Ignition Kinetics of Hydrocarbons and Propellants

Chung K. Law
Princeton University

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 \textit{n}-Heptane and \textit{iso}-Octane Pool by Heated Stagnating Oxidizing Flow

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

Temperature Controller
Top Air
Coflow N₂
Inner Heater
Outer Heater
Thermocouple
Optical Sensor & Reservoir
Syringe Pump
Vacuum
Water
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

Determinación de la tasa de estrés, 1/2

- Tasa de esfuerzo $K$: gradiente de la velocidad axial; cuantifica el campo de flujo
- Modelos: flujo potencial, flujo de manguera, flujo mixto
- El modelo de flujo mixto se ajusta bien con las mediciones
- En el modelo de flujo de manguera y condiciones experimentales, $K$ es una función de la ubicación

Determinación de $K$ no es sencilla!
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: $T_{\text{ign}}$ is minimally affected when $X_{\text{Fuel}}$ is beyond 0.4
  - Unbalanced counterflow: $V_{\text{oxidizer}} = 100$ cm/s, $V_{\text{fuel}} = 3$ cm/s
Fuel Concentration at Surface, 2/2

- $T_{\text{ign}}$ is insensitive to concentration change when $X_{\text{hep}}$ at the surface is above 0.4
- $X_{\text{hep}}$ ranges from 0.43-0.48 over the pressures and strain rates examined
- $X_{\text{hep}}$ 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, $p=1$ atm; with conversion for different strain rate definitions & thermocouple corrections
Measurement and Simulation of \( n \)-Heptane, 2/3

\[ P = 0.61 \text{ atm} \]

\[ P = 1.0 \text{ atm} \]
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.
- \( \lambda_{\text{exp}} \): 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: \( \text{H}_2/\text{CO} \) chemistry, \( \text{C}_2-\text{C}_3 \) reactions involving \( \text{C}_2\text{H}_4 \)
Ignition of the Butene Isomers: A Kinetics Study

1-butene  cis-2-butene  trans-2-butene  isobutene
Experimental Apparatus

Heated Air

Butene/N₂
Experimental Counterflow $T_{ign}$

- Ignition temperature increases with increasing *strain rate* and decreases with increasing *pressure*.

- $T_{ign}$: isobutene > trans-2-butene $\approx$ cis-2-butene > 1-butene
Modeling of Ignition Temperature

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

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
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

\[
\begin{align*}
\text{CH}_2=\text{CHCH}_2\text{CH}_3 + \text{R}\cdot & \rightarrow \text{CH}_2=\text{CHCH}_2\text{C}\cdot\text{H}_2 + \text{RH} \\
\text{CH}_3\text{CH}=\text{CHCH}_3 + \text{R}\cdot & \rightarrow \text{CH}_2=\text{CHCH}_2\text{C}\cdot\text{H}_2 + \text{RH}
\end{align*}
\]

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

\[
\begin{align*}
\text{CH}_2=\text{CHCH}_2\text{CH}_3 + \text{R}\cdot & \rightarrow \text{CH}_2=\text{CCH}=\text{CHCH}_3 + \text{RH} \\
\text{CH}_3\text{CH}=\text{CHCH}_3 + \text{R}\cdot & \rightarrow \text{CH}_2=\text{CCH}=\text{CHCH}_3 + \text{RH}
\end{align*}
\]

Unit: kcal/mol
Abstraction Rate of 1-Butene + OH

- Canonical Transition State theory
- Quantum mechanical tunneling effect

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

- 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 $T_{\text{ign}}$ of 1-butene
- Low temperature chemistry does not affect much the $T_{\text{ign}}$
- Small radical reactions are the most sensitive to model $T_{\text{ign}}$
- Captures correctly the trend of the $T_{\text{ign}}$ 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 \textit{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!