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AZEOTROPE OF HFC-125 AND HFC-143a AS AN ALTERNATIVE FOR R-502

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ABSTRACT

R-502 has been the primary refrigerant for low temperature commercial refrigeration applications for many years. The impending phase-out of CFCs dictates its elimination in the very near future. The identification of alternative(s) for R-502 therefore becomes a high priority. This paper addresses the factors to be evaluated in selecting the best replacement and identifies an azeotropic mixture of HFC-125 and HFC-143a as a leading candidate which satisfies the selection criteria.

HISTORICAL PERSPECTIVE

Early references indicated that HCFC-22 was introduced as a low temperature refrigerant to supplement CFC-12. One source (1) states that R-22 was developed for reciprocating compressor applications below -25 F which is typical for frozen food applications.

At that time, most compressors were of the open drive configuration and therefore less sensitive to the lower vapor heat capacity of HCFC-22. The compressor motors were air cooled rather than refrigerant cooled as most hermetic compressors are today. Furthermore, the motor heat was not added to the refrigerant, which kept the discharge temperatures at a more acceptable level. Water cooled condensers were much more common in the early days of retail food frozen food systems which resulted in lower condensing temperatures which also tended to maintain lower discharge gas temperatures.

In the 1950s, hermetic compressors combined with air cooled condensers started to predominate refrigeration systems. HCFC-22 was marginally acceptable with open drive compressors and water cooled systems where the condensing temperature rarely exceeded 105 F. Air cooled systems might have succeeded with generously sized condensers but the use of hermetic compressors placed an excessive burden on simple refrigeration systems. The change to a typical condensing temperature of 120 F combined with cooling a 75 percent isentropic efficient compressor would increase the discharge temperature from approximately 250 F to well above 350 F. Techniques developed to deal with the excessive temperatures generated in the compression process included multistage compression systems and/or liquid injection. These enhancements led to increased cost and introduced their own reliability problems as the overall system complexity was increased.

A patent was issued to A.F. Benning in 1953 (2) for an azeotrope of HCFC-22 and CFC-115. The patent did not address any specific application and for several years there did not seem to be any commercial interest in this azeotropic refrigerant. In 1961 the product was introduced commercially as R-502. Compressor manufacturers quickly endorsed its use for low temperature applications (3).

SELECTION CRITERIA

The specific heat of R-502 vapor is only incrementally lower than that of HCFC-22 but the lower heat of vaporization means that a higher mass flow rate is required for the same cooling load. The higher vapor density compensates for the greater mass flow requirement so that the volumetric flow rate is very close to that of HCFC-22. This allowed an easy conversion to R-502 with only minimal redesign of compressors and other capital intensive components. Retrofit was also facilitated although lubricant miscibility was decreased due to the CFC-115 content.

It is interesting to note that a major compressor manufacturer has published application information (4) which indicates that insufficient motor cooling is still the greatest problem for compressor reliability even with the use of R-502. This leads to the conclusion that an even greater vapor heat capacity would be desirable in a low temperature refrigerant.

With the imminent phase-out of R-502 for environmental reasons, it is obvious that a suitable alternative be identified. The initial reaction was to return to HCFC-22 as the replacement, recognizing that the issues of motor cooling and discharge temperatures were still valid. Again the proven methods of dealing with low vapor heat capacity were applied. In some cases, improvements in control technology permitted minor enhancements in liquid injection systems. Two stage compression offered the best energy efficiency option with high reliability but at a cost penalty. Internally compounded compressors provided a cost effective solution and became a much larger presence for retail food applications. Increasing concern over any chlorine containing refrigerants has cast a cloud over HCFC-22. Recent regulatory actions have embraced the eventual phase-out of this refrigerant and if history is any teacher, the phase-out dates will likely be accelerated.

As a result of both the operational limitations of HCFC-22, and more recently its perceived environmental unacceptability, there has been an intensive effort to identify a suitable replacement for R-502. Ideally, one would prefer an exact duplicate in both performance (capacity and efficiency) and operational (pressures and temperatures) characteristics. It becomes painfully obvious, rather quickly, that there are very limited choices that will be environmentally acceptable and will also meet all the other criteria such as performance, reliability and safety that the world has come to expect in a refrigerant.

HFC ALTERNATIVES

HFCs become leading candidates because they are one of the few chemical families that exhibit chemical stability combined with desirable environmental properties. They contain no chlorine and therefore are not implicated in stratospheric ozone depletion. They also tend to have low levels of toxicity and several of the compounds are nonflammable. There are several members of this chemical family that have physical properties which indicate suitability as refrigerants. Boiling point (or conversely vapor pressure) is the best indicator of refrigerant capacity for a given compressor displacement. Other properties such as vapor heat capacity are important as discussed above.

In reviewing potential HFC candidates as R-502 replacements, the list is distressingly small. A short list of candidates in order of decreasing boiling point are: HFC-152a, 134a, 143a, 125 and 32. There are, of course, other HFCs but their boiling points would be considered too distant from R-502 to be of interest. Of the above list HFC-32 has a considerably lower boiling point than R-502 and HFC-152a and 134a are substantially higher. Of the remaining candidates HFC-143a is flammable (as are HFC-32 and 152a). Therefore HFC-125 becomes the leading candidate to replace R-502. Closer examination shows that it has many properties which are desirable, e.g. nonflammable and low toxicity. It also has some less than desirable properties. Its low critical temperature limits its use in air cooled systems since both the capacity and efficiency degrade rapidly with increasing condensing temperatures.

One way to increase the number of options, in the search for an alternative to R-502, is to include the use of mixtures of HFCs. There are two types of mixtures which exist; simple mixtures where the properties of the mixture approximate an average of the properties of the constituents and azeotropic mixtures which have unique properties. The simple mixtures are described variously as zeotropes or non-azeotropic mixtures. Azeotropes are mixtures which behave like a single component fluid, i.e. they have the same composition in both the vapor and liquid phases. The characteristics of azeotropes are generally considered desirable to system designers and therefore are the only types of refrigerant mixtures which have seen significant use in the past.

One of the other non-obvious characteristics of an azeotrope is that the vapor pressure of the mixture is either higher or lower than that of either constituent. The more usual case is that the vapor pressure is higher, e.g. R-500, R-502 and R-503. One of the primary reasons for investigating mixtures is that flammable components may be used if mixed with nonflammable ones that suppress the flammability. R-500 is a perfect example where the use of HFC-152a, which is quite flammable is mixed with a nonflammable component, CFC-12, to form a nonflammable azeotropic mixture.

AN AZEOTROPIC ALTERNATIVE

An azeotrope consisting of HFC-125 and HFC-143a was discovered and patented. (5) This particular azeotrope is of the relatively rare type where the vapor pressure of the mixture is lower than that of either of the components. This is particularly desirable since both components have higher vapor pressure than R-502. Fig. 1 compares the thermodynamic capacity of R-502 with the azeotrope of HFC-125 and 143a and both components individually. It also shows qualitatively the expected performance if these refrigerants had not formed an azeotrope or if they had formed a more typical azeotrope with the positive vapor pressure characteristic. As can be seen, the projected performance of this azeotrope is remarkably close to that of R-502. Although it may be possible to achieve comparable performance with other combinations of HFCs, unless they also are azeotropes, it is unlikely that they would be favored by system designers.

This binary mixture forms an azeotrope in a 50/50 weight percent mixture at -40 F. The flammability of the HFC-143a is suppressed by the HFC-125 such that the mixture has been classified as "practically nonflammable" by Underwriters Laboratories (6). This is the same classification applied to both HCFC-22 and R-

502. Although complete toxicological data is not yet available, the preliminary results are encouraging enough to give it the most favorable ASHRAE Standard 34 classification. This particular azeotrope has been assigned the number R-507 with a classification of A1 by ASHRAE. Product availability in commercial quantities was announced in September, 1993.

Compressor calorimeter test results of the azeotrope and R-502 are compared in Figs. 2 and 3. At a typical retail frozen food evaporator temperature of -25 F, the capacity and efficiency match that of R-502 almost exactly. Based on the transport properties, the heat transfer would be expected to be somewhat improved with the HFC-125/143a azeotrope compared to R-502.

At the present time field conversions from R-502 to the HFC-125/143a azeotrope have been made by most of the major supermarket chains in the U.S. One of the best instrumented stores is one that is being used for research into alternative refrigerants and compression systems. This particular store located in Glens Falls, NY uses only HFC refrigerants in all refrigeration systems including the air conditioning. The low temperature systems were originally designed with HCFC-22. They were then converted to R-502 to establish a baseline for comparison purposes. The low temperature parallel rack was then converted to the HFC-125/143a azeotrope (designated as AZ-50). Fig. 4 shows recorded data for all three refrigerants. As can be seen, the HFC-125/143a azeotrope gave slightly improved performance over R-502 over a wide range of operating temperatures including at least one day which exceeded the local design temperature.

Other operational parameters such as pressures and temperatures are also of great interest. Over the complete temperature range from -40 to +140 F, the pressure of the HFC azeotrope is approximately 12 percent higher than R-502. Although one would prefer to match the vapor pressure exactly, this difference has been deemed acceptable by all major compressor manufacturers. The discharge temperature is illustrated by Fig. 5. The lower discharge temperature is a definite advantage and will assist in providing even greater long term reliability due to improved hermetic compressor motor cooling and reduced lubricant decomposition. This evidence of greater vapor heat capacity will also permit more effective use of liquid/suction heat exchange.

CONCLUSIONS

Of several alternatives proposed to replace R-502, one is an azeotrope which offers an excellent performance match. This azeotrope of HFC-125 and HFC-143a in a 50/50 ratio also provides desirable environmental and safety characteristics. In addition to the favorable thermodynamic capacity and efficiency match to R-502, this azeotrope has a greater vapor heat capacity which provides superior motor cooling and lower compressor discharge temperatures. The transport properties should result in better heat transfer and lower pressure drop than R-502. These vital characteristics suggest that ultimately, R-507 may prove superior to R-502 in performance once component and system engineers optimize designs around the properties of this new refrigerant.

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6. Private Communication, Underwriters Laboratories Report to AlliedSignal.

Capacity of Low Temperature Refrigerants -30 F Evaporating Temperature

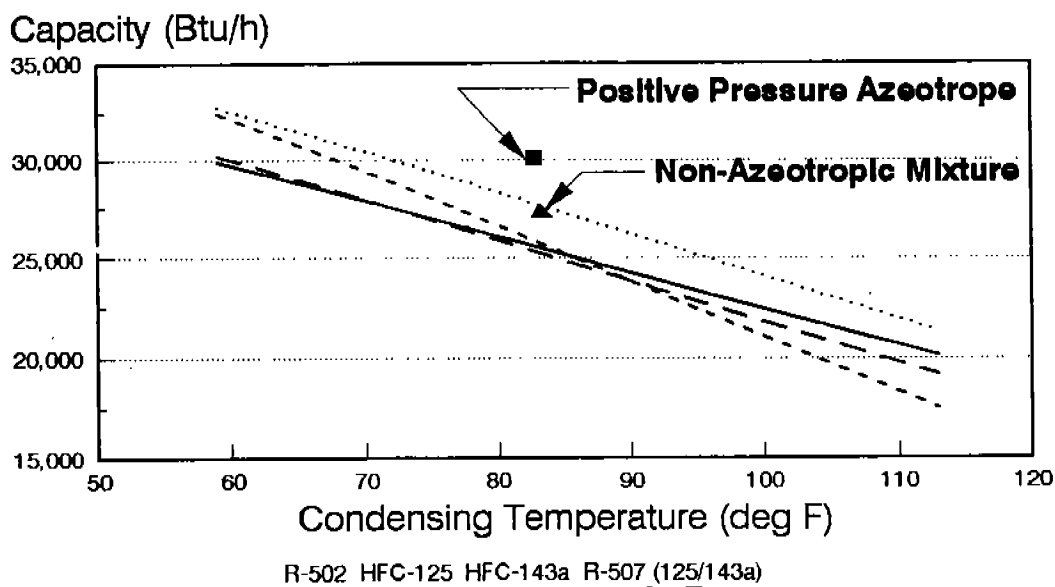
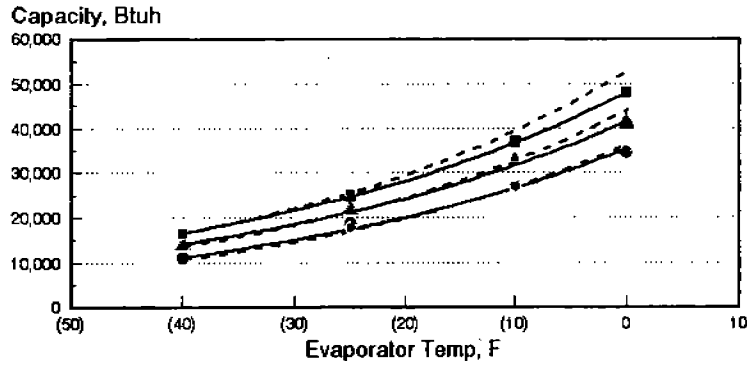


Fig. 1

Compressor Performance

R-502 vs. R-507 (125/143a)



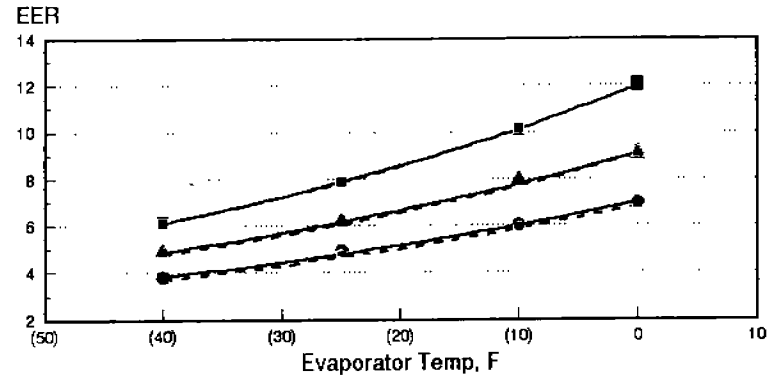
R-502_70F R-502_90F R-502_110F R-507_70F R-507_90F R-507_110F

65 F Return Temp; 0 F Subcooling
Copeland Model 2DL3-0400

Fig. 2

Compressor Performance

R-502 vs. R-507 (125/143a)



R-502_70F R-502_90F R-502_110F R-507_70F R-507_90F R-507_110F

65 F Return Temp; 0 F Subcooling
Copeland Model 2DL3-0400

Fig. 3

ASPEN SYSTEMS DEMONSTRATION RESULTS

-25 F System / Two Carlyle 06ER175

Test Site: Shop 'N Save, Glens Falls, NY

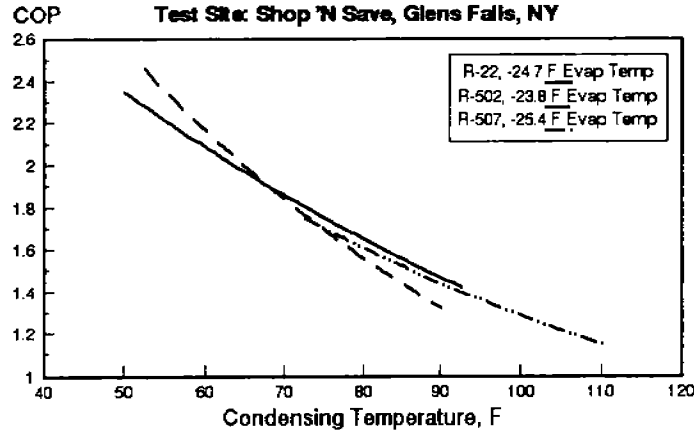


Fig. 4

Compressor Discharge Temperature

Several Refrigerants

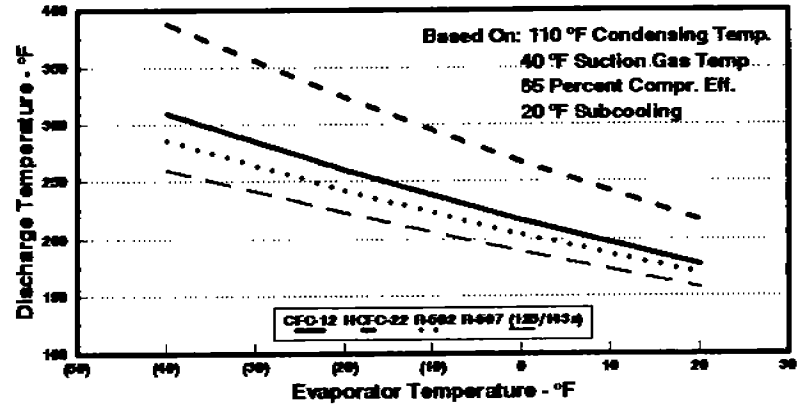


Fig. 5