Ignition Kinetics of Hydrocarbons and Propellants

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Research Projects:

- Stagnation pool ignition of heptane and iso-octane
- Ignition kinetics of the butene isomers
- Ignition kinetics of MMH pyrolysis and oxidation

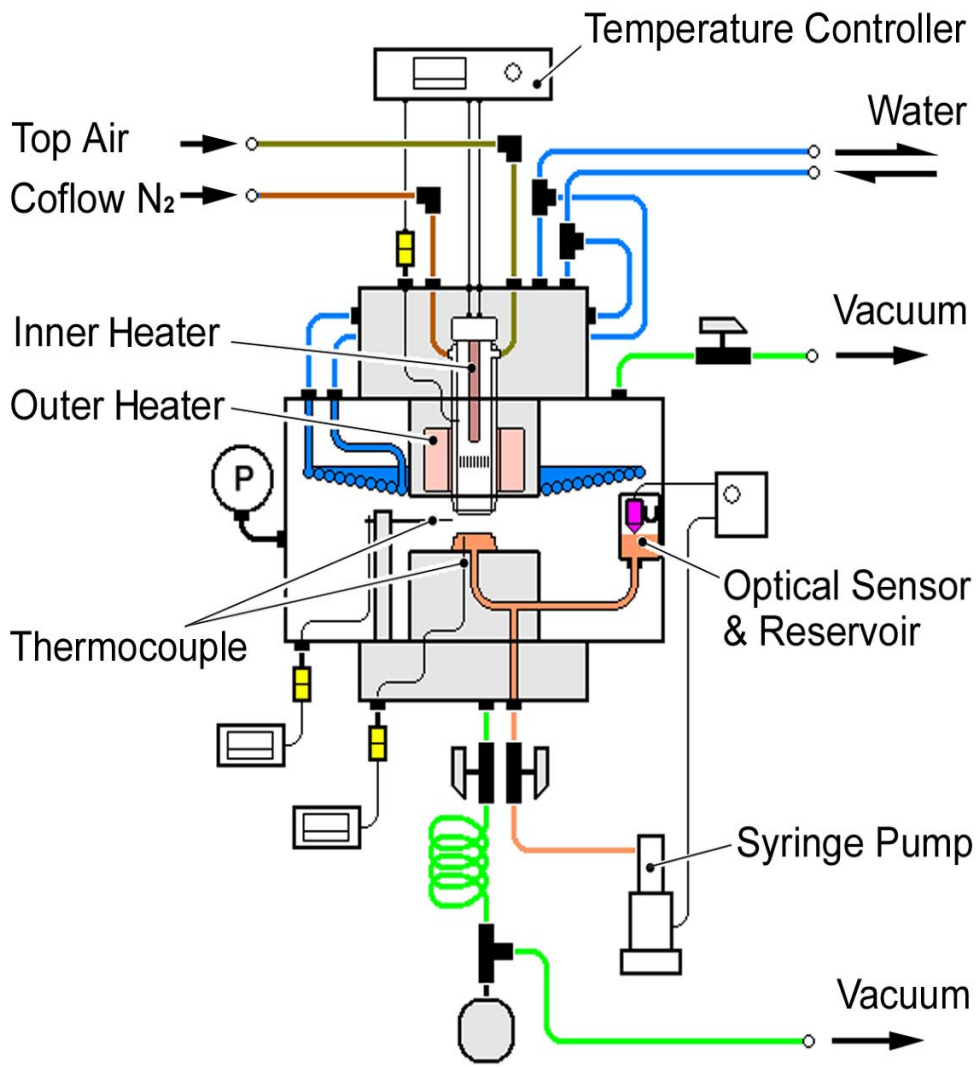
Ignition of *n*-Heptane and *iso*-Octane Pool by Heated Stagnating Oxidizing Flow*

* "Ignition of *n*-heptane pool by heated stagnating oxidizing flow," by W. Liu, D.L. Zhu, N. Wu and C.K. Law, *Combustion and Flame*, in press.

Background

- Interest in the diffusive ignition of hydrocarbons and propellants; low- to high-temperature chemistry
- Evolving concerns:
  - Most studies were on gaseous fuels in the counterflow
  - Interests in liquid fuels, especially those of low volatility
  - Pre-vaporization: limited to volatile fuels, low pressure & concentrations
- Our solution: stagnation flow

Experimental Apparatus



Numerical Solutions

- Steady state solution: stagnation-flow code, modified from the OPPDIF program with appropriate B.C. on the fuel side
- Ignition state: defined by the ignition turning point
- Kinetic Mechanisms:

***n*-Heptane:**

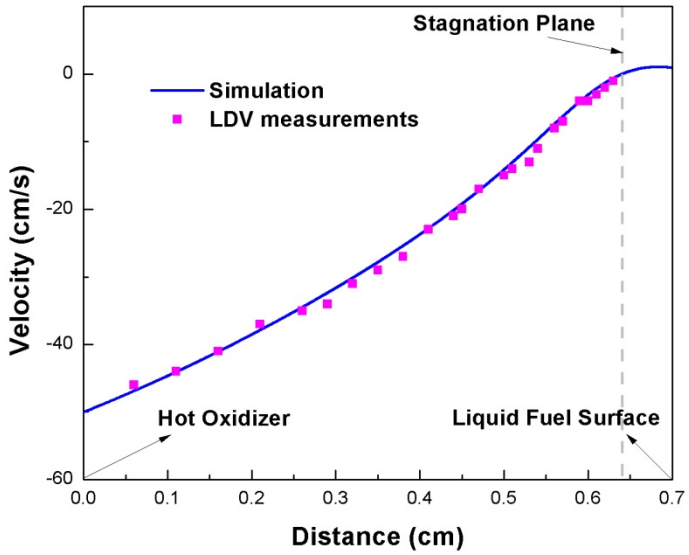
- Detailed, high-temperature model: Mech-130 (*H. Wang*)
- Reduced model: Mech-58, derived from a comprehensive detailed mechanism (*H.J. Curran & C.K. Westbrook*)

***iso*-Octane:**

- Reduced model: Mech-78, derived from a comprehensive detailed mechanism (*H.J. Curran & C.K. Westbrook*)

Determination of Strain Rate, 1/2

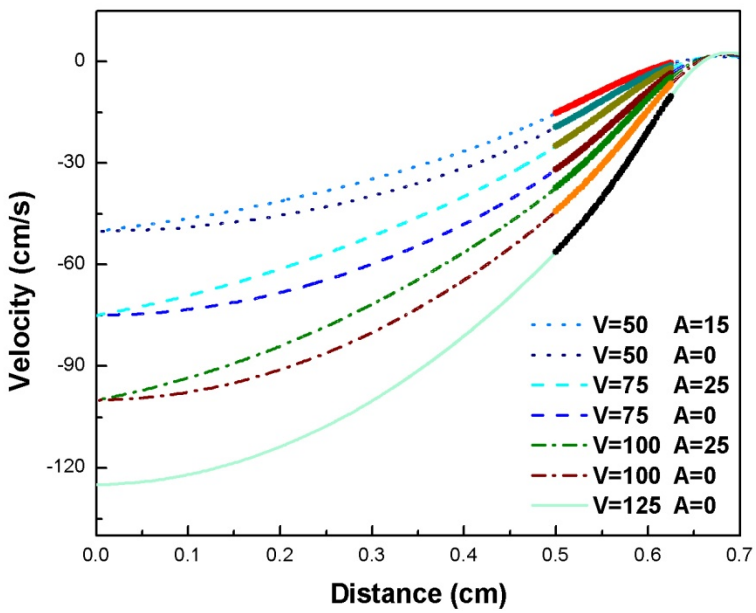
- Strain rate K: gradient of the axial velocity; quantifies the flow field
- Models: potential flow, plug flow, mixed flow
- Mixed-flow model agrees well with measurements
- In plug/mixed flow model and experimental conditions, K is a function of location

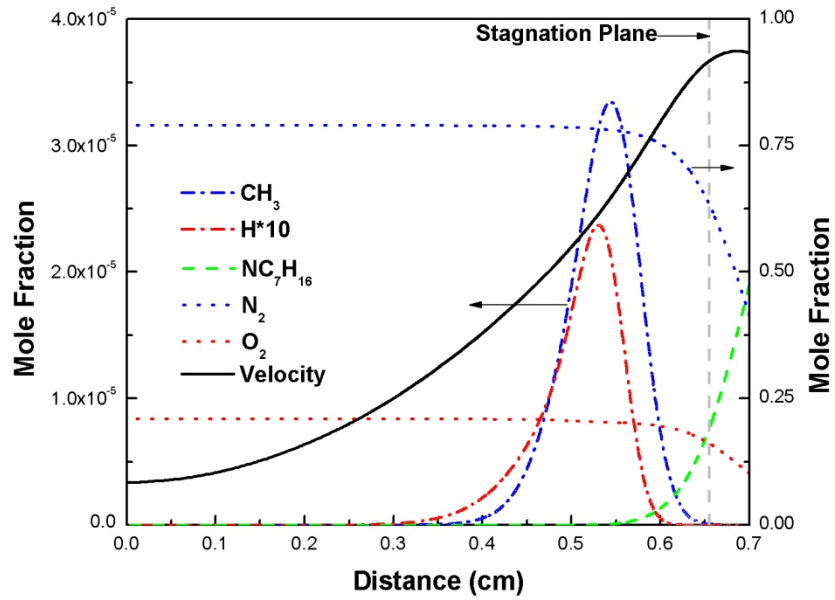


Determination of K is not straightforward!

Determination of Strain Rates, 2/2

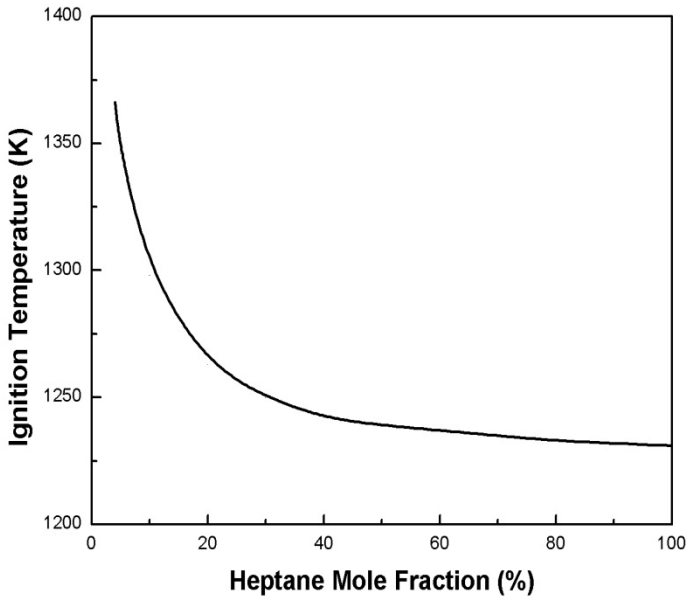
- Strain rate K: by fitting the axial velocity data (both experimental and numerical) within the region of 0.5 to 0.6 cm
  - Moderate linearity
  - Approximately in the center of the ignition kernel



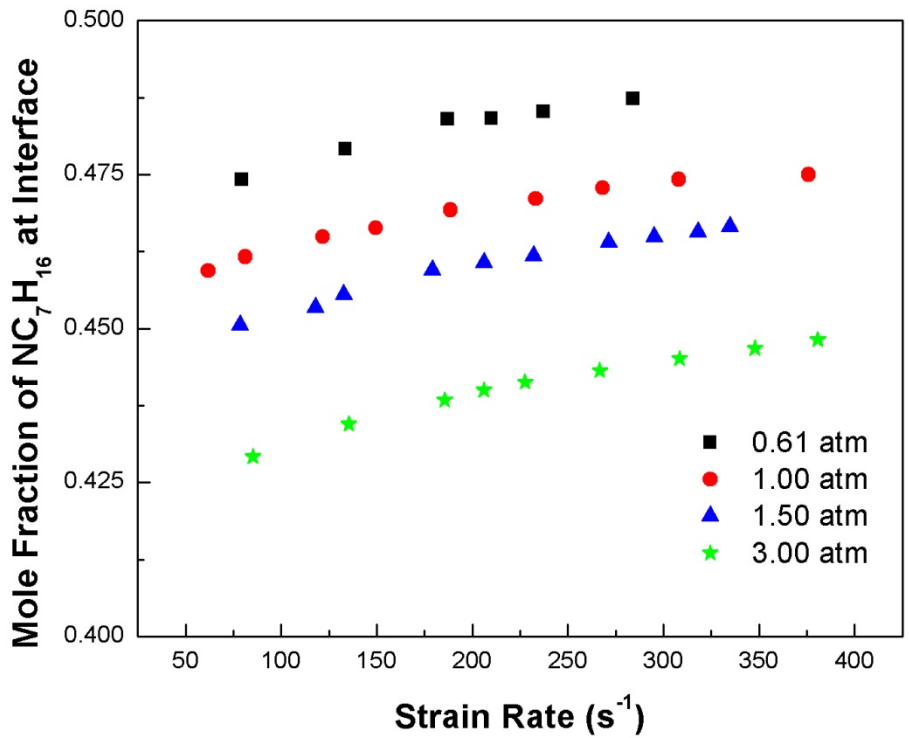


Fuel Concentration at Surface, 1/2

- Effect of fuel concentration on ignition
  - Stagnation flow: fuel concentration at liquid surface cannot be readily controlled
  - Counterflow: T_{ign} is minimally affected when X_{Fuel} is beyond 0.4
  - Unbalanced counterflow: $V_{oxidizer}$=100 cm/s, V_{fuel}=3 cm/s



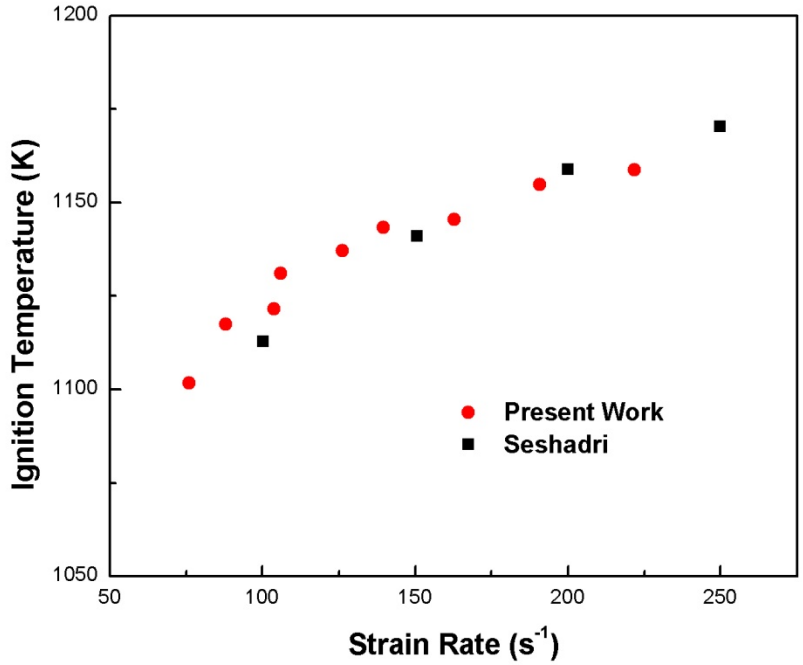
Fuel Concentration at Surface, 2/2



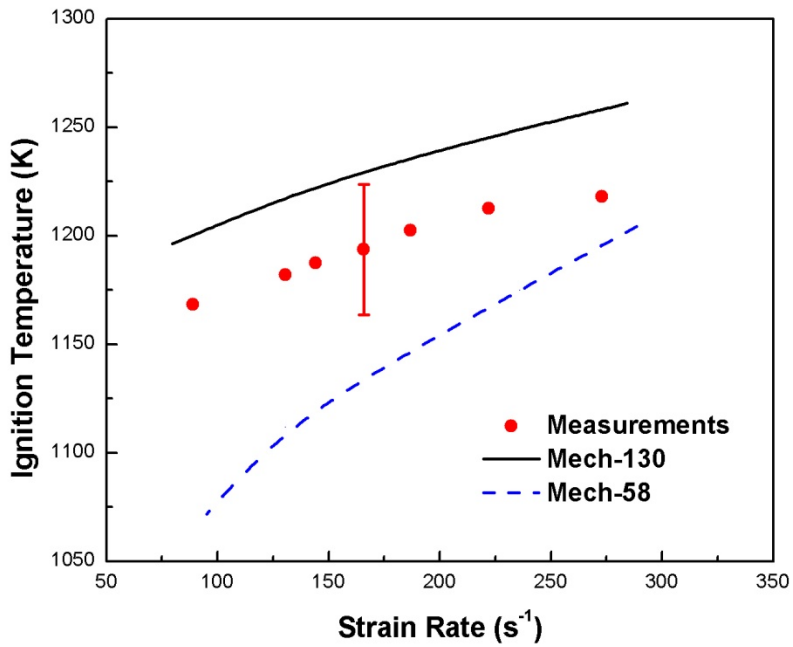
- T_{ign} is insensitive to concentration change when X_{hep} at the surface is above 0.4
- X_{hep} ranges from 0.43-0.48 over the pressures and strain rates examined
- X_{hep} could be considered to have minimal effect on ignition

Measurement and Simulation of *n*-Heptane, 1/3

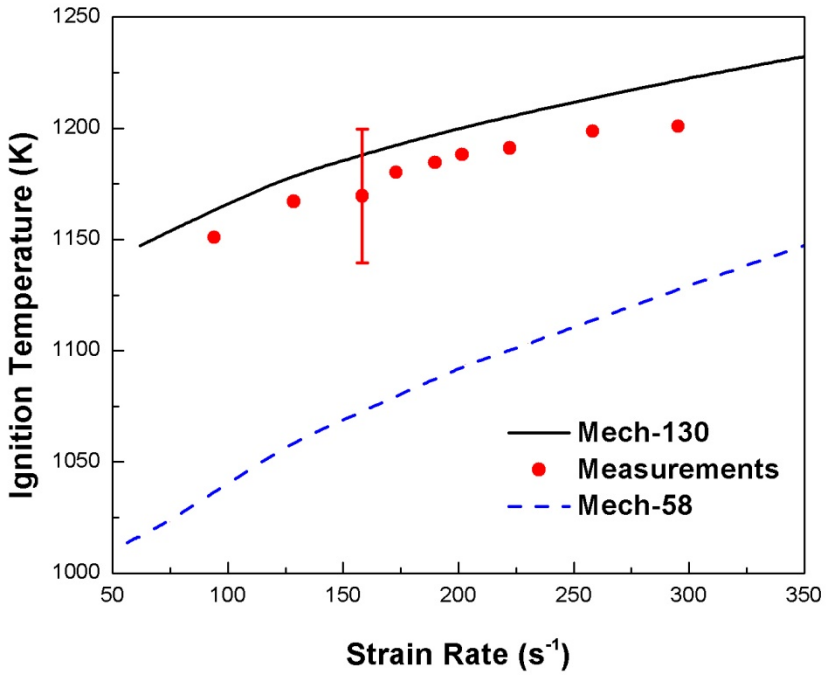
- Comparison of present experimental measurements and Seshadri's, *p*=1atm; with conversion for different strain rate definitions & thermocouple corrections



Measurement and Simulation of *n*-Heptane, 2/3

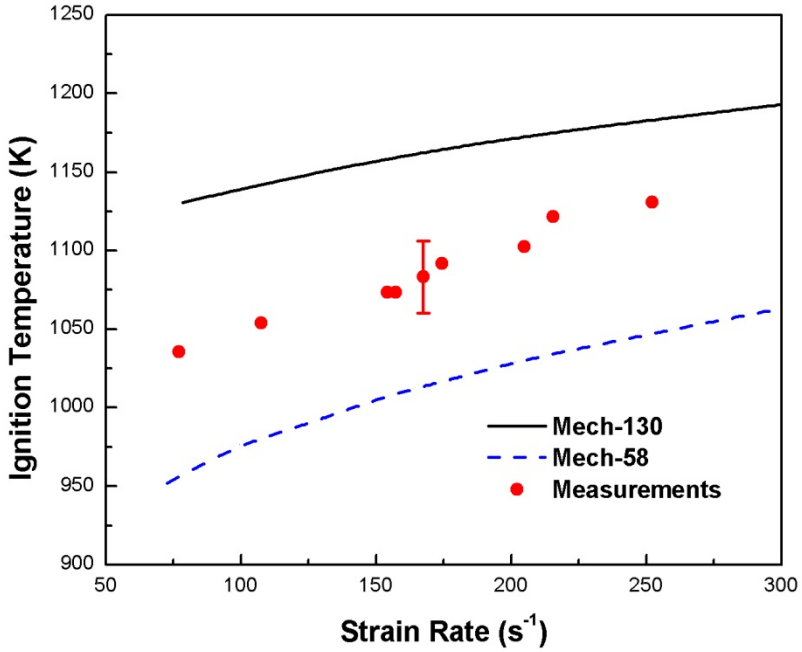


P=0.61atm

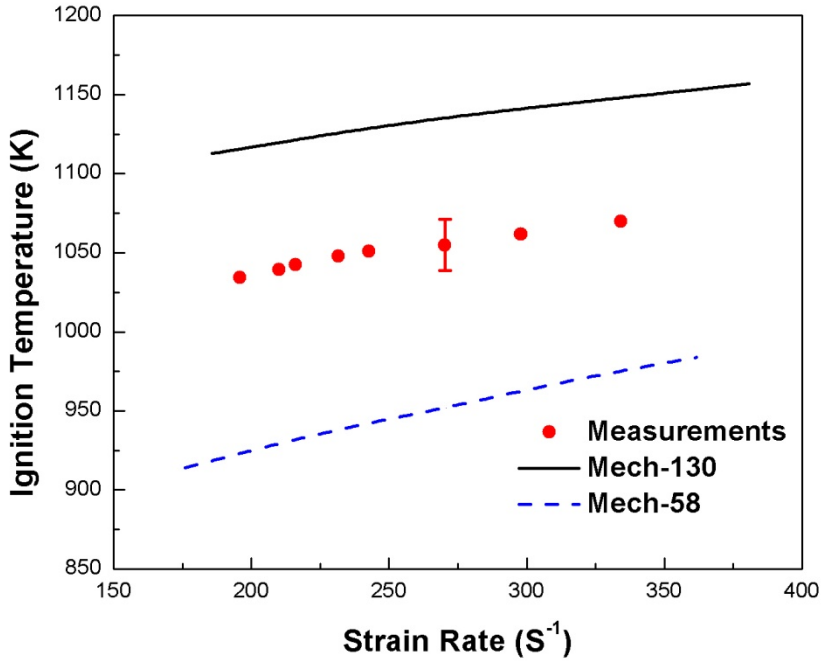


P=1.0 atm

Measurement and Simulation of *n*-Heptane, 3/3



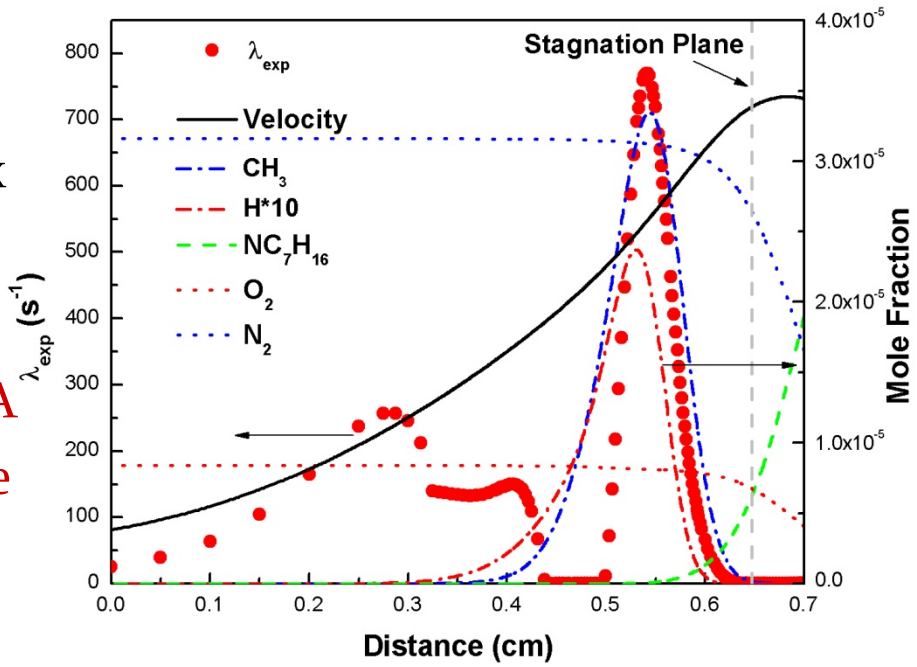
P=1.5 atm



P=3.0 atm

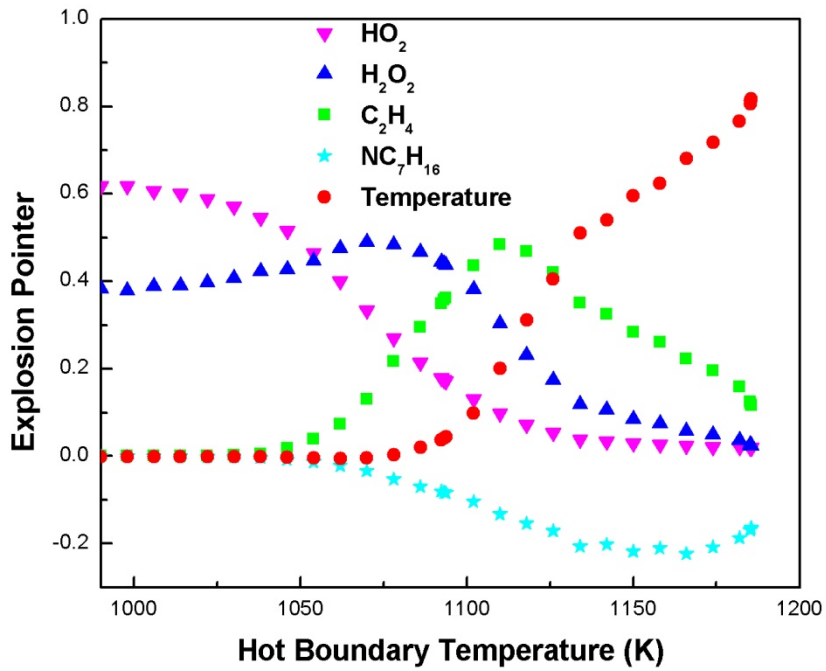
Chemical Explosive Mode Analysis of *n*-Heptane, 1/2

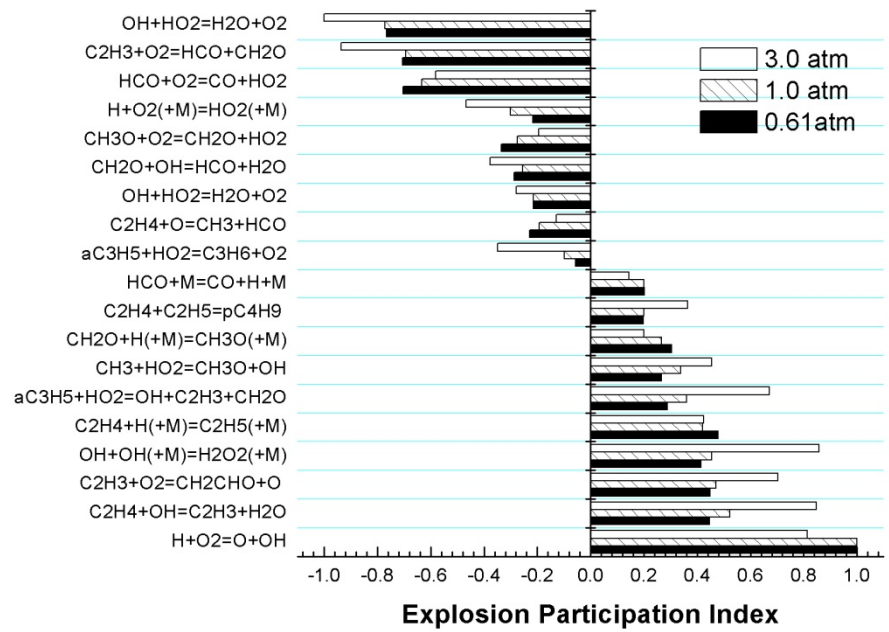
- CEMA (Tianfeng Lu) : chemical reactions are grouped into independent modes through eigen-decomposition of the Jacobian matrix of the chemical source term
- Important species and reactions to ignition could be identified by CEMA
- λ_{exp}: reciprocal of the explosive time scale; can be interpreted as the strength of the explosive mode; its spatial profile could be used to identify the "ignition kernel"



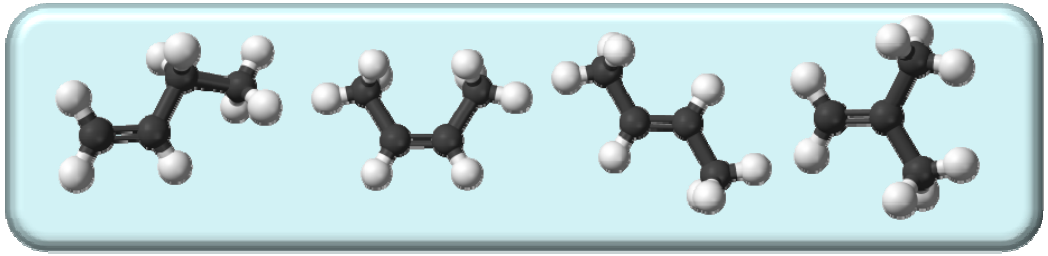
Chemical Explosive Mode Analysis of *n*-Heptane, 2/2

- A transition from radical explosion to thermal explosion
- Important reactions to ignition: H_2/CO chemistry, C_2-C_3 reactions involving C_2H_4



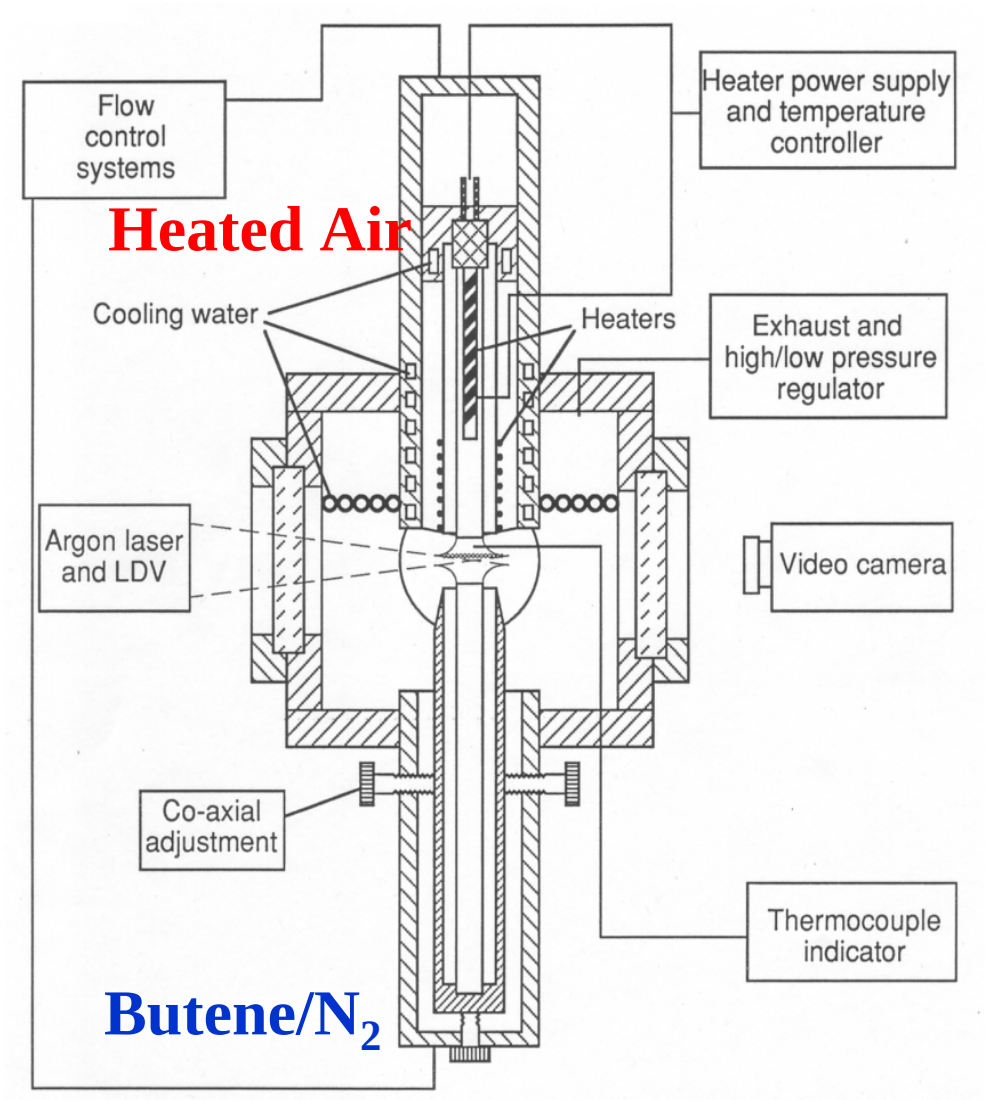


Ignition of the Butene Isomers: A Kinetics Study

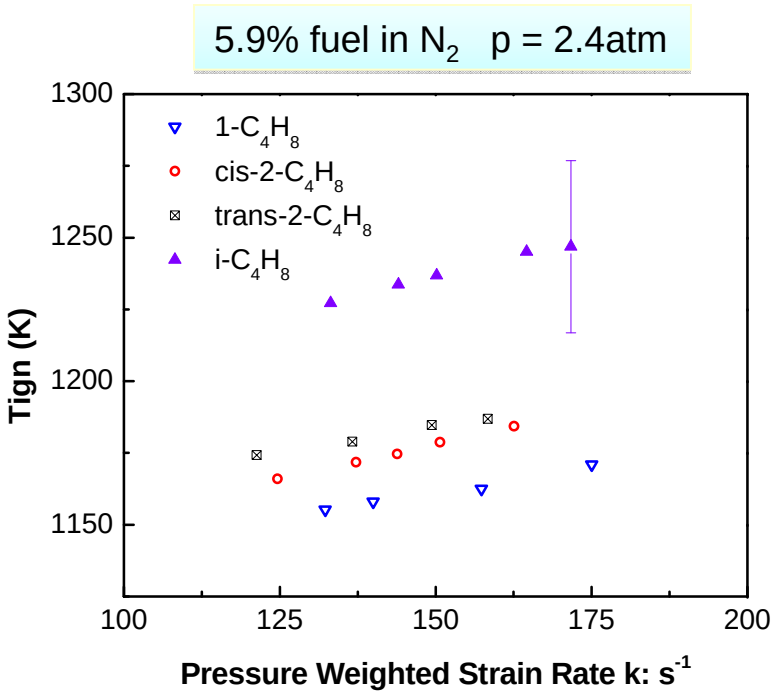


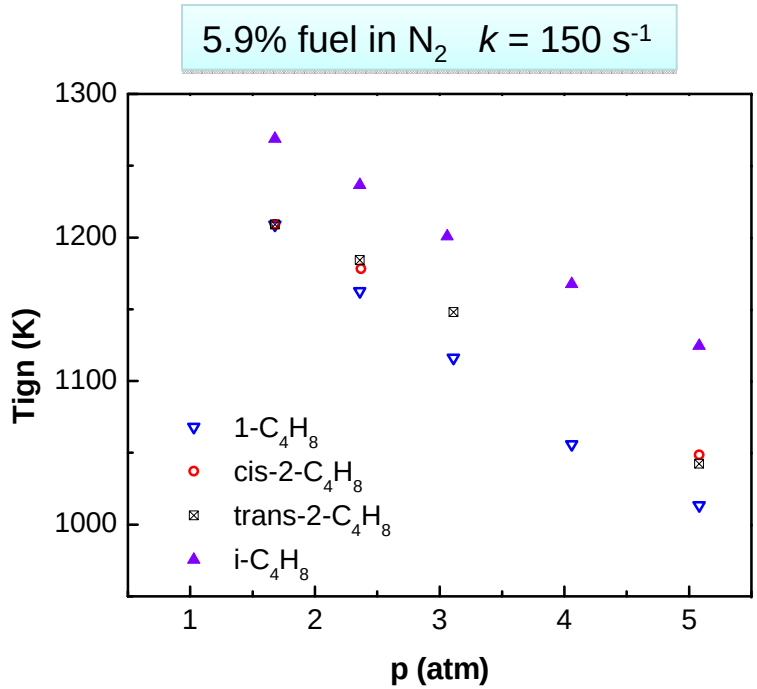
1-butene cis-2-butene trans-2-butene isobutene

Experimental Apparatus



Experimental Counterflow T_{ign}

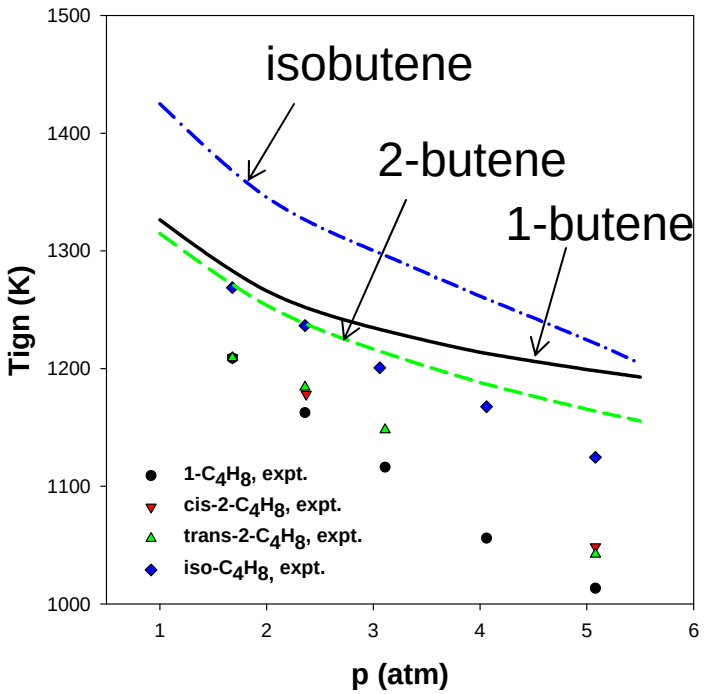




- Ignition temperature increases with increasing *strain rate* and decreases with increasing *pressure*
- T_{ign}: isobutene > trans-2-butene ≈ cis-2-butene > 1-butene

Modeling of Ignition Temperature

- **High-temperature reaction model of H_2/CO/C_1-C_4 compounds, *USC Mech Version II (May 2007):*** incorporates the recent thermodynamic, kinetic, and species transport updates relevant to high-temperature oxidation of H_2, CO, and C1-C4 hydrocarbons
- Counterflow ignition of alkanes initiated by fuel oxidation at p < 5 atm seems to follow the high-temperature mechanism of radical chain branching



- Overpredicts experimental data by ~ 75 – 100 K at 1 – 2 atm
- Difference becomes greater at high p and low T
- Experimental T_{ign}: isobutene > trans-2-butene > cis-2-butene > 1-butene
- Calculated T_{ign}: isobutene > 1-butene > 2-butene

Ignitability of isomeric butenes

- Allylic hydrogen bond dissociation energy (BDE) was calculated by $\Delta H_f^o{}_{298}$ of butene isomers and corresponding radicals (kcal mol^{-1}): isobutene: 89.3; trans-2-butene: 88.2; cis-2-butene: 87.5, 1-butene: 85.9
- Ignition temperature: isobutene > trans-2-butene > cis-2-butene > 1-butene

- The trend for the allylic hydrogen BDEs qualitatively agrees with that of measured counterflow ignition temperatures

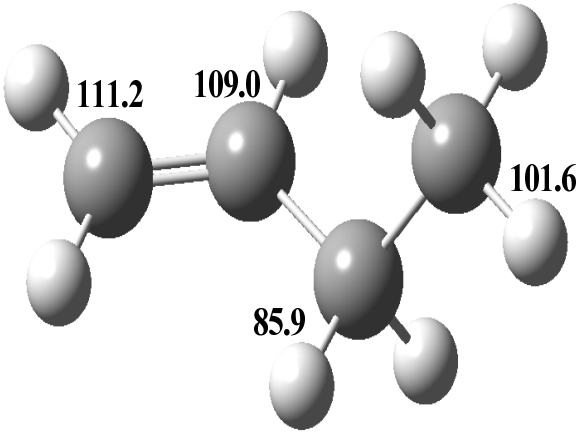
Kinetic Analysis of Oxidation Mechanism of Isomeric Butenes

• Key H-abstraction reactions in USC Mech-II, with estimated rates

$CH_2{=}CHCH_2CH_3 + R\bullet \rightarrow CH_2{=}CHCH_2C\bullet H_2 + RH$
$CH_3CH{=}CHCH_3 + R\bullet \rightarrow CH_2{=}CHCH_2C\bullet H_2 + RH$

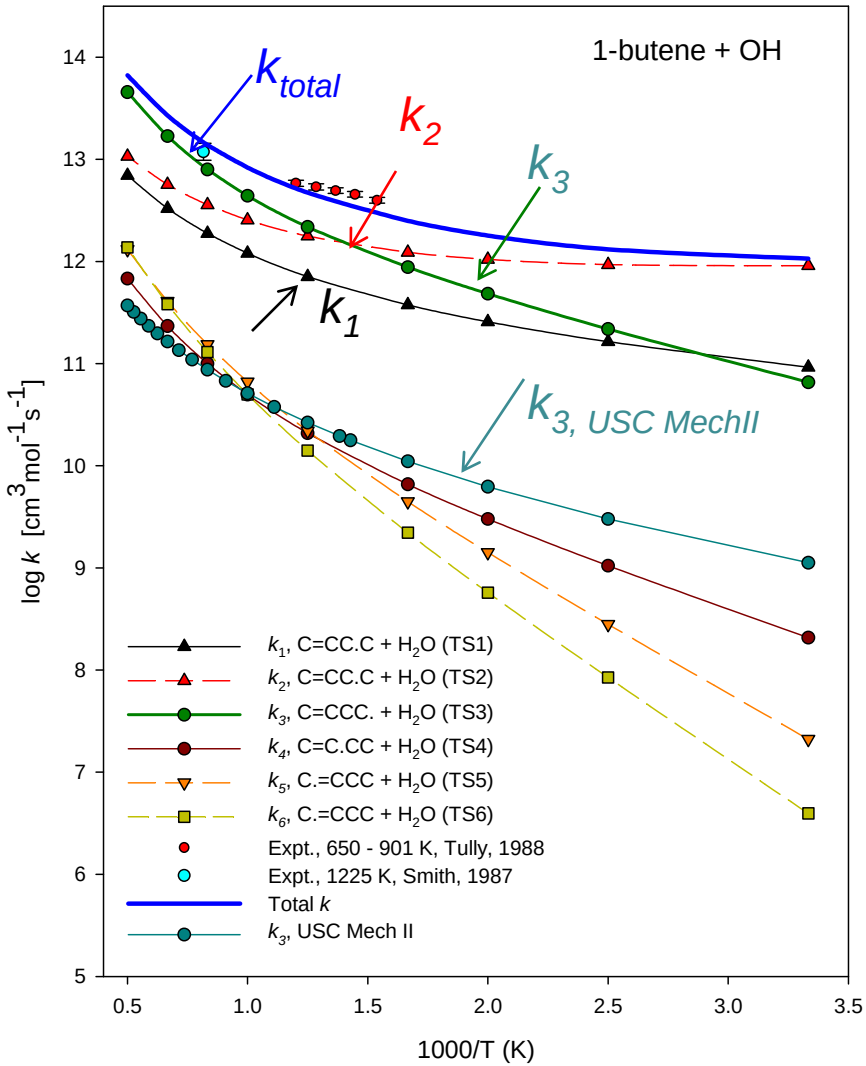
• Allylic H-abstraction channel (important in ignition) not included in USC Mech-II

$CH_2{=}CHCH_2CH_3 + R\bullet \rightarrow CH_2{\cdots}CH{\cdots}CHCH_3 + RH$
$CH_3CH{=}CHCH_3 + R\bullet \rightarrow CH_2{\cdots}CH{\cdots}CHCH_3 + RH$



Unit: kcal/mol

Abstraction Rate of 1-Butene + OH

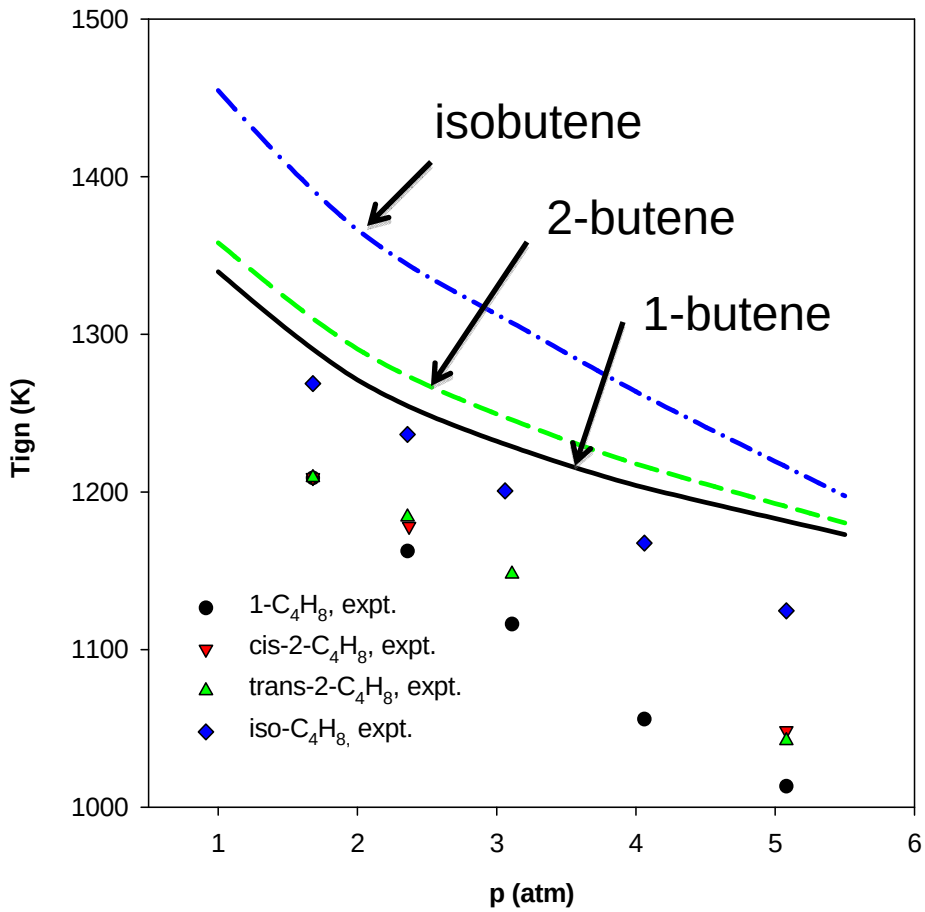


- Canonical Transition State theory
- Quantum mechanical tunneling effect

$$k_\infty = \Gamma \frac{k_B T}{h} e^{\Delta S^{\neq}/R} e^{-\Delta H^{\neq}/RT}$$

- ❑ Allylic H-abstraction channel (k_2) is dominant in low T
- ❑ Methyl H-abstraction channel (k_3) becomes dominant in high T
- ❑ Total abstraction rate agrees well with experimental data

Modeling of Ignition of Isomeric Butenes



- Allylic H-abstraction significantly reduces the T_{ign} of 1-butene
- Low temperature chemistry does not affect much the T_{ign}
- Small radical reactions are the most sensitive to model T_{ign}
- Captures correctly the trend of the T_{ign} on isomeric butenes

Summary: Ignition of *n*-Heptane & *iso*-Octane

- A variable-pressure stagnation-pool facility was designed & built for the study of diffusive ignition and combustion of low-volatility fuels
- Ignition temperature of *n*-heptane and *iso*-octane was experimentally determined at pressures of 0.61~3.0 atm
- Numerical simulation of the ignition response was conducted with detailed chemistry and transport
- Three kinetic models were employed and the simulation results were compared with the measurements
- CEMA was conducted on *n*-heptane: demonstrating a clear transition from radical explosion to thermal explosion

Summary: Ignition of Butene Isomers

- The trend for allylic H bond energies of four butene isomers qualitatively agrees with the experimental results on ignitability
- Reactions for controlling the ignition and flame speed were investigated with *ab initio and* kinetic theories
- New reaction paths and new rates were incorporated into USC Mech-II kinetic mechanism
- Updated mechanism prediction shows improved agreement with experimental ignition temperatures and flame speeds at different pressures

Supported by: ARO

Plan for Next Year

- Ignition of higher (liquid) hydrocarbons (C>7)
- Ignition of gaseous mixtures: interaction & hierarchy effects
- Oxidation chemistry of C4 to C6 hydrocarbons
- Development of detailed and reduced mechanisms for pyrolysis and oxidation of non-toxic propellants

Thank You!