EVOLUTION OF REFRIGERANT APPLICATION

Piotr A. Domanski
National Institute of Standards and Technology
Gaithersburg, MD, USA

Abstract

The paper reviews the development of chlorofluorocarbon refrigerants, the implemented replacements of ozone-depleting fluids, other considered alternatives, and the prospect for next-generation refrigerants in response to climate change concerns. Convincing evidence suggests that any future refrigerants will have large molecules with high molar heat capacities resulting in a lower thermodynamic efficiency than that of the contemporary refrigerants. If refrigerant availability is not affected by regulatory measures, hydrofluorocarbon refrigerants should continue to dominate the market. "Natural refrigerants" will gain some market share in selected applications. The search for new and the refinement of mature technologies will continue to produce environmentally friendly solutions for the future.

Introduction

The history of mechanical refrigeration is an exciting example of human ingenuity and technological progress. From the beginning of the 19th century, machines based on different refrigeration cycle concepts and using a variety of refrigerants were proposed. The majority of them disappeared from use when better alternatives were implemented. For almost two centuries, the stimulus for these changes were growing market demand for "artificial cold," development of component technologies, economics, and personal safety. These forces changed the preferred refrigeration technology from absorption at the outset to vapor-compression ammonia systems, and to vapor-compression systems using chlorofluorocarbons (CFCs) and hydrochlorofluorocarbons (HCFCs) (Thévenot, 1979). After their introduction in 1930, CFCs and HCFCs gradually became the preferred refrigerants for most applications with ammonia and air obtaining common presence in liquid chillers and aerospace applications, respectively. The dominating market share of CFCs and HCFCs was a result of their favorable attributes including safety and high efficiency.

The dominating market position of CFCs and HCFCs was unchallenged until their implication in the depletion of the ozone layer. This implication was started by the famous article by Molina and Rowland (1974) who argued that photodissociation of chlorine-containing methanes in the stratosphere produces significant amounts of chlorine atoms and leads to the destruction of the stratospheric ozone. The phase-out schedule of chlorine-containing refrigerants was first formulated by the Montreal Protocol in 1987 and was made more stringent during follow-up international meetings.

The mandated phase-out of the CFCs and HCFCs spurred unprecedented intense research to find alternative working fluids. The alternative refrigerants indicated by this effort came predominantly from the hydrofluorocarbon (HFCs) family. With growing concerns about climate warming, some countries oppose the use of HFCs although HFCs trap less infrared radiation than their predecessors. A review of evolution of refrigerants and their performance will help us to recognize the refrigerant options available to us for the future.

Development of CFC and HCFC Refrigerants

Several papers are available with a historic overview of refrigerant development and discussion of trade-offs in refrigerant selection. To pick a few, the papers by Downing (1984), McLinden and Didion (1987), Calm and Didion (1997) and Bhatti (1999) are excellent sources of information. Here, we will briefly discuss the key issues for completeness of presentation.

The list of desired refrigerant properties is extensive. In addition to having good thermophysical properties, an ideal refrigerant should be nonflammable, nontoxic, stable inside the system, and unstable in the atmosphere with harmless decomposition products. Practical considerations call for low cost and full compatibility with system materials including lubricants and machining fluids. Two environmental considerations, the impact of the refrigerant on the stratospheric ozone layer and climate, were added to the list in the 1980s.

For pioneers of refrigeration in the pre-CFC era, the primary refrigerant selection criterion was refrigerant availability. First refrigeration machines used the fluids that the inventors knew from other applications. The most popular refrigerants that were later used commercially for some extended time were carbon dioxide, ammonia, sulfur dioxide (SO_2), methyl chloride (CH_3Cl), and isobutane. Carbon dioxide was known for its low efficiency. The other refrigerants were either toxic or flammable, or both. Accidents were common, and the need for new safe refrigerants became obvious.

In 1928, T. J. Midgley was asked to find a nonflammable and nontoxic refrigerant for a home refrigerator. Considering limited information found in the published literature, he turned to the periodic table of elements. He realized that all refrigerants used at that time included a small group of elements that are located close to the upper-right corner of the periodic table, namely carbon, nitrogen, oxygen, sulfur, hydrogen, chlorine, and bromine. The layout of the elements on the periodic table allowed Midgley and his two associates, A. L. Henne and R. R. McNary, to observe definite trends in reactivity, volatility, toxicity, and flammability of compounds involving different elements. The erroneous boiling point published for carbon tetrafluoride (later it was found to have a much lower value) drew their attention to fluorinated compounds. While fluorine was known to be toxic, they suspected that fluorinated compounds were nontoxic. Therefore, they included fluorine for consideration. The progress Midgley and his two associates made is impressive by any measure. Within the first day of receiving their assignment, they focused on fluorinated compounds. Within three days they synthesized R-21 for initial evaluations. By the fall of 1929 they evaluated most of the physical properties of R-12 and proceeded to a methodical evaluation of a large number of fluorochemicals. In 1930 Midgley introduced R-12 during the meeting of the American Chemical Society. Commercial success came next. Commercial production of R-12 started in 1931, and was followed by production of R-11 in 1932. By the 1950s, with the introduction of other compounds, fluorochemicals became the dominant refrigerants in vapor-compression systems. Previously used refrigerants were abandoned except ammonia, which retained its notable position in water-chilling applications.

Figure 1. Upper-right corner of periodic table with Midgley's eight elements

CFCs, HCFCs and Considered Replacements
Table 1 lists predominant CFCs and HCFCs in the pre-Montreal Protocol years and their alternative candidates. Except for R-13B1, all CFCs and HCFCs contain chlorine. R-13B1 contains bromine, which is a stronger catalyst than chlorine in the ozone depletion process. The most important CFCs and HCFCs are from the methane series (based on one carbon atom). Only R-113, R-114, R-152a (component of R-500), and R-115 (component of R-502) are from the ethane series (based on two carbon atoms).

The phase-out of ozone depleting refrigerants spurred an intense research effort toward identification of alternative refrigerants. Hydrofluorocarbon refrigerants (HFCs) became the predominant zero ozone depletion potential (ODP) alternatives. It is not surprising that fluids of similar properties to CFCs and HCFCs came from the same carbon-based family where, with chlorine not allowed, all bonds are either carbon-hydrogen or carbon-fluorine. The phase-out also provided the opportunity to review the potentials of current commercially significant systems (ammonia, absorption, air) and other new not-in-kind technologies[1]. Besides ammonia, Table 1 includes propane (R-290), isobutane (R-600a), and carbon dioxide (R-744). These refrigerants, commonly called "natural refrigerants," have lately been the topic of considerable research interest with the goal to establish their viability as HFC substitutes.

To expand the range of possible replacement fluids with desired properties, mixtures of refrigerant were investigated. A mixture can be formulated to obtain vapor pressure similar to that of the original refrigerant, to suppress flammability or toxicity of one of the components that otherwise has excellent thermophysical properties, or to improve lubricant return to the compressor. Currently, ASHRAE Standard 34 (ASHRAE, 1997) lists 11 azeotropic and 23 zeotropic mixtures. Component-wise, the list of zeotropic mixtures involves only 13 unique combinations of single-component refrigerants. The extension up to 23 entries is due to seven molecule combinations being classified with a few compositions. For example, the molecule combinations of R-32, R-

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[1] Systems that do not use conventional refrigerants or are not vapor-compression machines

125, and R-134a (R-407) are classified for four mass compositions ((20/40/40 for R-407A, 10/70/20 for R-407B, 23/25/52 for R-407C, and 15/15/70 for R-407D). The mixtures developed in the pre-Montreal Protocol years and those considered as transitional mixtures involve ozone-depleting refrigerants. However, a majority of the mixtures consist of HFCs exclusively. All listed azeotropes are binary mixtures. Just two zeotropes involve only two components; one involves four components, and the remaining mixtures are ternaries.

Table 1. Components and mass fractions of selected refrigerant mixtures

Original Refrigerants		Replacement Refrigerants
Number	NBP* (°C)	
R-113	47.6	
R-11	23.8	R-123, R-245fa
R-114	3.8	R-236fa
R-12	-29.8	R-134a, R600a, R290, R290/600a, DME, R-717, R-744
R-500 [R-12/152a (73.8/26.2)]	-33.5	R134a
R-22	-40.8	R134a, R-407C [(R-32/125/134a (23/25/52)], R-410A [R-32/125 (50/50)], R-290, R-717, R-744
R-502 [R-22/115 (48.8/51.2)]	-45.4	R-404A [R-125/143a/134a (44/52/4)], R-507 [R-125/143a (50/50)]
R-13B1	-57.7	R-410A [R-32/125 (50/50)]
R-13	-81.4	R-23
R-503 [R-23/13 (40.1/59.9)]	-88.7	R-508B [R23/116 (39/61)]

*NBP - normal boiling point

From a commercial point of view, finding replacements for R-11, R-12, R-22, and R-502 has been the most important. The initial replacement for R-11 was R-123, an HCFC. R-123 was developed before the Montreal Protocol included HCFCs as controlled substances and was successfully commercialized in the U.S. The search for a chlorine-free R-123 replacement focused on propane series molecules and narrowed on the R-245 family (a two carbon, three hydrogen, and five fluorine molecules). This focus was based on the recognition that more then five fluorine atoms would result in excessive vapor pressure and more than four hydrogen atoms would result in the refrigerant being flammable (Hughes, 1997). Among five R-245 isomers, R-245fa has the best balance of properties and is seen as an R-123 alternative. It should be noted that R-245fa is far from being a drop-in replacement. Its normal boiling point of 15.1 °C is 8.7 °C lower than the normal boiling point of R-11 and 12.7 °C lower than that for R123. The vapor pressure of R-245fa is sufficiently high to require an ASME certified construction. Theoretical calculations of R-245fa coefficient of performance (COP) yield lower values than those obtained for R-123 and R-11. However, Hughes (1997) suggested that better transport properties of R-245fa and a multistage design may allow R-245fa systems to be competitive with R-11 and R-123 machines.

R-134a has become the dominant replacement fluid for R-12 and R-500. This transition has been the largest in terms of refrigerant quantities. Propane (R290), isobutane (R600a), and their mixture (R-290/600a) were also proposed as R-12 alternatives with notable success in Germany, where they were re-introduced in domestic refrigerators in 1993. Today, hydrocarbons have almost 100 % market share of German refrigerant/freezer production (Kruse, Tiedemann, 1997). This success is not uniform in all of Europe, and the marketing is mainly limited to Northern and Central European countries. Another "natural refrigerant", carbon dioxide, has received new worldwide interest as a working fluid in automotive air conditioners. This interest was initiated by Lorentzen who was the prominent proponent of carbon dioxide (Lorentzen, Pettersen, 1993). Extensive research and development programs were organized to establish the competitiveness of CO2-charged systems, e.g., the European RACE project (Wertenbach and Kauf, 1997).

Although R-22, an HCFC, is under a less rapid phase out schedule than R-11 and R-12, the search for R-22 replacements has been very vigorous. Depending on application, R-134a, R-407C, and R-410A are the leading alternatives. Each of these fluids offers different limitations. R-134a has a significantly lower vapor pressure. The zeotropic mixture R-407C has a similar vapor pressure to R-22, but its glide (approx. 5.5 °C) is large enough to complicate system charging and maintenance procedures because of the fractionation process. The glide of R-

407C is advantageous in liquid chillers where glide matching between refrigerant and water can be ensured using counter-flow heat exchangers. For systems using air as the external fluid, the glide is of a minimal advantage because practical air-to-refrigerant heat exchangers have a cross-flow configuration.

The zeotropic mixture R-410A has a very small glide (within 0.2 °C). From a practical standpoint, such a glide does not impact the operation or maintenance of the system. The higher pressure of R-410A (about 1 MPa higher than the R-22 pressure) and the proximity of the condenser temperature to the critical point result in a lower theoretical COP than that for R-22. However, the higher pressure of R-410A has the advantage of a lower drop of saturation temperature for the equal pressure drop in the heat exchangers (lower $dT/dP|_{sat}$). This allows higher refrigerant mass fluxes, which are synonymous with improved refrigerant-side heat transfer. This improvement is on the top of a higher heat transfer coefficient of R-410A due to superior transport properties. Also, higher compressor efficiencies were reported with R-410A due to a lower pressure ratio compared with R-22. The balance of property impacts provides the opportunity to produce R-410A air-to-air systems equivalent in COP to systems operating with R-22 (Hughes, 1997).

Propane has excellent transport properties and a slightly lower vapor pressure than R-22. If not for its flammability and safety concerns, propane would be an ideal R-22 alternative. Significant system design changes would have to be implemented before propane could be introduced on residential market in the U.S.

Carbon dioxide is also under consideration as R-22 replacement in residential systems, and some preliminary experimental studies have been performed. Because of the transcritical cycle realized by CO2 and significant temperature glide in the high-pressure-side heat exchanger (gas cooler), carbon dioxide offers the opportunity to increase the air supply temperature in the heating mode. The weak side of carbon dioxide is its low thermodynamic COP at high ambient temperatures. In a comparative evaluation of a CO2 and R-22 systems, Nekså and Aarlien (1998) measured a lower COP of CO2 in the cooling mode and higher in the heating mode than that for a R-22 system. Among other than residential applications, ammonia is expected to gain some market share of R-22. This is especially plausible for applications where ammonia lost a share of the market to R-22 in the past decades. No significant market is expected for small products in the short term. The new ammonia products are mostly in the field of small- and medium-capacity liquid and water chillers for air-conditioning, industrial, and commercial applications (De Larminat, 1997). About 20 innovative carbon dioxide/ammonia cascade systems have been commissioned in Europe (Pearson, 1998).

Global Warming and Refrigerant Selection
In the eighties, when depletion of the stratospheric ozone layer received predominant attention and regulatory action, many already considered global warming to be an equally important problem. Global warming is related to the increased atmospheric concentrations of so called "greenhouse gases." These gases trap the infrared radiation emitted by the earth and increase the average temperature of the earth. Since the pre-industrial times (about 1750) concentrations of carbon dioxide increased from 280 ppmv to 360 ppmv. For methane and nitrous oxide the increases are from 700 ppbv to 1720 ppbv and from 275 ppbv to 310 ppbv, respectively. While chlorine-containing refrigerants (in addition to bromine-containing fire suppressants) are the main culprits of the ozone depletion, the main culprits in the climate change are carbon dioxide (82 %), methane (12 %), and nitrous oxide (4 %). HFCs have a minor contribution at this time, but their role is expected to increase with increasing use and emissions. The goal of the Kyoto Protocol is to reduce total emissions of six greenhouse gases (CO_2, CH_4, N_2O, HFC, PFC and SF_6) by at least 5 % (with respect to their 1990 emissions) over the 2008-2012 period (IIR, 1999).

Albritton (1997) gave an excellent presentation of the current scientific understanding of global warming. He stressed the importance of understanding which facts concerning the climate system we know well and which facts we state with less confidence. For example, the principles of a natural greenhouse effect are very well understood and are not disputed. Basic physics demonstrates that CO_2 and other greenhouse gases trap part of the infrared radiation emitted at the surface and warm the earth's climate. Also, convincing data show that greenhouse gases caused by human activities are increasing in the atmosphere and are trapping more heat. It seems reasonable to predict that continued emissions will cause global climate change. This change may be very significant, altering temperature and rainfall patterns and affecting vegetation and the well being of living species. Although we understand the global consequences of increased concentrations of greenhouse gases, the climate change mechanisms are too complex to predict confidently local variations of climate and detailed effects.

A refrigerant's contribution to climate change has a direct and indirect component. The direct component is a result of a refrigerant being a greenhouse gas. The measure of the direct effect for a given gas is its global warming potential (GWP). It is a ratio of its heat trapping capability to that of the reference gas, commonly carbon dioxide. The indirect component is related to the amount of carbon dioxide released in the process of producing electricity needed for operating the refrigeration system. The fuel or fuel mix used to generate electricity, the conversion rate, and other system effects impact the indirect effect. A refrigerant influences the indirect effect through its thermodynamic efficiency. For a given refrigerant and application, both direct and indirect components are combined in the Total Equivalent Warming Impact (TEWI). In tight applications, the indirect component has the dominant effect on the global warming (Calm (1993), Sand et al. (1997)). This shows that improving energy efficiency and reducing refrigerant emissions are the most effective methods of reducing the impact on global climate change.

The common attribute of "natural refrigerants" is their small GWPs, which result in an insignificant direct effect for any reasonable quantities of refrigerant that can leak from the system. Hydrocarbons have the highest GWP in this group, approximately 20. For a comparison, GWP of R-134a is 1300, and that of its original counterpart, R-12, 8100. The use of "natural refrigerants" is appealing, particularly in the systems prone to leaks providing that comparable efficiency can be obtained.

Propane and isobutane can achieve COPs comparable to those of HFC refrigerants. Because of their flammability, hydrocarbon systems usually will require some special design features to assure safe operation. These safety requirements may differ from country to country depending on the safety code. Keller et al. (1997) examined flammability mitigation strategies and the corresponding safety modifications needed for a split residential heat pump and window air conditioner designated for the U.S. market. They compared R-410A and propane designs to the R-22 baseline designs. Their study showed that the R-410A split system had a better TEWI reduction per unit investment than the propane unit. In the window air conditioner case, the study yielded a better TEWI reduction per unit investment for propane than for R-410A.

McEnany et al. (1998) experimentally demonstrated comparable performance of a carbon dioxide and R-12 automotive systems. Both systems required heat exchangers of the same volume; however, the carbon dioxide air conditioner used new-generation micro-channel heat exchangers, which are more effective in heat transfer and more expensive. Wertenbach (1997) estimated the cost of carbon dioxide automotive air conditioner to be 30% higher than the cost of a R-12 system. The examples of propane and carbon dioxide systems show that additional investment may be necessary for achieving a competitive efficiency with "natural refrigerants."

Refrigerant Performance
The goal of this section is to review the factors affecting refrigerant performance. In the first part we will consider single-component fluids and azeotropes to avoid the complication of a temperature glide exhibited by refrigerant zeotropic mixtures. We will refer to the Carnot cycle and vapor-compression cycle to gain the theoretical insight. In this analysis we will omit the transcritical cycle realized by carbon dioxide in human comfort applications.

Single-component refrigerants and azeotropic mixtures
Thermodynamically, all refrigerants have the same COP potential for a given application. At prescribed condenser and evaporator temperatures, this potential is defined by the COP of the reversed Carnot refrigeration cycle,

$$\text{COP}_C = \frac{T_{\text{evap}}}{T_{\text{cond}} - T_{\text{evap}}}$$

(1)

All refrigerants have also the same COP_C potential if we evaluate their performance at the same reduced temperatures in both heat exchangers. The evaluation at the same reduced temperature (e.g., $T_{\text{evap}}/T_{\text{cr}}=0.65$, $T_{\text{cond}}/T_{\text{cr}}=0.82$, $T_{\text{cr}}=$ critical temperature) allows comparing fluids of vastly different critical temperatures at suitable operating conditions.

The Carnot cycle consists of two isentropes and two isotherms. It is completely reversible. The vapor-compression cycle (Figure 2) incorporates some irreversibilities of the real vapor-compression system,
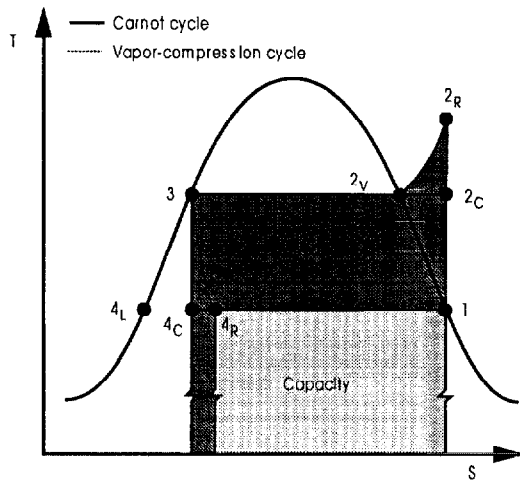
specifically, refrigerant superheating at the end of compression (point 2_R) and the isenthalpic (non-isentropic) expansion process (3-4_R). The work for the vapor-compression cycle includes that for the Carnot cycle plus the work depicted by the triangle 2_C-2_R-2_V and the rectangle located under the line 4_C-4_R. The loss of expansion work due to isenthalpic expansion is equal to the loss of refrigerating capacity. Because of its inherent irreversibilities, the COP of the vapor-compression cycle is lower than that of the Carnot cycle. In contrast to the fluid-insensitive Carnot cycle, the fluid thermodynamic properties will cause the vapor-compression cycle to have a fluid-dependent COP.

Figure 2. Carnot and vapor-compression cycles (capacity and work marked for the vapor-compression cycle)

For a set of specified condenser and evaporator temperatures, different refrigerants will realize different irreversibilities and, as a result, will achieve different COPs. The dominating thermodynamic parameters affecting these irreversibilities are the normal boiling point (or critical temperature) and molar heat capacity. Figure 3 depicts the impact of the critical temperature by showing the vapor-compression cycle realized by two fluids. The more volatile fluid (lower T_{cr}) starts evaporation at a higher vapor quality and has a larger superheated vapor horn – both attributes contribute to a lower COP. However, this refrigerant will have a higher volumetric capacity (Q_{vol}) since a lower critical temperature results in a higher pressure at the compressor inlet. This trade-off between the COP and volumetric capacity are unavoidable. It may be noted that differences in volumetric capacity are much sharper than differences in the COP.
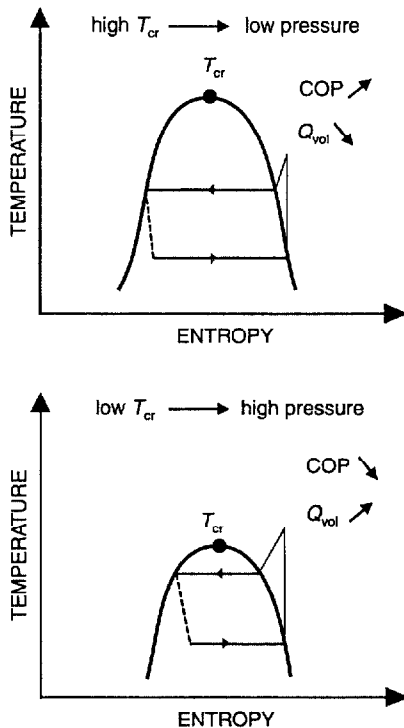
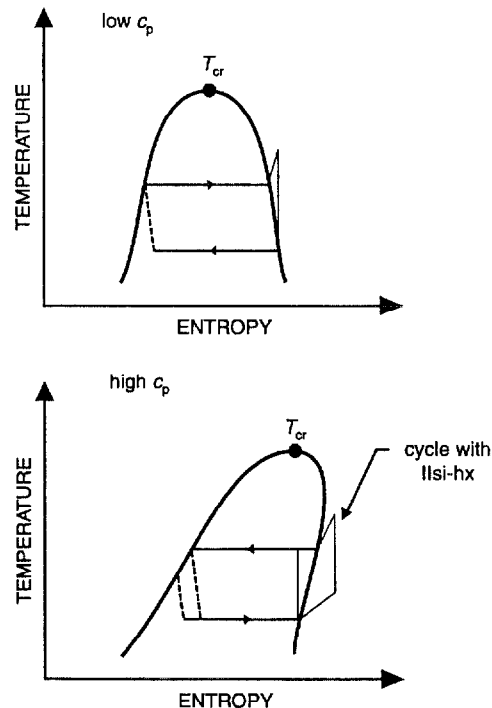Figure 3. Impact of critical temperature on capacity and COP

Figure 4. Impact of molar heat capacity on compression process and COP (c_p denotes molar heat capacity at constant pressure)

The molar heat capacity (c_p) affects the performance profoundly through its impact on the outline of the two-phase dome. The refrigerant with the high molar heat capacity has its two-phase dome skewed to the right, which may result in significant losses and undesirable "wet compression", as shown in Figure 4. A cycle with a liquid-line/suction-line heat exchanger (llsl-hx) – shown by a thin line on the diagram for the high-heat-capacity fluid – is relieved from "wet compression" and also may have a better COP than in a basic vapor-compression cycle (Domanski et al. (1994)).

Morrison (1994) discussed the influence of the molar heat capacity on the shape of the two-phase dome. He presented the following equation for the slope of the saturation line on the temperature-entropy (T-s) diagram:

$$\frac{dT}{ds}\Big|_\sigma = \left[\frac{1}{T}c_v + \left(\frac{\partial p}{\partial T}\right)_v \frac{dv}{dT}\Big|_\sigma \right]^{-1} \tag{2}$$

where σ denotes a property at a saturation line, and c_v, p, v are molar heat capacity at constant volume, pressure, and molar volume, respectively. If equation 2 is analyzed using molar quantities, the term $(\partial p/\partial T)_v dV/dT|_\sigma$ does not vary between different fluids as significantly as c_v/T indicating the dominating effect of the molar heat capacity on the slope of the saturation lines.

We can obtain a further insight on the importance of the molar heat capacity by analyzing the losses in the vapor-compression cycle in relation to the Carnot cycle quantities. Based on observation from Figure 2 and using a few simplifying assumptions, we can express the ratio of the lost refrigerating capacity (and work) to the capacity of the Carnot cycle, Q_{exp}/Q_C, by the following equation (Domanski (1995)):

$$\frac{Q_{exp}}{Q_C} = \frac{\dfrac{1}{COP_C} - \ln\dfrac{T_{cond}}{T_{evap}}}{\dfrac{h_{fg}}{T_{evap}\,\bar{c}_{p,l}} - \ln\dfrac{T_{cond}}{T_{evap}}} \tag{3}$$

where: h_{fg} is the latent heat, and $\bar{c}_{p,l}$ is the average heat capacity of liquid at constant pressure between points 3 and 4_L.

The relative loss of work due to isentropic expansion, W_{exp}/W_C, is related to Q_{exp}/Q_C through the Carnot efficiency, $W_{exp}/W_C = COP_C \cdot Q_{exp}/Q_C$, since $W_{exp} = Q_{exp}$ and $W_C = Q_C/COP_C$.

Only one term in the derived relation for Q_{exp}/Q_C is fluid-property dependent, while the remaining three terms depend on operating conditions. If we evaluate refrigerants at the same absolute or reduced temperatures in the evaporator and condenser, the three operating-regime-dependent terms will have the same values for all fluids. Thus, the relative loss of refrigerating capacity (and work loss) will depend solely on the latent heat, heat capacity of liquid at constant pressure, and the absolute temperature in the evaporator.

If selection of T_{evap} results in the same reduced temperature for the fluids studied, the h_{fg}/T_{evap} ratio does not vary significantly between the fluids. For 38 refrigerants evaluated by the author, the maximum deviation of h_{fg}/T_{evap} from the average value was found to be $\pm 16\%$ (Domanski, (1995)). The deviation of molar heat capacity was much larger (from -44% to $+52\%$), as shown graphically in Figure 5, making the molar heat capacity the most significant variable in the $h_{fg}/(T_{evap}\cdot c_{p,l})$ term.

It should be noted that the limited variation of h_{fg}/T, when evaluated for different fluids at the same reduced temperature, can be deduced from the way h_{fg}/T is correlated in the $0.6 < T_r < 1.0$ range with the Pitzer acentric factor, ω:

$$\frac{h_{fg}}{T} = \frac{R}{T_r}[7.08(1-T_r)^{0.354} + 10.95\omega(1-T_r)^{0.456}] \tag{4}$$

where $T_r=T/T_{cr}$, and $\omega = $ -log$_{10}(P_{0.7}/P_{cr})$-1 does not significantly influence the result (Reid et al., 1987). When refrigerant screening is performed at the same absolute temperature, the term h_{fg}/T_{evap} is not that uniform between different refrigerants because h_{fg} increases with distance from the critical point.
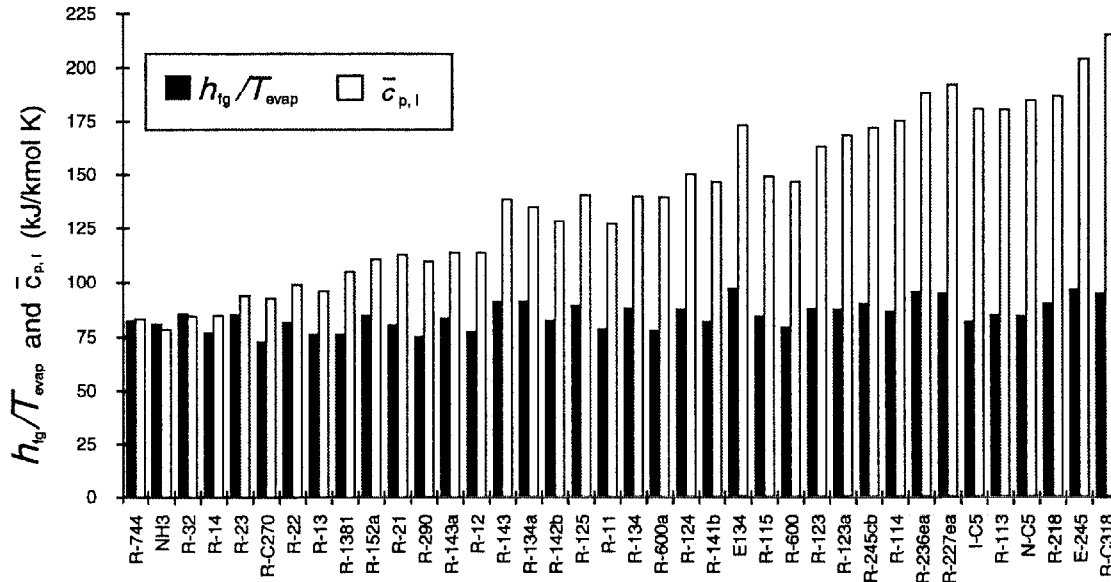

Figure 5. Liquid molar heat capacity and h_{fg}/T_{evap} at T_{evap}/T_{cr}=0.65 (Refrigerants are sorted according to increasing molar heat capacity of vapor. Domanski, 1995.)

The influence of the molar heat capacity on the superheat (and the additional compression work) can be explained considering the isentropic compression process on the T-s diagram (Figure 2). The amount of superheat (temperature difference between points 2R and 2V) depends on the entropy difference (ds) between points 1 and 2V and on the vapor heat capacity (c_p), as expressed by the equation:

$$dT=(Tds +vdp)/c_p \qquad (5)$$

(We may assume dp equal to zero for the 2_R-2_V process for this discussion). The value of ds is influenced by the molar heat capacity of vapor via the slope of saturated vapor line.

It is important to note that equation 2 reveals the significance of heat capacity not when mass-based units are used but rather when molar-based units are employed. This is consistent with the fact that the ideal gas equation of state, $pv=RT$, uses the universal gas constant (R) when a molar volume (v) is used. A practical evidence of the significance of the molar heat capacity is the case of ammonia, which is known to every practicing engineer for reaching high superheat at the compressor discharge. At 10 °C the mass-based heat capacity of saturated ammonia vapor is 2.84 kJ/(kg·K). This is greater than the mass-based heat capacity for R-114 (0.69 kJ/(kg·K), whose isentropic compression process results in wet vapor. However, with the molar mass of 17.03 kg/kmol, the molar heat capacity of ammonia is only 33.90 kJ/(kmol·K), while that for R-114, having the molar mass of 170.92, is 117.7 kJ/(kmol·K). Hence, the small value of molar heat capacity explains the high vapor superheat ammonia reaches as a result of the compression process.

The analysis of this section shows that the molar heat capacity has opposite effects on the loss of expansion work (and refrigerating capacity) on one side and the superheated vapor horn (and the additional compression work) on the other side. A refrigerant having a large molar heat capacity will have a large throttling and capacity loss and a small loss related to the superheated vapor horn, and vice versa. According to an analytical study by McLinden (1998), the optimal value of molar capacity at zero pressure limit ranges from 40 J mol^{-1} K^{-1} to 100 J mol^{-1} K^{-1}.
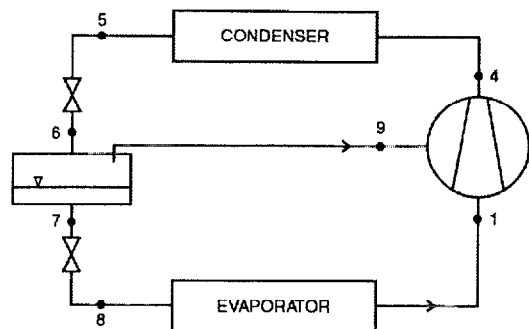
Figure 6. Schematic of a system with economizer

A turbine, liquid-line/suction line heat exchanger (llsl-hx), economizer, and ejector can reduce throttling losses. The author of this paper theoretically studied the last three options (Domanski 1995). The study showed that the economizer (Figure 6) is the most effective addendum to the basic cycle. Figure 7 shows the coefficient of performance of the basic cycle (COP) and economizer cycle (COP$_{ECO}$) referenced to the coefficient of performance of the Carnot cycle (COP$_C$). The selection of the reduced temperatures T_{evap}/T_{cr}=0.65 and T_{cond}/T_{cr}=0.82 results in the COP$_C$ limit of 3.82. All refrigerants benefited from using the economizer, and the best refrigerants in the basic cycle remained the best performers in the economizer cycle. The llsl-hx cycle improved the COP of refrigerants with large molar heat capacity (those that performed poorly in the basic cycle) but hurt the COP of some of refrigerants that performed well in the basic cycle. None of the large molar heat capacity refrigerant could exceed the COP of the best performers in the basic cycle for a practical llsl-hx. The ejector cycle showed least promise for the expected level of ejector efficiency.
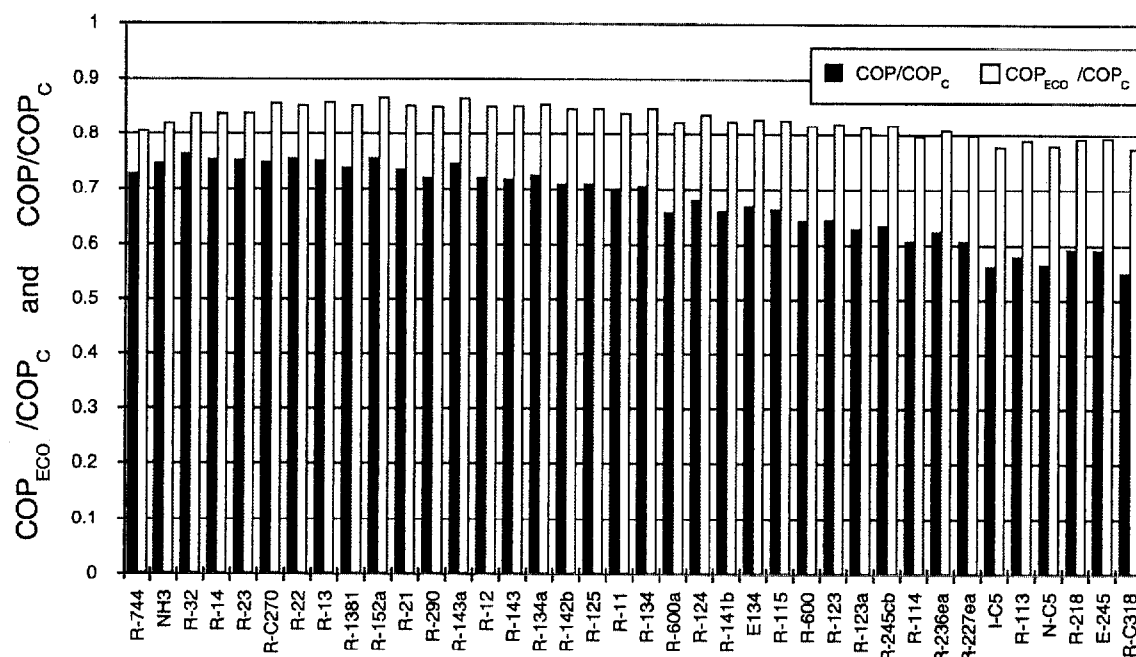

Figure 7. Relative COP in the basic vapor-compression cycle and economizer cycle. (Refrigerants are sorted according to increasing molar heat capacity of vapor. Domanski, 1995.)

Zeotropic mixtures

A temperature glide during phase change is the most differentiating feature of zeotropes when compared with single-component refrigerants. It offers the opportunity to improve performance by matching the zeotrope glide with the glide of the external fluid. Using counter-flow heat exchangers is essential for glide matching. The potential for COP improvement is greater in applications with a high refrigerant glide and low temperature lift ($T_{cond} - T_{evap}$). Kauffeld et al. (1990) measured a 32 % COP improvement for a R-22/114 mixture over R-22 in a laboratory water-to-water heat pump for selected operating regime. For a typical air-conditioning duty and R-407C, a simulation study by Marques and Domanski (1998) showed a 5 % COP improvement when switching from pure cross-flow heat exchangers to pure counter-flow heat exchangers (Figure 8). Their study also indicated that the COP degradation due to glide mismatch with parallel heat exchangers is 9 %; nearly twice as much as the potential for COP improvement with the counter-flow configuration. Considering that practical refrigerant-to-air heat exchangers are cross flow or cross-counter flow at best, a system using air as the external

fluid cannot reach the 5 % COP improvement potential presented in Figure 8. Regarding systems using shell-and-tube heat exchangers, another recent simulation study showed that zeotropic temperature glide causes a migration of a high-volatile mixture component to the condenser leaving the low-volatile component in the evaporator. This migration is undesirable because it raises the pressure differential and increases the compressor work (Swinney et al., 1998).
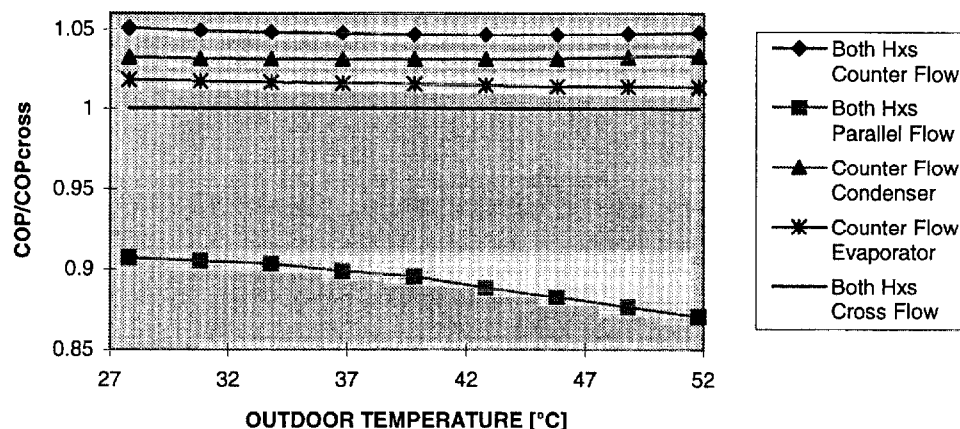

Figure 8. COP change due to the use of counter and parallel flow heat exchangers in a R-407C system at 26.7 °C indoor temperature (Marques and Domanski, 1998)
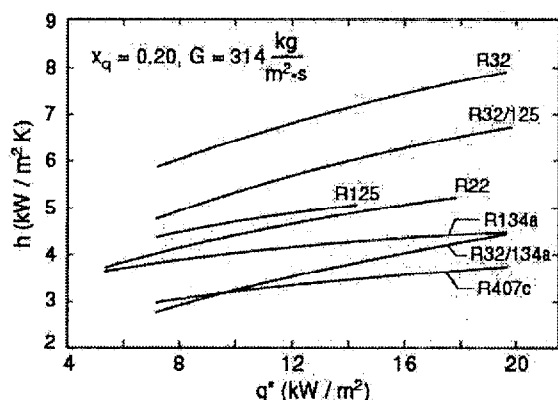

Figure 9. Flow boiling heat transfer coefficients for mixtures and mixture components (Kaul et al. 1996.)

Two-phase heat transfer studies showed that a zeotropic mixture has a lower heat transfer coefficient than either of the mixture components. Figure 9 demonstrates that the heat transfer coefficient for R-407C is lower than that of R-32, R-125, and R-134a. The main reasons for this heat transfer degradation are the degradation of transport properties (higher viscosity and lower conductivity) and mass transfer resistance associated with preferential evaporation of the high-volatile component. These phenomena do not preclude a zeotrope from having a better heat transfer performance than the original refrigerant if the mixture components have better heat transfer characteristic than the refrigerant to be replaced. On contrast to the R-407C zeotrope, the heat transfer performance of the R-32/125 (45/55) azeotropic mixture is bracketed by that of R-32 and R-125.

Prospects for New Refrigerants

Although HFCs satisfy performance requirements as CFCs and HCFCs replacements, investigations into next-generation refrigerants have continued in search of fluids superior to HFCs. The U.S. studies performed in the late eighties focused on ethers. A five-year Japanese program, initiated in 1990, screened about 500 compounds. Seventy of these compounds were 70 synthesized for a more detailed evaluation. The study covered fluorinated ethers, alcohols, amines, and silicon and sulfur compounds. None of the identified next-generation candidates can challenge HFCs based on the balance of its attributes, including safety (personal and environmental), performance, and production feasibility (Bivens and Minor (1998)). All possible replacements for R-11, R-134a, and R-22 fell short on the COP. Only one candidate replacement for R-114 showed an improved COP.

All contemporary refrigerant searches yielded fluids consisting exclusively of the elements identified by Midgley (less chlorine and bromine). The candidate alternative refrigerants tend to have larger molecules than the original fluids. We may note that R-11, R-12, and R-22 are one-carbon-based molecules. Except R-32, the refrigerants considered as CFC and HCFC replacement candidates are based on more than one carbon. Figure 10 illustrates

the progression of molecular complexity for R-11 replacements. All next-generation refrigerants identified by the Japanese study had at least three carbons.
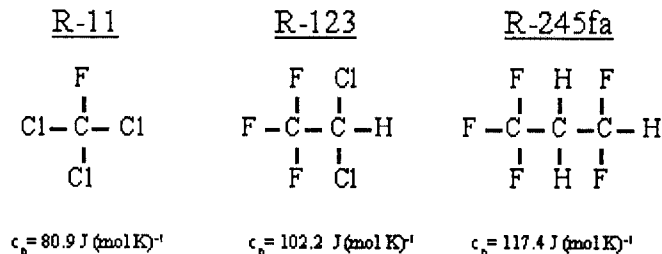
R-11

$$\begin{array}{c} F \\ | \\ Cl-C-Cl \\ | \\ Cl \end{array}$$

$c_p = 80.9 \ J\,(mol\,K)^{-1}$

R-123

$$\begin{array}{cc} F & Cl \\ | & | \\ F-C-C-H \\ | & | \\ F & Cl \end{array}$$

$c_p = 102.2 \ J\,(mol\,K)^{-1}$

R-245fa

$$\begin{array}{ccc} F & H & F \\ | & | & | \\ F-C-C-C-H \\ | & | & | \\ F & H & F \end{array}$$

$c_p = 117.4 \ J\,(mol\,K)^{-1}$

Figure 10. Increasing complexities and molar heat capacities of R-11 alternatives (c_p - molar heat capacity of vapor at constant pressure at 10 °C)

A relation exists between the molecular structure and molar heat capacity because each molecular bond provides a discrete contribution to heat capacity. The larger and more complex the molecule is, the more modes of motion to store energy (movement of the molecule, internal bond stretching and twisting), and the larger the molar heat capacity. Since further searches for new refrigerants are bound to produce fluids that have larger molecules, these refrigerants most likely will have lower COPs and may compress to the wet state.

Besides the lower COP and possibility of wet compression, there are other impediments in finding good refrigerants among large molecules. In general, larger molecules require multistep synthesis, which increase the cost of refrigerant. For this reason, the contemporary HFCs are more costly to produce than CFCs, and production of even larger molecules will be still more expensive. Also, the general trend is that larger molecules are less volatile. The Japanese study did not find alternatives that could match the performance of R22 and R134a. It only identified possible alternatives for the low-pressure R11 and R114. To get a proper perspective on the prospects for new refrigerants, we may contrast the results of the contemporary researchers during the last ten years to the immediate success of Midgley and his two colleagues who in the course of one Saturday afternoon focused on fluorinated methanes and then on R-12. It is quite possible that we already know all the refrigerants we will ever be using in the future.

Alternative technologies
A list of alternative concepts to traditional vapor-compression technology is long. We will mention here only the concepts receiving the most research attention and press. For more information, the reader may refer to Fisher (1998) or Fisher et al., (1994).

Currently, carbon dioxide is the most actively researched alternative technology. A recent review article on CO_2 studies cites 119 references covering transport and automotive applications, heat pumps, and commercial refrigeration (Kruse et al., 1999). Most advanced prototype work has been done on automotive air conditioners. From the thermodynamic point of view, water heating is probably the most attractive application.

Water and air deserve the term "natural refrigerants" more than any other fluid. Water realizes the vapor-compression cycle. Air uses the Joule cycle. Both fluids require mechanical compression. The future of these two refrigerants may depend on the availability of efficient compressors.

The Stirling cycle machines are efficient at low temperatures and have been commercialized as small cryocoolers. At evaporator temperatures above –26 °C the Stirling machine has a lower COP than a vapor compression machine. Additional barriers are a high first cost and reliability difficulties with seals and bearings (Fisher et al., 1994).

The practical advantage of acoustic compressors and thermoacoustic refrigerators is oil free operation. Laboratory results on thermoacoustic systems show low efficiencies. It appears that acoustic technologies require significant developments and technological breakthroughs.

Several alternative methods are based on imposing electrical current or magnetic field to establish temperature gradients for transferring heat. Most of these methods have a low efficiency. The magnetocaloric cooling

technology is an exception with high COPs reported. However, the high cost of high field permanent or superconducting magnets raises the cost of this technology above the vapor-compression technology.

Finally, absorption has been competing with the vapor-compression technology since the beginning of refrigeration. Absorption may be economically attractive in specific regions due to utility rate structure. Since the efficiency of absorption system is lower than the vapor-compression system, absorption does not offer an advantage over the vapor compression system in the context of global warming.

Concluding remarks
Within the last ten years, the air-conditioning and refrigeration industry made significant technical changes in its product offerings in response to stratospheric ozone layer depletion and pertinent regulations. New systems using new working fluid and lubricants were introduced and new maintenance practices were enforced to limit refrigerant emissions. New refrigerants included fluorinated compounds and, in some countries, hydrocarbons in small systems.

The highest-COP refrigerants in the vapor-compression cycle have small molecules. Since small molecule options have already been explored, the alternative refrigerants identified by contemporary searches have larger molecules and lower thermodynamic COPs than the original refrigerants. This decrease in COP may be mitigated in a system by favorable heat transfer properties of the alternative (where it is the case) or by system modifications. It is highly unlikely that a new refrigerant will be found with a thermodynamic COP better then the COPs of CFCs, HCFCs, and the best HFCs.

Considering the lack of promising next-generation refrigerants on the horizon, our refrigerant options in the future may be limited mainly to HFCs and "natural refrigerants", i.e., ammonia, carbon dioxide, hydrocarbons, water, air. These "natural refrigerants" were used in the pre-CFCs years and, except ammonia and air in selected applications, were abandoned by market forces due to their toxicity, flammability or low efficiency. In general, these shortcomings can be mitigated by upgrading system design. The cost for these changes will vary between applications.

A refrigeration system has a direct and indirect contributions to the global warming. An effective approach to mitigating the impact on climate change must include both contributions.

If refrigerant availability is not affected by regulatory measures, HFCs will continue to be dominant for the decades to come because of their high efficiency, personal safety, and the current strong position in the market. "Natural refrigerants" will be employed in selected applications. The search for new and the refinement of mature technologies will continue in an effort to produce environmentally friendly solutions for the future.

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