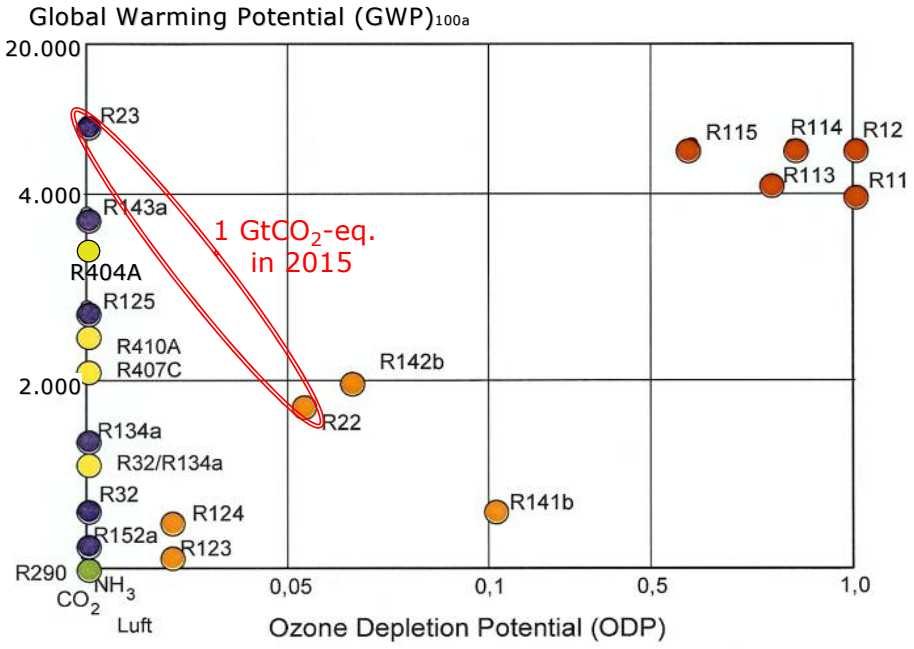
Fremtidens Kølemidler

Themadag 03.09.2007
Køleløsninger efter 1. januar 2007

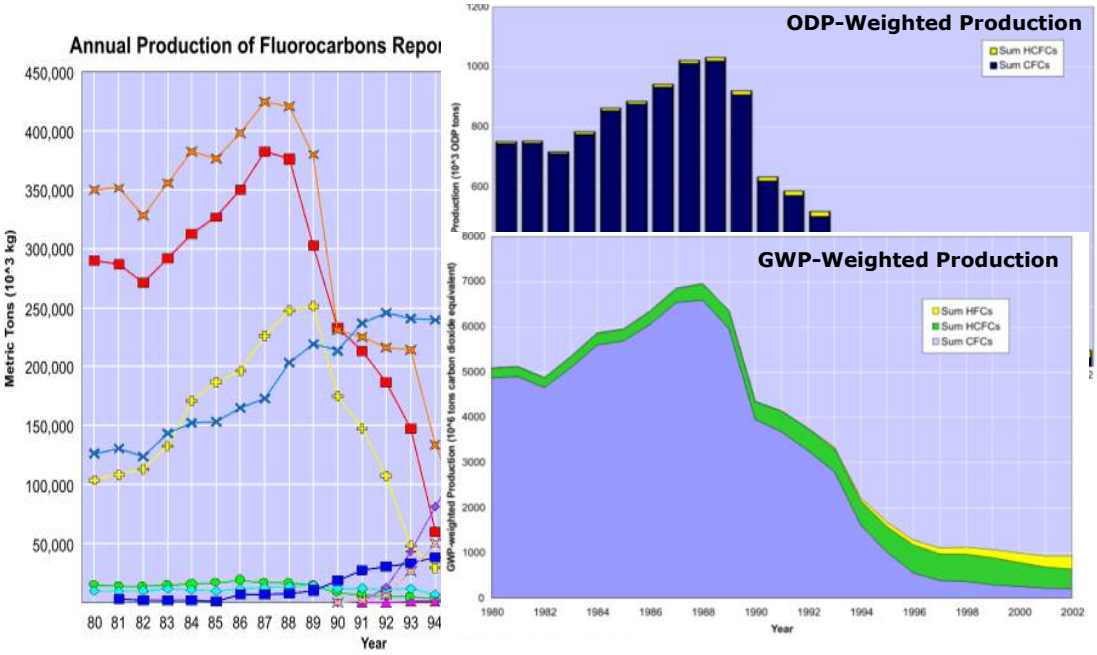
Dr.- Ing. Jürgen Süss
Advanced Engineering
Danfoss A/S, Nordborg

Aarhus, 3. September 2007

Ozone Depletion and Global Warming



CFC and HCFC phase-out achievements



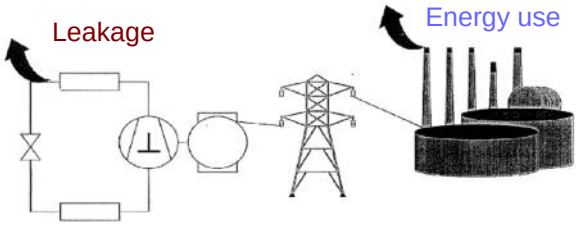
CFC, HCFC and other Montreal Protocol gases phase out has eliminated more than 5 Gigatons of CO2 equivalent (more than 25 % of all GHG emissions compared to 1990)

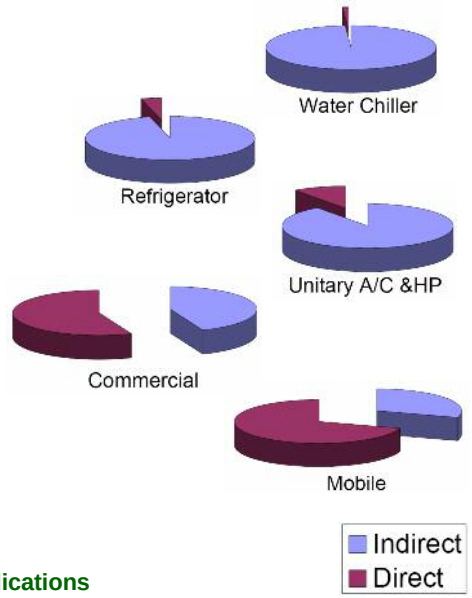
Refrigerants: Status of Regulations

Global Regulat	Regional implementation			
Montrea Ozone dep (ODP =0)				
Kyoto Protocol Global warming issue	F Gas Reg No. 842/2006 Applied July 4,2007 "minimization of GHG emission" leak preventive & checks, refrigerant & service records			Asia*

GHG emissions from refrigeration industry

- Direct Emissions
  - Refrigerant leakage
- Indirect Emissions
  - Energy use due to system operation

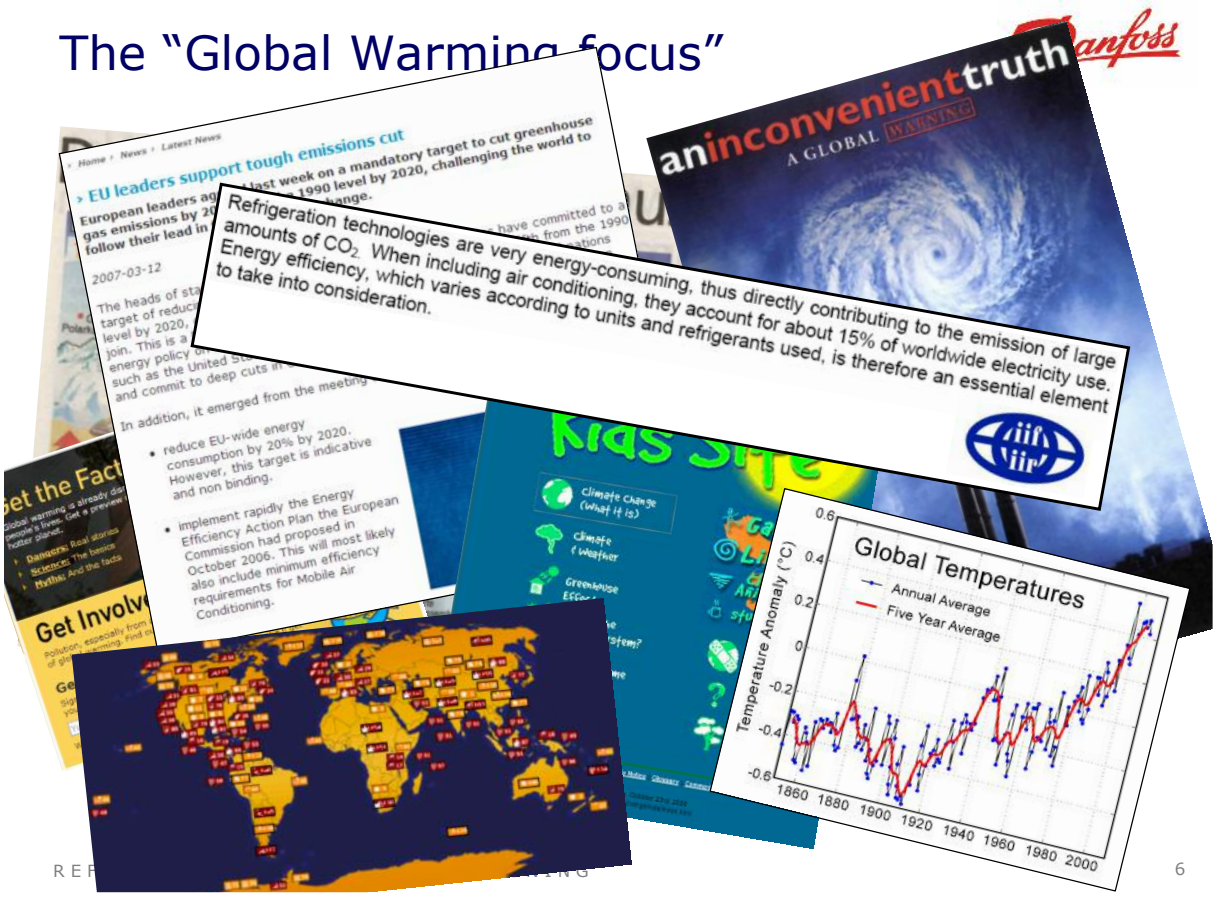




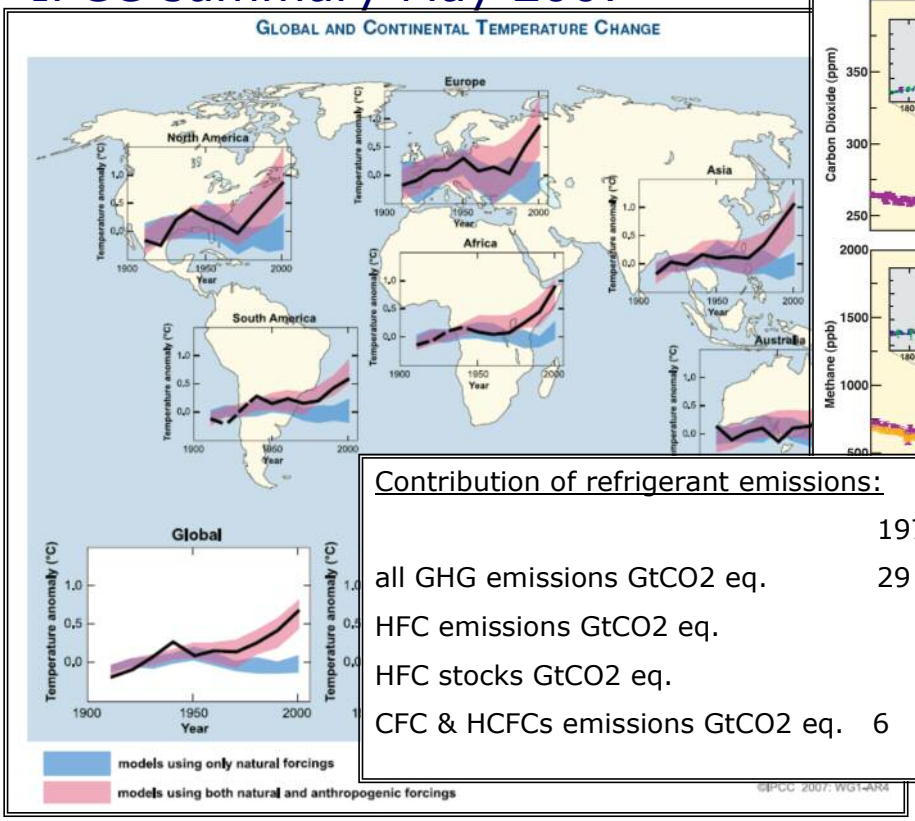
In stationary applications
indirect emissions are larger than
direct emissions due to refrigerant leakage

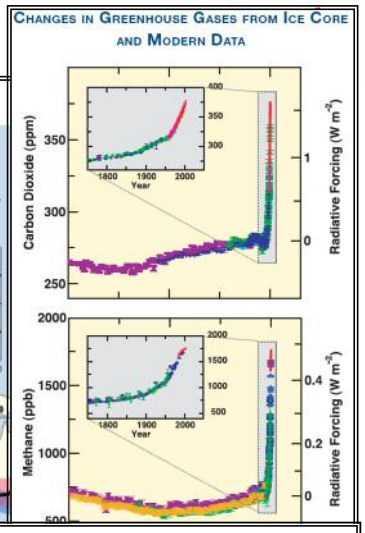
(Sources: IIF/IIR, AFEAS, DOE)

The "Global Warming focus"



IPCC summary May 2007





Contribution of refrigerant emissions:

	1970	2004
all GHG emissions GtCO2 eq.	29	50
HFC emissions GtCO2 eq.		2,5
HFC stocks GtCO2 eq.		21
CFC & HCFCs emissions GtCO2 eq.	6	3

Principles of refrigeration
or the potential of “not in kind technologies”

Reverse Rankine ← Process still offers highest energy efficiency

Stirling

Magneto caloric refrigeration

Vortex tube

Joule process

Peltier

Steam ejector

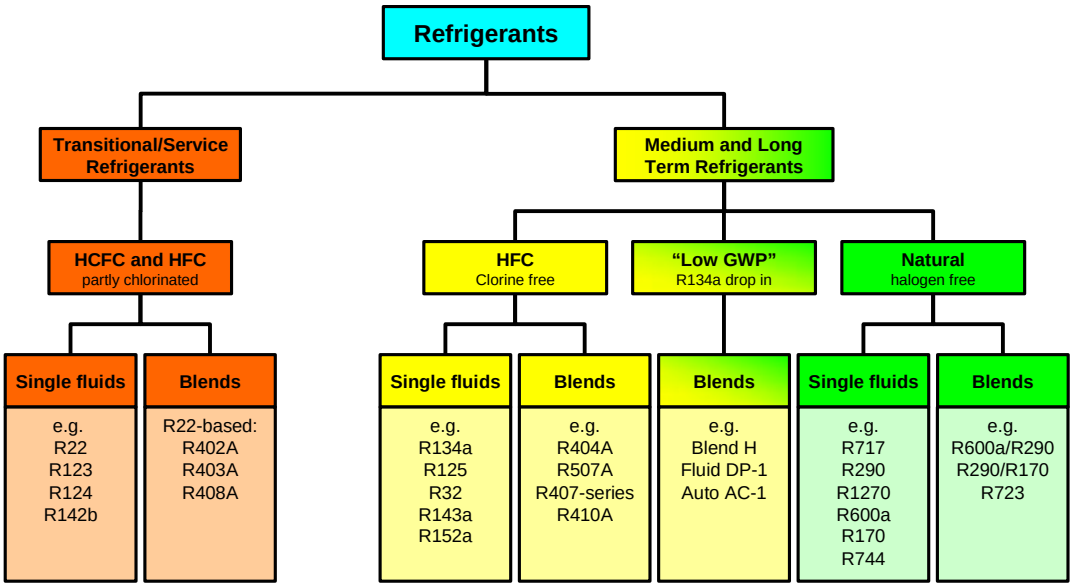
Absorption

Adsorption

…

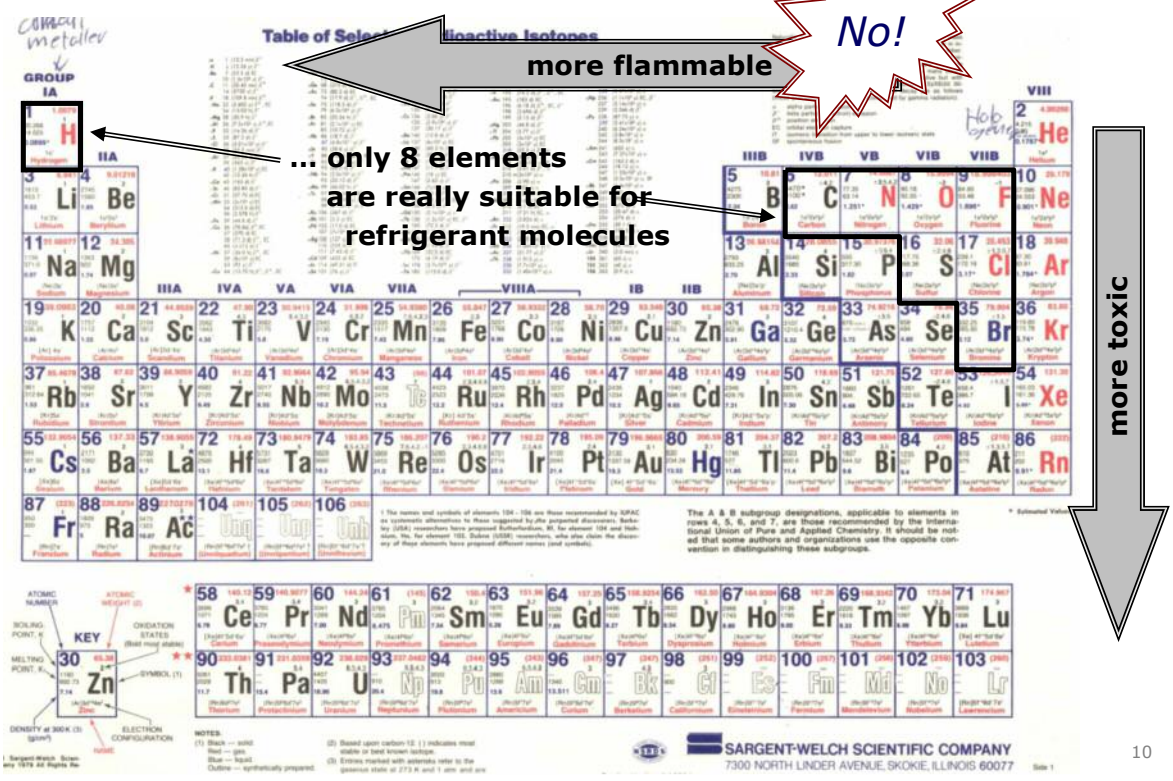
But which refrigerants should be used???

Refrigerant options

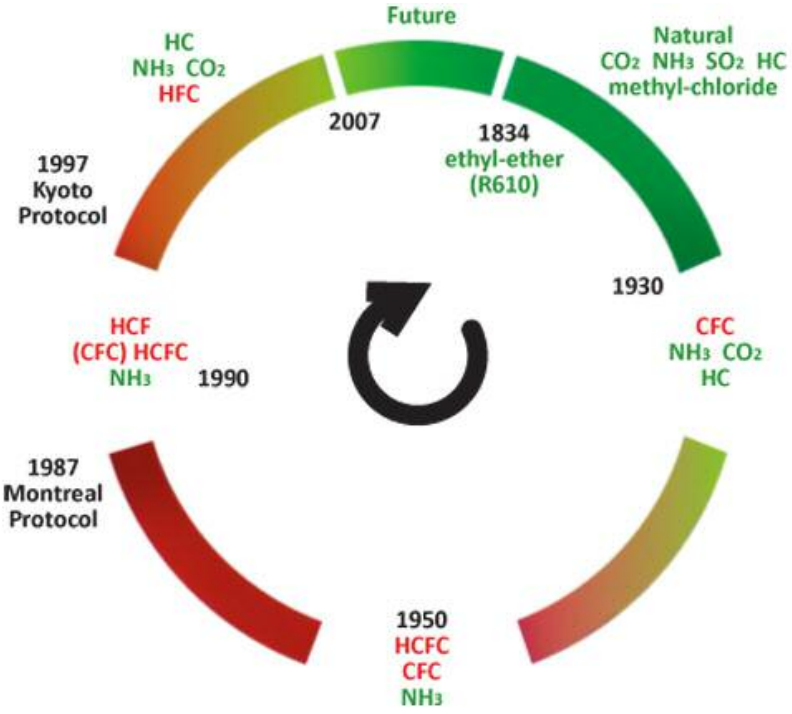


The choice of the refrigerant
has an impact on the (energetic) systems performance and reliability

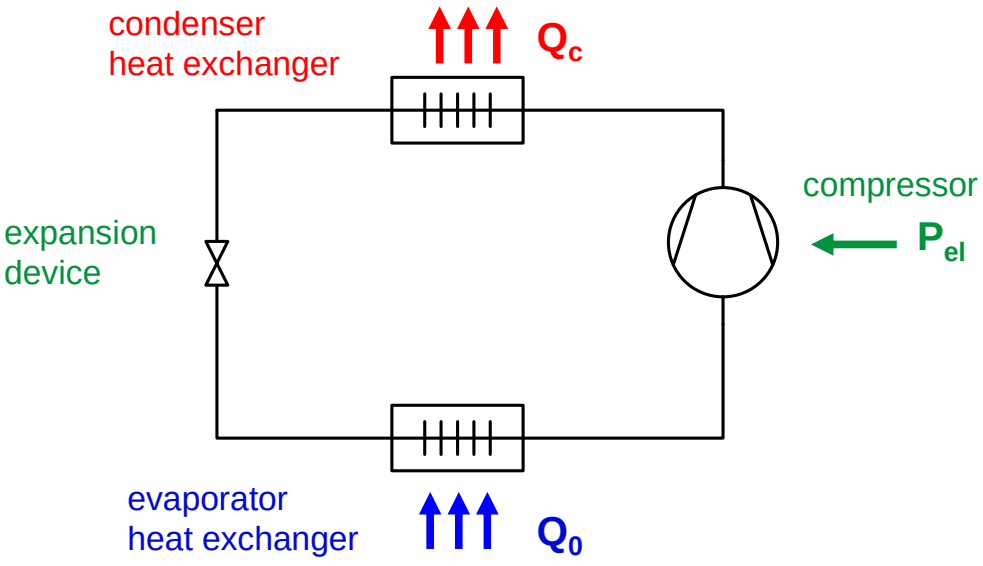
Is there a refrigerant *Wild Card*?



Refrigerants yesterday & today and in future?



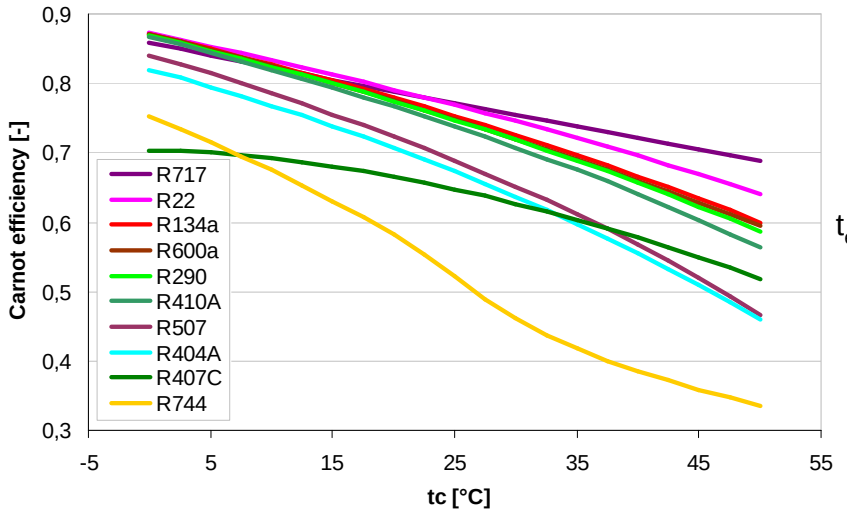
Reverse Rankine Cycle (conventional system)



Main energetic losses of the Reverse Rankine Cycle (in case technology is used right – normally it isn't)

Compressor losses	⇨	depend on compressor efficiency
Heat exchangers losses	⇨	depend on heat exchanger efficiency / size
Expansion losses Superheat losses	}	depend on refrigerant and system configuration

Expansion & Superheat losses



t_{evap} = -35°C

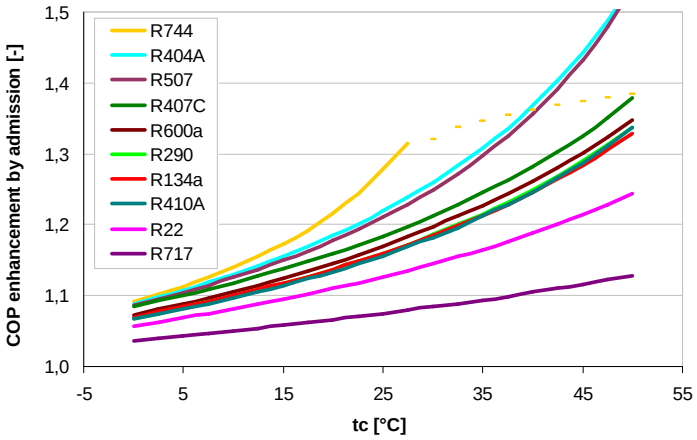
Poor thermodynamic performance of a refrigerant has to be compensated with enhanced component efficiency or system configuration

Performance enhancement of reversed Rankine Cycle

Internal admission
(economizer)

External admission
(two stage system with economi

No one wants to save energy,
but everybody wants to save money…



… and about the double as the enhancement of capacity…

Derived main potentials to minimize GHG emission from refrigeration industry

- Use the available technologies right - chose right components and service them
- Ensure most energy efficient system operation by adding intelligence:
  - detecting faults that increase efficiency losses and refrigerant leakage
  - detecting improper user behaviour
  - continuously search for the energy optimal operation point for the system
- Minimize refrigerant charge
- Enhance system tightness
- Enhance component efficiency
- Enhance system configuration
- Apply refrigerants with low GWP

Future Refrigerant Mix by application

AREA	APPLICATION	GLOBAL TRENDS
REFRIGERATION	Domestic	R134a R600a
	Light commercial	R134a, R404A R290, R744 (T)
	Commercial	R134a, R404A R744 (S+T)
	Industrial	R404A R717, R744 (S)
AIR CONDITIONING	Residential	R407C, R410A R290, R744 (T)
	Light commercial	R407C, R410A R290, R744 (T)
	Commercial	R134a, R410A R717, R290, R1270
HEAT PUMPS	Domestic	R407C, R410A R290, R744 (T)
	Industrial	R407C, R410A R717, R290, R744 (T)

Fluids:

R600a	Isobutane
R290	Propane
R744	Carbon Dioxide
R717	Ammonia

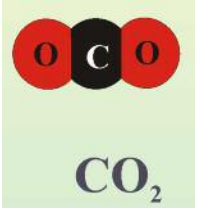
NOTE FOR R744:

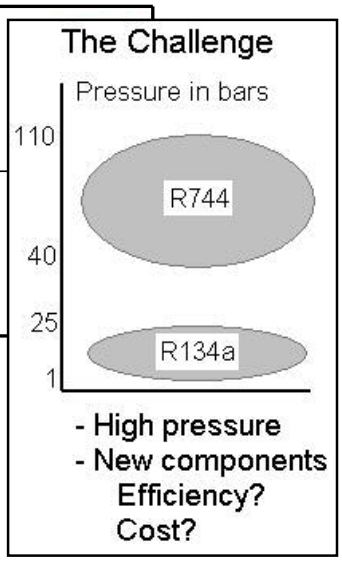
S	Subcritical
T	Transcritical

What about CO_2?

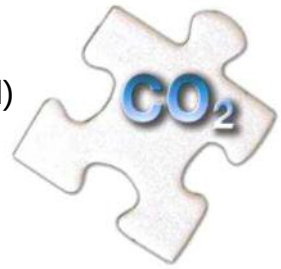
Environment - OK
- Refrigerant phase outs
- Companies policy
- Natural substance ✓

Safety - (OK)
- High concentrations ?
- High pressure ?
- Non flammable or toxic ✓



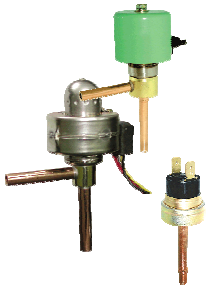


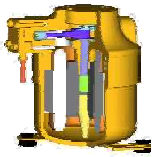
CO_2 activities at Danfoss

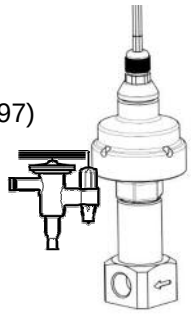


- Low pressure applications (Sub-critical)
  - Commercial controls and line components
  - Compressor tests

- High pressure applications (Transcritical)
  - RACE and COHEPS: EU funded CO_2-projects (1993-1997)
  - Controls R&D with > 70 partners (since 1998)
  - Compressor development (since 2001)
  - Danfoss Saginomiya Joint Venture (2002)







Investigated CO_2 applications

Food Retail
Sub critical CO2 applications

Valves, Controls, Driers and Safety equipment

Industrial
Sub critical CO2 applications

Valves, Controls, Driers and Safety equipment

Food Retail
Transcritical CO2 applications

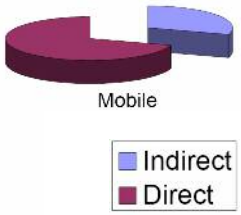
Controls

Heat Pumps & Bottle Coolers
Transcritical CO2 applications

Compressors, controls and complete cooling cassettes

The main objectives of MACs Directive

- The **control of leakage** of certain fluorinated greenhouse gases with a global warming potential (GWP) higher than 150 in MACs
- The **prohibition** of MACs using those gases from a certain date



CONTROL OF LEAKAGE – *(Art. 5.2 and 5.3)*

Leakage rate of F-gases with GWP>150

- not exceeding 40 grams/year for single evaporator system
- not exceeding 60 grams/year for dual evaporator system

From the date

- 12 months after the test procedure has been adopted (or 1 January 2007) for **new types of vehicles**
- 24 months after the test procedure has been adopted (or 1 January 2008) for **all new vehicles**

PHASE – OUT OF MACs DESIGNED TO USE F-GASES WITH GWP>150 - *(Art. 5.4 and 5.5)*

- From 1 January 2011 for **new types of vehicles**
- From 1 January 2017 for **all new vehicles**

RETROFITTING AND REFILLING - *(Art. 6)*

- Retrofitting with certain MACs not allowed from 2011 / 2017
- MACs refilling with F-gases with GWP > 150 not allowed from 2011/2017
  Exception for systems fitted before that date
- Provision for service providers (abnormal leak)

http://ec.europa.eu/enterprise/automotive/pagesbackgroud/pollutant_emission/index.htm#macs

INTERNATIONAL Herald Tribune

German auto industry to drop research on environmentally harmful cooling agents

The Associated Press
Tuesday, July 31, 2007

German carmakers choose R744

Industry insiders confirmed that German car manufacturers have decided to choose CO_2 (R744) for next generation mobile air conditioning systems. Grouped under the VDA, German manufacturers have also decided to stop all developments on new chemical blends.

2007-07-27

According to three reliable industry sources, the German Automotive Industry Association (VDA) has recently come together to choose CO_2 (R744) as the replacement to the current refrigerant, HFC 134a, in mobile air conditioning. This decision effectively puts an end in Germany to long discussions about which systems to choose to comply with the EU Directive banning high global warming refrigerants as from 2011.

Given its environmental performance and potential to significantly improve the system's efficiency, the German car industry is choosing CO_2 (744) instead of new blends proposed by chemical giants. The latter are still considered by other European manufacturers, even though they present open questions regarding their toxicity, flammability, long-term environmental effects etc..

"Should the VDA decision to go for R744 be officially confirmed, then the DUH welcomes this decision by the German car industry to take the lead in opting for the most sustainable solution available", says Jürgen Resch, Managing Director of the DUH (Deutsche Umwelthilfe).

Mr. Resch added that he also hopes "that other car manufacturer associations will follow the German lead."

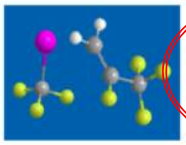
Next steps

R744.com will be reporting and sending regular updates concerning this important development on car air conditioning. In the meantime, readers are encouraged to react to this news by adding comments below.

Low Global Warming Refrigerant Development

Research & Development

- Started a number of years ago
- Designed for industry needs
- Broad IP on many families



- Fluid H: Binary Azeotrope
- 70% $CF_3CF=CH_2$ (1234yf)
- 30% CF_3I

Current Status

- Sampling since Jan '06
- More Than 40 companies sampled

- Good A/C performance
- Promising toxicological testing
- Notified EU regulators

Next Steps

- Mid 2007 industry decision
- Resolving key issues
- Complete validation

- Complete regulatory approvals
- Manufacturing plant construction
- Plant commissioning & start-up
- Launch

Source: Honeywell

Environmental Properties

Atmospheric Chemistry & Lifetime

- 1234yf reacts with OH radicals; 11 day lifetime
  - Forms trifluoroacetic acid, HF & CO_2 like 134a
- CF_3I breaks down by photolysis; 1-4 day lifetime
  - Forms HI, HF and CO_2 [Clemitshaw et al. 1995]

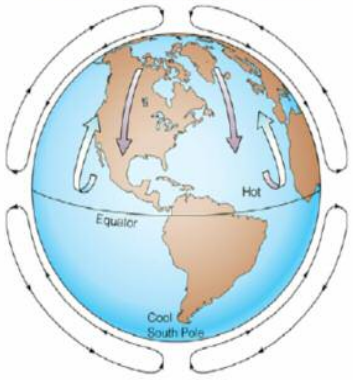
Global Warming Potential

- 1234yf GWP_{100} ~ 4 [Nielsen et al.]
- CF_3I GWP_{100} ~ 1 [Solomon, 1994]
- 1-Dimensional GWP calculations

CF_3I Ozone Depletion Potential

- ODP < 0.008, likely <0.0001 [Solomon, 1994]
- ODP = 0.000 [Montreal Protocol, TOC, 2002]
- ODP ~0.013 (N. hemisphere average) [Wuebbles, 2006]
  - However, 3D coupled calculations [5] are needed
- Honeywell is currently funding such calculations

Short Lived Molecules



- 6 months hemispheric mixing time
- 12 month global tropospheric mixing time
- Short lived molecules not well mixed
- GWP & ODP latitude & altitude dependant

1. Clemitshaw & Sodeau, J. Photochem. & Photobiol. A. Chemistry, 86 (1995) 9-14
2. O.J. Nielson, Chem. Phys. Lett., To be published
3. Solomon, Burkholder, Ravishankara & Garcia, J. Geophysical Res., 99, D10 (1994) 20,929-20,935
4. Montreal Protocol 2002 Assessment (Refrigerants & Heat Pump Technical Options Committee Report, Annex IV, p. 193
5. Wuebbles, Atmos. Chem. & Physics, 6, (2006) 4559-4568

Source: Honeywell

DuPont Leading Refrigerant Candidate: DP-1

- **Two component non-flammable blend**
  - Unique, innovative approach
  - Major component: non-flammable, fluorine based new compound
  - Minor component: commercially available refrigerant
- **Very encouraging toxicity data**
- **Zero-ODP, Very low GWP of ca. 40**
- **Operating conditions similar to R134a**
- **Compatible with conventional mobile air conditioning technology**

Source: DUPONT

WO 2005/068579 PCT/US2005/001508

TITLE OF INVENTION

1,1,1,2,2,3,3,4,4-NONAFLUORO-4-METHOXYBUTANE REFRIGERANT COMPOSITIONS COMPRISING A FLUOROETHER AND USES THEREOF

DuPont is aggressively pursuing the next generation MAC global industry solution

Path Forward

Internal

- Keep priority on toxicity testing
- Complete environmental testing
- Continue component testing and optimization
- Focus on process technology development to support a future commercialization plan that meets F-Gas requirements.
- Develop commercialization plans to meet MAC Directive R134a phase-out schedule, contingent upon global convergence to DP-1

External

- Broaden evaluations to additional OEMs and Tier 1 suppliers
- Support component level testing per OEM guidance
- Continue to support third party system/component testing and o
- Provide periodic updates at www.refrigerants.dupont.com

Source: DUPONT

Auto AC-1 composition and short history

At a glance:

- Nonazeotropic refrigerant
  - new and existing fluids
- Designed as a 'drop-in'
  - Similar thermodynamic characteristics to R-134a
- No additives in refrigerant
- Expected to be compatible with existing engineering materials
- Designed to be non-flammable
- Very low acute toxicity

History

- Ongoing refrigerant and process development as part of day to day business
- Development activity stepped up in response to renewed industry interest 2005/2006
  - Some apparent disadvantages of R-744 identified at OEM level
- Partnership approach adopted through SAE and industry in 2006
- Now a strategic focus for INEOS

R134a, R32 and HFO1225 Pentafluoropropene

Source: INEOS Fluor

Environmental performance

	Auto AC-1
ODP value	0
GWP	<150
Atmospheric lifetime	<20 days for new species
Decomposition process	OH- reaction mechanism
Decomposition products	Currently being measured but expected to be similar to other HFCs
Process for recovery & recycle	Objective to recycle locally where possible Handling practices: existing equipment expected to be usable. Liquid transfer of fluid from vessel to vessel

COP close to R-134a for low LCCP compared to alternatives

Source: INEOS Fluor

Sustainability …

… is an attempt to provide the best outcomes for the human and natural environments both now and into the indefinite future.

… relates to the continuity of economic, social, institutional and environmental aspects of human society, as well as the non-human environment.

… is intended to be a means of configuring civilization and human activity so that society, its members and its economies are able to meet their needs and express their greatest potential in the present, while preserving biodiversity and natural ecosystems, and planning and acting for the ability to maintain these ideals in a very long term.

…affects every level of organization, from the local neighborhood to the entire planet.

$$\text{Sustainability Index} = \frac{\text{Emergy Yield Ratio}}{\text{Environmental Loading Ratio}} = \frac{EYR}{ELR}$$

Emergy:
Embodied Energy refers to the quantity of energy required to manufacture, and supply to the point of use, a product, material or service.

Conclusions

- CFC/HCFC phase out is a success story (significant ODP & GWP reduction)
- HFCs are globally applicable and allow efficient & safe system operation, but they have typically a high GWP
- New blends with GWP<150
  - are designed as *"drop ins"* for R134a
  - consist of molecules containing H, F, C, I, O
  - still have unknown impacts and possibly showstoppers (toxicity, stability, cost, ODP…)
- Natural refrigerants will be applied where possible, but they are so far typically restricted to certain applications/regions or the technology is not mature yet

Recommendations:

- Maximize system efficiency & minimize refrigerant leakage to minimize the global warming effect of refrigeration industry
- Support the application of natural refrigerants, where feasible
- Consider new low GWP Blends as R134a substitutes, once they are commercial and have proven maturity as refrigerants (~ 3 year horizon)