Fundamental Kinetics Database for Jet Fuel Surrogates: Shock Tube/Laser Absorption Measurements

Fuel Summit at USC, September 15-17, 2009

R. K. Hanson, D. F. Davidson
Department of Mechanical Engineering
Stanford University

- Objectives/Facilities
- Kinetics Database Experiments
  - Ignition Delay Times
  - Multi-Species Time-Histories
  - Comparisons with JetSurF
- Future Work

Work supported by AF-IPT Program
Julian Tishkoff: contract Monitor
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Long-Term Objectives

- To develop improved detailed mechanisms for jet fuel surrogates through a *collaborative research effort* by the AF-IPT team

  ➤ Stanford contribution: Fundamental kinetics database for jet fuel surrogates using shock tube/laser absorption measurements; includes data for ignition delay times and multi-species concentration time-histories

  ➤ Stanford contribution: Improve knowledge of specific elementary reaction rates through *targeted* experiments (indirect and direct)
Advantages of Shock Tubes
- Near-Ideal Constant Volume Test Platform
- Well-Determined Initial T & P
- Clear Optical Access for Laser Diagnostics

Shock Tubes (4)
- Large Diameter Tubes (15 cm and 14 cm)
- High Pressure Tube (5 cm) heatable to 150°C
- Aerosol Tube (11 cm)

Optical Diagnostics
- Laser Absorption
  (VUV, UV, Vis, Near-IR, Mid-IR)
Topic 1: Ignition Delay Times - Current Status

- **Surrogate Fuels Studied**
  
  - **Year 1:** Large normal alkanes
    - n-pentane, n-hexane, n-octane, n-nonane
  
  - **Year 2:** n-dodecane, cyclo-alkanes,
    - n-dodecane (C_{12}H_{26})
    - cyclohexane (CH), methylcyclohexane (MCH), butylcyclohexane (BCH)

- **Goal:** High-quality dataset for jet fuel surrogates over a uniform range of conditions:  
  
  4% O_2, \( \phi = 0.5-1.0 \), 1.5-3.0 atm, 1200-1600 K
C₄ – C₉ N-Alkane Ignition (Year 1)

Stanford ST Study

- Achieve goal of high-quality, low scatter data
- Well-defined values for $E_A$
- Small systematic variation of ignition delay time with carbon no. ($\tau_{\text{ign}} \sim C^{-#0.4}$)
Achieve goal of high-quality, low scatter data

Well-defined values for $E_A$

Small systematic variation of ignition delay time with carbon no. ($\tau_{\text{ign}} \sim C^{\# -0.4}$)

JetSurF 0.2: some differences from experiment (but within USC uncertainty limits)

$\Rightarrow$ SU data will facilitate JetSurF 1.1 model refinements, especially at low T
N-Dodecane ($\text{C}_{12}\text{H}_{26}$) Ignition (Year 2)

Low P, High T

- Low P, High T: JetSurF 0.2 agrees with data at $T \sim 1500$ K, but overpredicts $E_A$
N-Dodecane ($C_{12}H_{26}$) Ignition (Year 2)

**Low P, High T**

- N-Dodecane/O$_2$/Ar
- JetSurF 0.2
- 2.2 atm, 0.75% O$_2$, $\phi = 1.15$
- Stanford (2009)

**High P, Low T**

- n-Dodecane/air
- 20 atm, $\phi = 1.0$
- Stanford (Vasu 2009)

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- **Low P, High T**: JetSurF 0.2 agrees with data at $T \sim 1500$ K, but overpredicts $E_A$
- **High P, Low T**: JetSurF 0.2 agrees with data near 1000 K, slightly overpredicts $\tau_{ign}$ at high $T$ and varies widely from data at $T < 800$ K
  - $\Rightarrow$ SU data will provide useful targets for refinements to JetSurF, especially at low $T$
Cyclo-Alkane Ignition (Year 2): Relative Ignition Delays for CH, BCH and MCH

- CH and BCH ignition delay times similar to n-hexane
- MCH ignition distinctly slower than BCH and CH
- Variation in ignition times can provide insight to decomposition pathways
Methylcyclohexane: Comparison with JetSurF 1.1 Model

MCH/4%O₂/Ar, 1.5 atm, \( \phi = 1.0 \)

- Excellent agreement between JetSurF 1.1 and Stanford data for \( \tau_{\text{ign}} \) and \( E_A \) at \( \phi = 1.0 \)
Methylcyclohexane: Comparison with JetSurF 1.1 Model

MCH/4%O₂/Ar, 1.5 atm, φ=1.0

- Excellent agreement between JetSurF 1.1 and Stanford data for $\tau_{\text{ign}}$
  and $E_A$ at $\phi = 1.0$

- Relatively good agreement at $\phi = 0.5$; but model slightly overpredicts $\tau_{\text{ign}}$
Cyclohexane: Comparison with JetSurF 1.1 Model

CH/4%O$_2$/Ar, 1.5 atm, $\phi=1.0$

- Relatively good agreement between JetSurF 1.1 and Stanford data, but model slightly underpredicts $\tau_{\text{ign}}$ at $\phi = 1.0$
Cyclohexane:  
Comparison with JetSurF 1.1 Model

CH/4%O₂/Ar, 1.5 atm, φ=1.0

- Relatively good agreement between JetSurF 1.1 and Stanford data, but model slightly underpredicts $\tau_{\text{ign}}$ at $\phi = 1.0$
- Very good agreement at $\phi = 0.5$
Butylcyclohexane: Comparison with JetSurF 1.1 Model

BCH/4%O₂/Ar, 1.5 atm, \( \phi = 0.83 \)

- Good agreement between JetSurF 1.1 and Stanford data, but model slightly underpredicts \( \tau_{\text{ign}} \) at \( \phi = 0.83 \)
Butylcyclohexane: Comparison with JetSurF 1.1 Model

BCH/4%O_{2}/Ar, 1.5 atm, \( \phi = 0.83 \)

BCH/4%O_{2}/Ar, 1.5 atm, \( \phi = 0.45 \)

- Good agreement between JetSurF 1.1 and Stanford data, but model slightly underpredicts \( \tau_{\text{ign}} \) at \( \phi = 0.83 \)
- Excellent agreement at \( \phi = 0.45 \)!
High-quality $\tau_{\text{ign}}$ dataset now available for key jet fuel surrogates at high $T$:

- Large normal alkanes ($C_5$-$C_{12}$)
  - n-pentane, n-hexane, n-octane, n-nonane, n-dodecane

- Cyclo-alkanes
  - Cyclohexane, methylcyclohexane, butylcyclohexane

Next Step: branched alkanes (year 3)
High-quality $\tau_{\text{ign}}$ dataset now available for key jet fuel surrogates at high $T$:

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Ignition Delay Times - Summary

- High-quality $\tau_{\text{ign}}$ dataset now available for key jet fuel surrogates at high $T$:
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  - Cyclo-alkanes
    - Cyclohexane, methylcyclohexane, butylcyclohexane

- Next Step: branched alkanes (year 3)
Topic 2: Multi-Species Time-Histories – Current Status

- **Surrogate Fuels Studied:**
  - N-Heptane
  - N-Dodecane
  - Methylcyclohexane (MCH)

- **Standard Conditions:**
  - $P = 2$ atm
  - $\Phi = 1.0$
  - $T = 1250-1650K$
  - $X_{\text{fuel}} = 300-500$ ppm

- **Goal:** develop multi-species database for oxidation and pyrolysis systems with time-histories of several key species: fuels, radicals, stable intermediates, products, and temperature
Multi-Species Diagnostics Methods

Currently In Use
- Fuels/Alkanes: \( \text{C}_7\text{H}_{16} \) (3.39 \( \mu \text{m} \))
- Stable Intermediates/Alkenes: \( \text{C}_2\text{H}_4 \) (10.57 \( \mu \text{m} \))
- Small Radicals: \( \text{OH} \) (306 nm)
- Products: \( \text{H}_2\text{O}, \text{CO}_2 \) (2.5, 2.7 \( \mu \text{m} \))

In Development
- Alkyl Radicals: \( \text{CH}_3, \text{C}_2\text{H}_5 \) (216 & 245 nm)
- Peroxide Species: \( \text{HO}_2/\text{H}_2\text{O}_2 \) (225 & 240 nm)
- Alkanes: Methane, Ethane, Propane (3.4 \( \mu \text{m} \))
- Alkenes: propene, butene (11 \( \mu \text{m}, 3 \mu \text{m} \))

➔ First multi-species application to jet fuel surrogate oxidation: 
  \( \text{n-heptane, n-dodecane, methylcyclohexane} \)

*Diagnostic development funded by other programs (mostly AFOSR)*
Laser Absorption Systems: Minimum Detectivity

- Ring-dye lasers with second harmonic generation (SHG): radical species
- Pulsed (ps) Ti:Sapphire laser with second (SHG), third (THG) and fourth (FHG) harmonic generation: radical species
- Distributed feedback (DFB) diode lasers: H$_2$O, CO$_2$, and T
- Difference-frequency-generation (DFG) diode lasers: HC fuels
- IR gas lasers: HC fuels (3.39 $\mu$m) and C$_2$H$_4$ (10.57 $\mu$m)

$\Rightarrow$ ppm and 10’s of ppm sensitivity available for species detection
Example Experimental Setup:
Ring Dye Laser for OH, CH, NH₂

Beer-Lambert Law:
\[
\frac{I}{I_0} = \exp \{- S(T) \Phi(T,P,x_i) P X_i L\}
\]

*Spectral parameters S & Φ determined at Stanford*
Multi-Species Time-Histories: n-Heptane Oxidation

- First test of multi-species strategy:
- N-Heptane mechanism well-developed
- High SNR data
- Excellent shock-to-shock repeatability (± 10K)
- Optimized fuel concentration selection allows useful data over entire ignition process (two orders of magnitude coverage in species concentration)

- Successful application of multi-species method to n-heptane
- Enables evaluation (and refinement) of model sub-mechanisms: e.g. decomposition pathways, induction time, exponential radical growth
Relative Performance of Well-Established Models for n-Heptane Oxidation

JetSurF 0.2 (2008)

1494K, 2.15atm
300ppm heptane, $\phi=1$

$C_2H_4$, $CO_2$, $H_2O$, $OH$

Mole Fraction [ppm]

Time [$\mu$s]
Relative Performance of Well-Established Models for n-Heptane Oxidation

JetSurF 0.2 (2008)

Chaos et al. (2007)

1494K, 2.15 atm
300ppm heptane, $\phi=1$

Mole Fraction [ppm]

Time [\mu s]

$C_2H_4$

$CO_2$

$H_2O$

$OH$

Mole Fraction [ppm]

Time [\mu s]

$C_2H_4$

$CO_2$

$H_2O$

$OH$
Both models perform well, but multi-species time-history data is sufficiently accurate to enable some refinements in both mechanisms.

Kinetic analyses (e.g. rate of production and sensitivity) provide critical links from data to model, and guide mechanism refinement.
Example: Heptane Decomposition Kinetic Analysis

1500K, 2 atm, $\phi=1$
300 ppm heptane

<table>
<thead>
<tr>
<th>Heptane ROP</th>
<th>Ethylene ROP</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_7H_{16} + H = C_7H_{15} + H_2$</td>
<td>$C_2H_5 = H + C_2H_4$</td>
</tr>
<tr>
<td>$C_7H_{16} = C_6H_{13} + CH_3$</td>
<td>$C_3H_7 = CH_3 + C_2H_4$</td>
</tr>
<tr>
<td>$C_7H_{16} = C_5H_{11} + C_2H_5$</td>
<td>$C_4H_9 = C_2H_4 + C_2H_5$</td>
</tr>
<tr>
<td>$C_7H_{16} = C_4H_9 + C_3H_7$</td>
<td>$C_5H_{11} = C_2H_4 + C_3H_7$</td>
</tr>
</tbody>
</table>

- ROP shows that primary n-heptane decomposition pathway (Dryer 2006) is: $n$-heptane $\rightarrow C_4H_9 + C_3H_7$
- Ethylene formed by secondary alkyl radical decomposition ($C_2H_4$ ROP)
- Large ethylene yields (2 $C_2H_4$ per $C_7H_{16}$) predicted by recent mechanisms confirmed with Stanford laser absorption data

Modeling using Dryer (2006)
Multi-Species Time Histories - Summary

- High-quality, multi-species datasets now available for oxidation of key jet fuel surrogates:
  - N-Heptane
  - N-Dodecane
  - Methylcyclohexane

- Next Steps:
  - Expand range (T, P, mixtures) of experiments
  - Measure additional intermediate species, including:
    - simple alkanes (methane, ethane)
    - higher alkenes (propene, butene)
Future Work (Year 3): Iso-Alkanes

- Need for branched alkane surrogate candidates
  - End-to-end symmetry?
  - Dimethyl alkane?
  - Large carbon number??
  - Economical??

- Potential candidates:
  - 2,5-dimethylhexane
  - 2,4-dimethylpentane
  - 2,2,4-trimethylpentane (iso-octane) allows for comparison with DMP
  - 2,2,4-trimethylpentane (iso-octane)
Stanford Program Summary/Plans:

Achievements:
- Measured ignition delay times (n-alkanes, cyclo-alkanes, branched alkanes)
- Measured multi-species time-histories (fuel, OH, C₂H₄, H₂O, CO₂) in decomposition and oxidation of 3 jet fuel surrogates (n-heptane, n-dodecane, MCH)

Next Steps:
- Expand range of databases (T, P, mixtures)
- Multi-species measurements of branched alkanes (e.g. di-methyl alkanes) and aromatics (e.g. toluene)
- Apply new IR diagnostics methods to measure methane, ethane, higher alkenes in pyrolysis/oxidation of targeted fuels
Acknowledgements


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  - A. Farooq (CO₂)
  - R. Cook (OH)