A Primer on HFOs

Hydrofluoro-olefins
Low-GWP Refrigerants

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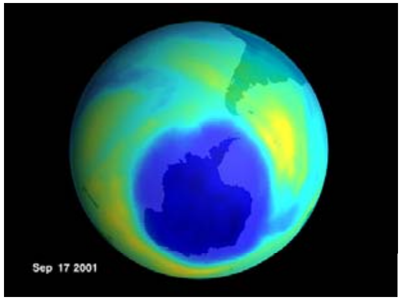
Learning Objectives for this Session

- Describe the climate change issue and associated with high GWP refrigerants and the leading low GWP options available
- Explain the refrigerant thermophysical property requirements needed for new low GWP refrigerants and how property data may be used
- Be able to explain the challenges with measuring the flammability properties of refrigerants that are only marginally flammable and options to make these measurements
- Explain the development history of hydrofluoro-olefin low GWP refrigerants such as HFO-1234yf
- Describe the codes and regulations in the US, Europe and Japan that govern the use of low GWP refrigerants such as CO_2, ammonia, hydrocarbons and HFOs and the barriers in current standards for their potential use
- Apply learnings from this seminar to begin selecting low GWP refrigerants for specific applications and begin designing new HVAC&R systems with these refrigerants

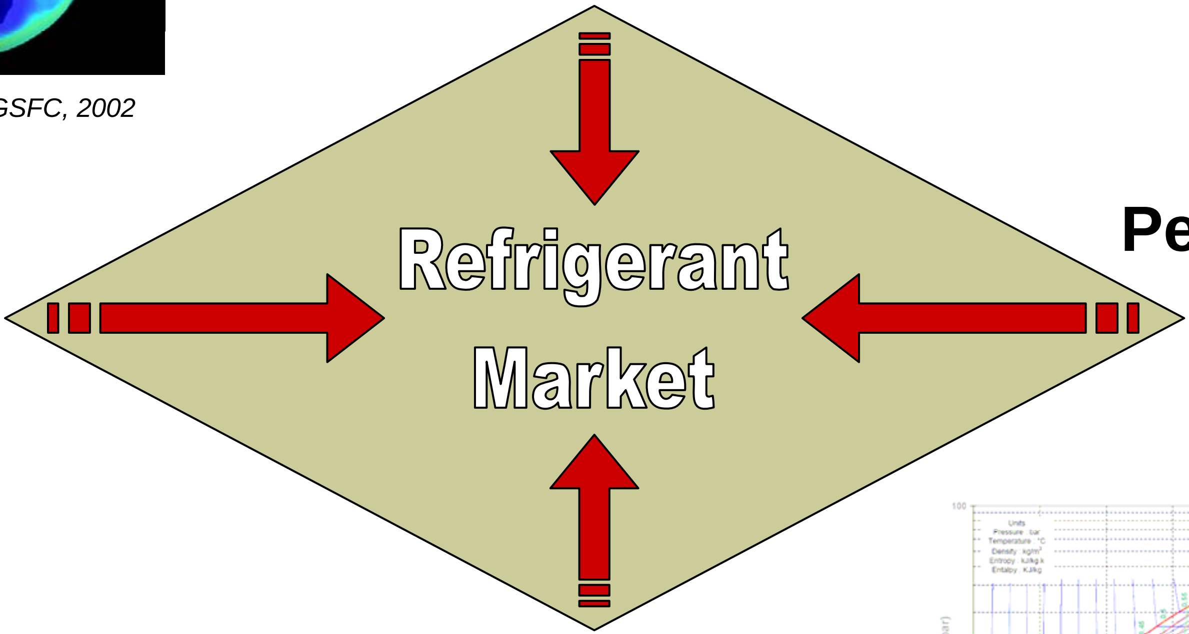
Drivers for Refrigerant Selection



NASA-GSFC, 2002

Environmental Sustainability

ODP, GWP, LCCP



Safety

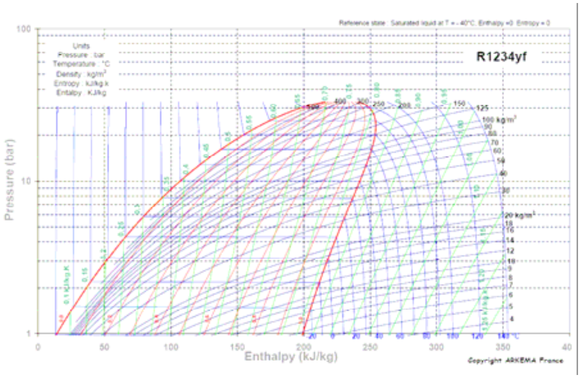
Flammability
Toxicity

Performance

Efficiency
Capacity

Supply

Cost, Availability



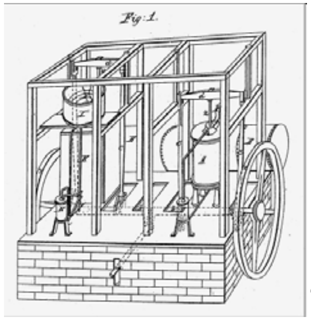
Refrigerant Timeline

Feasibility

1930 ***1950*** ***1970*** ***1990*** ***2010***

Ethyl Ether
NH_3
CO_2
CH_3Cl
SO_2
CCl_4
Etc.

1748: William Cullen: mechanical refrigeration
1805: Oliver Evans : concepts of mechanical refrigeration
1824: Nicolas Léonard Sadi Carnot: Carnot Cycle
1834: Jacob Perkins: refrigerating device
1844: John Gorrie: first “practical” refrigerator
1857: James Harrison: refrigerator



U.S. Patent 8,080

Refrigerant Timeline

Feasibility

Safety & Efficiency

1930 *1950* *1970* *1990* *2010*

Ethyl Ether
NH_3
CO_2
CH_3Cl
SO_2
CCl_4
Etc.

CFCs

HCFCs

1928: Midgley, Henne, McNary (GM): CFC refrigerants
1931: R-12
1932: R-11
1933: R-114
1934: R-113
1936: R-22

Refrigerant Timeline

Feasibility   Safety & Efficiency   **Ozone Protection**

1930   *1950*   *1970*   *1990*   *2010*

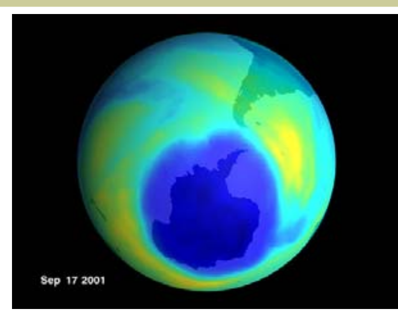
Ethyl Ether
NH_3
CO_2
CH_3Cl
SO_2
CCl_4
Etc.

CFCs

HCFCs

HFCs

1985: Vienna Convention
1987: Montreal Protocol
1996: CFC phase-out



NASA-GSFC, 2002

Refrigerant Timeline

Feasibility | Safety & Efficiency | Ozone Protection | **Climate Change**

1930 | *1950* | *1970* | *1990* | *2010*

Ethyl Ether
NH_3
CO_2
CH_3Cl
SO_2
CCl_4
Etc.

CFCs

HCFCs

HFCs

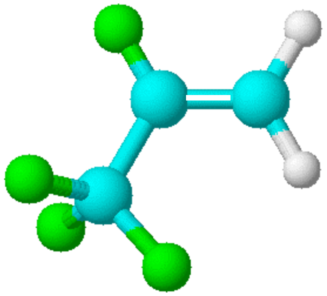
HFOs

Next Generation: HFO Refrigerants

- Can offer balance among:
  - Environmental profile
  - Safety and Durability
  - Performance

HFO: Nomenclature

Hydro-Fluoro-Olefin   2,3,3,3-tetrafluoroprop-1-ene



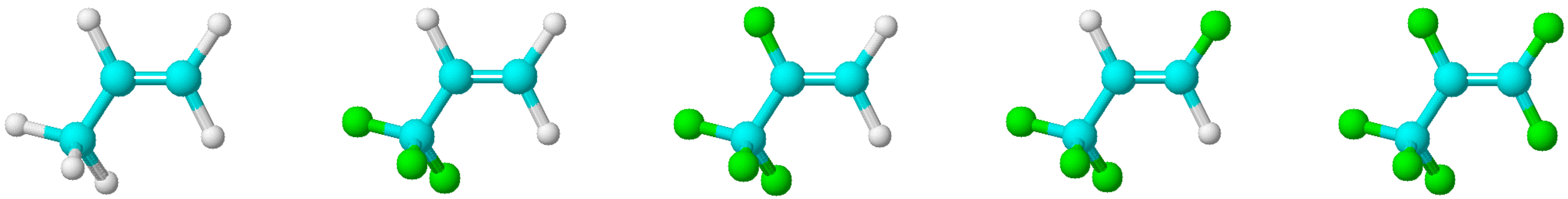
HFO – 1 2 3 4 y f

- 1: # of unsaturated bonds
- 2: # of carbon atoms - 1
- 3: # of hydrogen atoms + 1
- 4: # of fluorine atoms

Propene Series

- y: Substitution on central carbon:
  x: -Cl, y: -F, z: -H
- f: Substitution on terminal methylene carbon:
  a: $=CCl_2$ b: $=CClF$
  c: $=CF_2$ d: $=CHCl$
  e: $=CHF$ f: $=CH_2$

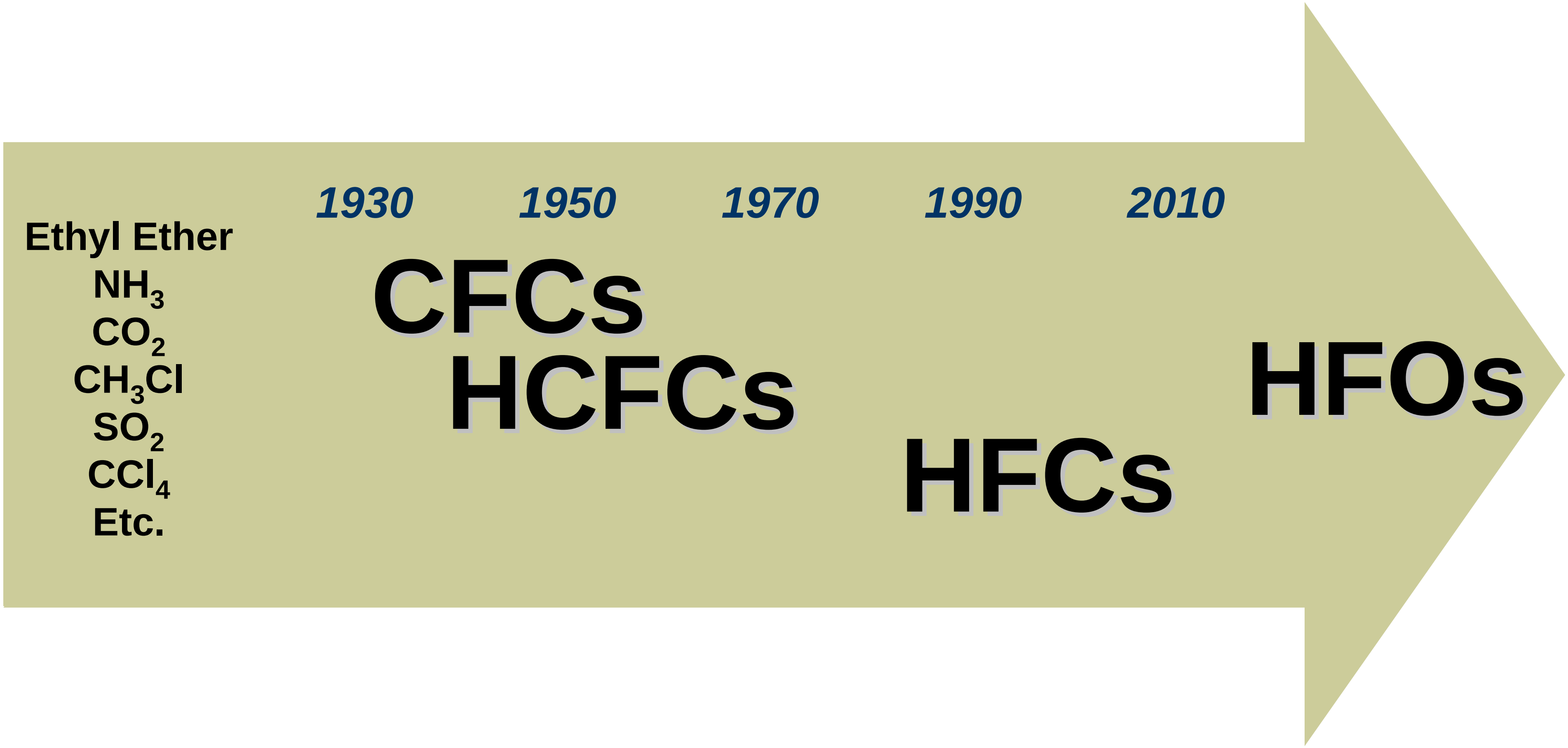
Propylene Series: examples



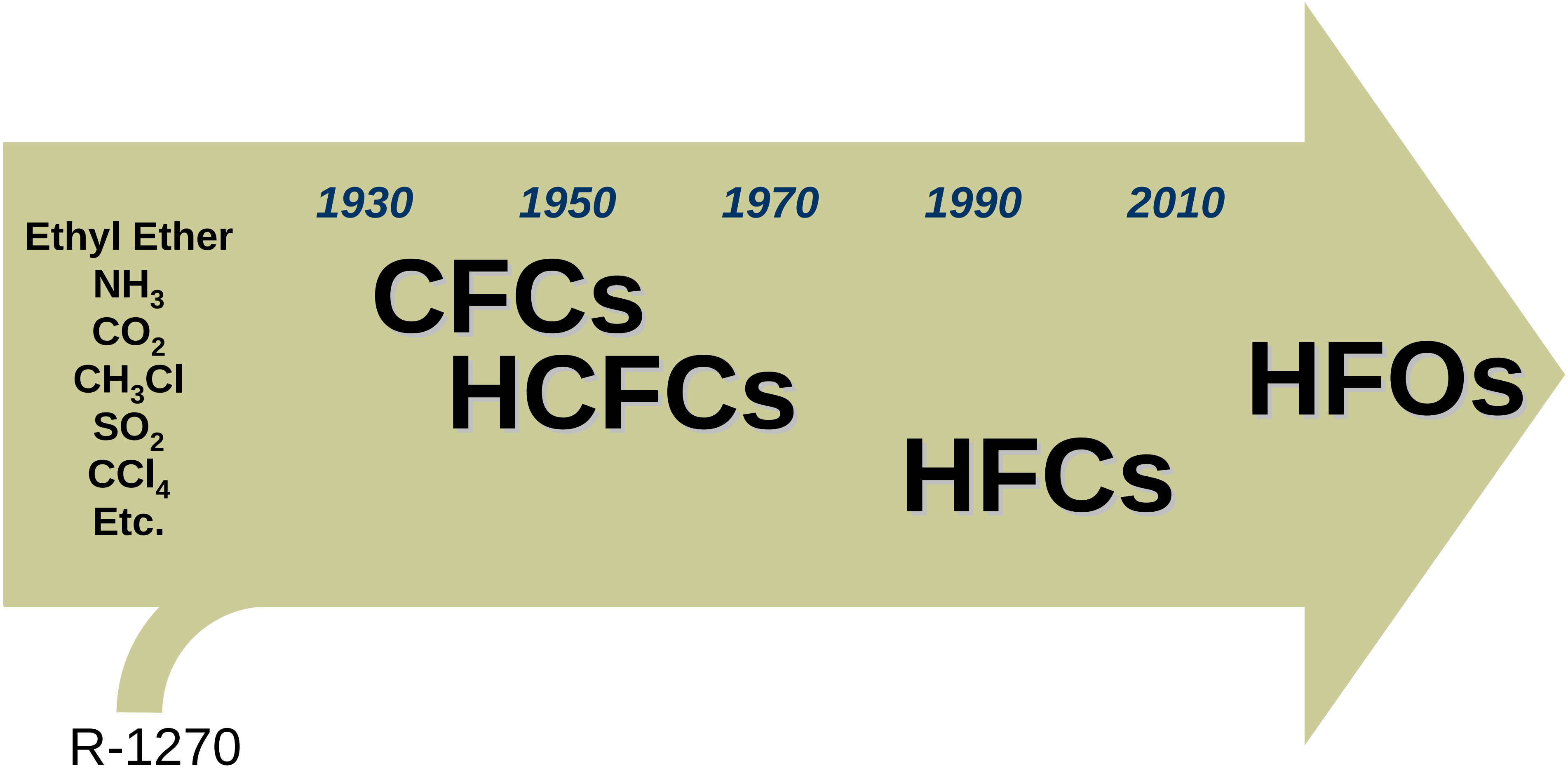
R-1270	R-1243zf	R-1234yf	R-1234ze(E)	R-1216
T_b = -48°C	T_b = -22°C	T_b = -29°C	T_b = -19°C	T_b = -29°C
Flammability				
3 #F = 0	2* #F = 3	2L #F = 4	2L^ #F = 4	1* #F = 6
Toxicity				
A	nc	A	A^	nc

*: estimated.   ^: as submitted to ASHRAE. nc: not classified by ASHRAE

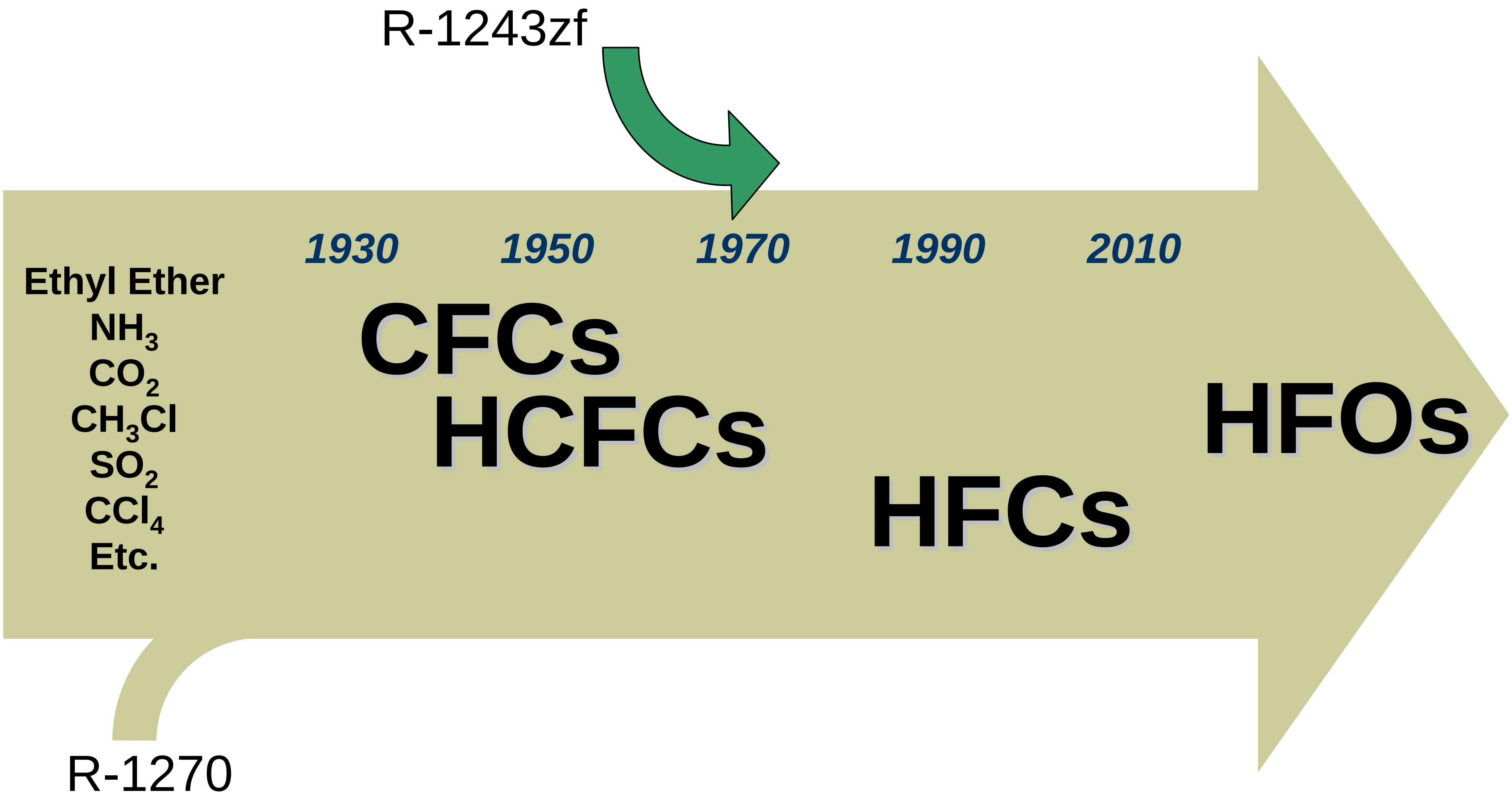
Refrigerant Timeline: Introduction of Propenes



Refrigerant Timeline: Introduction of Propenes



Refrigerant Timeline: Introduction of Propenes



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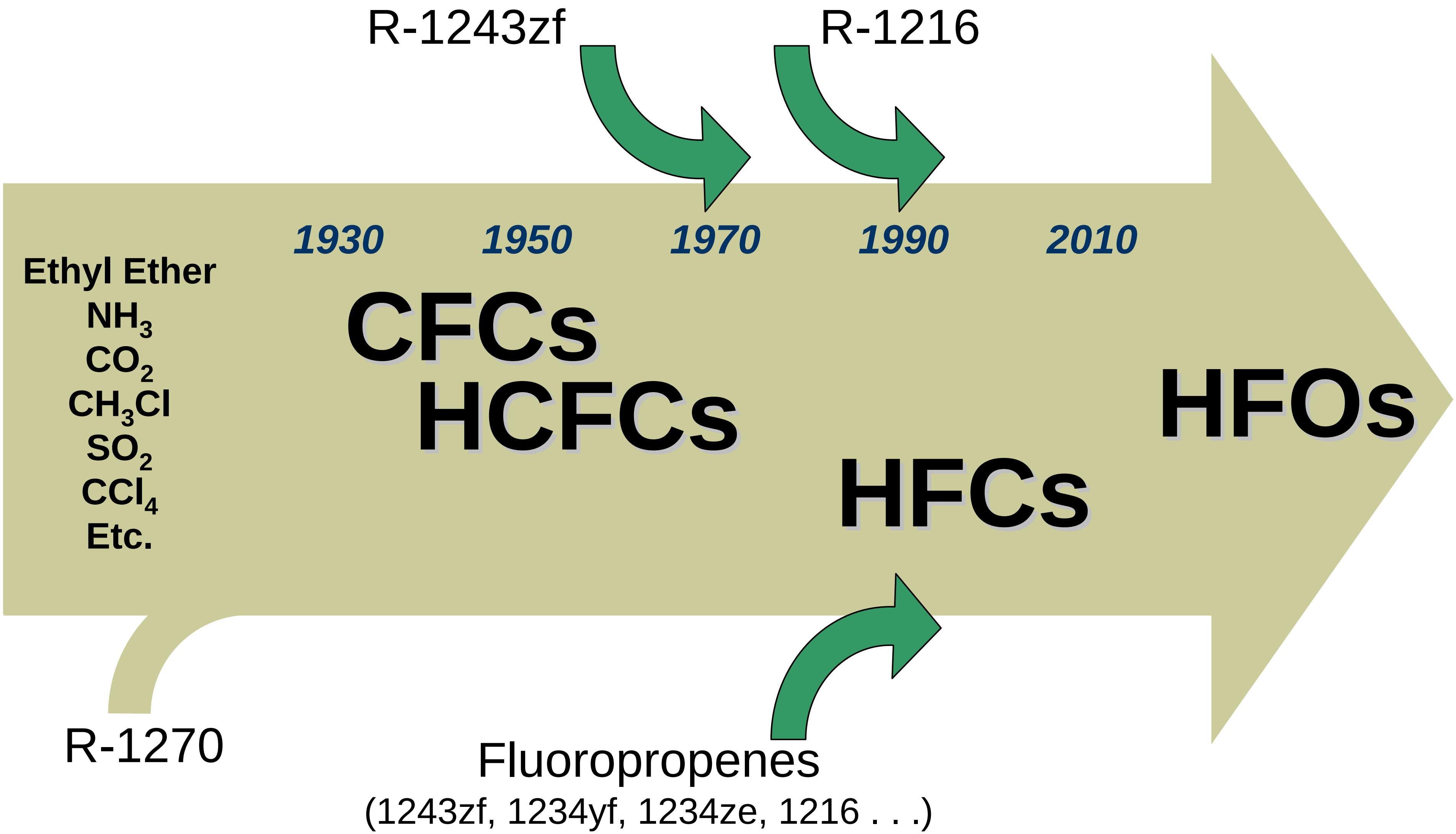
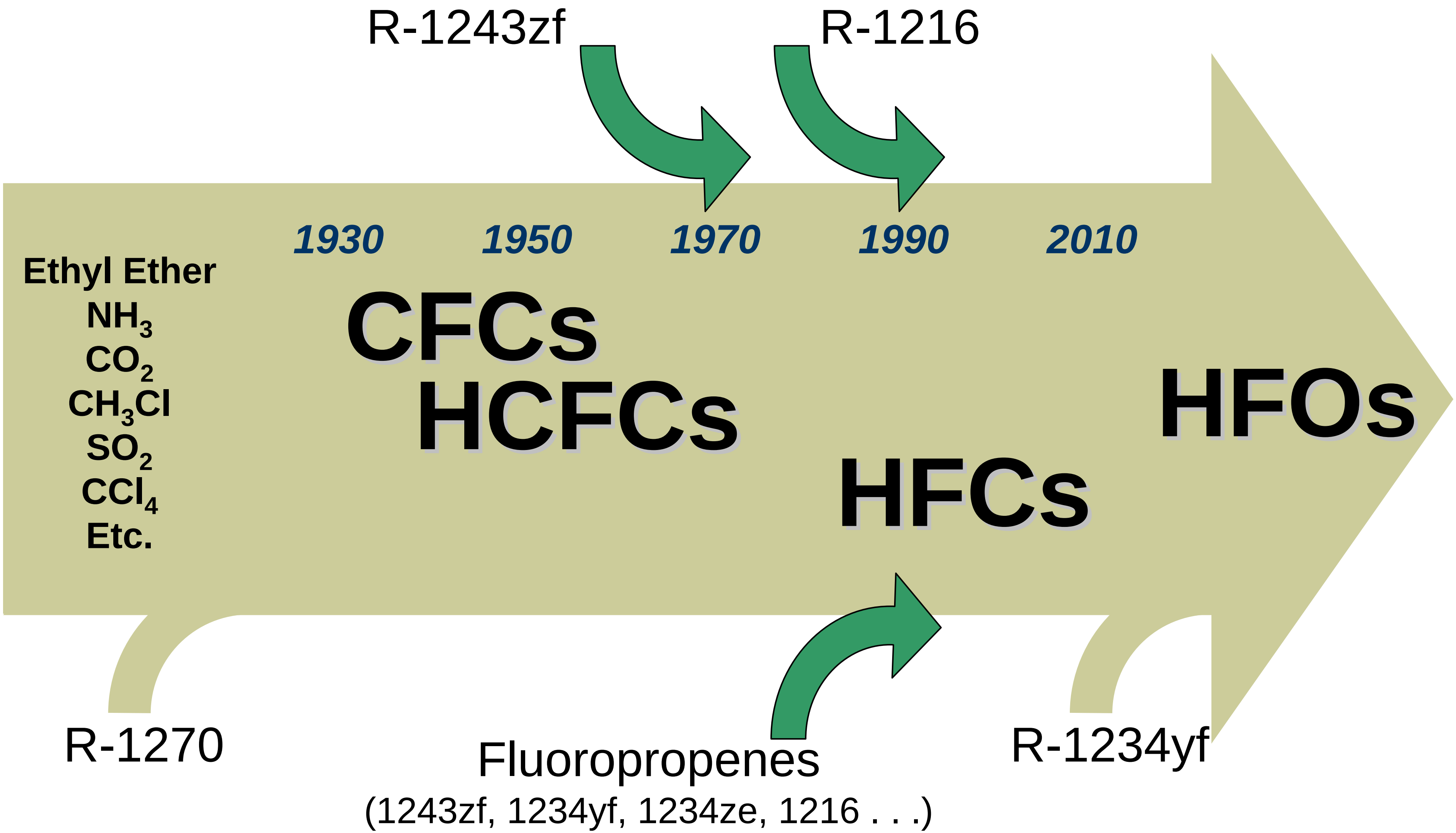
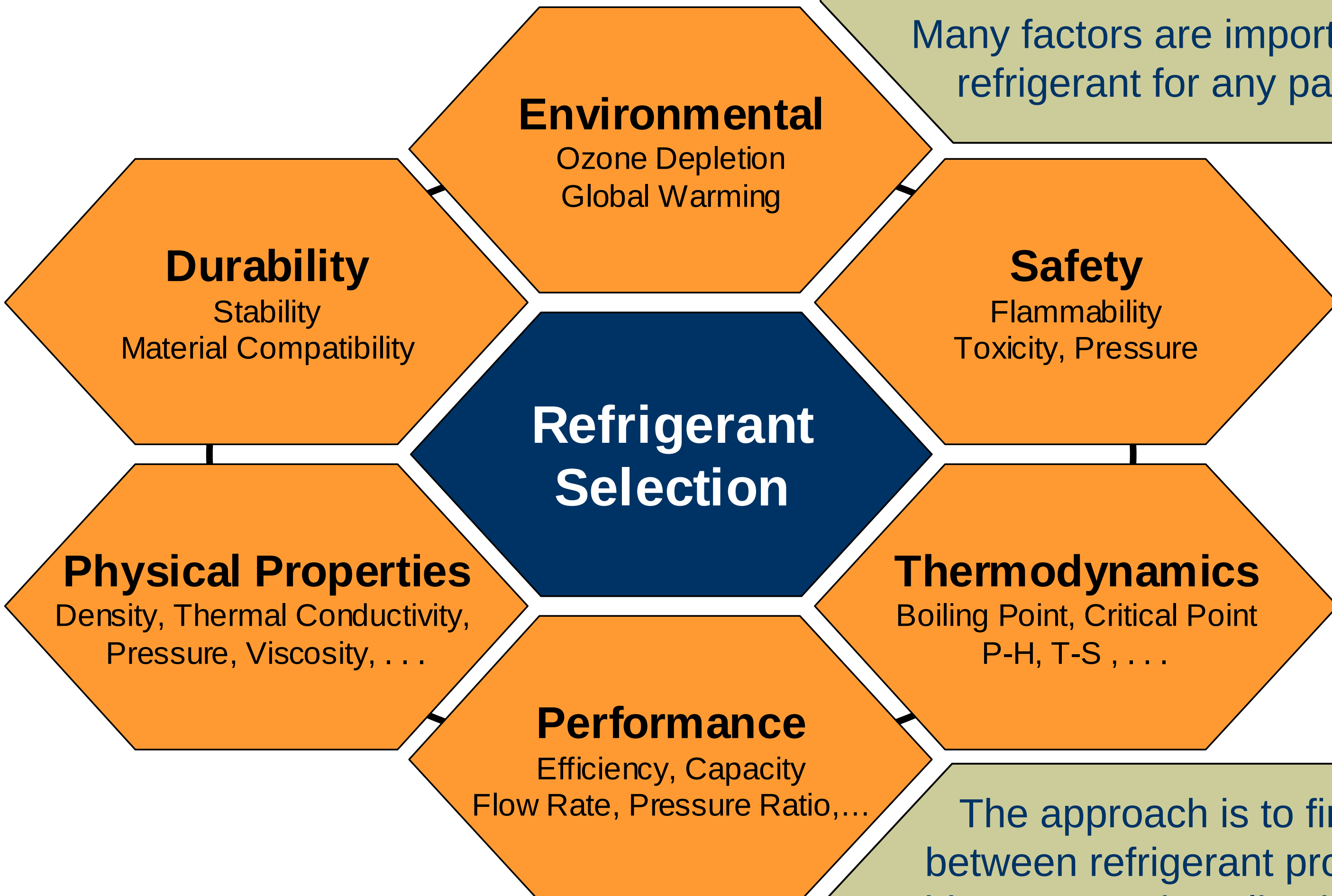


Refrigerant Timeline: Introduction of Propenes



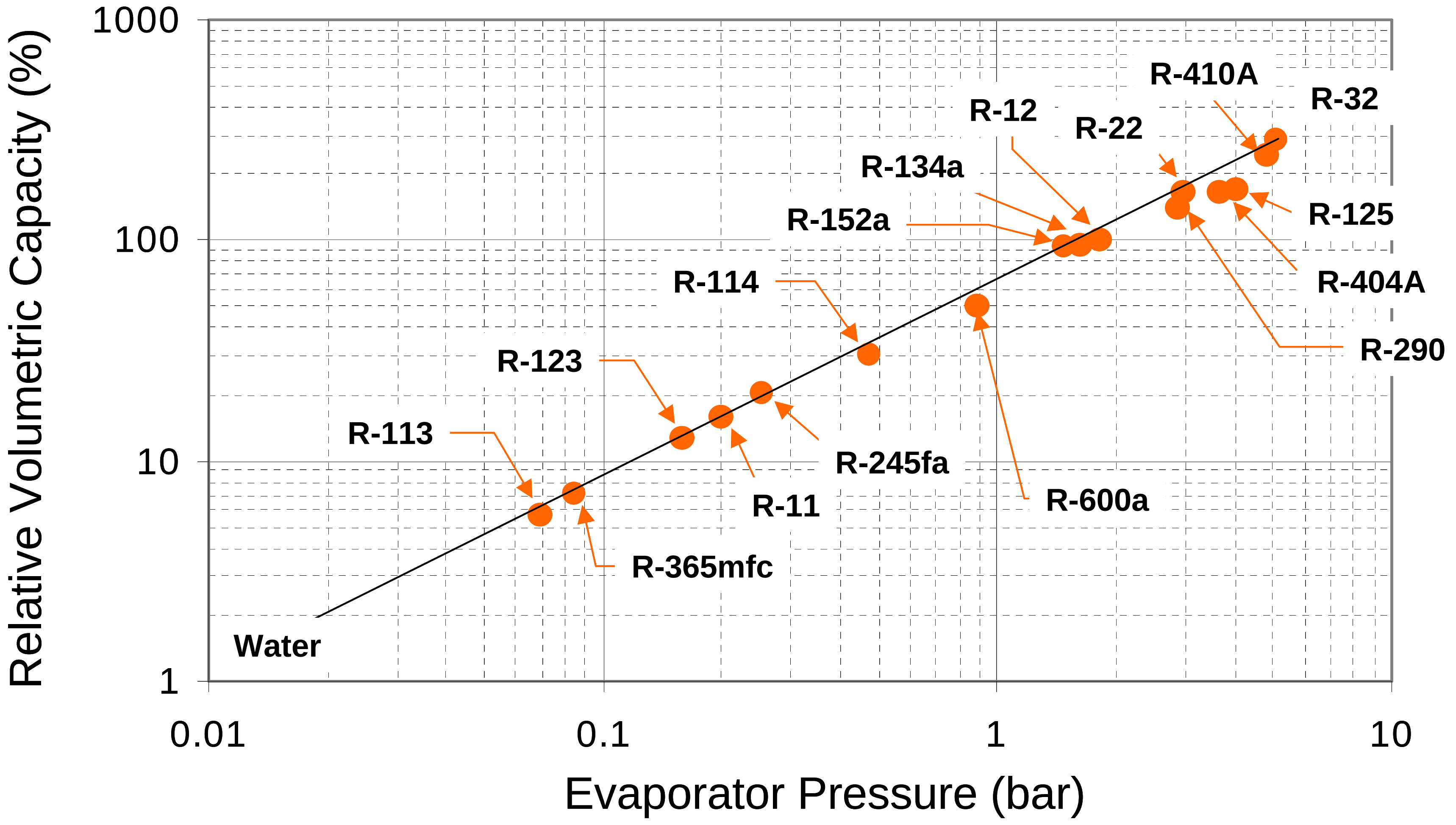
Refrigerant Selection



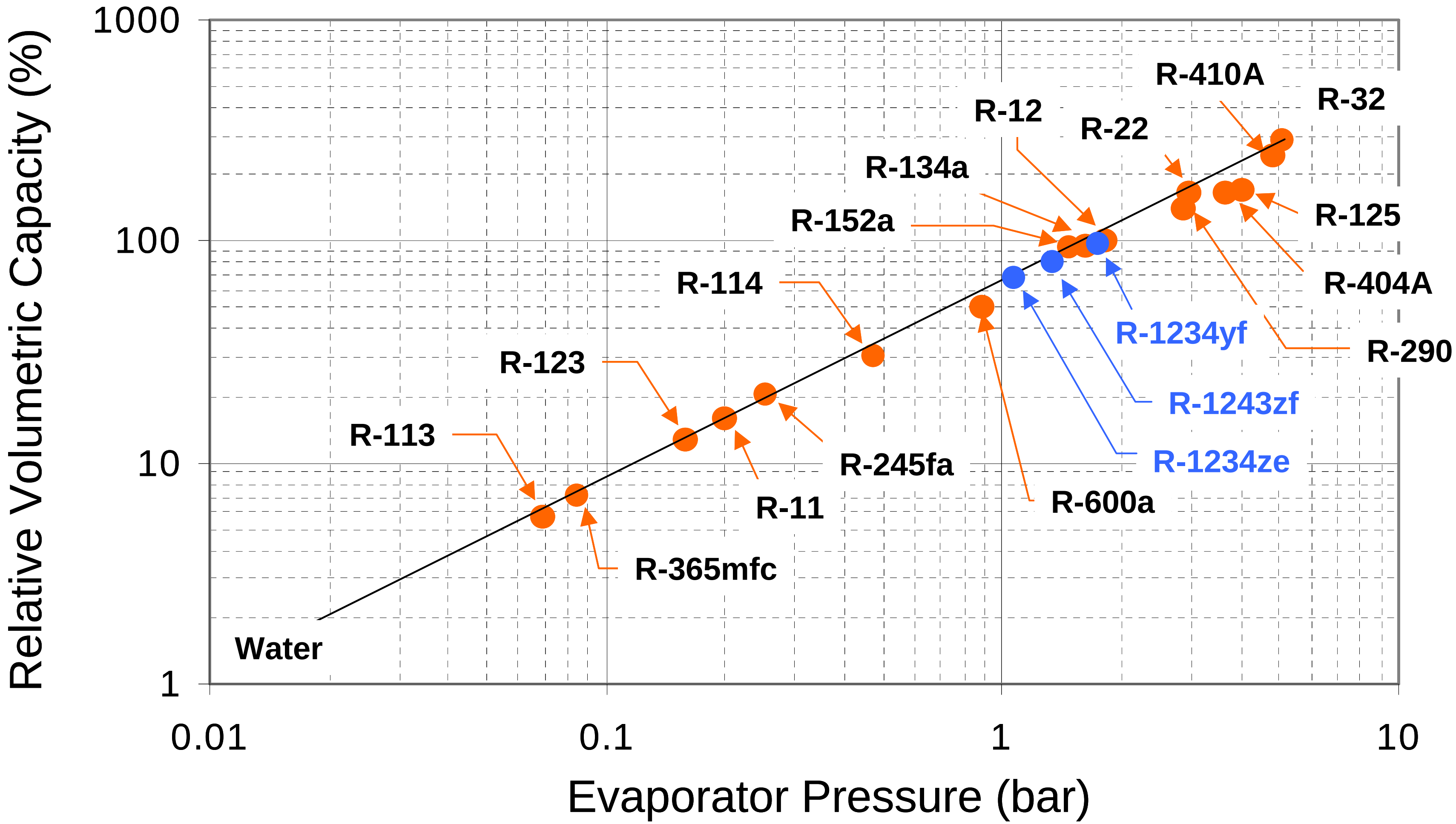
Many factors are important for selecting a refrigerant for any particular application

The approach is to find the best balance between refrigerant properties, system architecture, and application environment. Advances in refrigeration technology can affect refrigerant selection.

Refrigerant Volumetric Capacities (CAP)



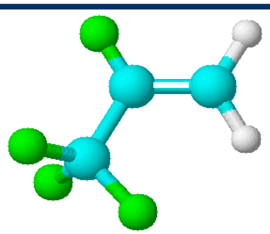
Refrigerant Volumetric Capacities (CAP)

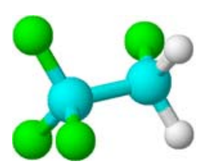


➢ **R-1234yf is a close match to R-134a**

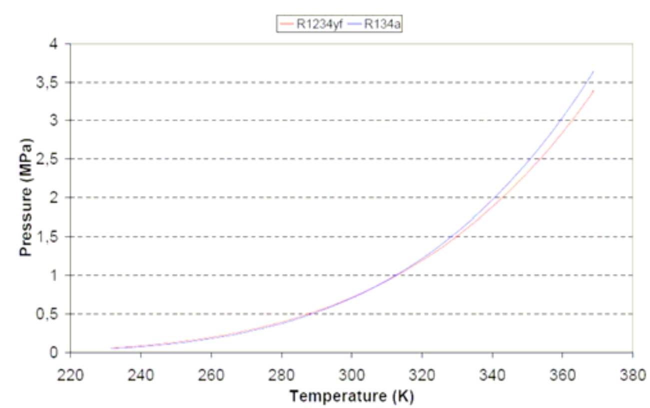
R-1234yf – Properties Summary

R-1234yf		R-134a
CF3-CF=CH2	Formula	CF3-CFH2
0	ODP	0
4	GWP	1430
11 days	Atm. Lifetime	13.8 years
114	mw (g/mol)	102
-29	Bp (°C)	-26
95	Tc (°C)	102
A	Toxicity	A
2 L	Flammability	1
6.5% / 12.3%	LFL/UFL (v/v)	none

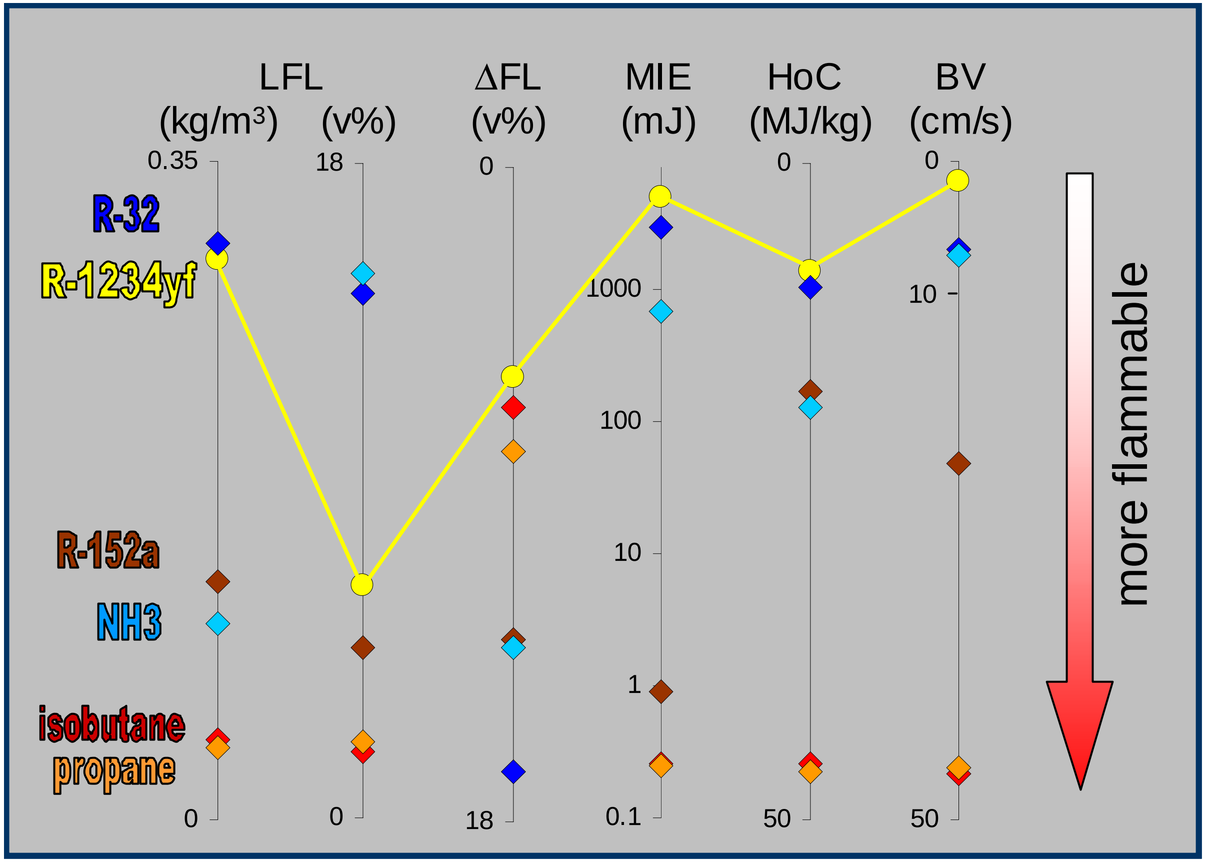


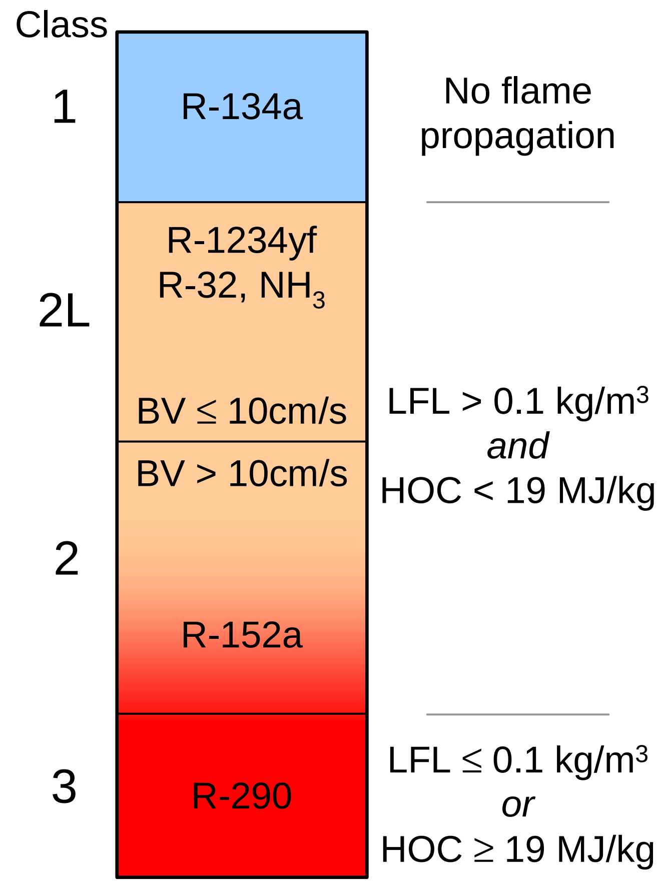


- ✓ **Low Toxicity**
- ✓ **Low Flammability**
- ✓ **Performance similar to R-134a**
  - ✓ **Pure component, no glide**
  - ✓ **Similar coefficient of performance and capacity**
  - ✓ **Good thermal stability and material compatibility**
- ✓ **Atmospheric chemistry is published**
  - ✓ **Same breakdown products as R-134a**
  - ✓ **No high-GWP breakdown products**
- ✓ **LCCP R-1234yf < LCCP R-134a**



R-1234yf – Flammability





R-1234yf

Low Flammable Range

- High LFL
- Narrow flammable window

Difficult to ignite

- High Min. Ignition Energy

Low impact of ignition

- Low Burning Velocity
- Low Heat of Combustion

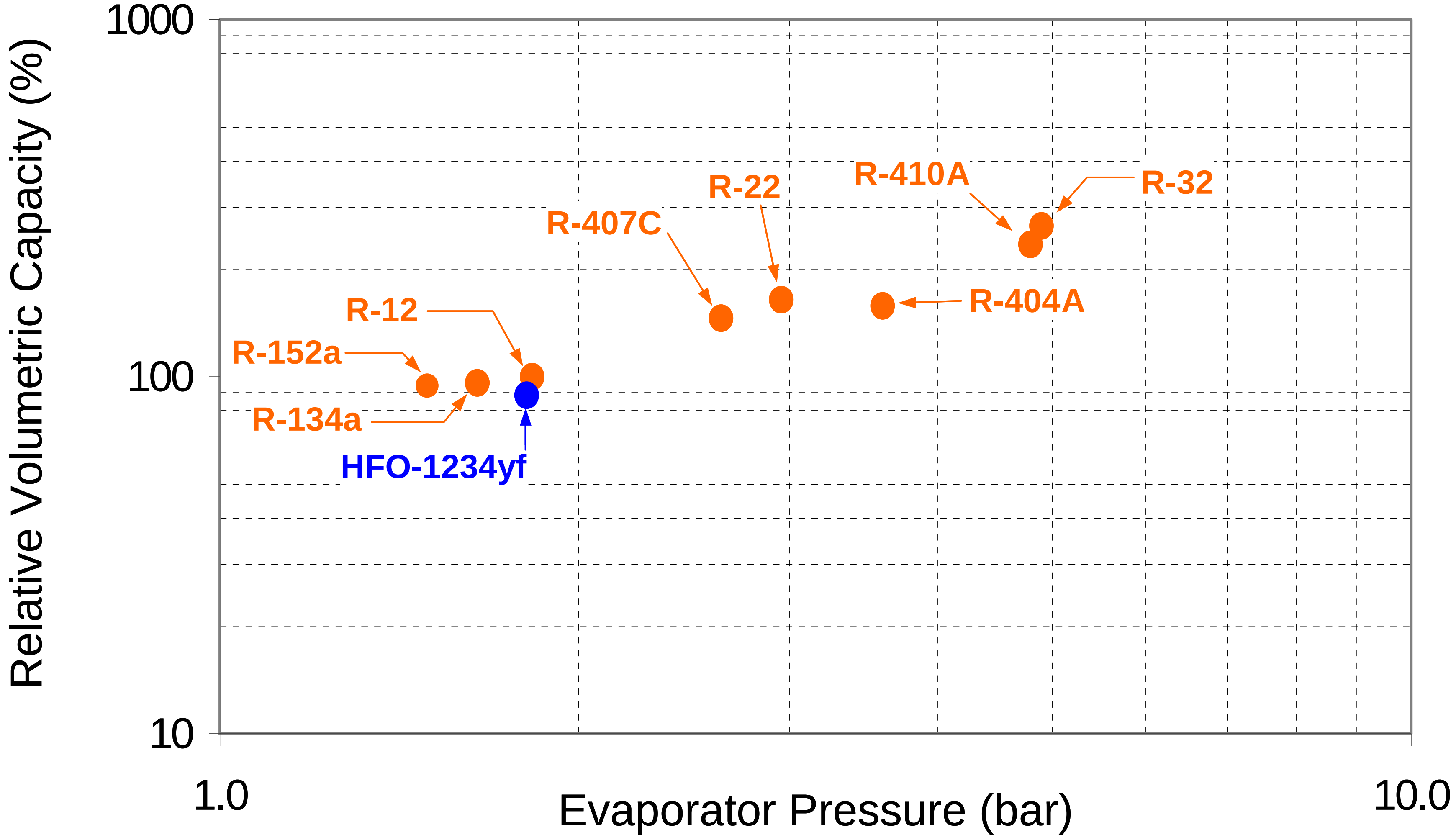
HVAC / R

Perspective on HFO Blends

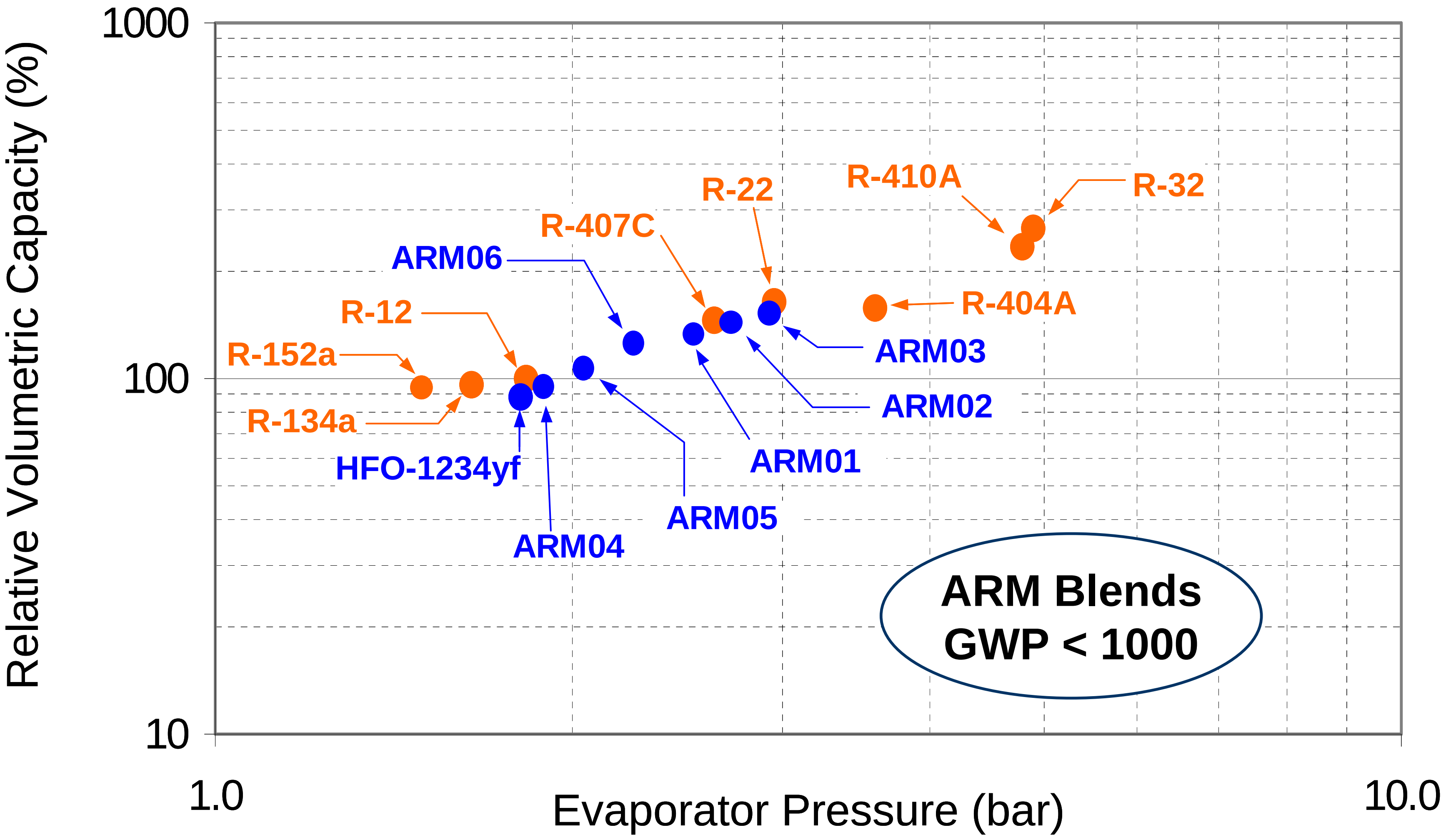
- Blend R-1234yf with other refrigerants to reduce the GWP and adjust refrigerant properties for market segments

- Tailor blend compositions for target applications & system architectures

Refrigerant Blends: Volumetric Capacities



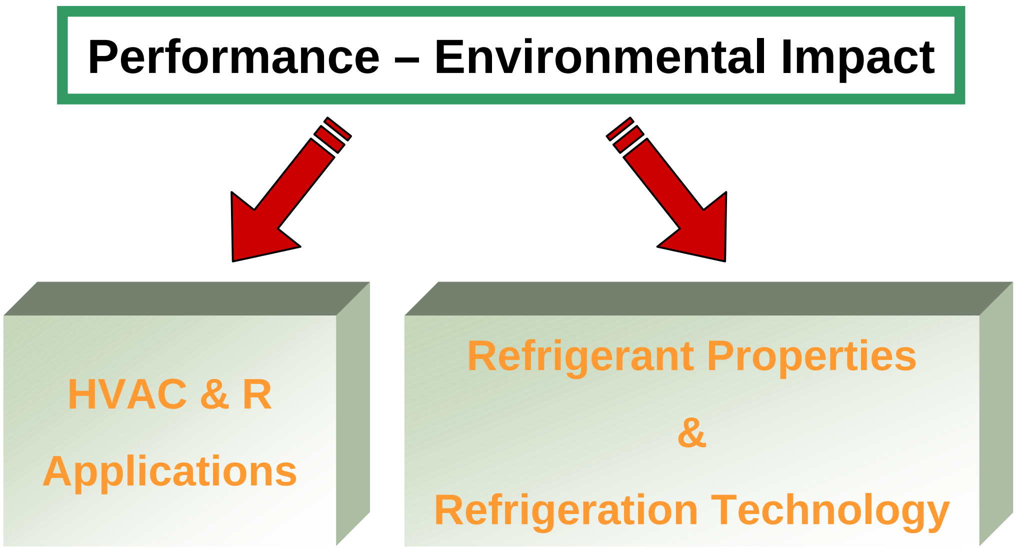
Refrigerant Blends: Volumetric Capacities

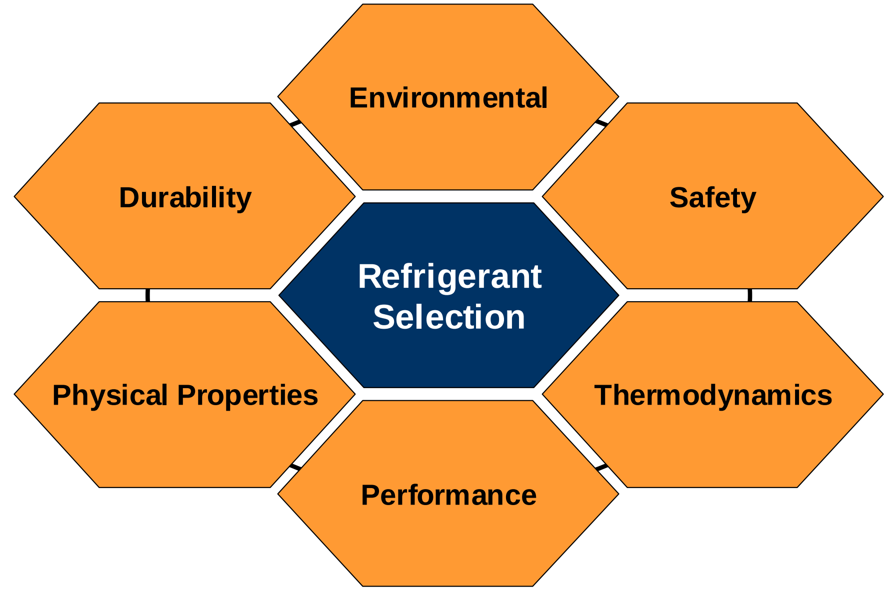


Refrigerant Blends: Conclusions

Other considerations for refrigerant blends

- **Safety classification, glide, application range, performance, . . .**





- **HFO-based blends allow for the development of reduced GWP solutions for various market segments of HVAC & Refrigeration**
- **Blend compositions are adapted for applications & systems architectures**
- **New technical challenges are ahead in the coming decades**

Thank you!