New Generation of HFO Refrigerants

Chuck Allgood, PhD
The Chemours Company
A Brief History of Refrigerants

1800 – 1920’s

Ammonia (NH₃), Methyl Chloride (CH₃Cl), and Sulfur Dioxide

1920’s

Fatal Accidents with CH₃Cl
People moved refrigerators to their backyards

Collaborative Search for Safer Refrigerants by General Motors, Frigidaire, & DuPont

1928  Thomas Midgley and Charles Kettering invent a “miracle compound” called Freon®
The Freon® Age Begins

KINETIC CHEMICALS, INC.
Du Pont Building
Wilmington Delaware

Technical Paper No. 1
March 13, 1931

THE THERMODYNAMIC PROPERTIES OF DICHLOORODIFLUOROMETHANE (F-12)

The Equation of State of Superheated Vapor

CFCs:

\[ \begin{align*}
& \text{F} \\
& \text{CHClF} \\
& \text{CHClF}_2 \\
\text{Freon-12}
\end{align*} \]

dichlorodifluoromethane
Why Do We Need New Refrigerants Now?

Worldwide focus on:

“Ozone Depletion”

“Climate Change”
Regulations Driving Change
What exactly is a Global Warming Potential (GWP) Anyway?

\[ GWP = \text{Atmospheric Lifetime} \times \text{Infrared Absorbance} \]

Atmospheric Life \rightarrow \text{rates of destruction reactions (hydroxyl radical)}

\[ \text{HFC} \quad \text{[OH-]} \quad k \]
### Designing a Low GWP Molecule

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Structure</th>
<th>Atmospheric Lifetime</th>
<th>GWP</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>PFC-116</strong></td>
<td>CF3-CF3</td>
<td>10,000 years</td>
<td>11,100</td>
</tr>
<tr>
<td></td>
<td>No hydrogen</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>HFC-134a</strong></td>
<td>CH2F-CF3</td>
<td>13 years</td>
<td>1300</td>
</tr>
<tr>
<td></td>
<td>2-H atoms</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>HFO-1234yf</strong></td>
<td>CH2=CF-CF3</td>
<td>10 days</td>
<td>&lt; 1</td>
</tr>
<tr>
<td></td>
<td>“Olefin”</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
How HFOs Work

HFC
Hydro fluorocarbon

HFO
Hydro fluoro olefin

Double bond in HFOs
Quicker breakdown in the atmosphere, yet stable in systems
HFO’s have Good Thermal Stability and Materials Compatibility

HFO-1234yf + POE Lubricants, 175° C TWO WEEKS

- No Breakdown, Fluoride or Acid Generation

HFO-1234yf + POE

R-134a + POE

HFO-1234yf + POE

R-134a + POE
Long Term Viability of HFO-1234yf in Stationary Refrigeration Systems

Dr. Charles Allgood, Joshua Hughes, Dr. Bianca Hydutsky, and Dr. Thomas Leck
DuPont Chemicals and Fluoroproducts
Wilmington, DE, USA

15th International Refrigeration and Air Conditioning Conference Purdue University, West Lafayette, IN
July 2014
HFO-1234yf Similar to HFC-134a
Very low GWP but Mildly Flammable

- Same operating conditions as 134a (similar P/T curve)
- Capacity and efficiency similar to HFC-134a

<table>
<thead>
<tr>
<th></th>
<th>R-134a</th>
<th>HFO-1234yf</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Formula</strong></td>
<td>CH₂FCF₃</td>
<td>CF₃CF=CH₂</td>
</tr>
<tr>
<td><strong>Molecular Weight</strong></td>
<td>102</td>
<td>114</td>
</tr>
<tr>
<td><strong>ODP</strong></td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td><strong>GWP&lt;sub&gt;100 (ARS)&lt;/sub&gt;</strong></td>
<td>1300</td>
<td>&lt;1</td>
</tr>
<tr>
<td><strong>T Critical Point</strong></td>
<td>102 °C</td>
<td>95°C</td>
</tr>
<tr>
<td><strong>Boiling Point</strong></td>
<td>-26°C</td>
<td>-29°C</td>
</tr>
</tbody>
</table>
HFO-1234yf – 2L Mildly Flammable

R-1234yf - Difficult to Ignite, Low Burning Velocity
Global Adoption of HFO-1234yf
By Automotive Industry

- SAE International – HFO-1234yf accepted
  - Safe for use; low environmental impact
- HFO-1234yf selected by Auto OEMs globally to meet EU MAC Directive

Million’s of 1234yf cars on the road, but:
What about Stationary Refrigeration?
Creating the Next Generation of Refrigerants

HFOs enable a safe, sustainable, cost effective future

- Zero ODP
- Low GWP
- No or low flammability

Efficiency + Capacity
---
Performance

Safety and Sustainability

Total Cost of Ownership

Performance

Commercial Availability

Capital Costs + Operation Costs
---
Total Cost of Ownership
The HFOs as Building Blocks

HFO- 1234yf  \( \text{CH}_2=\text{CF-CF}_3 \)

HFO- 1234ze  \( \text{CHF}=\text{CH-CF}_3 \)

HFCO- 1233zd  \( \text{CF}_3\text{CH}=\text{CH-Cl} \)

HFO- 1336mzz(Z)  \( \text{CF}_3\text{CH}=\text{CHCF}_3 \)

New Low GWP HFO Refrigerant Blends

<table>
<thead>
<tr>
<th>Replaced</th>
<th>HFO Blend</th>
<th>ASHRAE Class</th>
<th>GWP</th>
</tr>
</thead>
<tbody>
<tr>
<td>R-404A/507</td>
<td>R-449A</td>
<td>A1</td>
<td>1397</td>
</tr>
<tr>
<td>R-134a</td>
<td>R-454A</td>
<td>A2L</td>
<td>246</td>
</tr>
<tr>
<td>R-134a</td>
<td>R-513A</td>
<td>A1</td>
<td>631</td>
</tr>
<tr>
<td>R-1234yf</td>
<td>R-1234yf</td>
<td>A2L</td>
<td>4</td>
</tr>
</tbody>
</table>
### R-449A Compared to R-404A

<table>
<thead>
<tr>
<th>Property</th>
<th>R-404A</th>
<th>R-449A (XP40)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100 yr GWP</td>
<td>3922</td>
<td>1397</td>
</tr>
<tr>
<td>Flammability</td>
<td>None</td>
<td>None</td>
</tr>
<tr>
<td>Boiling Point °C (°F)</td>
<td>-47 (-53)</td>
<td>-46 (-51)</td>
</tr>
<tr>
<td>Critical Point °C (°F)</td>
<td>72 (162)</td>
<td>82 (180)</td>
</tr>
<tr>
<td>Vapor Pressure at 25°C in kPa (Psia)</td>
<td>1254 (182)</td>
<td>1274 (185)</td>
</tr>
<tr>
<td>Liquid Density at 25°C in kg/m³ (lb/ft³)</td>
<td>1044 (65.2)</td>
<td>1096 (68.4)</td>
</tr>
<tr>
<td>Vapor Density at 25°C in kg/m³ (lb/ft³)</td>
<td>65.3 (4.08)</td>
<td>49.2 (3.07)</td>
</tr>
</tbody>
</table>
2.5 m (8.0 ft) open food display case designed for R-404A, fully loaded with food simulator

- Reciprocating compressor with POE 32 oil
- Refrigerant charge size ~3.8 kg (8.4 lb), adjusted based on liquid density

- Tested per ASHRAE Standard 72-2005
- Tested at two ambient temps: 28ºC (82ºF) and 35ºC (95ºF) in outdoor room, 24ºC (75ºF) in indoor room
- Only minor TXV adjustment made (1.6 turns closed)
- Tested at low and medium temp conditions
### R-449A System Performance
Condensing Unit – Low Temp Results

<table>
<thead>
<tr>
<th></th>
<th>Energy Consumed Rel to R404A</th>
<th>Mass Flow Rate, lb/hr</th>
<th>Suct Press, Psia</th>
<th>Disch Press, Psia</th>
<th>Comp Ratio</th>
<th>Avg Food Temp, F</th>
<th>Comp Disch Temp, F</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Ambient T = 82 F</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>R-404A</td>
<td>100%</td>
<td>32 (71)</td>
<td>112 (16)</td>
<td>1438 (209)</td>
<td>13</td>
<td>-17 (1.4)</td>
<td>78 (172)</td>
</tr>
<tr>
<td>XP40 (R-449A)</td>
<td><strong>97%</strong></td>
<td>26 (57)</td>
<td>104 (15)</td>
<td>1407 (204)</td>
<td>14</td>
<td>-17 (1.4)</td>
<td>83 (181)</td>
</tr>
<tr>
<td></td>
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</tr>
<tr>
<td><strong>Ambient T = 95 F</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>R-404A</td>
<td>100%</td>
<td>33 (73)</td>
<td>127 (18)</td>
<td>1722 (250)</td>
<td>14</td>
<td>-16 (3.2)</td>
<td>87 (189)</td>
</tr>
<tr>
<td>XP40 (R-449A)</td>
<td><strong>96%</strong></td>
<td>26 (57)</td>
<td>115 (17)</td>
<td>1685 (244)</td>
<td>15</td>
<td>-15 (5.0)</td>
<td>92 (198)</td>
</tr>
</tbody>
</table>

- **~3% lower energy consumption**
- **Similar pressures and compression ratio**
- **Modest increase in discharge T and slightly lower mass flow rate**
<table>
<thead>
<tr>
<th></th>
<th>Energy Consumed Rel to R404A</th>
<th>Mass Flow Rate, lb/hr</th>
<th>Suct Press, Psia</th>
<th>Disch Press, Psia</th>
<th>Comp Ratio</th>
<th>Avg Food Temp, F</th>
<th>Comp Disch, F</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ambient T = 28°C (82°F)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>R-404A</td>
<td>100%</td>
<td>83</td>
<td>38</td>
<td>224</td>
<td>5.9</td>
<td>36</td>
<td>161</td>
</tr>
<tr>
<td>XP40 (R-449A)</td>
<td>92%</td>
<td>71</td>
<td>38</td>
<td>217</td>
<td>5.7</td>
<td>36</td>
<td>167</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ambient T = 35°C (95°F)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>R-404A</td>
<td>100%</td>
<td>91</td>
<td>36</td>
<td>265</td>
<td>7.4</td>
<td>36</td>
<td>180</td>
</tr>
<tr>
<td>XP40 (R-449A)</td>
<td>88%</td>
<td>74</td>
<td>41</td>
<td>260</td>
<td>6.3</td>
<td>37</td>
<td>183</td>
</tr>
</tbody>
</table>

- 8-12% lower energy consumption
- Similar pressures and compression ratio
- Less increase in discharge T and slightly lower mass flow rate
Dutch Retailer Conversion to R-449A

- System used screw compressors and electronic expansion valves
- MT/LT racks were converted first to R-407F, then to R-449A
- Refrigerant was removed and filter drier changed
- No seals or oil change was required
- Work took 3-4 hours
Dutch Retailer Conversion to R-449A

Medium Temp Energy Consumption Vs Ambient Temperature

Energy Savings 9-11% for R-449A vs R-507 at MT
Dutch Retailer Conversion to R-449A

Low Temp Energy Consumption Vs Ambient Temperature

Energy Savings 3-7% for R-449A vs R-507 at LT

Graph showing energy consumption in kW/hr/day vs ambient temperature in °F and °C.
Dutch Retailer Conversion to R-449A

Compressor Discharge Temperature

Ambient Temperature

Hourly Compressor Discharge Temperature

°C

°F

R-407F

R-449A

R-507A
Retrofit of Italian Cascade Supermarket

- R-404A/CO2 hybrid cascade system
- R-404A MT rack with six screw compressors
- System has programmable EEVs
- Covers 73 cabinets and 7 cold store rooms
- Filter drier replaced, EEVs programmed, no other changes
Retrofit of Italian Cascade Supermarket

Energy Consumption

![Graph showing energy consumption and ambient temperature relationship for R-404A and R-449A refrigerants. The graph indicates a 7% energy consumption increase at different ambient temperatures.]
Santa Rosa, California Retailer

Conversion from 404A to R-449A, Oct-2014
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td><strong>R-404A</strong></td>
<td><strong>R-449A</strong></td>
<td><strong>R-449A</strong></td>
</tr>
<tr>
<td>Condensing Pressure, psig</td>
<td>167.3</td>
<td>166.0</td>
<td>167</td>
</tr>
<tr>
<td>Discharge Temp, F</td>
<td>140.3</td>
<td>161.8</td>
<td>165.9</td>
</tr>
<tr>
<td>Ambient Temp, F</td>
<td>67.4</td>
<td>63.6</td>
<td>62.0</td>
</tr>
<tr>
<td>MT Suction P, psig</td>
<td>53.8</td>
<td>49.0</td>
<td>48.8</td>
</tr>
<tr>
<td>MT Suction Temp, F</td>
<td>54.0</td>
<td>62.9</td>
<td>66.5</td>
</tr>
<tr>
<td>LT Suction P, psig</td>
<td>16.2</td>
<td>12.3</td>
<td>12.3</td>
</tr>
<tr>
<td>LT Suction Temp, F</td>
<td>3.9</td>
<td>16.8</td>
<td>17</td>
</tr>
</tbody>
</table>
California Supermarket - Conversion to R-449A

Total Energy Usage for Days @ 60-68F

~8-9% Lower Energy Usage w/ R-449A vs R-404A
No changes to equipment, piping, lubricant or seals/gaskets

Adjusted TXVs (turn down) for optimized performance

Meets cooling demand, Stable operation

Energy benefit of 8-9%
## HFO Replacement Options for R-134a

<table>
<thead>
<tr>
<th></th>
<th>R-134a</th>
<th>R-1234yf</th>
<th>R-513A</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Chemical Formula</strong></td>
<td>CF₃CH₂F</td>
<td>CF₃CF=CH₂</td>
<td>Azeotrope</td>
</tr>
<tr>
<td><strong>100 yr GWP (AR4)</strong></td>
<td>1430</td>
<td>4</td>
<td>631</td>
</tr>
<tr>
<td><strong>Toxicity</strong></td>
<td>A1</td>
<td>A2L</td>
<td>A1</td>
</tr>
<tr>
<td><strong>Flammability</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Boiling Point °C</strong></td>
<td>-26</td>
<td>-29</td>
<td>-29</td>
</tr>
<tr>
<td><strong>Critical Point °C</strong></td>
<td>101</td>
<td>95</td>
<td>98</td>
</tr>
<tr>
<td><strong>Temperature Glide °C</strong></td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>
R-513A

- **HFC/HFO blend:** R1234yf / R134a (56% / 44%)
- **ODP:** Zero Ozone Depletion Potential
- **GWP:** 631
- **ASHRAE safety:** A1 non-flammable
- **Glide:** 0R (Azeotrope)
- **Can be topped off while servicing (do not mix with R-134a)**
- **Compatible with POE lubricants**
- **Major Compressor and OEM approvals**
Compressor Performance Modeling for R-513A

Calculations using Bitzer Software (v.6.4.3 rev1302) in 4FES-3Y Reciprocating compressor, at 40ºC Condensing Temperature

Graph showing the relationship between evaporating temperature and cooling capacity and COP for R-513A, R134a, and Opteon XP10.
R-513A Evaluation in Supermarket - Hybrid System
- Retrofitted from R-134a MT; CO₂ LT
- Running for three years
The New Generation of HFO Refrigerants

Where Do We Go From Here?
The New Generation of HFO’s Regulatory Approvals

Recent Additions

EPA publishes final rule prohibiting certain high-GWP HFCs as alternatives under SNAP (7/20/15)  →  R-404A, R-507, and others targeted for delisting

EPA publishes notice expanding list of acceptable climate-friendly alternatives under SNAP (7/16/15)  →  R-449A, R-513A and others approved

EPA final rule approves climate-friendly refrigerant alternatives under SNAP (4/10/15)
The New Generation of HFO’s
OEM Approvals/Adoptions

RS13A an option in new Trane chiller

Tecumseh backs R452A as R404A alternative

Carrier Transicold announces R452A option

FSDT member Carrier Transicold is the latest major transport refrigeration company to offer R452A as an optional alternative to R404A.

At this week’s Commercial Vehicle Show in Birmingham, UK, Carrier Transicold said that while it was actively working towards replacing current HFC refrigerants with CO2, it is to offer R452A as a lower GWP option to the existing R404A refrigerant. R452A, it says, has the same cooling capacity, fuel efficiency, reliability and refrigerant charge as R404A, but offers a 43% GWP reduction compared to R404A.
The New Generation of HFO’s Commercial Supply

HFO-1234yf - World’s First Commercial Plant
Why HFO’s?

• They’re environmentally sustainable
• We have the infrastructure
  – Trained work-force
  – OEM’s, Components, Tools
  – Decades of Experience in System Design and Optimization
  – Manufacturing and Supply chain is ready

• Energy Efficiency
• Safety and Health
• Cost Effective
• Applied to New/Remodel \textit{and} Installed Base