From the Beginnings of Artificial Cold to Climate-Friendly Fluids; Evolution of Refrigerants Application

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Acknowledgement
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J. S. Brown, R. Brignoli, J. Heo
Background

- **Refrigeration is used everywhere**
  Food industry, air conditioning, cryogenics, medicine and health products, energy, etc.

- **Use of refrigeration will increase, particularly in developing countries**

- **Use of refrigeration has environmental consequences**
  - Current refrigerants (HFCs) are greenhouse gases; need for low-GWP refrigerants
  - Emissions of CO$_2$ from fossil fuel power plants; need for high efficiency
  - Kigali amendment to the Montreal Protocol (2016); production & consumption of HFCs to be cut by more than 80% over the next 30 years.
    
  Weighed GWP across all sectors $\approx$ 300
Industrial revolution (1760–1840)

- Improved productivity through inventions and new production methods
  (Watt’s steam engine; iron production; textile industry)
- Sustained growth of income and population
- The most important event since the domestication of animals and plants (10,000 years ago)
**Beginnings of artificial cold**

1755 – apparatus to make ice by evaporation of water at reduced pressure; W. Cullen
1824 – genesis of thermodynamics; Carnot
1834 – refrigeration machine using compression of a liquefiable gas; Perkins
1834 – demonstration of the Peltier effect
   - reliable compressor; Harrison
   - absorption machine; F. Carre
   - air cycle machine; Gorrie
   - machine relying on evaporation of water (R-718) at reduced pressure; E. Carre
   - refrigerants: ethyl ether, methyl ether (R-E170), petrol ether + naphtha (chemogene), CO₂ (R-744), ammonia (R-717), SO₂ (R-764), methyl chloride (R-40)

1876 – ammonia compressors by Linde; application of thermodynamics

Main applications: ice making, transport of meat by sea, and brewing

1890 -> 1900 – collapse of ice harvesting
1918 – dominant refrigerants: ammonia, CO₂, SO₂
1920s – introduction of HCs
1931 – introduction of CFC refrigerants

Thevenot, R. (1979)
Application of refrigerants

Natural fluids

<table>
<thead>
<tr>
<th>Fluid</th>
<th>Normal boiling point (°C)</th>
<th>HFO-1234ze(E)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H2O</td>
<td>100.0</td>
<td></td>
</tr>
<tr>
<td>CO2</td>
<td>-78.4</td>
<td></td>
</tr>
<tr>
<td>Air</td>
<td>-194.2</td>
<td></td>
</tr>
</tbody>
</table>

Fluorinated fluids

2nd Generation (1931 – 1990s)
- Water chillers (centrifugal)
- Domestic refrigeration
- Air conditioners
- Industrial refrigeration

3rd Generation (1990 – 2010s)
- R-123 (HCFC) 27.8
- R-134a -26.1
- R-407C -43.6
- R-410A -51.4
- R-404A -45.7

4th Generation (2010s –)
- R-1336mzz(Z) 33.4
- R-1233zd(E) 18.3
- R-1224yd(Z) 14.6
- R-1234ze(E) -19.0
- R-1234yf -29.5

GWP ≤ 2

Calm (2008), Calm (2012), Myhre, G. et al. (2013)
Application of refrigerants

**Natural fluids**

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<td>air</td>
<td>-194.2</td>
</tr>
</tbody>
</table>

**Fluorinated fluids**

**2nd Generation (1931 – 1990s)**

- **CFCs & HCFCs**
  - R-11: 23.7
  - R-12: -29.8
  - R-22: -40.8
  - R-502 (R-115/22): -45.5

**3rd Generation (1990 – 2010s)**

- **HFCs & HCFC**
  - R-123 (HCFC): 27.8
  - R-134a: -26.1
  - R-407C (R-32/125/134a): -43.6
  - R-410A (R-32/125): -51.4
  - R-404A (R-125/143a/134a): -45.7

**4th Generation (2010s – )**

- **HFOs (Hydrofluoroolefins)**
  - R-1336mzz(Z): 33.4
  - R-1233zd(E): 18.3
  - R-1224yd(Z): 14.6
  - R-1234ze(E): -19.0
  - R-1234yf: -29.5
  - R-32: -51.7
  - R-32/HFC/HFO
  - R-32/HFC/HFO

**Safety & Durability**

- Water chillers (centrifugal)
- Domestic refrigeration
- Air conditioners
- Industrial refrigeration

**Ozone Protection**

- Whatever worked

**Global Warming Mitigation**

- GWP ≤ 2
- GWP = 677

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GWP = Global Warming Potential

Calm (2008), Calm (2012), Myhre, G. et al. (2013)
NIST search for low-GWP fluids  (2012 – 2017)

Objective: Identify molecules that might be good replacements for R-410A and R-22
- Air-conditioning and refrigeration applications
  - positive displacement compressors
  - forced-convection air-to-refrigerant heat exchangers

Approach: Perform screening using comprehensive database
(PubChem lists over 60 million unique chemical structures)

Important attributes/filters:

- Performance: COP, volumetric capacity ($Q_{\text{vol}}$)
- Environmental: ODP, GWP
- Safety: toxicity, flammability
- Materials: stability, compatibility (lubricant, seals, metals, etc.)
- Cost
NIST search for low-GWP fluids  (cont.)

PubChem database
- Component atoms: C, H, N, O, S, F, Cl, Br
- Maximum number of atoms: 18
- $\text{GWP}_{100} < 1000$
- Critical temperature: $46 \, ^\circ\text{C} < T_{\text{crit}} < 146 \, ^\circ\text{C}$
- Toxicity (MSDS, RCL, TLV, $=\text{CF}_2$)
- Stability
- Volumetric capacity $> 0.33 \, Q_{\text{vol,R-410A}}$ (Basic cycle simulations)

Evaluated manually

- 21 (primary interest) + 3 (commercial interest) + 3 (low $T_{\text{crit}}$) $\longrightarrow$ 27 fluids
- New toxicity data on R-1132a; 27 + 1 (low $T_{\text{crit}}$) $\longrightarrow$ 28 fluids

Performed detailed simulations with optimized heat exchangers for 24 fluids

15 - at least mildly flammable
6 - unknown hazards

Air conditioning (McLinden et al., 2017)
Refrigeration and heating (Domanski et al., 2017)
28 candidate fluids

Basic cycle; air conditioning; optimized heat exchangers

21 fluids of primary interest:
46 °C < \( T_{cr} \) < 146 °C
\( Q_{\text{vol}} > 0.33 \) \( Q_{\text{vol,R-410A}} \)
15 - at least mildly flammable
6 - unknown hazards

7 additional fluids:
- subcritical operation; 3 fluids [R-134, R-1123, R-1225ye(Z)]
- supercritical or near-critical operation; 4 fluids [R-170, R-41, R-1132a, R-744]

<table>
<thead>
<tr>
<th>Hydrocarbons and dimethylether</th>
<th>GWP</th>
<th>( T_{cr} ) (K)</th>
<th>COP</th>
<th>( Q_{\text{vol,R-410A}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>ethane CH(_3)-CH(_3)</td>
<td>R-170</td>
<td>6</td>
<td>305.3</td>
<td>1.033</td>
</tr>
<tr>
<td>propene (propylene) CH(_2)=CH-CH(_3)</td>
<td>R-1270</td>
<td>2</td>
<td>364.2</td>
<td>1.033</td>
</tr>
<tr>
<td>propane CH(_3)=CH-CH(_3)</td>
<td>R-290</td>
<td>3</td>
<td>369.9</td>
<td>1.014</td>
</tr>
<tr>
<td>methoxymethane (dimethylether) CH(_2)=O-CH(_3)</td>
<td>R-E170</td>
<td>1</td>
<td>400.4</td>
<td>0.996</td>
</tr>
<tr>
<td>cyclopropane -CH(_2)=CH-CH(_2)-</td>
<td>R-C270</td>
<td>86</td>
<td>398.3</td>
<td>1.018</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Fluorinated alkanes (HFCs)</th>
<th>GWP</th>
<th>( T_{cr} ) (K)</th>
<th>COP</th>
<th>( Q_{\text{vol,R-410A}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>fluoromethane CH(_2)F</td>
<td>R-41</td>
<td>116</td>
<td>317.3</td>
<td>1.038</td>
</tr>
<tr>
<td>difluoromethane CH(_2)=F</td>
<td>R-32</td>
<td>677</td>
<td>351.3</td>
<td>1.038</td>
</tr>
<tr>
<td>fluoroethane CH(_2)=CH-CH(_3)</td>
<td>R-161</td>
<td>4</td>
<td>375.3</td>
<td>1.026</td>
</tr>
<tr>
<td>1,1-difluoroethane CH(_2)=CH(_2)</td>
<td>R-152a</td>
<td>138</td>
<td>386.4</td>
<td>0.981</td>
</tr>
<tr>
<td>1,1,2,2-tetrafluoroethane CH(_2)=CH(_2)-</td>
<td>R-134</td>
<td>1120</td>
<td>391.8</td>
<td>0.967</td>
</tr>
<tr>
<td>Fluorinated alkenes (HFOs) and alkynes</td>
<td>GWP</td>
<td>( T_{cr} ) (K)</td>
<td>COP</td>
<td>( Q_{\text{vol,R-410A}} )</td>
</tr>
<tr>
<td>1-1-difluoroethene CF(_2)=CH(_2)</td>
<td>R-1132a</td>
<td>&lt;1</td>
<td>324.2</td>
<td>0.968</td>
</tr>
<tr>
<td>fluoroethene CH(_2)=CH(_2)</td>
<td>R-1121</td>
<td>1</td>
<td>327.1</td>
<td>0.956</td>
</tr>
<tr>
<td>1,1,2-trifluoroethene CF(_2)=CH(_2)</td>
<td>R-1123</td>
<td>3</td>
<td>343.0</td>
<td>0.988</td>
</tr>
<tr>
<td>3,3,3-trifluoroprop-1-yne CF(_3)=C=CH ( n.a. )</td>
<td>1.4</td>
<td>363.3</td>
<td>0.954</td>
<td>0.414</td>
</tr>
<tr>
<td>2,3,3,3-tetrafluoroprop-1-ene CH(_2)=CF-CH(_3)</td>
<td>R-1234yf</td>
<td>&lt;1</td>
<td>367.9</td>
<td>1.016</td>
</tr>
<tr>
<td>(E)-1,2-difluoroethene CH(_2)=CH(_2)-</td>
<td>R-1323(E)</td>
<td>1</td>
<td>370.5</td>
<td>0.964</td>
</tr>
<tr>
<td>3,3,3-trifluoroprop-1-ene CH(_2)=CF-CH(_3)</td>
<td>R-1243zf</td>
<td>&lt;1</td>
<td>376.9</td>
<td>0.973</td>
</tr>
<tr>
<td>1,2-difluoroprop-1-ene ( \dagger ) CH(_2)-CH(_2)-</td>
<td>R-1252ye ( \dagger )</td>
<td>2</td>
<td>380.7</td>
<td>0.939</td>
</tr>
<tr>
<td>(Z)-1,2,3,3-tetrafluoroprop-1-ene CH(_2)=CF-CH(_3)</td>
<td>R-1234ze(E)</td>
<td>&lt;1</td>
<td>382.5</td>
<td>0.922</td>
</tr>
<tr>
<td>1-fluoroprop-1-ene ( \dagger ) CH(_2)=CH(_2)-</td>
<td>R-1260ye ( \dagger )</td>
<td>1</td>
<td>390.7</td>
<td>0.975</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Fluorinated oxygenates</th>
<th>GWP</th>
<th>( T_{cr} ) (K)</th>
<th>COP</th>
<th>( Q_{\text{vol,R-410A}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>trifluoro(methoxy)methane CF(_3)-CH(_2)-</td>
<td>R-E143a</td>
<td>523</td>
<td>377.9</td>
<td>0.957</td>
</tr>
<tr>
<td>2,2,4,5-tetrafluoroprop-1,3-dioxole -O-CF(_2)-O-CF=CF(_2)-</td>
<td>n.a.</td>
<td>1</td>
<td>400.0</td>
<td>0.936</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Fluorinated nitrogen and sulfur compounds</th>
<th>GWP</th>
<th>( T_{cr} ) (K)</th>
<th>COP</th>
<th>( Q_{\text{vol,R-410A}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>N,N,1,1-tetrafluoroethaneamine CH(_2)=NF(_2)</td>
<td>n.a.</td>
<td>20</td>
<td>341.6</td>
<td>0.965</td>
</tr>
<tr>
<td>difluoromethanethiol CH(_2)=SH</td>
<td>n.a.</td>
<td>1</td>
<td>373.0</td>
<td>1.010</td>
</tr>
<tr>
<td>trifluoromethanethiol CHF(_3)=SH</td>
<td>n.a.</td>
<td>1</td>
<td>376.2</td>
<td>0.977</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Inorganic compounds</th>
<th>GWP</th>
<th>( T_{cr} ) (K)</th>
<th>COP</th>
<th>( Q_{\text{vol,R-410A}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>carbon dioxide CO(_2)</td>
<td>R-744</td>
<td>1.00</td>
<td>304.1</td>
<td>1.055</td>
</tr>
<tr>
<td>ammonia NH(_3)</td>
<td>R-717</td>
<td>&lt;1</td>
<td>405.4</td>
<td>1.055</td>
</tr>
</tbody>
</table>
COP and $Q_{vol}$

Air conditioning

Basic cycle

R-410A: $T_{\text{sat, evap}} = 10 ^\circ C; \quad T_{\text{sat, cond}} = 40 ^\circ C$
COP and $Q_{vol}$; air conditioning

Basic cycle

Simulations with optimized hx circuitry

Cycle with LL/SL-HX

Simulations with optimized hx circuitry
COP and $Q_{vol}$: air conditioning

Basic cycle

Simulations with optimized hx circuitry

Economizer cycle

Simulations with optimized hx circuitry

Domanski (1995)
COP and $Q_{vol}$; air conditioning

Simulations with optimized hx circuitry

Ideal cycle simulations

Domanski & Yashar (2006)
Why there are no low-GWP fluids that are nonflammable and have high $Q_{\text{vol}}$?

Trade-off between low GWP and flammability

GWP can be lowered by:

- **Replacing F or Cl with H.**
  It shortens the atmospheric life but leads to flammability.

- **Adding a C=C double bond.**
  Contributes to the reaction with oxygen.
Is it all? Why some other fluids did not make it?

- Peroxides [-O-O-]: unstable, one dropped
- Alkynes [-C≡C-]: generally less stable than =, one retained
- Ketenes [>C=C=O]: generally very reactive, three dropped
- Allenes [>C=C=C<]: very reactive
- Alcohol [-OH]: high $T_{cr}$
- = CF$_2$ group: high reactivity often associated with toxic effects; some exceptions
- = OF group: not stable, may lead to hydrofluoric acid
How reliable was the screening process?

Did we miss good fluids?

- PubChem database is complete (?)
  PubChem lists 30 three-carbon HFOs out of 31 possible. It is unlikely that the missing molecule would possess significantly different properties than those already listed.

- Component atoms: only C, H, N, O, S, F, Cl, Br (?) Maximum number of atoms: 18 (?) Additional screening of a different database with 2000 industrial fluids yielded small molecules with the above eight elements only.

- GWP$_{100}$ < 1000 (?)

- Critical temperature: 46 °C < $T_{cr}$ < 146 °C (?)
  Estimated with standard deviation of 16.5 K (4.5 %). $T_{cr,R-410A} = 71.3$ °C

- Stability and toxicity (?)
  Published data, which may be erroneous. E.g., toxicity of R-1132a Unstable fluid may be stabilized and used in the system. E.g., R-1123, R-13I1 (CF$_3$I)
**CF₃I - ASHRAE Standard 34 proposed addenda ‘t’ and ‘s’**

**Addendum ‘t’**

R-13I1  
Chemical name = trifluoriodomethane  
Chemical formula CF₃I  
OEL = 500 ppm v/v  
Safety Group = A1  
GPW = 0.4

**Addendum ‘s’**

R-466A  
Composition (mass %) = R-32/125/13I1 (49/11.5/39.5)  
OEL = 860 ppm v/v  
Safety Group = A1  
GWP = 733

- ODP = 0.008
- Good thermodynamic properties
- Fire suppression properties
- **Toxicity** of CF₃I was studied in the 1990s (McCain and Macko, 1999). CF₃I is SNAP-approved fire suppressing agent replacing halon 1301 (total flooding) and halon 1211 (streaming), with restrictions to unoccupied and non-residential uses, respectively.

- R-1234yf/CF₃I (70/30) was studied in the 2000s for automotive ACs, within the Cooperative Research Program CRP150 (SAE). Dropped over concerns related to the **non-zero ODP** and **reactivity** of CF₃I. (Brown, 2012)

**CF₃I is expected to see future application as a component of nonflammable blends.**

**Application challenge: reactivity**
Normalized Flammability Index $\bar{\Pi}$

**Novel empirical flammability estimate**
- Uses $F/(F+H)$ in reactants and adiabatic flame temperature $T_{ad}$
- Effects of humidity are included
- Based on the ASHRAE Std. 34 experimental database of refrigerant flammability

Linteris et al. (2017)

Initial temperature = 60 °C; mole fraction of H₂O in air = 0.014
Normalized Flammability Index $\bar{\Pi}$

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- Based on the ASHRAE Std. 34 experimental database of refrigerant flammability

**Flammability index**

$$\Pi = \arctan\left(\frac{T_{ad} - 1600}{2500 - 1600} \cdot \frac{F}{F + H}\right) \cdot \left(\frac{180}{\pi}\right)$$

$\Pi_{1,2L} = 36$; flammability boundary between classes 1 and 2L

**Normalized flammability index**

$$\bar{\Pi} = \frac{\Pi - \Pi_{1,2L}}{90 - \Pi_{1,2L}} \cdot 100$$

$\bar{\Pi} < 0$ No flame propagation

Initial temperature = 60 °C; mole fraction of H$_2$O in air = 0.014

Linteris et al. (2017)
Normalized Flammability Index $\bar{\Pi}$

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**Flammability index**
\[
\Pi = \arctan2 \left( \frac{T_{ad} - 1600}{2500 - 1600}, \frac{F}{F + H} \right) \cdot \left( \frac{180}{\pi} \right)
\]

\[\Pi_{1,2L} = 36; \text{ flammability boundary between classes 1 and 2L}\]

**Normalized flammability index**
\[
\bar{\Pi} = \frac{\Pi - \Pi_{1,2L}}{90 - \Pi_{1,2L}} \cdot 100
\]
\[\bar{\Pi} < 0 \quad \text{No flame propagation}\]
Search for nonflammable replacements for R-134a

- Comprehensive evaluation binary, ternary and four-component blends (13 compounds considered)

- Selection criteria:
  - Minimize flammability
  - Minimize GWP
  - Maximize COP
  - Match volumetric capacity to that of R-134a

### Blend components

<table>
<thead>
<tr>
<th>Blend components</th>
<th>Composition (molar)</th>
<th>GWP</th>
<th>COP</th>
<th>Q</th>
<th>Q_R-134a</th>
<th>( \bar{I} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>R-152a/1234yf</td>
<td>0.08/0.92</td>
<td>8</td>
<td>0.980</td>
<td>0.957</td>
<td>7.7</td>
<td></td>
</tr>
<tr>
<td>R-134a/1234yf</td>
<td>0.20/0.80</td>
<td>238</td>
<td>0.980</td>
<td>0.996</td>
<td>2.8</td>
<td></td>
</tr>
<tr>
<td>R-134a/152a/1234yf</td>
<td>0.20/0.16/0.64</td>
<td>270</td>
<td>0.987</td>
<td>0.984</td>
<td>8.7</td>
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</tr>
<tr>
<td>R-152a/1234yf/134</td>
<td>0.16/0.48/0.36</td>
<td>417</td>
<td>0.984</td>
<td>0.900</td>
<td>7.5</td>
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<tr>
<td>R-134a/1234yf</td>
<td>0.36/0.64</td>
<td>436</td>
<td>0.985</td>
<td>1.018</td>
<td>1.0</td>
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</tr>
<tr>
<td>R-134a/1234yf/1243zf</td>
<td>0.36/0.44/0.20</td>
<td>451</td>
<td>0.988</td>
<td>1.004</td>
<td>5.2</td>
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<tr>
<td>R-134a/152a/1234yf</td>
<td>0.36/0.20/0.44</td>
<td>496</td>
<td>0.994</td>
<td>0.994</td>
<td>8.3</td>
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<tr>
<td>R-134a/1234yf</td>
<td>0.44/0.56</td>
<td>537</td>
<td>0.987</td>
<td>1.025</td>
<td>-0.1</td>
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<tr>
<td>R-134a/1234yf</td>
<td>0.468/0.532 †</td>
<td>573</td>
<td>0.988</td>
<td>1.027</td>
<td>-0.4</td>
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</tr>
<tr>
<td>R-134a/1234yf/134</td>
<td>0.48/0.48/0.04</td>
<td>633</td>
<td>0.987</td>
<td>0.975</td>
<td>-1.1</td>
<td></td>
</tr>
<tr>
<td>R-134a/1234yf/1234ze(E)</td>
<td>0.52/0.32/0.16</td>
<td>640</td>
<td>0.987</td>
<td>0.989</td>
<td>-1.2</td>
<td></td>
</tr>
<tr>
<td>R-134a/1234yf</td>
<td>0.52/0.48</td>
<td>640</td>
<td>0.989</td>
<td>1.029</td>
<td>-1.2</td>
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<tr>
<td>R-134a/1234yf/134</td>
<td>0.4/0.44/0.16</td>
<td>665</td>
<td>0.986</td>
<td>0.958</td>
<td>-1.3</td>
<td></td>
</tr>
<tr>
<td>R-134a/125/1234yf</td>
<td>0.44/0.04/0.52</td>
<td>676</td>
<td>0.985</td>
<td>1.049</td>
<td>-1.5</td>
<td></td>
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<tr>
<td>R-134a/227ea/1234yf</td>
<td>0.40/0.04/0.56</td>
<td>681</td>
<td>0.984</td>
<td>1.007</td>
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<tr>
<td>R-134a/1234ze(E)</td>
<td>0.60/0.40</td>
<td>745</td>
<td>0.988</td>
<td>0.908</td>
<td>-2.4</td>
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<tr>
<td>R-134a/1234yf</td>
<td>0.60/0.40</td>
<td>745</td>
<td>0.990</td>
<td>1.031</td>
<td>-2.4</td>
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<tr>
<td>R-134a/1234yf/1243zf</td>
<td>0.60/0.36/0.04</td>
<td>750</td>
<td>0.990</td>
<td>0.966</td>
<td>-1.5</td>
<td></td>
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<tr>
<td>R-134a/1234yf/1234ze(E)</td>
<td>0.64/0.2/0.16</td>
<td>799</td>
<td>0.990</td>
<td>0.986</td>
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<tr>
<td>R-134a/152a/1234yf</td>
<td>0.64/0.04/0.32</td>
<td>817</td>
<td>0.993</td>
<td>1.023</td>
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<tr>
<td>R-134a/1234yf/134</td>
<td>0.52/0.32/0.16</td>
<td>824</td>
<td>0.990</td>
<td>0.966</td>
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<tr>
<td>R-134a/1234ze(E)</td>
<td>0.68/0.32</td>
<td>852</td>
<td>0.991</td>
<td>0.929</td>
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<tr>
<td>R-134a/1234yf/1243zf</td>
<td>0.68/0.2/0.12</td>
<td>870</td>
<td>0.994</td>
<td>1.020</td>
<td>-1.1</td>
<td></td>
</tr>
</tbody>
</table>

† R-513A

**Bell et al. (2019)**
# Low-GWP refrigerant options

## Natural fluids

<table>
<thead>
<tr>
<th>Fluid</th>
<th>Normal boiling point (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂O</td>
<td>100.0</td>
</tr>
<tr>
<td>CO₂</td>
<td>-78.4</td>
</tr>
<tr>
<td>Air</td>
<td>-194.2</td>
</tr>
</tbody>
</table>

Ammonia

## Fluorinated fluids

### CFCs & HCFCs

#### 2nd Generation
1931 – 1990s
- R-11: 23.7
- R-12: -29.8
- R-22: -40.8
- R-502: -45.3

### HFCs & HCFC

#### 3rd Generation
1990 – 2010s
- R-123 (HCFC): 27.8
- R-134a: -26.1
- R-407C: -43.6
  - (R-32/125/134a)
- R-410A: -51.4
  - (R-32/125)
- R-404A: -45.7
  - (R-125/143a/134a)

### Low-GWP options

#### 4th Generation
2010s –
- R-1336mzz(Z): 33.4
- R-514A(1): 29.0
  - B1: 2*
- R-1233zd(E): 18.3
  - A1: 1*
- R-1224yd(Z): 14.6
  - A1: 1
- R-1234ze(E): -19.0
  - A2L: 1
- R-1234yf: -29.5
  - A2L: 1
- R-513A(2): -29.2
  - A1: 573

### Notes:
- Low-GWP refrigerant options
- * Source other than IPCC AR5
- (1)R-1336mzz(Z)/1130(E) (74.7/25.3)
- (2)R-1234yf/134a (56/44)

---

1st Generation
1830 – 1930

Whatever worked

Water chillers (centrifugal)

Domestic refrigeration

Air conditioners

Industrial refrigeration

Calm (2008), Calm (2012), Myhre, G. et al. (2013)
Low-GWP refrigerant options

### Natural fluids

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</tr>
<tr>
<td>Air</td>
<td>-194.2</td>
</tr>
</tbody>
</table>

1. **Ammonia** (Normal boiling point: -33.3 °C)

### Fluorinated fluids

#### 2nd Generation

- **Water chillers** (centrifugal)
  - R-11: 23.7
  - R-12: -29.8
- **Domestic refrigeration**
  - Air conditioners
  - R-22: -40.8
- **Industrial refrigeration**
  - R-502: -45.3
    (R-115/22)

#### 3rd Generation

- **R-123 (HCFC)**: 27.8
- **R-134a**: -26.1
- **R-407C**: -43.6
  (R-32/125/134a)
- **R-410A**: -51.4
  (R-32/125)
- **R-404A**: -45.7
  (R-125/143a/134a)

#### Low-GWP options

- **R-1234yf**: -29.5
  (A₂L: 1)
- **R-600a**: -11.7
  (A3: 3*)
- **R-152a**: -29.2
  (A2: 138)
- **R-513A(¹)**: -29.2
  (A1: 573)

* Source other than IPCC AR5

[^1]: R-1234yf/134a (56/44)

Calm (2008), Calm (2012), Myhre, G. et al. (2013)
Low-GWP refrigerant options

Natural fluids

H₂O 100.0  R-717 -33.3  R-600a - 11.7  CO₂ -78.4  R-290 - 42.1  Air -194.2  R-1270 - 47.7

Fluorinated fluids

CFCs & HCFCs

1st Generation 1830 – 1930

Water chillers (centrifugal)
Domestic refrigeration
Air conditioners
Industrial refrigeration

2nd Generation 1931 – 1990s

R-11  23.7
R-12  -29.8
R-22  -40.8
R-502  (R-115/22)

3rd Generation 1990 – 2010s

HFCs & HCFC

R-123 (HCFC)  27.8
R-134a  -26.1
R-407C  -43.6  (R-32/125/134a)
R-410A  -51.4  (R-32/125)
R-404A  -45.7  (R-125/143a/134a)

4th Generation 2010s –

Low-GWP options

Safety  GWP

R-290  -42.0  A3  3
R-32  -51.7  A2L  677
R-32/.../...  A2L > 677
R-32/.../...  A1 > 1000

Calm (2008), Calm (2012), Myhre, G. et al. (2013)
Low-GWP refrigerant options

Natural fluids

<table>
<thead>
<tr>
<th></th>
<th>H₂O</th>
<th>R-717</th>
<th>R-600a</th>
<th>R-290</th>
<th>R-1270</th>
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<tbody>
<tr>
<td>1st</td>
<td>100.0</td>
<td>-33.3</td>
<td>-11.7</td>
<td>-42.1</td>
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<td>2nd</td>
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<td>3rd</td>
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<tr>
<td>4th</td>
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Fluorinated fluids

CFCs & HCFCs

<table>
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<tr>
<th></th>
<th>1st Generation</th>
<th>2nd Generation</th>
<th>3rd Generation</th>
<th>4th Generation</th>
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<tbody>
<tr>
<td>Domestic refrigeration</td>
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<tr>
<td>Air conditioners</td>
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<td></td>
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</tr>
<tr>
<td>Industrial refrigeration</td>
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<table>
<thead>
<tr>
<th></th>
<th>1st</th>
<th>2nd</th>
<th>3rd</th>
<th>4th</th>
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<tbody>
<tr>
<td>R-11</td>
<td>23.7</td>
<td></td>
<td>R-123 (HCFC)</td>
<td>27.8</td>
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<tr>
<td>R-12</td>
<td>-29.8</td>
<td>R-134a</td>
<td>-26.1</td>
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<tr>
<td>R-22</td>
<td>-40.8</td>
<td>R-407C</td>
<td>-43.6</td>
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<tr>
<td>R-502</td>
<td>-45.3</td>
<td>(R-32/125/134a)</td>
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</table>

<table>
<thead>
<tr>
<th>HFCs &amp; HCFC</th>
<th>safety &amp; durability</th>
<th>ozone protection</th>
<th>global warming mitigation</th>
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<tr>
<td>R-123 (HCFC)</td>
<td>27.8</td>
<td>R-123 (HCFC)</td>
<td>27.8</td>
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<tr>
<td>R-134a</td>
<td>-26.1</td>
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<tr>
<td>R-407C</td>
<td>-43.6</td>
<td>(R-32/125/134a)</td>
<td>-43.6</td>
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<tr>
<td>R-410A</td>
<td>-51.4</td>
<td>(R-32/125)</td>
<td>-51.4</td>
</tr>
<tr>
<td>R-404A</td>
<td>-45.7</td>
<td>(R-125/143a/134a)</td>
<td>-45.7</td>
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</table>

Low-GWP options

<table>
<thead>
<tr>
<th></th>
<th>B2L</th>
<th>1</th>
<th>A2L</th>
<th>100-300</th>
<th>A1</th>
<th>&gt; 1200</th>
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<tbody>
<tr>
<td>R-717</td>
<td>-33.3</td>
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<td>R-717 &amp; R-744</td>
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<td>R-32/..../...</td>
<td>B2L</td>
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<tr>
<td>R-32/..../...</td>
<td>B2L</td>
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</tbody>
</table>

Calm (2008), Calm (2012), Myhre, G. et al. (2013)
Cooling technologies
sorted by primary energy input

Acceptance criteria
• Coefficient of Performance
• Environmental
• Safety
• Cost
• Reliability
• Serviceability
• Physical size, weight

Best prospects for competing with vapor compression

Space conditioning
Food refrigeration
Concluding comments

- Availability of low-GWP refrigerants varies between applications
  - Good availability of low-pressure fluids (low GWP, nonflammable)
  - No direct HFO replacement candidate for R-22 or R-410A
    Single-component medium- and high-pressure replacement fluids are at least mildly flammable

- Prospects for finding new viable refrigerants are minimal.
  New equipment will have to be designed using the fluids we know already and their blends.

- Trade off between GWP and flammability↑
Concluding comments

- **Alternative cooling technologies?**
  - Alternative technologies will gain entry in niche applications
  - but
  - will need significant development effort and material breakthroughs to be competitive and enter the main stream.

- **We will have to use refrigerants judiciously, which includes:**
  - Selection of refrigerant for each application recognizing environmental and safety considerations
  - High-efficiency, leak-free equipment
  - Improved refrigerant handling practices (equipment commissioning, servicing, and decommissioning).
Thank you for your attention.


Bell, I., Domanski, P.A., McLinden, M.O., Linteris, G., 2019. The hunt for nonflammable refrigerant blends to replace R-134a, Int. J. Refrig., https://doi.org/10.1016/j.ijrefrig.2019.05.035


Calm, J.M., 2012. Refrigerant Transitions ...Again. ASHRAE/NIST Refrigerants Conference, Gaithersburg, MD.


