Characterization of RP-1 Kinetics during Pyrolysis and Oxidation

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5th Annual Fuels Research Review, September 17-20, 2012

RP-1 Pyrolysis
  Surrogate Decomposition Rates and Yields
  Formulation of RP-Fuel Surrogate Mixture

RP-1 Oxidation

Work sponsored by ERC, Inc. at the Air Force Research Laboratory, Edwards AFB
Contract Monitor: Matthew Billingsley
High Temperature Behavior of RP-Fuels

- Rocket engines that utilize RP-1
  - Atlas V (RD-180)
  - Delta II (RS-27A)
  - Falcon 9 (Merlin 1C)
- Decomposition chemistry is a building block for oxidation
- Study of decomposition chemistry helps understand coking in regeneratively cooled engines
- Need a surrogate and mechanism to predict decomposition rates and products

RD-180 Engine Test (NASA image)
### RP-1 Physical-Chemical Surrogate: Huber (2009)

<table>
<thead>
<tr>
<th>Fluid</th>
<th>Composition, mole fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>a-methyldecalin</td>
<td>0.354</td>
</tr>
<tr>
<td>5-methylnonane</td>
<td>0.150</td>
</tr>
<tr>
<td>2,4-dimethylnonane</td>
<td>0.000</td>
</tr>
<tr>
<td>n-dodecane</td>
<td>0.183</td>
</tr>
<tr>
<td>heptylcyclohexane</td>
<td>0.313</td>
</tr>
</tbody>
</table>

- Based on physical & thermochemical properties (NIST REFPROP)
- But not based on pyrolysis or oxidation kinetics!
Need for RP-Fuel Pyrolysis Surrogate

- RP-fuels are complex
  - Composed of hundreds of hydrocarbons
- No multi-component *kinetic* surrogates have been proposed for RP-fuels
- Pyrolysis surrogate needs components from multiple compound classes to accurately capture decomposition chemistry and products
- Multi-component surrogate candidate species
  - n-alkane (n-dodecane)
  - iso-alkane (iso-cetane)
  - cycloalkane (methylcyclohexane)

<table>
<thead>
<tr>
<th>Hydrocarbon Type</th>
<th>Mass %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Paraffins</td>
<td></td>
</tr>
<tr>
<td>( n- )</td>
<td>5</td>
</tr>
<tr>
<td>( iso- )</td>
<td>39</td>
</tr>
<tr>
<td>Total</td>
<td>44</td>
</tr>
<tr>
<td>Cycloparaffins</td>
<td></td>
</tr>
<tr>
<td>Cycloparaffins (nc) (^b)</td>
<td>34</td>
</tr>
<tr>
<td>Dicycloparaffins (c) (^b)</td>
<td>17</td>
</tr>
<tr>
<td>Tricycloparaffins (c) (^b)</td>
<td>4</td>
</tr>
<tr>
<td>Total</td>
<td>55</td>
</tr>
<tr>
<td>Aromatics</td>
<td></td>
</tr>
<tr>
<td>Alkylbenzenes</td>
<td>0.5</td>
</tr>
<tr>
<td>Indans + Tetralins</td>
<td>&lt;0.5</td>
</tr>
<tr>
<td>Naphthalene</td>
<td>&lt;0.5</td>
</tr>
<tr>
<td>Naphthalenes</td>
<td>0.5</td>
</tr>
<tr>
<td>Total</td>
<td>1(^a)</td>
</tr>
</tbody>
</table>

Billingsley et al. JPC 2010
AIAA-2010-6824
Strategy to Construct RP-Fuel Kinetics Surrogate

- Develop database of overall decomposition rates and ethylene yields for RP-1 and surrogate components (dodecane, MCH, iso-cetane) using shock tube/laser absorption

- Use linear addition of surrogate properties to mimic RP-1 behavior

- Develop reaction mechanism for 3-component surrogate (in collaboration with LLNL/C. Westbrook)
Laser Diagnostic Schemes

- Fuel measurement at 3.39 $\mu$m
- $\text{C}_2\text{H}_4$ measurement at 10.5 $\mu$m
- Corrections for interference
Shock Tube Laser Absorption Experiments

Beer’s Law

\[ \frac{I}{I_o} = \exp (-\sigma NL) \]

Absorption cross section
Laser Setup: 3.39 and 10.5 µm

- **HeNe laser:** 3.39 µm
  - Minimum detectivity: 100 ppm
- **CO₂ laser:** 10.5 µm
  - Minimum detectivity: 200 ppm
IR Fuel Diagnostic (3.39 µm)

- 3.39 µm strongly absorbed by all HC fuels
- Beer’s Law + Absorption cross sections → Fuel mole fraction

- Need fuel and surrogate cross sections at 3.39 µm

MacDonald et al., J. Prop. Power, 2011
MCH Cross Section at 3.39 µm

Absorption cross section determined from 300 - 1500 K

Current Study
P₂ ~ 5 atm
P₅ ~ 20 atm
2000 ppm MCH in argon
Iso-Cetane Cross Section at 3.39 µm

- Absorption cross section determined from 300 – 1300 K

- P₂ ~ 5 atm
- P₅ ~ 20 atm
- 2000 ppm iso-cetane in argon

- Current Study
Interference in Fuel Measurements at 3.39 µm

- Decomposition products also absorb at 3.39 µm
- HeNe is not tunable, cannot make an off-line measurement

Interference
- Major assumption: products form at the same rate that the fuel is removed
- Mathematical correction to fuel measurement

MacDonald et al., J. Prop. Power, 2011
**IR Ethylene Diagnostic (10.5 µm)**

- CO$_2$ gas laser P14 line is strongly absorbed by ethylene
- But also other alkenes
- Need to measure 2 wavelengths
  - 10.532 µm P14 line (on-line)
  - 10.675 µm P28 line (off-line)
IR Ethylene Diagnostic (10.5 µm)

- CO₂ gas laser P14 line is strongly absorbed by ethylene
- But also other alkenes
- Need to measure 2 wavelengths
  - 10.532 µm P14 line (on-line)
  - 10.675 µm P28 line (off-line)
- Need ethylene cross sections at both lines
Correction for Interference in Ethylene Measurements at 10.5 μm

- Other alkenes absorb at 10.5 μm
- But note! Interfering species have a constant cross section between the two laser lines
- Differential absorption at 2 wavelengths permits isolation of \( \text{C}_2\text{H}_4 \) absorption

Need to check cross sections of interfering species to ensure they are constant at 10.5 μm
Cross Sections of Interfering Species at 10.5 µm

- Small absorption by propene and 1-butene
Small absorption by propene and 1-butene with nearly-constant cross-sections at P14 & P28.
Pyrolysis Decomposition Results

- Fuel/ Ethylene time histories
- Ethylene yields
Dodecane Decomposition: Fuel and Ethylene Time-Histories

Species Time Histories

Dodecane Mole Fraction

Ethylene Mole Fraction

Time [ms]

C_{12}H_{26} 1306 K, 17.2 atm 0.17% nC_{12}H_{26} in argon

C_{2}H_{4}
Dodecane Decomposition: Ethylene Yields

Species Time Histories

\[ \text{Yield} = \frac{X_{C_2H_4, \text{final}}}{X_{C_{12}H_{26}, \text{initial}}} = 4.4 \]

1400 ppm dodecane in argon
19 atm

\( = 73\% \) C-atom Conversion
Dodecane Decomposition: Ethylene Yields

Species Time Histories

Dodecane Mole Fraction

C_{12}H_{26} 1306 K, 17.2 atm 0.17% nC_{12}H_{26} in argon

X_{fuel, initial}  X_{C_{2}H_{4}, final}

Ethylene Mole Fraction

Ethylene Yields

1400 ppm dodecane in argon
19 atm

1000 1200 1400 1600 1800

Temperature [K]

Peak Ethylene Yield

0 1 2 3 4 5 6
Dodecane Decomposition: Ethylene Yields

Species Time Histories

- C$_2$H$_4$ (Ethylene)
- C$_{12}$H$_{26}$ (Dodecane)

1306 K, 17.2 atm
0.17% nC$_{12}$H$_{26}$ in argon

Ethylene Yields

1400 ppm dodecane in argon
19 atm

Current work
JetSurF 2.0
Current models show low ethylene yields at high temperatures.
LLNL model captures ethylene yields at high T
- LLNL model captures decomposition rate below 1250 K
Ethylene produced at less than detection limit (200 ppm)
- LLNL model predicts ethylene yield increases with T
- LLNL model captures fuel time history well
Increasing ethylene yield with temperature
Kinetic surrogate will require mixture proportion decision
RP-1/ Surrogate Component Comparisons

Kinetic Surrogate Mixture Optimization
Comparison of Decomposition Rates: RP-1 and Surrogate Components

Overall decomposition rates:
- Iso-cetane is faster than RP-1 (needed to match RP-1 rate)
- n-Dodecane and MCH are slower than RP-1
- Iso-octane is similar to RP-1

![Graph showing decomposition rates]
Comparison of Ethylene Yields: RP-1 and Surrogate Components

Ethylene yields during pyrolysis:

- n-dodecane has greater yield than RP-1 (needed to match RP-1 yields)
- MCH and iso-cetane have smaller yields than RP-1
To determine the optimal 3-component pyrolysis surrogate, we use three constraints:

- the decomposition rates
- the ethylene yields
- total surrogate mole fraction = 1
Composition of RP-1 Surrogate

- Optimal composition is a function of temperature!

- Mid-T surrogate:
  - 23% n-dodecane
  - 9% iso-cetane
  - 68% MCH
Behavior of RP-1 Surrogate: Ethylene Yields

- Mechanism for three-component surrogate developed by LLNL/C. Westbrook
- Good agreement between surrogate/mechanism and experiment for ethylene yield
Behavior of RP-1 Surrogate: Overall Decomposition Rate

- Excellent agreement of surrogate predictions with overall decomposition rate
- Next step:
  - mechanism reduction
  - validation with other products (e.g. CH₄)
RP-1 Oxidation
- Ignition Delay Times
- $\text{C}_2\text{H}_4$ Species Time-Histories
Accurate $\tau_{ign}$ requires well-defined test conditions: non-reactive test have $dP/dt=0$
At high P (17-43 atm)

- \( \tau_{\text{ign}} \) varies as \( P^{-0.84} \)
- \( \tau_{\text{ign}} \) varies as \( \phi^{-0.09} \)
Simple two-component surrogate captures ethylene yield, but not $\tau_{\text{ign}}$
Summary

- Formulation of a 3-component RP-1 pyrolysis surrogate
  - Measured fuel decomposition and C₂H₄ production during pyrolysis for n-dodecane, MCH, iso-cetane, RP-1
  - Good agreement between model/surrogate with measured decomposition rates and ethylene yields
- Extend RP-fuel studies to oxidation
  - Measured RP-1 ignition delay times and C₂H₄ time-histories