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Dr Pearson then accepted the post of Senior Scientific Officer at Torry Research Station, Aberdeen and was involved in the practical development of freezing fish at sea on trawlers. Dr Pearson then remained with L. Sterne & Co. Ltd., Glasgow for 11 years, during which he became a Divisional Director and Chief Engineer of the Industrial Refrigeration Division. On the closure of the Industrial Refrigeration Division by Prestcold Ltd., Dr Pearson and some colleagues founded Star Refrigeration Ltd. in 1970.



At Star Refrigeration, Dr Pearson was responsible for the development of a patented range of high-efficiency blast freezers, for the low-pressure receiver type of refrigeration system, giving evaporator overfeed without the use of pumps, for four-port ball type reversing valves for reversed cycle defrost and for the introduction of the patented thermosiphon system of cooling for main frame computers. He developed the first practical drop-in replacements for R-502 and R-12 and has also patented drop-ins for R-22, R-12 in centrifugal compressors and R-13B1. He is currently working on methods of improving the efficiency of carbon dioxide refrigerating systems as well as on ways of replacing R-134a with a substitute which is more efficient at low temperatures. Dr Pearson is President of Star Refrigeration Ltd., is a past-President of the UK Institute of Refrigeration (IoR) and is currently Chairman of the Technical Committee of the IoR. He is a Past-Chairman of BSI Committee RHE/18 "Refrigeration Safety" and of the European TC182 WG2, also on refrigeration safety. Dr Pearson was awarded the Hall Thermotank Gold Medal of the IoR in 1991 and has also been awarded the Lightfoot Medal on 6 occasions. Dr Pearson was honoured to receive the prestigious IIR Gustav Lorentzen Medal in 2003 at the 21st IIR International Congress of Refrigeration in Washington DC. He is the holder of many patents on subjects relating to refrigeration and is the author of many papers.

Refrigerants Past, Present and Future

by

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INTRODUCTION

Refrigeration as we know it has its origins in the mid-19th century. It evolved during the Industrial Revolution when people began to understand the basic facts of thermodynamics. However, human use of refrigeration goes much further back than that. It is believed by some that our Palaeolithic ancestors stored frozen carcasses in pits dug into the permafrost, a practice which has persisted into recent times among the Caribou Eskimo. If this were indeed the case, then the first refrigerant was cold Arctic air, employed during an ice age. I am not completely convinced but it is certain that these ancestors dug pits for some purpose and that they could have been the first cold stores. It is therefore possible that the cold-storage industry predates the emergence of Homo sapiens, which may go some way towards explaining the type of person one meets in that industry.

If air were the first refrigerant, ice came somewhat later. The first written references to the use of ice houses in China date from before 1000 BC. The Romans and the Persians also used ice and snow, mainly for the cooling of drinks in the summer. Use of ice and snow is well documented from the 17th to the 19th centuries. Many ice

houses were constructed by the wealthy in that period, but the supply of ice depended to a large extent on the severity of winter, which could not be guaranteed.

As is often the case, the next step in the exploitation of ice came as the result of the vision of one man, Frederic Tudor of New York. He had travelled to the West Indies where he concluded that there would be a ready market for the abundant ice which was a by-product of winter in the Eastern states of the USA. It took many years for the vision to come true but by 1844, Wenham Lake ice was even being delivered to London as well as to many warmer parts of the USA, aided by the emerging rail network. Production of natural ice developed into a well-organized industry with standard ice block sizes, harvesting methods, large stores, a distribution network and even domestic ice boxes and the ubiquitous ice man with his tongs. The industry thrived on improved land and sea transport to the extent that, for many years, ice was delivered from the Eastern United States to India by ship.

Natural ice was cheap, readily available and easily understood. Its use might have continued but for the outbreak of the American Civil War,



which cut off the Confederate States from the supply of ice to which they had become addicted. It is not possible to construct a mint julep without ice. It is no coincidence that a Ferdinand Carré absorption refrigeration system was transported through the Union blockade into Mexico, and installed in San Antonio, Texas. This took place in 1862, only 3 years after the Carré patent had been granted in France. Absorption refrigeration machines operate at relatively low pressure and do not require any great precision in their manufacture. Though absorption refrigeration systems continue to be used to this day, they have been overtaken by vapour-compression systems, which are much more efficient.

I. REFRIGERANTS: THE PAST

The 19th century

The beginning of vapour-compression refrigeration can be traced back to Professor William Cullen of Glasgow, who produced ice in 1755 by the evaporation of water at low pressure. He also experimented with the evaporation of ethyl ether to produce a reduction in temperature.

Jacob Perkins, an American citizen, took out a patent in 1834 on a vapour-compression refrigerating system using ethyl ether in a closed circuit. The patent covers all the elements of the modern vapour-compression system; the compressor, the condenser, the expansion device and the evaporator. From this time there began a search for the ideal refrigerant, which has not yet been, and probably never will be, discovered.

Perkins used ethyl ether in his early experiments but later graduated to an organic material produced by the heating of India rubber. Ethyl ether is not a good refrigerant because it is both anaesthetic and flammable as well as requiring a large swept volume per unit of refrigerating effect. Ethyl ether is denser than air and has no strong smell, thus making it particularly dangerous in an age when illumination was by lamp or candle. It is not clear what components were contained in Perkins' distillate from India rubber, but all who came into contact with it reported that it had an indescribably bad smell. Presumably some sulphur was present.

By the time of Perkins, the classical refrigerants ammonia, sulphur dioxide and carbon dioxide had been isolated and were available for use, but complex compressors and prime movers were required to use them and, for a while, the original refrigerants, air and water, competed with the water/ammonia absorption machine in the production of artificial cold. None of these refrigerants can compete with the vapour-compression system in terms of efficiency. Air, which is used in the Brayton cycle, produces a very low thermodynamic efficiency because of the large temperature range through which the cycle must operate. Water is difficult to use efficiently because of the very low pressure and enormous pumped volumes which are involved. Absorption systems are notoriously inefficient but require a minimum of high-grade energy. However, it is impossible to imagine more benign substances than air or water. Ammonia, being part of the natural nitrogen cycle, is also completely benign in environmental terms.

Vapour-compression refrigeration continued to use the highly flammable ethyl ether, though in 1863 Charles Tellier took out a patent on the use of methyl ether, which operated at higher pressure and thus reduced the risk of drawing air into the system and forming an explosive mixture within the machine.

Vapour-compression systems were improved by James Harrison in Australia but continued to use methyl ether, which was also used by Carl von Linde in 1875. Linde is generally considered to have pioneered the use of ammonia, but the first ammonia compressor for refrigerating purposes was designed and constructed by David Boyle in 1872, 4 years before the first Linde ammonia machine. Boyle produced up to 200 ammonia compressors prior to 1884, mostly for the shipping of beef from Texas.

Ammonia is in many respects the ideal refrigerant but it has always had competition from less toxic substances. As early as 1862, Thaddeus Lowe developed a carbon-dioxide refrigerating system using a compressor he had developed for compressing hydrogen for observation balloons during the Civil War. Carbon dioxide has very low toxicity but requires high-pressure machinery and is difficult to use because of its low critical temperature (31.6°C).

Before the end of the 19th century, a fourth practical refrigerant, methyl chloride, had appeared in France, being used for the first time as a refrigerant in 1878. Methyl chloride was the forerunner of the vast family of halocarbon refrigerants, which came to prominence later. However, methyl chloride is odourless, but both

flammable and toxic, which gave rise to several serious accidents. In practice, methyl chloride proved to be much more dangerous to use than either sulphur dioxide or ammonia.

Sulphur dioxide is highly toxic but has a strong smell, which provided warning of any leak. Ammonia is also highly toxic and can be smelled

at even lower concentrations than sulphur dioxide.

Table 1 shows the theoretical performance of the 8 practical refrigerants available at the end of the 19th century. Of these, ammonia was by far the best from a thermodynamic point of view but, for safety reasons, air and carbon dioxide were preferred on board ships.

Table 1. Classical Refrigerants

Substance	Refrigerant	Formula	NBP °C	CT °C	Required Vapour Volume Flow relative to CO ₂	COP -15/30°C
Air ¹	R-279	-	-	-221.0	83.0	1.1
Water	R-718	H ₂ O	100.0	375.0	477.0	4.1 ³
Carbon dioxide	R-744	CO ₂	-55.6 ²	31.0	1.0	2.56
Ammonia	R-717	NH ₃	-33.3	135.0	3.44	4.76
Sulphur dioxide	R-764	SO ₂	-10.0	157.0	9.09	4.87
Diethylether	R-610	C ₂ H ₆ O	34.6	214.0	55.0	4.9
Dimethylether	E-170	C ₄ H ₁₀ O	-24.8	128.8	34.0	4.5
Methyl chloride	R-40	CH ₃ Cl	-24.2	143.0	5.95	4.9

¹Brayton cycle

²Triple point

³+5/30°C

Early 20th century

At the beginning of the 20th century, refrigeration was well-established on an industrial scale, but domestic refrigeration, using vapour-compression systems, had not yet been developed. Houses used a cool larder and sometimes an icebox. Commercial refrigeration was in its infancy, using belt-driven ammonia or sulphur dioxide machines. Some of these systems were surprisingly reliable and ran for long periods with minimal attention, but the use of packed glands for the crankshaft seal was less than ideal with such smelly and toxic refrigerants. Matters improved a good deal when the face-to-face seal was developed and the first domestic refrigerators began to appear.

Industrial refrigeration continued to be dominated by ammonia, with air and carbon dioxide being phased out because of their low efficiency. Commercial and domestic refrigeration used ammonia, methyl chloride, sulphur dioxide, propane and isobutane. Each of these refrigerants had serious drawbacks for use in domestic refrigeration. Methyl chloride was by far the most dangerous, but the statistically safer ammonia and sulphur dioxide were unpopular because a leak in the middle of the night could send the whole family out into the yard. Propane and isobutane are highly flammable but in fact had a surprisingly good safety record, probably because charges were relatively small and illumination was now usually by electric light.

Domestic refrigeration was still reserved for the rich. In 1921, only 5000 domestic refrigerators were manufactured in the whole of the USA.

To become more acceptable, the domestic refrigerator had to become a much cheaper, mass-produced article and it had to become safe, reliable and free of any maintenance requirement.

Two developments were required to make this possible. The first was the fully sealed system, having its electric motor contained within the system and exposed to the refrigerant. Refrigerants such as sulphur dioxide, methyl chloride, propane and isobutane are suitable for hermetic systems. Ammonia is not because it is a good conductor of electricity. Domestic refrigerators with fully sealed systems began to appear in the late 1920s and 1930s, but they suffered from lack of a really suitable refrigerant. Sulphur dioxide, though completely non-flammable, was toxic and smelly. It also formed sulphurous acid in the presence of any moisture drawn into the system.

Methyl chloride was both toxic and flammable, though it had no smell. It had a great affinity for water, in the presence of which it was unstable and broke down to form acids. It also reacted strongly with aluminium, to form unstable compounds. Propane and isobutane were ideal

refrigerants in every way except that they were highly flammable. The hydrocarbon refrigerants had a very good safety record but the introduction of the electric refrigerator was being strongly opposed by the ice companies, who could see a threat to their business. It was also opposed by unionized labour, who could see that many of their members might soon be out of a job. Tough safety regulations were imposed and, in some cases, it was laid down that union plumbers should install the machines. To overcome this opposition, and to win the confidence of the housewife, it was obvious that a much safer refrigerant would be required.

Charles F. Kettering of General Motors could see huge potential for the mass production of affordable electric refrigerators and air conditioners if only a better refrigerant could be found. The formidable task of finding the "ideal" refrigerant was given to an able engineer, Thomas Midgeley.

The required refrigerant had to be:

- stable,
- non-toxic,
- non-flammable,
- miscible with lubricating oil,
- capable of operating in a domestic refrigerator without going below atmospheric pressure,
- a good electrical insulator and a substance with a low index of compression so that the compressor would run cool.

The new refrigerant also had to operate at pressures similar to those of methyl chloride, propane and ammonia and to require a swept volume similar to the required swept volumes of these refrigerants.

Thomas Midgeley looked at the periodic table to find families of elements forming stable compounds, having vapour pressures in the desired range. He came to the conclusion that the halogens, iodine, bromine, chlorine and fluorine, formed compounds with carbon, which might be sufficiently stable. Methyl chloride, (CH₃Cl), is an example of such a compound; it was already being used as a refrigerant, but is not stable because of the hydrogen atoms not being strongly enough bonded to the carbon. Midgeley reasoned that if he could form compounds which did not include hydrogen, they would be very stable and certainly non-flammable.

Midgeley selected dichlorodifluoromethane (CCl₂F₂) as a possible refrigerant and it proved to be very good indeed. In addition to the desirable properties listed, the refrigerant had a relatively high critical temperature and the ability to improve bearing performance by forming minute quantities of chlorine compounds at the metal surface.

Table 2 shows how the properties of the refrigerant, now called R-12, compares with the properties of methyl chloride (R-40), ammonia (R-717) and R-134a, the best single substance replacement for R-12.

Table 2. R-12 and Similar Refrigerants

Refrigerant	Formula	NBP °C	CT °C	Required Vapour Volume Flow relative to CO ₂	COP -15/30°C	ODP	GWP
R-12	CCl ₂ F ₂	-29.8	112.0	5.81	4.7	0.82	10 600
R-40	CH ₃ Cl	-24.2	143.0	5.95	4.9	0.02	16
R-764	SO ₂	-10.0	157.0	9.09	4.87	0	0
R-717	NH ₃	-33.3	135.0	3.44	4.76	0	0
R-134a	CH ₂ F.CF ₃	-26.1	101.1	5.90	4.5	0	1300

* Source: UNEP, 2002 Report of the Refrigeration, Air Conditioning and Heat Pump Technical Options Committee – 2002 Assessment

The achievement of Thomas Midgeley in selecting R-12 out of the thousands of possible compounds of carbon, chlorine, fluorine and hydrogen, should not be underestimated. The simple derivatives of methane, ethane and propane account for 85 individual substances without taking account of compounds which are cyclic or have double carbon bonds. Of all these substances, R-12 is the one which most closely approximates to the "ideal" refrigerant which

Midgeley was seeking. Not all halocarbons are benign; some are toxic and some are flammable. Halocarbons which have found use as refrigerants have been selected for that purpose, out of a large number of compounds. R-12, used mainly in domestic and commercial refrigeration, was followed into use by R-11 (CCl₃F) for centrifugal air conditioning systems and, in 1945, by R-13 (CClF₃) for low-temperature refrigeration.

The only apparent, slight, disadvantage of R-12 was that it required a rather larger compressor to accomplish a given refrigerating effect than would be required when using highly toxic ammonia. Even that defect seemed to have been overcome with the development of non-toxic, non-flammable R-22 (CHClF₂), which required swept volumes similar to those for ammonia.

R-22 proved to be a highly practical choice of refrigerant and began to supersede R12 for marine work and ammonia for industrial work.

The apparent, slight, defects of R-22 were that it was less stable than R-12, produced higher compressor discharge temperatures and did not provide such good cooling for the motors of sealed compressors.

R-22 remained the workhorse for refrigeration and air conditioning for many years.

Problems of high discharge temperature and poor motor cooling were overcome by the development of R-502, an azeotrope of R-22 and R-115 (C₂ClF₅).

R-502 allowed the use of halocarbon refrigerants in simple, single-stage, systems under extreme conditions of high condensing pressure and low evaporating pressure.

The complete range of domestic, commercial, industrial and air conditioning applications could now be covered by the versatile range of halocarbon refrigerants. It appeared that there would soon be no room for any refrigerants other than halocarbons.

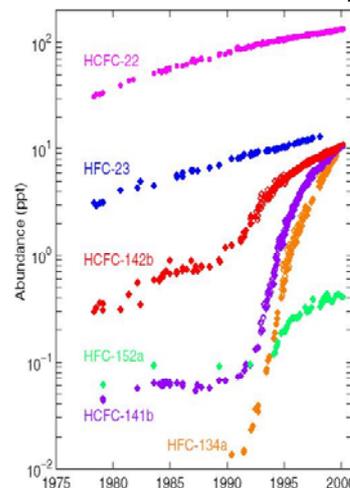
The boom years for production and use of halocarbon refrigerants were probably the 1960s and 1970s, but a cloud was coming up over the horizon.

It had been found that the stable, non-toxic, non-flammable, halocarbons were not only ideal refrigerants but were also very useful as aerosol propellants, as fire extinguishers and for foam blowing. By the mid-1960s, less than half of halocarbon production was being applied to refrigeration and of that, the majority was being used to top-up leaky systems.

It was not surprising that, by the 1960s, it became possible to detect the presence of halocarbons in the Earth's atmosphere. An intelligent and cynical friend of mine remarked that "Eventually there will be no need to buy Freon; you will be able to condense it out of the atmosphere".

In 1974, the researchers Roland and Molina produced the startling hypothesis that emissions of chlorinated halocarbons could damage the Earth's atmosphere by the catalytic destruction of ozone in the stratosphere. Stratospheric ozone is the main atmospheric shield against ultra-violet radiation which, though essential to life, is, like

HFC concentration in the atmosphere
Concentration des HFC dans l'atmosphère



oxygen itself, very deadly in overdose. First reactions were negative. Even the great Professor Lorentzen himself spoke out against proposed restrictions on the use of CFCs. However, as evidence accumulated, he changed his mind and became a determined advocate of "natural" refrigerants.

In 1985, it was established that the ozone layer over Antarctica was being progressively destroyed, just as Roland and Molina had predicted. International reaction was rapid, though the implication of CFCs was not yet proved at that stage.

In 1987, a unique International agreement, known as the Montreal Protocol, laid down that consumption of CFCs should be decreased by 50% over 10 years. The following year, after the release of further reports, DuPont committed itself to a phase-out of all CFC production as non-ozone-depleting substitutes could be found.

The hunt was now on for another set of "ideal" refrigerants, which would have to meet more stringent criteria than those which had been selected for Midgeley.

The new refrigerants must not contain chlorine, because it was chlorine which was damaging the ozone layer. The new refrigerants must also be efficient in use because attention was turning to the consequences of power requirement on global warming. Finally, and ideally, the new

refrigerants themselves should have low direct global warming impacts on their release.

It has not, so far, proved possible to accommodate all these requirements in a single, synthetic, refrigerant. The response of refrigerant manufacturers to the challenge was to co-operate in an unprecedented manner by exchanging information and funding development of significant new alternatives.

The first and most successful of the new alternatives was the refrigerant R-134a ($\text{CH}_2\text{F.CHF}_3$), which has properties very similar to those of R-12. R-134a was known to Midgeley but rejected because it was less stable than R-12, had a lower critical temperature than R-12, and was not miscible with conventional lubricants.

The second new refrigerant developed was R-123 (CHClF_3) as a replacement for R-11. However, as attitudes hardened against the use of any HCFCs, this otherwise excellent refrigerant did not find continuing favour and it will be phased-out along with all HCFCs, including R-22. It seems a pity to me that politicians and environmentalists cannot be persuaded that some HCFCs contribute so little to ozone depletion that their careful use could have been permitted. The production and destruction of ozone in the atmosphere is a continuous process. There is no evidence that continuing use of R-22 in sealed systems would have had serious consequences.

II. REFRIGERANTS: THE PRESENT

The phasing-out of all CFC and HCFC refrigerants brings us to the present day.

The only single-component HFC in common use as a refrigerant is R-134a, which is a good match for R-12.

Replacements for R-22 and R-502 have been created by blending components to produce the required properties. In general, blends of volatile substances will evaporate to dryness through a temperature range known as the "glide". Some blends however evaporate at a constant temperature. These blends are known as azeotropes. Glide is considered to be inconvenient so blends are generally selected to have zero, or minimal, glide. Such blends are azeotropes or near-azeotropes. Azeotropes are given refrigerant numbers in the 500 range. The actual numbers have no significance beyond indicating the order in which the blends were accepted by ASHRAE. Zeotropic and near-azeotropic blends are given numbers in the 400

range. It is worth noting that glide can be used to increase the available temperature difference when cooling a substance through a temperature range. Though circuit arrangements designed to take advantage of glide could increase efficiency of heat transfer, such circuits have not generally been adopted though they are standard practice in the gas liquefaction industry.

Selection of any refrigerant is a compromise. Because there are many applications of refrigeration, a bewildering variety of refrigerant blends has arisen to meet these applications. It is an indication of the inherent difficulty of satisfying the many, and sometimes contradictory, requirements for the ideal refrigerant that new blends continue to appear.

Current requirements for a successful blend are that it should have an Ozone Depleting Potential (ODP) of zero, that it should be efficient to use in conventional refrigeration machinery, that it should be non-toxic, non-flammable, and that it should have low global warming potential (GWP). It is very difficult to meet all these requirements. The only methane derivative which comes anywhere near is R-23, and it has a very high GWP. The only acceptable ethane derivatives are R-134a and R-125. It becomes obvious that flammable substances have to be pressed into service, provided they can be included in blends which are non-flammable and (ideally) do not fractionate to flammable. The flammable substances R-32, R-161, R-152a and R-143a can be added to the list of possible blend components. This still provides only seven substances from which to permute halocarbon refrigerants for today and for tomorrow. Attention turns to derivatives of propane but, out of 45 such compounds, only R-227, R-236 and R-245 are apparently suitable. None of these substances has a normal boiling point which makes it very suitable for commercial refrigeration. Another problem which arises when considering substances which are derivatives of propane, butane, or even heavier hydrocarbons, is that the critical temperature, and therefore the latent heat, of such substances tends to decrease as the molecular weight increases. It is a serious disadvantage for a refrigerant to have a low critical temperature and a low latent heat.

A major disadvantage of all the HFC refrigerants is that they have relatively high GWPs compared to the natural refrigerants.

Attention has returned to some of the natural refrigerants which were, to a large extent, superseded by the halocarbon refrigerants.

Natural refrigerants which have come back into use include propane, butane, isobutane and carbon dioxide.

Ammonia, which had never completely fallen out of use, came back into more common use, especially in systems designed to minimise the charge of ammonia.

Hydrocarbon refrigerants have become dominant for domestic refrigerators in Northern Europe. Over 50 million domestic refrigerators have been installed using the refrigerant, isobutane. Isobutane is highly efficient as a refrigerant because of its relatively high critical temperature

and it operates at very low noise levels because of the low pressures involved. I am not aware of any accidents in the field as a result of the use of this flammable refrigerant in domestic refrigerators.

Hydrocarbon refrigerants could also be used for small air conditioners but their use is, at present, restricted because of restrictions built into European and US safety standards. *Table 3* gives the properties of many of the refrigerants which are currently in use.

Table 3. Currently Used Zero-ODP Refrigerants

Refrigerant	Composition (formula)	NPB °C	Glide K	T _c (°C)	GWP	Safety Group
R-134a	CH ₂ F.CF ₃	-26	0.0	101	1300	A1
R-413A	R-134a.218/600a	-35	6.9	101	1900	A1/A2
R-404A	R-143a/125/134a	-47	0.7	73	3800	A1/A1
R-507A	R-143a/125	-47	0.0	71	3900	A1
R-407C	R-32/125/134a	-44	7.4	87	1700	A1/A1
R-417A	R-125/134a/600	-43	5.6	90	2200	A1/A1
R-410A	R-32/125	-51	0.2	72	2000	A1/A1
R-508	R-23/116	-86	0.0	13	12 000	A1
R-717	NH ₃	-33	0.0	133	0	B2
R-600a	CH (CH ₃) ₃	-12	0.0	135	20	A3
R-290	C ₃ H ₈	-42	0.0	97	20	A3
R-1270	C ₃ H ₆	-48	0.0	92	20	A3
R-744	CO ₂	-57 ¹	0.0	31	1	A1

¹Triple Point

* Source: UNEP, 2002 Report of the Refrigeration, Air Conditioning and Heat Pump Technical Options Committee – 2002 Assessment

Despite their high global warming potential and relatively low critical temperature, there will probably always be a place for the halocarbon range of refrigerants so ably developed originally by Thomas Midgeley. However, it is likely that the range of application of these refrigerants will be restricted due to increasing use of hydrocarbons at the small end of the range, and the increasing use of ammonia and carbon dioxide at the industrial end of the range.

Though some CFC refrigerants continue to be used in some parts of the world, they are rapidly being replaced. Each HCFC refrigerant, including R-22, is also being replaced. However, R-22 is a hard act to follow. Many of the proposed replacements have critical temperatures significantly below that of R-22. The replacements tend, therefore, to operate at lower cycle efficiencies than the R-22 systems which are being replaced.

Domestic refrigeration

The vast majority of domestic refrigerators use R-134a, which is a relatively close match for R-12. Disadvantages of R-134a include relatively poor performance at low evaporating temperatures compared to R-12 and a requirement to use synthetic lubricants.

Hydrocarbons have taken over from R-134a for domestic refrigerators in certain parts of the world. The most commonly used hydrocarbon is isobutane [CH(CH₃)₃]. Isobutane (R-600a) is, at first sight, a surprising choice because of the large

volumetric flow required but the high critical temperature, 135°C, and low cycle pressures combine to produce a very quiet and efficient system. The safety record has been excellent.

Automotive air conditioning

The dominant refrigerant for car air conditioning is R-134a. Emissions to atmosphere from this source are causing concern.

Commercial refrigeration

The dominant refrigerants in this field were R-22 and R-502. Zero ODP replacements for these substances tend to be blends of several HFC refrigerants, including R-32, R-125, R-143a, R-152a, R-134a, sometimes with the addition of a hydrocarbon to improve transport of lubricant within the system.

Replacement blends in the 400 and 500 series have performed relatively well in filling the gap left by R-22 and R-502 but serious concern is being expressed about their high global warming potentials and their low critical temperatures. More efficient substitutes are being sought but the availability of substances to replace the methane and ethane type HFCs is limited.

There has been some use of hydrocarbons in the commercial refrigeration industry but the practice is not widespread.

Air conditioning

Air conditioning has come to be almost completely carried out using halocarbon refrigerants. R-134a is used for small, fully sealed, systems and for centrifugal systems.

R-404A and R-407C are the most commonly used refrigerants for larger systems.

R-404A has very little glide but operates at higher pressures than R-22 and has lower theoretical efficiency at extreme pressure ratios.

R-407C has pressures more in line with R-22 and has a higher theoretical efficiency because of its higher critical temperature but it has a significant glide. R-407C is therefore not suitable for use in flooded evaporators and requires some caution to be applied to the design of DX systems.

A recently introduced refrigerant, R-417A, appears to produce higher efficiency than R-407C, but the reasons for this are not yet fully understood.

Industrial refrigeration

Ammonia continued to be used in the more traditional sections of the industrial refrigeration industry, though its use declined significantly with the advent of the non-toxic, non-flammable halocarbons.

Two unrelated events reversed the tendency away from ammonia. The first was the emergence of the oil-cooled screw compressor, which overcomes the high discharge temperature problems which have to be countered when using reciprocating compressors with ammonia. The second was the publication of their ozone depletion theory by Roland and Molina. Use of ammonia has been increasing in recent years and the use of ammonia is extending back down into regions which, in the past, would have been served by reciprocating compressors using halocarbon refrigerants.

Some traditional ammonia refrigerating practices are beginning to look distinctly old-fashioned. Modern refrigerating systems using ammonia tend to minimise the ammonia charge by various means. This tendency has been reinforced by legislation setting more stringent safety requirements for refrigerating systems containing large amounts of ammonia. The safety record of ammonia refrigerating systems has been very good over many years.

One method of limiting the ammonia charge and reducing potential exposure of people to ammonia vapour from leaking systems has been to use secondary refrigerants. Many new and improved secondary refrigerants have been produced. These include solutions of potassium formate and potassium acetate, which have even better properties than those of calcium chloride brine. Glycols and alcohols have also been used at higher temperatures but the high viscosity of water glycol solutions is a severe limitation to their use in industrial refrigeration.

An interesting development is the use of carbon dioxide, both as a volatile secondary refrigerant and as the low-temperature refrigerant in a cascade system. Both such applications provide

very high efficiency and are much safer than using an extensive ammonia distribution network.

III. REFRIGERANTS: THE FUTURE

I hope that some of the refrigerants currently in use will continue as refrigerants of the future but I am not holding my breath. Industry's record of safely containing synthetic refrigerants within their systems is not good. Atmospheric concentration of R-134a is rising exponentially, mostly from car air conditioning. Some supermarkets have suffered refrigerant losses of 30% per annum. Such prodigal use of refrigerant is obviously not sustainable.

Halocarbons

Halocarbons are so convenient to use that a strong case can be made for their continuing use. However, better methods of containment are essential and more efficient refrigerants with higher critical temperatures and lower GWPs should be sought.

It is clear that most losses of refrigerant come from "serviceable" systems, such as car air conditioning, and from distributed and serviceable systems, such as supermarket installations. By contrast, refrigerant loss from fully sealed, factory-constructed systems, such as domestic refrigerators and window air conditioners, is much less. The charge of such systems is also small.

If there is to be a long-term future for halocarbon refrigerants it might be necessary to restrict their use to fully sealed, factory-built systems. There is an inherent size limitation on such systems because of the need to cool the internal drive motor. The cooling problem is greater for low temperature systems and much less for air conditioning systems. Restricting halocarbons to factory-built systems would imply the use of secondary refrigerants for distributed systems, which could introduce further inefficiencies. It is, however, perhaps fair to say that present widely distributed systems with long suction lines are by no means close to maximum attainable efficiency so the penalty of using indirect systems might be less than one could imagine.

Restricting halocarbon use to fully sealed systems would raise the problem that this technique could also be applied to hydrocarbons, and even to the dreaded methyl chloride, without causing unacceptable risk. However, while it would be safe to recharge non-toxic, non-flammable halocarbons in the field, it would probably pose unacceptable risks for methyl chloride and for hydrocarbons.

As previously indicated, there are few possible compounds available which are not halocarbons. Sulphur hexafluoride would have some potential as a refrigerant but it has a very high GWP of 22,200. Hydrofluoroethers are theoretically possible but they too have high GWPs. E-125 ($\text{CHF}_2\text{-O-CF}_3$) has an ideal boiling point of -42°C but is prohibitively expensive to produce and has a GWP of 15 300.

I've long been an advocate of the use of R-218 (C_3F_8), perfluoropropane, because it forms an

azeotrope with a large number of halocarbons and therefore allows the production of a wide variety of potentially efficient blends. The GWP of R-218 is 7000 but, as far as I am aware, it has not been detected in the atmosphere despite being used in some industrial processes for many years.

Table 4 gives properties of some of the halocarbon refrigerants which might form the basis of future blends.

Table 4. Possible Future Blend Components

Refrigerant	Composition	NBP ($^\circ\text{C}$)	CT ($^\circ\text{C}$)	ODP	GWP
R-23	CHF_3	-82.1	25.9	0	12 000
R-32	CH_2F_2	-51.7	78.2	0	550
R-125	$\text{CHF}_2\text{-CF}_3$	-48.1	66.2	0	3400
R-143a	$\text{CH}_3\text{-CF}_3$	-47.2	72.9	0	4300
R-161	$\text{CH}_3\text{-CHF}_2$	-37.1	102.2	0	12
R-218	C_3F_8	-36.6	71.9	0	8600
R-134a	$\text{CH}_2\text{F-CF}_3$	-26.1	101.1	0	1300
R-152a	$\text{CH}_3\text{-CHF}_2$	-24.0	113.3	0	120
R-134	$\text{CHF}_2\text{-CHF}_2$	-23.0	119.0	0	1200
R-131l	CF_3l	-22.5	122.0	0	1
R-227ea	$\text{CF}_3\text{-CHF-CF}_3$	-15.6	102.8	0	3500
R-236fa	$\text{CF}_3\text{-CH}_2\text{-CF}_3$	-1.4	124.9	0	9400
R-143	$\text{CH}_2\text{F-CF}_2$	5.0	156.7	0	300
R-245fa	$\text{CHF}_2\text{-CHF-CF}_2$	15.1	154.1	0	950

* Source: UNEP, 2002 Report of the Refrigeration, Air Conditioning and Heat Pump Technical Options Committee – 2002 Assessment

Some of the substances listed in Table 4 may be toxic but preliminary indications are that R-161 and R-131l, which have very low GWPs, are not acutely toxic.

R-152, which is the symmetric form of the compound, is apparently toxic though the isomer, R-152a, is non-toxic. R-152 has a relatively low GWP of 43.

Hydrocarbons

There is a long history of hydrocarbon use in industrial systems where the area of the plant

is flameproof anyway. Hydrocarbons are good refrigerants, though the critical temperature of substances, such as propane, is disappointingly low. The only serious disadvantage of hydrocarbon refrigerants is their extreme flammability in air. The risk of combustion can be reduced to acceptable levels by the use of fully sealed systems, as has been demonstrated in Germany with domestic refrigerators. There is no fundamental reason why the use of hydrocarbons should not be extended to window air conditioners, water chillers and car air conditioning, provided fully sealed systems are

used. It should be possible to drive variable-speed, fully sealed compressors from an engine-driven alternator on a car. In my opinion, the risks associated with the use of hydrocarbons for car conditioning have been much exaggerated for commercial reasons. Tens of thousands of air conditioners have been unofficially converted to propane in the US and Australia. These vehicles have apparently been safe and reliable in operation but they could have been made even safer if specially designed for flammable refrigerants. The biggest threat to US standard of living comes from internal vested interests and threats of product liability.

It would seem unrealistic to be overly concerned about a few grams of hydrocarbon refrigerant in a car, which contains many kilograms of high octane fuel.

Hydrocarbon refrigerants have a useful future, but perhaps not in the US.

Ammonia

Ammonia is a unique refrigerant by virtue of its excellent thermodynamic properties and the benefits it brings to the environment. Natural production of ammonia dwarfs the amount of

ammonia which is produced by industry. Most industrial production is for the fertiliser industry. Refrigeration uses a very small fraction of the total industrial production of ammonia.

Ammonia will continue to be used in an increasing number of systems, but designs will have to change in order to limit the charge of individual systems.

Ammonia refrigeration already has a good safety record but more stringent laws to limit allowable charges of ammonia are being enacted in many places.

In many cases, it is possible to reduce the charge below that of traditional pump circulated ammonia systems by factors of 10 to 100 without compromising reliability or efficiency.

One method, recently pioneered in the US by Nestlé, is to use ammonia/carbon dioxide cascade systems, in which the ammonia charge is confined to the vicinity of the plant room. Such systems can be more efficient than conventional two-stage ammonia systems for a variety of reasons.

Ammonia is also making a comeback for air conditioning of large buildings. Low-charge chillers are used, usually chilling water. However, significant economies in power consumption and installation costs can be achieved by cooling carbon dioxide as a volatile secondary refrigerant for air conditioning.

Carbon dioxide

Carbon dioxide is also a unique refrigerant. Like ammonia, it is a natural substance and it is essential for life.

Carbon dioxide has a long history as a benign refrigerant but it completely fell out of use by the 1950s because of the advent of safe, non-toxic halocarbon refrigerants which were more efficient.

Carbon dioxide has made a successful comeback in refrigeration. It will be increasingly used in a variety of ways.

Most common uses at present are as an environmentally benign, low-temperature refrigerant in supermarkets and as the low temperature stage of large industrial freezing and cold storage systems.

Much work has been put into the development of transcritical carbon dioxide systems for car air conditioning. This is undoubtedly possible but much more difficult than using hydrocarbons. In the past, with reciprocating compressors, it was

not possible to get thermodynamic efficiencies comparable to those of ammonia or halocarbon systems. The advent of screw and scroll compressors, which can be "economised" allows much higher efficiencies to be obtained from carbon dioxide systems working near, or above, the critical temperature. At present, though screw compressors capable of pumping up to 100 bar gauge are manufactured, they are not designed for refrigeration and do not have economizer ports.

It is only a matter of time before high pressure carbon dioxide compressors for refrigeration are produced.

I confidently predict that carbon dioxide will be increasingly used as a volatile secondary, as the low-temperature stage of cascade systems and, when compressors are available, as a single stage system for air conditioning. There are already significant benefits to be gained from the use of carbon dioxide as a volatile secondary for air conditioning. These include better heat transfer, much smaller piping, reduced pumping power and elimination of chilled water.

CONCLUSION

We live at a time of transition in refrigeration. Such times are always interesting but sometimes painful and dangerous.

It is a time of challenge and opportunity for professional refrigeration engineers.

I trust that you will rise to the challenge.

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