Low GWP Refrigerant Solutions for Heat Pumps

Joshua Hughes, Jason Juhasz
The Chemours Company

January 12, 2019
Regional Regulations Connected with GWP Phase-Down:

- European F-gas
- Australia:
- Canada: HFC Phase-Down
- Japan: METI Material Conversion Limits
- US: State-level HFC Reg. activity & Federal Review (SNAP, etc.)
Opteon™ Lower GWP HFO Solutions

**R-404A/R-507**  
(HFC)  
**GWP: 3943**

- **XP40**  
  (R-449A)  
  **GWP: 1282**

- **XP44**  
  (R-452A)  
  **GWP: 1945**

- **XL40**  
  (R-454A)  
  **GWP: 237**

- **XL20**  
  (R-454C)  
  **GWP: 146**

**R-134a**  
(HFC)  
**GWP: 1300**

- **XP10**  
  (R-513A)  
  **GWP: 573**

- **YF**  
  (R-1234yf)  
  **GWP: <1**

**R-410A**  
(HFC)  
**GWP: 1924**

- **XL55**  
  (R-452B)  
  **GWP: 676**

- **XL41**  
  (R-454B)  
  **GWP: 467**

**R-22**  
(HCFC)  
**GWP: 1760**

- **XP40**  
  (R-449A)  
  **GWP: 1282**

- **XL20**  
  (R-454C)  
  **GWP: 146**

- **XP20**  
  (DR-93)  
  **GWP: 1147**

- **ASHRAE Number Pending**

**Incumbent Gas**  
**Non-Flammable Replacement**  
**Mildly Flammable Replacement**  
**Not Yet Commercial for Stationary n in US**
Increasing Interest & Market Adoption of XL41

**Opteon™ XL41 (R-454B)**

- Lowest GWP (466, AR4) alternative to R-410A on the market with comparable performance
- Minimizes re-design of R-410A equipment platform
- Selected by OEM’s in ducted residential and light commercial systems in North America and for Scroll Chiller systems in Europe, announced 2018

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**Carrier Introduces Puron Advance™: The Next Generation Refrigerant for Ducted Residential, Light Commercial Products in North America**

**INDIANAPOLIS - Dec. 19, 2018**

*Carrier, in collaboration with The Chemours Company, will offer Puron Advance (R-454B) to meet UN Montreal Protocol Kigali Amendment regulations*

Keeping with its long history of leading environmental responsibility, the world leader in high-technology residential, commercial, and light industrial HVAC, has announced Puron Advance™, a new synthetic refrigerant that meets the world’s commitment to controlling climate change.

Puron Advance™ is a new synthetic refrigerant that meets the world’s commitment to controlling climate change. It is the first refrigerant that carrier has developed in collaboration with the chemours company to help industry meet the goals of the UN Montreal Protocol Kigali Amendment regulations. The new refrigerant offers superior performance in residential, commercial, and light industrial HVAC systems.

**Carrier has been working with The Chemours Company to develop a new refrigerant that meets the world’s commitment to controlling climate change.**

The new refrigerant is expected to be used in residential, commercial, and light industrial HVAC systems. It is the first refrigerant that carrier has developed in collaboration with the chemours company to help industry meet the goals of the UN Montreal Protocol Kigali Amendment regulations. The new refrigerant offers superior performance in residential, commercial, and light industrial HVAC systems.

**Puron Advance™ offers superior performance in residential, commercial, and light industrial HVAC systems.**

**About R-454B refrigerant**

R-454B is a low-GWP (466, AR4) refrigerant that replaces R-410A in positive displacement, sealed refrigerant-containing and hermetically sealed, sealed systems, including Scroll Chillers, used in commercial and light industrial HVAC applications. R-454B is designed to provide a cost-effective, reliable, and environmentally friendly alternative to R-410A.

**YORK® YLAA Scroll Chiller with low-GWP R-454B**

Leading the transition to the next generation of low-GWP refrigerants, Johnson Controls is committed to helping the industry meet the goals of the UN Montreal Protocol Kigali Amendment regulations. The YORK® YLAA Scroll Chiller is designed to provide a cost-effective, reliable, and environmentally friendly alternative to R-410A.

**Why adopt the R-454B?**

- **Simplified service and maintenance:** R-454B is a direct replacement for R-410A, simplifying service and maintenance requirements.
- **Energy efficiency:** R-454B offers energy efficiency improvements compared to R-410A, helping to reduce operating costs.
- **Improved durability:** R-454B offers improved durability, reducing the need for frequent maintenance and repairs.
- **Positive environmental impact:** R-454B has a lower environmental impact compared to R-410A, helping to reduce greenhouse gas emissions.

**For more information:** www.york.com/en/europe
# <750 GWP Alternatives in Air Conditioning

<table>
<thead>
<tr>
<th>Air Conditioning</th>
<th>R-410A</th>
<th>XL55 (R-452B)</th>
<th>XL41 (R-454B)</th>
<th>XL40 (R-454A)</th>
<th>R-22 (R-454B)</th>
<th>XL20 (R-454C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GWP AR4 (AR5)</td>
<td>2088 (1924)</td>
<td>698 (676)</td>
<td>466 (467)</td>
<td>239 (238)</td>
<td>1810 (1760)</td>
<td>148 (146)</td>
</tr>
<tr>
<td>Capacity vs. R-410A</td>
<td>-</td>
<td>-3%</td>
<td>-4%</td>
<td>-23%</td>
<td>-32%</td>
<td>-33%</td>
</tr>
<tr>
<td>COP vs. R-410A</td>
<td>-</td>
<td>+1%</td>
<td>+1%</td>
<td>+3%</td>
<td>+6%</td>
<td>+5%</td>
</tr>
<tr>
<td>Evap Glide [K]</td>
<td>0.1</td>
<td>1</td>
<td>1</td>
<td>5</td>
<td>0</td>
<td>6</td>
</tr>
<tr>
<td>T Discharge [°C]</td>
<td>82</td>
<td>86</td>
<td>87</td>
<td>77.4</td>
<td>85</td>
<td>73.2</td>
</tr>
<tr>
<td>P Discharge [kPa]</td>
<td>2802</td>
<td>2663</td>
<td>2631</td>
<td>2131</td>
<td>1775</td>
<td>1842</td>
</tr>
</tbody>
</table>

Thermodynamic cycle model results for A/C Conditions:
10.0°C Avg Evap/ 46.1°C Avg Cond/ 8.3 K Subcool/11.1K Superheat, 70% Compressor Efficiency

- **Opteon™ XL41** provides the lowest GWP alternative to R-410A with comparable performance, minimizing need to re-design 410A equipment platform!
- Ultra-low GWP (<150) could be reached, with performance comparable to R-22, but higher glide.
- All products shown are ASHRAE Class A2L: Low Toxicity, Mildly Flammable
<750 GWP Alternatives in Heating

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<tr>
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<th>XL41 (R-454B)</th>
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<td>2088 (1924)</td>
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<td>239 (238)</td>
<td>1810 (1760)</td>
</tr>
<tr>
<td>Capacity vs. R-410A</td>
<td>-</td>
<td>-1%</td>
<td>-2%</td>
<td>-25%</td>
<td>-30%</td>
</tr>
<tr>
<td>COP vs. R-410A</td>
<td>-</td>
<td>+3%</td>
<td>+3%</td>
<td>+2%</td>
<td>+9%</td>
</tr>
<tr>
<td>Evap Glide [K]</td>
<td>0.1</td>
<td>1</td>
<td>1</td>
<td>4</td>
<td>0</td>
</tr>
<tr>
<td>T Discharge [°C]</td>
<td>102</td>
<td>111</td>
<td>111</td>
<td>95</td>
<td>107</td>
</tr>
<tr>
<td>P Discharge [kPa]</td>
<td>3435</td>
<td>3243</td>
<td>3207</td>
<td>2615</td>
<td>2175</td>
</tr>
</tbody>
</table>

Thermodynamic cycle model results for HP Conditions:
0°C Avg Evap/55°C Avg Cond/3K Subcool/10K Superheat, 70% Compressor Efficiency

- All products shown are ASHRAE Class A2L: Low Toxicity, Mildly Flammable
AC Performance Test Results

- Tested off-the-shelf 8.8 kW, 16 SEER ducted split AC/HP system in environmental chamber
- Optimized refrigerant charge size for peak COP in cooling
- Replaced OEM TXV with EEV to match R-410A superheat
- Tested at standard AHRI and ISO conditions
• Replaced OEM TXV with EEV to match R-410A superheat
• Close capacity match with improved COP with XL55 (R-452B) and XL41 (R-454B)
• Mass flow rate lower than R-410A
• Discharge temperatures only slightly higher than R-410A
• No discharge temperature management needed
Performance Test Results - Heating

- Charge size optimized in cooling mode
- Close capacity and COP with XL55 (R-452B) and XL41 (R-454B)
- Mass flow rate lower than R-410A
- Discharge temperatures only slightly higher than R-410A
- No discharge temperature management needed
- Similar performance to R-410A with minimal system design changes and 78% GWP reduction
XL41 (R-454B) exhibits similar behavior with existing lubricants as R-410A
Thermal Stability

- Thermal stability was evaluated using ASHRAE Standard 97 with RL32-3MAF as a lubricant
- Tubes were loaded with carbon steel, copper, and aluminum coupons, then filled with refrigerant and lubricant
- Some tubes contained refrigerant with air contamination (2000 ppm) and oil with moisture contamination (500 ppm)
- Tubes were sealed and aged at 175°C for 14 days

Indicators:

- High concentrations of fluoride ion $\Rightarrow$ fluid decomposition
- MDL (minimum detection limit) $\Rightarrow$ fluoride/chlorine ions were below procedure detection limit (MDL = 0.3 ppm)
Thermal Stability

No visual changes after 175°C for 14 days or visual differences vs. R-410A
## Thermal Stability

<table>
<thead>
<tr>
<th></th>
<th>Air (mmHg)</th>
<th>Water (ppm)</th>
<th>Metal Coupons</th>
<th>F- (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>R-410A</td>
<td>None</td>
<td>None</td>
<td>Yes</td>
<td>6.46</td>
</tr>
<tr>
<td>R-410A</td>
<td>7.6</td>
<td>None</td>
<td>Yes</td>
<td>11.70</td>
</tr>
<tr>
<td>R-410A</td>
<td>None</td>
<td>500</td>
<td>Yes</td>
<td>2.02</td>
</tr>
<tr>
<td>R-410A</td>
<td>7.6</td>
<td>500</td>
<td>Yes</td>
<td>3.07</td>
</tr>
<tr>
<td>XL41</td>
<td>None</td>
<td>None</td>
<td>Yes</td>
<td>3.46</td>
</tr>
<tr>
<td>XL41</td>
<td>7.6</td>
<td>None</td>
<td>Yes</td>
<td>6.06</td>
</tr>
<tr>
<td>XL41</td>
<td>None</td>
<td>500</td>
<td>Yes</td>
<td>8.06</td>
</tr>
<tr>
<td>XL41</td>
<td>7.6</td>
<td>500</td>
<td>Yes</td>
<td>7.41</td>
</tr>
</tbody>
</table>

Thermal stability similar to R-410A
High Temperature Heat Pumps
Low GWP Working Fluid?

Organic Rankine Cycle (ORC)

High Temp Heat Pump (HTHP)
Key Working Fluid Characteristics

- Nonflammable
- Good Environmental Footprint (Low GWP & No ODP)
- Good Reliability (Material Compatibility & Stability)
- Beneficial $T_c$ & $COP_H$
- Pay Back Time (ROI)

Opteon™ MZ, HFO-1336mzz(Z)

HFO-1336mzz(E)
# Refrigerant Properties

<table>
<thead>
<tr>
<th>Property</th>
<th>HCFC-141b</th>
<th>HFC-245fa</th>
<th>HFC-365mfc</th>
<th>HFO-1336mzz(Z)</th>
<th>HFO-1336mzz(E)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Boiling Point (°C)</td>
<td>32</td>
<td>15</td>
<td>40</td>
<td>33</td>
<td>7.5</td>
</tr>
<tr>
<td>ODP</td>
<td>0.11</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>GWP (AR5)</td>
<td>782</td>
<td>858</td>
<td>804</td>
<td>2</td>
<td>7</td>
</tr>
<tr>
<td>Vapor Thermal Conductivity at 25°C (mW/m-K)</td>
<td>9.7</td>
<td>12.7</td>
<td>10.5</td>
<td>10.7</td>
<td>11.5</td>
</tr>
</tbody>
</table>

**Opteon™ MZ**

<table>
<thead>
<tr>
<th><strong>Molecular Formula</strong></th>
<th>HFC-245fa</th>
<th>HFO-1336mzz(Z)</th>
<th>HFO-1336mzz(E)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CHF₂CH₂CF₃</td>
<td>Z-CF₃CH=CHCF₃</td>
<td>E-CF₃CH=CHCF₃</td>
<td></td>
</tr>
<tr>
<td>Flam. Limits</td>
<td>None</td>
<td>None</td>
<td>None</td>
</tr>
<tr>
<td>OEL, ppmv</td>
<td>300</td>
<td>500</td>
<td>400</td>
</tr>
<tr>
<td>Safety Class</td>
<td>B1</td>
<td>A1</td>
<td>A1</td>
</tr>
<tr>
<td>ALT, yrs</td>
<td>7.7</td>
<td>0.060 (22 days)</td>
<td>0.184 (67 days)</td>
</tr>
</tbody>
</table>
Performance Data at 30°C Lift

- For Higher Cycle Efficiency: R-1336mzz(Z)
- For Higher Volumetric Capacity: R-1336mzz(E)
Performance Data at 50°C Lift

- For Higher Cycle Efficiency: R-1336mzz(Z)
- For Higher Volumetric Capacity: R-1336mzz(E)
## Thermal Stability

HFO-1336mzz(E) at 175°C at 14 days with POE oil and Metal Coupons – Aluminium, Copper & Steel

<table>
<thead>
<tr>
<th>Fluid</th>
<th>Temperature (°C)</th>
<th>Duration</th>
<th>Oil</th>
<th>Coupon</th>
<th>IC - Anions (ppm wt%)</th>
<th>GC Results Purity (wt.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HFO-1336mzz-E</td>
<td>175</td>
<td>14 days</td>
<td>POE</td>
<td>Aluminum, Steel, Copper</td>
<td>F- 2.57</td>
<td>Before 99.9986 After 99.9981</td>
</tr>
</tbody>
</table>

HFO-1336mzz(E) at 250°C at 7 days with and without Metal Coupons

<table>
<thead>
<tr>
<th>Fluid</th>
<th>Temperature (°C)</th>
<th>Duration</th>
<th>Oil</th>
<th>Coupon</th>
<th>IC - Anions (ppm wt%)</th>
<th>GC Results Purity (wt.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HFO-1336mzz-E</td>
<td>250</td>
<td>7 days</td>
<td>N/A</td>
<td>Brass</td>
<td>F- 0.54</td>
<td>Before 3.31 After 1.79</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Zinc</td>
<td>Cl- 0.71</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Nickel</td>
<td>Before 1.17 After 0.77</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Aluminum</td>
<td>F- 0.91</td>
<td>Before 2.6 After 1.23</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Steel</td>
<td>Cl- 0.41</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Copper</td>
<td>Before 0.99 After 0.57</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>N/A</td>
<td>F- 2.66</td>
<td>Before 1.04 After 99.998</td>
</tr>
</tbody>
</table>

*Conducted in Sealed Tube Tests - ASHRAE Standard 97-2007*
Material Compatibility

Weight and Hardness Changes of Various Elastomers and Plastics with HFO-1336mzz(E) at 100°C at 14 days with POE Oil

<table>
<thead>
<tr>
<th>Material</th>
<th>Weight Changes</th>
<th>Hardness Changes</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Immediately after Exposure</td>
<td>24 hours after Exposure</td>
</tr>
<tr>
<td>Neoprene C1276-70</td>
<td>0.3%</td>
<td>-0.3%</td>
</tr>
<tr>
<td>Epichlorohydrin</td>
<td>4.9%</td>
<td>4.6%</td>
</tr>
<tr>
<td>Butyl Rubber</td>
<td>13.0%</td>
<td>12.3%</td>
</tr>
<tr>
<td>EPDM</td>
<td>8.1%</td>
<td>6.2%</td>
</tr>
<tr>
<td>NBR</td>
<td>7.8%</td>
<td>6.8%</td>
</tr>
<tr>
<td>Neoprene C0873-70</td>
<td>5.9%</td>
<td>5.4%</td>
</tr>
<tr>
<td>Polyester</td>
<td>8.2%</td>
<td>7.3%</td>
</tr>
<tr>
<td>Nylon resin</td>
<td>-1.1%</td>
<td>-1.1%</td>
</tr>
<tr>
<td>Polyamide-imide</td>
<td>-0.6%</td>
<td>-0.6%</td>
</tr>
<tr>
<td>Polyphenylene sulfide</td>
<td>0.0%</td>
<td>0.0%</td>
</tr>
<tr>
<td>PEEK</td>
<td>-0.1%</td>
<td>-0.1%</td>
</tr>
<tr>
<td>Nylon</td>
<td>-1.1%</td>
<td>-1.1%</td>
</tr>
<tr>
<td>PTFE</td>
<td>3.4%</td>
<td>2.9%</td>
</tr>
</tbody>
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- **Refrigeration**
  - Incumbent Gas
  - Non-Flammable Replacement
  - Mildly Flammable Replacement

- **Air Conditioning**
  - Not Yet Commercial for Stationary in US

*ASHRAE Number Pending*
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