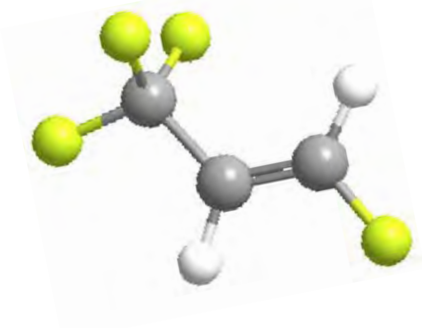


RECENT DEVELOPMENTS IN LOW-GWP REFRIGERANT ALTERNATIVES

Piotr A. Domanski

Ozone Operations Resource Group

International Conference of Sustainable Cooling

and

Fifth Annual CO_3OL Workshop

Washington, DC, November 28-30, 2018

Impact of refrigeration on climate

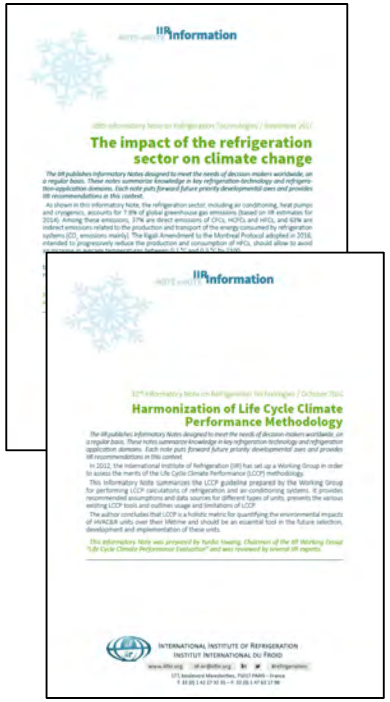
- The refrigeration sector accounts for 7.8 % of global greenhouse gas emissions

  Includes air conditioning, heat pumping and cryogenics (1,2)

  - 37 % are direct emissions of refrigerants (GWP)
  - 63 % are indirect emissions (efficiency)

- Emissions vary with applications

  - Mobile ACs; large direct emissions
  - Large chillers or domestic refrigerators; small direct emissions



(1) IIR, 2017. The impact of the refrigeration sector on climate change. 35th Informatory Note on Refrigeration technologies, Int. Institute of Refrigeration. November 2017. http://www.iifiir.org/

(2) IIR, 2016. Harmonization of Life Cycle Climate Performance Methodology. 32nd Informatory Note on Refrigeration technologies, Int. Institute of Refrigeration. October 2016. http://www.iifiir.org/

Availability of low-GWP refrigerants

- No flame propagation
- Lower flammability
- Higher flammability

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)
Unsaturated HFCs & HFC

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

Natural fluids

Ammonia

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

Normal boiling point (°C)

Availability of low-GWP refrigerants

- No flame propagation
- Lower flammability
- Higher flammability

Fluorinated fluids

Whatever worked

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safety & durability →

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ozone protection →

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

global warming mitigation →

HFOs (Hydrofluoroolefins)
Unsaturated HFCs & HFC

4th Generation
2010s –

		Options	
R-1336mzz(Z)	33.4	R-514A(*)	(B1)
R-1233zd(E)	18.3	√	(A1)
R-1224yd(Z)	14.6	√	(A1)
R-1234ze(E)	-19.0	√	(A2L)
R-1234yf	-29.5	√	(A2L)
		R-513A(#)	(A1)

(*)R-1336mzz(Z)/1130(E)
(#)R-1234yf/134a

Natural fluids

Ammonia

Normal boiling point (°C)

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

Availability of low-GWP refrigerants

No flame propagation	(blue)
Lower flammability	(orange)
Higher flammability	(red)

Fluorinated fluids

Whatever worked

1rd 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)
Unsaturated HFCs & HFC

4th Generation
2010s –

R-1234yf	-29.5

Options

R-600a	(A3)
√	(A2L)
R-513A (#)	(A1)

(#)R-1234yf/134a

Natural fluids

Ammonia

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

Normal boiling point (°C)

Availability of low-GWP refrigerants

No flame propagation
Lower flammability
Higher flammability

Fluorinated fluids

Whatever worked

1rd 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 -45.3 (R-115/22)

ozone protection →

HFCs & HCFC

3rd Generation
1990 – 2010s

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

global warming mitigation →

HFOs (Hydrofluoroolefins)
Unsaturated HFCs & HFC

4th Generation
2010s –

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

Options

- √ (A2L)
- R-290 (A3)
- R-........ (A2L)
- R-........ (A1)

Natural fluids

Ammonia

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

Normal boiling point (°C)

Availability of low-GWP refrigerants

- No flame propagation
- Lower flammability
- Higher flammability

Fluorinated fluids

Whatever worked

1rd 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)
Unsaturated HFCs & HFC

4th Generation
2010s –

R-32/HFC/HFO
R-32/HFC/HFO

Options

R-717 (A2L)
R-452A (#) (A1)
R-717 & R-744
Cascade system

(#)R-32/125/1234yf

Natural fluids

Ammonia

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

Normal boiling point (°C)

Search for R-410A low-GWP replacements

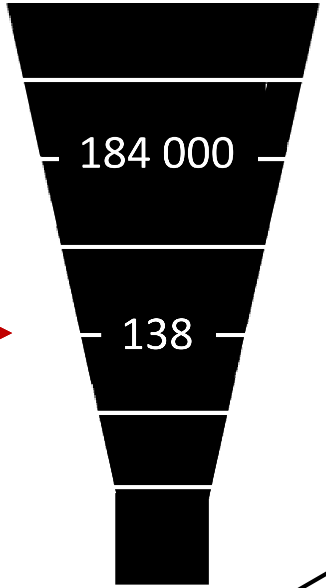
Screening study

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, REL, TLV, $=CF_2$)
- Stability
- Volumetric capacity > 0.33 $Q_{vol,R\text{-}410A}$
  (basic cycle simulations)

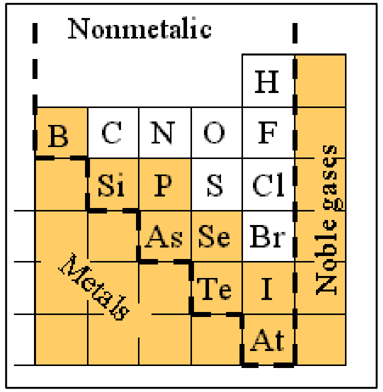
Molecule count

60 000 000



21

15 - at least mildly flammable
6 - unknown hazards

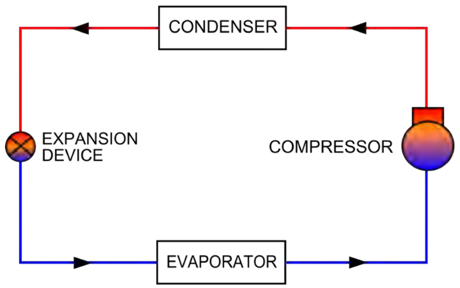


- 21 (primary interest) + 3 (commercial interest) + 3 (low T_{crit}) ⟶ 27 fluids
- New toxicity data on R-1132a; 27 + 1 ⟶ 28 fluids
  Performed detailed simulations with optimized heat exchangers of 24 fluids

Air conditioning: McLinden et al. (2017)

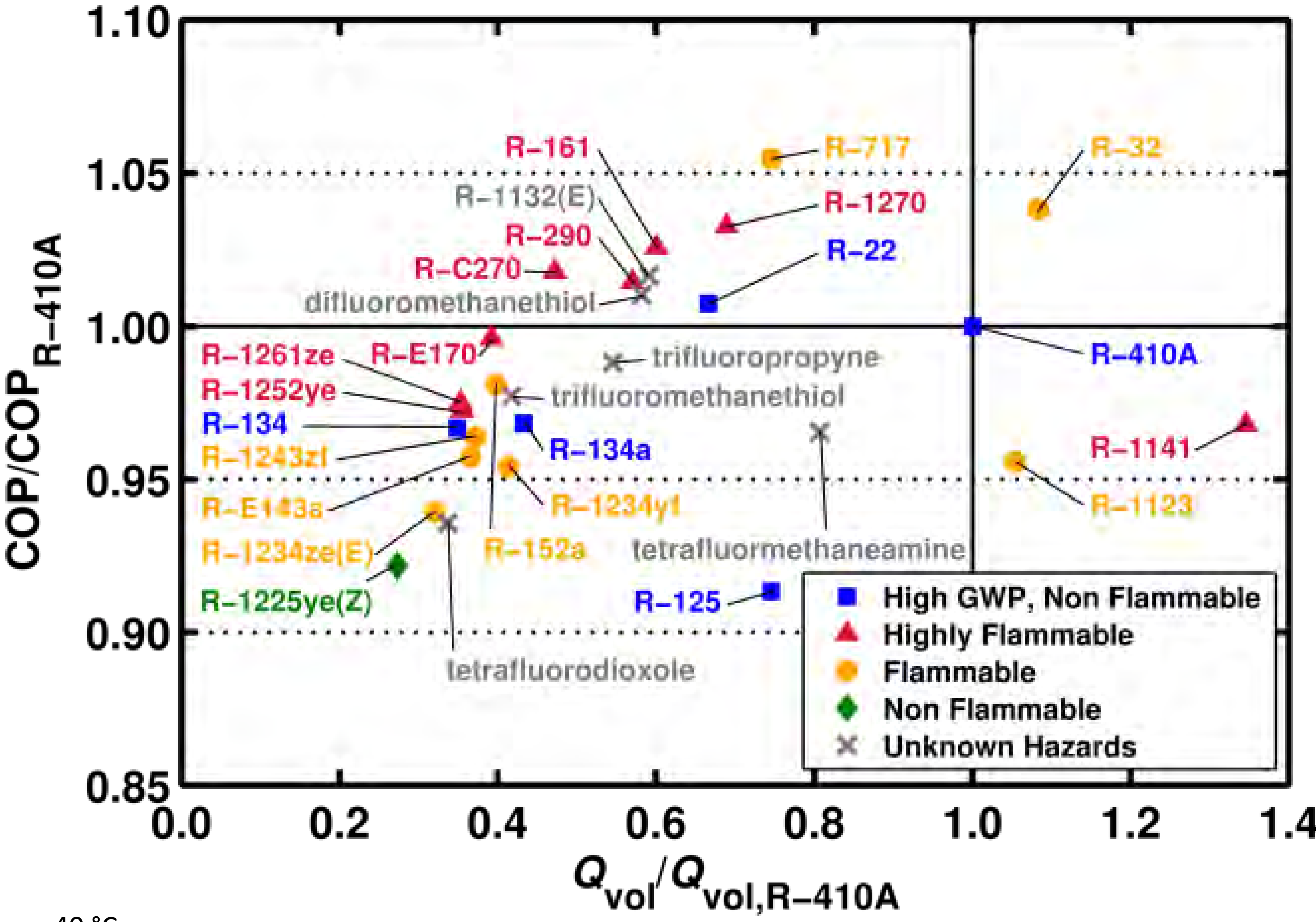
Refrigeration and heating: Domanski et al. (2017)

COP and Q_{vol}



Basic cycle, detailed simulations with optimized heat exchangers

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



Blends classified by ASHRAE Std. 34 – 2016

Zeotropes

ASHRAE Designation	Components	Composition (mass %)
R-401A	R-22/152a/124	53/13/34
R-401B	R-22/152a/124	61/11/28
R-401C	R-22/152a/124	33/15/52
R-402A	R-125/290/22	60/2/38
R-402B	R-125/290/22	38/2/60
R-403A	R-290/22/218	5/75/20
R-403B	R-290/22/218	5/56/39
R-404A	R-125/143a/134a	44/52/4
R-405A	R-22/152a/142b/C318	45/7/5.5/42.5
R-406A	R-22/600a/142b	55/4/41
R-407A	R-32/125/134a	20/40/40
R-407B	R-32/125/134a	10/70/20
R-407C	R-32/125/134a	23/25/52
R-407D	R-32/125/134a	15/15/70
R-407E	R-32/125/134a	25/15/60
R-407F	R-32/125/134a	30/30/40
R-407G	R-32/125/134a	2.5/2.5/95
R-408A	R-125/143a/22	7/46/47
R-409A	R-22/124/142b	60/25/15
R-409B	R-22/124/142b	65/25/10
R-410A	R-32/125	50/50
R-410B	R-32/125	45/55
R-411A	R-1270/22/152a	1.5/87.5/11.0
R-411B	R-1270/22/152a	3/94/3
R-412A	R-22/218/142b	70/5/25
R-413A	R-218/143a/600a	9/88/3
R-414A	R-22/124/600a/142b	51/28.5/16.5
R-414B	R-22/124/600a/142b	50/39/1.5/9.5
R-415A	R-22/152a	82/18
R-415B	R-22/152a	25/75
R-416A	R-124/R134a/600	39.5/59.0/1.5
R-417A	R-125/134a/600	46.6/50.0/3.4
R-417B	R-125/134a/600	79.0/18.3/2.7
R-417C	R-125/134a/600	19.5/78.8/1.7
R-418A	R-290/22/152a	1.5/96/2.5
R-419A	R-125/134a/E170	77/19/4
R-419B	R-125/134a/E170	48.5/48/3.5
R-420A	R-134a/142b	88/12
R-421A	R-125/134a	58/42
R-421B	R-125/134a	85/15
R-422A	R-125/134a/600a	85.1/11.5/3.4
R-422B	R-125/134a/600a	55/42/3
R-422C	R-125/134a/600a	82/15/3
R-422D	R-125/134a/600a	65.1/31.5/3.4
R-422E	R-125/134a/600a	58/39.3/2.7
R-423A	R-134a/227ea	52.5/47.5
R-424A	R-125/134a/600a/600/601a	50.5/47/0.9/1/0.6
R-425A	R-32/134a/227ea	18.5/69.5/12
R-426A	R-125/134a/600/601a	5.1/93/1.3/0.6
R-427A	R-32/125/143a/134a	15/25/10/50
R-428A	R-125/143a/290/600a	77.5/20/0.6/1.9
R-429A	R-E170/152a/600a	60/10/30
R-430A	R-152a/600a	6/24

Zeotropes

ASHRAE Designation	Components	Composition (mass %)
R-429A	R-E170/152a/600a	60/10/30
R-430A	R-152a/600a	6/24
R-431A	R-290/152a	71/29
R-432A	R-1270/E170	80/20
R-433A	R-1270/290	30/70
R-433B	R-1270/290	5/95
R-433C	R-1270/290	25/75
R-434A	R-125/143a/134a/600a	63.2/18/16/2.8
R-435A	R-E170/152a	80/20
R-436A	R-290/600a	56/44
R-436B	R-290/600a	52/48
R-437A	R-125/134a/600/601a	19.5/78.5/1.4/0.6
R-438A	R-32/125/134a/600/601a	8.5/45/44.2/1.7/0.6
R-439A	R-32/125/600a	50/47/3
R-440A	R-290/134a/152a	0.6/1.6/97.8
R-441A	R-170/290/600a/600	3/55/6/36
R-442A	R-32/125/134a/152a/227ea	31/31/30/3/5
R-443A	R-1270/290/600a	55/40/5

Blends with HFO

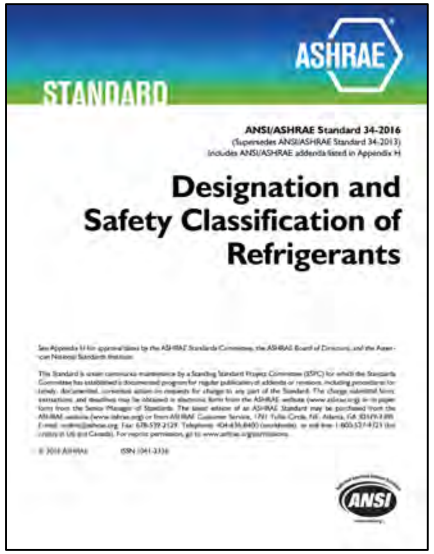
ASHRAE Designation	Components	Composition (mass %)
R-444A	R-32/152a/1234ze(E)	12/5/83
R-444B	R-32/152a/1234ze(E)	41.5/10/48.5
R-445A	R-744/134a/1234ze(E)	6/9/85
R-446A	R-32/1234ze(E)/600	68/29/3
R-447A	R-32/125/1234ze(E)	68/3.5/28.5
R-448A	R-32/125/1234yf/134a/1234ze(E)	26/26/20/21/7
R-449A	R-32/125/1234yf/134a	24.3/24.7/25.3/25.7
R-449B	R-32/125/1234yf/134a	25/24/23/27
R-450A	R-134a/1234ze(E)	42/58
R-451A	R-1234yf/134a	89.8/10.2
R-451B	R-1234yf/134a	88.8/11.2
R-452A	R-32/125/1234yf	11/59/30
R-452B	R-32/125/1234yf	67/7/26
R-452C	R-32/125/1234yf	12.5/61/26.5
R-454A	R-32/1234yf	35/65
R-454B	R-32/1234yf	68.9/31.1
R-454C	R-32/1234yf	21.5/78.5
R-455A	R-744/32/1234yf	3/21.5/75.5
R-456A	R-32/134a/1234ze(E)	6/45/49
R-457A	R-32/152a/1234yf	18/12/70

Azeotropes

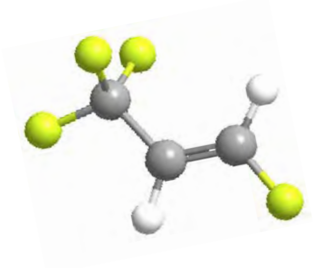
ASHRAE Designation	Components	Composition (mass %)
R-500	R-12/152a	73.8/26.2
R-501	R-22/12	75/25
R-502	R-22/115	48.8/51.2
R-503	R-23/13	40.1/59.9
R-504	R-32/115	48.2/51.8
R-507A	R-125/143a	50/50
R-508A	R-23/116	39/61
R-508B	R-23/116	46/54
R-509A	R-22/218	44/56
R-510A	R-E170/600a	88/12
R-511A	R-290/E170	95/5
R-512A	R-134a/152a	5/95

Blends with HFO

ASHRAE Designation	Components	Composition (mass %)
R-513A	R-1234yf/134a	56/44
R-513B	R-1234yf/134a	58.5/41.5
R-514A	R-1336mzz(Z)/1130(E)	74.7/25.3
R-515A	R-1234ze(E)/227ea	88/12



HFO blends classified by ASHRAE Std. 34 – 2016



Zeotropes

R-444A	R-32/152a/1234ze(E)	12/5/83
R-444B	R-32/152a/1234ze(E)	41.5/10/48.5
R-445A	R-744/134a/1234ze(E)	6/9/85
R-446A	R-32/1234ze(E)/600	68/29/3
R-447A	R-32/125/1234ze(E)	68/3.5/28.5
R-448A	R-32/125/1234yf/134a/1234ze(E)	26/26/20/21/7
R-449A	R-32/125/1234yf/134a	24.3/24.7/25.3/25.7
R-449B	R-32/125/1234yf/134a	25/24/23/27
R-450A	R-134a/1234ze(E)	42/58
R-451A	R-1234yf/134a	89.8/10.2
R-451B	R-1234yf/134a	88.8/11.2
R-452A	R-32/125/1234yf	11/59/30
R-452B	R-32/125/1234yf	67/7/26
R-452C	R-32/125/1234yf	12.5/61/26.5
R-454A	R-32/1234yf	35/65
R-454B	R-32/1234yf	68.9/31.1
R-454C	R-32/1234yf	21.5/78.5
R-455A	R-744/32/1234yf	3/21.5/75.5
R-456A	R-32/134a/1234ze(E)	6/45/49
R-457A	R-32/152a/1234yf	18/12/70

Azeotropes

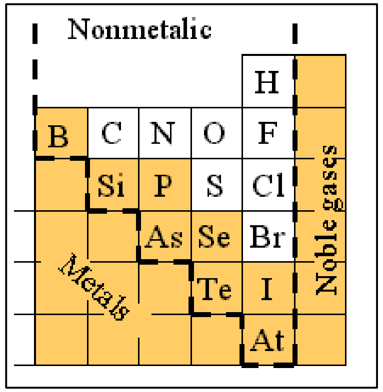
R-513A	R-1234yf/134a	56/44
R-513B	R-1234yf/134a	58.5/41.5
R-514A	R-1336mzz(Z)/1130(E)	74.7/25.3
R-515A	R-1234ze(E)/227ea	88/12

- R-32 is the most common component in HFO blends
- No low-GWP non-flammable replacement for high-pressure applications (R-22 and R-410A replacements)
- Trade-off in blend design: GWP versus flammability

16 new fluids introduced after 2016

- 2 single-component fluids
  - R-1224yd(Z) (A1)
  - R-1132a (A2)
- 1 azeotropic blend R-516A
  - R-1234yf/134a/152a (77.5/8.5/14) (A2L)
- 13 zeotropic blends
  - 10 blends contain R-32 (A1, A2L, A2, A3)

ASHRAE Standard 34 pending addenda ‘t’ and ‘s’



Addendum t

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

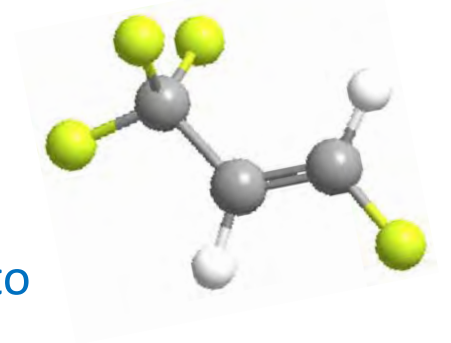
- ODP = 0.008;   GPW = 0.4
- Good thermodynamic properties
- File suppression properties
- **Toxicity** of **CF_3I** was studied in the 1990s (McCain and Macko, 1999). **CF_3I** is SNAP-approved fire suppressing agent replacing halon 1301 (total flooding) and halon 1211 (streaming), with restrictions to unoccupied and non-residential uses, respectively.
- R-1234yf/**CF_3I** (70/30) was studied in the 2000s for automotive Acs. Dropped over concerns related to the **non-zero ODP** and **reactivity** of **CF_3I**. (Brown, 2012)

Addendum s

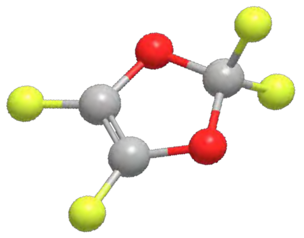
R-466A
Composition (mass %) = R-32/125/13I1 (49/11.5/39.5)
OEL = 860 ppm v/v
Safety Group = A1
GWP = 733

Addenda ‘t’ and ‘s’ were considered at the June 2018 ASHRAE Meeting. The ‘public comment period’ is closed.
Will be discussed at the January 2019 ASHRAE Meeting.

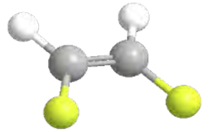
Concluding remarks



- Low-GWP refrigerants are limited to single-component refrigerants we know already and to their blends.



- Availability of low GWP refrigerants varies between applications
  - Good availability of low-pressure fluids (low GWP, non-flammable)
  - Mid-pressure and high-pressure low-GWP refrigerants are at least mildly flammable



- In general, new proposed fluids have large molecules and have somewhat lower efficiency in the basic vapor-compression cycle

- CF_3I (pending application to ASHRAE Std. 34) may see several future applications as a component of <u>non-flammable</u> blends

References

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