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Performance of Non-CFC Refrigerants for Low-Temperature Refrigeration

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Abstract: As a result of the worldwide ban on chlorinated refrigerants two widely used low temperature refrigerants; R13 and R503, are being made unavailable to the refrigeration industry. As for the present, alternative refrigerants for these fluids are very limited. This paper assesses the suitability of some logically screened non-CFC refrigerants and azeotropic mixtures for low temperature cooling applications. The analysis is based on thermal-physical properties and simulated vapour compression refrigeration cycle performance of the fluids. The screening process identified two fluorocarbons (R116 and R14) and one hydrocarbon (R170) as potential non-CFC replacements. Further, the study reveals that the properties of fluorocarbon R116, mixtures R508A and R508B correlate well with those of R13 and R503. It is also found that R14 possesses desired property behaviour of a refrigerant for cooling application close to –100 °C or below, however reasonable vapour pressures, volumes and discharge temperatures need to be obtained preferably by making a blend with a second fluid.

Keywords: Low-temperature refrigeration, mixtures, COP, efficiency, vapour compression systems

1. Background

Expanding knowledge on adverse environmental implications of chlorinated refrigerants intensified the global search for environmentally acceptable, chemically and thermally stable alternatives. However, current research on refrigerants reveal that the chances for the discovery of an ideal refrigerant that meets all the environmental and performance criterion are very unlikely [1,2,3,4]. Among different applications of refrigeration, one area that faces challenges and difficulties in finding suitable alternatives is low temperature applications; say those operating below - 50 °C. At such low temperatures, cascade or multistage refrigeration systems are usually employed; mostly in applications of food processing, pharmaceuticals and chemical processing [5].

In general, when selecting a refrigerant for a specified vapour compression application, a trade off situation exists between the cooling capacity and the efficiency [4]. The positions of the condensing and evaporating temperatures relative to the critical point temperature influence the mass and volume flow rates of a refrigerant. As a result, different refrigerants will have different system efficiencies when delivering a specified cooling duty. In addition, the slope of the saturated liquid line indicate the likely loss of refrigerating effect due to formation of flash gas during expansion from condensing to evaporating pressure. Further, limitations of the refrigerants themselves appear, such as considerable variation of properties, when working at very low temperatures [6].

Refrigerants R13 (CFC) and R503 (CFC/HCF), with normal boiling points -81.3 and – 87.5 °C respectively, possess most of the desired thermal-physical properties suitable for low-temperature applications. These two refrigerants have been very successful working fluids in lower cycles of cascade refrigeration systems. However both these refrigerants are being phased out. Presently hydorfluoro-carbons (HFC), fluorocarbons (FC), hydrocar-bons (HC) [2] and carbon dioxide [7], are considered as replacements. However, the complexity of the molecules and thermal-physical properties of the alternative refrigerants decide their efficiency and suitability for the intended low temperature applications. This paper investigates the suitability and asses associated parameters of certain appropriately screened refrigerants, FC, HC, HCFC etc., for low temperature cooling applications below –50 °C.

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2. Nomenclature

Notations

COP	Coefficient of performance
C_V	Constant volume specific heat (kJ/kgK)
dT	Degree of superheat or subcool
LFL	Lower flammability limit
P	Pressure (kPa)
s	Entropy (kJ/kgK)
T	Temperature (°C)
Tr	Reduced temperature
V	Volume (m3)

Subscripts

atm	Atmospheric
buble	Bubble point
cnd	Condensing, condenser
crt	Critical
evp	Evaporation, evaporator
NBP	Normal boiling point
sc	Subcool
sht	Superheat

3. Formulation

3.1 Property behaviours and their implications on refrigeration cycle performance

Boiling point and critical point temperatures, specific heat, latent heat of evaporation, specific volume of vapour, operating pressures at condensing and evaporating temperatures mainly form the thermal physical property creation in selecting a refrigerant for a specified application [4]. In addition, degree of environmental friendliness, flammability, chemical and thermal stability, compatibility with material and lubricants, odour, toxicity, broadly forms the basis for other important aspects of selection process [8]. The evaporator pressure is preferably maintained slightly above atmospheric to avoid inward leakages. A safe and moderate condensing pressure is preferred on safety grounds.

Further, as shown in Fig. 1, due to the inherent converging shape (towards critical point, though vapour domes not necessarily be symmetrical, as can be seen from actual shapes in Fig 5) of the vapour dome, operating too close to critical point has the disadvantage of relatively smaller condensing latent heat per unit mass of refrigerant circulated [3]. On one hand, this suggests need for a relatively larger single phase heat transfer area of the condenser. On the other hand, since only a smaller amount of heat is transported per unit mass flow of refrigerant, the coefficient of performance or the system efficiency is likely to be affected. On the contrary, operating further away from the critical point, the evaporation latent heat will be relatively larger and so will be the vapour volume, of which the former relates to a higher cooling effect per unit mass of refrigerant circulated and the latter corresponds to handling of larger refrigerant volumes. Therefore the refrigerant selection process needs to strike a balance between the cooling capacity and the efficiency of the cycle.

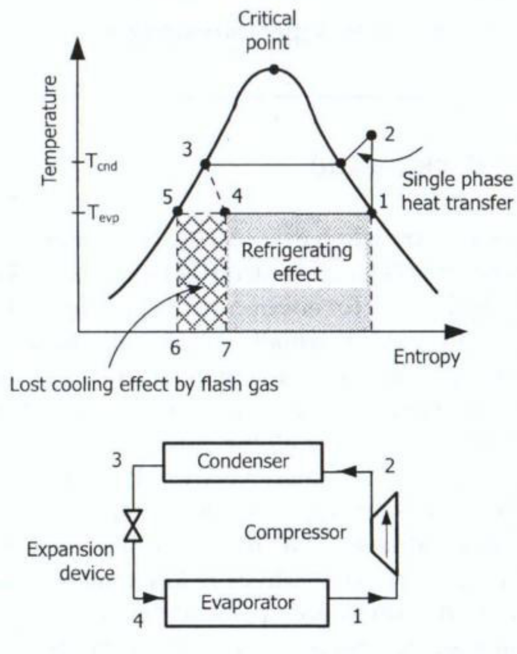

Figure 1: Influence of the critical point and operating temperatures on cooling capacity

The implications of the above is that for specified condensing and evaporating temperatures, different refrigerants will acquire different degree of irreversibilities, resulting in different cycle efficiencies. Using reduced temperature, Tr, defined as T/T_{crt}, the relative positions of evaporating and condensing temperatures on the vapour dome relative to critical point temperature can be conveniently described. This provides a common basis for performance comparison among different refrigerants for a specified application.

A refrigerant with moderate values of Tr in condenser and evaporator indicate a fair balance between the capacity an the efficiency, whereas Tr in condenser closer to unity or Tr in evaporator close to zero are the extreme cases which need avoiding on the above basis when selecting a refrigerant.

The slope of the saturated vapour and liquid lines are important criterion in selecting a refrigerant. Eq. 1 gives the slope of the saturated boundary on the vapour dome (T-s diagram) [9], where the subscript denotes that the respective gradients are taken along the saturation line.

$$\left[\frac{dT}{ds}\right]_\tau = \frac{1}{\left[\frac{C_v}{T} + \left[\frac{\partial P}{\partial T}\right]_v \left[\frac{dv}{dT}\right]_\tau\right]}$$

In equation 1, the term $(\partial P/\partial T)_v$ is positive for almost all saturated liquids and vapours, while $[dv/dT]_\tau$ is positive for saturated liquids and negative for saturated vapours. Among the terms in eq. 1, the term (C_V/T) shows the strongest influence on the slope of saturation line, vapour or liquid. On a practical note, the slope of the saturated vapour line, as given by eq.1, decides the fraction of liquid that will turn into flash gas during the expansion process; implying lower slopes corresponds to higher expansion losses (area 4-5-6-7, Fig 1).

3.2 Potential replacement refrigerants

Table 1 and 2 list selected properties and other related parameters of shortlisted alternatives (not necessarily on a commercial scale) for the low temperature refrigeration application below -50 °C, picked from the two lists of refrigerants and mixtures provided in the appendices A1 and A2.

Table 1: Selected refrigerants - Temperatures and enthalpies [10]

Refrigerant	T_{NBP} or T_{buble}	T_{crit}	h_{fg}
R14 (FC)	-128.1	-45.6	134.4
R170 (HC)	-88.6	32.2	489.5
R508A (HCFC/FC)	-87.4	11.0	156.9
R508B (HCFC/FC)	-87.4	12.1	166.1
R23 (HCFC)	-82.1	25.9	240.7
R116 (FC)	-78.2	19.9	116.2
R41 (HFC)	-78.1	44.1	488.8
R504 (HFC/CFC)	-57.7	62.1	195.7

In the selection of refrigerants, normal boiling point is used as a screening criterion based on the requirement of positive evaporator pressure at the lowest expected temperature. Though carbon dioxide too can be considered a potential refrigerant, only halogenated refrigerants and hydrocarbons are considered in the present study. Certain FCs such as R14, R116, are not presently used much as a common low temperature refrigerants. Both these fluids have relatively higher atmospheric life and global warming potential. However, R116 is used in making both R508A and R508B.

Table 2: Selected refrigerants - Environmental and safety parameters [7, 10]

Refrigerant	ODP (R11 = 1)	GWP (CO_2 = 1)	Safety group[(a)]
R14	0	5700	A1
R170	0	~ 20	A3
R508A	0	12 700	A1
R508B	0	13 000	A1
R23	0	12 240	A1
R116	0	10 000	A1
R41	0	97	-
R504	0.2	4 000	-

a - According to ASHRAE the capital letter indicates the toxicity; where A signifies non-toxic. The numeral denotes flammability; where 1 indicates no flame propagation, 2 signify refrigerants having moderate flammability (a lower flammability limit (LFL) of more than 0.10 kg/m3 at 21°C and 101 kPa and a heat of combustion of less than 19,000 kJ/kg), and 3 signify refrigerants having high flammability (an LFL of less than or equal to 0.10 kg/m3 at 21°C and 101 kPa or a heat of combustion greater than or equal to 19,000 kJ/kg).

3.3 Refrigerant and mixture properties

In this study the required thermal-physical properties of different refrigerants, the graphs of variation of properties on T-s plane and theoretical performance parameters of vapour compression cycles with selected refrigerants were obtained using a purpose written structured computer simulation. This simulation programme was written in Fortran 90, and consist of over 40 subroutines and data modules and validated using existing data for mixtures. Further, the simulation incorporate accurate and most recent mixing rules and equations of state for refrigerant mixtures [10].

4. Properties and performances

4.1 Saturation temperature, pressure and vapour volumes

Fig. 2 presents the variation of reduced temperatures (T/T_{crt}) of the selected refrigerants (given in table1) within evaporation temperatures in the range - 50 to -100 °C. It appears that the variation of reduced temperature of R116 closely follows that of R503. Also, the mixtures R508A and R508B have close reduced temperatures to those of R503. On the other hand, R23 and R170 show a behaviour very close to R13. Both R41 and R504 have lower reduced temperatures compared to R13 and R503. Among the refrigerant considered, R14 exhibit relatively higher reduced temperatures.

Fig. 3 presents the variation saturated vapour volumes, presented relative to those at -50 °C for each refrigerant. This demonstrates the order and the rate of change of vapour volume when operating at evaporation temperatures below -50 °C. Down to about -65 °C, the changes in vapour volumes are within about two folds of those at -50 °C. However, below -65 °C, vapour volume increases at a higher rate, with R504 showing the highest gradient, while R41 and R116 showing the lowest rate of change. The changes in vapour volume of R508A, R508B, R23 closely follow R13 and R503. Below about -90 °C, R14 show a lower rate of change of volume compared to R503 and R13.

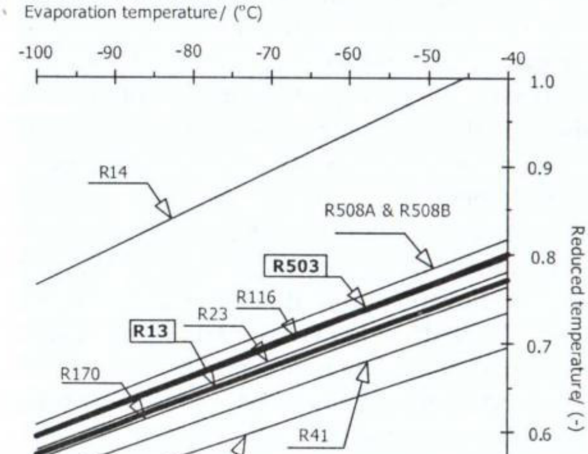

Figure 2: Reduced temperatures

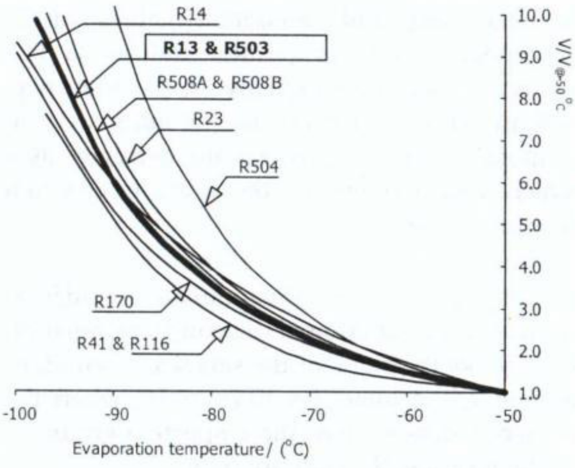

Figure 3: Saturated vapour volumes

Fig. 4 presents the variation of saturated vapour pressure with evaporation temperature, relative to the atmospheric pressure. The refrigerants show different degree of rate of change of pressure. R41, R116, R23 show evaporating pressures above atmospheric above -75°C, where for R170, R508A, R508B evaporation will be above atmospheric pressure at temperatures above -91°C. R504 will have lower evaporation pressure than the atmospheric pressure below about -55 °C. R14 shows relatively higher vapour pressure making it a good candidate for lower evaporating temperatures, even below -100 °C, a fact supported by its relatively higher reduced temperatures of evaporation and condensation of R14 (in Fig 2).

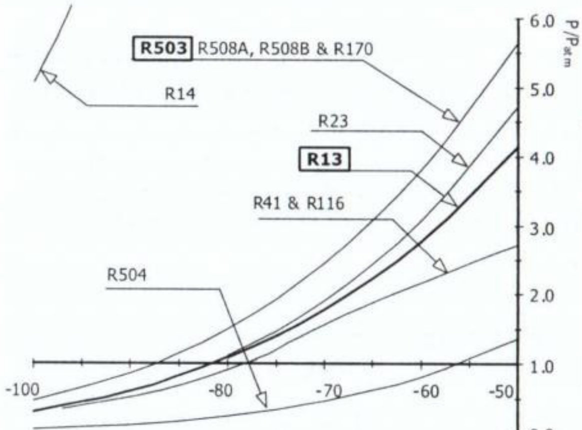

Figure 4: Saturated vapour pressures

As indicated in Fig. 4, the operating pressure of R14 at -100 °C is well above atmospheric pressure (≈ 514 kPa), indicating positive evaporator pressure down to about -128 °C (Table 2).

4.2 Factors affecting efficiency and performance

a) Compressor discharge temperature and flash gas losses

Fig. 5 presents the shape of vapour domes of the selected refrigerants on temperature - entropy (T-s) plane. For each refrigerant, temperatures -100 and - 50 °C are marked (in dotted lines) to provide an idea of the locations of corresponding saturation pressures relative to respective critical point. Among the refrigerants considered, R41 and R23 have fairly symmetrical vapour domes, where as R170 and R13 show somewhat sharp converging behaviour towards critical point. R116 and R14 have skewed vapour domes to the right to certain degree. However, the selected operating temperature ranges are situated very close to critical point in the case of R14, and much further away from critical point in the case of R116 and R41. Fig 5 also shows that R116 exhibit the risk of compression back into wet region under certain operating circumstances, which is not desirable feature for reciprocating compressors. Another observation is that R170 could be used at much lower temperatures compared to -100 °C.

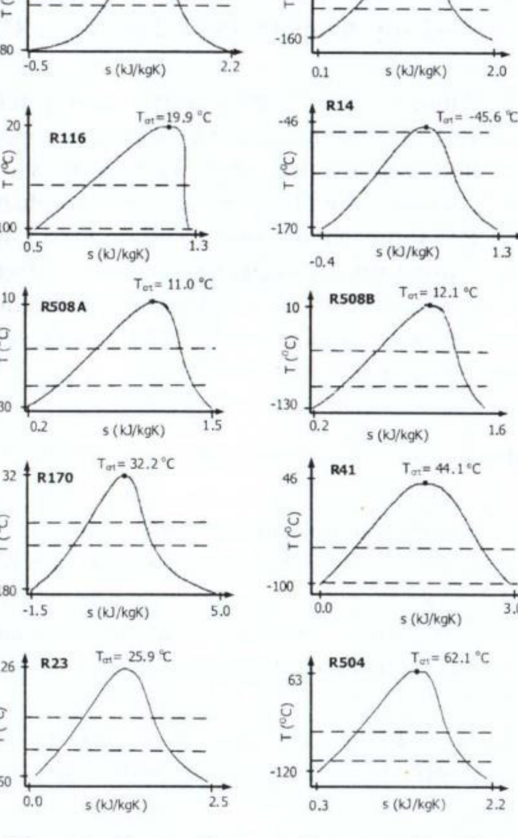

Figure 5: Shape of vapour domes on T-s plane

Fig. 6 presents the vapour quality at the evaporator entry when using each refrigerant in a vapour compression cycle with condensing and evaporating at -50 and -90 °C respectively. In the Fig., R14 shows the highest vapour quality; this is due to operation close to the critical point and relatively lower slope of saturated liquid line. R170, R504, R41, R508B and R23 all show lower vapour quality than R13 and R503. Among the refrigerants, R41 shows the lowest expansion losses, corresponding to the lowest fraction of cooling capacity losses during expansion.

Fig. 7 presents the vapour discharge temperatures from the compressor when isentropic compression is carried out from few selected evaporation temperatures to condensing temperature of -50 °C. R41 shows the highest discharge temperature whereas R116 shows the lowest. Though these two refrigerants, R41 and R116, exhibit similarities in certain behavioral aspects, such as vapour volumes and pressures, here they form the extreme cases among the considered refrigerants. Discharge temperatures of R508A and R14 follow closely those of R13 whereas R508B and R170 show somewhat similar temperatures as R503

In practice, there are fluctuations in the operating conditions of low temperature vapour compression systems; for example, the cascade condenser is exposed to fluctuations of temperatures and pressures during operation [5]. In such cases, if the discharge superheat is more than about 40 to 50 °C, to avoid the risk of thermal fatigue of the heat exchanger, desuperheating of entering refrigerant vapour will be required. The data show that R503, R170, R504, R41, R116, R508B and R23 show discharge superheat above 40 degrees at Tevp of -100 °C.

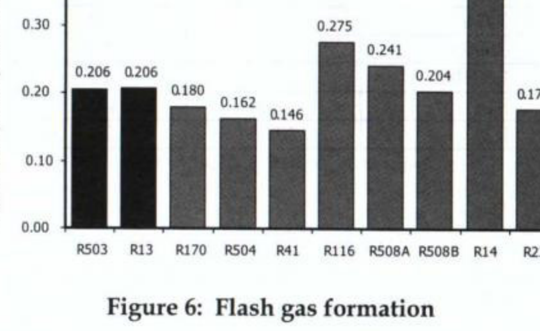

Figure 6: Flash gas formation

Cooling capacities of the refrigerants are presented in table 3 on both unit mass and volume bases. The first category corresponds to likely mass flow rate required to obtain a specified capacity, so that heat transfer and pressure drop estimates can be performed for the selected refrigerant and heat exchangers and pipe lines can be sized appropriately. The latter category directly relates to the size (volume flow rate) of the compressor. On mass basis R170 and R41 show the best performances where as on volume basis R14 has the best performances. One can see that, on the mass basis R23, R41, R504 and R170 have better performances than both replacing refrigerants R13 and R503. On volume basis, only R508A, R508B and R14 have superior performance to the two replaced refrigerants.

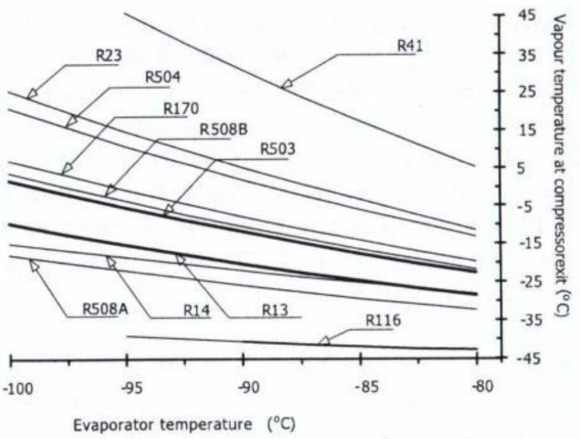

Figure 7: Discharge temperatures

b) Cooling capacity

Table 3 : Cooling and volumetric capacities

Refrigerant	Cooling capacity ($kW/kg\ s^{-1}$)	Volumetric capacity (kW/m^3)
R503	144.1	3.8
R13	122.0	3.2
R170	404.0	1.4
R504	216.9	0.4
R41	433.6	0.8
R116	88.3	3.4
R508A	121.1	4.3
R508B	129.5	4.0
R14	66.6	42.8
R23	203.5	2.1

$T_{evp} = -90, T_{cnd} = -50, dT_{sht} = 5, dT_{sc} = 5\,^{\circ}C$

5. Conclusions

Performances of R170, R41, R116, R504, R508A, R508B and R14 were evaluated for their suitability in low temperature applications with evaporation below - 50 °C. The analysis was based on the thermal-physical properties of the refrigerants and the performance of theoretical vapour compression cycle. The following can be concluded based on the findings.

- R116 exhibit a similar reduced temperature behaviour to R503, and R270 to R13
- Mixtures R508A and R508B closely follow saturated vapour volumes of both R13 and R503, making the two mixtures potential drop-in alternative refrigerants in system retrofit.
- None of the considered refrigerants show closely matching saturated vapour pressure behaviour to R13 or R513
- R170 shows better cooling performances per circulated unit mass at lower temperatures and can be used for evaporation at -100 °C or below.
- R14 and R508A follow refrigerant discharge temperatures behaviour of R13
- Among the refrigerants considered, R14 shows the highest flash gas losses and vapour pressures. However, when considered with its reduced temperature, R14 represent a good candidate for a low-temperature refrigerant mixtures where undesirable features of R14 (e.g. higher vapour pressure) could be made less prominent.

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Appendix 1

Table A1: Single component refrigerants [10]

Refrigerant	Halogen group	At 101.325 kPa T_{bpt} (°C)	h_{fg} (kJ/kg)
R14	FC	-128.1	134.4
R170	HC	-88.6	489.5
R23	HCFC	-82.1	240.7
R13	CFC	-81.3	149.3
R116	FC	-78.2	116.2
R41	HFC	-78.1	488.8
R32	HFC	-51.7	381.8
R125	HFC	-48.1	163.9
R1270	HC	-47.7	439.2
R143a	HFC	-47.2	227.1
R290	HC	-42.1	425.4
R22	HCFC	-40.8	233.7
R115	CFC	-38.9	125.4
R218	FC	-36.8	105.2
R12	CFC	-29.8	166.2
R134a	HFC	-26.1	217.0
R152a	HFC	-24.0	329.9
R227ea	HFC	-15.6	131.9
R124	HCFC	-12.0	165.8
R142b	HCFC	-9.0	222.7
RC318	FC	-6.0	116.8
R236fa	HFC	-1.4	160.3
R600	HC	0.5	385.7
R114	CFC	3.6	136.0
R236ea	HFC	6.2	165.2
R600a	HC	11.6	366.7
R245fa	HFC	14.9	196.7
R11	CFC	23.7	181.4
R245ca	HFC	25.1	197.4
R123	HCFC	27.8	170.2
R141b	HCFC	32.1	223.1
R113	CFC	47.6	144.3

Appendix 2

Table A2 : Refrigerant mixtures [10]

Refrigerant Mixture	Components	At 101.325 kPa T_{bub} (°C)	T_{dew} (°C)	h_{fg} (kJ/kg)
R503	R23/R13	-87.5	-87.5	179.0
R508A	R23/R116	-87.4	-87.4	156.9
R508B	R23/R116	-87.4	-87.0	166.4
R504	R32/R115	-57.7	-56.2	195.7
R410A	R32/R125	-51.6	-51.6	271.5
R410B	R32/R125	-51.5	-51.4	260.7
R402A	R125/R290/R22	-49.2	-47.1	194.3
R402B	R125/ R290/R22	-47.2	-44.9	210.1
R507A	R125/R143a	-47.1	-47.1	196.1
R407B	R32/R125/R134a	-46.8	-42.4	200.0
R404A	R125/R143a/R134a	-46.6	-45.8	200.1
R408A	R125/R143a/R22	-45.5	-45.0	224.9
R502	R22/R115	-45.3	-45.0	173.3
R407A	R32/R125/R134a	-45.2	-38.7	234.3
R407C	R32/R125/R134a	-43.8	-36.7	248.0
R407E	R32/R125/R134a	-42.8	-35.6	257.0
R411B	R1270/R22/R152a	-41.6	-40.3	243.4
R509A	R22/R218	-40.7	-40.6	159.8
R501	R22/R12	-40.5	-40.4	218.9
R411A	R1270/R22/R152a	-39.7	-37.2	249.6
R407D	R32/R125/R134a	-39.4	-32.7	240.3
R409B	R22/R124/R142b	-36.5	-29.7	219.6
R401B	R22/R152a/R124	-35.7	-30.8	228.3
R409A	R22/R124/R142b	-35.4	-27.5	220.2
R401A	R22/R152a/R124	-34.4	-28.8	226.7
R500	R12/R152a	-33.6	-33.6	202.5
R406A	R22/R600a/R142b	-32.7	-23.6	241.5
R401C	R22/152a/124	-30.5	-23.8	217.3

Note: Bubble point temperatures (T_{bub}) are given instead of boiling point temperature.