Refrigerants for Vapour Compression Refrigeration Systems

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With the mandate of Montreal Protocol banning ozone depleting substances, and Kyoto Protocol later on curtailing the use of substances which contribute to global warming, conventional refrigerants are to be replaced by environment-friendly working fluids. Chlorofluorocarbons (CFCs) and hydrochlorofluorocarbons (HCFCs) are being substituted by hydrofluorocarbons (HFCs), hydrofluorooelifins (HFOs), and a variety of mixtures. In view of the global warming potential of these newly synthesized refrigerants, the recent trend is to go back to the originally used natural fluids such as ammonia, carbon dioxide, hydrocarbons, water vapour, etc. In this article, various issues related to this changeover of refrigerants being used in vapour compression refrigeration systems are discussed.

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Keywords

Vapour compression refrigeration system, refrigerant, ozone depletion, global warming, CFC, HCFC, HFC, HFO, zeotropic mixture, natural fluids.

Introduction

Present day mankind depends very heavily on refrigeration (which can be defined as artificial production of cold) for daily needs. These cover a wide range of applications such as food processing, preservation and transport, comfort cooling, commercial and industrial air conditioning, manufacturing, energy production, health, recreation, etc. The first known machine to produce continuous cold was invented by the Frenchman Ferdinand Carre in 1859. This was the earliest version of 'aqua ammonia' absorption system. However, commercially successful compression refrigeration systems working with ammonia were introduced in 1875. Since then, the refrigeration technology has grown tremendously, influencing almost all aspects of human life.

Refrigeration systems can be broadly classified into two categories:

- Steady-state refrigeration systems in which the cooling effect is continuous; the refrigerant flow is steady and in one direction.
- Periodic refrigeration systems in which the cooling effect is cyclic or intermittent; the refrigerant flow varies periodically with time and is bidirectional.

The former is similar to direct current electrical systems and the latter to alternating current electrical systems, the refrigerant mass flow rate being analogous to current, and pressure being analogous to voltage. Vapour compression refrigeration systems used in domestic refrigerators and air conditioners are typical examples of steady-state refrigeration systems. Sterling refrigerators and adsorption systems are examples of periodic refrigeration systems. The efficiency of periodic refrigeration systems depends on the phase relationship between the mass flow rate and pressure vectors, just as the phase difference between current and voltage influences the performance of an alternating current electrical system. The performance of steady-state refrigeration systems, on the other hand, depends on the properties of the working fluid (refrigerant) used.

Refrigeration systems can also be classified depending on the type of energy input:

- Mechanical energy (compression refrigerators)
- Thermal energy (absorption/adsorption refrigerators)
- Electrical energy (thermo-electric refrigerators)
- Magnetic energy (magnetic refrigerators)
- Acoustic energy (acoustic refrigerators)
- Light energy (optical refrigerators).

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Figure 1 shows the different types of refrigeration systems. A large fraction (typically, about 80 %) of practical refrigerators are of vapour compression type and operate with mechanical energy input. In most cases the mechanical energy is derived from electric motors. Vapour absorption refrigerators that operate with heat input are the second most widely used refrigeration systems.

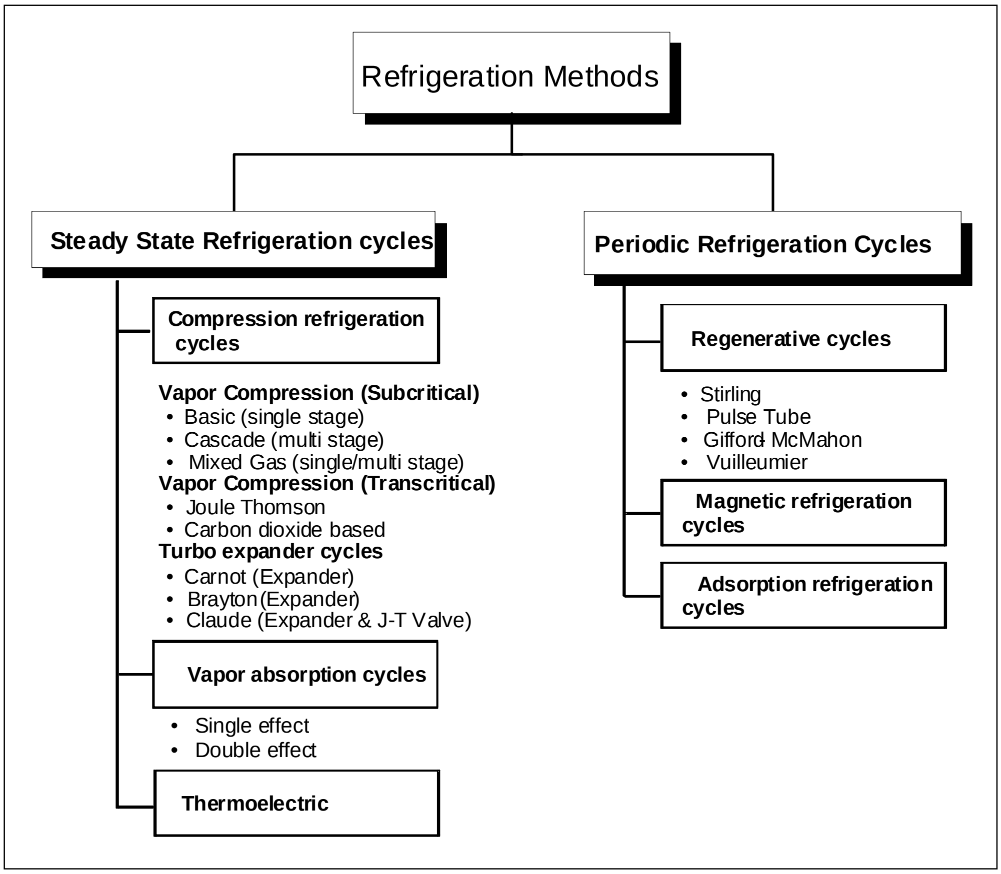

Figure 1. Classification of refrigeration methods based on type of the variation of pressure and flow rate in the cycle during steady-state operation.

Refrigerators that operate with other types of energy input are only used in niche applications.

This article deals with the refrigerants used in steady-state systems belonging to the broad category of vapour compression refrigeration systems (VCRS) that operate using mechanical power.

Vapour Compression Refrigeration Cycles

The Clausius–Rankine and the Lorenz–Meutzner cycles shown in *Figure* 2 are the two widely used basic vapour compression refrigeration cycles. Heat is absorbed/rejected by the refrigerant at constant temperature in the Clausius–Rankine cycle (*Figure* 3a) and over a range of temperatures in the case of the Lorenz–Meutzner cycle (*Figure* 3b). Processes shown in both

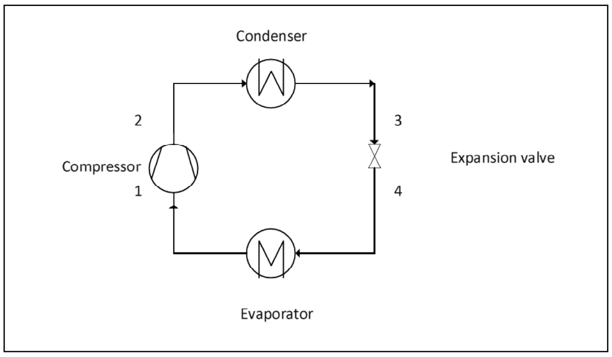

Figure 2. Schematic of a simple vapour compression refrigerator. The refrigerant vapour is compressed in the compressor (Process 1–2), condensed in the condenser (Process 2–3), expanded in a throttling device (Process 3–4) and evaporated in the evaporator (Process 4–1). Heat from the product to be cooled is added at the evaporator and rejected at the condenser to the ambient.

Figures 3a and 3b are realized as follows:

Process 1–2: Isentropic compression of the refrigerant.
Process 2–3: Constant pressure heat rejection[1] in a heat exchanger termed as the condenser.
Process 3–4: Isenthalpic expansion[2] of the refrigerant in an orifice, valve or a capillary tube.
Process 4–1: Constant pressure heat addition in a heat exchanger, usually termed as the evaporator.

[1] The heat added in the evaporator and the work supplied to the compressor are rejected in the condenser.

[2] Isenthalpic expansion process is an irreversible process, and is therefore normally shown in dotted lines on a *T-s* (temperature–entropy) diagram.

Processes in a real refrigeration system will be slightly different from those shown in *Figures* 2 and 3 due to irreversibilities such as pressure drop in heat exchangers caused by friction, acceleration of the refrigerant in the evaporator as the liquid turns into vapour, pressure drop in the suction and discharge valves, non-isentropic compression in the compressor, etc.

Air and water are the two most commonly used external heat

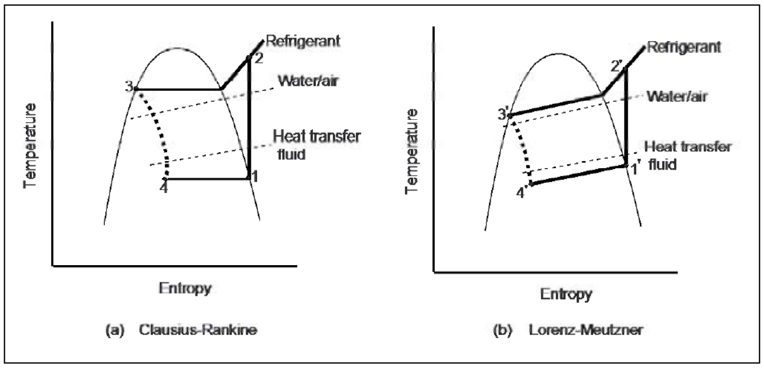

Figure 3. a) Clausius–Rankine (1-2-3-4) and b) Lorenz–Meutzner (1’-2’-3’-4’) cycles operating with heat transfer fluids that undergo a temperature change across the condenser/evaporator. The Clausius–Rankine cycle is used in refrigerators operating with single fluids and azeotropic mixtures, and the Lorenz–Meutzner cycle is used in refrigerators operating with zeotropic mixtures.

transfer fluids in the condenser to reject heat. Air is also generally used as the heat transfer medium in the evaporator of air conditioners. Fluids such as air, water, ethyleneglycol/water mixture, propyleneglycol/water mixture, brines, or other heat transfer fluids, etc., can be used at the evaporator depending on the temperature and requirements of the particular application. Except in a few cases, the temperature of the heat transfer fluid normally varies across the condenser and evaporator in most applications. The Lorenz–Meutzner cycle is preferable when the temperature change of the external heat transfer fluid (both at the evaporator and the condenser) is significant. The Lorenz–Meutzner cycle can be realized by using zeotropic (also called as non-azeotropic) refrigerant mixtures. It makes thermodynamic and also economic sense to match the temperature change of the refrigerant with that of the heat transfer fluid (the so-called 'glide-matching'). *Figure* 4 shows a comparison between the Clausius–Rankine and Lorenz–Meutzner refrigeration cycles. The shaded portion represents the energy saved when the Lorenz–Meutzner cycle is used instead of the Clausius–Rankine cycle.

Zeotropic refrigerant mixtures were not favored by the refrigeration community for a long time because of the possibility of change of composition of the mixture in case of leaks. However, zeotropic mixtures of hydrofluorocarbons (HFCs) are now widely used in place of chlorofluorocarbons (CFCs) banned by the Montreal Protocol. (See *Box* 1). This has led to a renewed interest in the refrigerators operating on the Lorenz–Meutzner cycle.

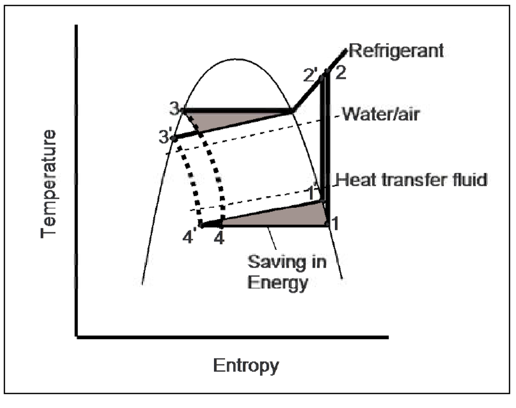

Figure 4. The shaded area gives the energy savings due to glide-matching when zeotropic refrigerant mixtures are used in a Lorenz–Meutzner cycle (1'-2'-3'-4') and glide of the refrigerant is close to that of the heat transfer fluid, compared to a refrigerator operating with a pure fluid as the refrigerant and the Clausius–Rankine cycle (1-2-3-4).

Box 1. The Ozone Depletion Effect

The atmosphere is divided into layers defined by the distance above the surface of the earth as follows:

- 0–15 kilometers (Troposphere)
- 15–50 kilometers (Stratosphere)
- 50–85 kilometers (Mesosphere)
- >85 kilometers (Thermosphere)

A proportion of the sun's energy is emitted as ultraviolet (UV) radiation which can be divided into three types according to the wave length:

- UVA : 3200 – 4000 Å
- UVB : 2900 – 3200 Å
- UVC : < 2900 Å (1 Å = 10^{-10} m).

It has been established that the short wavelength bands of the UV radiation are harmful to the life on earth in many ways. It has also been established that a layer of the stratosphere, 20–40 km thick and rich in ozone, filters out a major portion of this harmful UV radiation from reaching the earth's surface. Chemically stable chlorofluorocarbon (CFC) refrigerant molecules remain for a very long time in the atmosphere and can therefore reach the ozone layer. In the stratospheric area an energetic UV photon strikes the CFC molecule. The energy of the impact releases a chlorine atom, which is chemically very active and reacts with an ozone molecule. Through this interaction, the ozone molecule is destroyed. This is a complicated chain reaction leading to the 'ozone hole'.

Health and environmental effects of ozone depletion can be multifarious. Because biological life on this planet evolved only after the ozone shield developed, enormous potential for harm exists if the shield is damaged. DNA, the genetic code present in all living cells is damaged by UV radiation, UVC being the most damaging. A significant reduction in ozone in the upper atmosphere could result in long-time increase in skin cancer and cataracts, and probably damage the human immune system. Environmental damage and the resulting economic losses could be because of decreased yields of major agricultural crops, and reduced productivity of phytoplankton with possible implications for the aquatic food chain, resulting in substantial losses at the larval stage of many fish (e.g. anchovies, shrimps and crabs).

The extent of damage that a refrigerant can cause to the ozone layer is quantified by the Ozone Depletion Potential (ODP), which is the ratio of impact caused by the substance on ozone to that caused by CFC 11.

History of Refrigerants

Table 1 summarizes the different refrigerants used in the last 150 years. Many of the refrigerants used during the early periods did

Period	Refrigerants
1800–1900	Ethyl alcohol, methyl amine, ethyl amine, methyl chloride, ethyl chloride, sulphur dioxide, carbon dioxide, ammonia
1900–1930	Ethyl bromide, carbon tetrachloride, water, propane, isobutene, gasoline, methylene chloride
1931–1990	Chlorofluorocarbons, hydrochlorofluorocarbons, ammonia, water
1990–2010	Hydrofluorocarbons, ammonia, isobutene, propane, carbon dioxide, water
Immediate future	Hydrofluorooelifins, hydrofluorocarbons, hydrocarbons, carbon dioxide, water

Table 1. History of refrigerant usage.

not survive, mainly due to their toxicity. Ammonia, however, continues to be a refrigerant of choice for food freezing applications even today in spite of its toxicity, mainly due to its excellent thermodynamic and thermal properties. Carbon dioxide used in the early days of refrigeration is again being considered as a refrigerant in spite of its high operating pressures. Hydrocarbons used in the early part of the last century were quickly discontinued because of their flammability. However, hydrocarbons have made a successful comeback and are being used extensively in small domestic refrigerators and freezers in recent years.

The discovery of CFCs in the late twenties revolutionized the refrigeration industry. Both CFCs and hydrochlorofluorocarbons (HCFCs) are non-toxic, possess excellent thermodynamic properties, and are non-flammable. Both CFCs and HCFCs dominated the refrigeration industry for nearly 70 years till the Montreal Protocol imposed a ban due to their contribution to ozone depletion. In the last two decades, hydrofluorocarbons (HFCs), which possess zero Ozone Depletion Potential (ODP), have gradually replaced CFCs. Very recently, global warming due to emission of various gases into the atmosphere has been the issue being dealt with by the Kyoto Protocol (see *Box* 2). HFCs which have high Global Warming Potential[3] (GWP) are also being banned in spite of the fact that they are ozone friendly. Hydrofluorooelifins (HFOs), which have very low

[3] Global Warming Potential is the ratio of global warming impact caused by a substance to that caused by CO_2 of same mass in a certain period of time.

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Box 2. The Global Warming Effect

The earth and its atmosphere get heated as they continuously receive sun's energy in the form of high frequency radiation. A major part of this heat is returned as infrared radiation. Thus a delicate balance exists between the energy received and that returned to the outer space. The temperature of the earth depends on this. Many gases such as CO_2, methane (CH_4), nitrous oxide (N_2O), various hydrocarbons, CFCs, HCFCs, HFCs, etc., are released by mankind due to various agricultural and industrial activities. These gases, called 'green-house gases (GHG)', act as a screen, blocking out part of the infrared radiation of the earth towards outer space. Water vapour is also a powerful greenhouse gas but is not harmful as it is condensable and cannot build up in the atmosphere. This is the reason that HFCs, even though are safe from the ozone depletion point of view, are increasingly being blamed for contributing to the global warming.

In fact, man and animals emit significant amounts of GHGs due to their metabolic activity. Methane is a potent greenhouse gas produced by ruminant animals, such as dairy cows. Animal agriculture is responsible for more greenhouse gas (18%) than all of transportation (13%) according to a 2006 report of the UN-FAO. On Al Gore's website www.climatecrisis.org, he notes: "Eat less meat. Methane is the second most significant GHG, and cattle are the greatest methane emitters. Their grassy diet and multiple stomachs cause them to produce methane, which they exhale with every breath." By being vegetarian, we grow plants which not only produce food but also act as carbon sinks because they consume CO_2.

GWP and invented very recently are expected to replace HFCs in many applications. A detailed discussion on the different refrigerants is given below.

Desirable Properties of Refrigerants

The following are the important requirements of a refrigerant:

- Low GWP and zero ODP from a sustainable environment point of view.
- Non-toxic from human and animal safety point of view.
- Compatibility with the materials used in refrigeration systems (metals, polymers, lubricating oils, etc.) from design and operation points of view.
- Desirable thermodynamic and thermophysical properties from the operating efficiency point of view.

As already mentioned, the requirements of low GWP and ODP are relatively new as a consequence of Kyoto and Montreal Protocols respectively. *Tables* 2 and 3 list the GWP and ODP of various refrigerants.

Table 2. Refrigerants from different chemical groups.

No.	Refrigerant	Boiling Point @1 atm(K)	Freezing Point (K)	Critical Temp (K)	Critical Pr (bar)	ODP	GWP
CFCs (Chlorofluorocarbons)							
R113	Trichlorotrifluroethane	320.73	238.16	487.3	34.4	0.9	5200
R11	Trichloroflurometháne	296.98	162.05	471.2	44.1	1	4000
R114	Dichlorotetrafluroethane	276.94	179.27	418.9	32.6	0.7	16600
R12	Dichlorodiflurometháne	243.37	115.38	385.2	41.2	1	12200
R115	Chloropentafluroethane	233.83	167.05	353.1	31.5	0.6	39200
HCFCs(Hydrochlorofluorocarbons)							
R141b	Dichlorofluroethane	305.16	–	483.35	46.4	0.15	600
R123	Dichlrotrifluroethane	301.03	166.01	457.15	36.76	0.02	80
R22	Chlorodiflurometháne	232.40	113.16	363.15	49.78	0.05	1480
HFCs (Hydrofluorocarbons)							
R245fa	Pentafluropropane	288.44	166.49	383.4	31.5	0	790
R134a	Tetrafluroethane	247.00	176.55	374.25	40.67	0	1160
R507	Azeotrope - Blend	226.05	255.38	344.05	37.92	0	1400
R125	Pentafluroethane	224.59	170.01	339.25	36.2	0	3360
R32	Diflurometháne	221.44	137.05	351.4	58.08	0	440
R23	Triflurometháne	191.10	118.16	298.75	48.37	0	24000
HFOs (Hydrofluorooellifins)							
R1234yf	2,3,3,3-Tetrafluoropropene	244.15	220.00	367.85	33.82	0	4
FCs /PFCs (Fluorocarbons/Perfluorocarbons)							
R218	Octofluropropane	241.66	113.16	344.95	26.8	0	9300
R14	Tetraflurometháne	145.22	89.27	227.65	37.43	0	6500
Hydrocarbons							
R600	Butane	272.66	134.66	425.12	37.7	0	0
R290	Propane	231.07	85.49	369.83	42.1	0	0
R170	Ethane	184.35	90.38	305.32	48.5	0	0
R1150	Ethylene	169.44	104.27	282.34	50.3	0	0
R50	Methane	111.66	90.94	190.56	45.9	0	0
Inorganic Compounds							
R718	Water	373.16	273.16	647.13	219.4	0	0
R717	Ammonia	239.83	195.44	405.65	113.0	0	0
R744	Carbon dioxide	194.72	216.55	304.21	73.9	0	1
R728	Nitrogen	77.38	63.16	126.2	33.9	0	0
R702n	Hydrogen	20.38	13.99	33.19	13.2	0	0
R704	Helium	4.22	_	5.2	2.3	0	0
HFEs (Hydrofluoroethers)							
HFE-7100	Methoxynonafluorobutane	334.16	138.16	468.45	22.3	0	320
HFE-7200	Ethoxynonafluorobutane	349.16	135.16	482.0	19.8	0	55
HFE-7000	Methooxyheptafluropropane	307.16	150.38	438.15	24.8	0	400

No.	Blend/ Constituents	Compo- sition	Boiling Pt @1atm(K)	Dew Pt @1atm(K)	Critical Temp.(K)	Critical Pr.(bar)
R404a	Zeotrope (R125/143a/134a)	44/52/4	226.59	227.36	–	–
R407c	Zeotrope (R32/125/134a)	23/25/52	229.39	236.46	–	–
R410a	Zeotrope (R32/125)	50/50	221.6	221.65	–	-–
R507	Azeotrope (R125/143a)	50/50	226.4	226.4	344.1	37.9

Table 3. Commonly used HFC refrigerant blends (zeotropes and azeotropes).

Thermodynamic and Thermophysical Properties

The ideal refrigerant should have the following thermodynamic and thermophysical properties:

a) Low condensing pressure to allow the use of lightweight materials for heat exchangers, compressors, piping, etc.
b) Suction pressure above atmosphere for ease of leak detection and to prevent air and moisture ingress into the system.
c) Low compression ratio to give high volumetric efficiency and low power consumption.
d) High latent heat of vaporisation for large refrigerating effect or a small mass flow rate for a given cooling load.
e) Small specific volume for large mass flow rate per unit volume of compression (specifically for use with positive displacement compression systems).
f) Moderate temperature rise during compression to reduce the risk of compressor overheating and to avoid chemical reaction between refrigerant oil and other materials.
g) Low liquid specific heat capacity to increase liquid subcooling prior to expansion and to minimize flash gas.
h) High vapour specific heat capacity to reduce vapour superheat at suction.
i) High thermal conductivity of both liquid and vapour to improve heat transfer.
j) Low viscosity of both vapour and liquid to reduce pressure loss.

Items (c) and (d) are somewhat contradictory as both requirements are inter-related by the Clausius–Clapeyron equation according to which the evaporation enthalpy is directly proportional to the slope of the vapour pressure curve.

The critical temperature, normal boiling temperature and the heat capacity of the vapour are significant thermodynamic criteria which influence most of the properties such as latent heat of vaporization, evaporator pressure, etc. At a given reference evaporation temperature, the volumetric heating or refrigerating capacity will be lower for the gas with the higher critical temperature (see *Box* 3). This is due to the lower vapour pressures and thus lower vapour densities for refrigerants with higher critical temperatures (at fixed evaporator temperatures).

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The Coefficient of Performance[4] (COP, defined as the ratio of cooling output to the work input), however, is higher for refrigerants with higher critical temperatures. The COP drops as the temperature of the condenser approaches critical temperature of the refrigerant due to excessive compressor superheat and flash gas losses.

The normal boiling point[5] is also a good indicator of the critical temperature since their ratio is in the range of 0.6–0.7 for most fluids. Therefore, higher the normal boiling point of the refrigerant, higher will be the COP of the refrigerator.

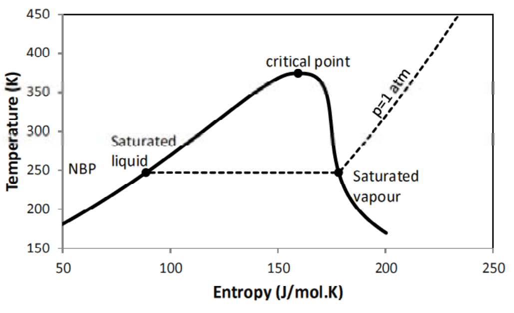
The heat capacity of vapour (c_p^o), has a smaller effect on the performance of the refrigerator than the critical temperature but is

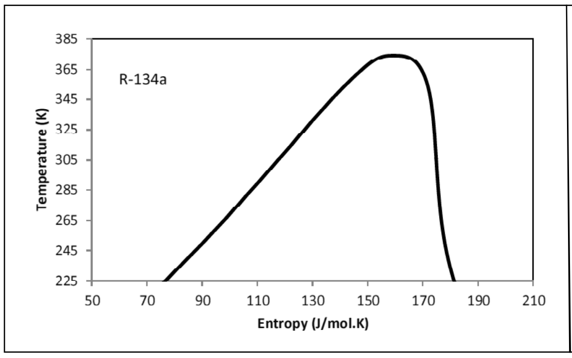
[4] COP of vapour compression cooling systems can be larger than 1 because heat quantity is divided by mechanical work. Therefore the typical COP of a home air conditioner is about 3, while the COP of –80°C deep freezer can be as low as 0.2.

[5] The boiling point of a pure fluid at a pressure of 1 atm. is known as the normal boiling point.

Box 3

The critical point is the highest temperature and pressure at which liquid and vapour phases can coexist in a pure fluid. The normal boiling point is the temperature at which a fluid boils (say saturated liquid to a saturated vapour state) at a pressure of 1 atm. The figure shows the different states of the fluid. The line connecting the saturated liquid states (at different pressures) is called the saturated liquid line and that connecting saturated vapour states is called the saturated vapour line.





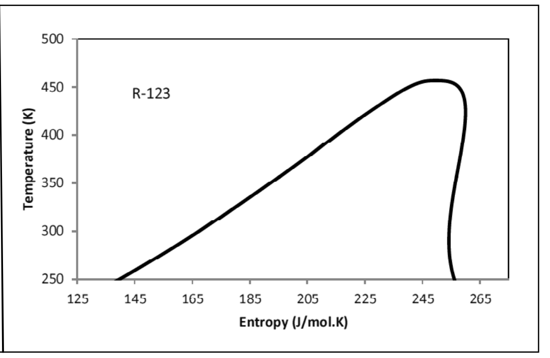


Figure 5(left). Vapour dome of a typical refrigerant (HFC134a) with negative slope of the saturated vapour line.

Figure 6 (right). Vapour dome of a typical refrigerant (HFC123) with positive slope of the saturated vapour line.

still significant. High volumetric capacities are associated with low values of c_p^o. For maximum COP, an optimum value of c_p^o exists. The heat capacity affects the performance of the vapour compression cycle primarily through its influence on the shape of the two-phase region or 'vapour dome' on the temperature – entropy diagram (see *Figures* 5 and 6). Low values of c_p^o give a vapour dome such that a compression process starting on the saturated vapour line terminates in the superheated vapour region. With a high value of c_p^o, however, the vapour dome is 'undercut' so that an adiabatic compression process terminates in the two-phase region. Such a 'wet' compression must be avoided for most types of compressors. The liquid and vapour sides of the two-phase region are connected and thus high values of c_p^o also result in greater flash losses (entropy generation) in the expansion device. The result of these offsetting effects is an optimum value for c_p^o lying between 40 and 100 J/mol-K depending on the critical temperature of the refrigerant. The optimum value of c_p^o results in a vapour dome that gives a small superheat; this is the behaviour observed with most common refrigerants.

Environmental and Safety Properties

In addition to thermodynamic and thermophysical properties, possible environmental impacts, safety, toxicity and flammability are also to be considered. In fact, environmental friendliness of the working fluid today is a major consideration. It is essential that all newly considered fluids should possess zero ODP, and low GWP. Decomposition and environmental assimilation of released substances may require many days to years to take effect. These effects are widespread and may affect locations far away from the source. Hence, these issues are to be tackled on a global basis.

In addition to thermodynamic and thermophysical properties, possible environmental impacts, safety, toxicity and flammability. It is essential that all newly considered fluids should possess zero ODP, and low GWP.

On the other hand, toxicity effects are generally localised and immediate. The margin of safety from the viewpoint of toxicity depends on the degree of concentration and the duration of exposure to cause harmful effects. An ideal refrigerant should be non-toxic to humans, animals and plant life even at low concentrations and with long time exposure.

The main concern with the use of hydrocarbon refrigerants is their flammability especially in case of leaks. Small- and medium-sized refrigeration systems use 'hermetic' compressors (compressor and motor placed inside a single sealed shell). Large systems, on the other hand, use open-type compressors that are difficult to seal completely. Similarly, a small amount of leakage also can occur from other components such as valves, measuring and safety equipment, etc. Refrigerant leaks are therefore difficult to avoid in large systems. The degree of hazard expected by the use of a refrigerant depends on factors such as the quantity of refrigerant used, volume of the space into which the refrigerant leaks, type of occupancy of the room, risk of naked flame or electric sparks.

Flammable refrigerants (isobutane, mixture of propane and isobutane, etc.) have been adopted widely for use in home refrigerators, including in India. Most low GWP refrigerants are flammable and their use is becoming the norm due to regulations such as the F-gas regulations in Europe which require refrigerants with GWP less than 150 to be used in new car models from this year. R1234yf, the low GWP refrigerant of choice, in the new car models has been accepted in spite of its flammability. Standards already exist on the type of safety features to be mandatorily used in plant rooms, the amount of refrigerant charge permitted to be used in plant rooms of given size (volume), etc. In cases where it is not recommended to use large amounts of hydrocarbon refrig-

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erants (supermarkets, concert halls, auditoria, etc.), hydrocarbon refrigerants can serve as primary refrigerants in the plant room while secondary refrigerants such as propyleneglyocol or ethyleneglycol can be used inside the building enclosure. With the increasing concern for global warming, it is likely that the refrigeration industry will have to learn to adopt flammable refrigerants even in large applications.

Another essential characteristic is the chemical stability within the refrigeration system so that the refrigerant does not decompose when it is repeatedly compressed/expanded and condensed/evaporated. It should not react with the lubricant or system construction materials to form harmful compounds. However, once emitted, a refrigerant should not be so stable that it persists indefinitely in the atmosphere to reach the upper layers of atmosphere. The ideal refrigerant should be totally stable while in use but decompose quickly into safe substances when released. These contradictory requirements essentially limit the number of fluids that can be used as refrigerants.

[6] High oil solubility ensures that the compressor lubricating oil carried over by the refrigerant returns to the compressor and does not accumulate in other components of the refrigerator such as heat exchangers, pipelines, etc. High vapour dielectric strength ensures that there is no electric short circuit between the motor windings and the outer shell through the refrigerant vapour in the case of hermetic compressors.

Other Properties

In addition to the various properties discussed so far, a number of other practical criteria are also necessary. Oil solubility and high vapour dielectric strength[6] are most important for hermetically-sealed compressors. HCs, CFCs and HCFCs are compatible with mineral oils, while HFCs are not. Synthetic lubricating oils such as polyolester (POE), polyalkyleneglycol (PAG), etc., need to be used with HFC refrigerants. Since these lubricating oils are also hygroscopic they cannot be exposed to the atmosphere for more than a few minutes during maintenance and service activities. Freezing point of lubricants should be below the lowest expected system temperature.

The ideal refrigerant should be totally stable while in use but decompose quickly into safe substances when released.

Economic operation is mainly related to thermodynamic and thermophysical properties which govern the efficiency and thereby the energy consumption of the system. Energy saving has significant indirect influence on the environment as it reduces the global warming caused by most of the energy production / conversion processes. The initial cost of the refrigerant is generally not very important as it usually forms a small percentage of the total system cost. Moreover, it is a one-time expenditure as against the energy cost which is a recurring one.

Properties of Specific Working Fluids

The basic thermodynamic and environmental properties of different fluids that have been used or can be used as refrigerants in vapour compression refrigeration and air conditioning equipment are discussed in this section.

The properties of different categories of refrigerants are summarized in *Tables* 2 and 3.

Chloroflurocarbons (CFC)

These are fully halogenated fluids that have high ODP and were found to be the most responsible for the creation of ozone hole. Use of formerly popular CFCs such as R12 and R11 in new equipment was banned by the Montreal Protocol. While R12 recovered from old systems may still be available, new lots of CFCs are no longer being produced.

Hydrochlorofluorocarbons (HCFC)

Unlike fully-halogenated CFCs, which contain only carbon and halogen atoms, in the case of partially-halogenated HCFCs, not all hydrogen atoms are replaced by halogen atoms. The remaining hydrogen atoms facilitate partial breakdown of the compounds in the troposphere. For this reason these compounds are less harmful to the stratospheric ozone layer, though they still have the some potential to damage the ozone layer. However, since they are known to cause global warming, HCFCs are no longer used in the industrialized countries of the West. Phase-out of HCFCs (mainly HCFC22, which is still widely used in India) is being accelerated.

Hydrofluorocarbons (HFC)

Hydrofluorocarbons contain fluorine but no chlorine or bromine in the molecule, so that their ODP is zero. Some examples of HFCs are R23, R32, R125, 134a, 143a and 152a. A problem with HFCs is that they are chemically stable and can accumulate in the atmosphere contributing to the global warming. Hence, HFCs need to be eventually replaced.

Hydrofluorooelifins (HFO)

These also belong to a class of HFCs, but are derived from unsaturated hydrocarbon molecules such as propylene. HFOs are relatively unstable, have a small atmospheric lifetime and therefore a small GWP. R1234yf and R1234ze are two HFO refrigerants invented recently. R1234yf has been widely accepted for use in cars by the automobile industry because of its very low GWP of 4. As soon as it becomes commercially available, R1234yf is expected to replace R134a, which is currently being widely used in air-conditioning plants, automobile air conditioners, domestic refrigerators, etc. There are also attempts to find mixtures of R1234yf and other HFCs such as R32 for use in other applications such as domestic air conditioners since mixtures containing R1234yf will have low GWP, typically less than 1000.

Fluoroiodocarbons (FIC)

These are a group of chemicals containing fluorine, iodine and carbon such as, trifluoromethyl iodide (CF_3I), perfluoroethyl iodide (C_2F_5I) and perfluoropropyl iodide (C_3F_7I). The FICs are reported to have zero ODP and negligible GWP due to their very short life periods. These can also be used in blends. A blend of CF_3I and HFC 152a (51/49 mole percent) was run in a refrigerator without oil change for over 1,500 hours without apparent ill effects. Measurements showed that the energy efficiency and capacity were equal to or slightly better than CFC 12.

Hydrocarbons

Several hydrocarbons have excellent thermodynamic properties and can be used as refrigerants. Though alkanes, ketones, alcohols and ethers can be used, alkanes are the most preferred group. As already mentioned, the main concern is that most of the hydrocarbons are flammable. Here, one should note that in certain industrial applications hydrocarbons have been used as refrigerants since the beginning of the 20th century. Hydrocarbons, for instance, are used in pure or mixture forms as refrigerants in petrochemical plants and in gas liquefaction plants. In LNG plants, mixtures of methane and n-pentane are in common use. With adequate safety precautions flammability will not pose a major problem in the usage of hydrocarbons. Home refrigerators have been sold in tens of millions worldwide, including India, during the last twenty years. The ODP of hydrocarbons is zero, while their GWP is very small.

The main concern is that most of the hydrocarbons are flammable.

While hydrocarbons have found acceptance in Europe, these were scarcely used in USA, mainly due to commercial reasons. However the Environment Protection Agency (EPA, USA) issued a ruling on December 14, 2011, approving propane, isobutane, and R-441A for use in small domestic and commercial refrigeration appliances. R-441A is a patented blend of ethane (3.1%), propane (54.8%), n-butane (36.1%) and isobutane (6.0%). This mixture is also considerably more energy efficient than HFC134a.Thus, hydrocarbons will now be allowed in domestic household refrigerators, freezers and window air conditioners in the USA.

Hydrocarbon refrigerants possess full chemical compatibility with nearly all lubricants commonly used in refrigeration systems. Good miscibility is maintained with most lubricants under all operating conditions. Due to the particularly high solubility with mineral oils, it may be necessary to use a lubricant with lower solubility or increased viscosity to compensate for possible thinning under situations where high solubility could occur. Almost all common elastomer and plastic refrigeration materials

The ODP of hydrocarbons is zero, while their GWP is very small.

used as 'O' rings, valve seats, seals and gaskets are compatible with hydrocarbon refrigerants. These include neoprenes, vitons, nitrile rubbers, PTFE and nylon. Evaporators and condensers using hydrocarbons tend to be virtually of the same design and size as those used for conventional fluorocarbon refrigerants that operate at similar pressures. Heat transfer coefficients tend to be higher for most hydrocarbons. Most compressor types are also suitable for use with hydrocarbon refrigerants. Compared to CFCs or HFCs, a much smaller refrigerant charge is normally required when hydrocarbons are used.

Natural Inorganic Fluids

Ammonia is an environmentally safe but toxic working fluid which is attracting renewed attention. It possesses the most advantageous thermodynamic and thermophysical properties needed for refrigeration. Ammonia-based compression systems, mainly for low temperature applications, are well developed. These are generally suited for industrial surroundings where sufficient knowledge and facilities exist to handle chemical leaks. There are proposals to extend its use into areas occupied by common public (e.g., comfort air conditioning, cooling of display cases in food shops, heat pumps, etc.). But this requires careful planning and design to avoid panic and accidents in case of leaks.

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Water has many desirable characteristics for cooling applications such as: thermal and chemical stability, neither toxic nor flammable, high COP and high heat transfer coefficients. Disadvantages of water include sub-atmospheric pressure operation, large specific compressor displacement, limitations of evaporation temperatures above 0°C and problems of lubrication.

Air has been used commercially for aircraft cooling since a long time. In spite of the low COP, this is being used because of the operating conditions (e.g., availability of compressed air and ram effect) and stringent specifications (e.g., low weight, small size, absolute safety, zero toxicity, etc.) which are exclusive to aircrafts. In the light of the new situation created due to the ban on synthetic refrigerants, possible use of air for on-ground applications is being considered actively. It should be noted here that the technology with air as refrigerant will be totally different from that with other working fluids due to the fact that air does not undergo phase change (condensation/evaporation) at the temperature levels encountered in conventional refrigeration applications.

Water has many desirable characteristics for cooling applications such as; thermal and chemical stability, neither toxic nor flammable, high COP and high heat transfer coefficients.

Use of carbon dioxide as refrigerant dates back to the early years of refrigeration. It is environmentally benign. Being the by-product of many energy conversion processes, it is cheap and easily available. Its use as a refrigerant can reduce its release to the atmosphere, thereby making a positive contribution to the environment. Very high operating pressure is a drawback. Because of its low critical point, most of the thermodynamic cycle operates in the single phase region. Since CO_2 enters the expansion valve as a superheated vapour, it results in a large energy loss during the throttling process. Carbon dioxide is an excellent refrigerant when both heating and cooling are desired. Also, it is not preferable for use in tropical countries such as India due to the high ambient temperatures which result in high condensing pressures.

Blends and Mixtures

A number of refrigerant mixtures are used for a variety of applications. Blends or mixtures are used either to obtain different desired properties such as bubble point temperature, oil solubility, flammability, as drop-in-substitutes for older refrigerants that are no longer produced, etc. by combining different fluids or to obtain variable temperature refrigeration. The mixtures used in refrigeration systems can be divided into four categories, namely, azeotropes, near-azeotropes, zeotropes and very wide boiling zeotropes.

Figure 7 shows the bubble and dew lines[7] of a typical azeotropic mixture. The bubble and dew point temperatures are the same at the azeotropic composition. The mixture essentially behaves as a pure fluid at this composition. The boiling point temperature of

[7] The dew point is the temperature at which the saturated vapour starts to condense. The bubble point is the temperature at which the liquid starts to boil. In the case of a single component fluid, both these temperatures have the same value, i.e., at a specified pressure, the fluid boils and condenses at the same temperature. However, in the case of fluid mixtures, as shown in *Figure* 8, the two temperatures are different and depend on the concentration of each component of the mixture. In the case of an azeotropic mixture, as seen in *Figure* 7, the dew point and the bubble point are identical just like a single component fluid. The line joining the dew points at different concentrations is known as the dew point line, whereas that joining the bubble points is called the bubble point line.

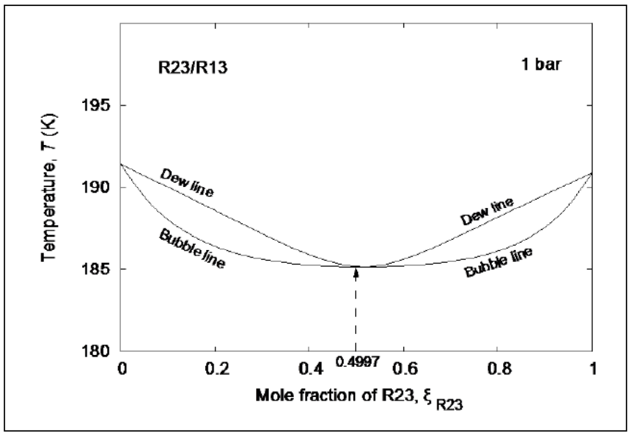

Figure 7. Dew and bubble lines of a typical azeotropic mixture (R23/R13).

azeotropic mixtures used in refrigeration industry is lower than the constituents of the mixture. Since azeotropic mixtures allow reaching temperatures lower than those with pure single component fluids, these have long been used in the refrigeration industry.

Figure 8 shows the bubble and dew lines of a typical binary zeotropic mixture. The difference between the dew and bubble point temperatures at any given concentration is known in the refrigeration industry as 'glide'[8]. Zeotropic HFC refrigerant mixtures with a small glide (0.5 K to 6 K) are widely used in air-conditioning and supermarket applications (in place of refrigerant HCFC22).

[8] The COP of a refrigerator will improve when the glide of the refrigerant is the same as that of the heat transfer fluid in the condenser/evaporator.

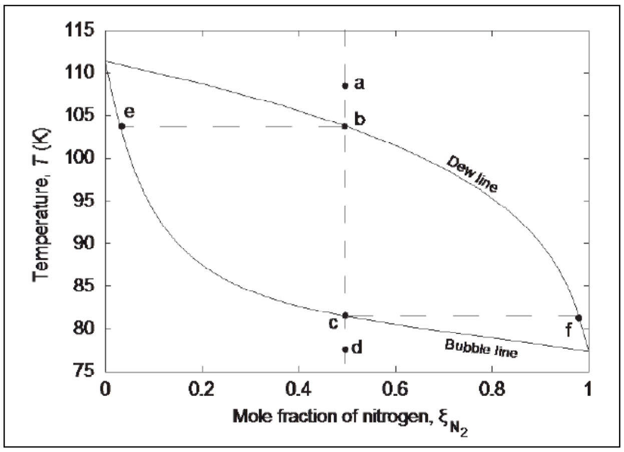

Figure 8. Dew and bubble lines of a typical zeotropic mixture (nitrogen-methane). The state of the mixture at different points are as follows: 'a': superheated vapour, 'b' : saturated vapour, 'c' : saturated liquid, and 'd': subcooled liquid. State points 'e' and 'f' correspond to that of the coexisting phases in equilibrium when the mixture is at state points 'b' and 'c' respectively.

Box 4.

Air conditioning for comfort and commercial applications such as office buildings, district cooling, malls, hospitals, information technology and telecom, etc., is a major area which is impacted by the need for change of refrigerants. Currently, many HFCs, HCFCs and mixtures such as R22, R134a, R404A, R407C and R410A are in use for this purpose. While these are known to be efficient, they suffer from high GWPs. The most recent alternatives offer dramatic reductions of GWP between 50 and 99 per cent. A new HFC mixture of particular interest is R407F (R32/125/134a in the proportion 30/30/40). As a replacement for R404A, this refrigerant yields nearly 50% GWP reduction, as well as energy savings. It is non-toxic, non-flammable, has properties similar to R22 and is of interest to supermarket operators. Environmentally-friendly chillers are also being developed and commercialized based on HFO1234ze, giving reduced energy consumption and also over 99 per cent reduction in GWP compared to R134a. In most cases, the HFO replacements are compatible with existing equipment designs and compressors, and therefore can yield quick and cost-effective solutions.

Refrigerant mixtures with glide less than 1 K are known as 'near azeotropes', and those with glide greater than 6 K are known as 'wide boiling zeotropes'. Though the boiling points of the components of near azeotropes are close, their mixture can have favourable properties such as lower flammability, better thermophysical properties, better oil solubility, etc.

It is well recognized that no direct replacement has been found for HCFC22, widely used for air-conditioning applications. Hundreds of mixtures have been tried as either drop-in-substitutes in existing systems or as a refrigerant in new systems, some of which are available commercially. Even today, the quest for a mixture with more favourable properties continues. The more recent efforts are in mixing low GWP refrigerants such as R1234yf with high GWP refrigerants such as R32 to form mixtures that have both favourable thermodynamic properties in addition to low GWP. Zeotropic mixtures with glide greater than 6 K are, in general, not preferred by the refrigeration and air-conditioning industry because of the large change in concentration of these mixtures if leaks occur and the difficulty in utilizing the glide efficiently.

Very wide boiling refrigerant mixtures that have a glide over 50 K, and up to 150 K can be effectively used in a relatively new

Box 5. Mixed Refrigerant Cascade (MRC) Refrigerators

Traditional cascade refrigeration systems used for production of very low temperatures employ separate compressors and different refrigerants in each of the stages. Mixed refrigerant cascade systems employ a single compressor operating with a zeotropic mixture of refrigerants to provide cooling with much smaller working pressures (Discharge:15-20 bar / Suction:3-5 bar) compared to conventional cryogenic cooling systems. Mixtures with at least four or more components are used in these systems. The refrigerant glide is very large and is typically over 100 K. In comparison, zeotropic mixtures used in traditional refrigeration systems have glides less than 6 K, and are made of only two or three components.

class of refrigeration systems known as mixed refrigerant cascade[9] (MRC) refrigerators and liquefiers (see *Box* 5). *Figure* 9 shows a schematic of the MRC refrigerator. Mixtures of nitrogen, methane, ethane, propane, and butanes are used in these systems. It is also possible to use HFC refrigerants in mixtures. Temperatures as low as 70K can be reached in a single stage with compressor operating pressures similar to those in air-conditioning systems. These refrigerators have replaced traditional cascade refrigerators (multistage refrigerators operating in series with different fluids in different stages) and conventional gas cycle systems, many in low temperature applications. The main advantages of MRCs are their higher COP, lower capital cost

[9] In a traditional cascade refrigerator, temperatures lower than –35°C are normally obtained by using two refrigeration systems operating with different refrigerants in each of the cycle, with the evaporator of the first stage cooling the condenser of the second stage.

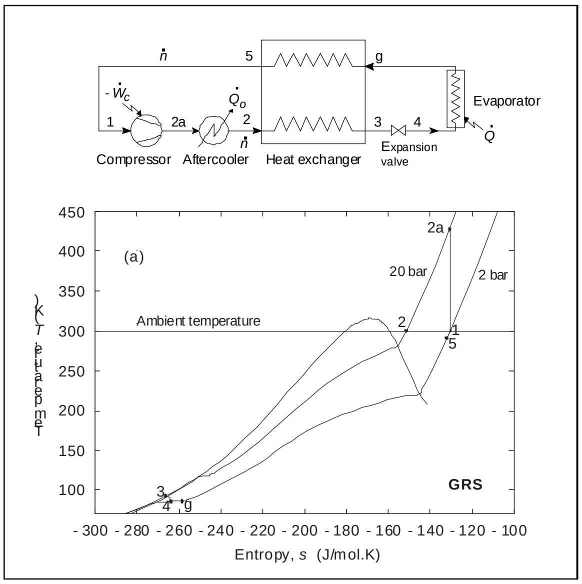

Figure 9. Mixed refrigerant cascade refrigerator: State points 1–5 of working fluid shown on the schematic correspond to those shown on the temperature – entropy diagram.

Refrigerant	Toxicity	COP	Cost of refri-gerant	Working pressures	Flammability	Materials of construction	Compatible lubricating oils
CFC/HCFC	Non toxic	High	Low	Low	Non-flammable commonly used	All oils/Synthetic oils materials	Mineral
HFC	Non toxic	High	Low	Low	Non-flammable	All commonly used materials	Synthetic oils only
HFO	Non toxic	High	?	Low	Flammable	All commonly used materials	Synthetic oils only
HC	Non toxic	High	Low	Low	Flammable	All commonly used materials	Mineral oils/ Synthetic oils
NH_3	Toxic	High	Low	Low	Mildly flammable	Only steels. Copper not compatible.	Mineral oils
CO_2	Mildly toxic	Low	Low	Very high	Non flammable	All commonly used materials	Mineral oils/ Synthetic oils

Table 4. Comparison of different refrigerants.

(single compressor instead of many compressors in cascade systems), lower operating pressures, and ease of control and operation. There is a worldwide effort including at the authors' laboratory to develop efficient MRC refrigerators and liquefiers for a variety of applications.

Concluding Remarks

The refrigeration industry has seen the rise and fall of a large number of refrigerants during the last 150 years. CFCs probably survived the longest till it was proved that they were the major cause of ozone depletion leading to the ozone hole. HFCs that replaced CFCs in the last decade have high GWP and need to be eventually phased out. Environment friendly natural refrigerants such as ammonia, carbon dioxide, hydrocarbons have specific practical deficiencies that limit their universal use. Recently suggested HFOs have low GWP compared to natural refrigerants, but are flammable.

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Thus, there are no refrigerants in the horizon that completely meet the safety, stability, energy efficiency and environmental friendliness. It seems that the refrigeration industry will have very little choice but to use flammable refrigerants (HFOs, low GWP HFCs, HCs, NH_3, etc). Since the energy efficiency of HFOs is somewhat low, mixtures of medium GWP fluids such as R32 and low GWP refrigerants such as R1234yf may be the working fluids of choice in the immediate future. Meanwhile, the quest for better molecules continues. Barring new inventions, natural refrigerants appear to be the best choice in the long term.

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