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<th>05 October 2015</th>
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<td>2. REPORT TYPE</td>
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<td>3. DATES COVERED (From - To)</td>
<td>15 September 2015 - 05 October 2015</td>
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<td>6. AUTHOR(S)</td>
<td>M. Billingsley, D. Pamplin, N. Keim, B. Hill-Lam, C. Wilhelm, R. Synovec</td>
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<td>7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)</td>
<td>Air Force Research Laboratory (AFMC) AFRL/RQRC 10 E. Saturn Blvd. Edwards AFB, CA 93524-7680</td>
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<td>9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)</td>
<td>Air Force Research Laboratory (AFMC) AFRL/RQ 5 Pollux Drive Edwards AFB, CA 93524-7048</td>
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<td>11. SPONSOR/MONITOR'S REPORT NUMBER(S)</td>
<td>AFRL-RQ-ED-VG-2015-367</td>
</tr>
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<td>12. DISTRIBUTION / AVAILABILITY STATEMENT</td>
<td>Approved for public release; distribution unlimited</td>
</tr>
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<td>13. SUPPLEMENTARY NOTES</td>
<td>For presentation at 14th International Symposium on the Stability, Handling, &amp; Use of Liquid Fuels; Charleston, SC; 05 Oct 2015 PA Case Number: #15588; Clearance Date: 9/24/2015</td>
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<tr>
<td>15. SUBJECT TERMS</td>
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<td>18. NUMBER OF PAGES</td>
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<td>19a. NAME OF RESPONSIBLE PERSON</td>
<td>M. Billingsley</td>
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<td>19b. TELEPHONE NO (include area code)</td>
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ADVANCED FUEL QUALITY ASSURANCE STANDARDS
BASED ON THERMAL TESTING & CHEMOMETRIC MODELING

Matt Billingsley (AFRL/RQRC)
D.Pamplin (DLA Energy/DQT)
N.Keim, B.Hill-Lam, C.Wilhelm (Johns Hopkins University / CADRE)
R.Synovec (University of Washington)

IASH 14th Int’l. Symposium
Charleston, SC
Oct 2015

Distribution A: Approved for Public Release. Distribution is Unlimited
Acknowledgments

- Jose Maniwang, Lindsey Hicks
  DLA Energy (DQT), Ft. Belvoir, VA

- Tim Edwards (AFRL/RQTF)
- Linda Shafer, Matt DeWitt, coworkers (UDRI)
- Steve Westbrook, George Wilson (SwRI)
- Joel Moreno, Indresh Mathur (Haltermann Solutions)
Outline

- Motivation/Background
- Approach
- Referee Fuel Set
- Thermal Integrity Test Method and Results
- Model Development and Results
- Future Work

LIQUID PROPELLANTS SYMPOSIUM

Sponsored by the TECHNICAL ADVISORY PANEL ON FUELS AND LUBRICANTS

Distribution A: Approved for Public Release. Distribution is Unlimited
Motivation: Fuel Quality Assurance

- Propulsion fuel performance, quality, and suitability **must be verified**
- This challenge is faced by:
  - Aerospace propulsion development/demonstration activities
  - Agencies who procure fuels for DoD use
  - Fuel manufacturers and suppliers
- Many requirements to consider:
  - Propellant cost
  - Support operations/infrastructure
  - Product availability & sustainability
  - **Functional performance**: combustion, cooling, lubrication…

**Fuel thermal stability and material compatibility**

### Aerospace Cooling System Conditions and Environments

<table>
<thead>
<tr>
<th>Application</th>
<th>$T_{\text{wall}}$ (°F)</th>
<th>$T_{\text{fuel, bulk}}$ (°F)</th>
<th>Pressure (psi)</th>
<th>Heat Flux (Btu/in²s)</th>
<th>Material</th>
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</thead>
<tbody>
<tr>
<td>Rockets</td>
<td>500-900</td>
<td>100-500</td>
<td>700-7000</td>
<td>10-120</td>
<td>Cu alloys</td>
</tr>
<tr>
<td>Hypersonics</td>
<td>1200-1500</td>
<td>100-1300</td>
<td>500-1000</td>
<td>0.5-2</td>
<td>Ni alloys</td>
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<tr>
<td>Aircraft</td>
<td>300-400</td>
<td>100-300</td>
<td>500-800</td>
<td>&lt;1</td>
<td>SS alloys</td>
</tr>
</tbody>
</table>
Liquid Rocket Engine (LOX/Kerosene)
Regenerative Cooling Environment

- Nonuniform heat flux, $q''$
- Deposition
- Supercritical
- Subcritical
- Compressibility: $\rho(r,z)$
- Transcritical process: sharp $\frac{\partial}{\partial T}$
- Compositional variability
- Surface corrosion/catalysis
- Competing rate processes:
  - Momentum & mass transfer, chemical kinetics

$R \cdot + O_2 \rightarrow ROO \rightarrow$ 
$ROOH \rightarrow P \rightarrow$ deposit 

$R \rightarrow R \cdot \rightarrow$ bulk deposits
# Background

## 1. Fuel Specification

<table>
<thead>
<tr>
<th></th>
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<th></th>
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</thead>
<tbody>
<tr>
<td>Requirement, Units</td>
<td></td>
<td>5624U</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>Distillation, °C</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>IBP</td>
<td>D86</td>
<td>report</td>
<td>&lt;205</td>
<td>&lt;205</td>
<td>(185-210)</td>
</tr>
<tr>
<td>10% recovered</td>
<td>D86</td>
<td>report</td>
<td>&lt;205</td>
<td>&lt;205</td>
<td>(185-210)</td>
</tr>
<tr>
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<td>D86</td>
<td>report</td>
<td>&lt;205</td>
<td>&lt;205</td>
<td>(185-210)</td>
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<tr>
<td>50% recovered</td>
<td>D86</td>
<td>report</td>
<td>&lt;205</td>
<td>&lt;205</td>
<td>(185-210)</td>
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<tr>
<td>90% recovered</td>
<td>D86</td>
<td>report</td>
<td>&lt;205</td>
<td>&lt;205</td>
<td>(185-210)</td>
</tr>
<tr>
<td>End point</td>
<td>D1298</td>
<td>&lt;300</td>
<td>&lt;300</td>
<td>&lt;300</td>
<td>&lt;300</td>
</tr>
<tr>
<td>Density/15°C, kg/L</td>
<td>D1298</td>
<td>0.788-0.845</td>
<td>0.775-0.840</td>
<td>0.799-0.815</td>
<td>0.799-0.815</td>
</tr>
<tr>
<td>Viscosity/-20°C, mm²/s</td>
<td>D445</td>
<td>&lt;8.5</td>
<td>&lt;8.0</td>
<td>&lt;16.5ᵇ</td>
<td>&lt;16.5ᵇ</td>
</tr>
<tr>
<td>Flash Point, °C</td>
<td>D93ᵇ</td>
<td>&gt;60</td>
<td>&gt;38</td>
<td>&gt;60</td>
<td>&gt;60</td>
</tr>
<tr>
<td>Freezing Point, °C</td>
<td>D2386ᵈ</td>
<td>&lt;=-46</td>
<td>&lt;=-40</td>
<td>&lt;=(-51)</td>
<td>&lt;=(-51)</td>
</tr>
<tr>
<td>Net Heat of Combustion, MJ/kg</td>
<td>variesᶠ</td>
<td>&gt;42.6</td>
<td>&gt;42.8</td>
<td>(&gt;43.0)</td>
<td>(&gt;43.0)</td>
</tr>
<tr>
<td>Hydrogen, mass %</td>
<td>variesᵍ</td>
<td>&gt;13.4</td>
<td>&gt;13.4ʰ</td>
<td>&gt;13.8</td>
<td>&gt;13.8</td>
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<tr>
<td>Aromatics, vol %</td>
<td>D1319</td>
<td>&lt;25.0</td>
<td>&lt;25.0</td>
<td>&lt;5</td>
<td>&lt;5</td>
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<tr>
<td>Olefins, vol %</td>
<td>D1319</td>
<td>&lt;2.0</td>
<td>&lt;1.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total sulfur, mass%</td>
<td>varies¹</td>
<td>&lt;0.3</td>
<td>&lt;0.3</td>
<td>&lt;0.003</td>
<td>&lt;0.00001</td>
</tr>
<tr>
<td>Mercaptan sulfur, mass%</td>
<td>D3227</td>
<td>&lt;0.002ʰ</td>
<td>&lt;0.003¹</td>
<td>&lt;0.0003</td>
<td>&lt;0.0003</td>
</tr>
<tr>
<td>Thermal Stability: ΔP change, mmHg</td>
<td>D3241ᵏ</td>
<td>&lt;25</td>
<td>&lt;25</td>
<td></td>
<td>report</td>
</tr>
</tbody>
</table>

- Specification review and development activities are important for fuel qualification.
- Physical, chemical spec limits are influenced by operational factors:
  - Performance
  - Handling/storage
  - Cost/Availability
- Neither engine performance nor fuel chemical composition are specified *per se*
2. Compositional Variation

Retention Time (min.)

Abundance (A.U.)

n-C$_8$  C$_9$  C$_{10}$  C$_{11}$  C$_{12}$  C$_{13}$  C$_{14}$  C$_{15}$  C$_{16}$  C$_{17}$

RP-2, Sample 1
RP-2, Sample 4
RP-1, Sample 19
JP-8, POSF 4751
JP-7, POSF 3327

data: G.Wilson, S.Westbrook (SwRI)

Distribution A: Approved for Public Release. Distribution is Unlimited
### Background

#### 3. (Lack of) Thermal Performance Test

**ASTM D3241 (JFTOT) Results**

<table>
<thead>
<tr>
<th>Fuel Type</th>
<th>Designation</th>
<th>Tube Deposit Rating Code</th>
<th>Maximum ΔP, mmHg</th>
<th>Data: G.Wilson, S.Westbrook (SwRI) R.Cook (AFRL), M.Thiede (AFPET)</th>
</tr>
</thead>
<tbody>
<tr>
<td>JP-7</td>
<td>POSF 3327</td>
<td>&lt;2</td>
<td>0.1</td>
<td></td>
</tr>
<tr>
<td>JP-8</td>
<td>POSF 4751</td>
<td>&gt;4AP&lt;sup&gt;a&lt;/sup&gt;</td>
<td>280.1</td>
<td></td>
</tr>
<tr>
<td>RP-1</td>
<td>Sample 19</td>
<td>&lt;2</td>
<td>0.1</td>
<td></td>
</tr>
<tr>
<td>RP-2</td>
<td>Sample 4</td>
<td>&lt;2</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>RP-2</td>
<td>Sample 1</td>
<td>&lt;2</td>
<td>0.1</td>
<td></td>
</tr>
<tr>
<td>RP-TS-5</td>
<td>Sample 14</td>
<td>&lt;2</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>RP-2</td>
<td>Sample 6</td>
<td>&lt;2</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>Fuel Type</td>
<td>Designation</td>
<td>Tube Deposit Rating Code</td>
<td>Maximum ΔP, mmHg</td>
<td></td>
</tr>
<tr>
<td>RP-1</td>
<td>Sample 18</td>
<td>35-38 (17)&lt;sup&gt;b&lt;/sup&gt;</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>RP-1</td>
<td>Sample X</td>
<td>5</td>
<td>0</td>
<td></td>
</tr>
</tbody>
</table>

<sup>a</sup> “A” denotes abnormal deposit; “P” denotes peacock deposit.

<sup>b</sup> Filtered

- Rocket kerosene is not quality tested for thermal stability or material compatibility prior to delivery
  - RP-1 is not tested. RP-2 is tested with ASTM D3241 (JFTOT) but results are “report only”
- JFTOT method may be valuable for screening very low performing fuels (contamination, alternative sources)...

**But the method is inadequate for ensuring fuel quality as increasingly demanding thermal environments arise**
AFQTMoDev Project Structure

Fuel Compositional Variation

1. Optimize Composition
2. Specification Limits

LECO RC612 Test section analysis

CRAFTI Thermal Integrity Index (TII)

GCxGC-TOFMS 3D Chemical Data

Compound Correlation to TII

Distribution A: Approved for Public Release. Distribution is Unlimited
Referee Fuel Set

- Criteria for fuel selection
  - Multicomponent: distribution of hydrocarbon species and/or types
  - Possess heteroatom species diversity
  - Span the compositional range of fuels meeting MIL-DTL-25576E: not necessarily “today’s fuel”
  - Meet aerospace fuel designations for health/flammability/reactivity, etc.

- What we ended up with
  - 51 compositionally unique fuels (or potential blend materials – single/multicomponent)...
  - 19 evaluated for thermal integrity and included in chemometrics/modeling
  - 3 available from previous SwRI project
  - Less than ideal compositional variation
    - Produced on demand – no repository of historical fuels
    - Relatively consistent production past 20 years
    - Several “interesting” fuels contained common feedstocks
Referee Fuel Set Variation

Distillation Temperature (°F)

% Distilled

Distribution A: Approved for Public Release. Distribution is Unlimited
Fuel Set Compositional Variation

RP-1 (18)
- Aromatics (3.35 Vol%)
  - 39.41
  - 35.85
  - 13.76
  - 5.69
- Iso-Paraffins
- n-Paraffins
- Monocycloparaffins
- Dicycloparaffins
- Tricycloparaffins
- Alkylbenzenes
- Alkynaphthalenes
- Cycloaromatics

RP-2 (1)
- Aromatics (0.25 Vol%)
  - 38.83
  - 35.42
  - 20.87
  - 2.59
- Iso-Paraffins
- n-Paraffins
- Monocycloparaffins
- Dicycloparaffins
- Tricycloparaffins
- Alkylbenzenes
- Alkynaphthalenes
- Cycloaromatics

RP-2 (4)
- Aromatics (0.62 Vol%)
  - 41.40
  - 23.99
  - 18.23
  - 14.23
- Iso-Paraffins
- n-Paraffins
- Monocycloparaffins
- Dicycloparaffins
- Tricycloparaffins
- Alkylbenzenes
- Alkynaphthalenes
- Cycloaromatics

Total Aromatics
- 0.0
- 1.0
- 2.0
- 3.0
- 3.5

Cycloaromatics
- 0.0
- 0.2
- 0.4
- 0.6
- 0.8
- 1.0

Alkynaphthalenes
- 0.0
- 0.2
- 0.4
- 0.6
- 0.8
- 1.0

Alkylbenzenes
- 0.0
- 0.2
- 0.4
- 0.6
- 0.8
- 1.0

Distribution A: Approved for Public Release. Distribution is Unlimited
Compact Rapid Assessment of Fuel Thermal Integrity (CRAFTI)

Standard Test Conditions

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<tr>
<th>Parameter</th>
<th>Value</th>
<th>Units</th>
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<td>Reynolds Number, Re</td>
<td>2000-20,000</td>
<td>-</td>
</tr>
<tr>
<td>Test article material</td>
<td>Cu (C10100)</td>
<td>-</td>
</tr>
<tr>
<td>Input power</td>
<td>4500 W</td>
<td></td>
</tr>
<tr>
<td>Wall temperature (dependent variable)</td>
<td>~1050±250</td>
<td>°F</td>
</tr>
<tr>
<td>Backpressure</td>
<td>1,000 (6.9)</td>
<td>psi (MPa)</td>
</tr>
<tr>
<td>Heated length</td>
<td>4 (10.2)</td>
<td>in. (cm)</td>
</tr>
<tr>
<td>Test duration</td>
<td>15 min.</td>
<td></td>
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</tbody>
</table>

Test Article Details & Naming

Test Article Analysis
Temperature Programmed Oxidation

Distribution A: Approved for Public Release. Distribution is Unlimited
Ten runs were performed at standard test conditions using baseline fuel (RP-2 Sample 1):
- 6 runs – initially
- 2 runs – 2/3 mo. later
- 2 runs – 9/10 mo. later
- Purge/flush/purge protocol between fuels; no disassembly

Pressure drop can be indicative of deposit formation:
- Variation from other sources should be minimized

Pressure drop variability from test to test was well within measurement uncertainty:
\[ \delta(\Delta P) \approx \delta(P_{in}) + \delta(P_{out}) \]
Repeatability: Deposit Formation

- For ten runs with baseline fuel, carbon deposit behavior is similar – and initially somewhat unexpected.
- Near detection limits → some noise likely due to instrument response.
- These results indicate "end-to-end" variation (fuel, experiment, test article handling, analysis, etc.)
- Will carbon deposit behavior vary with fuel composition?
### CRAFTI v1.1 Conditions/Results

(15 min., \( T_{\text{obulk}} \sim 650^\circ\text{F}, T_{\text{wc}} \sim 800-1200^\circ\text{F} \))

(Shaded fuels: Indistinguishable \( \Delta P \) with JFTOT)

<table>
<thead>
<tr>
<th>Fuel</th>
<th>Sample #</th>
<th># of Runs</th>
<th>Average Wall Temperature °F (°C)</th>
<th>Pressure Drop ( \Delta P ), initial psi (kPa)</th>
<th>( \Delta P ) Increase during Test psi (kPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>RP-2</td>
<td>1</td>
<td>10</td>
<td>1158 (626)</td>
<td>44 (306)</td>
<td>16 (113)</td>
</tr>
<tr>
<td>RP-2</td>
<td>4</td>
<td>4</td>
<td>1026 (552)</td>
<td>42 (288)</td>
<td>20 (136)</td>
</tr>
<tr>
<td>RP-2</td>
<td>7</td>
<td>2</td>
<td>1048 (564)</td>
<td>39 (269)</td>
<td>21 (142)</td>
</tr>
<tr>
<td>RP-1</td>
<td>3</td>
<td>7</td>
<td>1112 (600)</td>
<td>46 (320)</td>
<td>21 (146)</td>
</tr>
<tr>
<td>UL-RP-1</td>
<td>13</td>
<td>2</td>
<td>1115 (602)</td>
<td>33 (225)</td>
<td>22 (154)</td>
</tr>
<tr>
<td>RP-2</td>
<td>9</td>
<td>4</td>
<td>1110 (599)</td>
<td>31 (213)</td>
<td>23 (158)</td>
</tr>
<tr>
<td>RP-2</td>
<td>6</td>
<td>2</td>
<td>1145 (618)</td>
<td>47 (326)</td>
<td>23 (158)</td>
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<td>10</td>
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<td>26 (179)</td>
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<td>RP-2</td>
<td>12</td>
<td>2</td>
<td>1144 (618)</td>
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<td>30 (207)</td>
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<td>19</td>
<td>2</td>
<td>1074 (579)</td>
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<td>30 (210)</td>
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<td>11</td>
<td>2</td>
<td>1085 (585)</td>
<td>30 (205)</td>
<td>33 (225)</td>
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<td>RP-TS-5</td>
<td>14</td>
<td>2</td>
<td>1130 (610)</td>
<td>32 (222)</td>
<td>35 (242)</td>
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<td>JP-900</td>
<td>16</td>
<td>2</td>
<td>1015 (546)</td>
<td>31 (217)</td>
<td>45 (313)</td>
</tr>
<tr>
<td>JP-7</td>
<td>15</td>
<td>2</td>
<td>950 (510)</td>
<td>30 (205)</td>
<td>50 (343)</td>
</tr>
<tr>
<td>RP-1</td>
<td>8</td>
<td>2</td>
<td>964 (518)</td>
<td>35 (241)</td>
<td>79 (545)</td>
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<td>RP-1</td>
<td>5</td>
<td>2</td>
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<td>41 (281)</td>
<td>82 (563)</td>
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<tr>
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<td>2</td>
<td>7</td>
<td>1027 (553)</td>
<td>45 (311)</td>
<td>91 (625)</td>
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<tr>
<td>RP-1</td>
<td>17</td>
<td>1</td>
<td>964 (518)</td>
<td>31 (217)</td>
<td>103 (713)</td>
</tr>
<tr>
<td>RP-1</td>
<td>18</td>
<td>2</td>
<td>1005 (541)</td>
<td>30 (210)</td>
<td>188 (1293)</td>
</tr>
</tbody>
</table>

- Standard test conditions produce **measureable performance differences**
- Pressure drop increase varies from 40-630% of initial value
- Most fuels meet current RP-1/RP-2 limits (MIL-DTL-25576E)
- JFTOT results indicated indistinguishable performance (\( \Delta P \) increase after 5 hours) for these fuels
Wall Temperature Behavior (Heated Region Only)

- Wall temperature can be indicative of fuel thermal integrity, but is complicated by other factors:
  - Electrical connection → local current flux density
  - Deposit formation → effects on local heat transfer
  - Transcritical flow → property gradients
- Repeateable characteristic profile for fuels of different thermal quality...
- Difficult to explain temperature/time history variation
- Modeling & simulation underway to characterize fluid/solid thermal environment, flow behavior

Time-Averaged Wall Temperature (°F)

Axial Position (inches)

Error bars: ±5%
Time-Integrated (Total) Carbon Sensitive to Fuel Composition

Average Carbon Deposit (A.U.)

Section Number

Distribution A: Approved for Public Release. Distribution is Unlimited
Differentiated Carbon Data Provides Additional Insight

- Highest depositing fuels showed largest pressure drop increase
  - Exception: UL-RP-1 (13): significant deposit but small ΔP increase
- Heated region carbon deposits predominantly chemisorbed (0-200s)
- Amorphous carbon (200-450s) dominates exit region
- Only one fuel with strong filamentous carbon signal (450-800s): UL-RP-1 (13) in heated region
- Pressure drop increase correlated with amorphous deposit in exit region?
Chemometrics with CRAFTI, Carbon Deposit, & Comprehensive GC×GC-TOFMS Datasets

- **Purpose of chemometrics:**
  - Clarify role of fuel composition in cooling performance/quality
    - Guide fuel formulation
    - Advise specification methods/limits

- **Implementation:**
  - Principal component analysis (PCA)
    - Assign categorical quality
    - Identify important compositional differences
  - Fisher ratio (F-ratio) analysis
    - Refine GC×GC dataset for optimized models
    - Identify distinguishing chemical compounds
  - Partial least squares (PLS) modeling
    - Develop predictive models that relate thermal integrity behavior to fuel composition

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PCA Example: Correlate Carbon Deposit Types/Regions with Channel ΔP Increase

- Map of 3D TPO data
- Available for 19 referee fuels
- Multivariate data: excellent PCA candidate
- How can information be made useful?

- PCA Scores Plot: PC groupings capture variance in measured data (ideally 100%)
- In this case, high ΔP fuels (purple) and low ΔP fuels (green) group together – primarily along PC1
- A relationship between carbon deposit and pressure drop is confirmed – but what does PC1 represent?

- PCA PC1 Loadings Plot
  - Associates positive (blue) & negative (red) contributions to PC1 with original data matrices
  - Positive contributions to PC1 (blue) correlate with high pressure drop
  - ΔP most sensitive to amorphous carbon (200-450s) in exit region (sections 12-21)

Similar analyses performed for test article pressure drop, wall temperature, GC×GC-TOFMS chromatographic variation

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### Fisher Ratio Analysis: Identify Compounds Responsible for Group Assignment

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<tr>
<th>#</th>
<th>F-Ratio (min.)</th>
<th>t_r1 (sec)</th>
<th>t_r2 (sec)</th>
<th>Compound</th>
<th>Match Value</th>
<th>C-ratio</th>
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<td>p-cymene</td>
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<td>6.9</td>
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#### Top 300 F-Ratio Chromatographic Locations

- F-Ratio Analysis top hits are primarily aromatic...
- But their relative influence is quantified
- Hits represent class-distinguishing compounds, not necessarily direct influences on fuel thermal integrity
- Reduces superfluous chemical data in PLS model development

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PLS Modeling: Predict Thermal Integrity using GC×GC-TOFMS Data

- Leave One Out Cross Validation (LOOCV):
  - $N$ models generated, each with $N-1$ datasets
  - Datasets include CRAFTI, TPO, and GC×GC data
  - Each resulting model used to predict behavior for fuel left out during model generation
  - Statistical/graphical comparison of predicted vs. measured values

- Top 300 F-Ratio tiles used

- New parameter defined based on PCA, F-Ratio efforts:
  Thermal Integrity Index (TII):
  \[ TII \propto \left( \Delta P_{\text{max}} \times C_{A,\text{exit}} \right)^{-1} \]

- Good model agreement
  - Not inclusive of all compositional influences
  - Does not account for $\Delta P_{\text{init}}$

---

*Similar predictive models developed for test article pressure drop, wall temperature, carbon deposit*
Summary

- A compositionally diverse set of rocket kerosene fuels was acquired and systematically evaluated.
- A compact, rapid fuel thermal integrity assessment (CRAFTI apparatus) was developed and used to quantify fuel performance. Qualification criteria:
  - Operates at conditions relevant to intended application
  - Produces meaningful data quickly using small fuel quantity
  - Performance data collected with adequate repeatability
  - Discriminate between otherwise indistinguishable fuels
  - Results are traceable to existing experiments
  - Possesses characteristics of a standard test method
- Chemometric analyses applied to multiparametric datasets
  - Improvements in understanding of physicochemical influences and impacts of deposit formation were made
  - Predictive, composition-based models were developed – these models are adaptable to additional datasets and expandable to diversified fuel sets:
    - Pressure drop, wall temperature, carbon deposit, etc.
Thank You for Your Attention