Low GWP Working Fluid for Organic Rankine Cycles: DR-2

Chemical Stability at High Temperatures

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DuPont Fluorochemicals

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**Conventional Wisdom:**
Unsaturated fluorocarbons are not sufficiently stable to be used as refrigerants!

**Paradigm Shift:**
Unsaturated fluorocarbon refrigerants decompose rapidly in the atmosphere but can remain stable in a system!
Hydro-Fluoro-Olefins

CFCs $\rightarrow$ HCFCs $\rightarrow$ HFCs $\rightarrow$ HFOs

- CFC-12 $\rightarrow$ HFC-134a $\rightarrow$ HFO-1234yf, XP10, DR-14
- CFC-114 $\rightarrow$ HFC-245fa $\rightarrow$ DR-12, DR-40
- CFC-11 $\rightarrow$ HCFC-123 $\rightarrow$ DR-2

**Less Chlorine** | **No Chlorine** | **Double Bond**

**Conventional Wisdom:**
Unsaturated fluorocarbons are not sufficiently stable to be used as refrigerants!

**Paradigm Shift:**
Unsaturated fluorocarbon refrigerants decompose rapidly in the atmosphere but can remain stable in a system!
## Developmental Refrigerant: DR-2

<table>
<thead>
<tr>
<th></th>
<th>HFC-245fa</th>
<th>DR-2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical Formula</td>
<td>CF$_3$CH$_2$CHF$_2$</td>
<td></td>
</tr>
<tr>
<td>ASHRAE Std 34 Safety Class</td>
<td>B1</td>
<td>A1 (expected)</td>
</tr>
<tr>
<td>ALT [yrs]</td>
<td>7.6</td>
<td>0.0658 (24 days)</td>
</tr>
<tr>
<td>ODP</td>
<td>None</td>
<td>None</td>
</tr>
<tr>
<td>GWP$_{100}$</td>
<td>1,030</td>
<td><strong>9</strong></td>
</tr>
<tr>
<td>$T_b$ [°C]</td>
<td>15.1</td>
<td><strong>33.4</strong></td>
</tr>
<tr>
<td>$T_{cr}$ [°C]</td>
<td>154</td>
<td><strong>171.3</strong></td>
</tr>
<tr>
<td>$P_{cr}$ [MPa]</td>
<td>3.65</td>
<td><strong>2.9</strong></td>
</tr>
</tbody>
</table>

**Very Low GWP AND Non-Flammable**
Vapor Pressure

<table>
<thead>
<tr>
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<th>DR-2</th>
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<tr>
<td>$T_{cr}$, °C</td>
<td>154.0</td>
<td>171.3</td>
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</table>
DR-2 Temp-Entropy Diagram vs HFC-245fa

Temperature [°C] vs Entropy [kJ/kg-K]

DR-2

HFC-245fa
ORC Energy Efficiency

- HFC-245fa
- DR-2

**Parameters:**
- Vapor Superheat: 10 K
- Liquid Subcooling: 5 K
- Expander Efficiency: 0.7
- Pump Efficiency: 0.7

Temperature at Condenser ($T_{\text{cond}}$): 35 °C
Thermal Stability Testing

**ASHRAE Standard 97 Sealed Glass Tube Method**

1. Copper, steel and aluminum coupon bundles are placed in glass tubes.

2. Working fluid and optionally lubricant, air and/or moisture are loaded into tubes.

3. Tubes are sealed and aged at a selected temperature for selected times.

4. Post-aging, liquid is analyzed for:
   - Fluoride and Chloride concentration
   - Total Acid Number (TAN) when lubricant is present
Thermal Stability of DR-2: In the Presence of Metals

Aging for 14 Days at Increasing Temperatures

After 14 days @ 250 °C: Clear Fluid, Clean Coupons

<table>
<thead>
<tr>
<th>Aging Temp [°C]</th>
<th>F⁻ [ppm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>150</td>
<td>&lt;0.15</td>
</tr>
<tr>
<td>175</td>
<td>&lt;0.15</td>
</tr>
<tr>
<td>200</td>
<td>0.18</td>
</tr>
<tr>
<td>225</td>
<td>0.23</td>
</tr>
<tr>
<td>250</td>
<td>1.50</td>
</tr>
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Threshold F⁻ Value: 100 ppm
# Thermal Stability of DR-2: In the Presence of Metals

**Aging for 14 Days at Increasing Temperatures**

<table>
<thead>
<tr>
<th>Aging Temp [°C]</th>
<th>Newly Formed Compounds [ppm] by GCMS</th>
</tr>
</thead>
<tbody>
<tr>
<td>150</td>
<td>0.5</td>
</tr>
<tr>
<td>175</td>
<td>4.0</td>
</tr>
<tr>
<td>200</td>
<td>25.0</td>
</tr>
<tr>
<td>225</td>
<td>77.1</td>
</tr>
<tr>
<td>250</td>
<td>425.5</td>
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**After 14 days @ 250 °C:**
Negligible Formation of Decomposition Products
# Reference Fluids

<table>
<thead>
<tr>
<th>Working Fluid Family</th>
<th>Name</th>
<th>Formula</th>
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<tbody>
<tr>
<td>Hydro-Fluoro-Olefin</td>
<td>DR-2</td>
<td></td>
</tr>
<tr>
<td><strong>Hydro-Chloro-Fluoro-Carbon</strong></td>
<td>123</td>
<td>CHCl₂CF₃</td>
</tr>
<tr>
<td><strong>Hydro-Fluoro-Carbon</strong></td>
<td>245fa</td>
<td>CF₃CH₂CHF₂</td>
</tr>
<tr>
<td><strong>Hydro-Fluoro-Ether</strong></td>
<td>HFE-449sl</td>
<td>C₄F₉OCH₃</td>
</tr>
<tr>
<td><strong>Hydro-Chloro-Fluoro-Olefin</strong></td>
<td>1233zd-E</td>
<td>CF₃CH=CHCl</td>
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Thermal Stability in the Presence of Metals: DR-2 vs Reference Fluids

After 1 day @ 250 °C

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<th>Fluid</th>
<th>Visual Observations</th>
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<tr>
<td>HFO DR-2</td>
<td>clear liquid; clean coupons</td>
</tr>
<tr>
<td>HCFC-123</td>
<td>slight yellow tint</td>
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<tr>
<td>HFC-245fa</td>
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<tr>
<td>HCFC-123</td>
<td>dark brown liquid, brown on glass, brown on coupons</td>
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**AGING @ 250 °C**

## Fluoride Ion Concentration [ppm]

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<th>AGING [DAYS]</th>
<th>HFO DR-2</th>
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<tr>
<td>1</td>
<td>&lt;3</td>
<td>328</td>
<td>&lt;3</td>
<td>330</td>
<td>14</td>
</tr>
<tr>
<td>7</td>
<td>8</td>
<td>2,460</td>
<td>8</td>
<td>159</td>
<td>118</td>
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## Chloride Ion Concentration [ppm]

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<th>AGING [DAYS]</th>
<th>HCFC-123</th>
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<td>1</td>
<td>496</td>
<td>219</td>
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<td>7</td>
<td>63</td>
<td>530</td>
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Threshold Cl⁻, F⁻ Value: 100 ppm
## Thermal Stability in the Presence of Metals: DR-2 vs Reference Fluids

**AGING @ 250 °C**

### Fluoride Ion Concentration [ppm]

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Threshold Cl⁻, F⁻ Value: 100 ppm
DR-2 Thermal Stability: In the Presence of Metals, Air and Moisture

AGING @ 250 °C
Air: 7.6 mmHg; Moisture: 200 ppm

Metal Coupons:
No Significant Change in Appearance

Fluoride Ion Concentration [ppm]

<table>
<thead>
<tr>
<th>AGING [DAYS]</th>
<th>HFO DR-2</th>
<th>HFC-245fa</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>6</td>
<td>4</td>
</tr>
<tr>
<td>7</td>
<td>11</td>
<td>20</td>
</tr>
</tbody>
</table>

Threshold F⁻ Value: 100 ppm
Stability of POE Lubricants: CPI/Lubrizol POE

At 250 °C With Metal Coupons; No Refrigerant Added

<table>
<thead>
<tr>
<th>AGING [DAYS]</th>
<th>Acidity, TAN [mg KOH/g]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.2</td>
</tr>
<tr>
<td>7</td>
<td>1.3</td>
</tr>
</tbody>
</table>

Dried and De-aerated

7.6 [mm Hg] of Air and 200 [ppm] of Moisture

<table>
<thead>
<tr>
<th>AGING [DAYS]</th>
<th>Acidity, TAN [mg KOH/g]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.6</td>
</tr>
<tr>
<td>7</td>
<td>1.6</td>
</tr>
</tbody>
</table>

Threshold TAN Value: 3
Thermal Stability of DR-2/POE Blends: At 250 °C In the Presence of Metals

CPI/Lubrizol POE Lubricant
Dried and De-aerated

<table>
<thead>
<tr>
<th>AGING [DAYS]</th>
<th>HFO DR-2/POE (50/50 vol%)</th>
<th>HFC-245fa/POE (50/50 vol%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.4</td>
<td>?</td>
</tr>
<tr>
<td>7</td>
<td>1.5</td>
<td>1.5</td>
</tr>
</tbody>
</table>

Threshold TAN Value: 3
Thermal Stability of DR-2/POE Blends: At 250 °C In the Presence of Metals, Air and Moisture

CPI/Lubrizol POE Lubricant
7.6 [mm Hg] of Air and 200 [ppm] of Moisture

Acidity, TAN [mg KOH/g]

<table>
<thead>
<tr>
<th>AGING [DAYS]</th>
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<th>HFC-245fa/POE (50/50 vol%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.6</td>
<td>1.3</td>
</tr>
<tr>
<td>7</td>
<td>2.3</td>
<td>2.2</td>
</tr>
</tbody>
</table>

Threshold TAN Value: 3
In Summary

- DR-2, remarkably, exhibits comparable thermal stability to HFC-245fa at the severe conditions tested (up to 250°C) despite its unsaturated chemical nature!!

- DR-2 and HFC-245fa demonstrate the highest thermal stability among the fluids tested (HCFC-123, HCFO-1233zd-E and HFE-449sl).

- However, DR-2 provides the highest thermal stability with the lowest GWP (99 % reduction vs. HFC-245fa).

DR-2:
Attractive Safety, Health and Environmental Properties
Favorable Thermodynamics
High Thermal Stability
Thank you!

Claus-Peter Keller
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Du Pont de Nemours (Deutschland) GmbH

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Mobile: ++49 (0) 175 573 0043
e-mail: claus-peter.keller@dupont.com