Flame Kinetics of Surrogate Jet Fuel Components

C.K. Law
Princeton University
T.F. Lu
University of Connecticut

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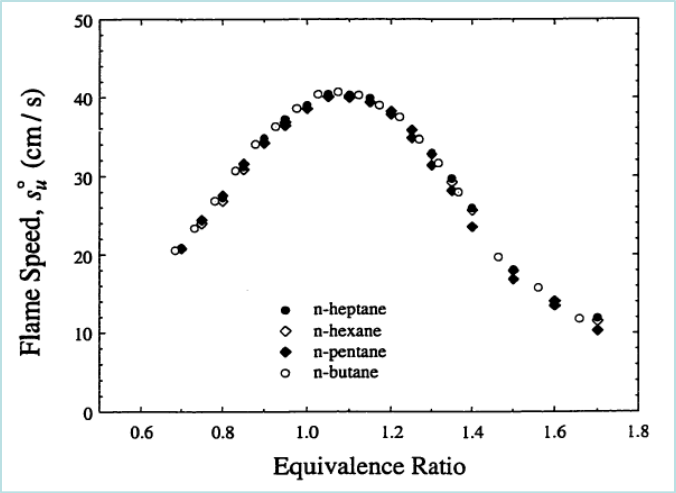
Outline of Presentation

1. Similarity of flame kinetics of large n-alkanes
2. Flame kinetics of cycloalkanes
3. PSR kinetics of ignition and extinction kinetics (T.F. Lu)

Similarity of Flame Kinetics of Large n-Alkanes

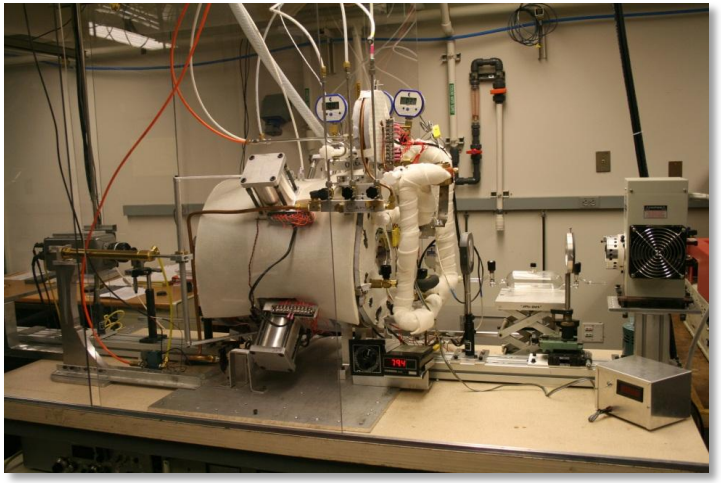
Motivation

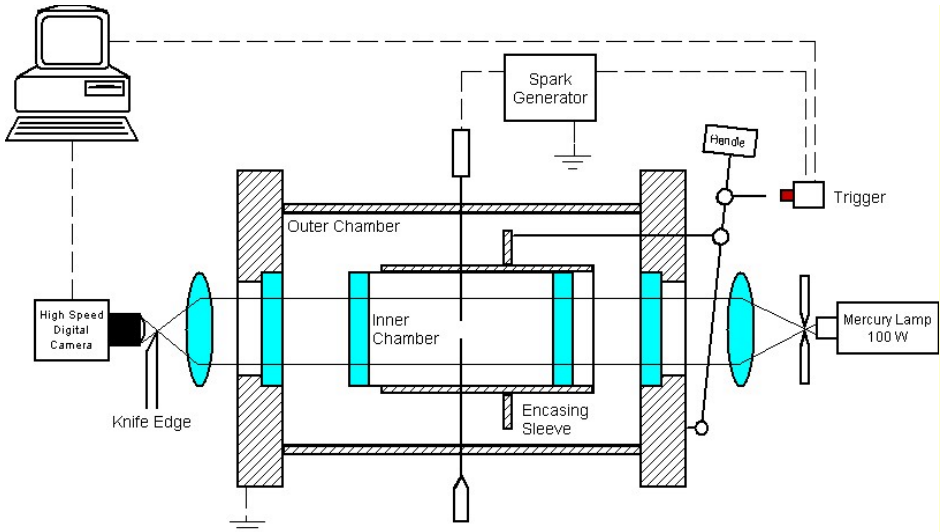


Davis & Law (1998)

- Fuel similarity in terms of flame speed demonstrated at 1 atm by Davis and Law (1998) for n-C4 to -C7 hydrocarbons
- Ji *et al.* demonstrated fuel similarity for n-C_5 to -C_{12} at 1 atm
- Does fuel similarity still hold at elevated pressures?
  - Elevated pressures change chemical kinetics, increasing the frequency of three-body reactions
  - High pressure relevant for practical engine conditions
  - Examine fuel similarity in the flame structure

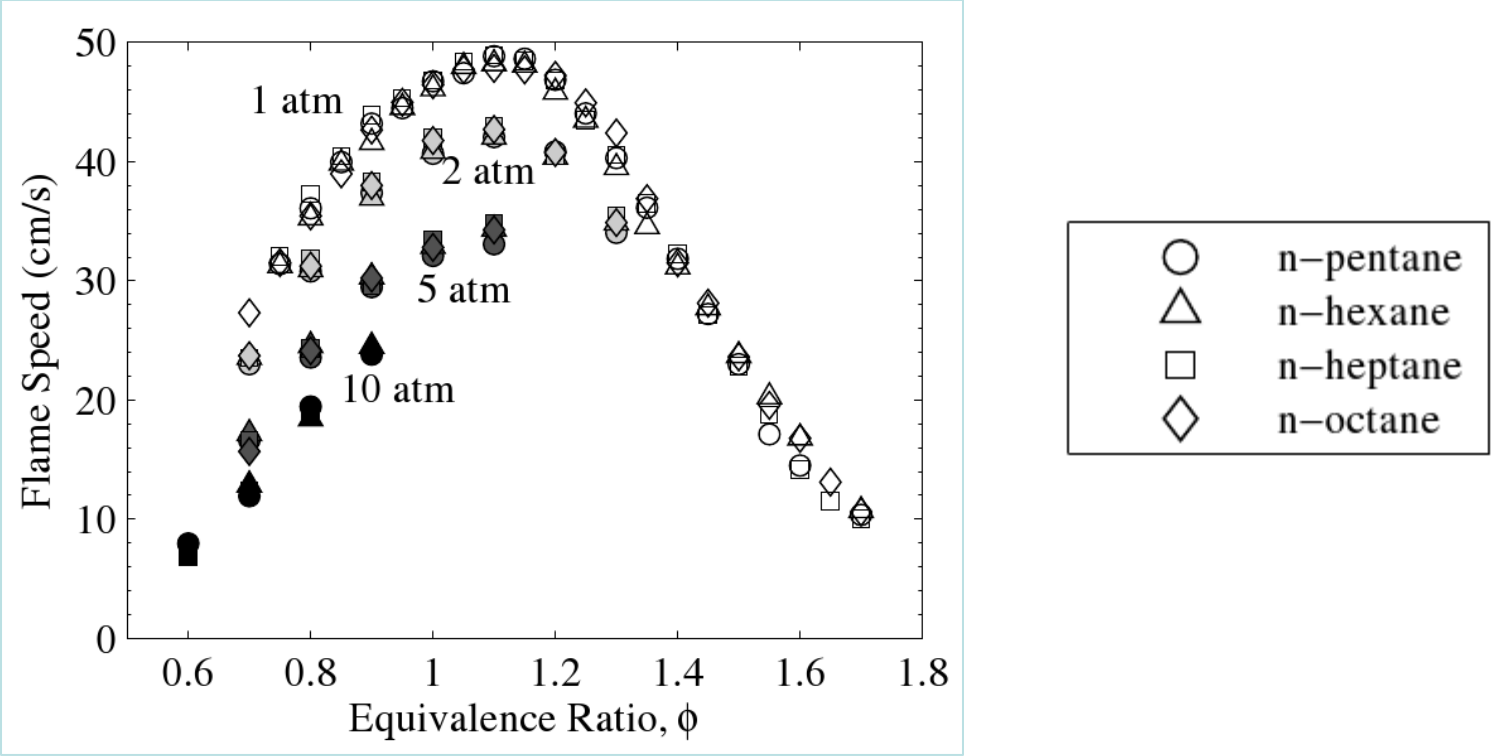
Constant & High-Pressure Chamber for High-Pressure Flame Studies



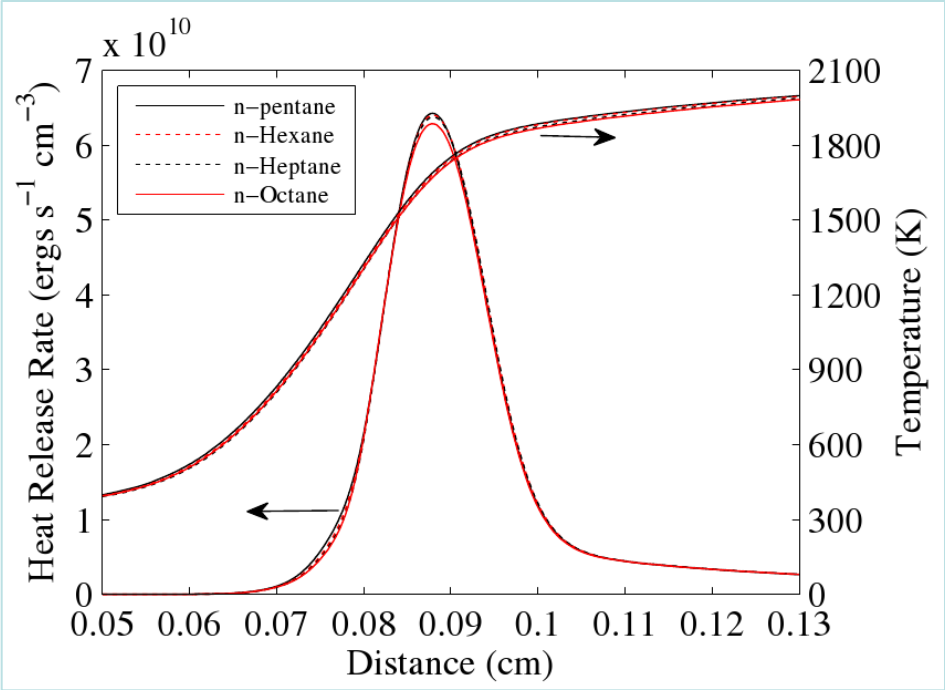


- Unique chamber design allows well-controlled study of expanding spherical flames in constant, high-pressure (up to 60 atm.) environment.

Flame Speed Similarity of C_5 to C_8 n-Alkanes at Elevated Pressures



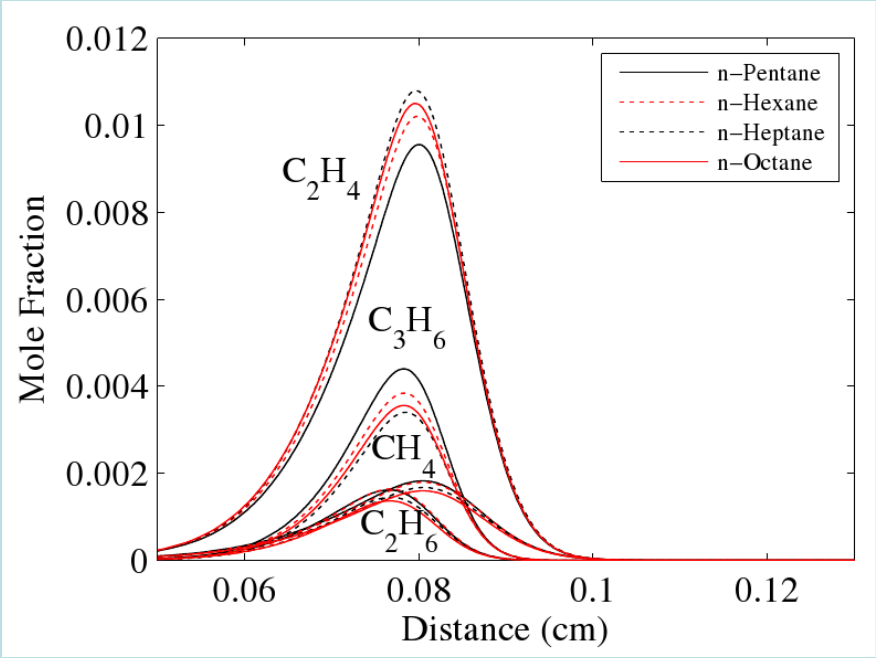
Similarity in Profiles of Heat Release and Temperature



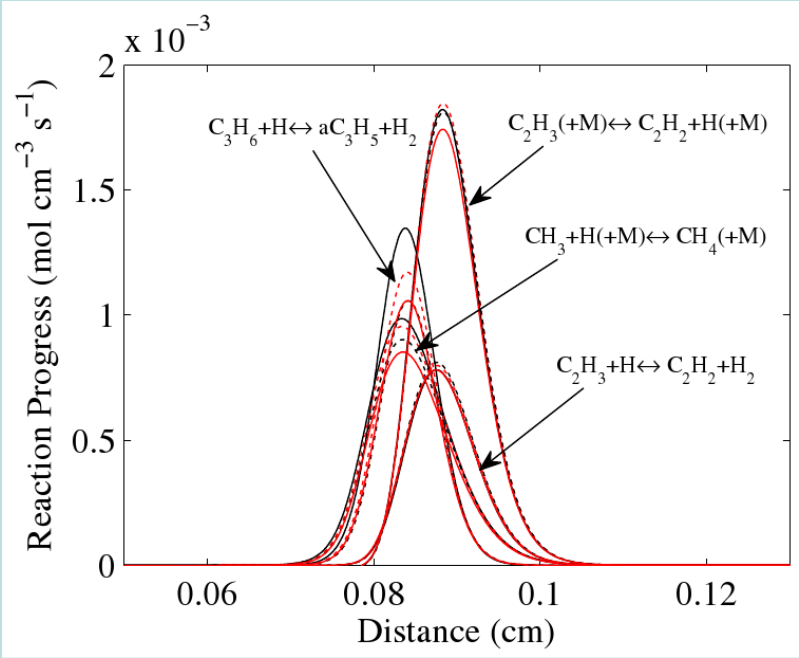
- Nearly identical heat release and temperature profiles
- Flame speed primarily depends on the adiabatic flame temperature, which is nearly identical for all fuels studied
- Temperature gradient controls heat transfer

Similarity in Profiles of Decomposed Fuel Species and Reactions

Species Profiles

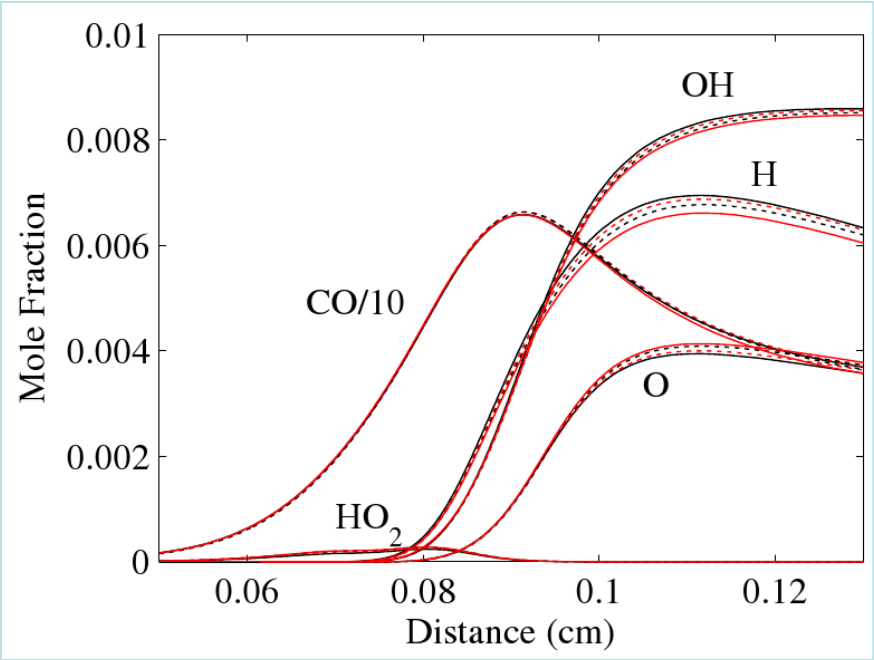


Reaction Progress

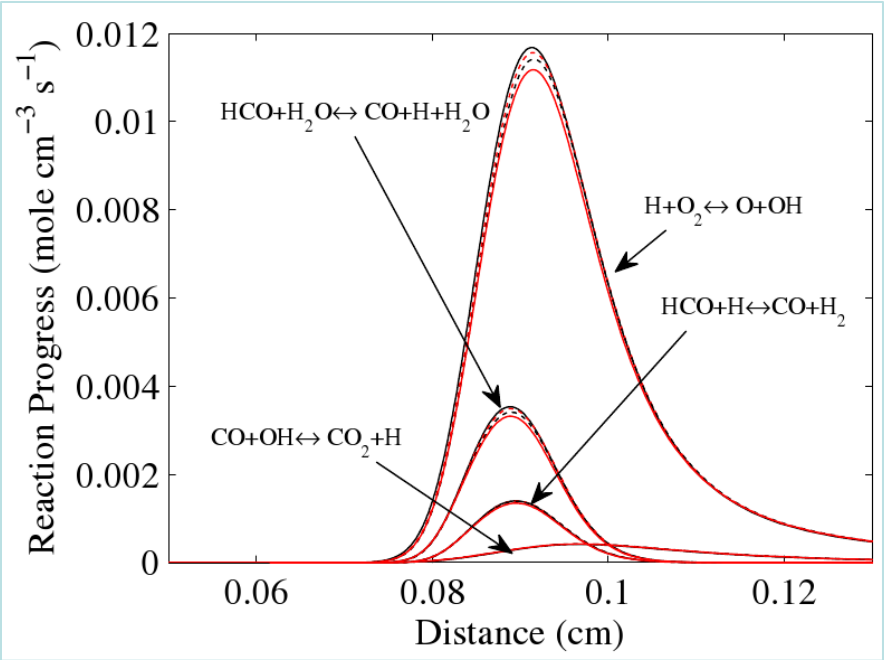


Similarity in Profiles of (Small Species) Radical Concentrations and Reactions

Species Profiles



Reaction Progress



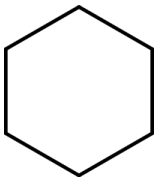
Interim Summary

- Experimental laminar flame speeds of C_5 to C_8 n-alkanes almost identical at atmospheric and elevated pressures
- Computation shows almost identical profiles for:
  - Concentrations of decomposed fuels species and their further reactions in the preheat zone
  - Concentrations of small molecule species and their reactions in the active reaction zone

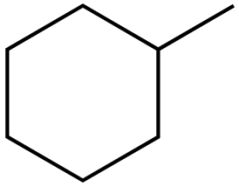
Flame Kinetics of Cycloalkanes

Interest in Cycloalkanes

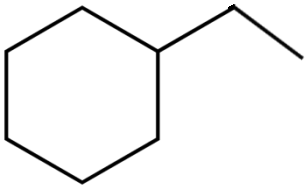
- To what extent is fuel similarity of n-alkanes carried over to other hydrocarbon fuels?
- Cycloalkanes are major components of fuel blends
- Ji *et al.* 2011 found: cyclohexane > n-hexane > mono-alkylated CH; difference seems to be caused by fuel cracking process



cyclohexane



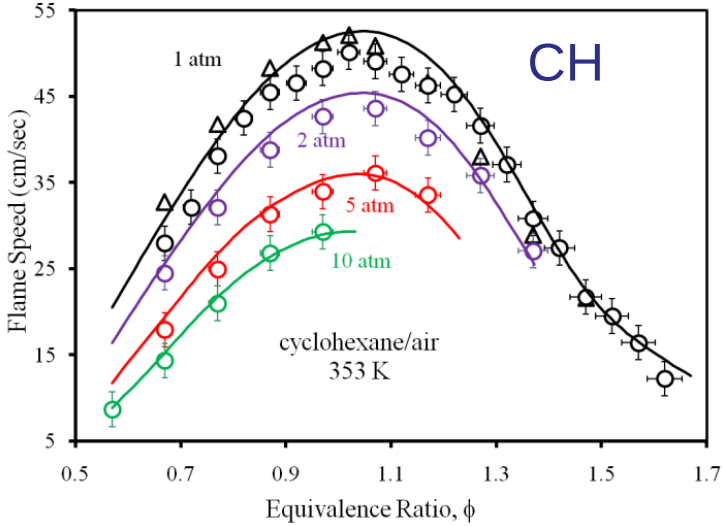
methyl-CH

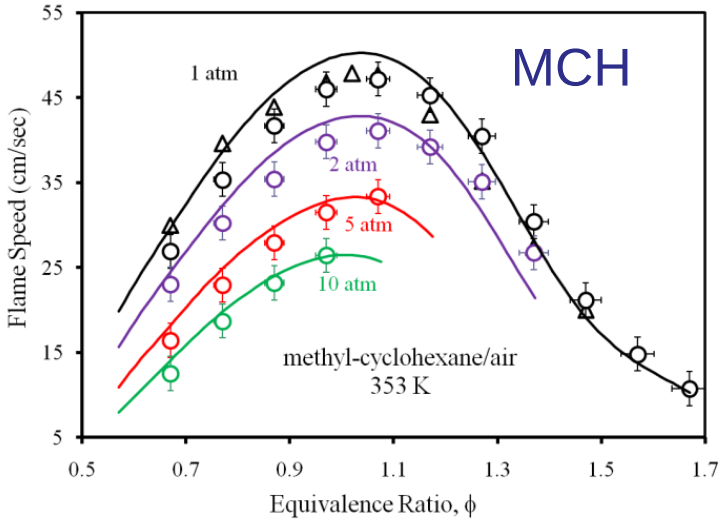


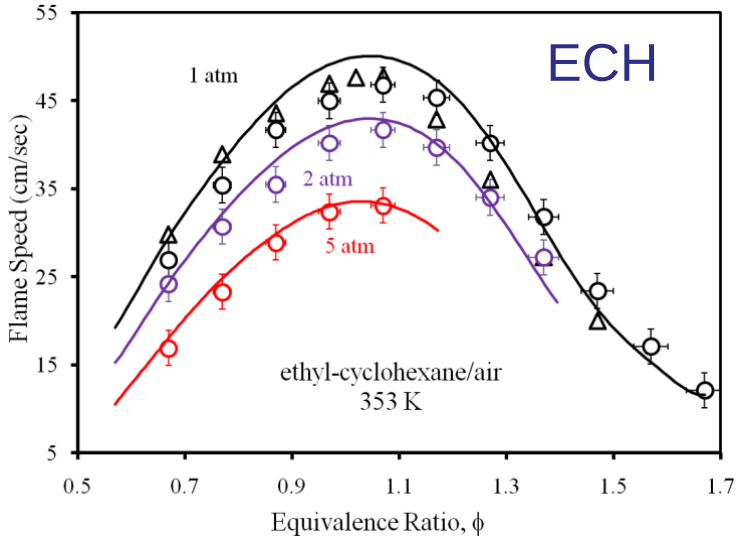
ethyl-CH

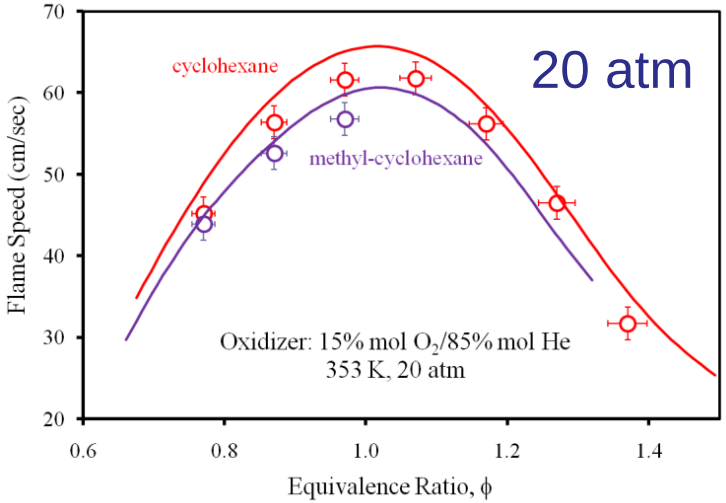
- Same trend holds at higher pressures?
- Further contrast difference between different fuels

Experimental and Calculated Flame Speeds





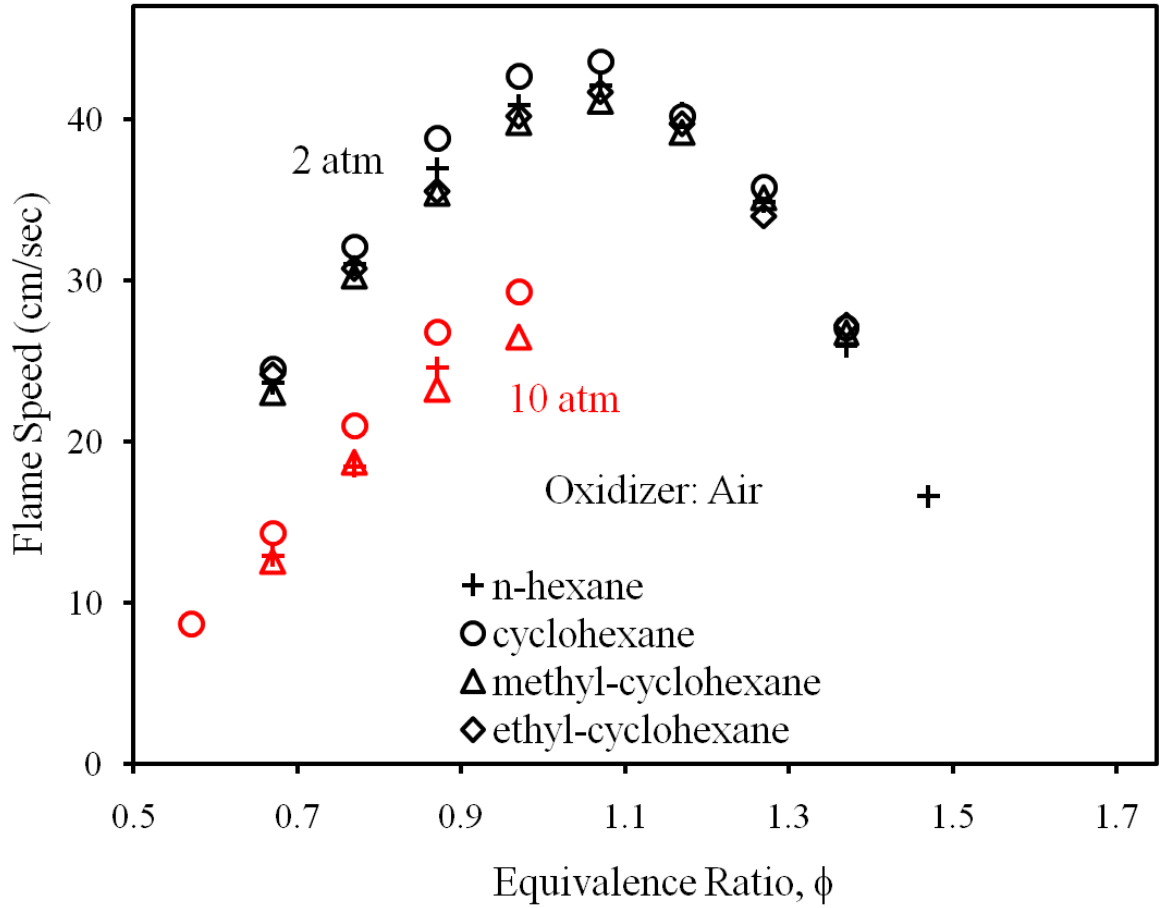




△ : **Ji et al. 2011**

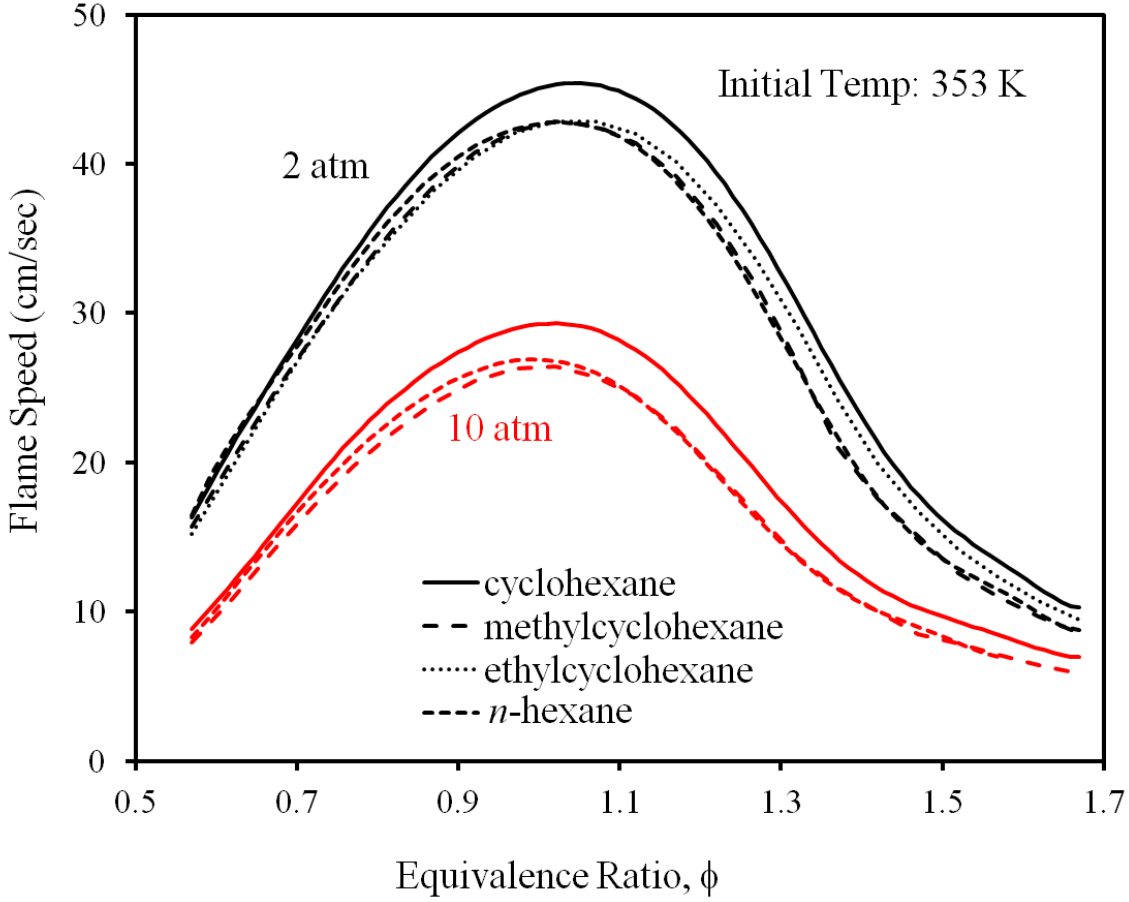
Calculation: JetSurF 2.0

Comparisons at Elevated Pressures: Experiment



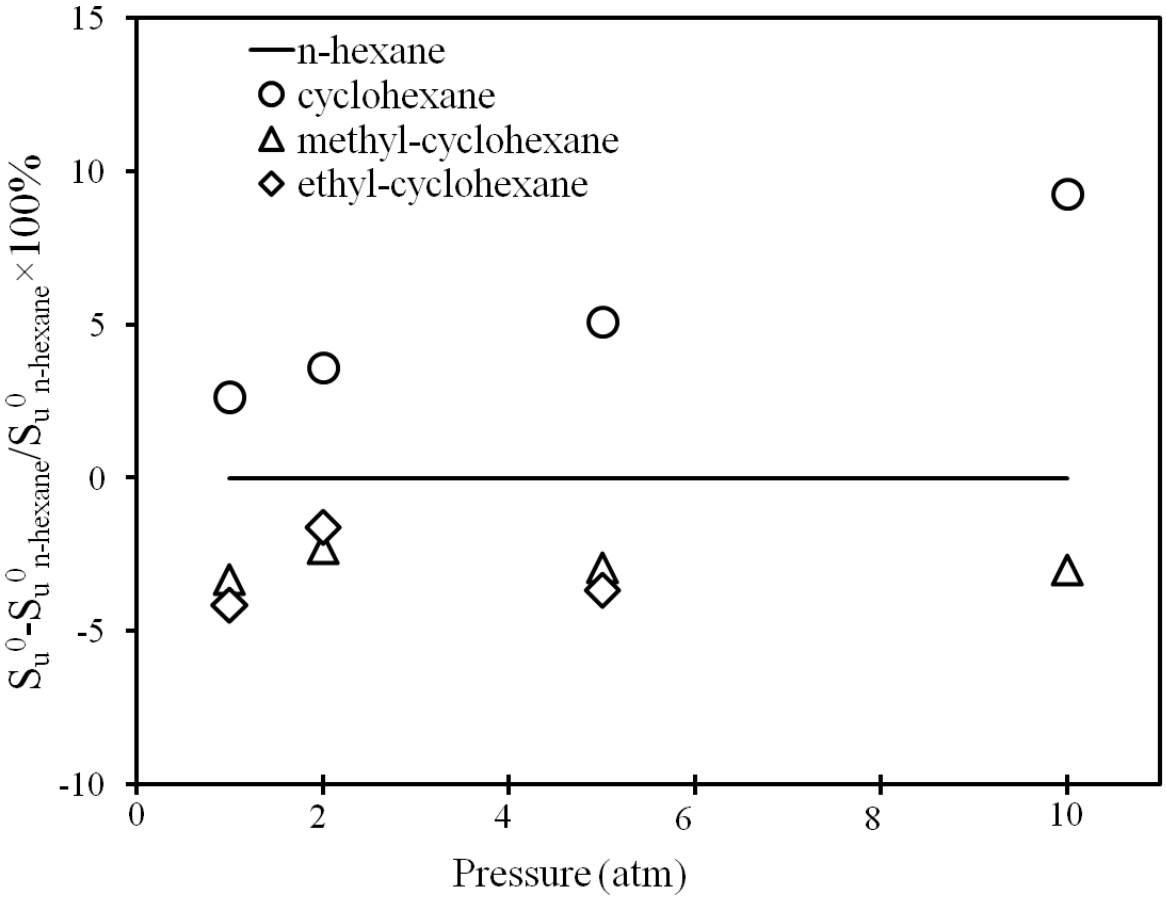
cyclohexane > n-hexane > methyl-CH ≈ ethyl-CH

Comparison at Elevated Pressures: Calculation



- Simulation by JetSurF 2.0 shows similar trend

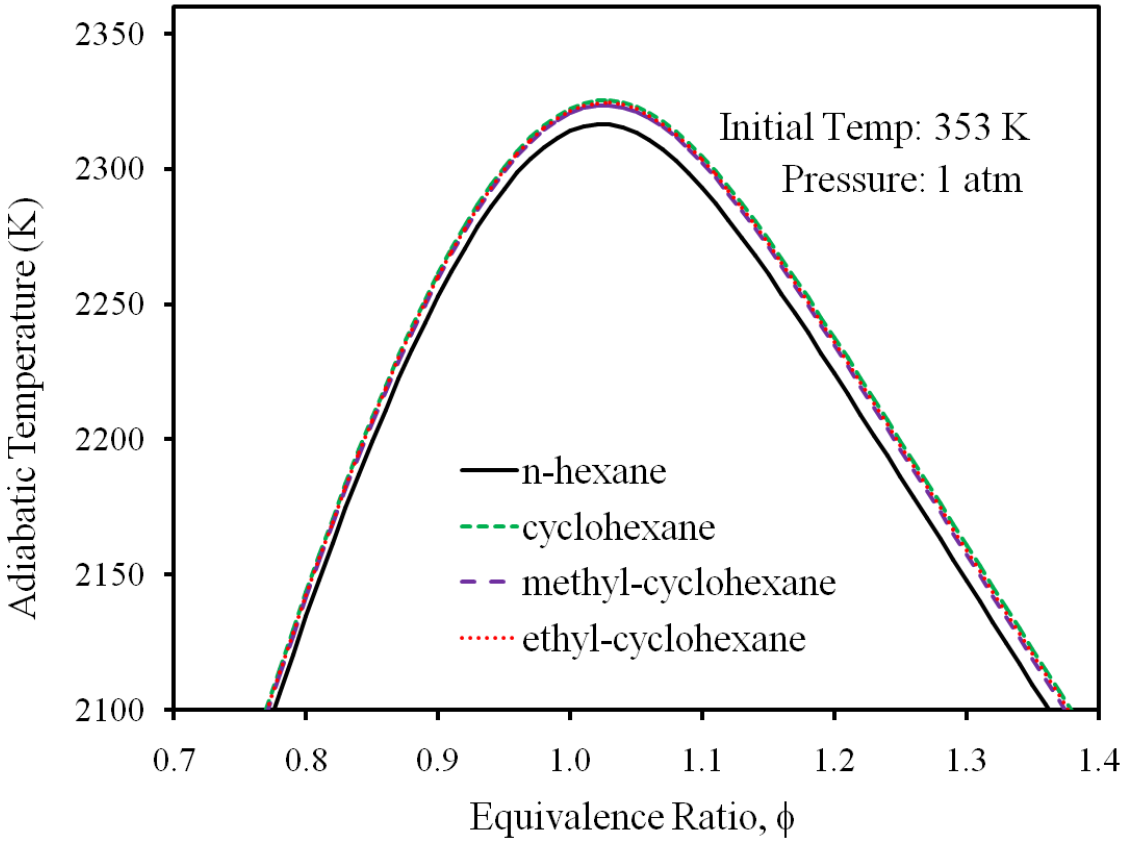
Assessment of Differences



- Difference increases with pressure: 5% at 1atm, 13% at 10 atm

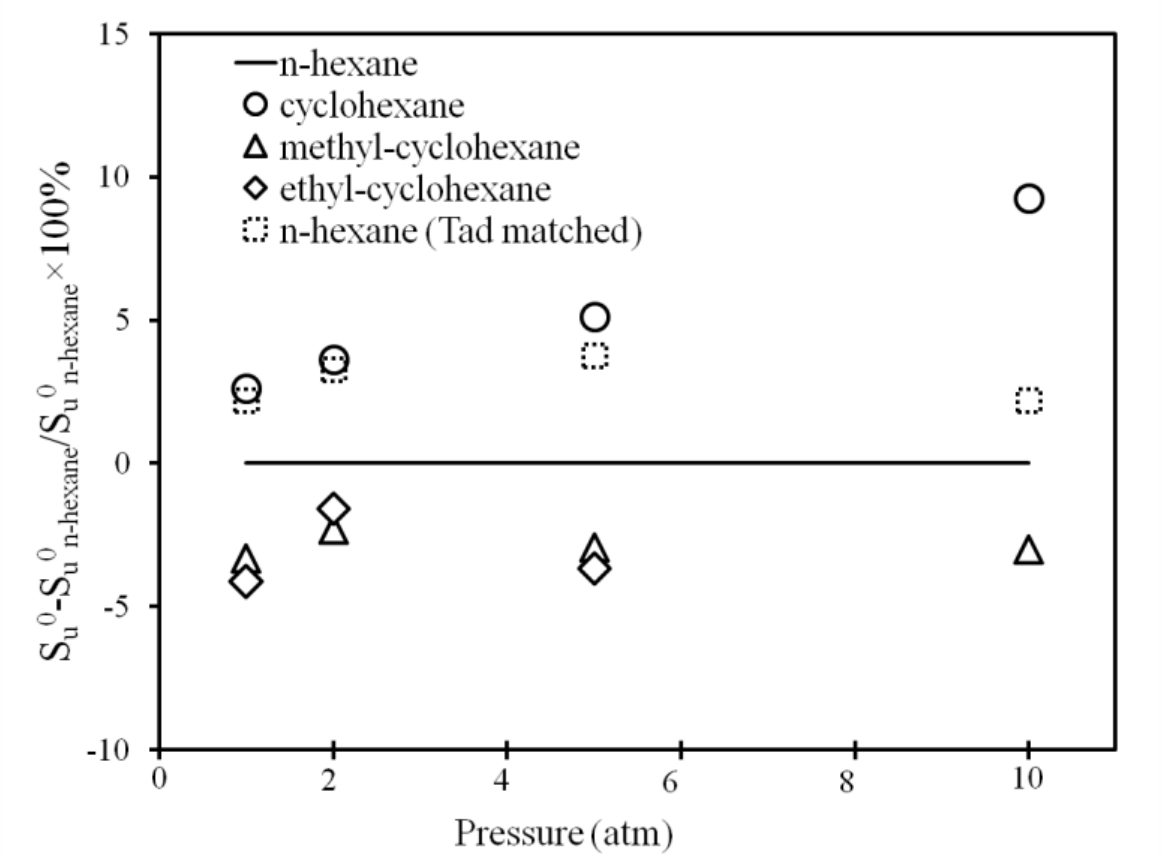
Assessment of Thermal Effect

- Identical flame temperature for cyclohexane and mono-alkylated CH
- n-hexane lower by 10 K at maximum

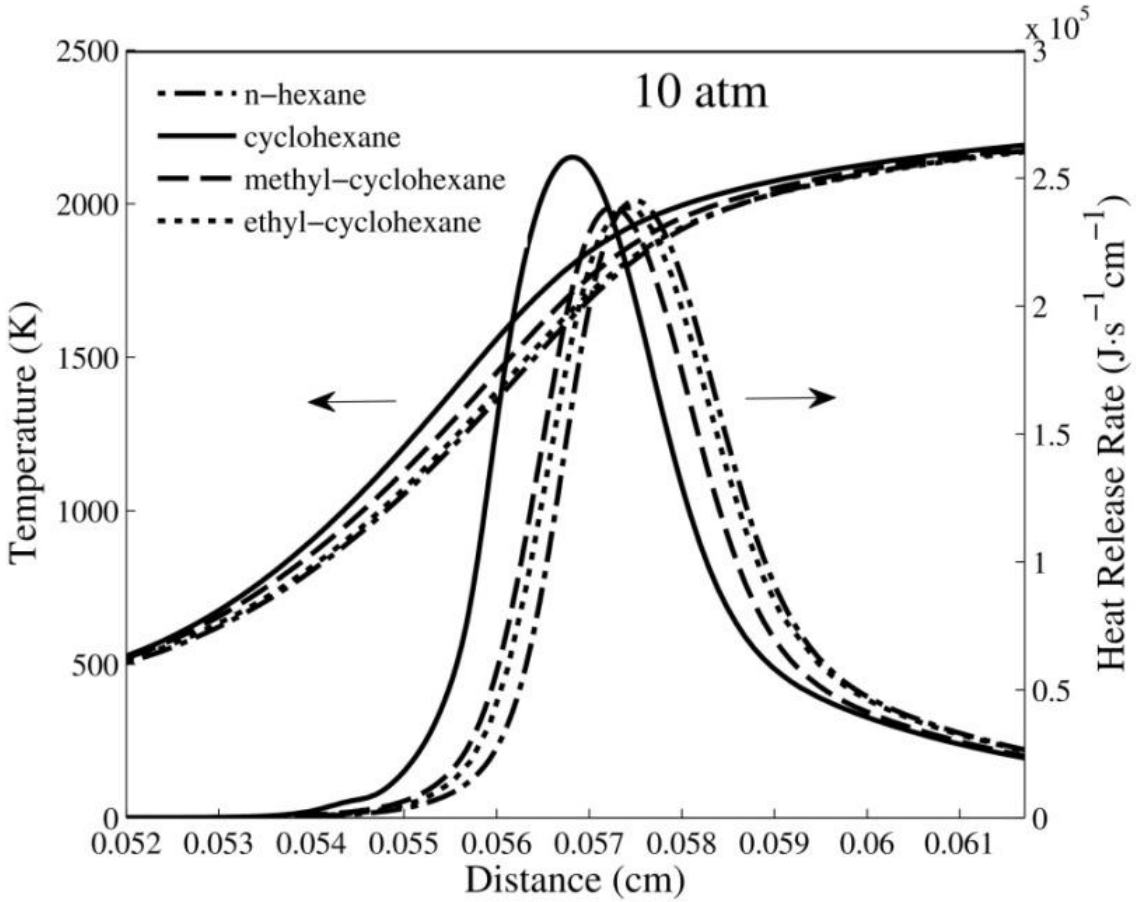


Assessment of Thermal Effect

- Thermal effect explains the difference between n-hexane and cyclohexane at 1 atm (Ji *et al.*), but not at 10 atm
- Suggesting a kinetic reason



Assessment of Kinetic Effect



- Distinctive heat release profile for cyclohexane

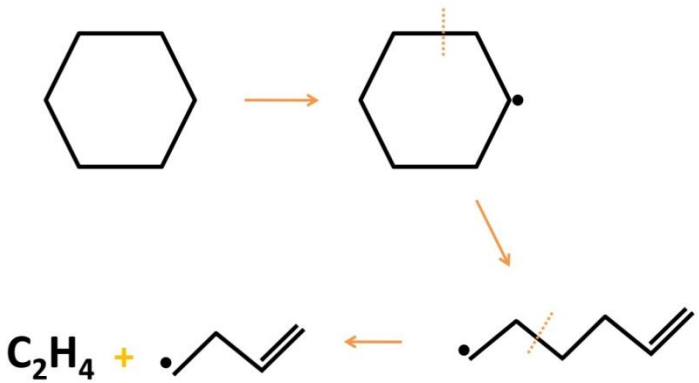
Assessment of Kinetic Effect

- Key termination reaction for hexane and methyl-CH

  $aC_3H_5 + H + M \rightarrow C_3H_6 + M$

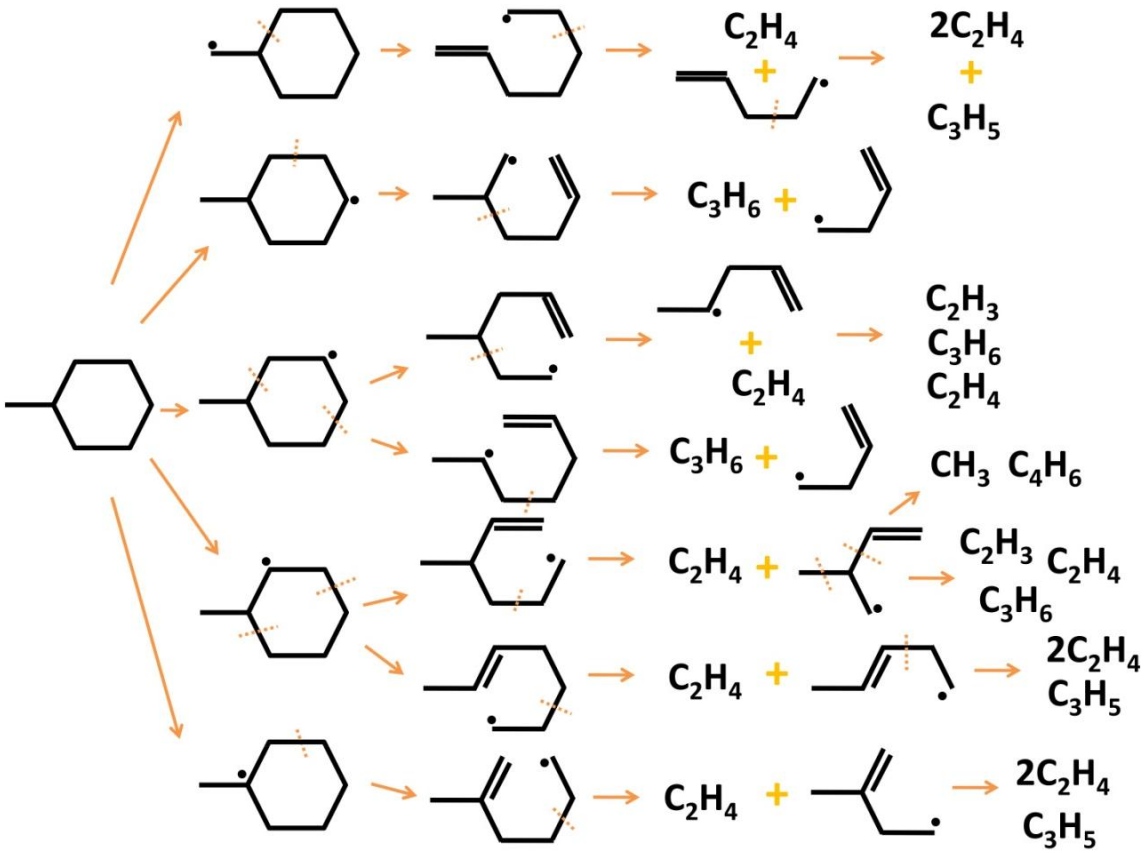
  which increases with pressure
- Cyclohexane cracks into much more C_2 and C_4 than C_3.

  - Dominant role of β-Scission



Assessment of Kinetic Effect

- Not so for methyl-CH



Interim Summary on Cycloalkanes

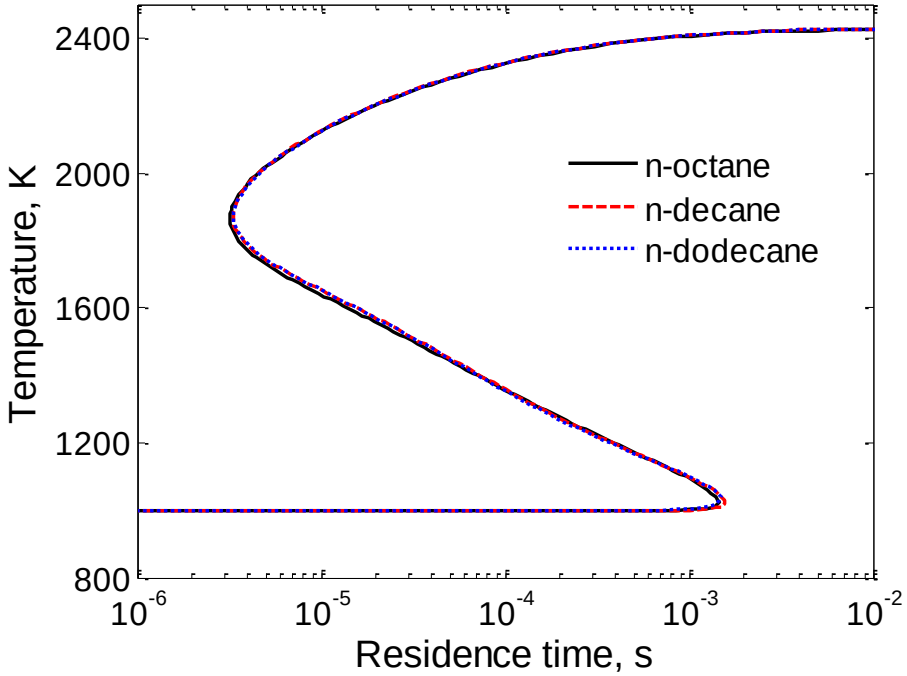
- Acquired flame speed data for cyclohexane, methyl-CH and ethyl-CH from 1 atm to 20 atm
- Good agreement with JetSurF 2.0 mechanism at all pressures
- Slight over-prediction of JetSurF 2.0 at 1 atm
- Revealed the trend for flame speed: cyclohexane > n-hexane > methyl-CH ≈ ethyl-CH with relative difference 5% at 1 atm, 13% at 10 atm
- Computed flame structure and sensitivity analysis reveal that cracking of cyclohexane favors C_2, C_4 over C_3 fragments
- The special feature of cyclohexane can be explained by its symmetric structure and the general applicability of β-scission rule

A PSR Study on Effects of Surrogate Fuel Composition on Ignition and Extinction

Tianfeng Lu

University of Connecticut

S-Curve of PSR for Jet Fuel Surrogates (1/2)

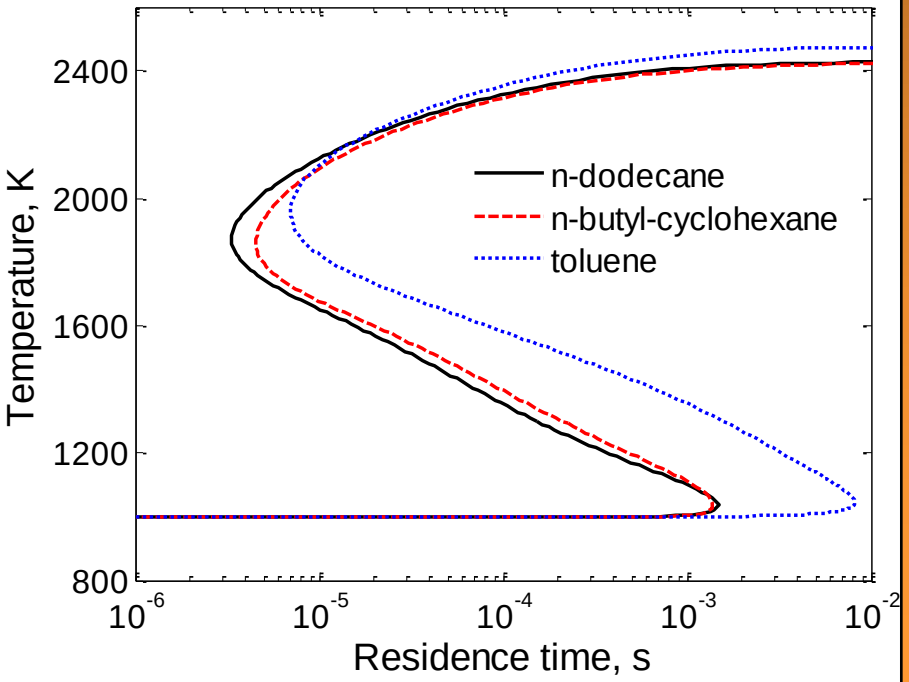


Mechanism: JetSurF 2.0

Inlet condition:

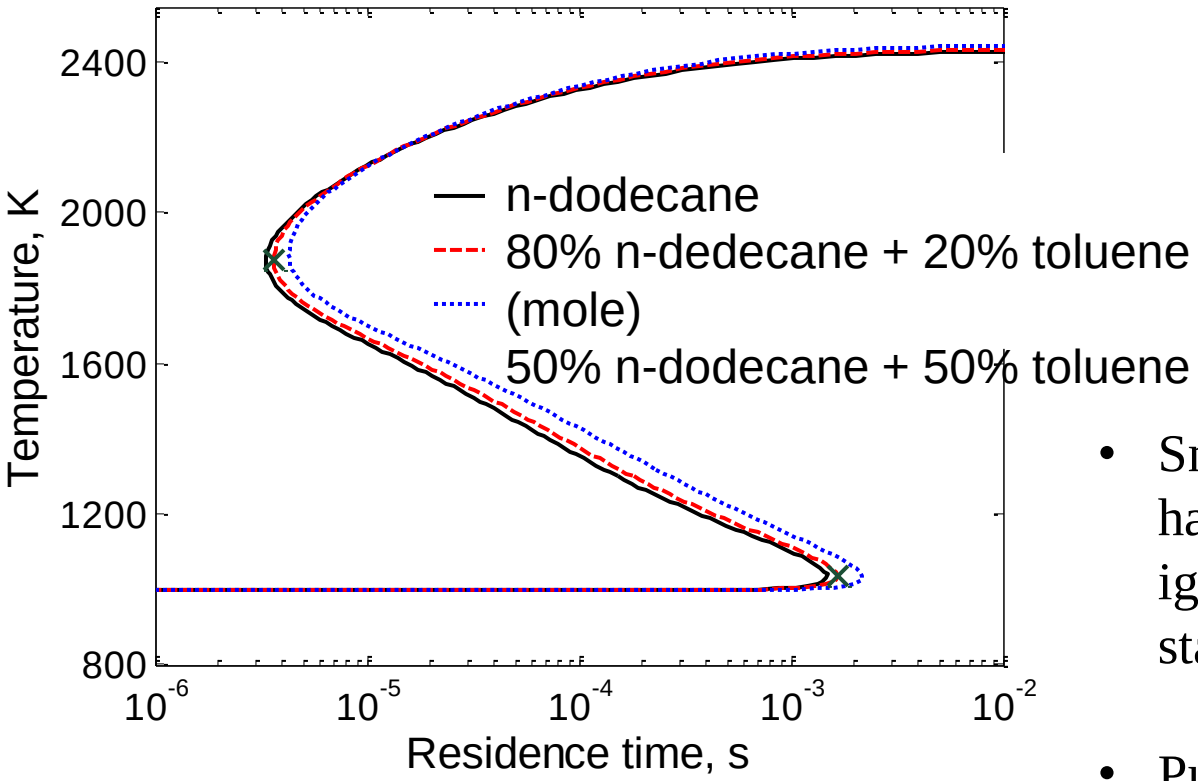
$T_{in} = 1000K$

$p = 10atm$



- Large n-alkanes feature mostly identical S-curves
- Pure n-alkane, cycloalkanes, and aromatics feature different ignition and extinction states

S-Curve of PSR for Jet Fuel Surrogates (2/2)



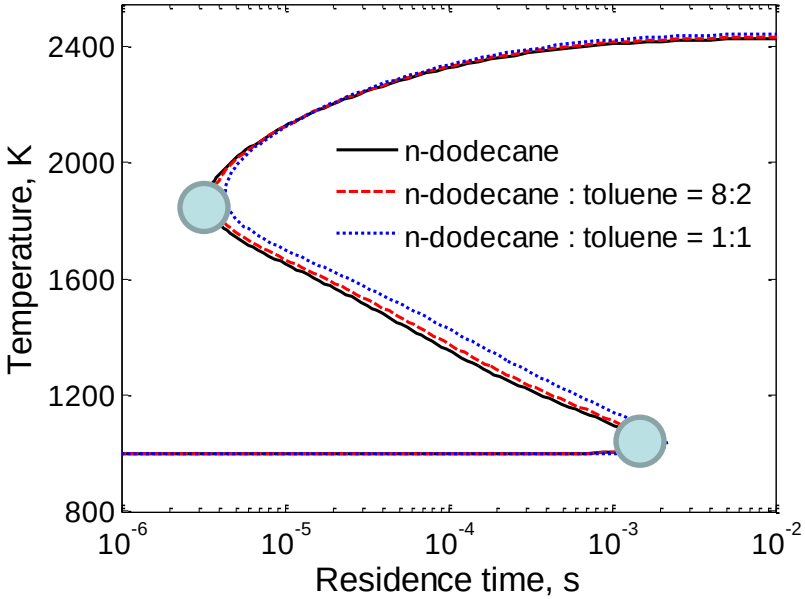
Inlet condition:

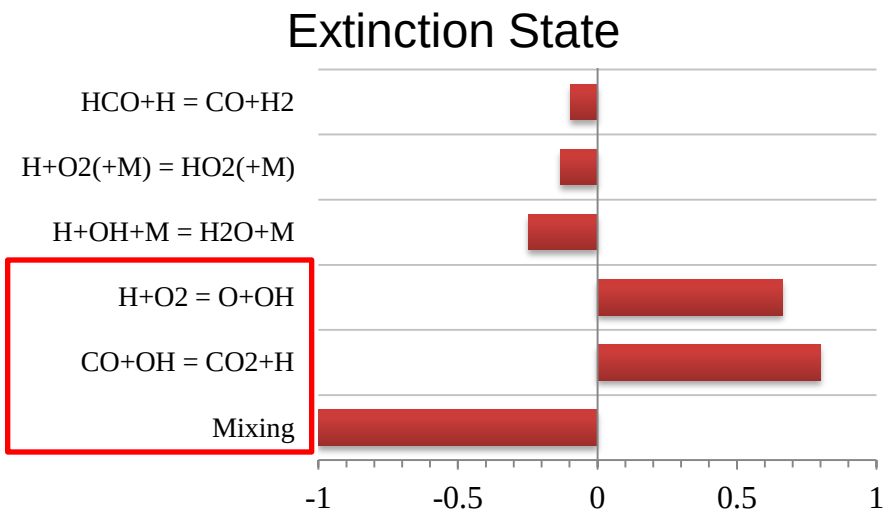
T_{in} = 1000K

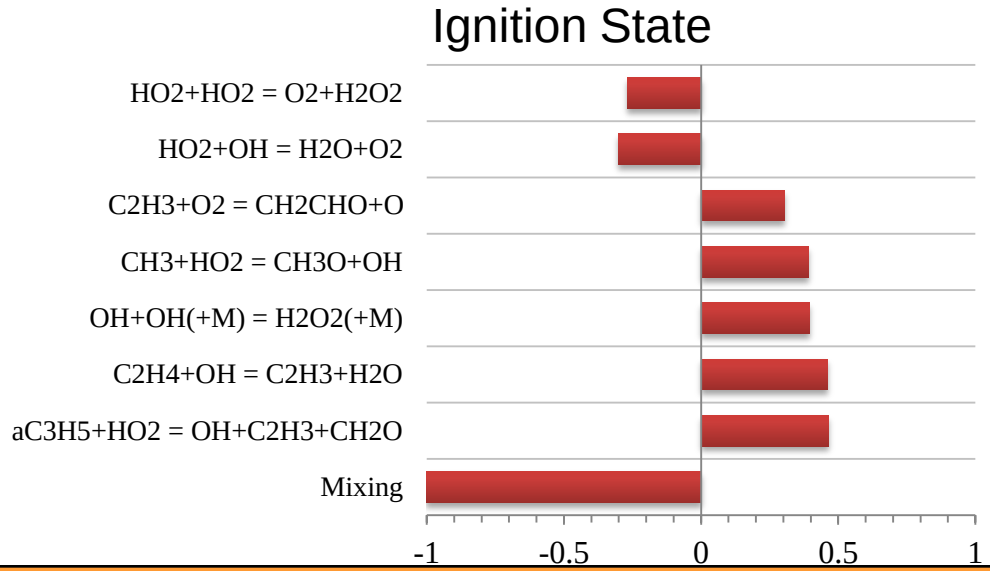
p = 10atm

- Small amount of aromatics has little effects on either the ignition or the extinction states
- Pure n-alkanes may be sufficiently good surrogates for capturing limit flame phenomena

Controlling Reactions for Ignition/Extinction (80% n-Dodecane + 20% Toluene)







- Both ignition (high-T) and extinction are determined by reactions involving small molecules (H, CO, C1-C3)
- A "low-dimensional manifold" may exist for high-T chemistry of large hydrocarbons

Interim Summary on PSR Study

- Pure components of jet fuel surrogate (e.g. n-alkanes, cyclo-alkanes, aromatics) may feature dramatically different ignition/extinction states
- Small amount of aromatics in n-alkanes has little effects on either ignition or extinction states
- Reaction pathways involving small molecules control ignition (high-T) and extinction of jet fuels
- A “low-dimensional manifold” may exist for chemistry of large molecules for ignition (high-T) and extinction