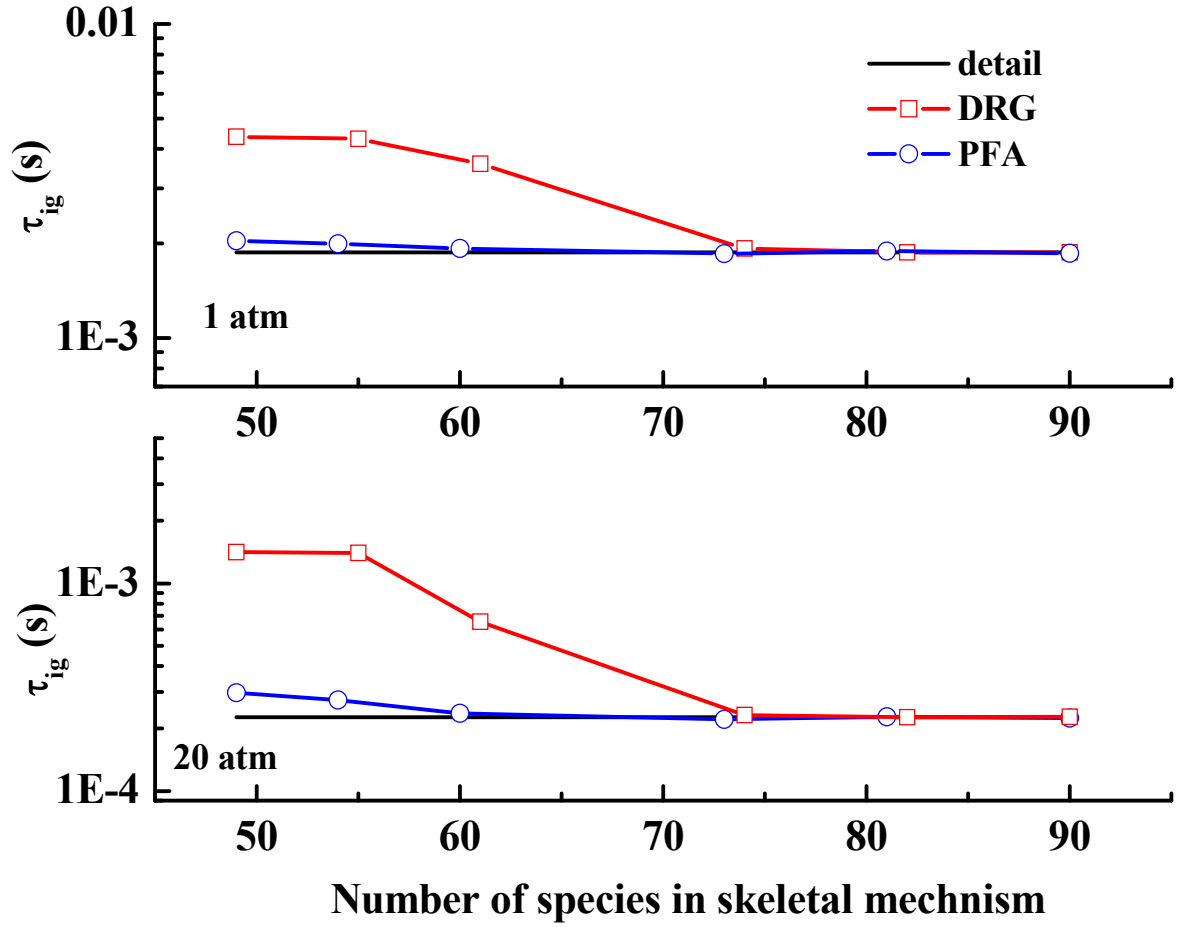



**Perfect Stirred Reactor**



# Skeletal mechanisms of different sizes
# Comparison of PFA with DRG

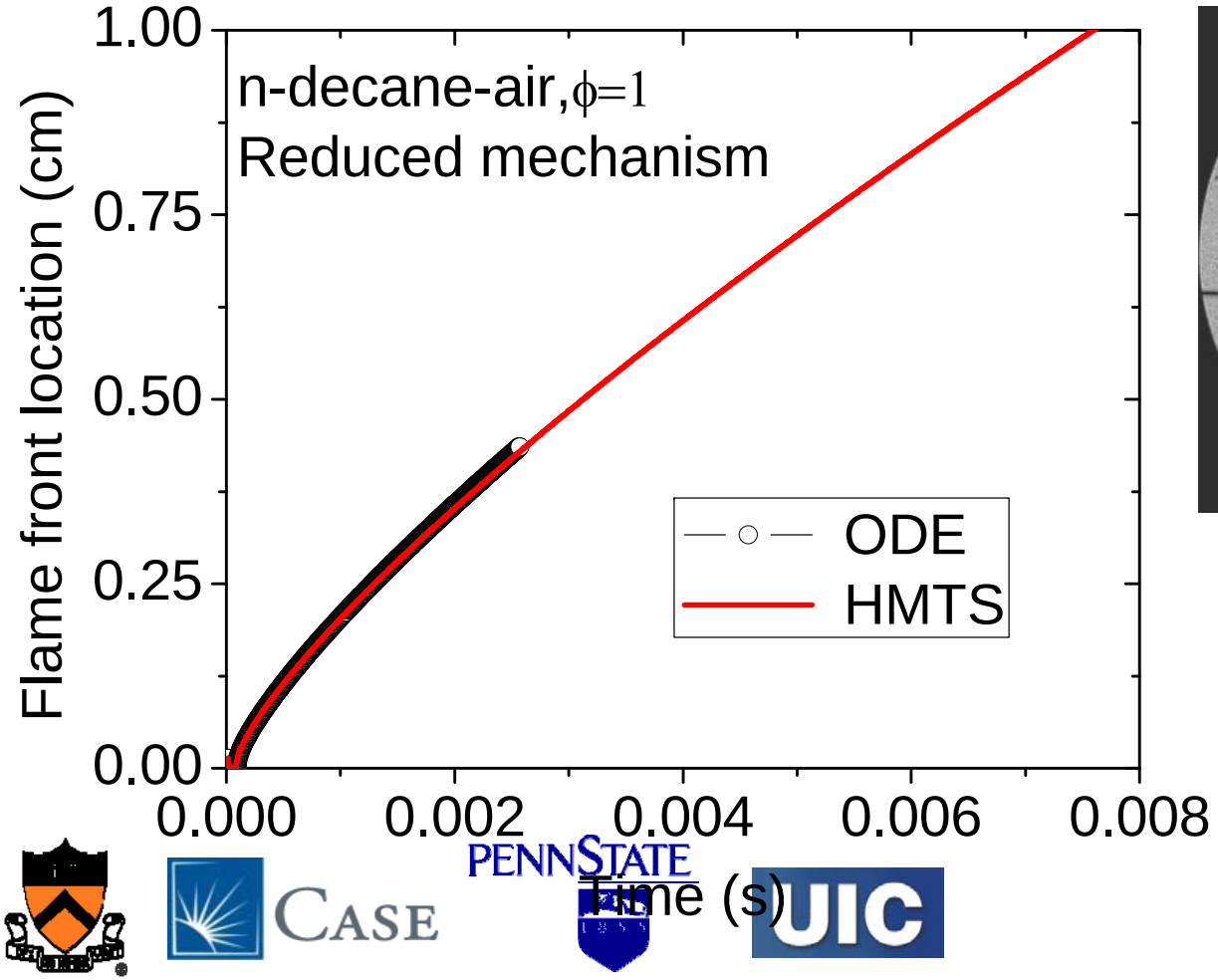
$T_0$=1200 K

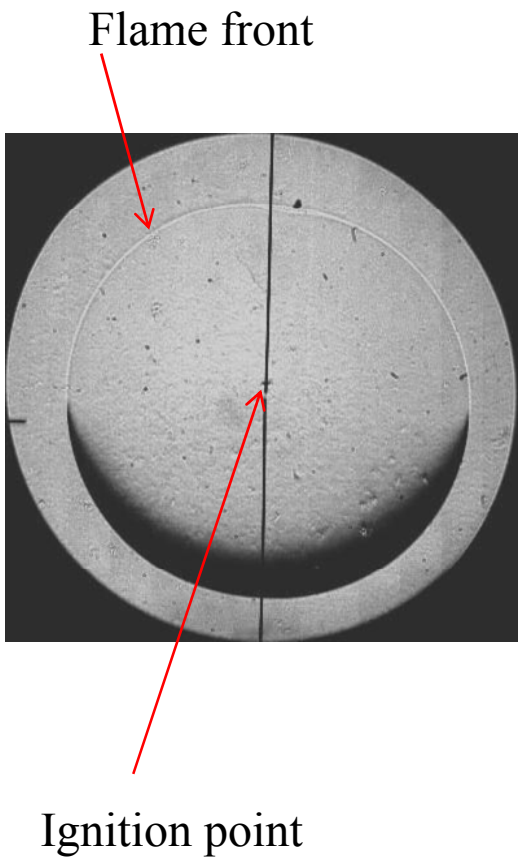


# Integration of HMTS & PFA : Comparison of ODE & HTMS

## Reduced mechanism

**Outwardly propagating spherical n-decane/air flame**



# Conclusion

- Kinetic coupling affects strongly the extinction limits of blended alkane and aromatic fuel mixtures.
- Measurements of aromatic fuel fragments and OH concentration are important to develop validated kinetic mechanisms for blended fuel mixtures.
- The extinction limits of toluene blended n-decane mixtures are found linearly dependent on the maximum OH concentration, suggesting as a radical index.
- A simple linear correlation between extinction limits and fuel properties is obtained for n-decane/toluene blended fuel mixtures.
- A new dynamic multi-timescale (MTS) model and a hybrid MTS model are developed. Both MTS and HMTS methods have excellent accuracy and improved computation efficiency for ignition and flames with detailed chemistry.
- A Path flux analysis (PFA) method is developed for mechanism reduction. The method has better model accuracy in a broad temperature and pressure ranges.
- The integration of MTS/HMTS with PFA mechanism reduction can dramatically enhance the computation efficiency.

# Future work:

- Kinetic effects on extinction limits of n-decane/n-dodecane with trymethylbenzene, n-propylbenzene
- Development of radical index to construct extinction correlation
- Experimental data of flame speeds at elevated pressures
- Reduced mechanism development using MTS/PFA for aromatic fuels

**Thanks Dr. Tishkoff for**
**the MURI research grant**