ASHRAE

ASHRAE MACAO CHAPTER
DL TALK
11th Dec 2018

Beyond Refrigerants: What's in store after HFOs & Naturals?

Ir TL CHEN DL&F.ASHRAE
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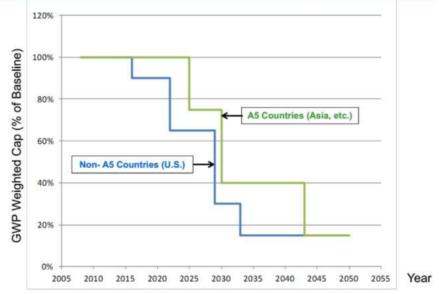
North American Proposal for HFC Phase-down



Synopsis

The first generation of refrigerants was all about accepting anything that works - the era of Natural refrigerants

The second generation came about to address concerns on safety (flammability), toxicity & durability - the era of Synthetic refrigerants

The third generation refrigerants sought to protect our ozone layer - the demise of CFCs followed by HCFCs

Today's fourth generation seeks to arrest global warming - completing the circle back to the first generation refrigerants

So what's next after HFOs and Naturals ?

Are we ready and prepared to move past the era of Synthetics and Naturals to a future of Non Rs ?

History of Refrigeration & Airconditioning

- 1830s - Jacob Perkins - vapor compression (ether)
- 1851 - John Gorrie - patent for air cycle
- 1859 - R-717 / R-718 (ammonia/water)
- 1866 - CO_2 - marine applications
- 1873 - R-717 (ammonia) commercial refrigeration - Carl Linde
- 1875 - R-764 (sulfur dioxide)
- 1920s -R-600a (isobutane) & R-290 (propane)
- 1922 - Willis Carrier - R-1130 (dielene)
- 1926 - R-30 (methylene chloride)

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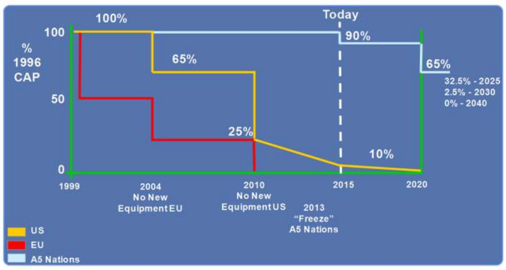
Montreal Protocol Agreement for Reducing ODP Refrigerants: R-22 Phase-out Timeline



Common Refrigerants in 1920s

• Ammonia (R-717)	NH_3
• Carbon Dioxide	CO_2
• Sulfur Dioxide	SO_2
• Hydrocarbons	C_nH_m
• Methyl Chloride	CH_3Cl
• Water	H_2O

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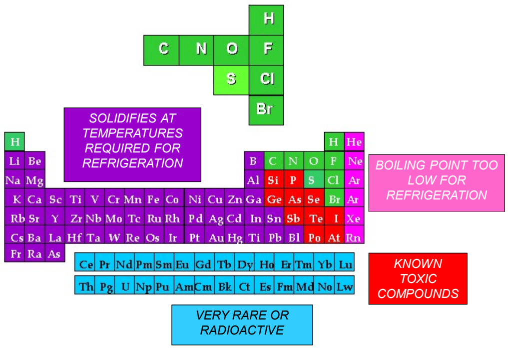
EARLY REFRIGERANTS ARE EITHER **FLAMMABLE** OR **TOXIC** !

THE PERIODIC TABLE



Challenge to Find Refrigerants

(before ODP & GWP)

- Non-flammable
- Good Stability
- Low Toxicity
- Atmospheric Boiling Point between -40^{0}C & 0^{0}C

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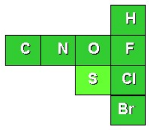


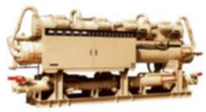
From these elements,
CFC refrigerants were formulated.

How are Refrigerants selected?

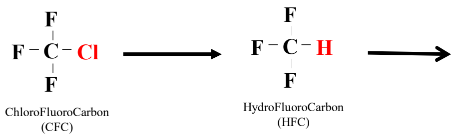
The Periodic Table

1931	CFC R12
1932	CFC R11
1936	HCFC R22
1980s	CFC, HCFC R123

CFC and HCFC extensively used as refrigerants in air-conditioning systems



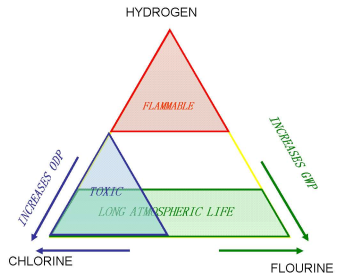
What are the potential replacements?
(post ODP & GWP)



Refrigerant			Property				
			Capacity ratio /gas volume	Condensation pressure kPa.a	ODP	GWP	Safety
<reference>	R22	single	100	1943	0.034	1900	O
Substitute Refrigerants	R134a	single	62	1319	0	1600	O
	R407c	Non-azeotropic	98	2111	0	1980	O
	R410a	Quasi-azeotropic	140	3066	0	2340	O
Other Refrigerants	R32	single	162	3141	0	880	△ (low inflammability)
	Propane	single	82	1713	0	3	X (high inflammability)
	Ammonia	single	118	2033	0	0	X (high inflammability; toxic)
	CO_2	single	153	5722	0	1	O

Advantage | Disadvantage

Group	Name	Elements	Commercial Name
CFC	ChloroFluoroCarbon	Chlorine, Fluorine, Carbon	R-11, R-12
HCFC	HydroChloroFluoroCarbon	Chlorine, Fluorine, Hydrogen, Carbon	R-22, R-123
HFC	HydroFluoroCarbon	Fluorine, Hydrogen, Carbon (alkane)	R-134a, R-32
HFO	HydroFluoroOlefin	Fluorine, Hydrogen, Carbon (alkene)	R-1234yf



SELECTING REFRIGERANTS (post Montreal Protocol)

- ✓ ***Physical Consideration***
  - Operating Pressure & Temperature
  - Critical Point
  - Normal Boiling Point
  - Bubble & Dew Point Temperature
  - Fractionalization (Temperature Glide)
  - Flammability
  - Toxicity
  - Operating Pressure
  - Lubrication
- ✓ ***Environmental Consideration***
  - Ozone Depletion Potential (ODP)
  - Global Warming Potential (GWP)
  - Atmospheric Lifetime
- ✓ ***Efficiency***
  - COP

2018
The World Scenario:

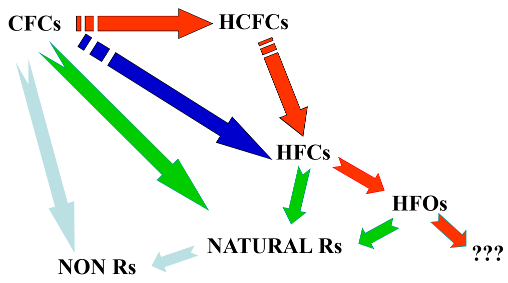
- CFCs successfully phased out (circa 2000)
- HCFC phase out program in progress
- HFC phase down commenced
- Low GWP and mildly flammable HFC/HFOs coming on stream
- HFOs gearing up to replace high GWP HFCs
- Natural refrigerants progressing at varying pace

2018

The Malaysian Scenario:

- CFC gone and dusted
- HCFC phase out program in place
- HFC phase down schedule on the way
- Naturals (HC) increasingly creeping on board
- HFC-32 introduced in Indonesia still to make its mark
- HFC-134a, HFC-410a are prevalent
- HFOs beginning to appear
- RRR practice remains insignificant
- HCs for domestic refrigerators are finally here (2017)!!

RECAP (1990):
Did we jump out of the frying pan into the fire?



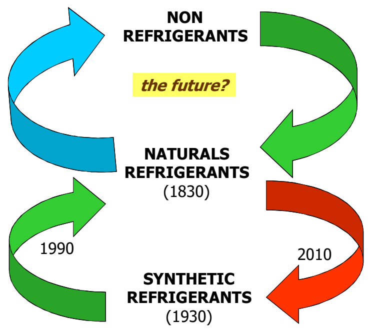
Overview - Advent of Flammable Refrigerants

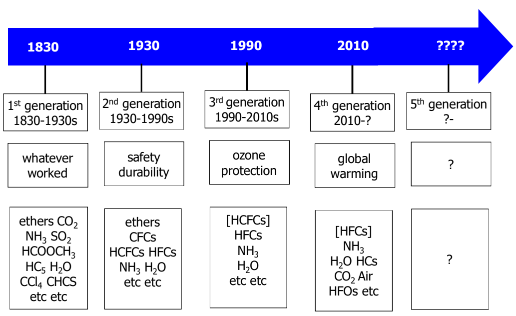
The first generation of refrigerants was all about accepting anything that worked - heralding the era of Natural refrigerants

The second generation addressed concerns on safety (flammability), toxicity & durability - the era of Synthetic refrigerants

The third generation refrigerants sought to protect our ozone layer - the demise of CFCs followed by HCFCs

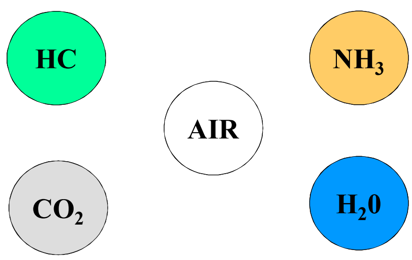
Today's fourth generation seeks to arrest global warming - completing the circle back to the first generation refrigerants



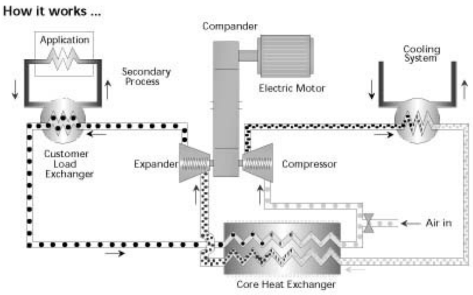


Refrigerant Progression

The Natural Five



AIR Refrigeration Cycle



Refrigerant Options Available in Future

Refrigerant	Self-contained Reach-in	Walk-in	Rack Refrigeration
Today Tomorrow	R404A R134a	R404A (R407A)	R404A R407A
<1,500 GWP Non-Flammable	R448A, R449A R450A, R513A R134a, etc	R448A, R449A R450A, R513A R134a, etc	R448A, R449A R450A, R513A R134a, etc
<300 GWP Mildly Flammable	R32+HFO Blends	R32+HFO Blends	R32+HFO Blends
<150 GWP Mildly Flammable	R32+HFO Blends	R32+HFO Blends	-
<10 GWP	Propane <150 gm HFO	CO2, Propane, HFO	CO2

Once a refrigerant is in production and SNAP approved, expect two to six years for all components and equipment to be available

AIR as Refrigerant

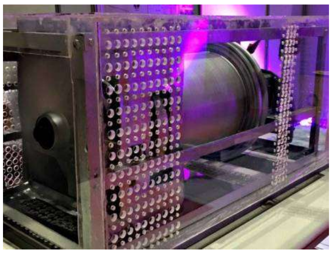
Application: Ultra low temperature (- 58^{0}F to - 148^{0}F)

- Cold storage for tuna/bonito
- Blast freezing for meat & other food products
- Freeze-drying
- Frozen milling in home appliance recycling process
- Semiconductors
- Medical and chemical industry

The Non Rs

Magnetic

Thermoacoustic



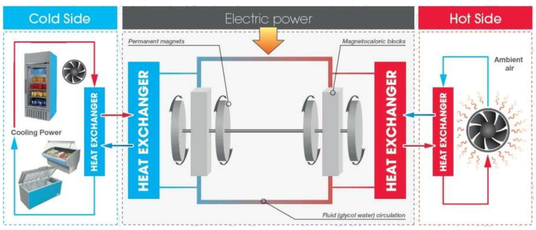
Air as Refrigerant

Instead of using a cooling medium, Palma's AC uses low compression and a high volume of air molecules as refrigerant replacement.

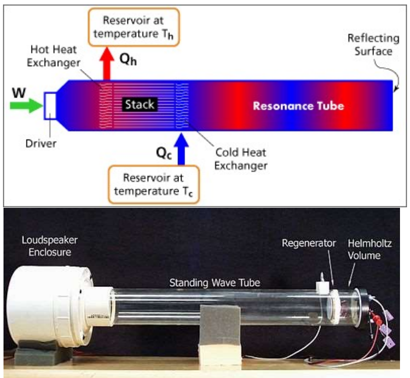
August 2018

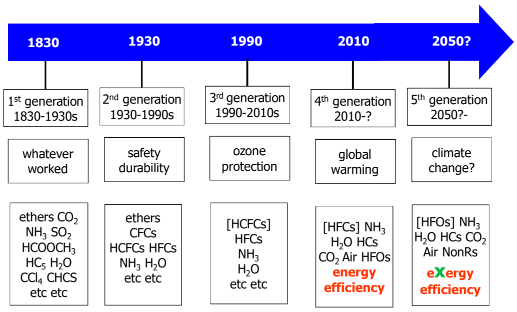
The heart of Yza Palma's AirDisc is a centrifugal compressor that uses rotating concentric air tanks with air inlets that continuously take in enough air molecules from a room for compression. The heat generated from the air compression is separated while the compressed air molecules with less heat are allowed to expand. This process effectively and continuously lowers the room temperature. *Philippine Star*

Magnetic Refrigeration



Thermoacoustic Refrigeration





Refrigerant Progression

LIFE SPAN

- **CFCs** about 50 years (now ended)
- **HCFCs** about 25 years - 10 years to go
- **HFCs** about 50 years - 35 years to go?
- **HFOs** about to begin life for the next 50 years?
- **HCs** 100 years the first time - now reborn
- **CO_2** since 1830 but never seriously took off
- **NH_3** since 1830 - now with renewed interest
- **H_2O** since 1830 - with its own niche market
- **Air** since 1850 - now with renewed interest
- **Magnetic** prototype in 1999 yet to commercialise
- **Sound** prototype in 2004 yet to commercialise
- **?** ???

Forecasting the future trend

Synthetic Refrigerants

- HFCs will be replaced by mildly flammable HFCs and HFOs and some other synthetics thereafter
- Any accelerated phase-out of each successive synthetics will be dictated by the Chemical Giants (not by any government)
- Cars (new) will be expected to convert to HFO rather than HC or other naturals

Table 1. Candidates Components	
candidates	**considerations**
"natural refrigerants" (NH_3, CO_2, HC_s, H_2O, air)	efficiency, for NH3 and HCs also flammability
low GWP HFCs (R-32, R-152a, R-161, ...)	flammability; most suppressants have high GWP
HFEs	disappointing thus far, still ?
HCs, HEs (R-290, R-600, R-E170, ...)	flammability
unsaturates (olefins) (R-1234yf, ...)	short atmospheric lifetime and therefore low GWP flammability? toxicity? compatibility?
HFICs, FICs (R-31I1 (CH2FI), R-13I1 (CF3I), ...)	expensive, ODP→0 but not in MP some are toxic; compatibility?
fluorinated alcohols (-OH) **fluorinated ketones** (-(C=O)-)	efficiency? flammability? toxicity? compatibility?
others	??? — no ideal refrigerants

Table 1: Candidates and Blend Components for Low GWP Refrigerants

Natural Refrigerants

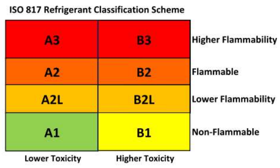
- Certainly European-led and it is heartening to note that the pace has been maintained if not increased since 1997
- Ammonia chillers for high-rise and commercial buildings are already established but ....
- HC airconditioners are prevalent in Scandinavian countries for the last decade
- HC domestic refrigerants are the norm in Europe; in Japan since 2005 .... and finally in Malaysia in 2017!!

MS on Flammable Refrigerant System

The need for this MS 2678 was initiated by the Fire & Rescue Department of Malaysia ....

.... more than 15 years after the author first presented HC (flammable) refrigerant to the local industry in Jan 2000

- Developing and under-developed nations of Asia and Africa will have little say, and for all intents and purposes will dutifully follow the World Bank directives so long as subsidies are given
- Resistance to flammable refrigerants appears to be finally receding with a newly created category of mildly flammable refrigerants (Class A2L)...... that is because Synthetics are involved and certainly not because of the non-patented HFC-32 but rather the patented HFOs!



Flammable Refrigerants

Refrigerant No.	Refri Prefix	Chemical Name	Formula	Safety Group
R32	HFC	methylene fluoride	CH_2F_2	A2L
R50	HC	methane	CH_4	A3
R142b	HCFC	chloro difluoroethane	CH_3CClF_2	A2
R143a	HFC	trifluoroethane	CH_3CHF_3	A2L
R152a	HFC	d fluoroethane	CH_3CHF_2	A2
R170	HC	ethane	CH_3CH_3	A3
R-E170		dimethyl ether	CH_3OCH_3	A3
R290	HC	propane	$CH_3CH_2CH_3$	A3
R600	HC	butane	$CH_3CH_2CH_2CH_3$	A3
R600a	HC	isobutane	$(CH_3)_2CHCH_3$	A3
R601	HC	pentane	$CH_3CH_2CH_2CH_2CH_3$	A3
R702		hydrogen	H_2	A3
R717		ammonia	NH_3	B2L

R&D for Non R Technologies

- The key for R & D unfortunately is dictated by USA
- Both government and private funding will be needed to advance on researching the technology of air, magnetic and sound refrigeration
- The former funding is more likely to appease the Europeans to prove there is concern for the natural climate, whilst the latter funding is likely to be individuals or organisations who truly believe in the cause.

Flammable Refrigerants

Refrigerant No.	Refri Prefix	Chemical Name	Formula	Safety Group
R1150	HC	ethylene	$CH_2=CH_2$	A3
R1234yf	HFO	tetrafluoropropene	$CF_3CF=CH_2$	A2L
R1270	HC	propylene	$CH_3CH=CH_2$	A3
R403A		R290/22/218		A1/A2
R406A		R22/600a/142b		A2/A2
R411A, R411B, R412A, R413A, R415A, R415B, R418A, R419A, R429A, R430A, R431A, R432A, R433A, R433B, R433C, R435A, R436A, R436B, R437				

- As for the Development part, this will certainly be artificially curtailed and delayed as long as possible, for obvious commercial reasons
- There will likely be **no quantum leap** in commercialization until the capital cost and more for setting up HFC plants (next HFO plants) are fully recovered, and each time-line is at least 20 years or more
- It is the author's prediction (and fervent hope) that synthetic refrigerant manufacturers will invest in the development of non refrigerant technologies as an **insurance** against the success of natural refrigerants which are **non patentable** and hence cannot be monopolized

CONCLUDING REMINDER

- Why let 1% continue to dictate 99%?
- Cooling due to chillers account for only 15% of our local market
- Refrigerant Efficiency rather than Hardware Efficiency will continue to rule aka Energy Efficiency instead of Exergy Efficiency

the end

THANK YOU

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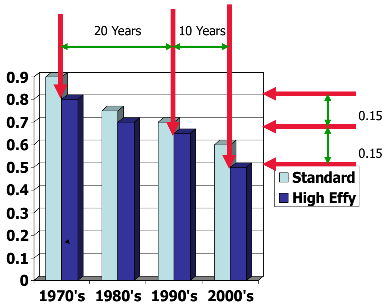
Thermal Efficiency Progression
Chiller Efficiency : kWe/RT



caution on misLEADERS!

ODP GWP ... refrigerants

CDM aka Carbon Trading

Y2K fiasco