

ADVANCED ENERGY SYSTEMS

Choosing the right refrigerant

Given today's environmental, safety, performance, and economic concerns, what options does a designer have? **By Siva Gopalnarayanan**

MORE THAN A DECADE has passed since the signing of the historic Montreal Protocol that restricted the use of ozone-depleting substances. Many conventional refrigerants have already been banned or are slated to be phased out. With several alternative refrigerants in place, is the process of selecting a refrigerant for a particular application straightforward? The answer is no. The driving forces in refrigerant development and selection are varied and sometimes conflicting. However, several options are currently available that take into account all aspects of the refrigeration system.

DESIGN CONSTRAINTS

There are five major factors that design engineers must consider in selecting a refrigerant for a particular application: performance, safety, reliability, environmental acceptability, and simple economics. In assessing these areas, design engineers should keep in mind that the relative importance of each depends upon the application and, of late, government regulations, which differ from one country to another.

Two of the primary criteria in the performance of a refrigeration system are refrigeration capacity and efficiency. The refrigeration capacity is the amount of cooling that the system can produce for a given volumetric flow rate of the refrigerant. Volumetric capacity is dependent not only on the latent heat of vaporization but also on the density of the refrigerant vapor that enters the compressor.

One good indicator of a refrigerant's capacity is its nor-

mal boiling point. The higher the boiling point, the lower the fluid's volumetric cooling capacity will be. On the other hand, fluids with higher boiling points tend to have greater efficiency. However, they also tend to have a higher pressure drop and, in some cases, lower heat-transfer coefficients. Thus there is a need for compromise. Other refrigeration system requirements include appropriate operating pressure, smaller compressor size, and lower compressor-discharge temperature.

As far as safety is concerned, toxicity, flammability, and pressure govern the proper use of a refrigerant. Refrigerants are broadly classified, based on their toxicity and flammability, by Standard 34-1997 of the American Society of Heating, Refrigerating, and Air-conditioning Engineers (ASHRAE). For toxicity, the classification is based on the chronic exposure limits (the level to which an individual can be exposed over his working life without ill effects), which are defined by the threshold limit value (TLV), the maximum exposure at any given time, and the time-weighted average (TWA). Refrigerants with no identified toxicity at concentrations less than 400 parts per million (ppm) based on TLV and TWA are considered Class A, while those that show evidence of toxicity at concentrations below 400 ppm are Class B. Most of the refrigerants in use are Class A. However, there are a few Class B refrigerants, such as R-123 and ammonia, that need additional equipment safety.

Refrigerants are classified in three groups, according to their flammability. Class 1 refrigerants are nonflammable—they show no flame propagation at ambient conditions at any concentration. Class 2 refrigerants, which are considered moderately flammable, show flame propagation at concentrations greater than 0.1 kilogram per cubic

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meter with heats of combustion less than 19 megajoules/kg. Class 3 refrigerants are highly flammable even for concentrations less than 0.1 kg/m³ with heats of combustion greater than 19 MJ/kg. All of the current halocarbon refrigerants (including refrigerant mixtures) are formulated to be Class 1. Hydrocarbon refrigerant falls into Class 3, with heats of combustion nearing 50 MJ/kg. Ammonia is a Class 2 refrigerant.

Some refrigerants exhibit high pressures. For example, systems using carbon dioxide can have pressures as high as 9,000 kilopascals (kPa). There are many national and international standards that govern the use of high-pressure refrigerants.

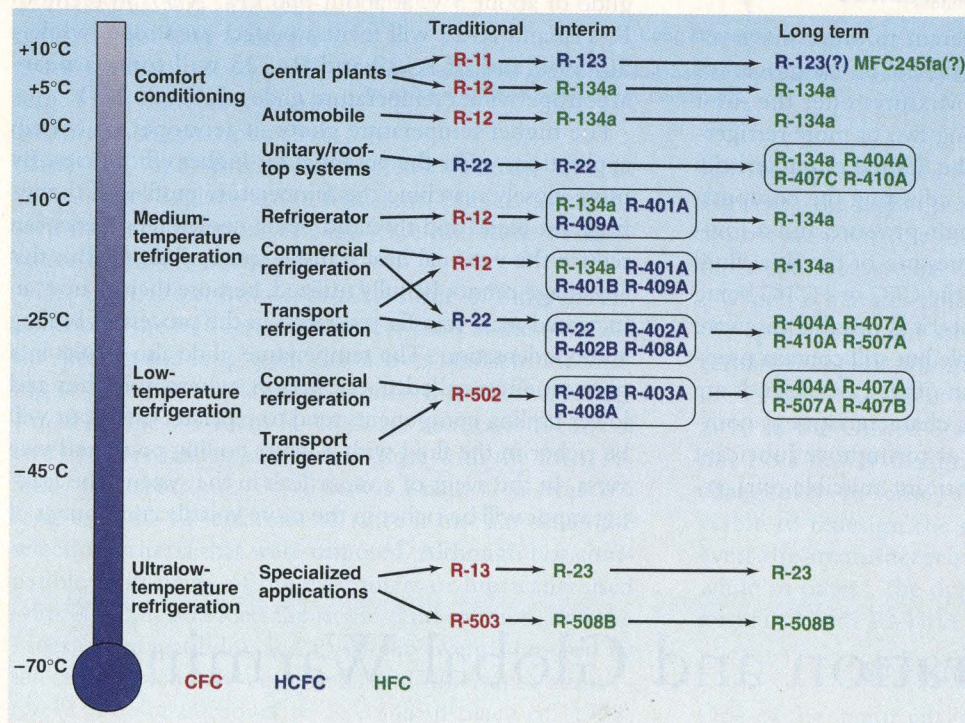
The reliability of a refrigeration system depends to a large extent on the chemical stability of the refrigerant and its compatibility with the various system compo-

Rowland shared the 1995 Nobel Prize in chemistry with Paul Crutzen of the Max Planck Institute for Chemistry in Mainz, Germany.

Ozone depletion potential (ODP) is an index that indicates the ability of a gas to deplete the ozone layer, relative to CFC11 (ODP = 1). The refrigerant should obviously have a low or zero ODP.

In addition to the ozone depletion issue, the general warming trend of the Earth has gained increased scrutiny. Some of the gases that are naturally present in the atmosphere, such as carbon dioxide, absorb infrared radiation, leading to the greenhouse effect that maintains an energy balance and the surface temperature of the Earth. However, increased emissions of carbon dioxide and other greenhouse gases, due to such human activity as the burning of fossil fuels, alter this balance and lead to the gradual

warming of the Earth's surface. Refrigerants, especially those that have long atmospheric lifetimes, have also been found to contribute to this effect. The amount of radiant energy that the refrigerants absorb is measured by an index called global warming potential (GWP). GWP is the amount of infrared radiation that the gas can absorb, relative to carbon dioxide (with an assigned GWP of 1), integrated over a period of 100 years. A more appropriate measure of a refrigerant's contribution to global warming is based on a concept called total equivalent warming impact, or TEWI (see the sidebar entitled "Refrigeration and Global Warming" for details). The refrigerant select-



For a variety of applications, a number of interim and long-term replacements are available.

nents and the compressor lubricant. The refrigerant should not decompose under the temperatures and pressures experienced in the system. It also should not dissolve, swell, or embrittle the elastomers and plastics used in the valve seals and motor components.

The refrigerant should be reasonably miscible at all temperatures with the lubricant used. Good miscibility of the refrigerant with the lubricant is considered important in ensuring proper return of the lubricant to the compressor where it belongs.

Environmental concerns about refrigerants received a major boost in 1974, when Mario Molina of the Massachusetts Institute of Technology in Cambridge and F. Sherwood Rowland of the University of California at Irvine established that the chlorine in chlorofluorocarbons (CFCs) catalytically destroys the ozone layer in the upper atmosphere that protects the Earth from the sun's harmful ultraviolet rays. For this work, Molina and

ed also should have a TEWI as low as possible.

Economics plays an important role in refrigerant selection. Some alternative refrigerants may require expensive system redesign—for example, to withstand higher pressures or to accommodate the use of alternative materials and lubricants made necessary by the new refrigerants. The extent of system redesign varies with the refrigerant selected.

ALTERNATIVE REFRIGERANTS

Although the selection criteria described above appear to be very restrictive, there are several refrigerants available that will meet or exceed all the requirements.

In the decade following the signing of the Montreal Protocol, an extensive search was undertaken for alternatives that would replace CFCs. Among several groups of alternatives, two—the hydrochlorofluorocarbons (HCFCs) and the hydrofluorocarbons (HFCs)—are the most useful. The HCFCs were developed to serve as in-

terim replacements for CFCs. They are used in existing equipment for the remainder of the equipment life and in new systems, until a permanent replacement becomes available. The HCFCs contain chlorine and therefore are still ozone-depleting substances. But their ODP is less than that of CFCs. For example, the ODP of R-12 is 1.0, while one of its interim replacements, R-409A, a blend of three HCFCs (R-22, R-124, and R-142b), has an ODP of 0.05. Some of the HCFCs, such as R-22, offer excellent performance characteristics and were in use even before the ozone depletion issue was raised. HFCs were developed to offer long-term alternatives to CFCs and HCFCs. They do not have any chlorine and hence have zero ODP. Many long-term alternative refrigerants are mixtures of two or more HFCs.

REFRIGERANT MIXTURES

Widely used in the past, refrigerant mixtures have received renewed interest from designers in the process of searching for new alternatives. Mixtures offer the most attractive solution, since by mixing two or more refrigerants a new working fluid with the desired characteristics can be created. For example, by adjusting the composition of a blend containing a high-pressure and a low-pressure refrigerant, the vapor pressure of the final fluid can be tailored to match that of the CFC or HCFC being replaced. By blending refrigerants, it is possible to create new blends that are nonflammable but still contain moderately flammable refrigerants. In other cases, blends are created to improve such system characteristics as compressor discharge temperature, or to improve lubricant circulation by adding a more lubricant-miscible refrigerant to the blend.

Refrigerant mixtures fall into two major groups, zeotropes and azeotropes. In zeotropic mixtures, as the name implies, the liquid-vapor phase change does not occur at a constant temperature (at a fixed pressure) as in the case of pure fluids, but over a range of temperatures. Azeotropic mixtures, on the other hand, boil at a single temperature, much as a pure fluid does. The temperature alteration during phase change is commonly called "temperature glide." An intermediate class of mixtures, dubbed "near-azeotropes," are really zeotropes that are close to an azeotropic composition, and have a very small temperature glide. In some cases, a pair of fluids may be called near-azeotropes if the maximum temperature glide for the pair is very small, even though they may not form an azeotrope. A 50/50 mixture of R-32 and R-134a, for example, forms a zeotropic blend with a temperature glide of about 5°C at about 950 kPa. A 50/50 blend of R-115 and R-22 will form a perfect azeotrope, while a 50/50 blend of R-32 and R-125 will form a near-azeotrope with a temperature glide of about 0.1°C.

The higher temperature glides in zeotropes, in certain applications, offer the potential for higher efficiencies. By more closely matching the temperature profiles of the refrigerant blend and the fluid being cooled, engineers can reduce the external heat transfer irreversibilities. But this advantage cannot be fully utilized, because there is now an increased mass-transfer resistance in the process of boiling and condensation. The temperature glide also results in a phenomenon called fractionation, whereby higher and lower boiling components tend to separate; the vapor will be richer in the fluid with a lower boiling point and vice versa. In the event of a vapor leak in the system, the leaking vapor will be richer in the more volatile component of

Refrigeration and Global Warming

IF HYDROFLUOROCARBONS (HFCs) were the obvious solution to the refrigerant quandary, why would there be so much activity in developing alternative refrigerants and technologies? One reason, it is thought, is the higher global-warming potential (GWP) of HFCs.

For purposes of comparison, R-134a has a GWP of about 1,300, while that of the hydrocarbon refrigerant isobutane is about 11. Both of these refrigerants are used as replacement fluids for R-12 in domestic refrigerators. Is the difference in GWP significant? The answer lies in realizing that the contribution to global warming comes not only from the refrigerant that may leak from the system, but also from the amount of carbon dioxide that will be emitted at the power plant in producing the energy needed to run the compressor.

The effect of a refrigeration system on global warming is more accurately described by the popular concept of total equivalent warming impact (TEWI), which takes into account both of these contributions to global warming. TEWI, therefore, ties in the energy efficiency of the system (and that of the power plant) in determining the effect upon global

warming. In the case of the refrigerator using R-12, only 4 percent of the TEWI comes from direct emission of the refrigerant. Considering that R-134a has only about one-fifth of the GWP of R-12, the contribution to TEWI of using either R-134a or isobutane makes a difference of only 1 percent over the lifetime of the refrigerator.

It is estimated that HFCs currently account for only 0.06 percent of human-induced global warming. Even assuming that HFCs will be fully emitted from the systems in which they are used, estimates place their contribution at about 0.6 percent in 2010, less than 2 percent in 2030, and approximately 2.6 percent by 2100.

Approaches to the global-warming issue taken by various countries are different. In the United States, the consensus is to reduce TEWI by attacking the energy efficiency of the equipment, since that seems to contribute the most to the TEWI. In some European countries, however, emphasis is placed only on reducing the direct contribution from the refrigerants. As in the case of politically sensitive issues like this, the approaches taken by various governments are not necessarily always based only on technical merit.

the blend. This could result in a change in the mixture's composition, which is undesirable, since it could alter the system's performance. However, performance changes will result even for pure fluid if there is a refrigerant leak, since change in refrigerant inventory will cause a change in performance. Class 1 zeotropic blends are formulated to be nonflammable even under the worst fractionation scenario.

Azeotropes and near-azeotropes, on the other hand, do not have a temperature-glide-induced problem. However, azeotropes and near-azeotropes that match the vapor-pressure characteristics of the CFC or HCFCs they replace are nonexistent. Hence, as can be seen in the illustration on page 93, a multitude of alternative blends are zeotropes.

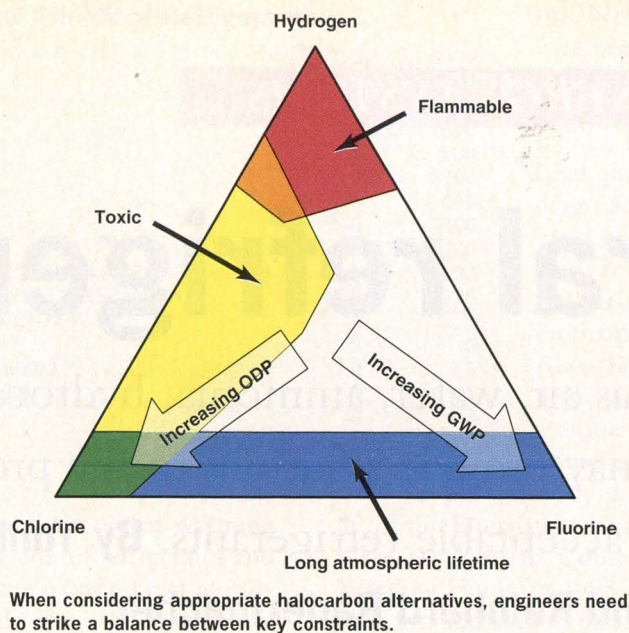
The illustration shows a broad outline of different applications, the refrigerants that were used in the past, and the interim and long-term alternatives available. According to ASHRAE's refrigerant-numbering scheme, refrigerants having the form R-4xxx are zeotropic blends of two or more refrigerants, while those with the form R-5xxx are azeotropes. R-134a was a natural answer as a long-term R-12 replacement, since it met almost all the selection criteria that were imposed. Although not compatible with many of the elastomers or lubricants used with R-12, it provided the single-fluid solution, and the issues of compatibility and miscibility were addressed by selecting alternative elastomers and lubricants, respectively. The changeover to R-134a in place of R-12, however, required a concerted effort and considerable expense on the part of equipment manufacturers.

COMFORT CONDITIONING

R-22 is being used extensively in comfort conditioning. Unlike R-12, however, there is no known single-fluid answer that would meet all the selection criteria. One of the alternatives proposed is propane. Although propane has a low GWP compared to other alternatives, it may have a higher TEWI. In addition, being flammable, it will require additional safeguards, resulting in a more expensive system.

Two alternatives that have become acceptable as replacements for R-22 in comfort-conditioning applications, R-407C and R-410A, are both refrigerant mixtures containing HFCs. HFCs are immiscible with conventionally used mineral or alkyl benzene lubricants, and so require either polyalkylene glycol or polyol ester lubricants.

R-407C is a ternary zeotropic mixture of R-134a, R-125, and R-32. One of the advantages of R-407C is that its vapor pressure is only slightly higher than that of



R-22, so it can be used as a "retrofit" fluid in R-22 systems with only a lubricant change. It also has performance comparable to R-22. One disadvantage of R-407C is its temperature glide, which can be as high as 6 to 7°C at typical system pressures, leading to problems related to the fractionation discussed earlier.

The other alternative, R-410A, is a near-azeotropic mixture of R-32 and R-125. The vapor pressure of this fluid is almost 50 percent higher than that of R-22, and thus R-410A cannot be used in existing systems.

Newly built systems will have to be redesigned to handle the increased pressures. However, the higher pressure and the fact that the fluid is almost an azeotrope provide an opportunity to design more compact systems with greater efficiency.

Which is a better fluid? Again, the choice depends on the application and local regulations. For example, in certain European countries, the phaseout date for R-22 use in new equipment is as early as 1998 (as opposed to 2010 in the United States). In this instance, there may not be a newly designed R-410A unit available for changeover. In some cases, it may not be economically viable to redesign the entire system, considering that even the manufacturing plant will require redesign, while in others, the opportunity for better system performance with R-410A may justify the investment.

STRIKING A BALANCE

One of the major challenges in identifying halocarbon alternatives to ozone-depleting substances is to strike a balance between the various affecting factors, namely ODP, TEWI, toxicity, flammability, performance characteristics, and cost. Due to halocarbons' level of GWP, some European countries have begun exploring alternatives to them. Certain naturally occurring compounds, such as hydrocarbons, carbon dioxide, and ammonia, would need significant processing or refining to be used as refrigerants. These processed refrigerants, as well as natural refrigerants such as air or water, continue to be considered and in some cases applied as viable alternatives to synthetic refrigerants. In the United States, there is considerable resistance to use of hydrocarbons or ammonia in applications that use halocarbons. This is due to liability concerns arising from their flammability and, in the case of ammonia, also toxicity. Even considering their higher direct GWP, halocarbon refrigerants appear to offer the most complete solution, by fully meeting all the safety, performance, economic, and environmental constraints that are placed on today's refrigerants. ■