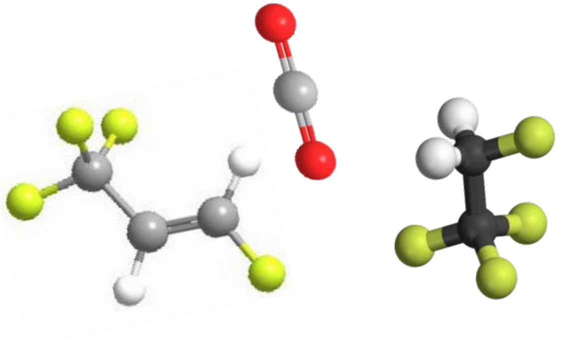
Screening for Next Generation Refrigerants



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Gaithersburg, MD, USA

Acknowledgement

M.O. McLinden, A. Kazakov, J. S. Brown,

R. Brignoli, J. Heo

Background

- **Refrigeration is used everywhere**

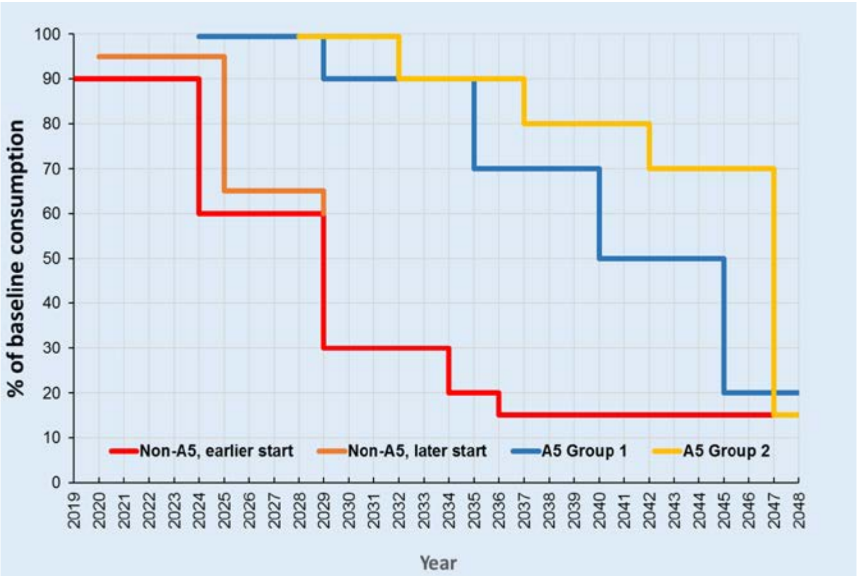
  Food industry, air conditioning, cryogenics, medicine and health products, energy, etc.

- **Use of refrigeration will increase, particularly in developing countries**

  Hotter countries tend to be less developed. Air conditioning offsets adverse effects of high temperature on human physical and cognitive performance. (Heal and Park, 2013)

- **Use of refrigeration has environmental consequences**
  - Current refrigerants (HFCs) are greenhouse gases; need for low-GWP refrigerants
  - Emissions of CO_2 from fossil fuel power plants; need for high efficiency
  - Kigali amendment to the Montreal Protocol (2016); production & consumption of HFCs to be cut by more than 80 % over the next 30 years.

  Weighed GWP across all sectors ≈ 300



Beginnings of artificial cold

1755 – apparatus to make ice by evaporation of water at reduced pressure; W. Cullen

1824 – genesis of thermodynamics; Carnot

1834 – refrigeration machine using compression of a liquefiable gas; Perkins

1834 – demonstration of the Peltier effect

- – reliable compressor; Harrison
- – absorption machine; F. Carre
- – air cycle machine; Gorrie
- – machine relying on evaporation of water (R-718) at reduced pressure; E. Carre
- – refrigerants: ethyl ether, methyl ether (R-E170), petrol ether + naphtha (chemogene), CO_2 (R-744), ammonia (R-717), SO_2 (R-764), methyl chloride (R-40)

1876 – ammonia compressors by Linde; application of thermodynamics

Main applications: ice making, transport of meat by sea, and brewing

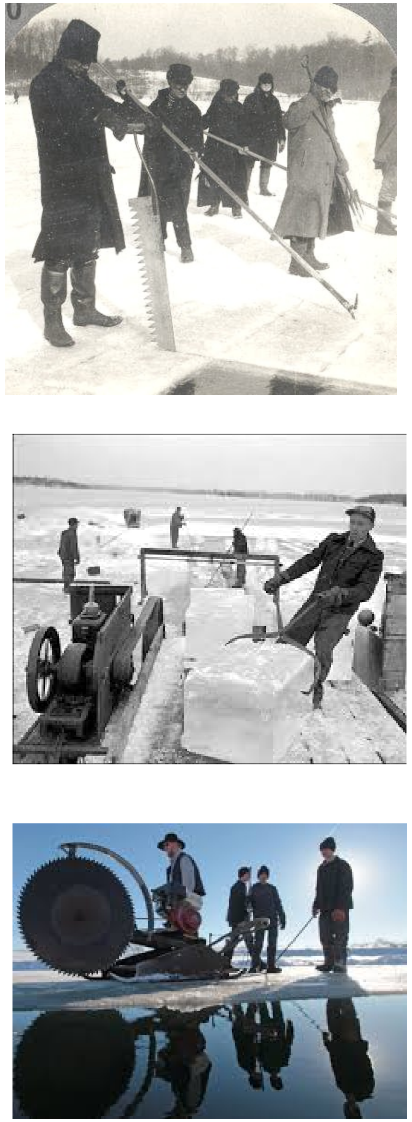
1890 -> 1900 – collapse of ice harvesting

1918 – dominant refrigerants: ammonia, CO_2, SO_2

1920s – introduction of HCs

1931 – introduction of CFC refrigerants

Ice harvesting



Thevenot, R. (1979)

Application of refrigerants

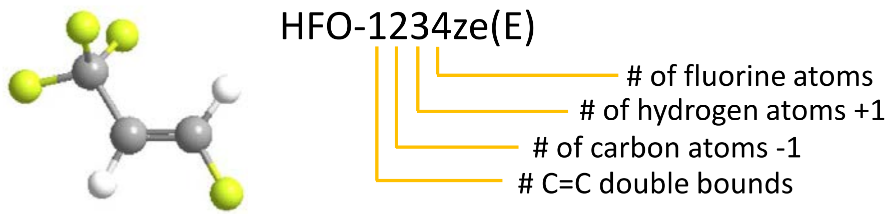
🟦	No flame propagation
🟧	Lower flammability
🟥	Higher flammability

Natural fluids

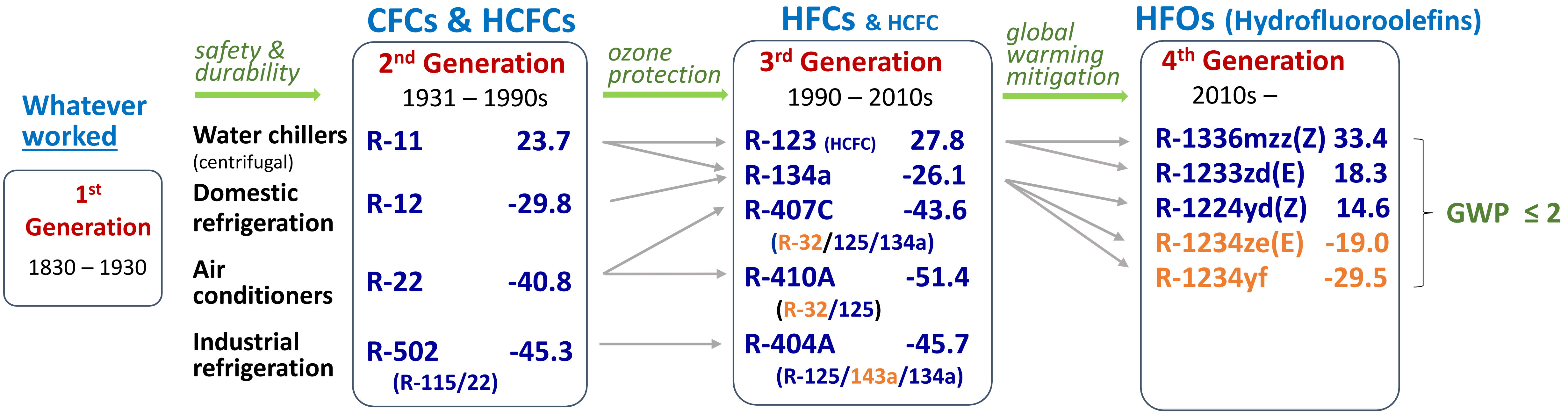
H_2O	100.0	R-717	-33.3	R-600a	- 11.7
CO_2	-78.4			R-290	- 42.1
air	-194.2			R-1270	- 47.7

Ammonia

Normal boiling point (°C)



Fluorinated fluids



Whatever worked

1st Generation
1830 – 1930

safety & durability

Water chillers (centrifugal)
Domestic refrigeration
Air conditioners
Industrial refrigeration

CFCs & HCFCs

2nd Generation
1931 – 1990s

R-11	**23.7**
R-12	**-29.8**
R-22	**-40.8**
R-502 (R-115/22)	**-45.3**

ozone protection

HFCs & HCFC

3rd Generation
1990 – 2010s

R-123 (HCFC)	**27.8**
R-134a	**-26.1**
R-407C (R-32/125/134a)	**-43.6**
R-410A (R-32/125)	**-51.4**
R-404A (R-125/143a/134a)	**-45.7**

global warming mitigation

HFOs (Hydrofluoroolefins)

4th Generation
2010s –

R-1336mzz(Z)	**33.4**
R-1233zd(E)	**18.3**
R-1224yd(Z)	**14.6**
R-1234ze(E)	**-19.0**
R-1234yf	**-29.5**

GWP ≤ 2

Calm (2008), Calm (2012), Myhre, G. et al. (2013)

Application of refrigerants

🟦 No flame propagation
🟧 Lower flammability
🟥 Higher flammability

Natural fluids

H_2O	100.0	R-717	-33.3	R-600a	- 11.7
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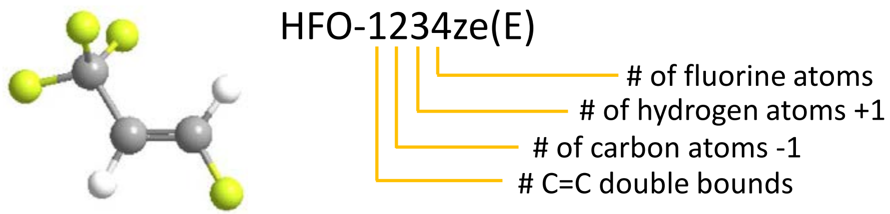
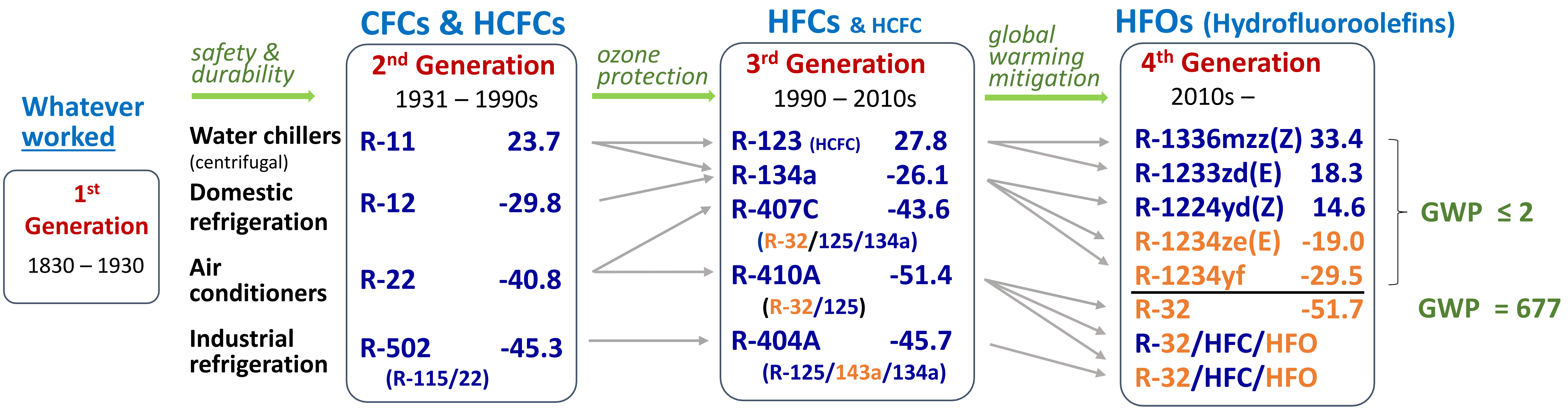


HFO-1234ze(E)

Fluorinated fluids



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R-32	**-51.7**
R-32/HFC/HFO	
R-32/HFC/HFO	

GWP ≤ 2

GWP = 677

Calm (2008), Calm (2012), Myhre, G. et al. (2013)

NIST search for low-GWP fluids (2012 – 2017)

Objective: Identify molecules that might be good replacements for R-410A and R-22

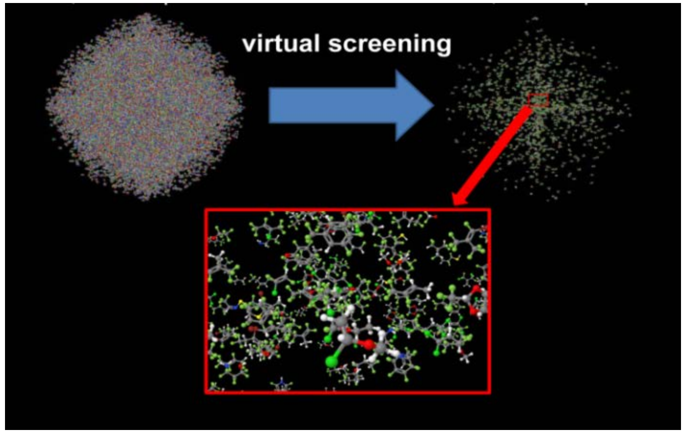
Air-conditioning and refrigeration applications
- positive displacement compressors
- forced-convection air-to-refrigerant heat exchangers

Approach: Perform screening using comprehensive database

(PubChem lists over 60 million unique chemical structures)

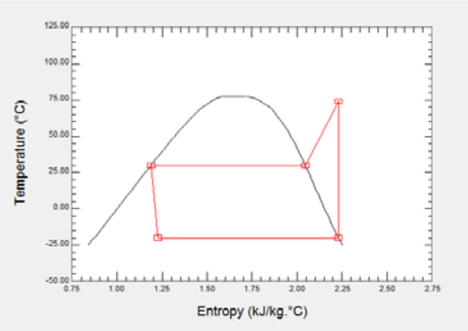
Important attributes/filters:

- Performance: COP, volumetric capacity (Q_{vol})
- Environmental: ODP, GWP
- Safety: toxicity, flammability
- Materials: stability, compatibility (lubricant, seals, metals, etc.)
- Cost



Performance limit of the vapor-compression cycle

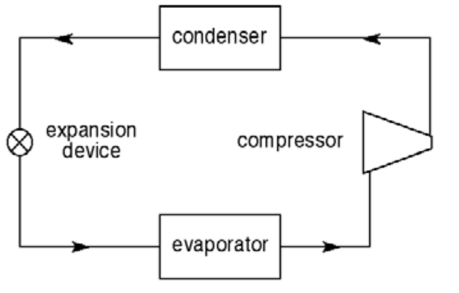
- **What are thermodynamic limits of performance?**
  COP; volumetric capacity
- **What are optimum thermodynamic parameters?**
- **How do current fluids compare?**
  Can we do better?



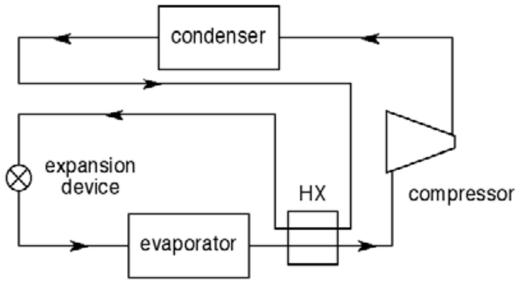
Studied applications:

- **Cooling: T_{evap} = 10 ˚C, T_{cond} = 40 ˚C**
- Heating: T_{evap} = –10 ˚C, T_{cond} = 30 ˚C
- Refrigeration: T_{evap} = –20 ˚C, T_{cond} = 30 ˚C

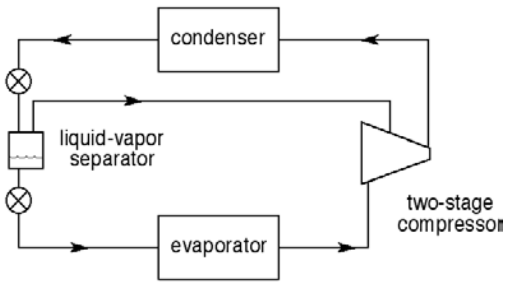
simple vapor compression cycle (baseline)



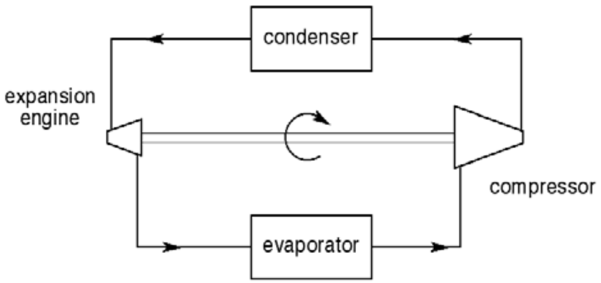
liquid-line/suction-line HX



flash economizer



work recovery



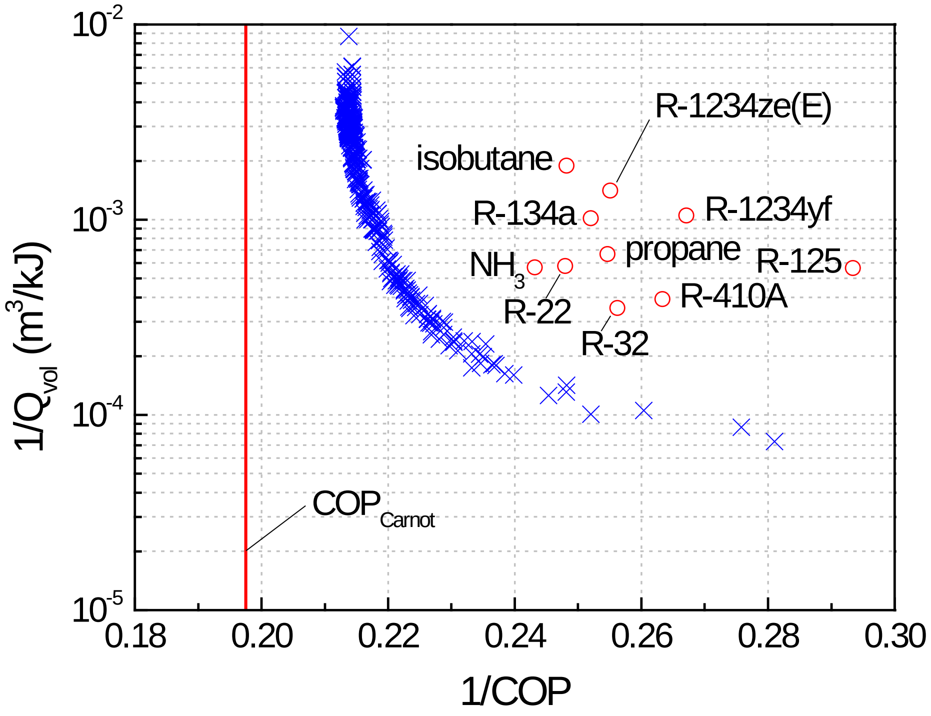
Domanski et al. (2014)

Performance limit of the vapor-compression cycle

- **Vapor compression cycle model**
- **Extended Corresponding States (ECS) model for representation of refrigerant properties**
- **Search for optimum ECS parameters**

Bi-objective optimization for COP and Q_{vol} using evolutionary algorithms

Parameter	Units	Range	Granularity
T_{crit}	K	305 ~ 650	0.5
P_{crit}	MPa	2.0 ~ 12.0	0.05
ω	–	0.0 ~ +0.6	0.005
α_1	–	–0.3 ~ +0.3	0.01
α_2	–	–0.8 ~ 0.0	0.1
β_1	–	–1.0 ~ +1.0	0.01
β_2	–	–0.8 ~ +0.8	0.1
C_p°(300 K)	$J\cdot mol^{-1}\cdot K^{-1}$	20.8 ~ 300	0.2
γ	K^{-1}	0.0 ~ 0.0025	0.0001



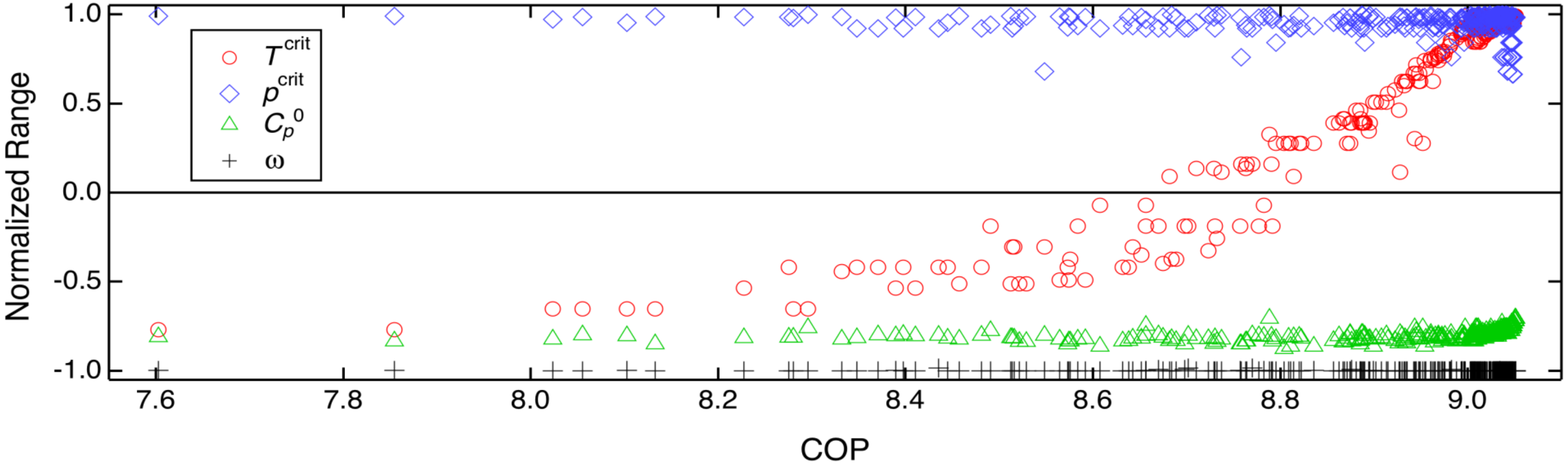
$$\mathrm{COP} = \frac{T_{evap}}{T_{cond} - T_{evap}}$$

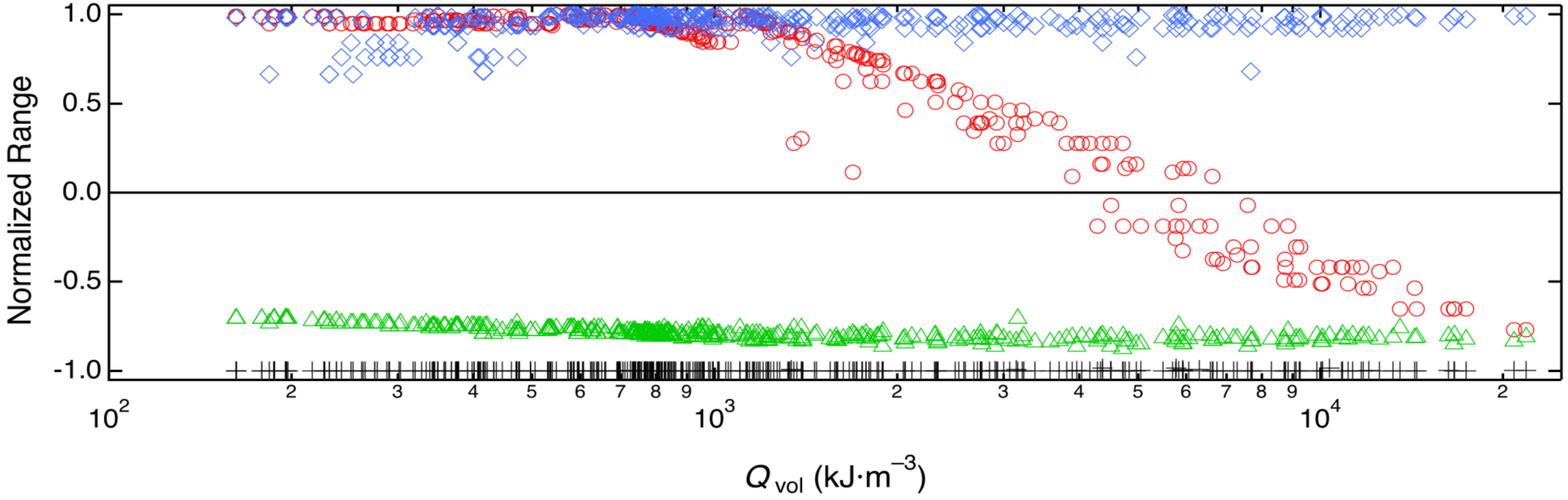
Refrigerant parameters along Pareto front

Basic cycle

T_{evap} = 10 ˚C
T_{cond} = 40 ˚C

ΔP_{evap} = 0 kPa
ΔP_{cond} = 0 kPa





Database screening

PubChem database

- Component atoms: C, H, N, O, S, F, Cl, Br
- Maximum number of atoms: 18

- $GWP_{100} < 1000$
- Critical temperature: 46 °C < T_{crit} < 146 °C

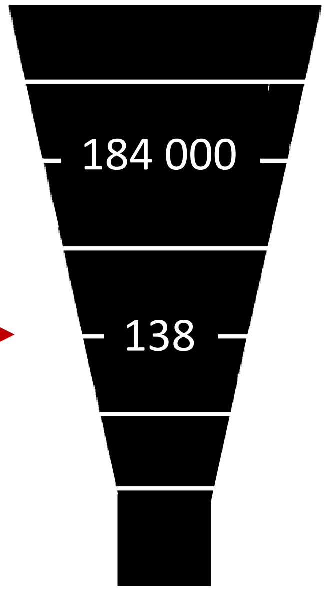
- Toxicity (MSDS, RCL, TLV, $=CF_2$)
- Stability

Evaluated manually

- Volumetric capacity > 0.33 $Q_{vol,R\text{-}410A}$
  (Basic cycle simulations)

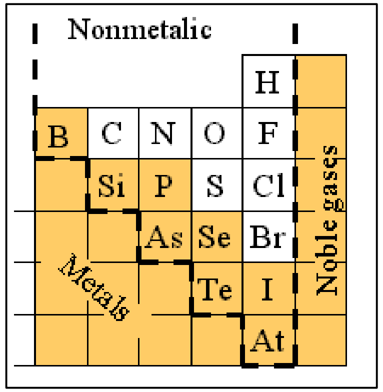
Molecule count

60 000 000



21

15 - at least mildly flammable
6 - unknown hazards



- 21 (primary interest) + 3 (commercial interest) + 3 (low T_{crit}) → 27 fluids
- New toxicity data on R-1132a; 27 + 1 (low T_{crit}) → 28 fluids

Performed detailed simulations with optimized heat exchangers for 24 fluids

Air conditioning (McLinden et al., 2017)

Refrigeration and heating (Domanski et al., 2017)

28 candidate fluids

Basic cycle; air conditioning;
optimized heat exchangers

21 fluids of primary interest:

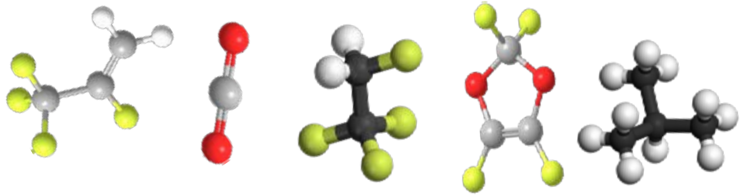
$46\ °C < T_{cr} < 146\ °C$

$Q_{vol} > 0.33\ Q_{vol,R\text{-}410A}$

15 - at least mildly flammable
6 - unknown hazards

7 additional fluids:

- 🔵 subcritical operation; 3 fluids
  [R-134, R-1123, R-1225ye(Z)]
- 🔴 supercritical or near-critical operation; 4 fluids
  [R-170, R-41, R-1132a, R-744]

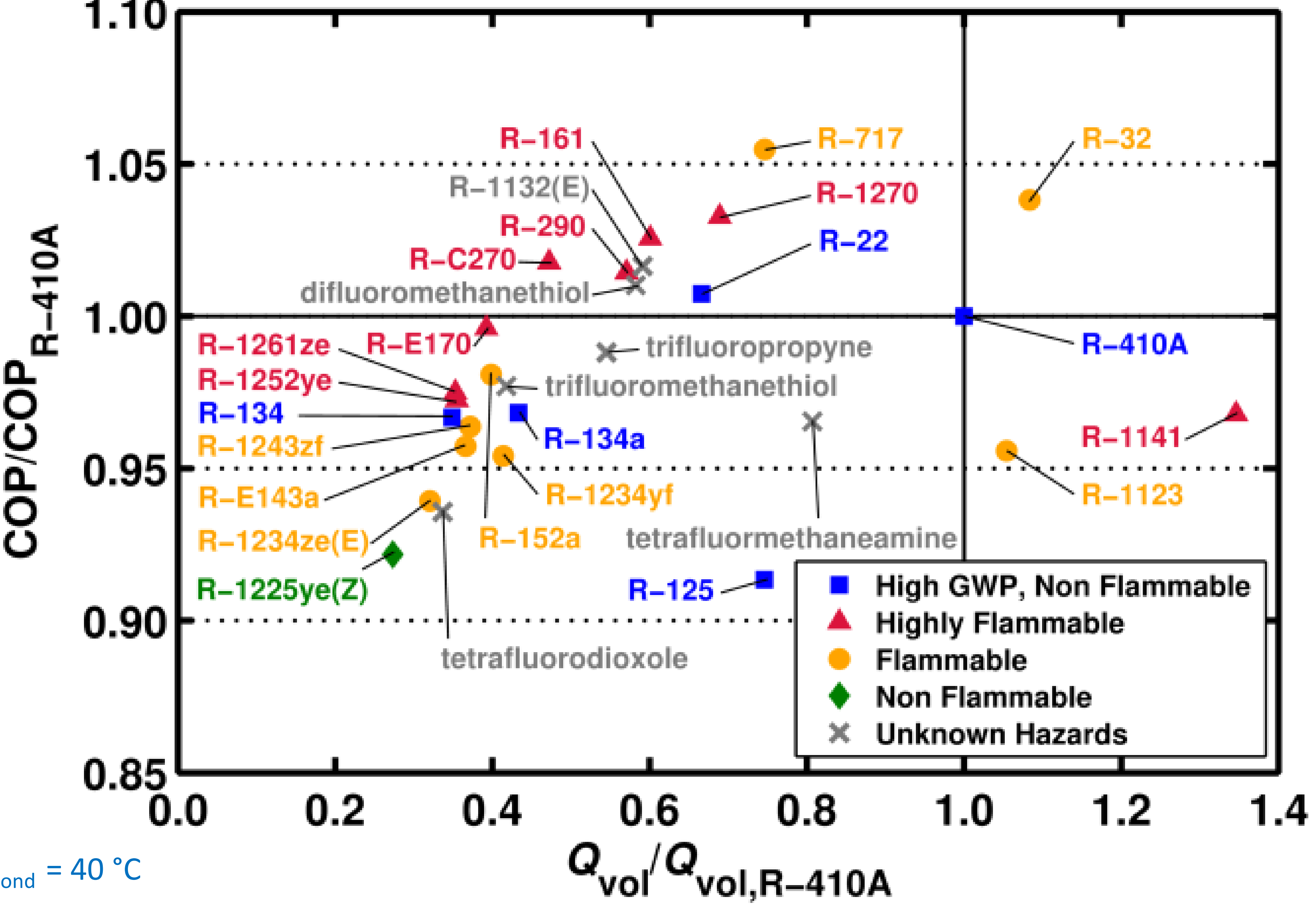


				GWP	T_{cr} (K)	$\frac{COP}{COP_{R410A}}$	$\frac{Q_{vol}}{Q_{vol, R410A}}$
Hydrocarbons and dimethylether							
ethane	CH_3-CH_3	🔴	R-170	6	305.3		
propene (propylene)	CH_2=CH-CH_3		R-1270	2	364.2	1.033	0.689
propane	CH_3-CH_2-CH_3		R-290	3	369.9	1.014	0.571
methoxymethane (dimethylether)	CH_3-O-CH_3		R-E170	1	400.4	0.996	0.392
cyclopropane	-CH_2-CH_2-CH_2-		R-C270	86	398.3	1.018	0.472
Fluorinated alkanes (HFCs)							
fluoromethane	CH_3F	🔴	R-41	116	317.3		
difluoromethane	CH_2F_2		R-32	677	351.3	1.038	1.084
fluoroethane	CH_2F-CH_3		R-161	4	375.3	1.026	0.601
1,1-difluoroethane	CHF_2-CH_3		R-152a	138	386.4	0.981	0.399
1,1,2,2-tetrafluoroethane	CHF_2-CHF_2	🔵	R-134	1120	391.8	0.967	0.348
Fluorinated alkenes (HFOs) and alkynes							
1-1-difluoroethene	CF_2=CH_2	🔴	R-1132a	<1	324.2		
fluoroethene	CHF=CH_2		R-1141	<1	327.1	0.968	1.346
1,1,2-trifluoroethene	CF_2=CHF	🔵	R-1123	3	343.0	0.956	1.054
3,3,3-trifluoroprop-1-yne	CF3-C≡CH		n.a.	1.4	363.3	0.988	0.545
2,3,3,3-tetrafluoroprop-1-ene	CH_2=CF-CF_3		R-1234yf	<1	367.9	0.954	0.414
(E)-1,2-difluoroethene	CHF=CHF		R-1132(E)	1	370.5	1.016	0.591
3,3,3-trifluoroprop-1-ene	CH_2=CH-CF_3		R-1243zf	<1	376.9	0.964	0.372
1,2-difluoroprop-1-ene‡	CHF=CF-CH_3		R-1252ye‡	2	380.7	0.973	0.355
(E)-1,3,3,3-tetrafluoroprop-1-ene	CHF=CH-CF_3		R-1234ze(E)	<1	382.5	0.939	0.320
(Z)-1,2,3,3,3-pentafluoro-1-propene	CHF=CF-CF_3	🔵	R-1225ye(Z)	<1	384.0	0.922	0.273
1-fluoroprop-1-ene‡	CHF=CH-CH_3		R-1261ze‡	1	390.7	0.975	0.353
Fluorinated oxygenates							
trifluoro(methoxy)methane	CF_3-O-CH_3		R-E143a	523	377.9	0.957	0.366
2,2,4,5-tetrafluoro-1,3-dioxole	-O-CF_2-O-CF=CF-		n.a.	1	400.0	0.936	0.337
Fluorinated nitrogen and sulfur compounds							
N,N,1,1-tetrafluormethaneamine	CHF_2-NF_2		n.a.	20	341.6	0.965	0.807
difluoromethanethiol	CHF_2-SH		n.a.	1	373.0	1.010	0.582
trifluoromethanethiol	CF_3-SH		n.a.	1	376.2	0.977	0.418
Inorganic compounds							
carbon dioxide	CO_2	🔴	R-744	1.00	304.1		
ammonia	NH_3		R-717	<1	405.4	1.055	0.746

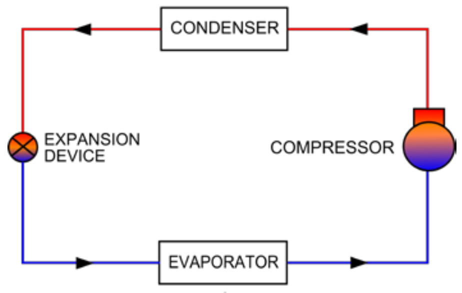
COP and Q_{vol};

air conditioning

Simulations with optimized hx circuitry



Basic cycle



R-410A: $T_{sat,evap}$ = 10 °C; $T_{sat,cond}$ = 40 °C

COP and Q_{vol}; air conditioning

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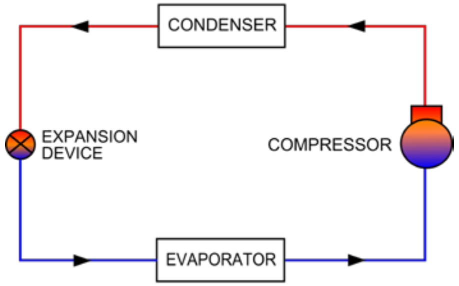

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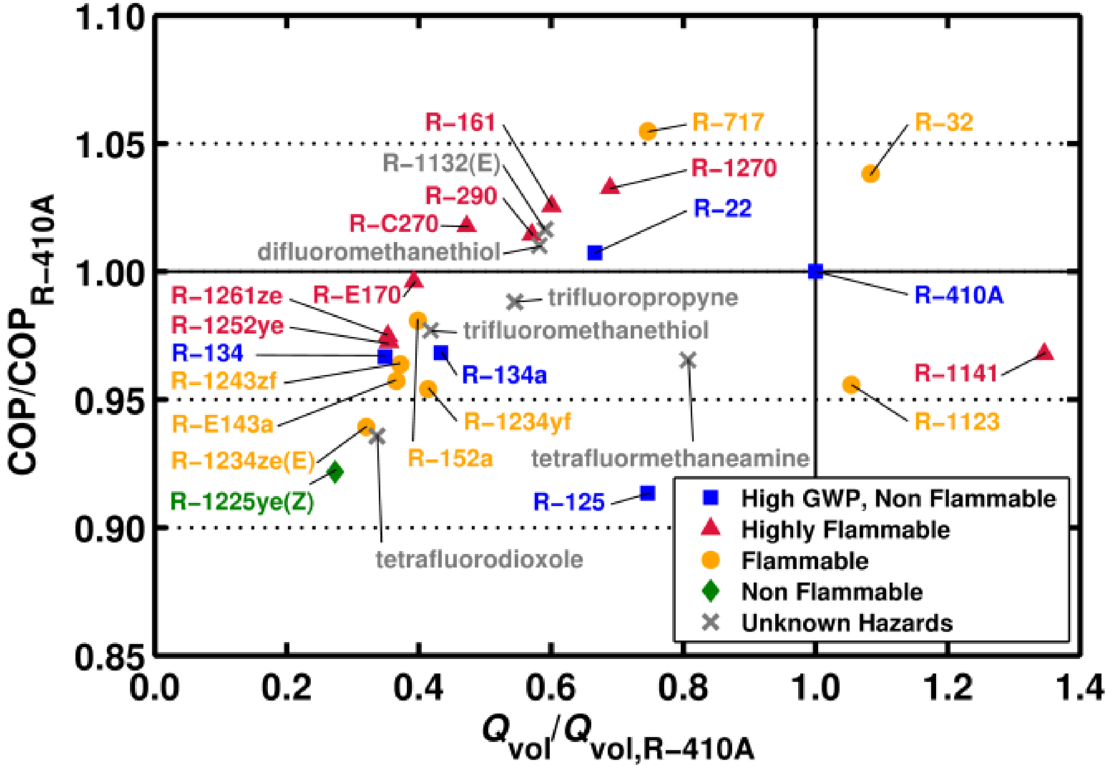
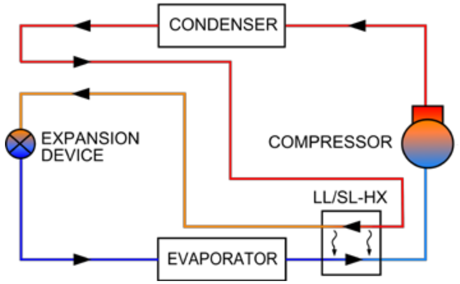


Cycle with LL/SL-HX



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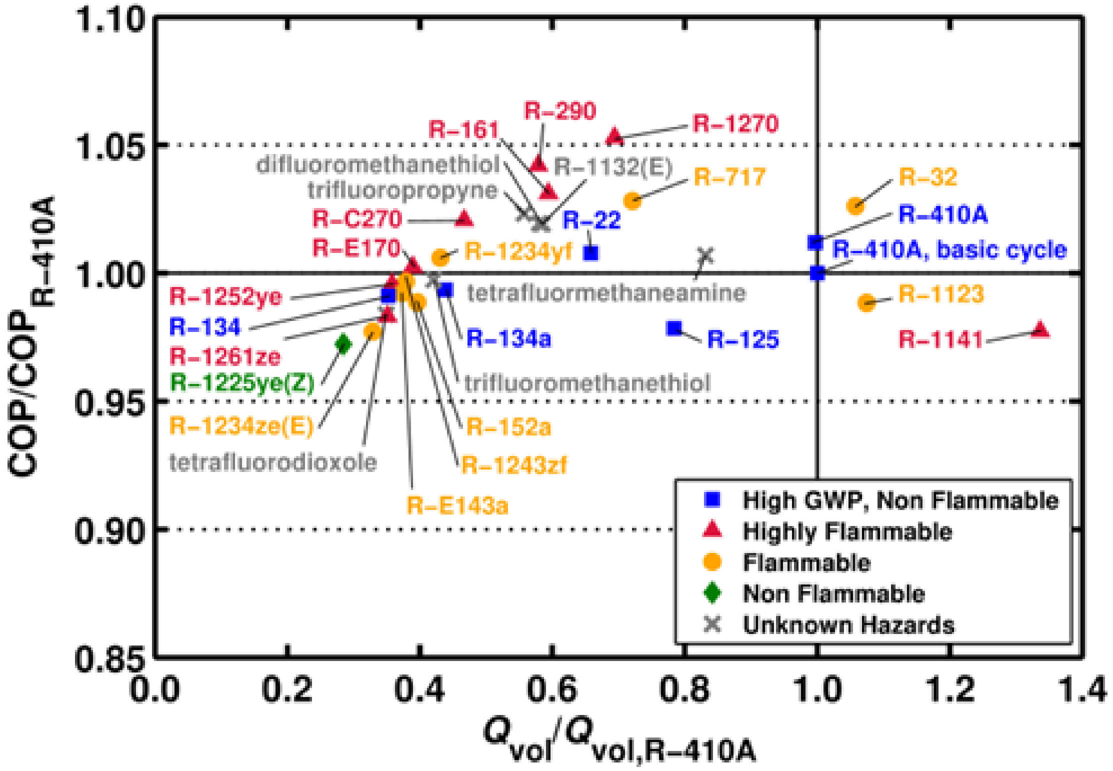
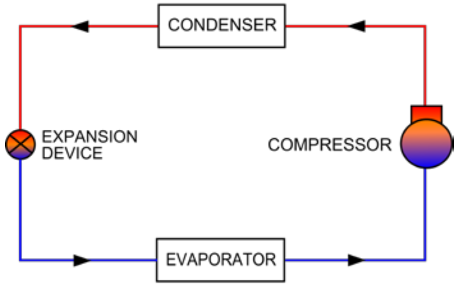
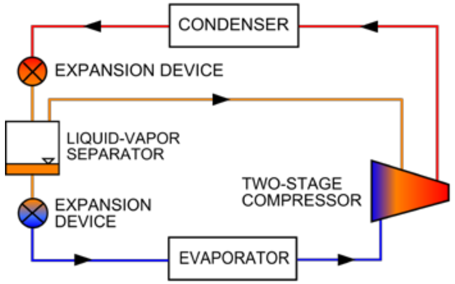


COP and Q_{vol}; air conditioning

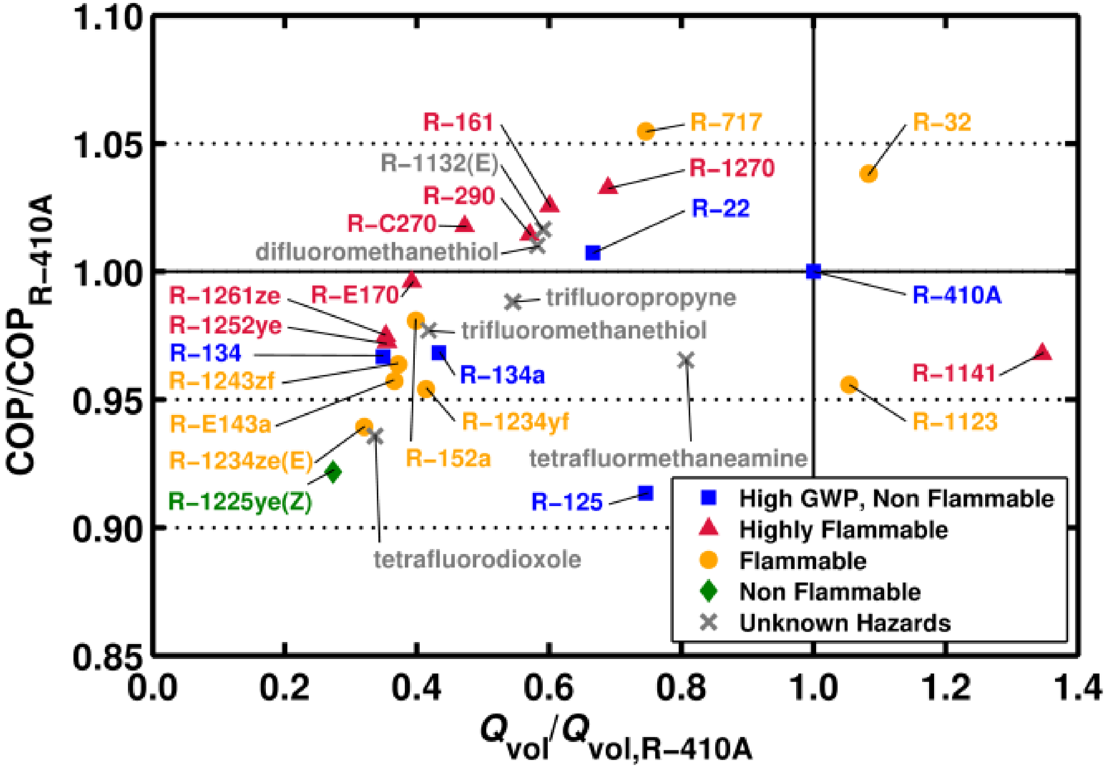
Basic cycle



Economizer cycle



Simulations with optimized hx circuitry



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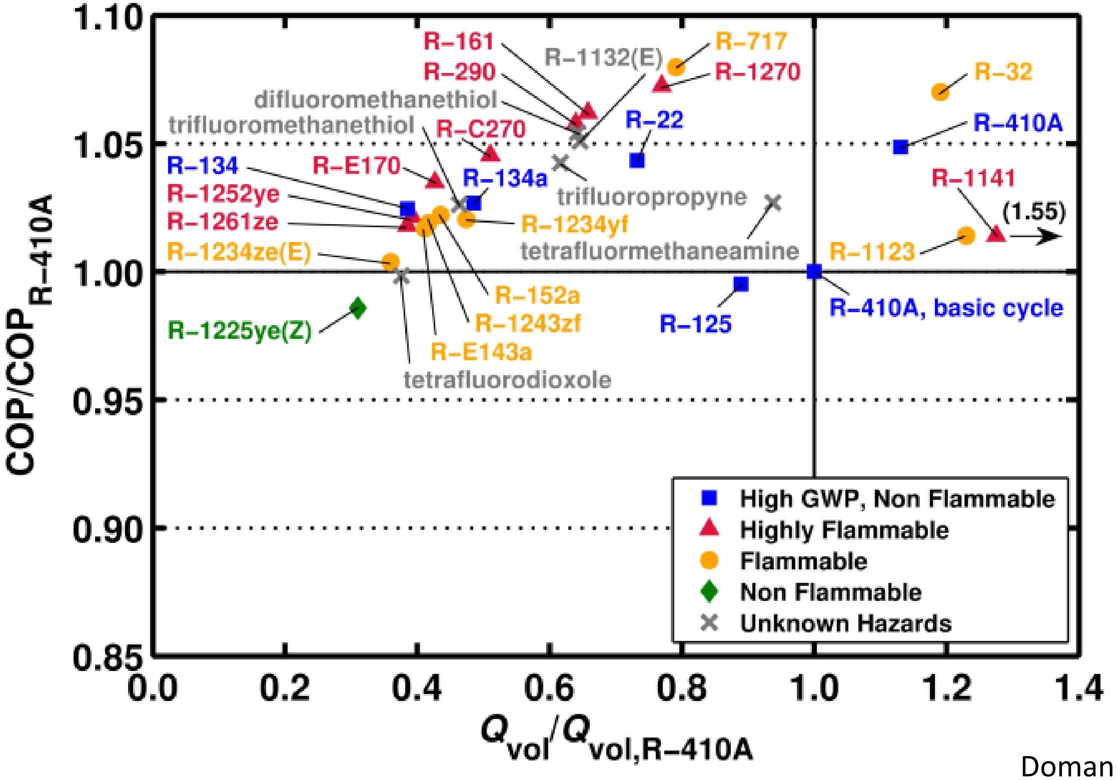
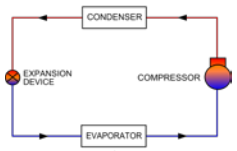
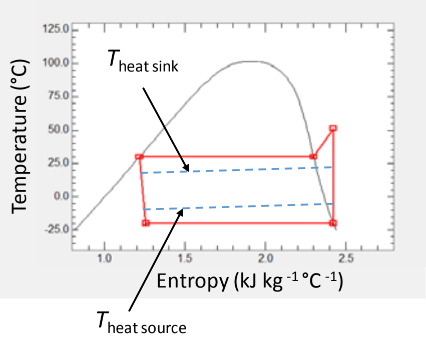


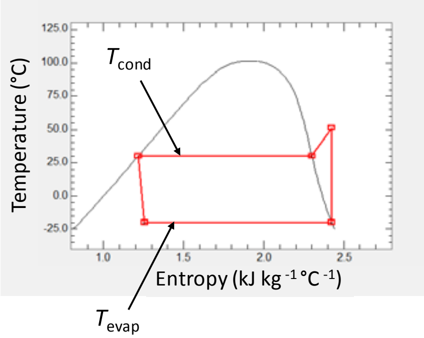
Domanski (1995)

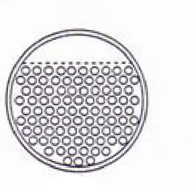
COP and Q_{vol}; air conditioning

Basic cycle









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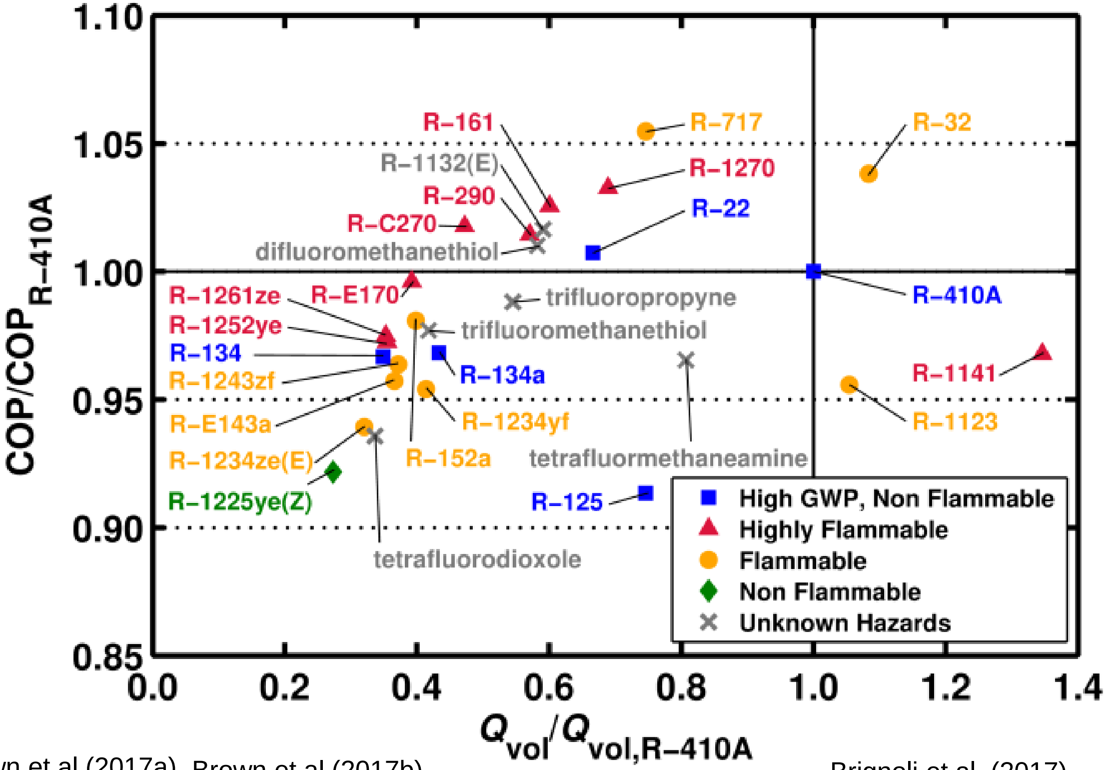
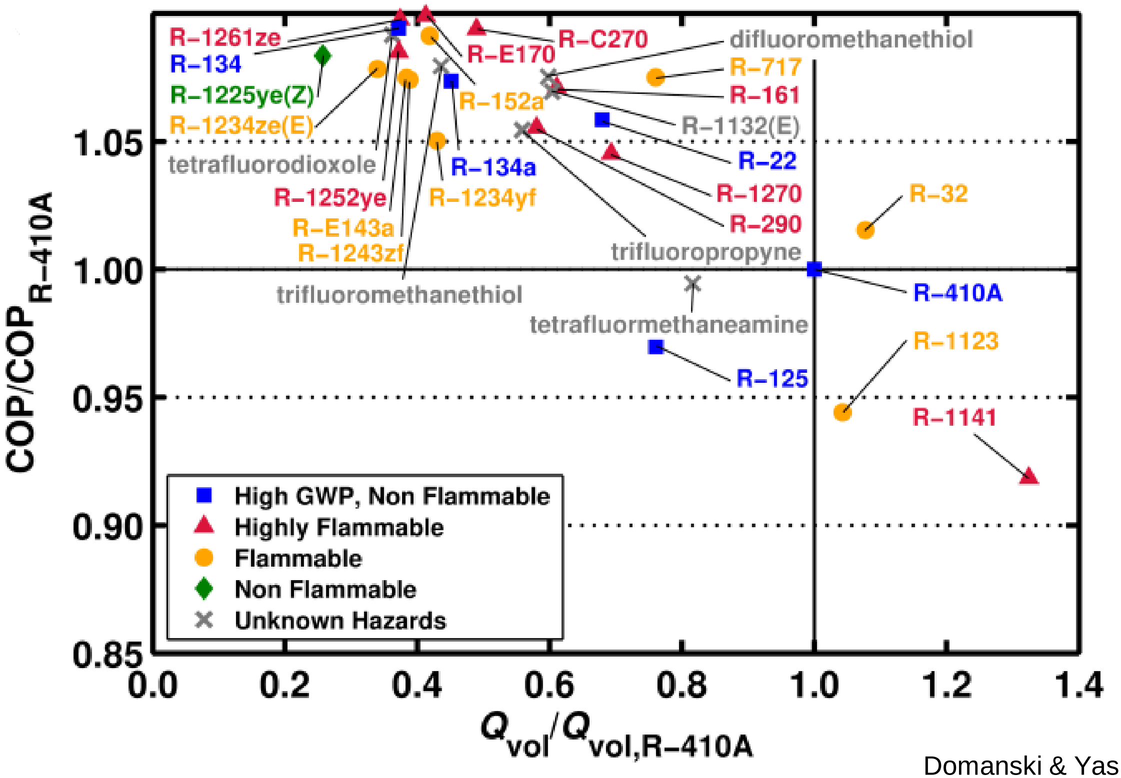


Brown et al.(2017a), Brown et al.(2017b)

Brignoli et al. (2017)

Ideal cycle simulations (zero hx pressure drop)



Domanski & Yashar (2006)

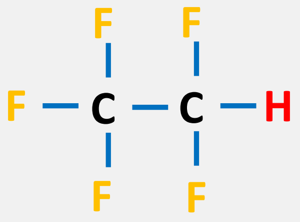
Why there are no low-GWP fluids that are nonflammable and have high Q_{vol}?

Trade-off between low GWP and flammability

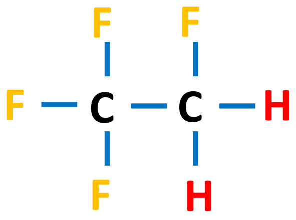
GWP can be lowered by:

- **Replacing F or Cl with H.**
  It shortens the atmospheric life but leads to flammability.

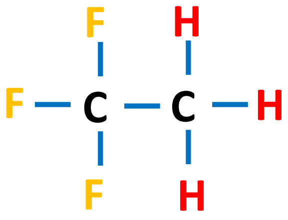
- **Adding a C=C double bond.**
  Contributes to the reaction with oxygen.



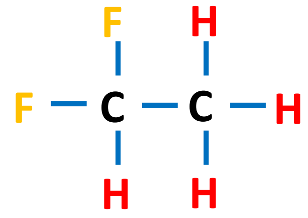
R-125
GWP = 3170; T_{cr} = 66.0 °C
Class: 1



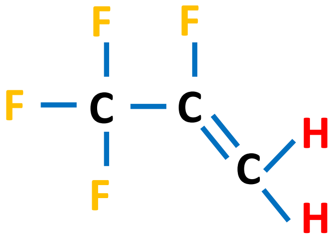
R-134a
GWP = 1300; T_{cr} = 101.1 °C
Class: 1



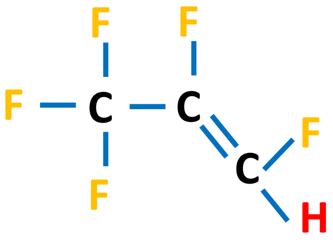
R-143a
GWP = 4800; T_{cr} = 72.7 °C
Class: 2L



R-152a
GWP = 138; T_{cr} = 113.3 °C
Class: 2



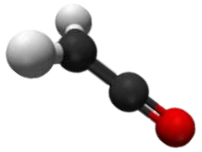
R-1234yf
GWP = < 1; T_{cr} = 94.7 °C
Class: 2L



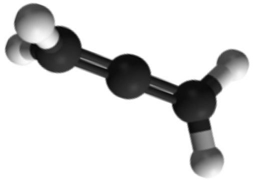
R-1225ye(Z)
GWP < 1; T_{cr} = 110.9 °C
Class: 1

Is it all ?
Why some other fluids did not make it ?

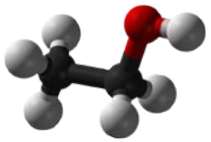
- Peroxides [-O-O-]: unstable, one dropped
- Alkynes [-C≡C-]: ≡ generally less stable than =, one retained
- Ketenes [>C=C=O]: generally very reactive, three dropped



- Allenes [>C=C=C<]: very reactive



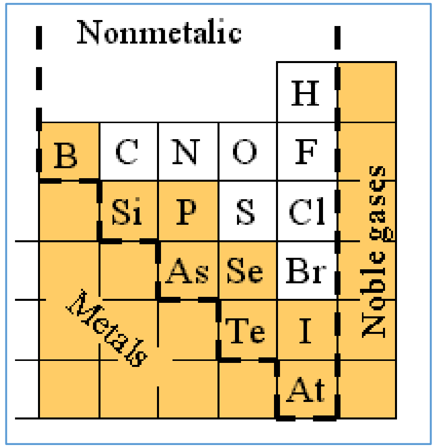
- Alcohols [-OH]: high T_{cr}



- = CF_2 group: high reactivity often associated with toxic effects; some exceptions
- = OF group: not stable, may lead to hydrofluoric acid

How reliable was the screening process?

Did we miss good fluids?



- PubChem database is complete (?)

  PubChem lists 30 three-carbon HFOs out of 31 possible. It is unlikely that the missing molecule would posses significantly different properties than those already listed.

- Component atoms: only C, H, N, O, S, F, Cl, Br (?) Maximum number of atoms: 18 (?)

  Additional screening of a different database with 2000 industrial fluids yielded small molecules with the above eight elements only.

- GWP$_{100}$ < 1000 (?)

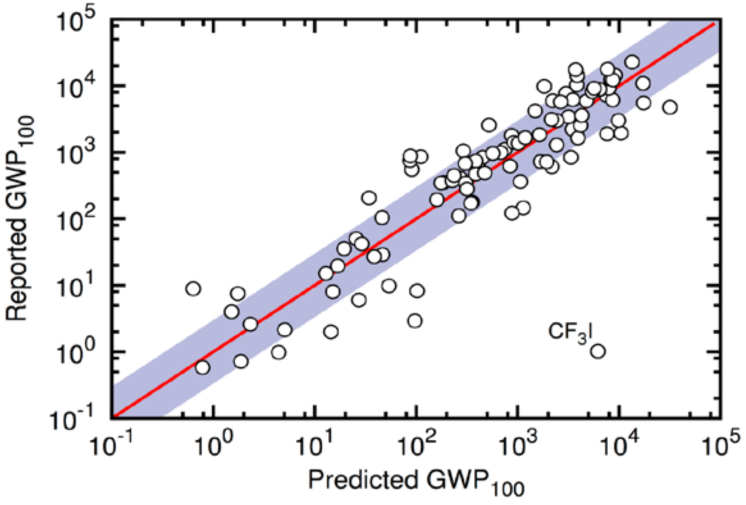
- Critical temperature: 46 °C < T_{cr} < 146 °C (?)

  Estimated with standard deviation of 16.5 K (4.5 %). $T_{cr,\ R\text{-}410A}$=71.3 °C

- Stability and toxicity (?)

  Published data may be erroneous. E.g., toxicity of R-1132a

  Unstable fluid may be stabilized and used in the system. E.g., R-1123, R-13I1 (CF$_3$I)



RMS deviation: factor of 3

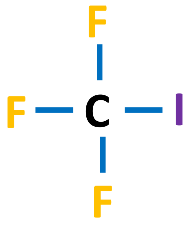
CF_3I - ASHRAE Standard 34 proposed addenda ‘t’ and ‘s’

Addendum ‘t’

R-13I1
Chemical name = trifluoroiodomethane
Chemical formula **CF_3I**
OEL = 500 ppm v/v
Safety Group = A1
GPW = 0.4

Addendum ‘s’

R-466A
Composition (mass %) = R-32/125/13I1 (49/11.5/39.5)
OEL = 860 ppm v/v
Safety Group = A1
GWP = 733



- ODP = 0.008
- Good thermodynamic properties
- Fire suppression properties

- **Toxicity** of **CF_3I** was studied in the 1990s (McCain and Macko, 1999). **CF_3I** is SNAP-approved fire suppressing agent replacing halon 1301 (total flooding) and halon 1211 (streaming), with restrictions to unoccupied and non-residential uses, respectively.

- R-1234yf/**CF_3I** (70/30) was studied in the 2000s for automotive ACs, within the Cooperative Research Program CRP150 (SAE). Dropped over concerns related to the **non-zero ODP** and **reactivity** of **CF_3I**. (Brown, 2012)

CF_3I is expected to see future application as a component of nonflammable blends.
Application challenge: reactivity

Low-GWP refrigerant options

🟦 No flame propagation
🟧 Lower flammability
🟥 Higher flammability

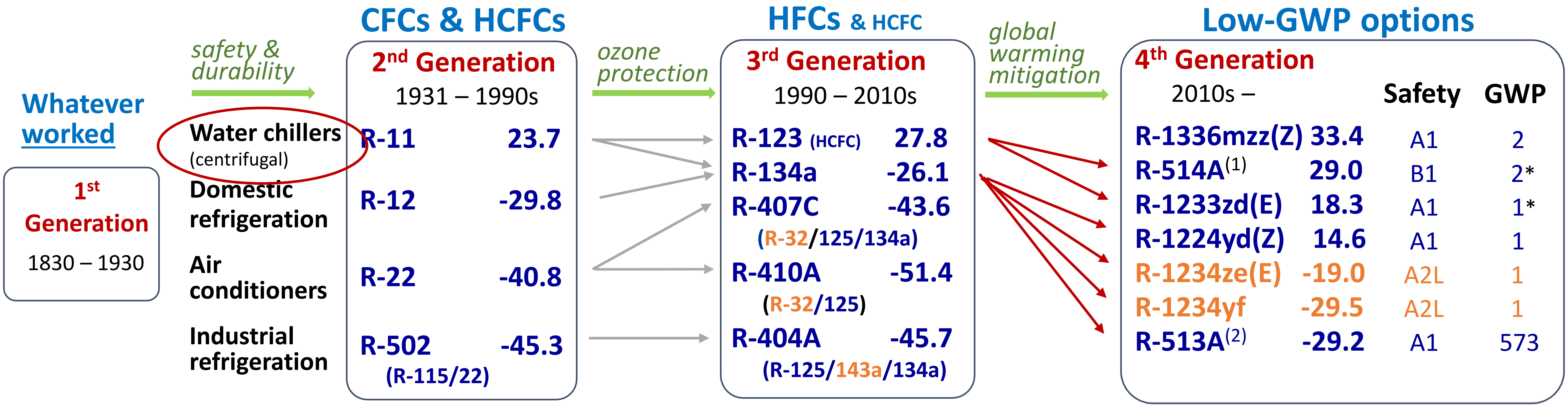
Natural fluids

H_2O	100.0	R-717	-33.3	R-600a	- 11.7
CO_2	-78.4			R-290	- 42.1
air	-194.2			R-1270	- 47.7

Ammonia

Normal boiling point (°C)

Fluorinated fluids



CFCs & HCFCs

2nd Generation

1931 – 1990s

R-11	23.7
R-12	-29.8
R-22	-40.8
R-502 (R-115/22)	-45.3

HFCs & HCFC

3rd Generation

1990 – 2010s

R-123 (HCFC)	27.8
R-134a	-26.1
R-407C (R-32/125/134a)	-43.6
R-410A (R-32/125)	-51.4
R-404A (R-125/143a/134a)	-45.7

Low-GWP options

4th Generation

2010s –		Safety	GWP
R-1336mzz(Z)	33.4	A1	2
R-514A(1)	29.0	B1	2*
R-1233zd(E)	18.3	A1	1*
R-1224yd(Z)	14.6	A1	1
R-1234ze(E)	-19.0	A2L	1
R-1234yf	-29.5	A2L	1
R-513A(2)	-29.2	A1	573

Calm (2008), Calm (2012), Myhre, G. et al. (2013)

* Source other than IPCC AR5

(1)R-1336mzz(Z)/1130(E) (74.7/25.3)

(2)R-1234yf/134a (56/44)

Low-GWP refrigerant options

🟦 No flame propagation
🟧 Lower flammability
🟥 Higher flammability

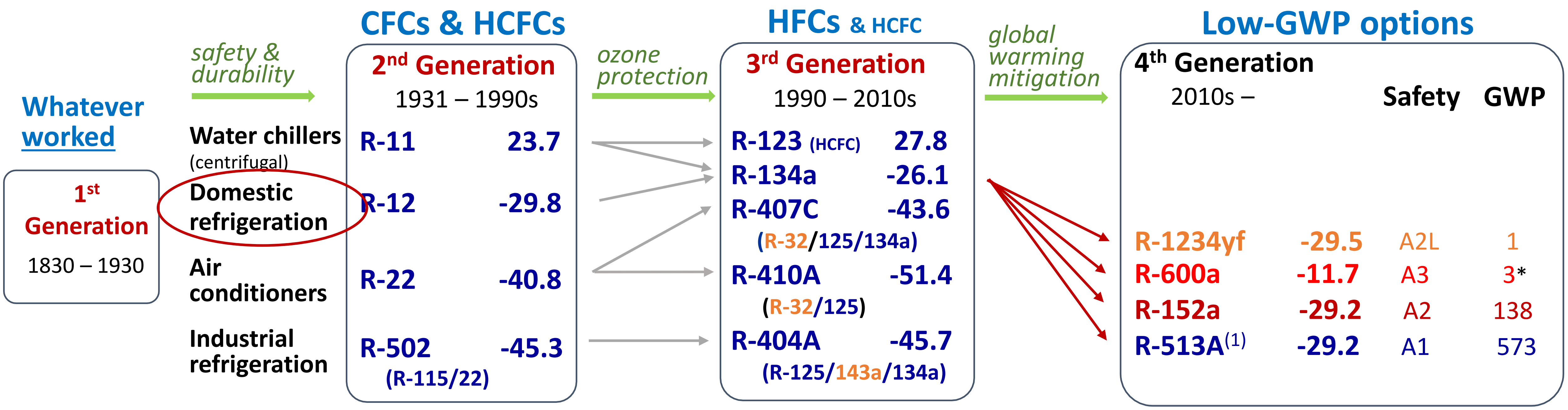
Natural fluids

H_2O	100.0	R-717	-33.3	R-600a	- 11.7
CO_2	-78.4			R-290	- 42.1
air	-194.2			R-1270	- 47.7

Ammonia

Normal boiling point (°C)

Fluorinated fluids



Whatever worked

1st Generation
1830 – 1930

safety & durability

Water chillers (centrifugal)	R-11	23.7
Domestic refrigeration	R-12	-29.8
Air conditioners	R-22	-40.8
Industrial refrigeration	R-502 (R-115/22)	-45.3

CFCs & HCFCs

2nd Generation
1931 – 1990s

ozone protection

HFCs & HCFC

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R-410A (R-32/125)	-51.4
R-404A (R-125/143a/134a)	-45.7

global warming mitigation

Low-GWP options

4th Generation
2010s –

		Safety	GWP
R-1234yf	-29.5	A2L	1
R-600a	-11.7	A3	3*
R-152a	-29.2	A2	138
R-513A(1)	-29.2	A1	573

Calm (2008), Calm (2012), Myhre, G. et al. (2013)

* Source other than IPCC AR5

(1)R-1234yf/134a (56/44)

Low-GWP refrigerant options

🟦	No flame propagation
🟧	Lower flammability
🟥	Higher flammability

Natural fluids

H_2O	100.0	R-717	-33.3	R-600a	- 11.7
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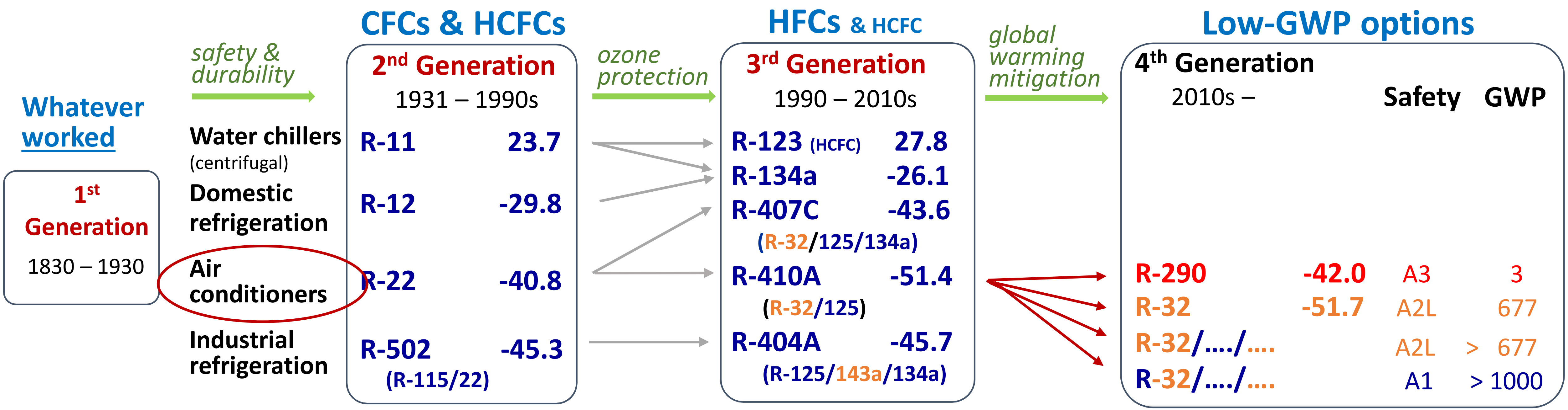
Ammonia

Normal boiling point (°C)

Fluorinated fluids



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R-410A (R-32/125)	-51.4
R-404A (R-125/143a/134a)	-45.7

global warming mitigation

Low-GWP options

4th Generation
2010s –

		Safety	GWP
R-290	-42.0	A3	3
R-32	-51.7	A2L	677
R-32/..../....		A2L	> 677
R-32/..../....		A1	> 1000

Calm (2008), Calm (2012), Myhre, G. et al. (2013)

Low-GWP refrigerant options

🟦 No flame propagation
🟧 Lower flammability
🟥 Higher flammability

Natural fluids

H_2O	100.0	R-717	-33.3	R-600a	- 11.7
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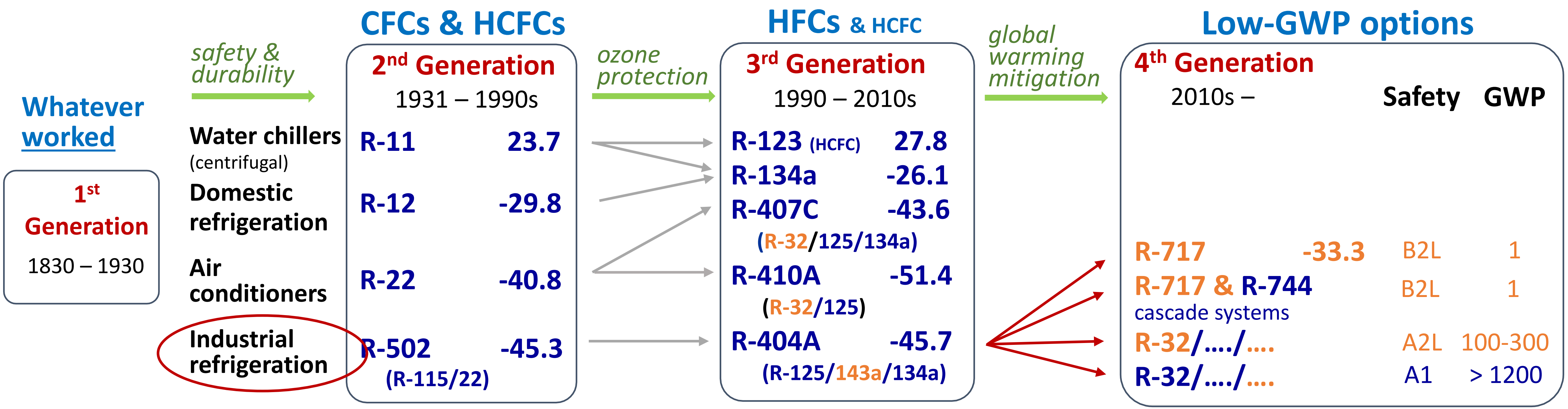
Ammonia

Normal boiling point (°C)

Fluorinated fluids



Whatever worked

1st Generation
1830 – 1930

safety & durability

CFCs & HCFCs

2nd Generation
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ozone protection

HFCs & HCFC

3rd Generation
1990 – 2010s

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R-134a	**-26.1**
R-407C (R-32/125/134a)	**-43.6**
R-410A (R-32/125)	**-51.4**
R-404A (R-125/143a/134a)	**-45.7**

global warming mitigation

Low-GWP options

4th Generation
2010s –

		Safety	**GWP**
R-717	**-33.3**	B2L	1
R-717 & R-744 cascade systems		B2L	1
R-32/..../....		A2L	100-300
R-32/..../....		A1	> 1200

Calm (2008), Calm (2012), Myhre, G. et al. (2013)

Cooling technologies

sorted by primary energy input

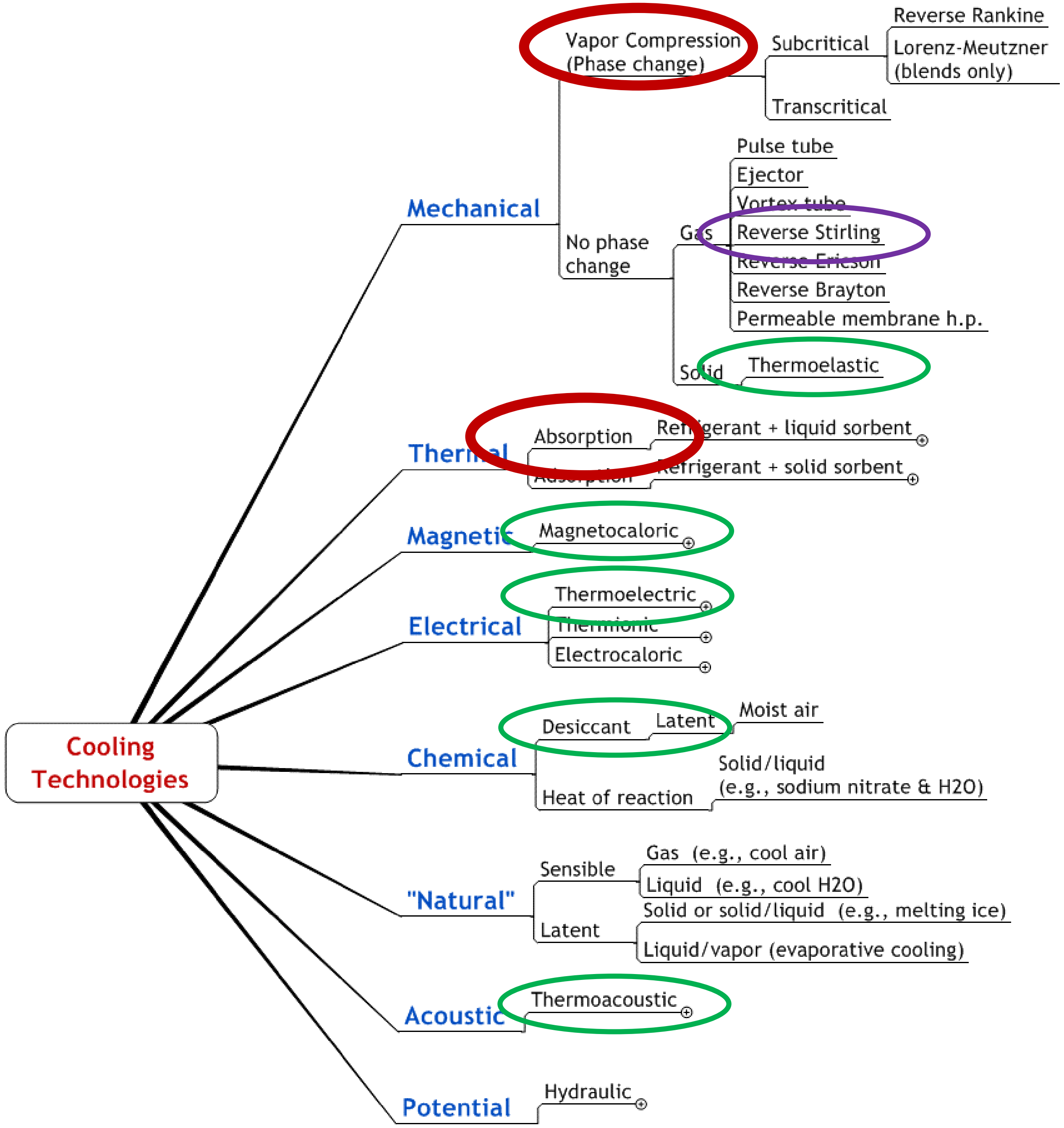
Acceptance criteria

- Coefficient of Performance
- Environmental
- Safety
- Cost
- Reliability
- Serviceability
- Physical size, weight

Best prospects for competing with vapor compression

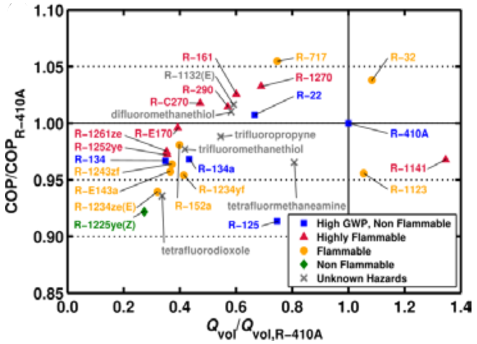
🟢 Space conditioning

🟣 Food refrigeration



- Cooling Technologies
  - Mechanical
    - Vapor Compression (Phase change)
      - Subcritical
        - Reverse Rankine
        - Lorenz-Meutzner (blends only)
      - Transcritical
    - No phase change
      - Gas
        - Pulse tube
        - Ejector
        - Vortex tube
        - Reverse Stirling
        - Reverse Ericson
        - Reverse Brayton
        - Permeable membrane h.p.
      - Solid
        - Thermoelastic
  - Thermal
    - Absorption
      - Refrigerant + liquid sorbent
    - Adsorption
      - Refrigerant + solid sorbent
  - Magnetic
    - Magnetocaloric
  - Electrical
    - Thermoelectric
    - Thermionic
    - Electrocaloric
  - Chemical
    - Desiccant
      - Latent
        - Moist air
    - Heat of reaction
      - Solid/liquid (e.g., sodium nitrate & H2O)
  - "Natural"
    - Sensible
      - Gas (e.g., cool air)
      - Liquid (e.g., cool H2O)
    - Latent
      - Solid or solid/liquid (e.g., melting ice)
      - Liquid/vapor (evaporative cooling)
  - Acoustic
    - Thermoacoustic
  - Potential
    - Hydraulic

Concluding comments



- **Availability of low-GWP refrigerants varies between applications**
  - Good availability of low-pressure fluids (low GWP, nonflammable)
  - No direct HFO replacement candidate for R-22 or R-410A

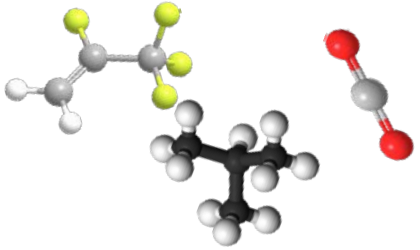
    Single-component medium- and high-pressure replacement fluids are at least mildly flammable

- **Prospects for finding new viable refrigerants are minimal.**

  New equipment will have to be designed using the fluids we know already and their blends.

- **Trade off between GWP ↓ and flammability ↑**

Concluding comments



o Alternative cooling technologies?

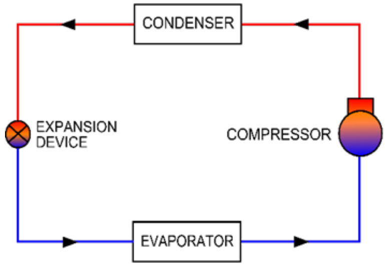
Alternative technologies will gain entry in niche applications

<u>but</u>

will need significant development effort and material breakthroughs to be competitive and enter the main stream.

Ice harvesting

Vapor compression



?

o We will have to use refrigerants judiciously, which includes:

- Selection of refrigerant for each application recognizing environmental and safety considerations
- High-efficiency, leak-free equipment
- Improved refrigerant handling practices (equipment commissioning, servicing, and decommissioning).

Thank you for your attention.

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