

THE APPLICATION OF HFCS AS REFRIGERANTS

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ABSTRACT

The technical criteria for using hydrofluorocarbons (HFCs), as refrigerants in the vapor compression cycle, is presented. If thermodynamic performance is to be optimized, particular attention must be paid to the fluid's critical point and molar heat capacity. A reasonable balance between volumetric capacity, which implies equipment size, and coefficient of performance is best achieved by selecting a refrigerant of appropriate vapor pressure. To achieve these balances for the many different applications, both azeotropic and zeotropic mixtures of HFCs are now in use. The characteristics and performance advantages and disadvantages of these mixtures are discussed. Additional physical properties of these refrigerants dealing with lubricant compatibility and safety considerations, i.e. toxicity and flammability, are also discussed.

1. INTRODUCTION

Although hydrofluorocarbons (HFCs) have been considered for working fluids in refrigeration systems since the halogens were first developed, they have been used sparingly until the recent ozone crisis. Ironically, the very reason that they are now the preferred choice over chlorofluorocarbons (CFCs) is the reason that they were not selected initially. In 1928 the inventor of the halogen refrigerants family, Thomas Midgley determined that only eight elements are suitable to be combined into molecules that could act as refrigerants (Midgley, 1937). All others would form solids, are unstable or toxic, or are so inert (e.g., noble gases) that they could not be reasonably combined with other elements. In 1987 a search of a database of some 860 industrially important fluids was conducted to seek refrigerant candidates (McLinden, *et al.*, 1987). The criteria for sorting out the candidates was that the liquid / vapor phases would exist at reasonable pressures and temperatures and that the fluid would have an acceptable volumetric heat capacity. In short, the study showed that Midgley's postulate stood the test of time. All but two of the selected 51 fluids contained only Midgley's elements. The two were highly reactive and toxic and thus unsuitable from chemical and health criteria viewpoints. Interestingly, Midgley and associates chose the CFC path as opposed to the HFC path for the very reason that caused the refrigerants to be capable of destroying the stratospheric ozone, molecular stability. Chemical stability is of course a most desirable quality for any fluid intended to be used for twenty years or more. In fact, the first HFC, what we now call R-134a, was synthesized in 1936 by Midgley's associates Henne and Renoll for the purpose of proving that CFCs were more stable than HFCs and to establish the strength of the C-F bond (Bhatti, 1999). This latter point is the very reason HFCs are a global warming issue.

The ozone crisis has eliminated two of Midgley's original eight elements: chlorine and bromine. The surviving six elements are carbon, nitrogen, oxygen, sulfur, hydrogen and fluorine. Molecules constructed from these elements have strict thermodynamic limitations associated with their molar heat capacity and critical point. The implication of the heat capacity being that complex molecules cannot yield an acceptable efficiency when used in the vapor compression cycle. In addition to these thermal properties criteria there are at least ten other chemical, health,

safety and miscellaneous criteria that a refrigerant must satisfy to be considered for operation in a modern vapor compression cycle system (Threlkeld, 1970). Of these physical properties, lubricant compatibility, toxicity, and flammability have had significant influence on the selection of the refrigerants. While too much chlorine was likely to lead to a toxic refrigerant a little chlorine enabled the solubility between the refrigerant and mineral oil, as well as enhanced the lubricity. These attributes, alone, contributed greatly to the implantation of the CFC as the preferred molecule for a refrigerant. Only occasionally was a HFC utilized and then with care. The highly flammable HFC-152a was used along with CFC-12 to form the non-flammable azeotrope R-500. The flammable HFC-32 was introduced as refrigerant for industrial systems in the early '60s but in spite of its superior thermal performance it was short lived in the marketplace. Thus it was not until the realization of the ozone crisis in the mid '80s and the rediscovery of the HFC-134a that the wide spread usage of the HFCs began.

2. SINGLE COMPONENT HFCs

Although each refrigerant has different numerical property values, all fluids have similar vapor domes. A typical shape is shown in Figure 1. A saturated liquid line (left side) and a saturated vapor line (right side), with different slopes for each fluid, meet at a critical point (CP) of unique temperature and pressure. Using the CP as one index of refrigerant performance, one can see some consequences different working fluids have on the cycle's performance. Given an ideal vapor compression cycle for a fixed application temperature range, a refrigerant with an excessively high CP will result in a decreased density at state 3, the point of suction into the compressor. Since most refrigeration compressors run at constant speed and are thus constant volume pumps, this decrease in density translates to a decrease in mass flow rate and thus system capacity, which is equal to the product of mass flow rate times refrigerating effect. On the other hand, since evaporation is taking place in that part of the vapor dome where the refrigerating effect is large, the system efficiency is high. Conversely, selecting a fluid that has a lower CP results in a larger mass flow rate for per unit volume displacement but a higher reduced condenser temperature. (Reduced temperature, T_r , is defined as the ratio of the particular state temperature to the CP temperature.) Since the slope of the liquid saturation line decreases as it approaches the CP, the operation at higher reduced temperatures will result in the constant enthalpy expansion process using more flash gas to reduce the remaining liquid to evaporator conditions. Also the latent condensing heat per unit mass flow is less because of the narrowing of the vapor dome near the critical point. These reductions in refrigerating effect result in a decrease in COP since less heat can be transported per unit mass flow and thus per unit work. As a general rule when selecting a working fluid, an inherent trade-off exists between the vapor compression cycle's efficiency and capacity. The former is proportional to the CP value and the latter is inversely proportional to it. Therefore no single refrigerant can be optimum for all applications (McLinden, 1988).

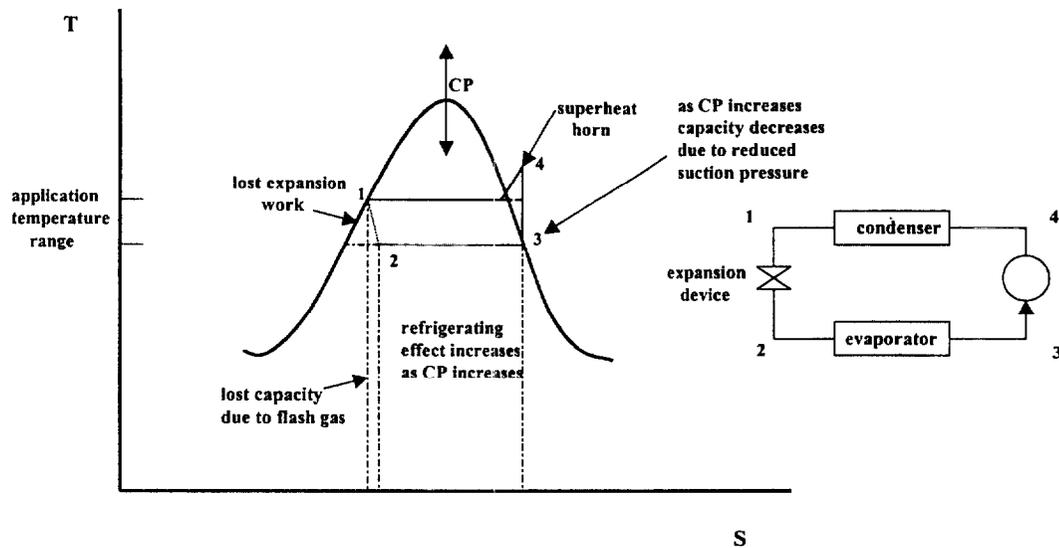


Figure 1. Inherent Tradeoffs for Refrigerants in the Vapor Compression Cycle

Morrison showed that the slope of the saturation lines are related to thermodynamic properties of fluids in such a way that estimates of its expected field performance could be made that based on a prospective refrigerant's molar heat capacity (Morrison, 1994). His analysis showed the slope of the saturation lines to be represented by:

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

where the subscript σ implies along the saturation line. It should be noted that $\left(\frac{\partial P}{\partial T}\right)_v$ is positive

for virtually all saturated liquids and vapors and $\left(\frac{dv}{dT}\right)_{\sigma}$ is positive for saturated liquids and negative for saturated vapors. Among these terms, the magnitude of the variation of the constant volume molar heat capacity is the greatest and will have a strongest influence on the slope of either saturation line. In the case of the vapor side, it can be a matter of whether it will be a positive or negative slope (see Figure 2). By the second law, the slope of the saturated liquid line cannot be negative. Thus, the heat capacity will be the dominant influence as to how positive the slope will be. Molar heat capacity is generally a function of molecular complexity (and to a lesser degree molar mass). This is because temperature is a measure of translation energy only. Chain molecules have the ability to absorb energy in the rotational and vibration modes, which is not reflected by an increase in the substance's temperature. A rule of thumb might be that the more complex the molecule the higher the molar heat capacity and the more likely the saturated vapor line will bend so that its slope will become negative at the lower pressures and positive at the higher pressures. Figure 2 illustrates the saturation domes of HFCs of increasing molecular chain length. For refrigerants with three or more in a carbon chain (e.g., HFC-236fa), the isentropic vapor compression process starting from the saturation vapor line at a low pressure, rising vertically, can enter the two-phase region. This 'wet compression' process over an extended period of time is unacceptable for most compressors; thus, all such fluids are considered doubtful as potential alternative refrigerants. One might be tempted to suggest that the re-entry into the two-phase region could be avoided with a sufficient amount of superheat

prior to the compressor suction point. Indeed, limited superheat is always advisable so as not to 'slug' the compressor with liquid. However, for all fluids, superheat is detrimental to the system COP. This is because the slope of the isentropes on the ln P-h diagram decreases as they get further from the saturation line. This may be reasoned mathematically by comparing the combination of the 1st and 2nd laws to the expansion of enthalpy as a function of entropy and pressure, and for simplicity, consider the ideal gas equation of state to obtain

$$\left(\frac{\partial P}{\partial h}\right)_s = \frac{1}{v} = \frac{P}{RT}$$

Thus as the superheat temperature increases the isentrope slope decreases and the work (dh) increases for a fixed difference between the saturation pressures of the evaporator and condenser. In other words, it takes more work to compress a hot gas than a cool gas over the same pressure lift. In addition, the suction gas density (and thus the volumetric capacity) decreases. Fundamentally, superheat is so detrimental to performance that it is doubtful that any potential working fluid is likely to have other properties that offset this degradation. Therefore, it is safe to say that any halogen or hydrocarbon of carbon chains longer than three or four is unlikely to have acceptable performance, particularly in these energy and environmental conscious days. Bivens and Minor conducted a rather extensive study of halogenated ethers and failed to show any likely prospects for refrigerants with NBP < 0 °C (Bivens *et al.*, 1998).

Higher molar heat capacity fluids have another problem, on the saturated liquid side. Here decreased slope implies an increase in expansion losses. Another explanation is that the increased liquid molar heat capacity requires more latent heat, via more flash gas, to bring the condenser liquid down to the evaporator temperature. Figure 1 illustrates the area that represents the potential work that could be recovered by an isentropic expansion turbine being placed between the condenser and evaporator in lieu of the usual constant enthalpy expansion device. This old idea has recently been developed by at least one manufacturer (apparently overcoming the practical difficulties of two phase turbine) in order to make the HFC-134a centrifugal water chiller more energy competitive with the HCFC-123 chiller. The HCFC-123 chiller has a theoretical COP advantage of 12.8 to 12.2 largely because of its higher critical point. However, the potential increase in COP, using a perfect expansion turbine, is another 11.7 %, or for the ideal cycle a COP of 13.7 for the HFC-134a chiller. In practice however, the HCFC-123 top-of-the-line chiller has been redesigned to optimize the machinery components and system. The current result is that the HCFC-123, two stage, economizer cycle chiller has a COP rating of 7.33 while the HFC-134a, expansion turbine model has a COP of 6.76. Given the same effort

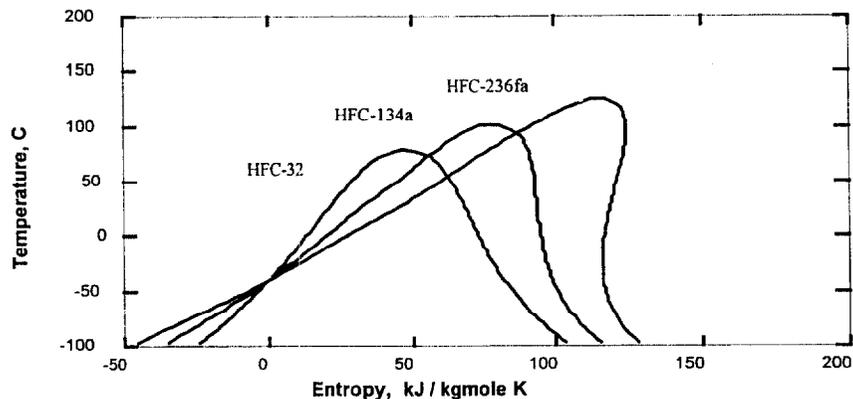


Figure 2. Saturation Domes of HFCs with increasing Molecular Complexity

(cost) put forth for both systems there is no reason to think that the HFC-134a chiller can ever equal the efficiency of the HCFC-123 chiller, because of the latter's higher critical point.

Figure 3 illustrates the vapor pressure curves of HFC-134a which is an alternative for CFCs 500 and 12 and a competitor of HCFC-123, which is the alternative for CFC-11. For each curve the uppermost point is the approximate CP and the point at which the curve (straight line) crosses the atmospheric pressure line is the approximate normal boiling point (NBP). For reasons illustrated in Figure 1 there is an inherent tradeoff between capacity and COP when selecting a refrigerant for a given application. Therefore, comparing HFC-134a to HCFC-123 results in a poorer COP. Comparing it to HCFC-22 (i.e., using a HFC-134a system for HCFC-22 applications) will result in a lower volumetric capacity (i.e., the need for larger equipment) but higher efficiency. In practice, at least one major manufacturer offered a HFC-134a air conditioner among its residential and light commercial product lines for the purposes of quick response to the ozone problem; however now that HFC-410A has been developed, these products have been discontinued.

The vapor pressure line similarity of each CFC to its alternative HFC suggests similar sized equipment is appropriate. One manufacturer's dimensional analysis indicated that a conversion of either of their CFC-500 or CFC-12 flooded evaporator, centrifugal machines to HFC-134a would result in the same efficiency and 90% capacity with no hardware changes at all. (Note the relative position of their respective vapor pressure curves with the lower pressure, and thus lower density, for the HFC indicating a lower mass flow for the same volumetric displacement rate.) Since the CFC-12 machine would require a gear change to achieve the higher isentropic lift of the HFC-134a, a smaller impeller wheel would be necessary to sustain the same capacity. (Note the steeper slope of the HFC-134a vapor pressure line relative to CFC-12 implies more work.) Otherwise a 17% capacity increase would result (Johnson *et al.*,1993). From a thermophysical properties viewpoint, it has been quite possible to convert many existing machines from CFCs to HFCs in a cost effective way.

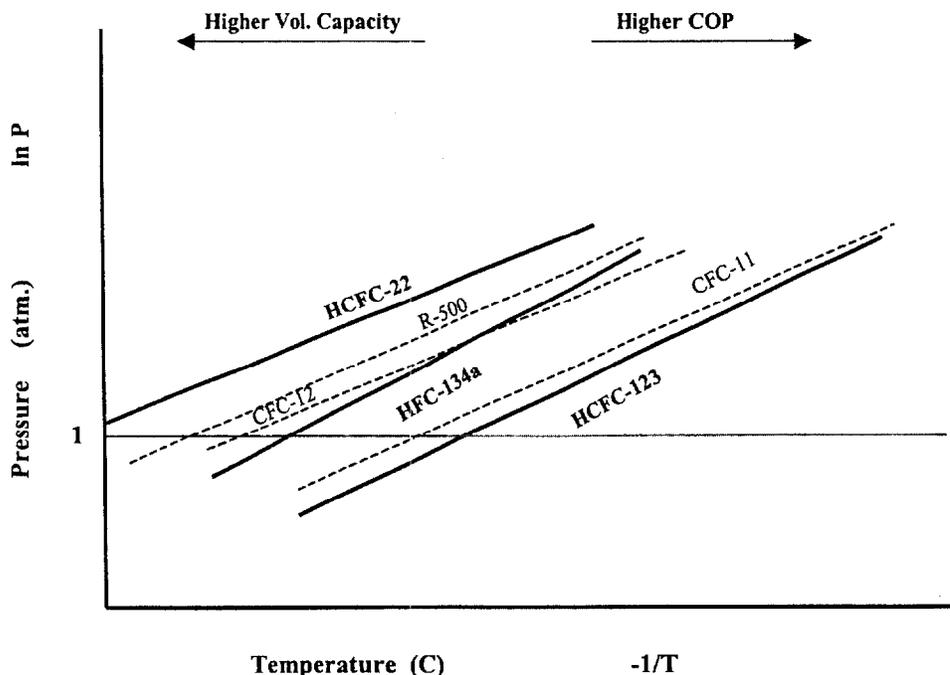


Figure 3. Vapor Pressure of HFC-134a and Similar Refrigerants

Obviously the most successful, and long lasting, applications for HFC-134a are the previous CFC-12 applications. In many systems the vapor pressures are close enough that a drop-in conversion (except for the lubricant change) is possible. New systems will have a similar size and efficiency. However, since the crossover point of the vapor pressure lines is at 16.6 °C, the evaporator will be at a lower pressure and the condenser at a higher pressure with the HFC-134a. Those systems that were traditionally CFC-12, notably automotive air conditioning, domestic refrigerators, middle-temperature commercial refrigeration, vending machines, transport refrigeration, which have been redesigned for HFC-134a, will probably remain such. Also some of the larger CFC-12 equipment have been retrofitted for HFC-134a. These include both centrifugal and screw compressor water chillers. All the major chiller manufacturers have a new HFC-134a screw compressor product line which will undoubtedly grow because of the popularity of the compressor. Some of the centrifugal manufacturers have abandoned the lower pressure HCFC-123 compressor in favor of the HFC-134a compressor as their primary high capacity machine.

3. ZEOTROPIC REFRIGERANT MIXTURES

No acceptable single component alternative refrigerant has been discovered for HCFC-22. As a result, the industry has searched for and developed several mixtures from which two types of zeotropes have emerged; one with a vapor pressure similar to HCFC-22 and one of considerably higher vapor pressure. The similar vapor pressure mixture is the ternary zeotrope, R-407C whose composition is HFC-32/125/134a (23/25/52 % mass). It is intended to be used as a 'drop-in' for existing HCFC-22 equipment or for new equipment where it may be competitive. An alternative of the other category is a binary near-azeotrope, R-410A, which is a composite of R-32/125 (50/50 % mass). Thermodynamically speaking, all are zeotropes, (a.k.a., non-azeotropes) but the binary has a rather small maximum difference between the dew-point temperature and the bubble-point temperature and is thus distinguished by the jargon word 'near-azeotrope' because it has some of the practical qualities of an azeotrope. This temperature difference is called the temperature glide and is used to characterize the degree of temperature change a particular mixture has during a liquid / vapor phase change. Zeotropic mixtures' tendency to shift composition during the phase change process may be illustrated best on a composition phase diagram. Figure 4 is a phase diagram of a binary zeotrope of R-32/134a (30/70 % by mass) which has been considered as an alternative to HCFC-22. The maximum temperature glide for the evaporation process is 7 °C. (It should be noted that where the evaporation process is preceded by a flashing process the glide within the evaporator will be less than 7 °C.) The maximum amount of the flammable HFC-32 that exists during operation occurs in the evaporator. The liquid charge initially has 30% and as the evaporation process proceeds this quantity decreases to 15%. The HFC-32 vapor composition is initially 57% at the bubble point and decreases to 30% HFC-32 when the evaporation process is completed. At the condenser condition all the variations are similar but to a lesser degree. The temperature glide is 5 °C, and the liquid and vapor HFC-32 compositions shift from 30% to 21% and 41% to 30%, respectively. A leak during a two-phase condition would permanently change the operating composition and thus the performance of the system. The composition shift characteristic of zeotropes also causes difficulties in applications where a large portion of the working fluid remains in the liquid state during operation. That is, if only a minor part of the total charge is circulating throughout the vapor compression system at any given time it is difficult to know what the circulating fluid's composition is and thus difficult to size or rate the hardware components. This difficulty is exacerbated when such a system is expected to meet a varying load and the liquid pool becomes a variable during operation. For this reason, only zeotropic mixtures whose components have similar NBPs (i.e., near-azeotropes) are being considered for flooded evaporator systems, such as water chillers.

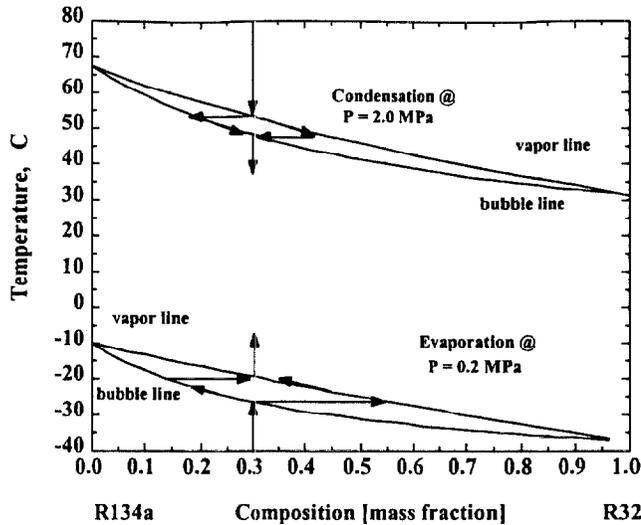


Figure 4. Phase Diagram of a Zeotropic Mixture

A 'drop-in' alternative for HCFC-22 can be achieved then by straddling the desired vapor pressure curve with at least one alternative above and one below. The first example is the binary R-32 /134a (30/70% by mass) which is illustrated in Figures 4 and 5. However, the 57 % proportion of HFC-32 that this binary mixture's vapor can achieve (e.g., during a leak), at very low evaporator quality, is considered flammable according to the ASHRAE test procedure. As seen in Figure 5 a ternary was created by adding the non-flammable HFC-125, to create R-407C. This resulted in some sacrifice in performance because the CP was lowered and, in the heat transfer process, the mass diffusion dependency among components was increased. However, since the resultant zeotropic vapor pressures are similar to that of HCFC-22, these alternatives constitute a reasonable drop-in for HCFC-22 systems. This near drop-in status of R-407C made it the likely alternative for meeting the time schedule for eliminating HCFCs in several European countries. Because most equipment manufacturers have, as one of their important criteria, to "meet the required performance rating with minimum manufacturing cost", it is not clear if this current popularity for R-407C will remain. However, for applications where the condenser temperature is above 40 °C (e.g., light commercial rooftop units) the future would appear stable, largely because of lack of competition. It is expected that the R-407C will require the same number of heat exchanger circuits as HCFC-22 however, the zeotropic temperature glide is significant enough that, when possible, the designer should consider a cross-counter flow configuration so as to minimize heat exchanger ineffectiveness. Compressor tests are generally touted to show a 5 % decrease in performance from that of HCFC-22 which it is replacing. Proprietary laboratory tests of residential sized air conditioners show R-407C/HCFC-22 ratio values of 95 to 102 % for capacity and 94 to 101 % for COP.

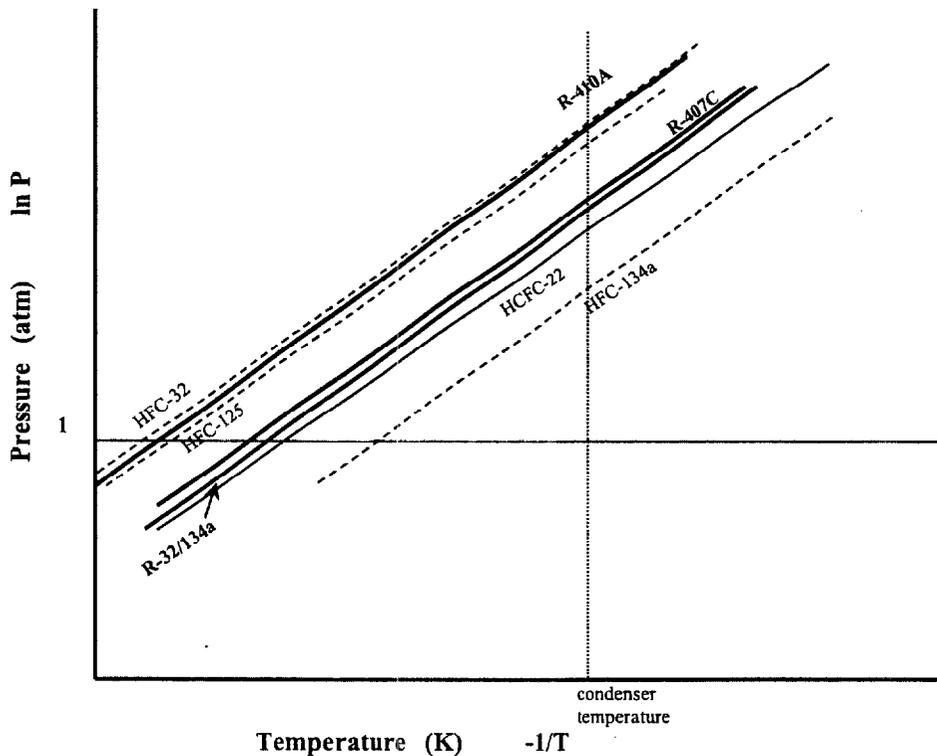


Figure 5. HCFC-22 Alternatives and Their Components

The primary alternative for new systems of HCFC-22 applications up to 35 kW capacity is R-410A. Its component's NBPs are only 3.6 °C apart, which means the mixture is a near-azeotrope and acts similar to a single component refrigerant. As can be seen from Figure 5, it is at a significantly higher vapor pressure than HCFC-22 and lies between the vapor pressures of its components, as all zeotropes do. R-410A's high pressure makes it unsuitable for a 'drop-in' for an existing HCFC-22 system. But the fact that the R-410A system will be considerably smaller and probably will have a decrease in material costs needed for manufacture will make it the system of choice for new residential sized air conditioners and heat pumps. It is these products which, in the USA at least, must meet minimum performance standards and are subjected to mandatory test and rating procedures. Coupling this with the typical manufacturer's philosophy of 'designing to meet the performance requirements with minimum manufacturing costs' makes the R-410A system the obvious choice. Early designs have shown that it should be possible to decrease the evaporator heat exchanger tubing from 3/8" diameter to 5/16" for the same number of circuits as HCFC-22 system. If it is decided to keep the same tube size then as much as 40% less tubes would be needed. What is important is to maintain the same refrigerant velocity (Reynolds Number) so as not to diminish the heat transfer coefficient.

Figure 6 shows the measured flow heat transfer coefficient values of the pertinent HFCs and their mixtures for the conditions found in a typical evaporator (Kaul *et al.*, 1996). The relative values of the single component fluids follow their thermal transport property predictions rather well. The fluids with higher thermal conductivity and lower viscosity have the higher heat transfer coefficient. The mixture R-410A (titled by its components R32/125) values fall between its component values because it actually forms an azeotrope at higher compositions of HFC-32. Thus no significant zeotropic molecular diffusion phenomena is exhibited by R-410A, as it is by the other two mixtures which have a wider temperature glide (Didion, 1999). It can be noted

then that the substitution of R-410A for HCFC-22 will result in an improvement of heat exchanger performance, whereas with the substitution of R-407C the opposite can be expected. Of course heat exchanger design must also include pressure drop considerations. Here again R-410A exhibits superior thermodynamic performance potential in that refrigerants of higher vapor pressure have a smaller dew point temperature change due to pressure drop (Kim *et al.*, 1997) Thus, it is the excellent thermophysical properties of HFC-32 that makes R-410A a competitive refrigerant.

The higher density R-410A offers the designer a choice relative to the HCFC-22 systems. Using a compressor of the same volumetric rate (i.e., size) offers less mechanical irreversibilities, such as pipe friction and valve pressure drops, for the same capacity. Using a

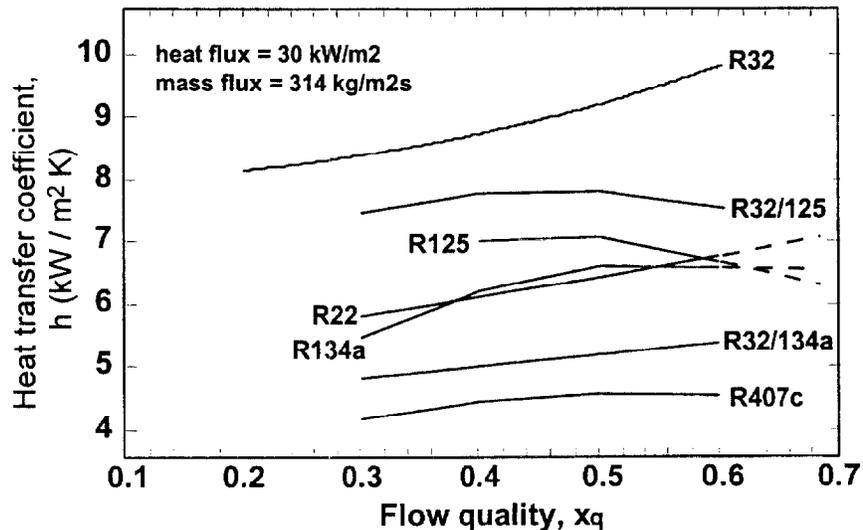


Figure 6. Internal Evaporative Flow Heat Transfer Coefficients

smaller compressor will increase the irreversibilities but provides the potential for lower cost unit of the same quality. A series of proprietary tests were run with R-410A in a HCFC-22 sized compressor and in one 'optimized' for its own density to determine the respective irreversibilities. This data was then applied to an isentropic compression process of ideal cycles operating under air conditioning conditions. The COP of the R-410A in a system with a compressor optimized for R-410A was 2.9 as compared to a 3.3 for a system designed for and using HCFC-22. In other words the R-410A had a performance detriment of 12%. Comparing the performance of R-410A to HCFC-22, where both were operated with the compressor of the HCFC-22 system, a detriment of only 6% occurred. However R-410A tests in a system totally designed for this fluid shows near equal to the performance of the HCFC-22 system it is replacing. These simple comparisons suggest then, that, what is lost in the R-410A system compressor is regained in the heat exchangers and that there is potential improvement available through the use of larger compressors. Indeed, at least one manufacturer is currently marketing a R-410A residential air conditioner line with a COP > 4.0. Such performance would certainly include several improved hardware components (e.g., higher performance compressors and micro-finned heat exchanger tubes) that might not have been used in the HCFC-22 systems it is replacing. It is these hardware improvements that are being incorporated during the refrigerant conversion period that are, and will be, the source of performance increases rather than the working fluid itself. And, as always, the amount of hardware improvements will depend upon cost and/or government regulation.

Over the past few decades CFC-12 systems were often replaced by HCFC-22 systems for applications where equipment size (i.e., footprint) or cost was important. It stands to reason that the even smaller R-410A system should thrive in such an application area, as well.

4. AZEOTROPIC REFRIGERANT MIXTURES

The use of more than one working fluid in a refrigerant system usually increases both the complexity and the flexibility of its design and operation. The increase in flexibility comes in the form of more fluids to choose from, which can result in a closer match of the optimum working fluid to the application. The complexity is the introduction of another independent variable, composition, which has both theoretical and practical ramifications as discussed in the previous section. Some refrigerant mixtures have been in use by the Industry for several decades. However, the ones that have been in use have been restricted to a rather rare category called azeotropes. The unique property azeotropes have is that, over a locus of specific temperature and pressure values, the mixture's vapor and liquid compositions are exactly the same and at these points the temperature and pressure are either a maximum or a minimum of all possible compositions. A maximum pressure (thus a minimum temperature) azeotrope is illustrated in Figures 7a and 7b. It can be seen that an azeotropic saturation condition exists only at a single composition. However, there is also a wide band of very minimal composition differences between vapor and liquid. For all practical purposes, the typical azeotrope acts as a single component refrigerant throughout the various pressure and temperatures of a refrigeration system. As such, azeotropes offer additional opportunity to better match working fluids to a given application without additional complications. They are the preferred form of mixed working fluids but are relatively rare.

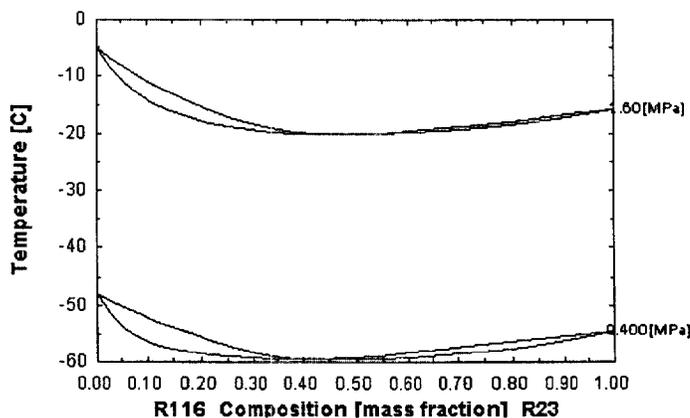


Figure 7a. Temperature – Composition Phase Diagram for R-508A

Two new azeotropes based on HFCs have been found: R-507, which is comprised of HFC-125/143a (50/50% by mass), and R-508A, which is HFC-23/116 (39/61 % mass). The R-508A azeotrope is the usual positive pressure type which means its vapor pressure is higher than either of its components. As can be seen in Figures 7a and 7b the azeotropic region is sufficiently wide that a second azeotropic mixture has been patented and dubbed R-508B with a composition of HFC-23/116 (46/54 % mass). The R-508s have a vapor pressure similar to that of CFC-503, which they are intended to replace. Also with their pseudo-critical points of the order of 11°C their application is usually limited to a low temperature loop of a cascade refrigeration system.

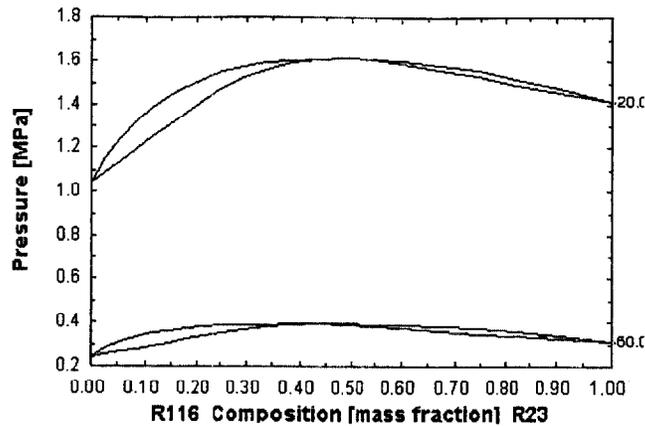


Figure 7b. Pressure -- Composition Diagram for R-508A

R-507 is a substitute for CFC-502. Figure 8 illustrates the vapor pressure lines for this mixture and its components, as well as the azeotrope it is replacing. Careful examination reveals that this new azeotrope is a very rare negative pressure mixture. This was fortunate in that this unusual property lowers the azeotrope's vapor pressure closer to that of R-502 than either of the components. Typically azeotropes do not exist over all possible temperature and pressure ranges. In the case of the R-507 the azeotrope 'drift' causes it to go out of existence at a lower saturation temperature than most refrigeration applications. However, this is of little practical consequence since the components, HFC-125 and HFC-143a, have NBPs that are only 1°C apart. Thus any composition change due to liquid pooling within the system or leaks will be so minimal that performance changes would not occur.

However, R-507 is very close to being flammable because HFC-143a is flammable. For this reason, one refrigerant manufacturer has added 4% HFC-134a to this mixture, trapping the flammable fluid between the two non-flammable ones and ensuring safety under most any condition. This very near-azeotropic ternary is known as R-404A. Although the third component has a significantly different NBP, its small quantity only creates a difference in dew and bubble point temperatures of 0.8 °C. This suggests that only very little composition shift is possible. HFC-143a and HFC-125 have relatively high global warming potentials, so both the azeotropic binary and the near-azeotropic ternary must be used in equipment with careful attention to refrigerant containment.

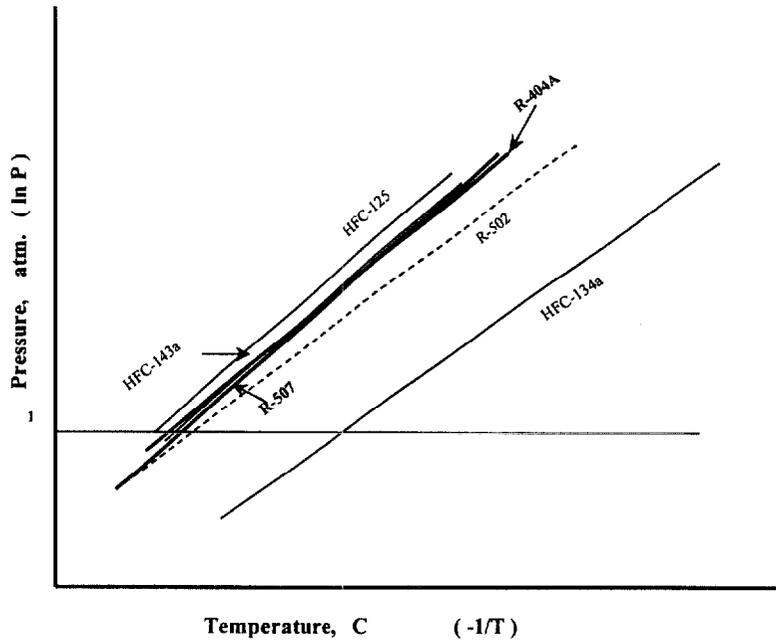


Figure 8. R-502 and Its HFC Alternatives and their Components

5. SAFETY

In 1930 Thomas Midgley stood on the stage of the American Chemical Society and introduced the first halogen as a refrigerant by inhaling a lung full of what we now call CFC-12 vapor and blowing out a candle. From that point on, the refrigeration industry had a solution to the problem of unsafe working fluids. In order to ensure that status continued, the American Society of Heating, Refrigerating and Air Conditioning Engineers (ASHRAE) assumed the responsibility for assigning identification numbers to any new refrigerant only after sufficient test data has been presented to their Standing Standard Project Committee 34 (SSPC 34). Whereupon the committee assigns the proper flammability and toxicity ratings (ANSI/ASHRAE, 1997). Table 1 illustrates the ASHRAE group classifications for safety. See Appendix B for a listing of the more popular HFC refrigerants' ratings. A double rating for a mixture refers to 'as-formulated/worst-case'. The latter being the rating of a resulting composition, during a fractionation process, that would be the most flammable or most toxic. Virtually all of the CFCs were in the category A1, which means they are nonflammable and nontoxic. To date, the conversion to HFCs has been to only fluids in this A1 category. Although flammable HFCs (i.e., 32, 143a and 152a) are currently in production, they are only shipped and used in a mixture that is nonflammable.

Safety ratings for refrigerants are, at the same time, both vague and rigorous. There exists well defined laboratory test apparatuses and procedures, but whether these conditions represent the field operations is an eternally debatable question. This is particularly true when one considers that the most likely time of human exposure to the refrigerant is during installation or repair. Thus it is necessary to consider safety relative to application. For this purpose ASHRAE has a Standing Committee 15 which provides guidelines, for the different refrigerants, about refrigeration system and the space that it occupies (ANSI/ASHRAE, 1994). The work between the two committees is closely coordinated.

Table 1. ASHRAE Std. 34-1997 Safety Group Classification

	no identified toxicity at concentrations ≤ 400 ppm	evidence of toxicity below 400 ppm	
Higher Flammability	A3 (C ₃ H ₈)	B3	LFL ≤ 0.10 kg/m ³ $\Delta H_{\text{comb}} \geq 19$ MJ/kg
Lower Flammability	A2 (HFC-32)	B2 (NH ₃)	LFL ≤ 0.10 kg/m ³ $\Delta H_{\text{comb}} < 19$ MJ/kg
No Flame Propagation	A1 (HFC-134a)	B1 (HCFC-123)	
	Lower Toxicity	Higher Toxicity	

5.1 Toxicity

Two types of toxicity are considered: acute and chronic. The first is defined as the adverse health effect from a single short-term exposure as might occur during an accidental release of refrigerants. Chronic is defined as an adverse health effect from long-term, repeated exposures, which require various intensity and time definitions. Refrigerants are divided into toxicity groups of two levels - A and B, which are called lower and higher levels of toxicity. These are meant to represent no toxicity evidence or some toxicity evidence, respectively, for a Threshold Limit Value - Time Weighted Average (TLV-TWA) of 400 ppm of refrigerant in air. This sort of definition, albeit inclusive of a rigorously defined test procedure, alludes to the recognition that all substances can be toxic, depending on the quantity and conditions. The toxicity determination of the HFCs, et.al., listed in Appendix B, was largely the responsibility of the Programme for Alternative Fluorocarbon Toxicity Testing (PAFTT) which was sponsored by the major producers of refrigerants from nine countries. Each alternative was subjected to over one hundred individual toxicity tests over a two year period at a cost of three to five million US dollars. The net result is that more is known about the HFCs than was ever known about the CFCs. A long time member of this ASHRAE sub-committee, James Calm, summed up this work in one sentence (Calm, 1994):

“Based on current toxicity findings, HFC-134a is regarded as one of the safest refrigerants yet introduced.”

However, this statement alone was not intended to be taken out of context and applied equally to all field installations. For example, consider an unintended leak of HFC-134a, with its rating of A1, relative to the less safe HCFC-123, with its A2 rating. The more volatile HFC-134a (NBP = -26.1°C) might exceed its 1000 ppm allowance before the HCFC-123 (NBP = 27.8°C) meets its 50ppm limit in a 25°C room. On the other hand, the existence of a warm surface in the proximity of the leaking refrigerant may well bring about the opposite effect. To put these scenarios in perspective, a properly maintained mechanical room is likely to have a ventilation rate such that either refrigerant is < 1 ppm. All of this is to say that the degree of ‘unsafe’ is largely a matter of hardware design, installation, maintenance procedure and limitation on amount of refrigerant at a given site.

5.2 Flammability

The flammability groups are divided into three classes: 1, 2 and 3, which mean no, lower and higher flammability, respectively. These classes are based on the ASTM E681-85 test procedure which the ASHRAE SSPC34 has modified with several specifications in an attempt to make a more distinct identification of flame propagation. Since the goal is to identify the lower flammable limit (LFL) of a vapor that is usually only slightly flammable, this is necessarily a difficult process requiring numerous laboratory tests by experienced personnel. Following the tradition of the industry since the 1930s, all of the HFCs in use as single component refrigerants are simply not flammable under near atmospheric conditions (class 1).

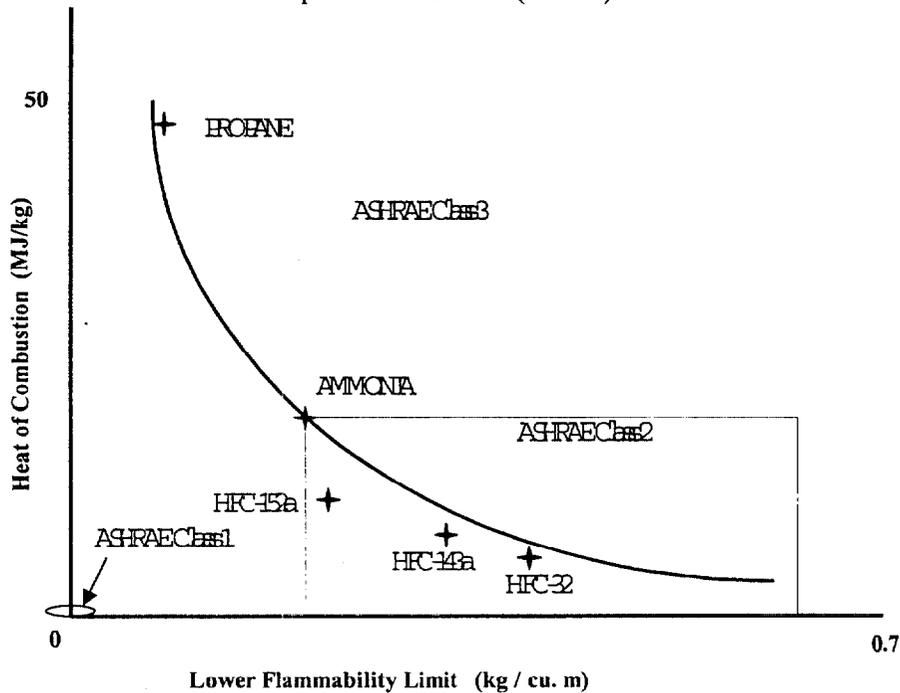


Figure 9. Flammability Trends in Refrigerants

Classes 2 and 3 are distinguished by assigned numerical values of lower flammability limit and heat of combustion (HoC), which might be thought of as ease of ignition and thermal energy created upon ignition, respectively. Figure 9 is a generic representation of how fluids, of all types (e.g., hydrocarbons, halogens, ethers, ketones, nitrogen and sulfur compounds, etc.), would plot on such a coordinate system (McLinden, 1994). Virtually all flammable halogens fall into class 2 and hydrocarbons into class 3. It is important that a significant gap exists between Classes 2 and 3 so that the levels of these two flammable refrigerant classes are quite distinguishable. As a general rule halogens whose molecule has a fluorine to hydrogen atom ratio of 1.7 or less is flammable under ASHRAE test conditions and all hydrocarbons are flammable. Dealing with a flammable halogen is quite different from dealing with a hydrocarbon. However, this significance may be more important for the manufacturer who has to deal with the fluids, in thousands of kilograms size, at the factory. If the individual product goal is to have no increased risk at the installation site, then the protection required for any flammable refrigerant may be the same. Studies have predicted that a typical USA residential central air conditioner (~ 10 kW/ 3 kg charge) with a class 3 refrigerant would increase the product cost by at least 30 % for it to attain Underwriters Laboratory (UL) safety approval.

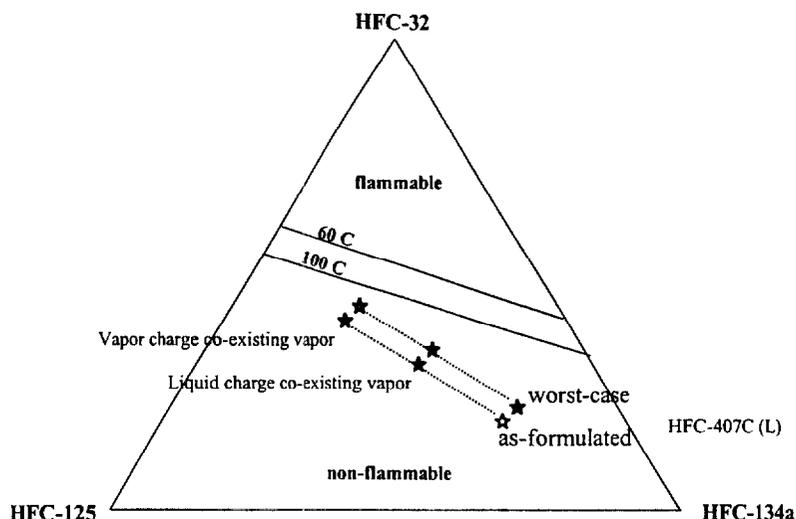


Figure 10. Flammability Regimes of HFC-32/125/134a

The evolution of mixtures flammability is more complex. Mixtures evolved from the desire to maximize thermodynamic performance so some flammable components were used, but only to the degree that the mixture itself was still nonflammable. Determining the flammability of a zeotropic mixture first requires the determination of the entire flammability zone of all possible compositions of the mixture. Figure 10 outlines the flammability zones of the possible mixture compositions, of HFCs 32/125/134a, for two refrigerant temperature conditions. The 100°C criteria is required for the as-formulated liquid state, and the 60°C criteria is for the worst-case liquid and all vapor states. The R-407C liquid composition, as formulated, is shown to be well within the nonflammable zone, as is its coexisting vapor state. A worst-case composition shifting criteria have been established for the possible field conditions that include scenarios of partial refrigerant leaks from a system that is then recharge with an as-formulated composition. (To this end NIST has developed a LEAK/RECHARGE computer simulation program to assist in the prediction of these worst-case scenarios.) (Didion *et al.*, 1999) However, for any of the compositions of the 32/125/134a ternary the worst case will be the coexisting vapor of the as-formulated liquid mixture because the only flammable fluid, HFC-32, is the most volatile one of the three. A further, non-regulatory but possible, analysis is shown in Figure 10 for both as-formulated and worse-case conditions. It is what could happen if the field charging was mistakenly taken from the vapor level of the refrigerant container. The container's vapor composition would become the system's liquid composition and an additional stage of fractionation would result in the system's coexisting vapor composition, as shown. For R-407C, as-formulated case, is well within the nonflammable zone, as is the worst-case flammability composition of R-407C is 25/23/35 % mass, which allows for a manufacturing tolerance of +2% with the flammable component. Superimposing a fallacious vapor charging would still result in a nonflammable composition. Thus, it can be seen that it is not just the initial composition of a zeotropic that must be safe but rather the addition of any number of possible production and field mishaps that might cause a different composition to exist.

To reiterate, while safety testing can be rigorously defined and carried out by different laboratories to everyone's satisfaction; the question of the defined laboratory specifications simulating any or all field possibilities is eternally debatable. For example, it should be noted that the lubricant is not included in the laboratory tests but it is an integral part of the working fluid in some part of any field system. The best that can be done is that independent, objective committees develop and apply reasonable criteria to monitor the growing body of field

experience. However in the case of zeotropic mixtures where field experience is limited, manufacturers are cautious to risk the complexities of field operations since most of these HFC mixtures contain at least one flammable component. And while there are many positive performance attributes, not discussed in this paper, this is one of the negative attributes opposing the long-term use of wide-glide zeotropes. The field experience being gained through the use of R-407C, however, may eventually mitigate this caution.

6. LUBRICANTS

The single most important reason refrigeration systems have a typical operation life of more than twenty years is due to compressor lubrication. A lubricant must be stable, provide increased lubricity between the machine's moving parts, and be soluble in the refrigerant. Other qualities are desirable for particular compressors but these three are fundamental to all machines. With the elimination of chlorine in refrigerants, two of these three were diminished, causing the compressor manufacturers to view the conversion of CFCs to HFCs as a lubricant crisis more than a refrigerant one. Only stability benefited. Chlorine was the solubility link between the refrigerant and the mineral oil and it reacted with the iron in the solid surfaces to increase the overall lubricity between the moving parts. The lack of solubility issue forced the industry to seek a new family of lubricants for the majority of HFC systems. However, some small compact systems, such as packaged air conditioners, vending machines, and home refrigerators, where the lubricant will return to the compressor in spite of poor solubility, have continued to use alkylbenzene lubricants.

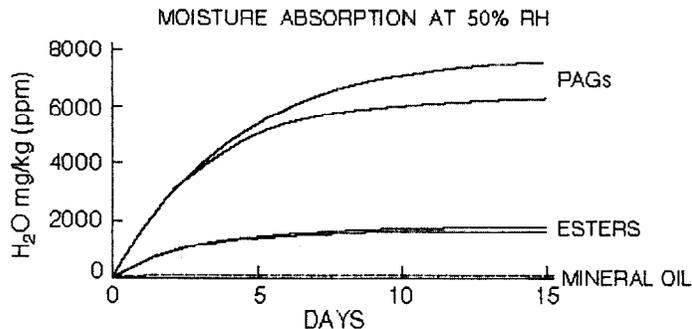
The first lubricant family to emerge, for use with HFCs, was the polyalkylene glycols (PAGs). The automotive industry quickly adopted these for their vehicular air conditioning systems. They now have a variety of specific products that have been working in the marketplace for as long as five years. Even conversion of old CFC/mineral oil systems to HFC/PAG systems are now routine.

The stationary systems industry, with its demands of longer system life (i.e., more hours of operation) and wider temperature range, found the PAGs less than satisfactory for many of its lower temperature applications. Of particular concern was that the water absorption rate was considerably higher and the hydrolytic stability lower. Figure 11 illustrates the general trends of water absorption rates for the PAGs relative to that of mineral oils. Also included in Figure 11 are the rates of polyolester lubricants (POEs) which the industry has now adopted for most of its applications. The two curves for each lubricant refers to 'dry' and 'wet' initial conditions. Dry means the lubricant was subjected to good manufacturing, storage and handling practices prior to test. Wet is the condition that resulted from poor practices where the lubricant was overexposed to the atmosphere. A POE or PAG with a water content of > 500 to 1000 ppm is likely to fail in the machine. The fact that the POE's water absorption rate is still higher than the mineral oil/CFC level suggests the need to obtain advice about the filter/ dryer system to match the specific HFC/POE being used. In spite of the increased stability of the HFC/POE mixture, free water in the system has the long range potential to breakdown the POEs into acids and alcohols. The time scale in Figure 11 is a matter of days, so care must be taken in the storage and transfer stages so as not to expose a POE to air more than necessary.

CFC-12 MINERAL OIL
10-20 PPM (Nominal)

HFC-134a/ESTER
PPM (Nominal)
50-100 "Dry"
100-300 "Wet"

HFC-134a/PAG
PPM (Nominal)
50-200 "Dry"
200-1200 "Wet"



Courtesy of Dr. Hans Spauschus
Spauschus Associates

Figure 11. Moisture Absorption by Lubricants

Lubricants have always been somewhat enigmatic to machine owners and operators due to the numerous additives that are required to enhance or minimize lubricant side effects. POEs are no exception. Manufacturers rely on the lubricant/refrigerant mixture to perform a variety of ways for different compressors. Reciprocating compressors rely on foaming for a quieting effect and splashing for cylinder wall lubrication, screws need rotor to wall sealing, all compressors rely on the lubricant to have the strength to withstand thrust or journal bearing pressures and the loss of the chlorine-iron lubrication effect should be replaced. This last item is perhaps the most serious in that now there has been time for some extensive wear tests. It appears that the HFC/POE mixture does not provide the same wear protection that the CFC/mineral oil mixture did. The foaming/ noise issue, which is particularly sensitive for residential systems, is somewhat mitigated by the fact that the inherently quieter scroll is rapidly replacing the reciprocating compressor. However, for some reciprocating compressors, the lack of lubrication due to foaming has required a redesign in the hardware. For this reason the low temperature systems have been moving more cautiously towards the HFC/POE systems. In general if a lubricant has sufficient viscosity to withstand the bearing pressures, it will be sufficient to perform any sealing effect required. As always, dilution of the lubricant's viscosity by the refrigerant in critical bearing areas is of prime concern. The HFC/POE mixture appears to be performing as well as the CFC/mineral oil mixture in this area. However, designers of systems with lubricant separators have discovered that it is somewhat more difficult to separate the POE from the HFC. In some systems, the effect the lubricant has on the heat transfer in the heat exchangers may be so important that additives are used to minimize any degradation. This issue will continue to grow in importance as the use of micro-enhanced surfaces grows. All of this is to say that it is imperative to use exactly the lubricant the manufacturers recommend, as well as, the associated filters and procedures.

Conversion of CFC/mineral oil systems to HFC/POEs is being done routinely. Various organizations have recommended procedures for the different systems. The important issue is to rid as much of the old oil from the system as possible. Usually two or three flushings are required to attain something of the order of 95 to 99 % of the original oil charge. Interestingly PAGs are sometimes used for the flushing purposes because of their solvent-like properties.

POEs solubility has been reasonably satisfactory if not uneven. It appears that the refrigerants with a high dipole moment, such as HFC-143a, have poor solubility with POEs; whereas small dipole moment refrigerants, such as HFC-125, have good solubility. Another interesting property of the POE is that it is a better solvent than the refrigerant. As a result some care has to be taken in selecting materials and fluids used within the system and during the manufacturing process, so as not to have wax-like substances form from chemical interactions with the refrigerant/lubricant mixture. In addition, now that there has been time to conduct long term wear tests, some concern has been reported that the HFCs/POEs might not provide protection for as many years as the CFCs/mineral oils did. To this end, lubricant research has continued in the direction of more highly stabilized POE lubricants. A new lubricant family of PolyVinylEthers is under serious consideration because of its superior lubricity characteristics. So it would seem that the lubricant issue is not completely settled.

7. FUTURE DEVELOPMENTS

It is not possible to say, with any certainty, what changes will come about in the future. This is largely because of the strong political influence that has resulted from predicted environmental problems. If environmental regulations remain the same, there will be a methodical improvement in the average performance of refrigeration systems as the industry gains experience with HFCs and incorporates new hardware improvements. If the global warming issue becomes a political reality, worldwide, it will be very important that we not repeat some of the mistakes of the ozone crisis. The use of a prescriptive measure, the regulation to ban all chlorine-containing refrigerants from production, led to the future elimination of the most efficient refrigerant we currently know, HCFC-123 (Calm *et al.*, 1998). Whereas if efficiency would have been considered as an environmental factor, as it surely must be for global warming, HCFC-123 would have proven to be the most overall environmentally friendly working fluid there is for centrifugal compressor systems.

For efficiency sake, it is reasonable to say that the predominance of refrigeration systems will remain based on the vapor compression cycle and operate with its condenser as close to the environmental temperature as economically feasible. Also, no one refrigerant or system will be optimum for all applications. This suggests that any prospective refrigerant may have its performance estimated by its critical point (CP) and molar heat capacity. The effect of both critical point and liquid molar heat capacity on ideal cycle performance may be seen in Figure 12. The data of eighteen, arbitrarily selected, different fluids from REFPROP 6.0 (McLinden *et al.*, 1998) was correlated for two sets of reduced temperatures of the ideal vapor compression cycle. It is assumed that the efficiency of a refrigerant may be indicated by how much of the mass flow rate is utilized to transport the heat (i.e., the ratio of the refrigerating effect to the latent heat). The analysis shows that the lower critical point or higher molar liquid heat capacity fluids will be poorer performers. Since for all fluids, the molar heat capacity is inherently tied to molecule complexity primarily, and weight secondarily, the number of future alternatives is severely limited. That is only simple or light weight molecules make reasonable refrigerants. This rather stringent criteria does include a few hydrocarbons. However, in the 1920s, when Thomas Midgley first was given the charge of finding a new family of refrigerants, he was told that if refrigeration is going to ever 'go anywhere' it would be necessary to have nonflammable, nontoxic refrigerants. Lest we forget the problems of the past there are thousands of USA lawyers anxious to remind us. We should at least try not to create a very local environmental problem, safety, while seeking a solution to a global environmental problem. It is possible to design safe systems for unsafe refrigerants; however, at this time, it does not appear to be cost-effective. The reason for the added cost is to make the HC system both leak-proof and

explosion-proof. Since the HFC system needs only to be leak-proof, it is and always will be more cost effective.

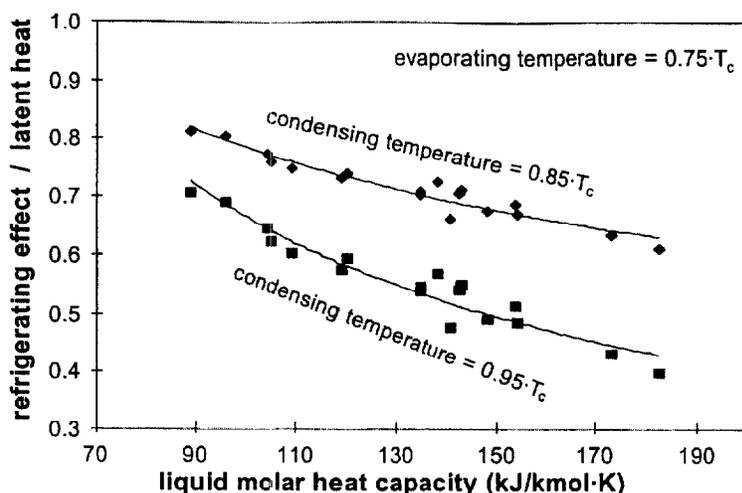


Figure 12. Refrigerant Performance versus Liquid Molar Heat Capacity

It is important to realize that the amount of atmospheric damage is a function of emission rate (Albritton, 1997). This means that a measure of global warming potential should take into account the rate at which the emission is released into the atmosphere. Stationary refrigeration and air conditioning systems are typically designed to retain the refrigerant within the system throughout its life. To encourage a continuation of improvements in the containment of this refrigerant, it is necessary to have a measure that will be able to give credit for system designs and refrigerant handling procedures that tend the emission rate towards zero.

It is not uncommon for a stationary refrigeration system to have a life of 25+ years. By any measure, the electrical power demand over this lifetime will have a significant, if not a dominant, impact on the environment. Thus is important to establish a proper measure by which this secondary environmental impact may be accounted for. The industry has been using the Total Equivalent Warming Impact (TEWI). This index is a composite of the direct environmental warming effect and the indirect warming effect. The direct effect is due to the release of the refrigerant into the atmosphere. The indirect effect is due to the warming stemming from combustion emissions to provide power to the refrigeration system. As a result of the ozone crisis, the direct impact has been continually mitigated with new machine designs that require less refrigerant charge and approach minimal leakage. Furthermore, recycled CFC cost increases and new regulations have caused considerable improvements in refrigerant handling and shipping procedures. All of which reduces the emissions of the existing refrigerants. With the stationary refrigeration systems having such a long operational period, it should not be surprising that it is the indirect warming effect that dominates. In fact, studies have shown that replacing a centrifugal water chiller, using hundreds of kilograms of CFC-11, by a double effect absorption chiller, with environmentally benign fluids, will result in more harm to the environment due to the differences in efficiency over the lifetime of the units (Fairchild *et al.*, 1991).

What is needed then, is a relative measure; one that quantifies improvement in a new design or shows that one product is better than another. A performance document criteria that gives credit for system efficiency improvements and emission reductions, coupled with minimum environmental standards, will enable the designers and manufacturers to use their ingenuity and

experience to met this challenge just as they have met all the other challenges that have given us the safe, reliable, cost effective systems we have today.

What is not needed are regulations that inadvertently dictate refrigerant or refrigeration system design, by forbidding specific products that are presumed harmful to the environment.

Finally, there is an old African adage which seems to be metaphorically appropriate:

*“ when a man sets aside his traditional ways he must
have something of value to replace them with”.*

To determine the value of what potential replacements will be, I suggest we:

1. recognize that the environmental damage is a rate problem and that it is the rate of emissions that needs to be controlled,
2. realize that the importance of refrigerant energy efficiency will severely limit the number of fluids available for candidacy and thus the danger in regulating against current HFCs without having a proven equal already in the field,
3. recognize that the global warming factor must be satisfied in light of the economic, performance, safety, and reliability factors and, in the end, only the manufacturers and system designers have the necessary experience to find the appropriate balance to optimize the next generation of products,
4. establish an environmental impact measure that includes indirect impacts associated with a system's lifetime operation such that both system emissions and efficiency are accounted for,
5. establish a performance criteria that addresses the environmental problem, not the presumed cause of the problem, so as to provide the manufacturers the freedom to use their experience to develop the best possible product.

NOMENCLATURE

P – pressure

T – temperature

v – specific volume

c_v - molar heat capacity (constant volume)

σ - along the saturation line

h – specific enthalpy

R – ideal gas constant

S - entropy

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ACKNOWLEDGEMENTS

The author wishes to thank several outstanding engineers in the refrigeration industry, with who, he had detailed technical conversations about their recent experiences with the process of converting from CFCs to HFCs. They are Kenneth Hickman and Joseph Pillis of York International; Donald Bivens of DuPont; James Calm an engineering consultant; Thomas Watson of McQuay; Paul Glamm, Dick Ernst, and Dick Cawley of Trane; and Charles Bullock of Carrier, Carl Laverrenz of Tyler Refrigeration, David Henderson of Spauschus Associates. Thanks is also extended to Jeffrey Schein of the U.S.Navy Laboratory in Annapolis, MD for his assistance in determining the ideal cycle data referred to in this paper. It should be noted that

this paper was originally written for, and published in the proceedings of the Centenary Conference of the Institute of Refrigeration, London, England, November 1999.

APPENDIX A

In order to quantitatively define the thermodynamic state, of a mixture, it is necessary to introduce an additional dimension, composition, to the pure fluids' three-dimensional (P-v-T) system. Constructing a two dimensional plane of one constant thermodynamic property then will not necessarily be sufficient to define all of the saturation states. When a pure fluid is represented on a $\ln P$ vs $(-1/T)$ diagram the two-phase lines, one for saturated liquid and one for saturated vapor, are projected on top of one another in the constant specific volume plane. For a zeotropic mixture, the surface of thermodynamic equilibrium states is not flat and normal to the constant specific volume plane, and therefore both the saturated liquid line and saturated vapor line are visible. Figure A1 illustrates the zeotropic mixture HFC-32/134a (30/70%mass) as it truly should be. The two saturation lines are the boundaries of the two-phase region, albeit somewhat distorted and not particularly helpful qualitatively. Nevertheless, the temperature glide through the two-phase region is seen explicitly; where the lower pressure evaporator glide is always larger than the higher pressure condenser glide (that is the temperature difference between the saturation lines).

Throughout the text of this paper a single saturation line was used to represent a zeotropic mixture for the sake of clarity. Since this single line represents an average value somewhere between the two saturation lines and thus does not accurately represent a quantitative value, the numerical scales were left off. The purpose of the single saturation line is to approximate the mixture's relative position to that of its components.

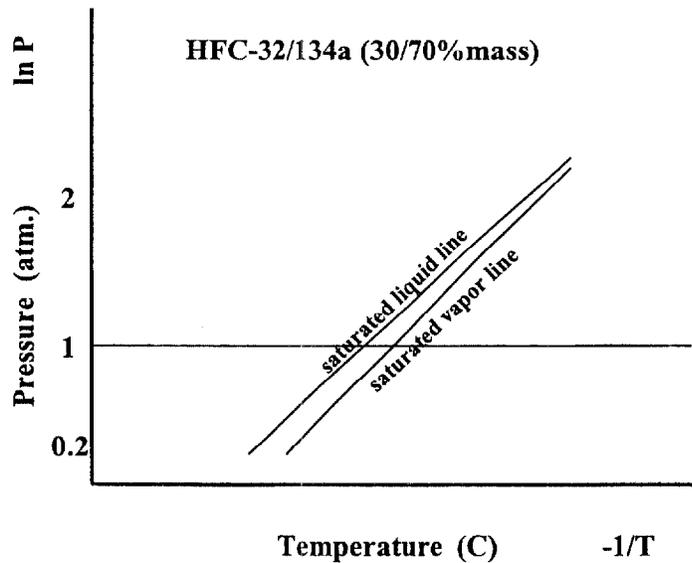


Figure A1. True Representation of a Zeotropic Mixture

APPENDIX B

Data for Selected HFC Refrigerants and Mixtures

Refrigerant		Physical Data				Safety Data				Environmental Data		
No.	Formula	Molecular Mass	NBP (°C)	Critical Point (°C) (MPa)		TLV-TWA (ppm)	LFL (%)	HoC (MJ/kg)	ASHRAE Safety Group	Atm. Life (yr.)	ODP	GWP (100yr)
23	CHF ₃	70.01	-82.1	25.9	4.84	1000	-	-12.5	A1	243	0	14800
32	CH ₂ F ₂	52.02	-51.7	78.2	5.78	1000	13.3	9.4	A2	5.6	0	880
116	CF ₃ CF ₃	138.01	-78.2	19.9	3.04	1000	-		A1	10000	0	11400
125	CHF ₂ CF ₃	120.02	-48.1	66.2	3.63	1000	-	-1.5	A1	32.6	0	3800
134a	CH ₂ FCF ₃	102.03	-26.1	101.1	4.06	1000	-	4.2	A1	13.6	0	1600
143a	CH ₃ CF ₃	84.04	-47.2	72.9	3.78	1000	7.1	10.3	A2	53.5	0	5400
152a	CH ₃ CHF ₂	66.05	-24.0	113.3	4.52	1000	3.1	17.4	A2	1.5	0	190
404A	R-125/143a/134a (44/52/4 %)	97.6	-46.6	72.1	3.74	1000	-	-6.6	A1/A1		0	4540
407C	R-32/125/134a (23/25/52 %)	86.20	-43.8	87.3	4.63	1000	-	-4.9	A1/A1		0	1980
410A	R-32/125 (50/50 %)	72.58	-51.6	72.5	4.95	1000	-	-4.4	A1/A1		0	2340
507A	R-125/143a (50/50 %)	98.86	-47.1	70.9	3.79		-	-5.5	A1		0	4600
508A	R-23/116 (39/61 %)	100.10	-87.4	11.0	3.7	1000	-		A1/A1		0	12700
508B	R-23/116 (46/54 %)	95.39	-87.4	14.0	3.93	1000	-		A1/A1		0	13000

Courtesy of James M. Calm P.E.
Engineering Consultant

Where:

NBP - normal boiling point; i.e., the boiling temperature at atmospheric pressure.(101.33 kPa)
 TLV-TWA – threshold limit value-time-weighted average; as referenced in ASHRAE Standard 34-1997.
 LFL – lower flammability limit; as defined in ASHRAE Standard 34-1997.
 HoC – heat of combustion; as defined in ASHRAE Standard 34-1997.
 ODP – ozone depletion potential
 GWP – global warming potential; 100 year integration

L'application des HFC en tant que réfrigérants

Nous discutons les critères techniques pour l'utilisation des hydrofluorocarbones (HFC) en tant que réfrigérants dans le cycle de compression de la vapeur. Pour optimiser la performance thermodynamique il importe de considérer le point critique du fluide et la capacité calorifique molaire. Un compromis raisonnable entre la capacité volumétrique, qui influence les dimensions de l'équipement, et le coefficient de performance est réalisé de façon optimale par la sélection d'un réfrigérant ayant une pression adéquate de la vapeur. Des mélanges azéotropiques ou zéotropiques sont utilisés afin de réaliser les compromis exigés par des applications diverses. Nous discutons les caractéristiques de ces mélanges et les avantages et inconvénients de leurs performances. Nous discutons en outre les propriétés de ces réfrigérants concernant la lubrification et la sécurité de leur emploi.