The Properties of RP-1 and RP-2
MIPR F1SBAA8022G001

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Executive Summary:

AFOSR-MIPR F1SBAA8022G001

• Characterization of a real fuel: JP-8
  – i.e., chemical analysis, \( \text{VLE} \), \( \rho \), \( \nu \), \( \lambda \), \( \text{C}_v \)

• Complete RefProp fluids files for RP-1 and RP-2

• Perform thermal decomposition studies on RP-2:
  – no additives
  – with THQ, tetralin, +100 package
NIST Staff:

• Tom Bruno
• Arno Laesecke
• Stephanie Outcalt
• Richard Perkins
• Jason Widegren
• Marcia Huber
• Eric Lemmon
and Students:

• Beverly Smith
• Lisa Ott
• Kari Brumbeck
• Amelia Hadler
• Tara Lovestead
First, a bit of history
RP-1:

- Rocket Propellant 1 (refined petroleum 1)
- Kerosene base, used with LOX in rockets such as the Saturn V
- Density 0.81 - 1.02 g/mL
- Oxidizer to fuel ratio = 2.56
- Temperature of combustion = 3,670 K
RP-2

- A highly hydrotreated kerosene
- Little or no sulfur
- Few if any aromatics
- Clear at present, no added dye
We obtained a sample of RP-1, 2002:
  - P000016660
  - Chemical analysis revealed presence of many aromatics and alkenes

An extensive series of measurements and correlations was done.

At the December ’03 workshop, it was decided that the lot was “unusual”.

A follow-on project determined compositional variability.
Our results were summarized in NISTIR 6646, and the preliminary RP-1 fluid file was developed
We start with:

- Comprehensive chemical analysis
- Distillation curves (of the advanced variety)
Curve is far more typical of a complex fluid.

Curve is dominated by a few major components.

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RP-1 and RP-2 are very similar in volatility, while TS-5 is slightly less volatile.
Now, complete the property suite:

\( \rho, \upsilon, \lambda, C_v, \text{etc.} \)
Density:

Experimental details were discussed earlier.
And for RP-2:
Speed of sound of RP-1 and RP-2 as a function of temperature at ambient pressure.
Adiabatic compressibility data of RP-1 and RP-2 as a function of temperature at ambient pressure.
Kinematic viscosity of RP-1 and RP-2 as a function of temperature at ambient pressure.
Thermal Conductivity of RP-1 (New Sample)

$\lambda / \text{W m}^{-1}\text{K}^{-1}$ vs $P / \text{MPa}$

- 300 K
- 350 K
- 400 K
- 450 K
- 500 K
- 550 K

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Thermal Conductivity of RP-2

![Graph showing thermal conductivity vs. pressure for different temperatures.]

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In parallel, a study of decomposition was done:

- Decomposition studies have been part of the NIST protocol since we left cryogenics.

- With RP-2, the decomposition is important as a measurement.
  - straight RP-2, RP-2 with additives, corrosivity studies.
Explicit consideration of sample decomposition was begun of necessity:


Experimental effort involves numerous high value, one-of-a-kind apparatus:

- VLE Instruments
- Viscometers
  - torsional crystal
  - Stabinger
  - gravitational
- Densimeters
  - dual sinker
  - rapid screening
- Thermal Conductivity
  - low and high temperature hot wire
- Speed of Sound
- Etc.
At only 100 °C, the sample decomposed into CO, H₂, and synthetic products.
Samples are thermally stressed in stainless steel ampoule reactors

Diagram:
- Ampoule reactor
- Thermostat
- Insulated box
- Slots for reactors
- Stainless steel block (one of two)
- Temperature probe
- Heaters
- PID temperature controller
Ampoule reactors:

Temperatures to 450 °C
Pressures to 10,000 psi
(once, by accident, to 36,000 psi)
Extent of decomposition determined by analysis

**GC-FID of RP-2**

Unheated sample

After 10 min at 450 °C

Emergent suite of decomposition products

The light decomposition products are used for the kinetic analysis

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Pseudo-first-order kinetics on the emergent suite of decomposition products

\[ A \xrightarrow{k'} B \]

\[- \frac{d[A]}{dt} = \frac{d[B]}{dt} = k'[A] \]

\[ t_{1/2} = \frac{\ln 2}{k'} \]

The assumption of first-order kinetics is a necessary approximation for these complex mixtures.
Separate phase analysis is performed
determine thermal or catalytic mechanisms

Liquid and gas phases analyzed by FTIR, GC-FID and GC-MS

Decomposition kinetics of RP-2

The rate constant for decomposition, $k'$, is obtained from the fit.
Decomposition kinetics of RP-2

The rate constant for decomposition, $k'$, is obtained from the fit.
Decomposition kinetics of RP-2

![Graph showing decomposition kinetics at different temperatures: 450 °C, 425 °C, 400 °C, and 375 °C. The x-axis represents reaction time in minutes, and the y-axis represents product suite area.](image)
Rate constants for RP-2 decomposition

<table>
<thead>
<tr>
<th>$T / ^\circ C$</th>
<th>$(k' \pm 1\sigma) / s^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>375</td>
<td>$(1.33 \pm 0.30) \times 10^{-5}$</td>
</tr>
<tr>
<td>400</td>
<td>$(9.28 \pm 2.01) \times 10^{-5}$</td>
</tr>
<tr>
<td>425</td>
<td>$(1.33 \pm 0.33) \times 10^{-4}$</td>
</tr>
<tr>
<td>450</td>
<td>$(5.47 \pm 0.80) \times 10^{-4}$</td>
</tr>
</tbody>
</table>

The Arrhenius plot shown in the diagram illustrates the relationship between $\ln k'$ and $1000/T$. The data points are plotted, showing a linear trend that indicates the rate constants decrease with increasing temperature, as expected from the Arrhenius equation.

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Decomposition kinetics of RP-1

The decomposition of RP-1 and RP-2 is very similar.

Comparison of RP-1 and RP-2 decomposition

![Graph showing comparison of RP-1 and RP-2 decomposition at 450 °C. The graph plots reaction time in minutes on the x-axis and product suite area on the y-axis. The temperatures are indicated by different markers: red for RP-2 and blue for RP-1.](image-url)
Comparison of Jet A with RP-1 and RP-2

![Graph showing comparison of Jet A with RP-1 and RP-2]
# Comparison of RP-1 and RP-2 decomposition

<table>
<thead>
<tr>
<th>$T / ^\circ$C</th>
<th>$k' \pm 1\sigma) / s^{-1}$ RP-1</th>
<th>$k' \pm 1\sigma) / s^{-1}$ RP-2</th>
</tr>
</thead>
<tbody>
<tr>
<td>375</td>
<td>$(1.13 \pm 0.04) \times 10^{-5}$</td>
<td>$(1.33 \pm 0.30) \times 10^{-5}$</td>
</tr>
<tr>
<td>400</td>
<td>$(1.19 \pm 0.33) \times 10^{-4}$</td>
<td>$(9.28 \pm 2.01) \times 10^{-5}$</td>
</tr>
<tr>
<td>425</td>
<td>$(3.08 \pm 0.77) \times 10^{-4}$</td>
<td>$(1.33 \pm 0.33) \times 10^{-4}$</td>
</tr>
<tr>
<td>450</td>
<td>$(5.84 \pm 1.33) \times 10^{-4}$</td>
<td>$(5.47 \pm 0.80) \times 10^{-4}$</td>
</tr>
</tbody>
</table>
Decomposition of RP-2 with additives

- RP-2 with 5% tetralin
- RP-2 with 5% THQ
- RP-2 with 256 ppm of the additive mixture in JP-8 +100
  - contains a chelator, antioxidant, and surfactant

Hydrogen donors increase thermal stability by interrupting radical decomposition pathways.
Decomposition of RP-2 with additives

5% THQ lowers the rate of decomposition by about an order of magnitude.
Decomposition of RP-2 with additives

The stabilizing effect is smaller at higher temperature.
Concentration of THQ during decomposition

375 °C

425 °C

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Parallels results with B100 (biodiesel):
Lower is better!

A clear high-temperature stabilization effect occurs.
Stabilization of RP-2:

\[
\text{tetrahydroquinoline} \quad >> \quad \text{tetralin} \quad >>>>
\]

Stabilization of B100:

\[
\text{tetrahydroquinoline} \quad \sim \quad \text{t-decalin} \quad >> \quad \text{tetralin}
\]
Corrosivity of decomposed RP-1

An improved copper strip corrosion test, developed at NIST, was used to determine the corrosivity of four liquids based on RP-1:

1. RP-1
2. RP-1 + 0.14 % allyl sulfide
3. RP-1 after 2 h at 400 °C
4. RP-1 + 0.14 % allyl sulfide after 2 h at 400 °C
Corrosivity of decomposed RP-1

Decomposition greatly increased the corrosivity of the mixture, and slightly increased the corrosivity of RP-1.

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## Corrosivity of decomposed RP-1

<table>
<thead>
<tr>
<th>Sample</th>
<th>CSCT</th>
<th>L*</th>
<th>[sulfur] / ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>RP-1 + 0.14 % allyl sulfide, decomposed</td>
<td>4a</td>
<td>160</td>
<td>3.1</td>
</tr>
<tr>
<td>RP-1 + 0.14 % allyl sulfide</td>
<td>1a</td>
<td>199</td>
<td>28.8</td>
</tr>
<tr>
<td>RP-1, decomposed</td>
<td>1b</td>
<td>189</td>
<td>not detected</td>
</tr>
<tr>
<td>RP-1</td>
<td>untarnished</td>
<td>197</td>
<td>not detected</td>
</tr>
</tbody>
</table>

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Rocket and Hypersonic Vehicle Propellant Workshop:

Place: NIST Boulder Laboratories

Time: Sept. 25 - 26, 2008

“Rollout of RP fluid files”
Acknowledgements:

• AFRL-EAFB

• Matt Billingsley, Ron Bates and Steve Hanna

• Tim Edwards, AFRL-WPAFB
Decomposition of RP-2 with additives

- RP-2
- RP-2 + 100 additive
- RP-2 + 5% decalin
- RP-2 + 5% tetralin
- RP-2 + 5% THQ

Product Suite Area

Reaction Time / min

Temperature: 425 °C