Introduction to Refrigerants - Part II

In this lecture...

- Comparison between refrigerants.
- Alternate refrigerants.
- Flammability and Toxicity.
- Contemporary trends.
Comparison of refrigerants

Why choose/replace one with another?

Comparison between different refrigerants

- Synthetic refrigerants were commonly used for RAC/cold storage applications such as R 11, R 12, R 22, R 502 (CFC 12+R 22) and NH$_3$.

- Of these, R 11 was primarily used with centrifugal compressors in air conditioning applications. R 12 was used primarily in small capacity refrigeration and cold storage applications, while the other refrigerants were used in large systems such as large AC/CS.

- Among these refrigerants, except ammonia, all the others are synthetic and are 'non-toxic' and 'non-flammable'.

- However, these refrigerants have to be phased out due to their Ozone Depletion Potential (ODP).
Comparison between different refrigerants

- The synthetic replacements for the older refrigerants are: R-134a (HFC-134a) and blends of HFCs, which are generally non-toxic and non-flammable.

- However, compared to the natural refrigerants the synthetic refrigerants offer lower performance and they also have higher Global Warming Potential (GWP).

- Hence, these synthetic refrigerants also need eventual replacement.

Comparison between different refrigerants

- The most commonly used natural refrigerant is ammonia. This is also one of the oldest known refrigerants. It has excellent thermodynamic, thermophysical and environmental properties.

- However, it is toxic and is not compatible with some of the common materials of construction such as copper, which somewhat restricts its application.

- Other natural refrigerants that are being suggested are hydrocarbons (HCs) and carbon dioxide (R-744). Though these refrigerants have some specific problems, they are being studied widely and their prominence is again increasing very rapidly.
Comparison between different refrigerants

◉ The depletion of stratospheric ozone layer was attributed to Cl and Br containing chemicals such as Halons, CFCs, HCFCs etc.

◉ Since ozone layer depletion could lead to catastrophe on a global level, global community is aiming to phase out the OD substances.

◉ In addition to ozone layer depletion, most of the conventional synthetic refrigerants also cause significant global warming.

◉ Search for suitable replacement continues! → low ODP, low GWP

Alternate refrigerants

◉ The alternate refrigerants can be classified into two broad groups:
  ○ Non-Ozone depleting synthetics based on Hydro-Fluoro-Carbons (HFCs) and their blends and Unsaturated Olefins
  ○ Coming back to natural refrigerants
    ■ Ammonia, Carbon dioxide, Hydrocarbons and their blends
## Replacement Chart/General Properties

<table>
<thead>
<tr>
<th>Refrigerant</th>
<th>Application</th>
<th>Substitute Suggested</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>R 11 (CFC)</strong>&lt;br&gt;NBP = 23.7°C&lt;br&gt;$h_g$ at NBP=182.5 kJ/kg&lt;br&gt;$T_{cr}$ = 107.06°C&lt;br&gt;$C_p/C_v$ = 1.13&lt;br&gt;ODP = 1&lt;br&gt;GWP = 3500</td>
<td>Large air conditioning systems&lt;br&gt;Industrial heat pumps</td>
<td>R 123 (R,N)</td>
</tr>
<tr>
<td><strong>R 12 (CFC)</strong>&lt;br&gt;NBP = -29.8°C&lt;br&gt;$h_g$ at NBP=165.8 kJ/kg&lt;br&gt;$T_{cr}$ = 112.04°C&lt;br&gt;$C_p/C_v$ = 1.126&lt;br&gt;ODP = 1&lt;br&gt;GWP = 7300</td>
<td>Domestic refrigerators&lt;br&gt;Small air conditioners&lt;br&gt;Water coolers&lt;br&gt;Small cold storages</td>
<td>R 22 (R,N) R 134a (R,N) R 227ea (R,N) R 401A, R 401B (R,N) R 411A, R 411B (R,N) R 717 (N)</td>
</tr>
<tr>
<td><strong>R 22 (HCFC)</strong>&lt;br&gt;NBP = -40.8°C&lt;br&gt;$h_g$ at NBP=233.2 kJ/kg&lt;br&gt;$T_{cr}$ = 96.02°C&lt;br&gt;$C_p/C_v$ = 1.166&lt;br&gt;ODP = 0.05&lt;br&gt;GWP = 1500</td>
<td>Air conditioning systems&lt;br&gt;Cold storages</td>
<td>R 410A, R 410B (N) R 417A (R,N) R 407C (R,N) R 507 R 507A (R,N) R 404A (R,N) R 717 (N)</td>
</tr>
<tr>
<td><strong>R 134a (HFC)</strong>&lt;br&gt;NBP = -26.15°C&lt;br&gt;$h_g$ at NBP=222.5 kJ/kg&lt;br&gt;$T_{cr}$ = 101.06°C&lt;br&gt;$C_p/C_v$ = 1.102&lt;br&gt;ODP = 0.0&lt;br&gt;GWP = 1200</td>
<td>Used as replacement for R 12 in domestic refrigerators, water coolers, automobile A/Cs etc</td>
<td><strong>No replacement required</strong>&lt;br&gt;High global warming potential&lt;br&gt;*Highly hygroscopic</td>
</tr>
<tr>
<td>Refrigerant</td>
<td>Application</td>
<td>Substitute suggested Retrofit(R)/New (N)</td>
</tr>
<tr>
<td>-------------</td>
<td>-------------</td>
<td>-----------------------------------------</td>
</tr>
<tr>
<td><strong>R 717 (NH₃)</strong>&lt;br&gt;NBP = -33.36°C&lt;br&gt;h_g at NBP=1389.9 kJ/kg&lt;br&gt;T_α = 133.0°C&lt;br&gt;Cp/Cv = 1.31&lt;br&gt;ODP = 0.0&lt;br&gt;GWP = 0.0</td>
<td>Cold storages&lt;br&gt;Ice plants&lt;br&gt;Food processing&lt;br&gt;Frozen food cabinets</td>
<td>No replacement required&lt;br&gt;* Toxic and flammable&lt;br&gt;* Incompatible with copper&lt;br&gt;* Highly efficient&lt;br&gt;* Inexpensive and available</td>
</tr>
<tr>
<td><strong>R 744 (CO₂)</strong>&lt;br&gt;NBP = -78.4°C&lt;br&gt;h_g at 40°C=321.3 kJ/kg&lt;br&gt;T_α = 31.1°C&lt;br&gt;Cp/Cv = 1.3&lt;br&gt;ODP = 0.0&lt;br&gt;GWP = 1.0</td>
<td>Cold storages&lt;br&gt;Air conditioning systems&lt;br&gt;Simultaneous cooling and heating (Transcritical cycle)</td>
<td>No replacement required&lt;br&gt;* Very low critical temperature&lt;br&gt;* Eco-friendly&lt;br&gt;* Inexpensive and available</td>
</tr>
<tr>
<td><strong>R600a (Iso-butane)</strong>&lt;br&gt;NBP = -11.73°C&lt;br&gt;h_g at NBP=367.7 kJ/kg&lt;br&gt;T_α = 136.0°C&lt;br&gt;Cp/Cv = 1.085&lt;br&gt;ODP = 0.0&lt;br&gt;GWP = 3.0</td>
<td>Replacement for R 12&lt;br&gt;Domestic refrigerators&lt;br&gt;Water coolers</td>
<td>No replacement required&lt;br&gt;* Flammable&lt;br&gt;* Eco-friendly</td>
</tr>
</tbody>
</table>
What is ODP and GWP?

Environmental impact of refrigerants
Environmental effects of refrigerants

- Depletion of the ozone layer in the stratosphere.
- Global warming:
  - Refrigerants directly contributing to global warming when released to the atmosphere
  - Indirect contribution based on the energy consumption of among others the compressors (CO₂ produced by power stations)

Ozone depletion potential (ODP)
Global warming potential (GWP)

The chart shows the Global Warming Potential (GWP) of various substances used in refrigeration and air conditioning. The substances are compared with R1234ze, R290, R744 (CO2), and R717 (NH3). The GWP values are indicated along the y-axis, with R507A, R404A, R407A, R410A, R407F, R407C, R134a, R32, HFO 1234ze, R290, R744 (CO2), and R717 (NH3) listed from top to bottom.

- **R507A**
- **R404A**
- **R407A**
- **R410A**
- **R407F**
- **R407C**
- **R134a**
- **R32**
- **HFO 1234ze**
- **R290**
- **R744 (CO2)**
- **R717 (NH3)**

The chart indicates that R717 (NH3) has the highest GWP, followed by R744 (CO2) and R290. R507A and R404A have lower GWP values compared to others. The GWP values range from 0 to 4000 along the x-axis.
Carbondioxide as refrigerant

- Non Flammable
- Non toxic
- Inexpensive and widely available
- Its high operating pressure provides potential for system size and weight reducing potential.

**Drawbacks:**

- Operating pressure (high side) : 80 bars
- Low efficiency
Hydrocarbon refrigerants

- Used since the 1880's → natural → Zero ODP and negligible GWP
- Good substitutes for CFC's, HCFC's, and HFC's.
- Compatible with copper, miscible with mineral oil, lubricating oils
- Retrofitting of existing systems is relatively cheap.
- Energy saving: up to 20%
- When HC's burn they produce carbon and steam; when synthetic refrigerants burn they all produce highly toxic fumes.
- Proving to be good for Domestic Refrigeration and Air Conditioning and also for Mobile Air Conditioning Systems (MACS)
- Commercial/Industrial Refrigeration and Air Conditioning

**Drawback:**
- Flammable

Ammonia – A natural refrigerant

- Ammonia is produced in a natural way by human beings and animals; 17 grams/day for humans.

<table>
<thead>
<tr>
<th>Natural production</th>
<th>3000 million tons/year</th>
</tr>
</thead>
<tbody>
<tr>
<td>Production in factories</td>
<td>120 million tons/year</td>
</tr>
<tr>
<td>Used in refrigeration</td>
<td>6 million tons/year</td>
</tr>
</tbody>
</table>
Advantages of using ammonia as refrigerant

◉ ODP = 0; GWP = 0
◉ Excellent thermodynamic properties small molecular mass, large latent heat, large vapor density and excellent heat transfer characteristics.
◉ High critical temperature (132°C): highly efficient cycles at high condensing temperatures
◉ Its smell causes leaks to be detected and fixed before reaching dangerous concentration
◉ Relatively low price

Some drawbacks of ammonia as refrigerant

◉ Toxic
◉ Flammable (16 – 28% concentration)
◉ Not compatible with copper
◉ Temperature on discharge side of compressor is higher compared to other refrigerants.
Properties of ammonia

<table>
<thead>
<tr>
<th>Concentration (ppm)</th>
<th>Effect</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>Noticeable by smell</td>
</tr>
<tr>
<td>25</td>
<td>Irritation noticeable</td>
</tr>
<tr>
<td>50</td>
<td>Irritation of nose, mouth and throat; acclimatization after a while</td>
</tr>
<tr>
<td>500</td>
<td>Immediate irritation of mucous membranes, respiration difficult</td>
</tr>
<tr>
<td>3500</td>
<td>Lethal after a short period of exposure</td>
</tr>
<tr>
<td>20000</td>
<td>Causes blisters and chemical burns</td>
</tr>
<tr>
<td>Lower explosion limit</td>
<td>16 % by volume in air</td>
</tr>
<tr>
<td>Higher explosion limit</td>
<td>25 % by volume in air</td>
</tr>
<tr>
<td>Ignition temperature</td>
<td>650 °C</td>
</tr>
<tr>
<td>Ignition energy required</td>
<td>.01 to 1 Joule</td>
</tr>
</tbody>
</table>

Refrigeration properties of ammonia

- Evaporation enthalpy 0°C 1262 KJ/KG
- Pressure at 0°C 4.9 bar
- Pressure ratio 0/35°C 3.15
- COP 0/35°C 6.77
- Discharge temperature 0/35°C 81°C
- Volumetric refrigerating capacity 3800 KJ/m³
- Volumetric refrigerating capacity of R134a 2000 KJ/m³
### Energy efficiency – reciprocating compressor

**Performance: t-evap = -10 °C; t-cond = 35 °C**

<table>
<thead>
<tr>
<th>Refrigerant</th>
<th>Refrigerating capacity</th>
<th>Shaft power</th>
<th>COP</th>
<th>1/COP</th>
</tr>
</thead>
<tbody>
<tr>
<td>[-]</td>
<td>[kW]</td>
<td>[kW]</td>
<td>[-]</td>
<td>[%]</td>
</tr>
<tr>
<td>R717 (NH₃)</td>
<td>425.8</td>
<td>112.9</td>
<td>3.771</td>
<td>100.0</td>
</tr>
<tr>
<td>R22</td>
<td>380.3</td>
<td>121.3</td>
<td>3.135</td>
<td>120.3</td>
</tr>
<tr>
<td>R134a</td>
<td>218.8</td>
<td>74.7</td>
<td>2.929</td>
<td>128.7</td>
</tr>
<tr>
<td>R404A</td>
<td>352.4</td>
<td>132.6</td>
<td>2.658</td>
<td>141.9</td>
</tr>
<tr>
<td>R507</td>
<td>356.7</td>
<td>136.0</td>
<td>2.623</td>
<td>143.8</td>
</tr>
</tbody>
</table>

### Energy efficiency – screw compressor

**t-evap = -30 °C; t-cond = 35 °C**

<table>
<thead>
<tr>
<th>Refrigerant</th>
<th>Refrigerating capacity</th>
<th>Shaft power</th>
<th>COP</th>
<th>1/COP</th>
</tr>
</thead>
<tbody>
<tr>
<td>[-]</td>
<td>[kW]</td>
<td>[kW]</td>
<td>[-]</td>
<td>[%]</td>
</tr>
<tr>
<td>R717 (NH₃)</td>
<td>435.9</td>
<td>228.0</td>
<td>1.912</td>
<td>100.0</td>
</tr>
<tr>
<td>R22</td>
<td>443.2</td>
<td>228.4</td>
<td>1.940</td>
<td>98.6</td>
</tr>
<tr>
<td>R134a</td>
<td>221.5</td>
<td>139.4</td>
<td>1.589</td>
<td>120.3</td>
</tr>
<tr>
<td>R404A</td>
<td>394.7</td>
<td>257.5</td>
<td>1.533</td>
<td>124.7</td>
</tr>
<tr>
<td>R507</td>
<td>408.4</td>
<td>262.7</td>
<td>1.555</td>
<td>123.0</td>
</tr>
</tbody>
</table>
Interim summary

Different groups of refrigerants and their ozone-depletion and global warming potentials (IPCC, 2007)

<table>
<thead>
<tr>
<th>Substance group</th>
<th>Abbreviation</th>
<th>ODP</th>
<th>GWP</th>
<th>Example (refrigerant/foam blowing agent)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Saturated chlorofluorocarbons</td>
<td>CFC</td>
<td>0.6-1</td>
<td>4750-14,400</td>
<td>R11, R12</td>
</tr>
<tr>
<td>Saturated hydrochlorofluorocarbons</td>
<td>HCFC</td>
<td>0.02-0.11</td>
<td>77-2310</td>
<td>R22, R141b</td>
</tr>
<tr>
<td>Saturated hydrofluorocarbons</td>
<td>HFC</td>
<td>-</td>
<td>124-14,800</td>
<td>R32, R134a</td>
</tr>
<tr>
<td>Unsaturated hydrochlorofluorocarbons</td>
<td>u-HCFC</td>
<td>&lt;0.001</td>
<td>0-10</td>
<td>R123zd</td>
</tr>
<tr>
<td>Unsaturated hydrofluorocarbons</td>
<td>u-HFC</td>
<td>-</td>
<td>&lt;1-12</td>
<td>R1234yt, R1234ze, R1234yz</td>
</tr>
<tr>
<td>Natural refrigerants</td>
<td></td>
<td></td>
<td>0-3</td>
<td>R744 (carbon dioxide) R717 (ammonia) R290 (propane)</td>
</tr>
</tbody>
</table>

Green Cooling
- Natural refrigerants...
- Energy efficiency
Typical manufacturing cycle/life cycle

1. Adoption of Low Global Warming Impact Refrigerants (Examples)
   - Adopt optimal next-generation refrigerant for each type of air conditioner
   - Develop and manufacture air conditioners with less environmental impact by utilizing the characteristics of next-generation refrigerants

2. Stable Supply of Low Global Warming Impact Refrigerants (Examples)
   - Build distribution networks

3. Prevention of Refrigerant Leakage During Air Conditioner Use
   (Examples)
   - Raise technical level of air conditioner installation

4. Thorough Refrigerant Recovery
   (Examples)
   - During air conditioner repair, removal, and disposal

Flammability and Toxicity

Classification and more...
**Flammability of refrigerants**

- The question of refrigerant flammability is often raised when discussing low GWP refrigerant alternatives for the future.
- Flammability of a refrigerant is its ability to burn or ignite, causing fire or combustion. It is a property of a mixture in which a flame is capable of self-propagating for a certain distance.
- The degree of difficulty required to cause the combustion of a substance needs quantification.
- When the substance is flammable depends on the upper and lower flammability limits and the supplied energy for ignition.
- The consequences of the flammability event depend on the burning velocity, heat released and by-products of combustion.

**Lower flammability limit (LFL, % by volume or g/m³):** minimum concentration of the refrigerant that is capable of propagating a flame through a homogeneous mixture of the refrigerant and air under the specified test conditions at 23.0 °C and 101.3 kPa.

- At a concentration in air lower than the LFL, gas mixtures are too weak to burn. For example, Methane gas has a LFL of 4.4%. If the atmosphere has less than 4.4% methane, combustion cannot occur even if a source of ignition is present.

**Upper flammability limit (UFL):** is the highest concentration of a gas or a vapor in air capable of producing a flash of fire in presence of an ignition source (arc, flame, heat). Concentrations higher than UFL are ‘too rich’ to burn.
Minimum ignition energy and lower flame limit

- **Burning velocity** is velocity relative to the unburnt gas (normally in cm/s), at which a laminar flame propagates in a direction normal to the flame front, at the concentration of refrigerant with air giving the maximum velocity.

- **Heat of combustion** is the heat evolved from a specified reaction of a substance with oxygen.
Burning velocity and heat of combustion

Flammability and Toxicity
- Standards provide limitations and recommended practices on how to properly handle different refrigerants, including flammable ones.
- ASHRAE standard 34 "Designation and Safety Classification of Refrigerants" classifies refrigerants based on their flammability and toxicity characteristics.
- Non-flammable A1 to highly flammable A3, depending on refrigerant’s LFL value, heat of combustion and maximum burning velocity.
Auto ignition temperature

Approximate auto ignition temperatures

- R22 630 ºC
- R12 750 ºC
- R134a 740 ºC
- R290 465 ºC (Propane)
- R600a 470 ºC (Iso-butane)
- Oil 222 ºC

Flammability and Toxicity

Mildly flammable: a substance which burns at a velocity no greater than 10 cm/s. By comparison, Usain Bolt’s world record 100-metre time equates to 1043 cm/s, while hydrocarbons burn many times faster.
Flammability and Toxicity

<table>
<thead>
<tr>
<th>Classification</th>
<th>A3</th>
<th>A2</th>
<th>A2L</th>
<th>B2L</th>
</tr>
</thead>
<tbody>
<tr>
<td>Substance</td>
<td>Propane</td>
<td>HFC-152a</td>
<td>HFC-32</td>
<td>Ammonia</td>
</tr>
<tr>
<td>Burning velocity</td>
<td>39 cm/sec</td>
<td>23 cm/sec</td>
<td>6.7 cm/sec</td>
<td>7.2 cm/sec</td>
</tr>
<tr>
<td>Heat of combustion</td>
<td>46 MJ/kg</td>
<td>16 MJ/kg</td>
<td>9 MJ/kg</td>
<td>19 MJ/kg</td>
</tr>
</tbody>
</table>

The TEWI factor

- The Total Equivalent Warming Impact (TEWI) rating measures the efficiency of a refrigerant by combining its direct and indirect global warming contribution.
- It is expressed in kg of CO₂.
- TEWI = leakage rate + Recuperation Rate + Indirect emissions due to energy consumption
Leakage rate

- Leakage rate is the amount of greenhouse gases released into the atmosphere by the refrigeration system. It is given by the mass of refrigerant emissions in kilograms times the GWP of the refrigerant.

- Leakage Rate = Mass of refrigerant leaking from system × GWP of Refrigerant

- Typical leakage rates:
  - Hermetic compressor: 1 - 2%
  - Split units: 6 - 8%
  - Automotive air conditioning: 10 - 20%

Recuperation rate

- Recuperation rate = \( \text{GWP}_{\text{ref}} \times \text{Charge}_{\text{ref}} \times (1 - \text{recuperation factor}) \)

- Recuperation factor is the percentage of refrigerant recovered when a refrigeration or air conditioning equipment reaches the end of its useful life.
Indirect emissions

- Indirect emissions are emissions of CO₂ which occur by generation of electricity needed to run the RAC equipment during its lifetime.

  \[ \text{CO}_2 \text{ contrib} = \text{Machine life} \times \text{Energy cons. PA} \times \text{Emission factor} \]

- The emission factor is the amount of CO₂ released into the atmosphere when fuel is burned to produce one kWh of electricity.

Example of TEWI calculation

- Chiller unit running on R407c with a charge of 426 kg.
- Average leakage rate pa: 4 kg
- Lifespan of equipment: 25 years
- GWP of R407c: 1610 kg CO₂
- Average power rating of unit: 298.3 kW
- Chiller working on an average of 20 hours per day
- Recuperation factor assumed to be 50 %
Calculation of TEWI

- Leakage Rate = $4 \times 1610 \times 25 = 128,800$ kg CO$_2$
- Recuperation rate = $1610 \times 426 \times (1 - 0.5) = 342,930$ kg CO$_2$
- Indirect contribution due to energy consumption =
  
  $25 \times (298.3 \times 20 \times 365) \times 0.6 = 32,663,850$ kg CO$_2$

  \{Emission factor is assumed to be 0.9 for Mauritius\}

- TEWI factor for the chiller unit calculated over its lifetime of 25 years:
  
  $128,800 + 342,930 + 32,663,850 = 33,135,580$ kg CO$_2$

  This implies that the chiller will contribute to the equivalent of **33,135,580 kg of CO$_2$** over its useful life of 25 years.

- **Direct emissions = 1.4 % of the indirect emissions**

Conclusions

- In the aftermath of the Montreal protocol, HFC’s have predominantly replaced CFC’s and HCFC’s in RAC equipment.
- However, due to their high GWP, HFC’s are not a good replacement solution.
- The solution are the natural refrigerants:
  - Ammonia, Hydrocarbons and Carbon dioxide
- System need to have low TEWI factor
- High efficiency with ammonia and lower power consumption with hydrocarbons
Thanks!

Any questions?

You can write to me

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Thanks!