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<td>5b. GRANT NUMBER</td>
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<td>Air Force Research Laboratory (AFMC) AFRL/PRS 5 Pollux Drive Edwards AFB CA 93524-7048</td>
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<td>19b. TELEPHONE NUMBER</td>
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20030312 061
MEMORANDUM FOR PRS (Contractor/In-House Publication)

FROM: PROI (TI) (STINFO) 24 Oct 2000

Suri, Suresh; Tinnierlo, M. & Marcischak, J. (ERC), “Synthesis and Screening of Advanced Hydrocarbon Fuels”


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PHILIP A. KESSEL          Date
Technical Advisor

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Synthesis & Screening of Advanced Hydrocarbon Fuels

Suresh C. Suri*, Michael Tinnirello¹ & Jacob Marcischak¹

*Air Force Research Laboratory/PRSP; ¹ERC Inc.
10 East Saturn Blvd., Edwards Air Force Base, CA 93536
Presentation Outline

- Goal
  - HEDM program
  - NASA program
  - IHRPRT program (propellant perspective)
- Criteria for fuel selection
- Approach
- Results
- Accomplishments (FY-2000)
- Planned Efforts (FY-2001)
HEDM Goal

- To Develop fuels with increased Isp over LOX/RP-1
  - LOX/RP-1 (Calculated Isp) = 300 sec
  - LOX/RP-1 (Delivered Isp) = 263 sec

Determined at sea level and 1000 psi chamber pressure
IHPRPT GOAL
(Propellant Contribution)

<table>
<thead>
<tr>
<th>Phase</th>
<th>Time</th>
<th>Improvement Over SOTA* Isp (del)</th>
</tr>
</thead>
<tbody>
<tr>
<td>II</td>
<td>2005</td>
<td>+ 5 Sec</td>
</tr>
<tr>
<td>III</td>
<td>2010</td>
<td>+ 11 Sec</td>
</tr>
</tbody>
</table>

*SOTA: LOX/RP-1 Propellant Isp(del) = 263 Sec.
Isp (calc) = 300 Sec.
NASA Goal

- **FY-1999**
  - Deliver three advanced hydrocarbon fuel in 8-10 lb quantity.
    - Quadricyclane
    - 1,7-Octadiyne
    - Bicyclopropylidene
- **FY-2000**
  - Screen four hydrocarbons for their physical and hazardous properties.
Criteria for Fuel Selection

- Predicts better performance (Isp) over LOX/RP-1 system
- Most desirable physical properties
  - Lower vapor pressure compared to RP-1
  - Higher density ($\geq$ RP-1 = 0.801 g/ml)
  - Freezing point ($\leq$ -10 °C; RP-1 = -41.4 °C)
  - Boiling point $\geq$ B. P. Of RP-1
- Storable
- Compatible with the current system
Approach

- Structural requirements
- Survey of energetic hydrocarbons
- Selection of hydrocarbons based on improved theoretical performance
- Synthesis of target hydrocarbons at bench scale.
  - Easy preparation, cost effective and safe
- Translate bench-scale synthesis to pilot scale.
# Heat of Formation of Saturated Hydrocarbons

<table>
<thead>
<tr>
<th>Compound</th>
<th>Structure</th>
<th>ΔHf (Obs)</th>
</tr>
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<tbody>
<tr>
<td>Ethane</td>
<td>CH₃CH₃</td>
<td>-20.04</td>
</tr>
<tr>
<td>Propane</td>
<td>CH₃CH₂CH₃</td>
<td>-25.02</td>
</tr>
<tr>
<td>Butane</td>
<td>CH₃(CH₂)₂CH₃</td>
<td>-30.03</td>
</tr>
<tr>
<td>Pentane</td>
<td>CH₃(CH₂)₃CH₃</td>
<td>-35.08</td>
</tr>
</tbody>
</table>

ΔHf/added CH₂ = ~ -5 Kcal/mole
## Heat of Formation of Unsaturated Hydrocarbons

<table>
<thead>
<tr>
<th>Compound</th>
<th>Structure</th>
<th>$\Delta H_f$(Obs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethylene</td>
<td>$\text{CH}_2=\text{CH}_2$</td>
<td>+12.5</td>
</tr>
<tr>
<td>1,3-Butadiene</td>
<td>$\text{CH}_2=\text{CH-CH-CH}=\text{CH}_2$</td>
<td>+26.11</td>
</tr>
<tr>
<td></td>
<td>$\Delta H_f/C = \sim +6.25 \text{ Kcal/mole}$</td>
<td></td>
</tr>
<tr>
<td>Acetylene</td>
<td>HC≡CH</td>
<td>+54.36</td>
</tr>
<tr>
<td></td>
<td>$\Delta H_f/C = \sim +27.1 \text{ Kcal/mole}$</td>
<td></td>
</tr>
</tbody>
</table>
Structural Requirement for High Energy Contents (Cont..)

- The energy content is also increased by incorporating strain in the molecule

<table>
<thead>
<tr>
<th>Compound</th>
<th>ΔHf</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ring compound</td>
<td>+ 12.73 kcal/mole</td>
</tr>
<tr>
<td>Cyclopropane</td>
<td>+ 6.78 kcal/mole</td>
</tr>
<tr>
<td>Cyclobutane</td>
<td>- 18.44 kcal/mole</td>
</tr>
<tr>
<td>Cyclopentane</td>
<td></td>
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</table>
Structural Requirements For High Energy Contents (Summary)

Incorporation of small ring (strain) and unsaturation in a molecule increases its energy contents
# Performance Comparison of Energetic Hydrocarbons (Theoretical)

<table>
<thead>
<tr>
<th>Hydrocarbons</th>
<th>H/C ratio</th>
<th>Density (g/ml)</th>
<th>Calc. ΔHf (Kcal/mole)</th>
<th>Calc. Isp (sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>RP-1</td>
<td>1.9</td>
<td>0.80</td>
<td>-5.76</td>
<td>300.0</td>
</tr>
<tr>
<td>Quad</td>
<td>1.14</td>
<td>0.98</td>
<td>72.2</td>
<td>307.0</td>
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<tr>
<td>BCP</td>
<td>1.33</td>
<td>0.85</td>
<td>76.1</td>
<td>312.5</td>
</tr>
<tr>
<td>AFRL-1</td>
<td>1.2</td>
<td>0.77</td>
<td>64.0</td>
<td>311.3</td>
</tr>
<tr>
<td>AFRL-2</td>
<td>1.25</td>
<td>0.87</td>
<td>73.4</td>
<td>307.2</td>
</tr>
<tr>
<td>AFRL-3</td>
<td>1.0</td>
<td>0.93</td>
<td>123.6</td>
<td>307.2</td>
</tr>
<tr>
<td>AFRL-4</td>
<td>1.0</td>
<td>-</td>
<td>129.6</td>
<td>321.4</td>
</tr>
<tr>
<td>AFRL-5</td>
<td>1.33</td>
<td>0.80</td>
<td>56.3</td>
<td>308.7</td>
</tr>
</tbody>
</table>
Results

Synthetic Sequence of BCP

1. EtMgBr/cat. Ti(OR-)-/Ether
2. 10% Aq. H₂SO₄

Ph₃P/Br₂

CO₂CH₃

Br

t-BuOK/DMF

# Characterization of BCP

## Physical properties

- B.P. = 101 °C
- M.P. = -12 °C
- F.P. = -6.4 °C
- Density = 0.8454 g/ml
- $\Delta H_f$ (exp.) = 67.4 kcal/mole
- $\Delta H_f$ (calc.) = 76.1 kcal/mole

## Hazardous properties

- Zero card gap (negative)
- Drop test > 200 kg/cm
- Friction test 133 newton

### Toxicity

( Inhalation LC50 )

- 1.95 mg/L

### Adiabatic Compression (psi)

- 3000 Neg.
Is BCP Hypergolic?

- Qualitative Test
  - BCP is found to be hypergolic using nitrogen tetroxide (NTO). Spontaneous reaction with visible flame.
  - Hypergolic with inhibited red fuming nitric acid (IRFNA) as oxidizers. (Darren M. Thompson, U.S. Army missile command).

- Ignition Delay
  - The work is in progress under SBIR phase-1 with TDA Research, Inc.
Synthesis of AFRL-1

- Two steps synthesis
- Involves readily available materials
- Yield in both steps is > 90 %
Characterization of AFRL-1

**Physical Properties**
- B.P. = 52-55 °C
- Density = 0.77 g/ml
- ΔHf (Exp.) = 67.4 Kcal/mole
- ΔHf (Calc.) = 64.0 Kcal/mole

**Hazardous Properties**
- “0” card gap (Negative)
- Liq. Impact test > 200 Kg-cm
- Friction Test 78 Newtons

**Adiabatic Compression (psi)**

| 3000 | Neg. |
Synthesis of AFRL-3

- One step synthesis from AFRL-1.
- Requires oxidative coupling of AFRL-1.
- Yield is 92%.
Characterization of AFRL-3

<table>
<thead>
<tr>
<th>Physical Properties</th>
<th>Hazardous Properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>B.P. = 102 °C</td>
<td>• &quot;0&quot; card gap (negative)</td>
</tr>
<tr>
<td>M.P. = -13 °C</td>
<td>• Liq Impact test &lt;20 kg-cm</td>
</tr>
<tr>
<td>Density = 0.93 g/ml</td>
<td>• Friction Test = 64.8 Newton</td>
</tr>
<tr>
<td>ΔHₚ (Calc.) = 123.6 kcal/mole</td>
<td>Adiabatic Compression (psi)</td>
</tr>
<tr>
<td>ΔHₚ (Exp.) = 117.0 kcal/mole</td>
<td>500            Neg.</td>
</tr>
<tr>
<td></td>
<td>2000            Neg.</td>
</tr>
<tr>
<td></td>
<td>3000            Neg.</td>
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</tbody>
</table>
Synthesis of AFRL-5

- Higher homologue of AFRL-1
- Two step synthesis
- Yield in both steps is greater than 90%
Characterization of AFRL-5

Physical properties
B.P. = 78 °C
M.P. = -92.8 °C
Density = 0.7957 g/ml
ΔH_f (Exp.) = 50.39 kcal/mole
ΔH_f (Calc.) = 56.3 kcal/mole

Hazardous properties
“0” card gap (TBD)
Liq. Impact Test > 200 kg-cm
Friction Test = 43.12 newton
Adiabatic Compression (psi)

3000 | Neg.
Accomplishments (FY 00)

- Delivered four hydrocarbons to NASA/ Marshall.
  - Cyclopropyl acetylene (AFRL-1).
  - Bicyclopropyldiene
  - Quadricyclane
  - 1,7-Octadiyne
- Synthesized two advanced hydrocarbons (AFRL-1 & AFRL-3) at bench-scale level.
- 200 gm of AFRL-3 was synthesized in the laboratory.
Planned Efforts of Fiscal Year 2001 (Technical)

- To continue exploring bench scale synthesis of advanced hydrocarbon (AFRL-4).

- Evaluate physical & hazardous properties of AFRL-4 & AFRL-2.
Alliances

- **Industry**
  - Boeing
  - TRW
  - Kistler
  - Aerojet

- **NASA**
  - Marshall
  - Glenn

- **DOD**
  - Navy- China Lake
  - Army- Huntsville
Team Efforts

Research
- Suresh C. Suri
- Michael Tinnirello
- Jacob Marcischak

Theoretical Efforts
- Jeffrey Mills

Physical Properties
- Paul Jones, JoAnne Larue, Jeff Yinn

Hazardous Properties
- Tommy W. Hawkins, Adam Brand, Milton Mckay, Ismail Ismail
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