Fundamental Combustion Data for Surrogate Components, Blends, and Jet Fuels

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Multi-Agency Coordination Committee for Combustion Research – Summit on Fuels
Generation of Comprehensive Surrogate Kinetic Models and Validation Databases for Simulating Large Molecular Weight Hydrocarbon Fuels

National Institute of Standards and Technology
Gaithersburg, MD 20899

September 8, 2008
Key Tasks

• Acquire extensive and comprehensive experimental validation database for neat surrogate components, binary fuel blends, and real jet fuels.

• *Rapid Compression Machine Experiments*:
  – Obtain experimental data for autoignition delays and pre-ignition species evolutions at elevated pressures and low-to-intermediate temperatures.

• *Counterflow Flame Experiments*:
  – Determine fundamental flame properties, including laminar flame speeds and extinction stretch rates.
Year 1 Progress

- Autoignition of neat hydrocarbon components under high pressure conditions.
  - \textit{n-decane} \quad \textit{toluene}
  - \textit{dimethyl ether (DME)} \quad \textit{iso-octane}
  - \textit{methylcyclohexane (MCH)} \quad \textit{diisobutylene-1 (DIB-1)}

- Chemical kinetic interactions in binary fuel blends.
  - \textit{toluene}+\textit{iso-octane} and \textit{toluene}+\textit{DIB-1}.

- Autoignition of real jet fuels, including \textit{Jet-A}, \textit{JP-8}, and \textit{S-8}.

- Laminar flame speeds of preheated \textit{Jet-A/air} and \textit{S-8/air} mixtures.
Outline of Presentation

• Characterization of Rapid Compression Machine

• Autoignition of Jet-A

• Autoignition of Fuel Blends

• Laminar Flame Speeds of Jet-A

• Future Work
Characterization of Rapid Compression Machine (RCM)
Issues/Concerns

• “You don’t know anything about gas motion and heat loss inside an RCM!”
  – A main reason why kinetics people are quite critical, even dismissive, of results from RCMs.
• Much of our effort was expended to make the RCM technique sound and convincing.
  – improved temperature homogeneity using creviced piston
    • Acetone PLIF experiments confirm these attributes
  – model the heat loss effect using *effective volume approach*
• Is zero-dimensional modelling *hunky dory?*
  – need much more sophisticated numerical approaches to model RCM studies?
CFD Modeling

- Influence of physical and operating parameters on RCM performance
- Hydrogen ignition in an RCM
  - representing single-stage ignition phenomenon
  - considering conditions above the extended second limit to examine pre-ignition heat release effect on hot ignition event
- *Hydrocarbon fuels with two-stage ignition behavior (in progress)*
Modeling Objectives

• Assess RCM performance over a range of physical and operating conditions
  – Effect of pressure
  – Effect of compression stroke
  – Effect of clearance volume

• Compare CFD simulation and zero-dimensional calculation for reactive mixtures

• Assess various heat loss models
Computationa l Grids

Length dimensions are in mm.

A=0.50, B=4.0, C=0.15, D=20.0, and E=1.50.
Effect of Pressure (1)

Stroke Length = 25.4 cm, Clearance = 1.4 cm

(a) $P_C = 15.27$ bar

(b) $P_C = 36.18$ bar

Stroke Length = 25.4 cm, Clearance = 1.4 cm
Stroke Length = 25.4 cm, Clearance = 1.4 cm

at TDC (time = 30 ms), $T_C = 1070$ K

- $P_C = 8.82$ bar, $0.85$ m/s
- $P_C = 14.71$ bar, $0.57$ m/s
- $P_C = 25.95$ bar, $0.18$ m/s
- $P_C = 37.58$ bar, $0.10$ m/s

(mass-weighted average velocity)
Effect of Clearance

Stroke Length = 25.4 cm, $P_c \sim 15.3$ bar

<table>
<thead>
<tr>
<th>Time</th>
<th>Temperature (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>30 ms (TDC)</td>
<td></td>
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<tr>
<td>70 ms</td>
<td></td>
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<tr>
<td>120 ms</td>
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</table>

(a) Clearance = 1.4 cm

(b) Clearance = 2.1 cm

(c) Clearance = 2.8 cm
Effect of Compression Stroke

Clearance = 1.4 cm, $P_C \approx 15.3$ bar

(a) Stroke Length = 25.4 cm
(b) Stroke Length = 21.59 cm
(c) Stroke Length = 17.78 cm
Performance Summary (1)

Significant Vortex Effect

Compression Stroke

 Clearance at TDC

Low Pressure

Compression Stroke

 Clearance at TDC

High Pressure
Typical Stroke-Clearance Range for RCM Experiments

- **1100 K**: Compression Stroke (cm) decreases from 24 to 18 as Clearance at TDC (cm) increases from 1.5 to 5.5.
- **650 K**: Compression Stroke (cm) decreases from 24 to 18 as Clearance at TDC (cm) increases from 1.5 to 5.5.
$T_{\text{max}} = \text{maximum instantaneous temperature}$

$T_{\text{mavmain}} = \text{mass averaged temperature of the main reaction chamber (without crevice)}$

$T_{\text{mav}} = \text{mass averaged temperature of the entire reaction chamber (including crevice)}$
FLUENT vs. SENKIN (1)

**FLUENT (lines)**

**SENKIN with effective volume specification (circles)**
FLUENT vs. SENKIN (2)

FLUENT-Simulated Ignition Delay (ms) vs. SENKIN-Simulated Ignition Delay (ms)

- 15.25 bar, 962 K
- 15.2 bar, 967.6 K
- 17.7 bar, 1028 K
- 28.6 bar, 964.25 K
- 32.52 bar, 939 K
Modeling Remarks

• Important to assess RCM performance over the associated range of operating conditions in order to obtain reliable chemical kinetics data.

• For the H₂ cases investigated, zero-dimensional modeling along with the effective volume approach is acceptable in terms of mechanism validation for ignition delays.
  – Expected to be valid for the ignition cases of other hydrocarbons exhibiting single-stage ignition characteristics.

• Preliminary results on two-stage ignition modeling.
Autoignition of Jet-A
under High Pressure Conditions
Mixture Preparation

• Homogeneous test mixture prepared in a *stirred, heated* stainless steel tank of known volume
  – Gaseous components in the test mixture are determined manometrically
  – Liquid fuel components are added on a gravimetric basis
• Add air/fuel under ambient temperature conditions
• Preheat temperature 97–134 °C (below the boiling points of the liquid fuel components)
  – Continuous magnetic stirring
  – Soak time ~ 2 hours for complete vaporization of the liquid components
Composition Confirmation

Mixture Molar Percentages:
- $n$-decane (0.49%),
- oxygen (20.91%),
- nitrogen (76.24%),
- and methane (2.36%).
## Test Matrix

### Mass Proportion

<table>
<thead>
<tr>
<th>Jet-A</th>
<th>$O_2$</th>
<th>$N_2$</th>
<th>$Ar$</th>
<th>$O/F$</th>
<th>$\phi$</th>
<th>7 bar</th>
<th>15 bar</th>
<th>30 bar</th>
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<tbody>
<tr>
<td>5.00</td>
<td>33.21</td>
<td>61.79</td>
<td>0.00</td>
<td>19.00</td>
<td>0.51</td>
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<td>7.14</td>
<td>32.46</td>
<td>60.40</td>
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<td>1.16</td>
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<td>84.85</td>
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</tbody>
</table>

*Jet-A (supplied by Tim Edwards): composite blend, labeled 04POSF4658*
# Jet-A Surrogate

<table>
<thead>
<tr>
<th>COMPONENT</th>
<th>Mass % in Fuel</th>
<th>Mole % in Fuel</th>
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<tbody>
<tr>
<td>iso-Octane</td>
<td>5.00</td>
<td>6.47</td>
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<td>Methyl Cyclohexane</td>
<td>5.00</td>
<td>7.53</td>
</tr>
<tr>
<td>m-Xylene</td>
<td>5.00</td>
<td>6.96</td>
</tr>
<tr>
<td>Tetradecane</td>
<td>15.00</td>
<td>11.18</td>
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<tr>
<td>Tetralin</td>
<td>5.00</td>
<td>5.59</td>
</tr>
<tr>
<td>Dodecane</td>
<td>20.00</td>
<td>17.36</td>
</tr>
<tr>
<td>Cyclo-Octane</td>
<td>5.00</td>
<td>6.59</td>
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<tr>
<td>n-Decane</td>
<td>15.00</td>
<td>15.58</td>
</tr>
<tr>
<td>Butyl Benzene</td>
<td>5.00</td>
<td>5.51</td>
</tr>
<tr>
<td>1,2,4,5-Tertamethylbenzene</td>
<td>5.00</td>
<td>5.51</td>
</tr>
<tr>
<td>1-Methylnaphthalene</td>
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<td>5.20</td>
</tr>
<tr>
<td>Hexadecane</td>
<td>10.00</td>
<td>6.53</td>
</tr>
</tbody>
</table>

Experimental Reproducibility

- Representative trace from at least 4 concordant runs for determining ignition delay.

Jet-A/Air, $\phi=1.12$, $P_C=15$ bar

$T_C=765$ K

$T_C=661$ K

End of Compression
Definition of Ignition Delay

Jet-A/Air, $\phi=1.12$, $P_C=15$ bar

The location of inflection point in the pressure trace identifies the ignition time for both first and second stage.
- $\tau_1 =$ First stage ignition delay
- $\tau_2 =$ Second stage ignition delay
Development of NTC Behavior

(a) Jet-A/Air, $\phi=1.12$, $P_C=7$ bar
(Air-to-Fuel Mass Ratio = 13.0)

(b) Jet-A/Air, $\phi=1.12$, $P_C=7$ bar
(Air-to-Fuel Mass Ratio = 13.0)

(c) Jet-A/Air, $\phi=1.12$, $P_C=7$ bar
(Air-to-Fuel Mass Ratio = 13.0)

(d) Jet-A/Air, $\phi=1.12$, $P_C=7$ bar
(Air-to-Fuel Mass Ratio = 13.0)
Ignition Delay Comparison

Jet-A/Air, $\phi \approx 1$, $\sim 21$ bar

Overall Ignition Delay (ms)

$1000/T_5$ or $1000/T_C$ (K$^{-1}$)

Vasu et al. (2008)
Current
Effect of Pressure

- The first-stage ignition delay is relatively insensitive of pressure
Effect of Equivalence Ratio (1)

- Equivalence ratio has a strong influence on the overall delay.
  - Effect is relatively stronger at lower pressures.
Effect of Equivalence Ratio (2)

- Equivalence ratio has relatively less influence on first-stage delay.
  - The influence of pressure is also limited.
• Equivalence ratio has a strong effect

Overall Ignition Delay: Jet-A/Oxidizer, $P_C=15$ bar

- Oxidizer/Fuel = 84.9 (Mass)
- $O_2/N_2/Ar = 1/3.76/4.90$ (Moles)
- $A/F = 19$ (Mass)
- $A/F = 13$ (Mass)

- Equivalence ratio has a strong effect

- Overall Ignition Delay: Jet-A/Oxidizer, $\phi=0.42$

- Oxidizer-to-Fuel Mass Ratio = 84.9

- $O_2/N_2/Ar = 1/3.76/4.90$

- 7 bar
- 15 bar
- 30 bar

- $1000/T_C (K^{-1})$

- $\phi=1.12$
- $\phi=0.77$
- $\phi=0.42$
Autoignition of Binary Fuel Blends

Raw pressure traces and heat loss parameters are available at
http://www.mae.case.edu/facilities/cdl/projects/rapidcomp/rapiddatabase
Background

• Hydrocarbon classes differ vastly in reactivity and ignition chemistry.
• It is important to understand the nature of interactions in blended fuels.
• Obtain experimental data for autoignition of neat components and blends under well characterized conditions
  ➢ iso-octane \((Alkane)\)
  ➢ diisobutylene-1 \((Alkene)\)
  ➢ toluene \((Aromatic)\)
  ➢ toluene + DIB-1
  ➢ toluene + iso-octane
<table>
<thead>
<tr>
<th>Mixture #</th>
<th>R&lt;sub&gt;1&lt;/sub&gt;</th>
<th>iso-octane</th>
<th>toluene</th>
<th>O&lt;sub&gt;2&lt;/sub&gt;</th>
<th>N&lt;sub&gt;2&lt;/sub&gt;</th>
<th>Ar</th>
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<td>1</td>
<td>1</td>
<td>0.5</td>
<td>0</td>
<td>8.333</td>
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<td>2</td>
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<td>0.375</td>
<td>0.125</td>
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<td>4.667</td>
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<td>4</td>
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<td>0.375</td>
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<td>6.990</td>
<td>45.360</td>
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<td>5</td>
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<td>0.025</td>
<td>0.475</td>
<td>6.117</td>
<td>8.900</td>
<td>43.917</td>
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<tr>
<td>6</td>
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<td>9.323</td>
<td>43.610</td>
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<tr>
<td>7</td>
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<td>16.850</td>
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<table>
<thead>
<tr>
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<th>DIB-1</th>
<th>toluene</th>
<th>O&lt;sub&gt;2&lt;/sub&gt;</th>
<th>N&lt;sub&gt;2&lt;/sub&gt;</th>
<th>Ar</th>
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<tbody>
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<td>0.25</td>
<td>0.25</td>
<td>7.000</td>
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<td>46.510</td>
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<tr>
<td>11</td>
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<td>0.025</td>
<td>0.475</td>
<td>6.100</td>
<td>9.063</td>
<td>43.770</td>
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<td>12</td>
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<td>1</td>
<td>0</td>
<td>16.000</td>
<td>7.500</td>
<td>52.660</td>
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</table>

- R<sub>1</sub> (R<sub>DIB</sub>) is the mole fraction of iso-octane in the combined toluene + *iso*-octane (toluene+DIB-1) fuel mixture.
- Total fuel mole fraction is kept constant at 0.0084.
- Mixtures for blends have the same specific heat ratio.
Autoignition of Neat Components

![Graphs showing ignition delay versus 1000/T_C for different mixtures and pressures.]

- **(a)**
  - Toluene (Mixture #6) with P_C = 45 bar
  - Isooctane (Mixture #1) with P_C = 45 bar

- **(b)**
  - DIB-1, P_C = 35 bar
    - \( X_{DIB-1} = 0.0084 \) (Mixture #13)
    - \( X_{DIB-1} = 0.013 \) (Mixture #14)
  - Isooctane (Mixture #7) with P_C = 36 bar

Graphs illustrate the relationship between the ignition delay (ms) and 1000/T_C (1/K) for various mixtures and pressures.
Autoignition of iso-Octane/Toluene Blends

Combined Fuel Mole Fraction=0.0084, Equivalence Ratio=0.75, $P_0$=930 Torr,
Conditions at TDC: $T_C$=992–996 K and $P_C$=45 bar

\[ R_I = \frac{F_I}{(F_I + F_T)} \]

$F_I$ and $F_T$ are respectively the mole fractions of iso-octane and toluene in the fuel mixture.
Autoignition of DIB-1/Toluene Blends

Combined Fuel Mole Fraction=0.0084, Equivalence Ratio=0.75 and $P_C=45$ bar

F_DIB and F_T are respectively the mole fractions of DIB-1 and toluene in the fuel mixture.
• The presence of a double bond and its position can significantly alter autoignition characteristics.
  – Overall kinetic behavior of alkenes is a result of competition between the addition reactions to a double bond and the reactions through hydrogen abstraction of alkyl chain.
  – Less pronounced features of NTC behavior for DIB-1 imply that the addition reactions at the double bond dominate over the peroxidation reactions of the alkenyl chain.
• Nonlinear sensitization of toluene by iso-octane or DIB-1 similar to that of methane by ethane or propane (Westbrook 1979, 1983).
  – Radicals produced by H atom abstraction from either toluene or methane do not have a decomposition reaction to produce chain branching agents.
  – Early radical generation by small addition of more reactive fuel component accelerates the ignition of the less reactive fuel component.
Laminar Flame Speeds of Jet-A
Extrapolation

n-Dodecane/Air, $\phi=1.4$, $T_u \sim 400$ K

Reference Flame Speed (cm/s)

Stretch Rate ($s^{-1}$)

- USC
- CWRU
Laminar Flame Speed Results

Fuel/Air Mixtures, $T_u = 400$ K

- **n-Decane**
- **n-Dodecane**
- **Jet-A**

Air-to-Fuel Mass Ratio vs. Laminar Flame Speed (cm/s)
Future Work

• Acquire autoignition data of neat surrogate components.
  – high priority: \( n \)-dodecane.

• Acquire autoignition data of binary fuel blends.
  – fuel blends with relatively high Cetane numbers.
  – high priority: \( n \)-dodecane + MCH; \( n \)-decane + \( iso \)-octane.

• Conduct extinction stretch rate measurements of real jet fuels – Jet-A and S-8.

• Complete the setup of a new high-pressure counterflow burner system for flame measurements.
Acknowledgements

• Tim Edwards of AFRL for jet fuel supplies.

• Fred Dryer and Marcos Chaos of Princeton as well as Hai Wang and Xiaoqing You of USC for thermodynamic property calculations.

• CWRU participants –
  Post-Doctoral Research Associates: Kamal Kumar and Gaurav Mittal

  Graduate Students: Bryan Weber and Xin Hui