Project Summary: Increased Fuel Affordability through Deployable Refining Technology (Briefing Charts)

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For CRDF update - used to satisfy the once-every-2-years requirement for work unit Q014
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Viewgraph/Briefing Charts
PROJECT SUMMARY: INCREASED FUEL AFFORDABILITY THROUGH DEPLOYABLE REFINING TECHNOLOGY

May 2016

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Applied Materials Group
Propellants Branch (RQRP)
Aerospace Systems Directorate
Air Force Research Laboratory

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Overall Process
Sulfur in Fuels

The presence of sulfur in fuels leads to many detrimental effects:

- Coking on rocket engine injector plates
- Deposit formation in hypersonic cooling channels
- Clogging of diesel engine fuel-injectors
- Fouling of automobile catalytic converters
- \( \text{SO}_x \) emissions
  - Environmental pollution
  - Corrosion issues on military equipment
Extraction Curves

The slope of these lines is the partition coefficient (K). We need $K > \sim 0.1$ for a feasible extraction process.

Equilibrium curve for compounds extracted from dodecane with IPA:water 10:1 v:v ratio
New Hydrophobic Membrane: Whatman Phase Separator Filter

- These surfaces have ~10 µm roughness, ~10 µm fibers, and ~15 µm pores, with a wide range of pore sizes and re-entrant features.
- Testing of hydrophilic membranes showed that pore sizes below ~5 µm result in high operating pressure drops and mechanical failure at >~2 gal / min / ft².
- Current hydrophilic membranes from Hygratech have ~25 µm pores, can withstand at least ~ 5 gal / min / ft², and have been 100% effective at separation.
- Hygratech hydrophobic membrane appears to have a surface energy near 29 dyn / cm, whereas the Whatman membrane is ~26 dyn / cm.

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Limiting factor in extraction fluid selection is surface tension (must exceed that of all potential fuels to be utilized) when operating at flow rates high enough that phases do not coalesce within a single stage.

Membrane surface energy must lie between the surface tension of the extraction fluid and that of the fuel to be treated.

Sensitivity of surface tension to composition also plays a key role (smaller is better)
Increased water content results in less efficient extraction (lower $K$)

Because of surface tension constraints, the design choice falls along the thin lines indicated, not along the horizontal axis

Actual design trade is relatively insensitive to alcohol choice
Diffusion Coefficient Calculations

Fo = D t / L²; in this case L = 0.97cm, solving for D yields 3 (±1) x 10⁻⁵ cm² / s

This value implies that for ~1 mm droplets, mass transfer will take ~30 s.

Why Measure?

This is a value we do not control; it is a fundamental constraint on the process.

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Extraction Apparatus

IPA / Water Inlet Spray

Hydrophobic / Oleophillic Membrane (passes oil, not water)

RP Inlet Spray

Oleophobic / Hydrophillic Membrane (passes water, not oil)

RP Outlet

RP Phase

Emulsion Phase

IPA / Water Outlet

Water (IPA) Phase

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Extraction of Sulfur from RP-1

<table>
<thead>
<tr>
<th>Sulfur Compounds by GC-SCD (Sulfur Speciation)</th>
<th>Concentration (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C2 Thiophenes</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>C3-C4 Thiophenes</td>
<td>1.6</td>
</tr>
<tr>
<td>C5 Thiophenes</td>
<td>6.3</td>
</tr>
<tr>
<td>C6 Thiophenes</td>
<td>6.1</td>
</tr>
<tr>
<td>C7 Thiophenes</td>
<td>5.8</td>
</tr>
<tr>
<td>C8-C9 Thiophenes</td>
<td>4.9</td>
</tr>
<tr>
<td>C10 Thiophenes</td>
<td>1.3</td>
</tr>
<tr>
<td>C11 Thiophenes</td>
<td>0.9</td>
</tr>
<tr>
<td>C12+ Thiophenes</td>
<td>2.0</td>
</tr>
</tbody>
</table>

**Standard Grade RP-1**
(Errors are ±0.3 ppm)

<table>
<thead>
<tr>
<th>Sulfur Compounds by GC-SCD (Sulfur Speciation)</th>
<th>Concentration (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C2 Thiophenes</td>
<td>0.3</td>
</tr>
<tr>
<td>C3-C4 Thiophenes</td>
<td>1.4</td>
</tr>
<tr>
<td>C5 Thiophenes</td>
<td>3.7</td>
</tr>
<tr>
<td>C6 Thiophenes</td>
<td>3.5</td>
</tr>
<tr>
<td>C7 Thiophenes</td>
<td>4.1</td>
</tr>
<tr>
<td>C8-C9 Thiophenes</td>
<td>2.9</td>
</tr>
<tr>
<td>C10 Thiophenes</td>
<td>0.6</td>
</tr>
<tr>
<td>C11 Thiophenes</td>
<td>0.6</td>
</tr>
<tr>
<td>C12+ Thiophenes</td>
<td>&lt;0.1</td>
</tr>
</tbody>
</table>

**Standard Grade RP-1 after extraction with 10:1 IPA water in extraction apparatus**

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### Extraction of Sulfur from Spiked Diesel #2

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Input Fuel Source</td>
<td>Diesel #2 procured at Kramer’s Junction, CA</td>
</tr>
<tr>
<td>Contaminant</td>
<td>Benzothiophene</td>
</tr>
<tr>
<td>Initial Contaminant Level</td>
<td>2700 ± 100 ppm</td>
</tr>
<tr>
<td>Final Contamination Level</td>
<td>1200 ± 100 ppm</td>
</tr>
<tr>
<td># Stages</td>
<td>5</td>
</tr>
<tr>
<td>Expected Extraction Efficiency per Stage</td>
<td>K = 0.2</td>
</tr>
</tbody>
</table>

- Key question = how does extraction curve for other components compare to that of benzothiophene?

---

Open Loop, Fresh Extraction Fluid, K = 0.2

Estimated stages needed for 15 ppm = 30 (range: 28-38)
Sulfur Chemiluminescence Detector

The Agilent 355 sulfur chemiluminescence detector (SCD) relies on the detection of light emitted from the reaction of sulfur monoxide (from sulfur-containing analytes) with ozone (produced by the detector) in an internal reaction cell.

\[
\text{Sulfur compound (analyte) } \rightarrow \text{SO} + \text{H}_2\text{O} + \text{other products}
\]

\[
\text{SO} + \text{O}_3 \rightarrow \text{SO}_2 + \text{O}_2 + \text{hv} \ (<300-400 \text{ nm})
\]
Sulfur Speciation by GC/SCD

<table>
<thead>
<tr>
<th>Calibration Standard</th>
<th>Retention Time (minutes)</th>
</tr>
</thead>
<tbody>
<tr>
<td>hydrogen sulfide</td>
<td>1.15</td>
</tr>
<tr>
<td>carbonyl sulfide</td>
<td>1.35</td>
</tr>
<tr>
<td>methyl mercaptan</td>
<td>2.44</td>
</tr>
<tr>
<td>ethyl mercaptan</td>
<td>3.99</td>
</tr>
<tr>
<td>methyl sulfide</td>
<td>4.37</td>
</tr>
<tr>
<td>carbon disulfide</td>
<td>4.84</td>
</tr>
<tr>
<td>2-propanethiol</td>
<td>5.24</td>
</tr>
<tr>
<td>2-methyl-2-propanethiol</td>
<td>6.17</td>
</tr>
<tr>
<td>1-propanethiol</td>
<td>6.50</td>
</tr>
<tr>
<td>ethyl methyl sulfide</td>
<td>6.65</td>
</tr>
<tr>
<td>1-methyl-1-propanethiol</td>
<td>8.02</td>
</tr>
<tr>
<td>thiophene</td>
<td>8.07</td>
</tr>
<tr>
<td>2-methyl-1-propanethiol</td>
<td>8.30</td>
</tr>
<tr>
<td>diethyl sulfide</td>
<td>8.86</td>
</tr>
<tr>
<td>1-butane thiol</td>
<td>9.20</td>
</tr>
<tr>
<td>methyl disulfide</td>
<td>9.96</td>
</tr>
<tr>
<td>2-methylthiophene</td>
<td>10.93</td>
</tr>
<tr>
<td>3-methylthiophene</td>
<td>11.04</td>
</tr>
<tr>
<td>diethyl disulfide</td>
<td>14.16</td>
</tr>
<tr>
<td>benzothiophene</td>
<td>19.75</td>
</tr>
<tr>
<td>5-methylbenzothiophene</td>
<td>21.75</td>
</tr>
<tr>
<td>3-methylbenzothiophene</td>
<td>21.85</td>
</tr>
<tr>
<td>diphenyl sulfide</td>
<td>26.27</td>
</tr>
</tbody>
</table>

Chromatogram of 8 ppm sulfur standards in toluene
Instrument conditions followed were from ASTM D 5623

- SCD detector allows for determination of individual sulfur compound concentration (speciation) and total sulfur concentration
- Retention time depends on instrument conditions and molecular weight of sulfur compound
Determination of Sulfur Concentration in RP1 by GC/SCD

- SCD allows for a determination of a wide range of concentration, typically from 1 ppm to >3000 ppm for most sulfur compounds.
- Typical sulfur compounds present in RP-1 are high molecular weight species such as benzothiophene and methylated isomers resulting in a fairly complex chromatogram.

Typical chromatogram of RP1 rocket fuel
Instrument conditions followed were from ASTM D 5623
As expected, contaminants in Jet A match elution times for C10-C12 S compounds.
Provisional Speciation Scheme for Jet A

Chromatogram is split into seven regions using the three largest peaks, plus the two intervening and two external regions.
Calibration Curve for Benzothiophene

Although generally linear, some run to run variation is present.
Extraction efficiency of 10% in first pass is typical of shake tests, but then decreases significantly in later passes, perhaps due to contamination of fuel by extraction fluid.
The heavier components appear to be less affected in later stages, with 5-10% extracted per stage.
Analysis of Total Sulfur Concentration

Sulfur impurity level in fuel vs. number of separations, using 70% absolute ethanol/30% water; single-stage apparatus

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Understanding the Effects of Miscibility on Extraction

\[ \Delta H_{\text{mix}} = \phi_1 \phi_2 V_{\text{ref}} \left[ (\delta_{D1} - \delta_{D2})^2 + (1/4) (\delta_{P1} - \delta_{P2})^2 + (1/4)(\delta_{H1} - \delta_{H2})^2 \right] \]

\[ \delta^2 = \delta_D^2 + \delta_P^2 + \delta_H^2 \]

\[ \delta^2 = (\Delta H_{\text{vap}} - RT) / V \]

\[ K = C_{0,2} / C_{0,1} \]

\[ \text{RT} \ln K = V_0 \left[ (\delta_{D1} - \delta_{D0})^2 + (1/4) (\delta_{P1} - \delta_{P0})^2 + (1/4)(\delta_{H1} - \delta_{H0})^2 - (\delta_{D2} - \delta_{D0})^2 - (1/4) (\delta_{P2} - \delta_{P0})^2 - (1/4)(\delta_{H2} - \delta_{H0})^2 \right] + \text{RT} \ln \left( V_1 / V_2 \right) \]

\[ \text{RT} \ln K = V_0 (D_{1-0}^2 - D_{2-0}^2) + \text{RT} \ln \left( V_1 / V_2 \right) \]

D_{i-0} is the distance in “solubility parameter space” between liquid i and impurity 0. For reference, phase 1 = fuel, phase 2 = extraction fluid.

D_{i-0} is fixed, so to maximize K, minimize D_{2-0} subject to constraint that 1 and 2 are not miscible (i.e. maximize D_{1-2}).
Optimal extraction fluid will lie along the line connecting points 1 and 0 in HSP space, but outside the sphere of solubility for 1.

Extraction efficiency (K) depends on the difference in lengths of the lines connecting points 1-0 and points 2-0.

When fuel becomes saturated with extraction fluid, its solubility parameters change, shortening the distance 1-0, and lowering K.
## Quantitative Predictions: Oil Red B4 in Dodecane / IPA:Water 9:1 (vol)

<table>
<thead>
<tr>
<th>Case #</th>
<th>Scenario</th>
<th>$\delta_D$</th>
<th>$\delta_D$</th>
<th>$\delta_D$</th>
<th>$\delta_D$</th>
<th>$\delta_D$</th>
<th>$D_{1.0}^2$</th>
<th>$D_{2.0}^2$</th>
<th>$K$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Baseline</td>
<td>16</td>
<td>0</td>
<td>0</td>
<td>15.8</td>
<td>7.1</td>
<td>16.4</td>
<td>178</td>
<td>148</td>
</tr>
<tr>
<td>2</td>
<td>Miscibility</td>
<td>16</td>
<td>1.4</td>
<td>3.7</td>
<td>15.8</td>
<td>7.1</td>
<td>16.4</td>
<td>115</td>
<td>148</td>
</tr>
<tr>
<td>3</td>
<td>Water HSP</td>
<td>16</td>
<td>0</td>
<td>0</td>
<td>15.8</td>
<td>7.1</td>
<td>17.4</td>
<td>178</td>
<td>165</td>
</tr>
<tr>
<td>4</td>
<td>Dye HSP*</td>
<td>16</td>
<td>0</td>
<td>0</td>
<td>15.8</td>
<td>7.1</td>
<td>16.4</td>
<td>217</td>
<td>189</td>
</tr>
</tbody>
</table>

Baseline case assumes no miscibility of dodecane in IPA. Miscibility (case 2) estimates HSP for ~5 vol% IPA in dodecane, based on experience with RP-1.

HSP for IPA: water mixture is estimated based on either apparent values from miscible solvent / water mixtures (cases 1, 2, and 4) and a slightly higher value based on uncertainty in $\delta_H$ for water in mixtures (case 3).

*HSP for Oil Red B4 are $\delta_D = 20.4 \ (J/cc)^{1/2}$ $\delta_p = 5.0 \ (J/cc)^{1/2}$ $\delta_H = 8.7 \ (J/cc)^{1/2}$ for cases 1, 2, and 3. For case 4, $\delta_D = 21.4(J/cc)^{1/2}$ $\delta_p = 5.0 \ (J/cc)^{1/2}$ $\delta_H = 8.7 \ (J/cc)^{1/2}$

Proper assessment of uncertainties, in particular even slight mutual miscibility, is critical for quantitative predictions of $K$.
Taking speciation and saturation into account results in large changes in the number of predicted passes needed to achieve a given level of sulfur removal.
Process Development Roadmap

- **Bench reactive desulfurization**
  - Year 1

- **Scaled-up reactive desulfurization**
  - Year 2

- **50 gal / hr LLE, open loop**
  - Year 2

- **200 gal / hr LLE, closed loop**
  - Year 3
Equipment Status

Unit 1: **Operational**
Location: EAFB Bldg 8498
Initial Operating Capability: 4 Feb 2016
Current status: Performing several test runs per month.
Current Experiments: Testing of different membrane / disperser configurations and hold-up configurations

Unit 2: **Operational**
Location: WPAFB, Bldg 490 Storage
Initial Operating Capability: 20 Jan 2016
Current status: Performing several test runs per month
Current experiments: Testing 2-membrane modified spray column configuration
Scale-Up of Liquid/Liquid Extraction

**Side View**

- Stainless steel perforated inserts (IP2-10), stainless steel holder plate (IH2-10 A), and fasteners (IA2-10 B)
- Filters, stainless steel holder plate (IH2-10 A), and fasteners (IA2-10 A). Blue represents an extraction fluid selective filter (IF2-10 B) between two guard filters (IG2-10 B and IU2-10 B), and red represents a fuel selective filter (IF2-10 A) between two guard filters (IG2-10 A and IU2-10 A).
- Top holder plate (IH1 B), pre-filter guard (IG1 A), fuel selective filter (IF1 A), post-filter guard (IU1 A), and fasteners (IA1 A)
- Bottom holder plate (IH11 B), pre-filter guard (IG11 B), extraction fluid selective filter (IF11 B), post-filter guard (IU11 B), and fasteners (IA11 A)

**Expanded Single Component**

- Membrane or metal clips
- Stainless steel
- Stainless steel mesh
- Coated filter paper
- Labeled halves to differentiate
- Stainless steel mesh
- Membrane or metal clips

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Scale-Up of Liquid/Liquid Extraction

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Future Plans

Finish optimization of configuration using Units 1 and 2

Design and build Unit 3 (200 gph, closed loop system) in a portable container

Refine a 1000-gal batch of Jet A to meet ultra-low sulfur diesel specifications using Unit 3. Perform 40-hr ground engine test using refined fuel.

Retain bench unit and Unit 1 @ Edwards AFB for production of custom-composition batches of rocket fuel for future research; retain Unit 2 @ AFRL/RQ for future fuels research.

Maintain Unit 3 as available for future demonstration activities.