NEW, NATURAL AND ALTERNATIVE REFRIGERANTS

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INTRODUCTION

It is an honour to be invited to present this paper despite the rather daunting title.

Originally the title given was ‘‘New and Alternative Refrigerants’’ but I was also asked to represent the International Institute of Refrigeration by presenting a paper on natural refrigerants so the subjects have been combined.

It is good to be able to pass on the best wishes of the International Institute of Refrigeration (IIR) and to remind you that the IIR will be holding its Gustav Lorentzen Memorial Conference in Glasgow next year. I hope that the IIR conference will be as well supported and as valuable as this CIBSE/ASHRAE conference. You are warmly invited to attend the Gustav Lorentzen conference in Glasgow, which would give you an opportunity to learn about another face of Scotland. It would be presumptuous of me to speculate which face is anterior and which is posterior.

Refrigerants which are ‘‘new’’ cannot be ‘‘natural’’ but refrigerants which are ‘‘alternative’’ could be almost anything and should include alternative systems in which the refrigerant may hardly be discernible. I therefore intend to start with ‘‘alternative’’ refrigerants, which I shall define as refrigerants and refrigerating systems which are practicable but which do not at present extend beyond certain niche markets.

ALTERNATIVE REFRIGERANTS

The vast majority of refrigerating systems use the practical reversed Rankine cycle. Some alternative systems use the Rankine cycle with refrigerants which restrict their fields of application but many alternative systems are cycles or methods which are fundamentally different.

Some of these are considered below.

Acoustic Refrigeration

Acoustic refrigeration depends on the fact that the energy travelling through gas in sound consists of pressure fluctuations in the gas, which themselves produce variations in temperature. If the sound is produced within a pressurised tube it is possible to cool an object within the tube and to refrigerate a fluid passing through the object. Typical acoustic refrigerators work at 20 bar absolute and involve sound intensities of about 180 decibels. I have been told that such refrigerators have been used in the space programme. The fluid used was hydrogen. It is not likely that this technique will find acceptance in building services.

Magnetic Refrigeration

Magnetic refrigeration is used to produce very low temperatures in the region of absolute zero. It works by extracting energy from already cold substances by de-magnetising them.

Articles have been published recently describing a form of magnetic refrigeration produced by alternately magnetising and de-magnetising a special alloy rotating in a magnetic field. This type of magnetic refrigeration is said to produce refrigeration at temperatures suitable for domestic refrigeration.

Thermo-Electric Refrigeration

Thermo-electric refrigeration is thoroughly practicable on a small scale. It depends on the Peltier effect, which is that when a current is passed round a circuit containing two dissimilar materials, there is rejection of heat at one junction and absorption of heat at the other. When the dissimilar materials are metallic, as in a thermocouple, the conductivity of the metals is so high that the apparent cooling and heating effects are negligible. However, if materials of low conductivity, such as semi-conductors, are used, then the heating and cooling effects can clearly be demonstrated at the junctions. The benefit is a silent refrigerator with no moving parts. The disadvantage is that the efficiency of such refrigerators, using best available semi-conductive materials, is much lower than the efficiency of vapour compression systems. Thermo-electric refrigeration is established for the localised cooling of small objects and for the production of cold without need of mains electricity, from solar power for example. At present, thermo-electric refrigeration is not appropriate for building services but the situation could change if better semi-conductors were found.

Air Cycle Refrigeration

Air is a natural refrigerant but the Brayton cycle differs from the Rankine cycle and air cycle refrigeration displays such low efficiency that it cannot compete with conventional refrigeration systems except in certain niche markets.

The market dominated by air cycle refrigeration is that of cabin air conditioning for aircraft. Compressed air at appropriate pressure is available from the jet engines and the running gear is very light. Air cycle has not dominated any other market though it has been demonstrated for rail carriage air conditioning and, on a large scale, for low temperature freezing. Because of its low efficiency, air cycle refrigeration is unlikely to be accepted by the building industry despite the simplicity of the concept.

Water Vapour Compression

Water is also a natural refrigerant but, despite the fact that water vapour compression systems work on the Rankine cycle, the equipment required is so different from conventional refrigerating equipment that I shall treat water vapour compression systems as alternative systems. Water has a very high latent heat of evaporation and a high critical temperature. It is therefore potentially a very efficient refrigerant. However, water suffers from the enormous disadvantage of having an extremely high specific volume. Valiant efforts have been made to overcome this disadvantage by using high speed, multi-stage, axial compressors but it is too early to say that they have been crowned with success. Water vapour systems could eventually be applied as standard in building services but it is more likely that the much more dense carbon dioxide will be even better and just as environmentally friendly.

Evaporative Cooling

Evaporating water is also used as a refrigerant in evaporative cooling systems. Such systems are effective in arid regions where the relative humidity is low. Appropriate conditions can also be obtained by using a desiccant which can be regenerated. Such systems could have a market in building services. At present the market occupies a relatively small niche but the market size could increase if the trend towards legislating against the use of halocarbon refrigerants continues.

Another form of evaporative cooling is the use of trees and shrubs, which produce a degree of cooling by the evaporation of water from their leaves. Some trees, such as the aspen, are designed to increase mass transfer by shaking their leaves in the slightest breeze. As far as I am aware no work has been done on the relative cooling effectiveness of various trees.

The Moorish gardens at the Alhambra are a good example of evaporative cooling using fountains, streams and plants to provide both cooling and shade.

Absorption Refrigeration

Absorption refrigeration produces its refrigerating effect by evaporating a refrigerant, which is then absorbed into solution in a suitable liquid. The concentrated solution is pumped to high pressure and the refrigerant driven out of solution by heat, to be condensed at the higher pressure in a condenser. The condensed liquid is fed through an expansion valve to the evaporator, where the cycle recommences. The absorption refrigerator does not require a compressor but it tends to be bulky and inefficient. However the energy required is mainly low-grade heat as distinct from the high-grade energy which would be required for a vapour compression system. Absorption refrigeration systems can be operated using waste heat if it is available. There are also obvious opportunities to make use of waste heat from combined heat and power systems, thus providing power, heat and refrigeration from a single system.

The fluid pairs in general use are ammonia/water and water/lithium bromide. Ammonia is the refrigerant in the water/ammonia system, which can operate at low temperature. Water is the refrigerant in the water/lithium bromide system, which consequently cannot operate below 0^oC.

The water/lithium bromide system is more efficiency than the ammonia/water system and is widely used for air conditioning in Japan, where the heat source is usually natural gas. Double-effect systems have been developed, which are more efficiency that the simpler, single –effect, system. Having said that, the coefficient of performance (CoP) of a double-effect system would be around 1 compared to a CoP for an R410A system of around 4.5.

Ammonia absorption systems have been used for domestic refrigeration for many years. By a clever trick, the need for a pump has been eliminated by adding a third fluid, hydrogen, which allows the ammonia to evaporate at low partial pressure, and thus low temperature. An arrangement of liquid seals restricts the hydrogen to the vicinity of the evaporator. The efficiency of such domestic refrigerators is lower than the efficiency of vapour compression systems but comparable to the efficiency of thermo-electric domestic refrigerators.

Absorption refrigeration has a place in some modern buildings. The main drawback is the low efficiency and the large amount of heat which has to be rejected compared to a vapour compression system.

Stirling Cycle Refrigeration

The Stirling Cycle engine was invented by the Reverend Robert Stirling of Kilmarnock in 1812 in an attempt to produce an engine which was much safer than the lethal combination of low pressure steam boiler and crude steam engine, which was coming into use at that time. The Stirling cycle engine is an external combustion engine. Heat is applied to a quantity of gas sealed within the engine. This moves the piston of the engine and produces rotation via a crankshaft. The expanded gas is then passed, at more or less constant volume, through a regenerative heat exchanger, to a position where the gas is compressed isothermally to the maximum cycle pressure. The compressed gas is then routed back through the regenerative heat exchanger, where it warms up to the point where it can be further heated by the external heat source to provide the expansion required for the power source. Reverend Robert Stirling was successful in his attempt to produce a safe, non-polluting, engine. Pressures and temperatures were comparatively low. Accidents were unheard of. However, being an external combustion engine, where the heat was transferred through the cylinders, there was a distinct limit to the amount of heat transfer surface which could be included. Early Stirling Cycle engines had piston diameters of the order of 2 feet. Such large, slow running, engines were capable of running for many years without maintenance. It is a feature of the Stirling Cycle engine that, if it is driven by an external power source, the sealed gas within the system will absorb heat during the expansion process and reject heat during the isothermal compression process. The Stirling Cycle machine is, in principle, a very efficient refrigerator. However Stirling Cycle machines are rather complex, containing compression pistons, displacer pistons and regenerative heat exchangers, together with a mechanism of some sort to regulate the relative motion of the power pistons and the displacer pistons.

The main field of operation of the Stirling Cycle refrigerator has so far been in the efficient production of low temperature on a relatively small scale. It is possible to purchase standard Stirling Cycle machines which will produce liquid nitrogen and liquid oxygen from atmospheric air.

Hydrogen is the best gas to use in a Stirling Cycle refrigerator because of its low molecular weight but nitrogen is often used in standard commercial machines because it is much cheaper and safer.

Stirling Cycle machines have a fascination for many ingenious engineers. Modern materials and designs are continually improving the efficiency and reliability of Stirling Cycle refrigerators. Hermetic versions are now available. An ingenious Dutch design uses oscillating pistons and displacers to provide a small, sealed, machine, which could be used in domestic refrigerators. The efficiency of such refrigerators would compare favourably with the efficiency of the three fluid absorption systems and the thermo-electric systems previously described. There is thus the intriguing possibility of three new forms of domestic refrigerator competing for the position of main competitor with the vapour compression system. The Stirling Cycle is not likely to be important to building services engineers except perhaps as part of a combined heat and power system.

The Vortex Tube Refrigerator

The vortex tube is an extremely simple device which works in a very complex manner. The device consists of a tube with a tangential entry for compressed air. There is a baffle plate within the tube and a concentric hole at one end. It is found that, when compressed air is fed tangentially into the centre of the tube, cold air exits at one end and hot air exits at the other. The tube separates the low energy air molecules from the high energy air molecules in the compressed air stream, thus producing a surprisingly large reduction in temperature.

The vortex tube is very inefficient but it is so robust and simple that it is often the best means of providing a small amount of spot cooling in a harsh, high temperature, environment.

NEW REFRIGERANTS

The number of substances suitable for use as refrigerants by virtue of their thermodynamic properties is relatively limited. When those synthetic substances which are toxic, flammable, or which have the potential to damage the ozone layer, are removed, very few remain. Of the methane derivatives studied by Thomas Midgeley, only R32 is remotely practicable and it is flammable. Of the ethane derivatives, R125 and R134a are apparently suitable and R143a, R152a and R161 have appropriate properties but are flammable. The propane derivatives tend to evaporate at too high a temperature but R218 and R227 are practicable. R245 and R236 would be suitable for centrifugal compressors but apparently some of the isomers of R245 are flammable.

Industry's response to lack of pure substances which can serve as non-toxic, non-flammable, zero-ozone depleting refrigerants has been to blend the few available substances, sometimes with the addition of hydrocarbons. R134a, R404A and R407 are well established and cannot therefore be classed as ''new''. Other promising blends which are not yet well established are R410A and R417A. R410A is a high pressure refrigerant giving much greater capacity per unit of swept volume than substances like R22 or R12. This should result in cheaper compressors for the same duty or more profitable compressors for the same duty, or perhaps a compromise. Unfortunately, R410A has a rather high global warming potential (GWP). Another new refrigerant which seems promising is R417A. This is similar to R407C but with slightly reduced glide, and it apparently gives significantly better efficiency in practice. The reasons for this are not clear but the claims of the manufacturer appear to be backed up by experimental evidence.
Attempts have been made to use some fluorocarbon esters as refrigerants but these have surprisingly high GWPs and are very expensive. Other substances which could be used as

synthetic refrigerants, such as sulphur hexafluoride, prove to have extremely high GWPs. The dominant requirements for non-toxic hydro fluorocarbon refrigerants are that they should be efficient in operation and that they should have low GWPs. It is also important, but not essential, that they should be non-flammable.

Efficiency in operation is largely predicated by the critical temperature of the refrigerant. I have attempted to rate refrigerants in terms of the ratio of their critical temperature compared to the critical temperature of R11, which has one of the highest halocarbon critical temperatures. Assuming that condensing temperatures of up to 55°C would be required I have produced a rating factor given by the formula below:

$$Rf = \frac{100.(T_c ref - NBP\,ref)(T_c ref - 55)}{(T_c R11 - NBP\,R11)(T_c R11 - 55)}$$

Though the rating factor is not an absolute comparison and neglects the deleterious effect of high specific volume it does give an indication of the problem facing those trying to develop new refrigerants. The following table indicates rating factors for some synthetic and some natural refrigerants. It should be emphasised that the rating factor is a means of arranging the refrigerants in order of probable efficiency. The absolute values are not significant, for example R717 is not twice as efficient as propane. It can be seen however that most of the new refrigerants come low down in the order, which is bad news in terms of system efficiency. One interesting comparison is between R404A and R125, which indicates that blending R125 with R143a and R134a has significant benefits.

TABLE 1 – Refrigerant Rating Factors

Refrigerants	**Rating Factor**
R11	100
R123	81
R717	52
R12	32
R134a	24
R1270	21
R290	23
R22	23
R407C	17
R417A	18
R502	13
R410A	8.7
R404A	8,2
R507	7.5
R218	7.4
R125	5.1

Three possible alternative synthetic refrigerants which have been neglected are R161, trifluoro-iodide (CF_3I) and R218. R161 has been neglected because it is flammable. Trifluoro-ioidide has been neglected because it is considered to be expensive to manufacture. At present, iodine is not manufactured on a large scale. R218 has been neglected because it is alleged to have a very long atmospheric life. Table 2 shows the properties shows the properties of these neglected alternatives.

TABLE 2 – Neglected Alternatives

	Normal B.P.	Critical Temp	Temp Glide	ODP	GWP_{100}	Flammability	Toxicity	Molecular Weight	Smell	Lubricant	Trouton Ratio T/M	Rating Factor
	^oC	^oC	^oC			LFL						
R161	-37.1	102.2	0	0	10	3.8	no	48	no	M	4.9	26
CF_3I	-22.5	122	0	0	0	no	no	196	slight	M	1.28	39
R218	-36.6	72	0	0	8600	no	no	188	no	S	1.26	7.4

Blends of these substances appear to produce refrigerants with very acceptable properties, however industry has not so far been prepared to make any significant investment in the toxicity testing of R161 and trifluoro-iodide. It is accepted that R218 is completely stable and entirely non-toxic. Perhaps the most promising of the synthetic blends in the long term is R410A, which has a GWP of 1890, even less than the relatively moderate GWP of R22. However the critical temperature of R410A is only 72^{o}C, which is much lower than ideal and which will tend to make it inefficient in its main application of air conditioning. It is possible that efficiency of R410A systems could be improved by economising. I understand that the Copeland Corporation has done some experiments in this direction, using modified scroll compressors.

There will always be a market for synthetic refrigerants but the size of the market will depend on the market share taken by natural refrigerants of various types.

NATURAL REFRIGERANTS

Apart from air and water, natural refrigerants par excellence, which have already been covered, natural refrigerants divide conveniently into hydrocarbons, ammonia and carbon dioxide.

Hydrocarbons

The dominant characteristic of the hydrocarbon refrigerants is their high flammability. Provided precautions are taken to mitigate the consequences of their flammability, hydrocarbons make excellent refrigerants in practice. They are miscible with mineral oils and have relatively high critical temperatures.

Propane (R290) and propylene (R1270) have normal boiling points below –40^{o}C and are therefore suitable for general refrigeration applications. Butane (R600) and isobutane (R600a) have much higher boiling points but they also have high critical temperatures, which tends to make them very efficient in operation.

It appears that the key to success in the use of hydrocarbons is to use them in fully sealed systems of relatively low charge.

The greatest success of hydrocarbons has been in the application of R600a to domestic refrigerators. Over 50 million such refrigerators have been produced and I am not aware of a single accident due to the flammability of R600a. Domestic refrigerators using isobutane are at least as safe as domestic refrigerators using halocarbons and they are more efficient and less noisy.

Propane, and blends containing propane, could safely be used in window air conditioners provided appropriate precautions were taken and provided they were used in fully sealed systems. There appears to have been much resistance to this development from what must be considered as vested interests.

Propane could also be used, with an acceptable degree of risk, for car air conditioning, again provided that appropriate precautions were taken. Some tens of thousands of car air conditioning systems have been ‘‘unofficially’’ converted to operate on propane by private individuals in USA and Australia. Despite the total lack of official sanction or control there has not been a noticeable increase in automobile fires. This is hardly surprising considering that the typical car contains up to 70 litres of highly flammable petroleum. The additional risk posed by a few grammes of hydrocarbon refrigerant would appear to be negligible. Again, there are strong vested interests opposing the use of hydrocarbons for automobile air conditioning.

R1270 is a refrigerant similar in performance to propane but much more expensive and therefore unlikely to find general favour.

Hydrocarbons would not appear attractive for large-scale air conditioning applications but they will certainly appear as a refrigerant for window air conditioners of low charge.

Ammonia

The dominant characteristics of ammonia are its penetrating smell and its acute toxicity. Despite these defects, ammonia has been widely used for well over 100 years and has a good safety record. This is perhaps partly due to the unpleasant and penetrating smell, which ensures that leaks are not tolerated.

The properties of ammonia make it an ideal refrigerant. If properly applied it is very efficient to use.

Provided ammonia systems are designed, installed, operated and maintained in accordance with national safety standards and codes of practice, they do not present an unacceptable degree of risk.

The use of ammonia for air conditioning is increasing. Several large systems have been installed within the city of London in recent years. So far these have proved to be very acceptable to end-users.

It is anticipated that use of ammonia for large-scale air conditioning systems will continue to increase.

Carbon Dioxide

Carbon dioxide is present in the bread we eat, the beer we drink, the breath we breathe out. It is present in the atmosphere and it is non-flammable and non-toxic.

Despite the high pressures associated with its use, carbon dioxide has been used as a refrigerant since 1862. Carbon dioxide continued in use in marine refrigeration as a non-toxic alternative to ammonia and to methyl chloride. However, the advent of halocarbons in the 1930s led to the abandonment of the much less efficient carbon dioxide, which finally went out of use in the 1950s.

The reason for poor efficiencies obtained when using carbon dioxide as a refrigerant is that it has a low critical temperature.

There are several ways in which this defect can be overcome. As a result of modern methods and developments, carbon dioxide is coming back into use as a refrigerant in systems which have efficiencies at least as great as the efficiencies of halocarbon and ammonia systems.

Carbon dioxide can be used as a refrigerant in several different ways.

Carbon dioxide in cascade systems

Carbon dioxide has been introduced as the low temperature refrigerant in carbon dioxide/ammonia cascade systems. Such use removes toxic ammonia from the low temperature evaporators and confines it to a special machinery room. The use of carbon dioxide as the low temperature refrigerant in a cascade system also overcomes the problems caused by the very high specific volume of ammonia vapour at temperatures below about –35^{o}C. Depending on the pressure at which the carbon dioxide can be condensed, it is found that such cascade systems are more efficient than two-stage ammonia systems for evaporating temperatures in the range –40^{o}C to –55^{o}C.

The first such system was installed by Nestlé, near London, for the freeze-drying of coffee. Nestlé subsequently installed similar systems for food freezing in USA. Asda/Wallmart have installed several such systems in UK for distribution depots. For a variety of reasons, these systems show cost and efficiency benefits compared to conventional systems.

Carbon dioxide as a volatile secondary refrigerant

Carbon dioxide can also be used as a volatile secondary refrigerant in accordance with UK Patent No: GB 2258298 of 1992. Liquid carbon dioxide is circulated to evaporators, where it extracts heat and returns to a vessel, where it is condensed by the action of a conventional refrigerant. No compressor is required for the carbon dioxide. The mass flow of circulating carbon dioxide is very much less than the mass flow which would have been required to circulate a non-volatile secondary refrigerant, such as glycol. This results in greatly reduced pumping power. The carbon dioxide system can also be oil-free, which gives rise to improved heat transfer coefficients. Such systems have been installed in UK, Sweden and France.

It is obvious that significant reductions in total power consumption could be achieved by using pumped carbon dioxide secondary instead of water for large air conditioning systems. Unfortunately, most consultants are priests of the cult of ''what has been done before''. It is no surprise therefore that the technique of using a pumped volatile secondary has not yet been applied to air conditioning, though it has successfully been applied to cold stores and to supermarkets.

The new headquarters of the Royal Bank of Scotland, currently under construction in Edinburgh, provided an opportunity for comparison between conventional best practice and what could have been done using proven volatile secondary techniques.

With the co-operation of consultants, a design study on the potential of volatile secondary systems was carried out using load profiles of the headquarters complex.

The system under construction represents best practice using circulation of chilled water to the air coolers and circulation of glycol solution from condensers of the R134a systems to dry air coolers. Dry air coolers are used to eliminate any risk of legionnaire's disease and to minimise the charge of R134a.

The system is designed so that at ambients of 14^{o}C or lower it is possible to circulate chilled water to the chilled beams without running the refrigeration compressors. This is sometimes known as ''free cooling''. Nothing is free in this life but systems of this type represent ''best practice'' when halocarbon refrigerants are used to chill circulating water. The power required to circulate chilled water and glycol solution is significant in this application.

Studies of a volatile secondary system using carbon dioxide as the secondary and ammonia as the primary indicated that the overall cost of ownership would have been about 45% of that for a best practice system using R134a and chilled water.

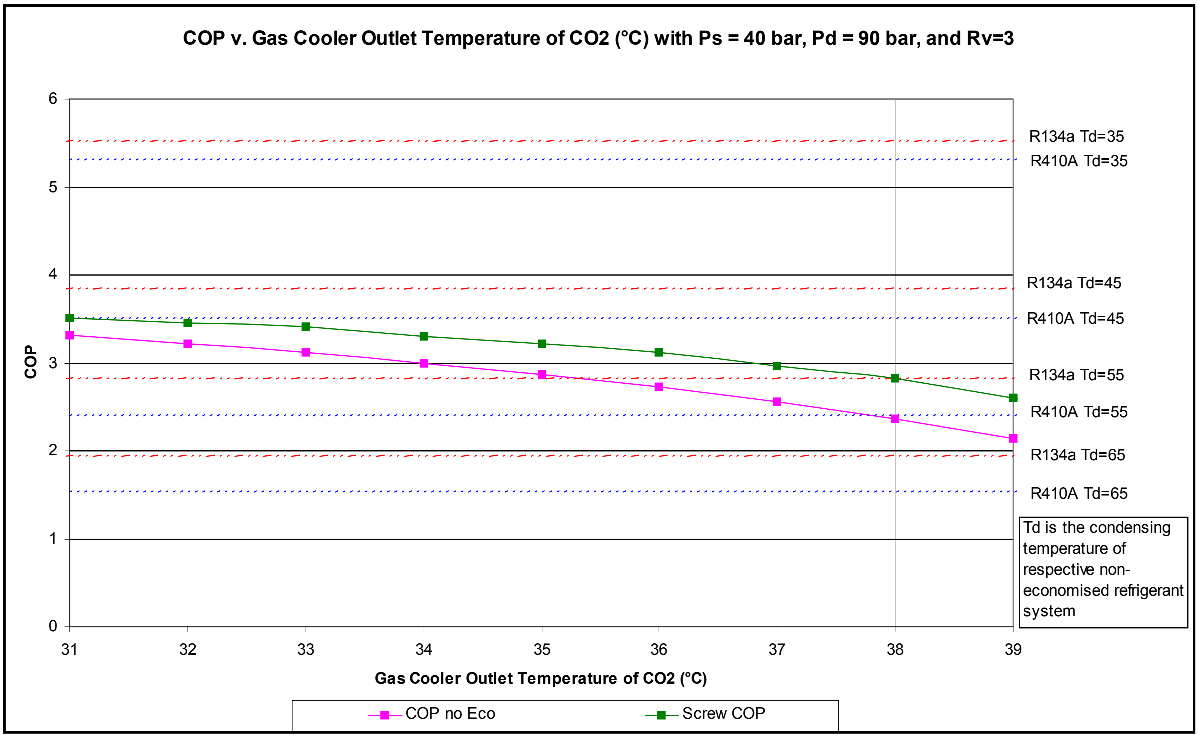
Reasons for the superiority of the volatile secondary system include the very much reduced pipe sizes throughout the building, 6 inch as opposed to 18 inch, and the reduction in pump power from 240kW to 24kW.

The benefits of using carbon dioxide as a volatile secondary system are so great that it would appear to be only a matter of time till the system becomes generally accepted.

At present, demonstration units are being constructed so that those who do only what has been done before can see the rather simple system in operation.

Carbon dioxide as a direct refrigerant

Use of carbon dioxide as direct refrigerant, especially for air conditioning, implies that the high-pressure side of the system will operate at pressures above the critical pressure. It is conventional wisdom that such systems cannot compete in terms of efficiency with conventional refrigerating systems using refrigerants like R134a, R410A and ammonia. However it has been discovered that the use of economised screw compressors would significantly improve the efficiency of transcritical carbon dioxide refrigerating systems. Figure 1 shows the coefficient of performance of an economised carbon dioxide refrigerating system with refrigerant evaporating at 5°C and rejecting its heat as supercritical fluid at a pressure of 90 bar absolute. Superimposed on the graph are coefficients of performance for R134a and R410A at various condensing temperatures. It can be seen that R134a is rather more efficient than R410A, which is to be expected because of the difference in their critical temperatures. It can also be seen that the efficiency of the economised screw system using transcritical carbon dioxide is comparable to the efficiency of the conventional systems when condensing at around 55°C.



55°C is not an unusual condensing temperature for air conditioning systems operating in high ambients. It is difficult to compare the operation of a supercritical fluid cooler with a refrigerant condenser. It is significant that the supercritical fluid is cooled through a wide temperature range compared to the conventional condenser, which rejects most of the heat at a constant temperature. The log mean temperature difference available to the supercritical fluid cooler is therefore rather similar to the log mean temperature difference available to the conventional condenser operating at 55°C.

Screw compressors are available to compress to pressures up to 100 bar absolute. These compressors are designed for fuel gas compression and not for refrigeration. They are also much larger than would be required for even the largest air conditioning system. Their existence demonstrates that economised screw compressors for carbon dioxide air conditioning could be produced.

CONCLUSIONS

Alternative refrigerants and alternative refrigerating systems are unlikely to find great acceptance in the building services industry except for absorption refrigerating systems, which will continue to be employed where conditions are appropriate.

There will continue to be a market for halocarbon refrigerants, especially when used in sealed systems. However, the scope for developing new halocarbon systems is limited.

The field of application of hydrocarbon refrigerants in fully sealed systems will continue to expand but rate of expansion will be slowed by opposition from vested interests.

Use of ammonia will continue, especially for larger industrial systems and for larger air conditioning systems. However, the acute toxicity of ammonia suggests that methods of limiting ammonia charge will be implemented.

After an absence of 50 years, carbon dioxide has returned to the field of refrigeration and its use is increasing rapidly. Carbon dioxide will be used as a low temperature refrigerant in cascade systems, as a volatile secondary refrigerant to avoid the high pumping power associated with the circulation of chilled glycol or chilled water and, possibly, as a direct refrigerant though that depends on the production of suitable refrigerating compressors.