Alternative Refrigerants

Types of Refrigerants

1. HaloCarbons
2. Azeotropic Refrigerants
3. Zeotropic Refrigerants
4. Inorganic Refrigerants
5. Hydrocarbon Refrigerants

Halocarbon Refrigerants

- Halocarbon Refrigerant are all synthetically produced and were developed as the Freon family of refrigerants.

Examples :

- CFC's : R11, R12, R113, R114, R115
- HCFC's : R22, R123
- HFC's : R134a, R404a, R407C, R410a

Inorganic Refrigerants

- Carbon Dioxide
- Water
- Ammonia
- Air
- Sulphur dioxide

Azeotropic Refrigerants

- A stable mixture of two or several refrigerants whose vapour and liquid phases retain identical compositions over a wide range of temperatures.

- Examples : R-500 : 73.8% R12 and 26.2% R152
  R-502 : 8.8% R22 and 51.2% R115
  R-503 : 40.1% R23 and 59.9% R13

Zeotropic Refrigerants

- A zeotropic mixture is one whose composition in liquid phase differs to that in vapour phase. Zeotropic refrigerants therefore do not boil at constant temperatures unlike azeotropic refrigerants.
- Examples :R404a : R125/143a/134a (44%,52%,4%)

  R407c : R32/125/134a (23%, 25%, 52%)

  R410a : R32/125 (50%, 50%)

  R413a : R600a/218/134a (3%, 9%, 88%)

Hydrocarbon Refrigerants

- Many hydrocarbon gases have successfully been used as refrigerants in industrial, commercial and domestic applications.
- Examples: R170, Ethane, C_2H_6

  R290 , Propane C_3H_3

  R600, Butane, C_4H_{10}

  R600a, Isobutane, C_4H_{10}

  Blends of the above Gases

Important Dates in Refrigeration History

- 1834 : Jacob Perkins patented refrigeration by vapour compression which was based on the reverse Rankine cycle
- *Use of Natural Refrigerants:*

  1880's : NH_3, SO_2, CO_2, HC's
- Toxic and flammable refrigerants led to fatal accidents
- *Use of Synthetic Refrigerants: (Stability, Non-toxicity and efficiency)*

  1930 : R11, R12

  1936 : R22

  1961 : R507

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 (CO_2 produced by power stations)

Survey Of Refrigerants

Refrigerant	Group	Atmospheric life	ODP	GWP
R11	CFC	130	1	4000
R12	CFC	130	1	8500
R22	HCFC	15	.05	1500
R134a	HFC	16	0	1300
R404a	HFC	16	0	3260
R410a	HFC	16	0	1720
R507	HFC	130	1	3300
R717	NH3	-	0	0
R744	CO_2	-	0	1
R290	HC	< 1	0	8
R600a	HC	< 1	0	8

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 CO_2.

- TEWI = leakage rate + Recuperation Rate + Indirect emissions due to energy consumption

Leakage Rate

- Leakage rate is the amount of green house 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 x GWP of Refrigerant
- **Typical leakage rates**:

  Hermetic compressor : 1 - 2%

  Split units : 6 - 8%

  Automotive air conditioning : 10 - 20%

Recuperation Rate

- Recuperation rate = GWP_{ref} x $Charge_{ref}$ x (1 – 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 CO_2 which occur by generation of electricity needed to run the RAC equipment during its lifetime.

$CO_{2\ contrib}$ = Machine life x Energy cons. Pa x Emission factor

The emission factor is the amount of CO_2 released into the atmosphere when fuel is burned to produce one kWh of electricity. The emission factor for electricity varies from country to country and according to the primary source of energy.

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 CO_2
- 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 x 1610 x 25 = **<u>128 800 kg CO_2</u>**
- Recuperation rate = 1610 x 426 x (1 – 0.5) = **<u>342 930 kg CO_2</u>**
- Indirect contribution due to energy consumption =

  = 25 x (298.3 x 20 x 365) x 0.6 = **<u>32 663 850 kg CO_2</u>**

  {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 **<u>33 135 580 kg of CO_2</u>** over its useful life of 25 years.

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

Improving TEWI of a System

- Using refrigerant with lower GWP
- Eliminating leakages in the system
- Improving the electrical efficiency of the system

What are the Alternatives ?

HFC's are definitely not a good option for the replacement of CFC's and HCFC's

The best choices from an environmental point of view are the natural refrigerants:

- Ammonia
- Hydrocarbons
- Carbon dioxide : Mainly for Vehicle AC and mobile refrigeration

Carbon Dioxide 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
- Zero ODP and negligible GWP
- Good substitutes for CFC's, HCFC's, and HFC's.
- Drop in solution
- Compatible with copper
- Miscible with mineral oil
- A third of original charge only is required when replacing halocarbons refrigerant in existing equipment
- Energy saving : up to 20% due to lower molecular mass and vapour pressure

Drawback :

- Flammable

Introduction to HC's

- HC refrigerants were first used in the late 1800's/early 1900's
- They are naturally occuring
- They have zero ODP and Minimal GWP
- They are compatible with most lubricants
- They are 'more' compatible with materials normally used in the industry
- HC's can reduce/eliminate acids forming

Introduction to HC's

- HC's are more efficient than chemical refrigerants
- MACS
- Domestic Refrigeration and Air Conditioning
- Commercial/Industrial Refrigeration and Air Conditioning
- Exceptions Flooded evaporator and Centrifugal

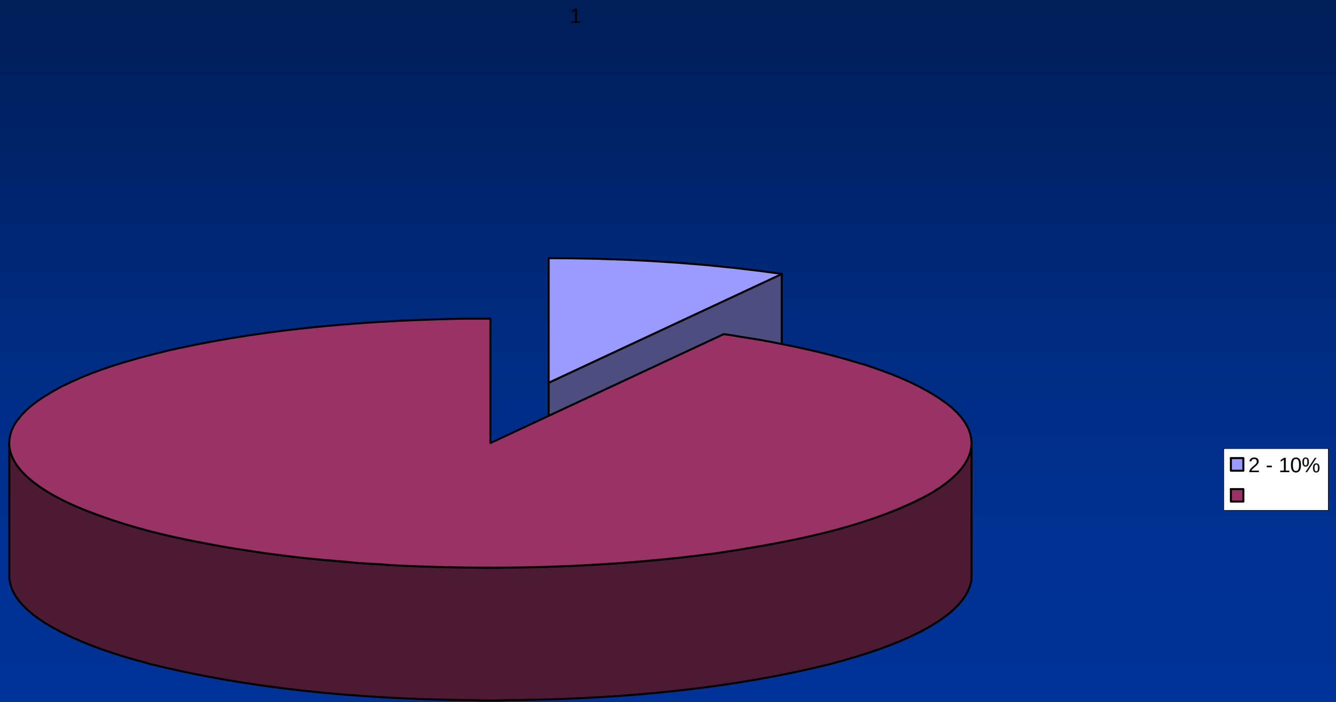
WHY Does It Work?

Characteristic/ Refrigerant /Commercial	R22	HR22
Class Classification	**HCFC**	**HC**
Molecular Formula	**$CHClF_2$**	**CH_3CH_3 + $CH_3CH_2CH_3$**
Molecular Mass	86.5	41.1
Critical Temperature (°C) [2]	96.2	> 130
Boiling Point (°C)	- 41	- 42
Refrigerant Efficiency (J/g)	160.8	359.1
Lubricant Miscibility	**Mineral**	**All Type**

Flammability

- ALL refrigerants are flammable at some point
- Lubricants, heated and under pressure have a lower flash point to refrigerant
- Source of ignition, Air, Fuel
- Most HC’s are only flammable at between 2 and 10% when mixed with air

Flammability



ONLY BETWEEN 2% AND 10%

Flammability

- Approximate auto ignition temperatures
- R22 630 ºC
- R12 750 ºC
- R134a 740 ºC
- R290 465 ºC
- R600a 470 ºC
- **Oil** **222 ºC**

Flammability

- When HC’s burn they produce carbon and steam
- When chemical refrigerants burn they ALL produce highly toxic fumes.

Modifications of Electrical Equipment

- Replaced with solid state equivalents
- Sealed to ensure that any sparks do not come into contact with leaking gas
- Relocated to a position where the component would not come into contact with leaking gas

Modifications of Electrical Equipment

- Faulty components.
- Poor, corroded, loose, or dirty electrical connections.
- Missing or broken insulation which could cause arcing/sparks.
- Friction sparks, like a metal fan blade hitting a metal enclosure.

Modifications of Electrical Equipment

- Modifications must meet local regulations and standards

Ammonia – A Natural Refrigerant

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

Natural production	3000 million tons/year
Production in factories	120 million tons/year
Used in refrigeration	6 million tons/year

Advantages of using Ammonia as Refrigerant

- ODP = 0
- GWP = 0
- Excellent thermodynamic characteristics: small molecular mass, large latent heat, large vapour density and excellent heat transfer characteristics
- High critical temperature (132C) : 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

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

Refrigeration Properties of NH_3

Evaporation enthalpy 0 ^{o}C	1262 KJ/KG
Pressure at 0 ^{o}C	4,9 bar
Pressure ratio 0/35 ^{o}C	3,15
COP 0/35 ^{o}C	6,77
Discharge temperature 0/35 ^{o}C	81 ^{o}C
Volumetric refrigerating capacity	3800 KJ/m^{3}
Volumetric refrigerating capacity of R134a	2000 KJ/m^{3}

Energy efficiency – Reciprocating compressor

Performance Grasso 612: t-evap = -10 ^{o}C; t-cond = 35 ^{o}C				
Refrigerant	**Refrigerating capacity**	**Shaft power**	**COP**	**1/COP**
[-]	[kW]	[kW]	[-]	[%]
R717 (NH_3)	425.8	112.9	3.771	100.0
R22	380.3	121.3	3.135	120.3
R134a	218.8	74.7	2.929	128.7
R404A	352.4	132.6	2.658	141.9
R507	356.7	136.0	2.623	143.8

Energy efficiency – Screw compressor

t-evap = -30 ^{o}C; t-cond = 35 ^{o}C				
Refrigerant	**Refrigerating capacity**	**Shaft power**	**COP**	**1/COP**
[-]	[kW]	[kW]	[-]	[%]
R717 (NH_3)	435.9	228.0	1.912	100.0
R22	443.2	228.4	1.940	98.6
R134a	221.5	139.4	1.589	120.3
R404A	394.7	257.5	1.533	124.7
R507	408.4	262.7	1.555	123.0

General Safety measures for refrigerating plants

- **Reduction of refrigerant contents:**
  - Components with reduced contents
  - Indirect systems with secondary refrigerant: distinction between generation and transport of cold

- **Scheduled maintenance and leak testing**

- **Governmental surveillance –** Refrigerant Audits for

  systems operating with HFC's. Recovery, Stock of used refrigerants, Recycling of refrigerants.

- For the Netherlands, the combined measures resulted in a leak rate reduction of 35% (1995) to 8% (2001) for R22-systems

Conclusions

- In the aftermath of the Montreal protocole HFC's have predominantly replaced CFC's and HCFC's in RAC equipment.
- 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