The autoignition of jet fuels, surrogates, and components

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Goal: \textit{a priori} predictive kinetic modeling for real fuels

\begin{itemize}
  \item \textbf{Real fuels}
    \begin{itemize}
      \item Jet fuels: traditional (Jet A, JP-x) and alternative (FT, other)
      \item Components and surrogates
    \end{itemize}
  \item \textbf{Predictive}
    \begin{itemize}
      \item Experimental uncertainties: \(\sim 10\text{-}20\%\) for ignition delay
      \item Modeling uncertainties: at present significantly larger than those for experiments; perhaps \(\times 2\) at high T and \(\times 10\) at low T for ignition delay for large HCs at elevated pressures
      \item Status: \textit{a priori} kinetics schemes differ \(\times 1\text{-}10\) with experimental ignition delay
        \begin{itemize}
          \item experiment - model = \textit{function} (conditions, fuel)
        \end{itemize}
    \end{itemize}
\end{itemize}
Kinetic targets, including ignition delay, provide...

- Validation/assessment/development of detailed and reduced kinetic mechanisms
- Direct insight into fuel chemistry
  - Influence of molecular structure on reactivity
  - Influence of fuel variability
- Assessment of surrogates and surrogate formulation methodologies
- Data that can be used directly in combustor design via reduced-order models

*Should* come from...

- Well-characterized experiments at *practical/useful* conditions where transport processes are well understood or of negligible importance
- e.g., *shock tubes*, rapid compression machines, flow reactors, flames, JSRs, etc.
Jet fuels are **compositionally complicated** (100s of distinct components) and **variable**

- Requires an integrated research focus on individual components, surrogate mixtures for specific jet fuels, and jet fuels
RPI jet fuel studies

- **Shock tube ignition delay time** studies for:
  - Jet fuels: specific Jet A w/ and w/o JP-8 additive package
  - Surrogates: AFOSR-MURI, RPI, literature
  - Components: chosen due to relevance to Jet A (JP-8) and diversity of organic structure

**Payoff**
- Fundamental kinetics: support the development of detailed kinetic mechanisms, classify the reactivity of variety of organic structures
- Surrogate formulation: provide surrogate vs jet fuel comparisons/assessment and targets for the development of surrogate models
- Direct path for implementation of kinetics in design: reduced-order models
Compounds recently studied at RPI

- alkanes (C7-C16)
- cycloalkanes
- aromatics

JP-8 chromatogram

Edwards and Maurice

Compounds

- n-alkanes, 28%
- iso-alkanes, 29%
- cycloalkanes, 20%
- aromatics, 18%
- other, 5%

Gas-phase experiments require heating

Boiling point, °C

174 216 253
RPI shock tube facility

- Inner diameter = 5.7 cm
- Reflected shock pressures up to 200 atm
- Initial temperatures up to 200°C
- Designed for kinetic studies of low vapor pressure fuels (jet fuels) at engine-like elevated pressures
Shock tube characteristics

**Heated Shock Tube Temperature**

Heated Shock Tube Temperature Profiles

**Incident Shock Velocity**

- JP-8 surrogate (Violi_3) / air, phi = 1.0
- Shock tube heated to 137°C
- Reflected shock condition: 1367 K, 16.6 atm
- Incident shock attenuation: 1.3%/m

**Non-Ideal Gasdynamics**

- pure N₂ driven
- 20% N₂/He driver
- Initial reflected shock conditions:
  - 961 K, 9.7 atm
  - dP/dt = ~2% / ms
- Estimated conditions at 4 ms:
  - 980 K, 10.5 atm

**Ignition Time Measurement**

- Jet A / air, phi = 1
- 674 K, 20.8 atm

- sidewall pressure
- Ignition delay time
- endwall OH*
Example component data: aromatics

- Measurements have been made for seven monocyclic and two bicyclic compounds
- Ignition delay times illustrate the influence of the side chains
- Wide range in high-temperature ignition for aromatics: important in surrogate selection
Aromatics

**toluene**

- 104 kcal/mol
- C-C

**n-propylbenzene**

- 77 kcal/mol
- C-C

**Side chains:**
- Primary C-H bonds ~89-90 kcal/mol
- Secondary C-H bonds ~87-88 kcal/mol

C₂ and longer alkyl side chains introduce weak C-C bonds
- Faster fuel consumption via decomposition and metathesis reactions
- Potential for radicals other than benzyl

**toluene**

**1,3,5-trimethylbenzene**

- Additional of methyl groups stabilizes the ring: increases the probability of unreactive benzylic radicals and decreases probability of more reactive phenylic radicals
Aromatic kinetic modeling

Preliminary data removed

n-propylbenzene
- Good agreement with NUI Galway shock tube measurements
- Good agreement with Won et al. kinetic modeling for $T > 900$ K
- Low-T deviation: gas dynamics or other non-kinetic experimental phenomena or $RO_2$ chemistry in the propyl side chain (not included in model)?
nPb reflected shock pressure profiles

Preliminary data removed

Ignition delay times
- Good agreement at \(~\text{950 K}\)
- Experiment is faster than model at \(~\text{850 K}\)

Induction period energy release
- Good agreement at \(950 \text{ K}\)
- Experiment exhibits greater energy release prior to ignition than model at \(\sim 850 \text{ K}\)
Reactivity of HC components

- Series of RPI autoignition studies for components provides quantitative kinetic targets and leads to following observations regarding reactivity
- **Large n-alkanes:** ignition times slightly decrease with increasing chain length; at high to moderate T, to first order, autoignition independent of chain length
- **Branched alkanes:** High- to moderate-T autoignition controlled by fraction of non-primary H atoms and rate of thermal decomposition
- **Substituted-aromatics:** side chain length/proximity/number primarily controls high-T autoignition; very little low-T reactivity
- **Substituted-cyclohexanes:** slight stabilization with increased side chain length

- Reactivity observations are important for surrogate formulation
  - First step might be to compare jet fuel and component data
- Data have led to refinements/validation of kinetic modeling
Ignition delay for jet fuels

• Jet-A (POSF 4658): average Jet-A blended at WPAFB (Tim Edwards) from several Jet-A fuels

• JP-8: POSF 4658 w/ JP-8 additive package

• No discernible influence on autoignition by additive package

• Good agreement with RCM data (Sung, UConn) at lower temperatures
Reflected shock pressure histories

- Well behaved pressure profiles for <10 ms with N\textsubscript{2}/He tailored driver gases
- Very little gasdynamic pressure rise (<1%/ms) for jet fuel/air and surrogate/air mixtures at very low temperatures (670-680 K) for reflected shock experiments
- Gasdynamic pressure rise varies from 0-2%/ms depending on desired reflected shock pressure and temperature
Comparison with literature jet fuel data

- Dean et al. GE/Minsk, shock tube: scaled from ~8 atm to 20 atm using $\tau \sim P^{-1}$
- Vasu et al. Stanford, shock tube: no pressure scaling
- Spadaccini and Tevelde UTRC, flow reactor: no pressure scaling

Most of the deviations in data sets are due to pressure differences/scaling and differences in fuel/air mixtures.
Jet fuel vs alkanes

- n-alkane ignition delay times shorter than jet fuel
- Highly branched iso-alkane ignition delay times longer than jet fuel
  - Dependent on degree of branching
Jet fuel vs methylcyclohexane

- MCH ignition delay times similar to jet fuel at high temperature and longer at low temperature
- Other substituted cyclohexanes likely behave similarly but have received little kinetic investigation
Jet fuel vs aromatics

Preliminary data removed

• Aromatic ignition delay times longer than jet fuel
• Significant differences in aromatic reactivity
  – Aromatic must be chosen carefully for reactivity and soot formation considerations
Surrogates and targets

**JP-8 composition**
- n-alkanes, 28%
- iso-alkanes, 29%
- cycloalkanes, 20%
- aromatics, 18%
- other, 5%

100s of distinct species

Jet fuel prohibitively complex to model
→ must model w/ surrogate

**JP-8 physical properties**
- H/C ratio = 1.84-2.07, $H/C_{avg} \approx 1.9$
- MW $\approx 153$ kg/kmol
- Aromatic liquid content $\approx 20\%$
- Liquid density $\approx 804$ kg/m$^3$

**Potential targets**
- Physical properties
- Organic compositional distribution
- Ignition/oxidation
  - ignition times, species histories/profiles, flame speed/extinction/ignition
- Cetane number, CN = 32-57, $CN_{avg} \approx 44$
- Soot, $TSI = 16-26$, $TSI_{avg} \approx 18$
- Distillation curve
- Transport

**Other factors**
- Simplicity vs complexity
  - number and structure of components
- State of kinetic modeling
- Cost
MURI surrogate 1

Methodology:
• Restricted to three components for which models are widely available
• Match H/C, DCN, and aromatic content of POSF 4658 ("average" Jet A from Dr. Tim Edwards, AFRL)
• Test surrogate vs POSF 4658: flow reactor, flame extinction, ignition delay (shock tube and RCM)

<table>
<thead>
<tr>
<th>Fuel</th>
<th>H/C</th>
<th>MW</th>
<th>Aromatic liquid %</th>
<th>Liquid density [kg/m³]</th>
<th>Cetane</th>
<th>TSI</th>
</tr>
</thead>
<tbody>
<tr>
<td>JP-8, literature</td>
<td>1.84-2.07, avg = 1.9</td>
<td>~153</td>
<td>~20</td>
<td>~804</td>
<td>CN = 32-57, avg = 44</td>
<td>16-26, avg = 18</td>
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<tr>
<td>POSF 4658</td>
<td>1.957</td>
<td>142</td>
<td>18.4</td>
<td>799</td>
<td>DCN = 47.1</td>
<td>21.4</td>
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<tr>
<td>MURI Sur 1</td>
<td>2.01</td>
<td>121</td>
<td>15.8</td>
<td>750</td>
<td>DCN = 47.1</td>
<td>14.1</td>
</tr>
</tbody>
</table>
• Surrogate experimentally mimics jet fuel autoignition well
• Fairly good agreement between ST and RCM
- **a priori** kinetic modeling longer than experiment by $\sim 2\times$
- Transition temperature from high-$T$ to NTC differs: model $\sim 950$ K, experiment $\sim 900$ K
MURI surrogate 2

Methodology:
• Use larger n-alkanes and aromatics representative of those found in Jet A
  ➢ n-dodecane, iso-octane, n-propylbenzene, and 135-trimethylbenzene

• Match H/C, DCN, aromatic content, TSI, and MW of POSF 4658

• Test surrogate vs POSF 4658: flow reactor, flame extinction, ignition delay (shock tube and RCM)

Preliminary data removed
MURI surrogate 2 vs jet fuel

Preliminary data removed

• More complex four-component surrogate experimentally mimics jet fuel autoignition well
MURI surrogate 2 vs kinetic modeling

Preliminary data removed

- *a priori* kinetic modeling only slightly longer than experiment at high to moderate $T$, longer at low $T$
- Transition temperature from high $T$ to NTC differs: model $\sim 950$ K, experiment $\sim 900$ K
RPI surrogate 1

Methodology:
• Choose HC components to approximate the relative distribution of typical jet fuel by organic class (n-alkane, iso-alkane, cycloalkane, aromatic)
• Match H/C, DCN, aromatic content, TSI, MW, and liquid density of literature average JP-8: heavier components chosen to match MW and liquid density

<table>
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<th>Fuel</th>
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<th>MW</th>
<th>Aromatic liquid %</th>
<th>Liquid density [kg/m³]</th>
<th>Cetane</th>
<th>TSI</th>
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<td>JP-8, literature</td>
<td>1.84-2.07, avg = 1.9</td>
<td>~153</td>
<td>~20</td>
<td>~804</td>
<td>CN = 32-57, avg = 44</td>
<td>16-26, avg = 18</td>
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<tr>
<td>POSF 4658</td>
<td>1.957</td>
<td>142</td>
<td>18.4</td>
<td>799</td>
<td>DCN = 47.1</td>
<td>21.4</td>
</tr>
<tr>
<td>RPI Sur 1</td>
<td><strong>1.87</strong></td>
<td><strong>151</strong></td>
<td><strong>20</strong></td>
<td><strong>792</strong></td>
<td><strong>DCN = 42.8</strong></td>
<td><strong>16.7</strong></td>
</tr>
</tbody>
</table>
• Captures high-temperature autoignition
• Slight deviations at moderate to low temperatures consistent with differences in DCN: 42.8 for surrogate vs 47.1 for Jet A (POSF 4658)
  – Motivates studies jet fuels and surrogates with variation in DCN
Summary

• Ignition delay data is available for jet fuels, components, and surrogates
  – Provide direct insight into fuel chemistry (reactivity vs structure)
  – Aide in development of kinetic mechanisms
  – Allow assessment of surrogates and surrogate formulation methodologies

• Surrogate formulation methodology hypothesized by the MURI team has been successful for formulating surrogates with reactivity (ignition delay) mimicking a specific jet fuel (POSF 4658)
  – Tested for three surrogates
    • n-decane, iso-octane, toluene
    • n-dodecane, iso-octane, n-propylbenzene, 135-trimethylbenzene
    • n-tetradecane, iso-cetane, methylcyclohexane, n-propylbenzene
Closing points on surrogates: jet fuel composition

NIST (Bruno) characterization of POSF 4658

<table>
<thead>
<tr>
<th>name</th>
<th>CAS no.</th>
<th>area percentage</th>
<th>name</th>
<th>CAS no.</th>
<th>area percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td><em>n</em>-heptane</td>
<td>142-82-5</td>
<td>0.125</td>
<td>2,3-dimethyl decane</td>
<td>17312-44-6</td>
<td>0.681</td>
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<tr>
<td>ethyl cyclohexane</td>
<td>108-87-2</td>
<td>0.198</td>
<td>1-ethyl-2,2,6-trimethyl cyclohexane</td>
<td>71186-27-1</td>
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<tr>
<td>2-methyl heptane</td>
<td>592-27-8</td>
<td>0.202</td>
<td>1-methyl-3-propyl benzene</td>
<td>1074-43-7</td>
<td>0.569</td>
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<tr>
<td>toluene</td>
<td>108-88-3</td>
<td>0.320</td>
<td>aromatic</td>
<td>NA</td>
<td>0.625</td>
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<tr>
<td>cis-1,3-dimethyl cyclohexane</td>
<td>638-04-0</td>
<td>0.161</td>
<td>5-methyl decane</td>
<td>13151-35-4</td>
<td>0.795</td>
</tr>
<tr>
<td><em>n</em>-octane</td>
<td>111-65-9</td>
<td>0.386</td>
<td>2-methyl decane</td>
<td>6975-98-0</td>
<td>0.686</td>
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<tr>
<td>1,2,4-trimethyl cyclohexane</td>
<td>2234-75-5</td>
<td>0.189</td>
<td>3-methyl decane</td>
<td>13151-34-3</td>
<td>0.969</td>
</tr>
<tr>
<td>4-methyl octane</td>
<td>2216-34-4</td>
<td>0.318</td>
<td>aromatic</td>
<td>NA</td>
<td>0.540</td>
</tr>
<tr>
<td>1,2-dimethyl benzene</td>
<td>95-47-6</td>
<td>0.575</td>
<td>aromatic</td>
<td>NA</td>
<td>0.599</td>
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<tr>
<td><em>n</em>-nonane</td>
<td>111-84-2</td>
<td>1.030</td>
<td>1-methyl-(4-methylthyl) benzene</td>
<td>99-87-6</td>
<td>0.650</td>
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<tr>
<td><em>x</em>-methyl nonane</td>
<td>NA</td>
<td>0.597</td>
<td><em>n</em>-undecane</td>
<td>1120-21-4</td>
<td>2.560</td>
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<tr>
<td>4-methyl nonane</td>
<td>17301-94-9</td>
<td>0.754</td>
<td><em>x</em>-methyl undecane</td>
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<td>1.086</td>
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<tr>
<td>1-ethyl-3-methyl benzene</td>
<td>620-14-4</td>
<td>1.296</td>
<td>1-ethyl-2,3-dimethyl benzene</td>
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<td>1.694</td>
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<td>2,6-dimethyl octane</td>
<td>2051-30-1</td>
<td>0.749</td>
<td><em>n</em>-dodecane</td>
<td>112-40-3</td>
<td>3.336</td>
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<td>1-methyl-3-(2-methylpropyl) cyclopentane</td>
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<td>1-ethyl-4-methyl benzene</td>
<td>622-96-8</td>
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<td><em>n</em>-tridecane</td>
<td>629-50-5</td>
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<td>1-methyl-2-propyl cyclohexane</td>
<td>4291-79-6</td>
<td>0.370</td>
<td>1,2,3,4-tetrahydro-2,7-dimethyl naphthalene</td>
<td>13065-07-1</td>
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<td>1,2,4-trimethyl benzene</td>
<td>95-63-6</td>
<td>1.115</td>
<td>2,3-dimethyl dodecane</td>
<td>6117-98-2</td>
<td>0.657</td>
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<tr>
<td><em>n</em>-decane</td>
<td>124-18-5</td>
<td>1.67</td>
<td>2,6,10-trimethyl dodecane</td>
<td>3891-98-3</td>
<td>0.821</td>
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<tr>
<td>1-methyl-2-propyl benzene</td>
<td>1074-17-5</td>
<td>0.367</td>
<td><em>x</em>-methyl tridecane</td>
<td>NA</td>
<td>0.919</td>
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<td>4-methyl decane</td>
<td>2847-72-5</td>
<td>0.657</td>
<td><em>x</em>-methyl tridecane</td>
<td>NA</td>
<td>0.756</td>
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<tr>
<td>1,3,5-trimethyl benzene</td>
<td>108-67-8</td>
<td>0.949</td>
<td><em>n</em>-tetradecane</td>
<td>629-59-4</td>
<td>1.905</td>
</tr>
<tr>
<td><em>x</em>-methyl decane</td>
<td>NA</td>
<td>0.613</td>
<td><em>n</em>-pentadecane</td>
<td>629-62-9</td>
<td>1.345</td>
</tr>
</tbody>
</table>
Closing points on surrogates: jet fuel composition

To match many macroscopic combustion properties (ignition delay, DCN, TSI, H/C, etc.)
• Not necessary to restrict the surrogate to the organic distribution and/or the organic structures found in jet fuels (e.g., iso-octane and iso-cetane are not found in jet fuels)

In order to match other physical properties (distillation), microscopic kinetic targets (detailed speciation), and perhaps some macroscopic targets (ignition delay) for a larger range of conditions it may be desired to make the surrogate look more like the jet fuel, in terms of structure and diversity of structure (larger number of components).
Closing points on surrogates: branching/substitution

If greater structural similarity is desired, need to consider:
- Lightly branched alkanes
  - extension of current n- and iso-alkane kinetics
- Cyclo-hexanes (C$_8$-C$_{11}$) with multiple small alkyl side chains
  - extrapolation of MCH kinetics
- Aromatics (C$_8$-C$_{10}$) with 2 or 3 small alkyl side chains
  - extrapolation of toluene kinetics
Future work

Jet Fuels
• Fuel variability: range of fuels (Jet A, JP-8, S-8, IPK, etc) with differing DCN
• Conditions
  – Lower and higher pressures of relevance to main combustors, after burners, and diesel engines
  – Equivalence ratio
  – Vitiation? – afterburners

Surrogates
• Sensitivity to compositional perturbations: variation of the same set of components to mimic a range of jet fuels

Components
• Lightly branched alkanes
• More complex cyclo-hexanes and aromatics
• Olefin compounds that are found in the intermediate soup during the oxidation of paraffins
Acknowledgements

• Sponsor: Air Force Office of Scientific Research, Dr. Julian Tishkoff

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• Students: Haowei Wang, Dr. Jeremy Vanderover (GE), Dr. Shawn Shen (Raytheon)

• Fuel: Dr. Tim Edwards (AFRL)
Questions?