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International Refrigeration and Air Conditioning Conference

School of Mechanical Engineering

1992

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S. G. Sundaresan
Copeland Corporation

NEAR AZEOTROPE REFRIGERANTS TO REPLACE R502 IN COMMERCIAL REFRIGERATION

Sonny G. Sundaresan
Copeland Corporation, 1675 W. Campbell Road
Sidney, Ohio, 45365, U.S.A.

ABSTRACT

The Refrigerant R502, an azeotrope of CFC115 and HCFC22, is an important refrigerant in commercial refrigeration, especially for low temperature applications using single stage compressors. Current users of R502 are faced with an earlier than anticipated phase-out and are under great pressure to find suitable alternates for retrofit and O.E.M. (new) applications. Single components like HCFC125, HFC143a, and HFC32 are not viable candidates. Some candidates which are being evaluated are near azeotropes containing HCFC22 and propane as components. This paper discusses the challenges involving the near azeotropes and also includes status on lubricants and materials compatibility requirements. The final solution for R502 involves finding a suitable zero ozone depletion potential refrigerant candidate with an appropriate lubricant.

INTRODUCTION

The Refrigerant R502, an azeotrope of CFC115 (Chloropentafluoroethane) and HCFC22 (Chlorodifluoromethane) is widely used in commercial refrigeration industry for low and medium (evaporator) temperature single-stage applications. With mineral oil and/or alkylbenzene as lubricant, R502 offered a reliable and robust combination for a variety of compressor and system designs. Its ability to meet the efficiency, capacity, and discharge temperature requirements over a wide range of evaporating (-40°C to -4°C) and condensing (21°C to 55°C) temperature was the key factor for its success. HCFCs, HFCs, FC, HCs, and other fluids are being evaluated to replace R502 in retrofit and new applications [1] [2]. Individual components like HFC134a, HFC125, and HFC143a were considered and eliminated due to poor low temperature performance, low efficiency at high condensing temperature, and flammability, respectively. The direct and total global warming impacts of CFC alternatives are receiving greater scrutiny and some HFC and FC components with higher direct GWP values fall into this category [3]. Near azeotrope candidates were designed to overcome these barriers and came in two categories: (a) those containing HCFC22 offering immediate availability and some flexibility with lubricants, and (b) those with zero Ozone Depletion Potentials (ODP) and meeting the Total Equivalent Warming Impact (TEWI) goals for total global warming effects. In addition to lubricant and materials compatibility requirements, the near azeotropes were critically evaluated for change in composition due to leakage in the two-phase regions. This paper presents the results to date in the evaluation of R502 replacements both for (immediate) retrofit and (long-term) final solutions.

MATERIALS AND METHODS

Candidate refrigerants to replace R502 were in two categories: (1) containing HCFC22 candidates HP81*, HP80*, 69-S+, and 69-L+ from first category, and (2) zero ODP: HP62. Lubricants for the first category candidates included mineral oil, alkylbenzene, blend of mineral oil and alkylbenzene, and polyol ester; only polyol esters were considered for HP62. The lubricants were selected to match the

*HP81, HP80, HP62 are products from DuPont under the trade name "SUVA"

+69-S and 69-L are products from Rhone-Poulenc Chemicals under the trade name "ISCEON".

performance of naphthenic mineral oil (32 centistokes) with R502.

Compressor performance testing was conducted in a (secondary) calorimeter, and the results (capacity, efficiency, and discharge temperature) were compared to the expected theoretical values. To achieve a fair comparison of a near azeotrope to a single refrigerant or a (true) azeotrope, the refrigerant cycle was defined at the mid-point of the temperature glide as a close approximation. Figure A illustrates this procedure using the pressure enthalphy diagram of the refrigeration cycle. Near azeotropes exhibit the dew point and the bubble point lines (isotherms) in the two-phase regions of condensation and evaporation. For the condenser and the evaporator, the set points M and N were chosen in such a way that M is the mid-point of BC and N is the mid-point of E'F. As can be seen from the figure, temperature at C is defined by $T_C=T_M-1/2$ the temperature glide at the condenser, and temperature at F is defined by $T_F=T_N+1/2$ the temperature glide at the evaporator. For this procedure, in addition to the traditional saturation pressure tables and superheated vapor tables, a table of temperature glide (as a function of pressure and liquid enthalpy) is needed for the near azeotropes.

Lubricant screening consideration included physical properties, miscibility with the refrigerant, lubricity in bench tests and/or compressor life tests [4]. Materials compatibility evaluations with metals, plastics, elastomers, and motor insulation are conducted in sealed tube aging tests conducted in accordance with the ASHRAE 97-88 procedures [4] [5]. Long-term tests for lubricity and materials compatibility will continue for the next two years.

Fractionation studies were conducted theoretically and experimentally to understand the effect of composition shifts of near azeotropes under different scenarios ranging from storage and handling, long-term system shutdown, normal operation, and leakages. The experimental studies included leak tests in static pressure vessels and in actual refrigeration systems. Also in a compressor calorimeter system, the differences and the effect due to composition shifts from the bulk (liquid) to the compressor inlet conditions were studied. The static pressure vessel test was a stainless steel cylinder with 300 cc capacity charged with 120 grams of liquid refrigerant HP62. After reaching the equilibrium, and after leakage at 25% and 50% levels approximately, the compositions of the liquid and the vapor phases were determined using the gas chromatography techniques.

In the other study, near azeotrope refrigerants were evaluated in a low temperature frozen food cabinet to verify the performance, the system behavior, and the effect of the change of composition by leakage [6].

RESULTS AND DISCUSSION

Refrigerants

Table 1 lists the physical, environmental, and safety properties of two, single component candidates, HFC125 and HFC143a; two azeotropes, HFC32/HFC125 (60%/40%) and HFC125/HFC143a (45%/55%); and five near azeotropes, 69-S (HCFC22-85%, HC290-6%, FC218-9%), 69-L (HCFC22-55%, HC290-6%, FC218-39%), HP81 (HCFC22-60%, HC290-2%, HFC125-38%), and HP80 (HCFC22-38%, HC290-2%, HFC125-60%) (blends containing HCFC22) and HP62 (HFC blend). Candidate HFC125's low critical temperature results in lower efficiency at high condensing temperatures and is not suitable. HFC143a is flammable and was not further considered for testing. Azeotropes of HFC-32/HFC125 and HFC125/HFC143a were not available for testing. Table 2 addresses the energy and global warming impact considerations in greater detail. The direct global warming potential of the candidates is listed in terms of HGWP (reference CFC11=1.00) in Table 1. In order to evaluate a refrigerant in a valid and comprehensive manner, the energy efficiency of the refrigeration cycle (eg, C.O.P. values in Table 1), the actual refrigeration system leakage potential, and the

CO_2 emissions resulting from the power generation plant, etc., must be taken into account. A new index called "Total Equivalent Warming Impact" combines the direct effects and the indirect effects for specific applications [3]. Table 2 lists the data for the five near azeotrope candidates for a low temperature supermarket condition (-40°C/54.4°C/no subcooling/18.3°C return gas) using CO_2 equivalent values for 500-year life, 33% power house efficiency, and typical fuel mix for North America [3]. As can be seen, many of the alternatives meet the requirement of not exceeding the TEWI for R502.

Figures B and C show the vapor pressure-temperature and pressure-enthalpy relationships. Figures D, E, and F present the theoretical capacity, efficiency, and discharge temperature values over the application range. Tables 3-1, 3-2, and 3-3 compare the actual capacity, efficiency, and discharge temperature values to the theoretical values at conditions -31.6°C/43.3°C and -40.0°C/54.4°C.

At the rating point (-31.7°C/43.3°C), HP81 and 69-S exhibit nearly equal capacity and efficiency. With respect to R502, the capacity is slightly higher and the efficiency is slightly lower. From the discharge temperature point of view, both 69-S and HP81 were higher than R502 and is expected to get worse at -40°C/54.4°C conditions. This resulted in the reformulation of these two candidates to HP80 and 69-L, respectively. As seen, HP80 and 69-L meet the general overall requirements to replace R502 in retrofit applications for capacity, efficiency, and compressor discharge temperature. HP62 meets the capacity, efficiency, and discharge temperature requirements to replace R502 in new (OEM) applications.

Table 3-4 provides values of the ratio of specific heats, the pressure ratios, the latent heat of vaporization, the vapor density, the theoretical capacity, and the theoretical power at -31.7°C/43.3°C rating conditions. The lower discharge temperature values of 69-L and HP80 in relation to 69-S and HP-81 respectively, can be explained in terms of lower ratio of specific heats and lower pressure ratios. For HP62, the lower discharge temperature value in relation to R502 is only due to the decreased value of ratio of specific heat and in spite of slightly higher pressure ratio. The capacity values comparison can be explained due to increased latent heat of vaporization and in most cases in spite of decreased suction gas density. For all the five candidates, both values of theoretical power and capacity were higher in comparison to R502. The efficiency ranking merely follows the ranking of the ratios of the power to capacity.

LUBRICANTS

Table 4 lists lubricants that were evaluated for the different refrigerant candidates. Hydrocarbon lubricants, naphthenic mineral oil (32 Cst), alkylbenzene (32 Cst), and a blend of mineral oil and alkylbenzene (40 Cst) offer proven experience (with R502), availability, and excellent resistance to moisture absorption. Their selection with near azeotrope refrigerants containing HCFC22 depends upon the compressor design (for lubricity) and system design (for oil return). Miscibility, the critical solubility data, and relative indices for system oil return and lubricity are provided. The relative "lubricity rating index" is a measure of long-term compressor reliability based on life testing at life testing under high compression ratio test conditions. A rating of 4-5 is the screening criteria used, and the specific candidates with a rating lower than 5 require continued improvement for oil return and/or lubricity without the sacrifice of the other.

Polyol ester lubricants meet the lubricity requirements for both categories of refrigerants: HFCs and mixtures containing HCFC22. In retrofit applications, miscibility of esters with residual hydrocarbon lubricants and compatibility with residual chlorine are favorable characteristics. These considerations must be carefully compared in contrast to proven reliability and excellent resistance to water absorption characteristics of hydrocarbon lubricants.

Lubricants research with HFC134a has provided an excellent starting point in terms of understanding the tradeoffs between structure of base stock and additives with respect to lubricity, oil return characteristics, and stability [4, 7, 8, 9]. For near azeotrope candidate, HP62, a mixture of three HFCs, only polyol ester lubricant was evaluated and found to meet the screening requirements. In all cases, the selection of lubricant requires careful screening and approval by the compressor manufacturers after extensive testing in actual systems for specific applications.

MATERIALS COMPATIBILITY

Table 5 lists the relative materials compatibility indices for the refrigerant/lubricant combinations. Existing information on CFC/HCFC refrigerants with hydrocarbon lubricants [10, 11] and materials compatibility research with HFC134a and polyglycol and polyol ester lubricants [2, 4, 5, 12] were the starting points. The list of materials includes metals, plastics, elastomers, and motor insulation system components normally encountered in hermetic systems. A rating of 4-5 is the screening criteria used for the specific refrigerant/ lubricant pairs and the candidates with rating lower than 5 require continued testing to assess the risks for the specific application environment. As seen from the list, there are no critical barriers in this area. Long-term tests with fluorinated polymers and HFCs are underway.

FRACTIONATION

Zeotropic mixtures are characterized by the changes in composition of the vapor and the liquid phases during any phase change process that occurs over a range of temperatures (glide). Mixtures with large temperature glides can be engineered to take advantage of this feature for example, by counter flow heat exchanger designs and improving the overall energy efficiency of the system [13]. Mixtures with large glides also have a greater tendency to segregate, and this feature must be evaluated carefully to determine its effect on factory and field service practices including storage, handling, charging, recharging, etc. [14]. Information from laboratory studies and actual field installations by chemical producers [15, 16, 17] and end users [18] indicate that near azeotropes are viable candidates.

Figure G explains what happens during a leak in a ternary near azeotrope (with one flammable component). Table 6 lists the effects on pressure capacity, efficiency, and discharge temperature with HP62 when there is a vapor leak under a worst case scenario (50°C). Points A, B, and C indicate the initial composition, after 10% leak and after 50% leak respectively. Point D indicates the composition after recharging from point C. It is clear that the mixture is still in the nonflammable region, and the effects are minimal at 10% leak condition and after recharge.

Leak test studies were conducted in a static pressure vessel to verify the expected behavior of components in a near azeotrope: (1) the component with the highest boiling point leaks the slowest, and (2) the effect of the leaks at 25%, 50%, etc., is negligible. The relative composition differences were measured by GC techniques from the vapor leak and Table 7 summarizes the expected effect on performance parameters. As seen, the expected effects in pressure, capacity, efficiency, and discharge temperature are negligible.

Near azeotrope candidate HP81 was evaluated in an actual supermarket refrigeration cabinet system to verify its system performance, including oil return and discharge temperature. The experiment included leakage scenarios from 10% to 50% levels. The results confirmed the theoretically predicted values and provided a basis for continuing development work with near azeotropes like HP80, 69-L, and HP62 [6].

To understand what composition differences exist between the bulk and at the compressor inlet, an experimental study was conducted in a secondary calorimeter (7.5 kw) at three different operating conditions: -31.7°C/43.3°C, -40.0°C/32.2°C, and at -40.0°C/54.4°C. Gas chromatographic evaluation of HP62 refrigerant at the liquid and compressor inlet conditions were determined and Table 8 provides the relative composition differences and the theoretically calculated effect on pressure, capacity, efficiency, and discharge temperatures. As can be seen, the variations in composition are negligible and within the ±0.5% error typical to GC techniques; also the effect on pressure, capacity, efficiency, and discharge temperature is negligible.

CONCLUSIONS AND SIGNIFICANT NEW FINDINGS

- Near azeotrope mixtures with very low temperature glides can be formulated to overcome the inefficiency and flammability barriers of some individual components and meet the safety and performance requirements during handling, storage, charging, and leakage scenarios.
- The TEWI (Total Equivalent Warming Impact) is the most appropriate index to screen candidates to meet the energy and the total effect of greenhouse warming potential.
- For R502 replacements, near azeotrope mixtures containing HCFC22 can offer acceptable non-CFC solutions in retrofit applications.
- Near azeotropes with zero ODP and acceptable TEWI indices can meet the R502 replacement criteria for long-term final solutions.

ACKNOWLEDGEMENTS

The author would like to express his gratitude for the direction of this work to Mr. Earl Muir, Copeland Corporation; and for the experimental work of Dr. William Finkenstadt, Donald Baird, and Ronald Watkins, Copeland Corporation. The timely help and assistance in obtaining the properties for the candidates from the E. I. DuPont deNemours, Wilmington, Delaware, USA, and The Star Refrigeration, Glasgow, Scotland, is also well appreciated.

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TABLE 1

R502 ALTERNATIVES
PHYSICAL AND ENVIRONMENTAL PROPERTIES

Candidate And Type	R502 Azeotrope	HFC 125 Single	HFC 143a Single	69-S Near Azeotrope	69-L Near Azeotrope	HP81 Near Azeotrope	HP80 Near Azeotrope	HP62 Near Azeotrope	32/125 Azeotrope	125/143a Azeotrope
Components				HCFC22 HC290 FC218	HCFC22 HC290 FC218	HCFC22 HC290 HFC125	HFC22 HC290 HFC125	All HFC		
Boiling point °C	-45	-48.6	-47	-46.7	-50.2	-47.9	-49	-47.8	-53	-45.8
Critical temp °C	82	66	73	89	76.3	81.7	75.2	72.6	74	71.1
ODP	0.23	0	0	0.043	0.028	0.03	0.02	0	0	0
HGWP	3.74	0.84	1.1	1.19	4.09	0.52	0.63	0.94	0.44	0.98
Toxicity (TLV/ppm)	1,000	1,000	1,000	N/A	N/A	1,000*	1,000*	1,000*	N/A	N/A
Flammability	NO	NO	YES	NO	NO	NO	NO	NO	NO	NO

(*AEL, 8-12 hour TWA)
N/A = not available

TABLE 2

DIRECT, INDIRECT, AND TOTAL EFFECTS OF GLOBAL WARMING

	DIRECT CO_2	INDIRECT CO_2	TEWI
R502	3,240	3,000	6,240
69-S	1,444	2,837	4,281
69-L	4,935	3,044	7,979
HP81	644	2,979	3,623
HP80	771	3,183	3,954
HP62	1,143	3,135	4,278
125/143A	1,180	3,135	4,315
32/125	480	3,336	3,816

Low temperature supermarket equipment with
20 year life; 10% per year leak rate; CO_2 values for 500 year life
Reference: (3)

TABLE 3.1

PERFORMANCE COMPARISON
(CAPACITY RATIOS)

	-31.7°C/43.3°C		-40°C/54.4°C)	
	Actual	(Theoretical)	Actual	(Theoretical)
R502	1.00	(1.00)	1.00	(1.00)
69-S	1.04	(1.04)	1.07	(1.07)
69-L	1.14	(1.14)	1.08	(1.06)
HP81	1.03	(1.07)	0.94	(1.09)
HP80	1.03	(1.10)	0.86	(1.08)
HP62	1.07	(1.04)	1.09	(1.02)

TABLE 3.2

PERFORMANCE COMPARISON
(EFFICIENCY RATIOS)

	-31.7°C/43.3°C		-40°C/54.4°C	
	Actual	(Theoretical)	Actual	(Theoretical)
R502	1.000	(1.00)	1.00	(1.00)
69-S	0.980	(1.03)	1.04	(1.05)
69-L	1.000	(0.95)	0.96	(0.92)
HP81	0.998	(1.004)	0.97	(1.04)
HP80	0.980	(0.95)	0.85	(0.92)
HP62	1.010	(0.98)	0.96	(0.95)

TABLE 3.3

PERFORMANCE COMPARISON
(DISCHARGE TEMPERATURE DIFFERENCES)

	-31.7°C/43.3°C		-40°C/54.4°C	
	Actual	(Theoretical)	Actual	(Theoretical)
R502	0	0	0	0
69-S	+15.6°C	(20.0)	15.0°C	(25.6)
69-L	-2.2°C	(0.2)	3.9°C	(2.2)
HP81	+9.4°C	(8.9)	0.6°C	(13.3)
HP80	0°C	(-1.1)	0°C	(-1.1)
HP62	-9.4°C	(-8.3)	+7.2°C	(-10.6)

TABLE 3.4

PERFORMANCE ANALYSIS (at -31.7°C/43.3°C)

	R502	69-S	69-L	HP80	HP81	HP62
*Ratio of Specific Heats	1.125	1.160	1.128	1.128	1.145	1.110
Pressure Ratio	9.85	10.17	9.97	10.06	10.25	9.97
Latent Heat of Vaporization (kJ/kg)	169	221	176	184	200	184
*Vapor Density (kg/m³)	8.70	6.50	9.18	8.97	7.64	8.19
Theoretical Capacity (kJ/m³)	982	1033	1066	1076	1054	1016
Theoretical Power (kJ/s)	760	785	862	867	832	803

(* at 18.3°C compressor inlet conditions)

TABLE 4
LUBRICANTS SUMMARY

Refrigerant	Lubricant	Miscibility	Critical Solubility Temperature @ 20% Lubricant Lower	Upper	System Oil Return Index	Lubricity** Rating Index
R-502	Mineral Oil	Partial	Na	(82.2°C)*	5	5 Baseline
69-S/69-L	Mineral Oil	Partial	Na	(76.3°C)*	3	2 - 3
69-S/69-L	Alkyl Benzene	Partial	Na	(76.3°C)*	4	3 - 4
69-S/69-L	AB + MO	Partial	Na	(76.3°C)*	3.5	2 - 3
HP81/HP80	Alkyl Benzene	Partial	Na	(81.7°C)*	4.75	4 - 5
HP81/HP80	Alkyl Benzene + Mineral Oil	Partial	Na	(81.7°C)*	4.5	4 - 5
HP81/HP80	Ester	Partial	90.6°C	(76.1°C)*	5	4 - 5
HP62	Ester	Inverse	34.4°C	(70.6°C)*	5	4 - 5

*LIMITED BY CRITICAL TEMPERATURE OF REFRIGERANT

**BASED ON LIFETESTING IN SEMI-HERMETIC COMPRESSORS

Na = Not applicable

TABLE 5
MATERIALS COMPATIBILITY INDEX SUMMARY

Materials	R502/ Mineral Oil	HFC 134a/ Ester	HP62/ Ester	Mixtures Contlaning R22 (69-S, 69-L, HP80, HP81)/ Mineral Oil, Ester
1. Metals (Al, SS/Cu)	5	5	5	5
2. Magnet wire enamel	5	5	5	5
3. Magnet wire coated with epoxy	5	4 - 5	4 - 5	4.5 - 5.0
4. PET film slot liner insulation	5	4 - 5	4 - 5	4.5 - 5.0
5. Fluorinated Polymers				
5A (PTFE)*	5	4.5 - 5	4.5 - 5	4.5 - 5.0
5B (VFHFP)+	5	3 - 4	3 - 4	3.5 - 4.5
6. Polyamide (nylon 6,6)	5	4 - 5	4 - 5	4.5 - 5.0
7. Polyimide	5	5	5	5
8. Polyetherketone	5	5	5	5
9. Non-asbestos gasket	5	4 - 5	4 - 5	4.5 - 5.0
10. Chloroprene (O-ring)	5	4 - 5	4 - 5	4.5 - 5

*(PTFE = Polytetra Fluoroethylene)

+(VFHFP = Vinylidene Fluoride-hexafluoropropylene)

TABLE 6
LEAKAGE SCENARIO WITH HP62 AT 50°C CONDITIONS (THEORETICAL STUDY)

	Discharge Pressure (Bars)	Suction Pressure (Bars)	Capacity (kJ/Hr)	Efficiency (Watt/Watt)	Discharge Temperature (Degrees Celsius)
A Start	19.88	1.99	25,495	2.10	99.7
B (At 10% leak)	19.83	1.98	25,278	2.09	99.9
C (At 50% leak)	19.52	1.93	24,030	2.02	100.2
D After Recharge	19.70	1.96	25,158	2.09	100.0

TABLE 7

STATIC LEAK TEST: EXPECTED EFFECT ON PERFORMANCE DUE TO MEASURED COMPOSITIONAL CHANGES DURING VAPOR LEAK.

	Discharge Pressure (Bars)	Suction Pressure (Bars)	Capacity (kJ/Hr)	Efficiency (Watt/Watt)	Discharge Temperature (Degrees Celsius)
Start	19.88	1.99	25,495	2.10	99.7
25% Leak	19.66	1.94	25,004	2.09	99.9
50% Leak	19.57	1.95	25,199	2.09	99.9
75% Leak	19.57	1.95	25,199	2.11	100.4

TABLE 8

COMPOSITION CHANGES AND ITS EFFECTS AT COMPESSOR INLET CONDITIONS

	-40°C/32.3°C	-31.7°C/43.3°C	-40°C/54.4°C
Component A	◄———	Change = -0.71	———►
Component B	◄———	Change = +0.25	———►
Component C	◄———	Change = +0.46	———►
(total = 100%)		(Total = 0%)	
Capacity Ratio	0.9917	0.9939	1.0000
Efficiency Ratio	1.0000	1.0000	1.0000
Discharge Temp. Difference, °C	0.0	+0.56	1.0000

Pressure - Enthalpy Diagram

Indicating the Effect of Temperature Glide.

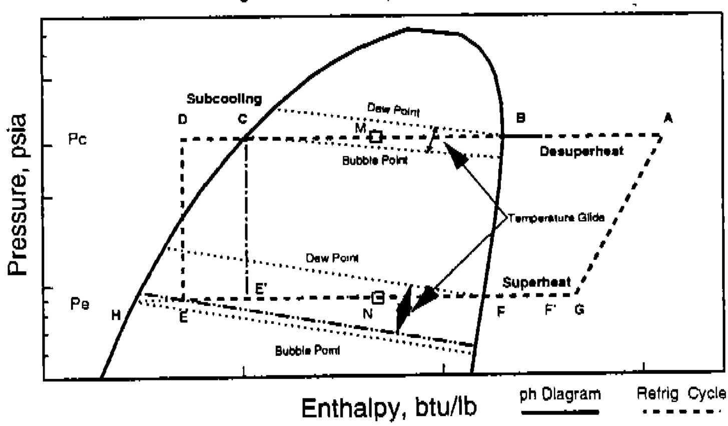

Figure A.

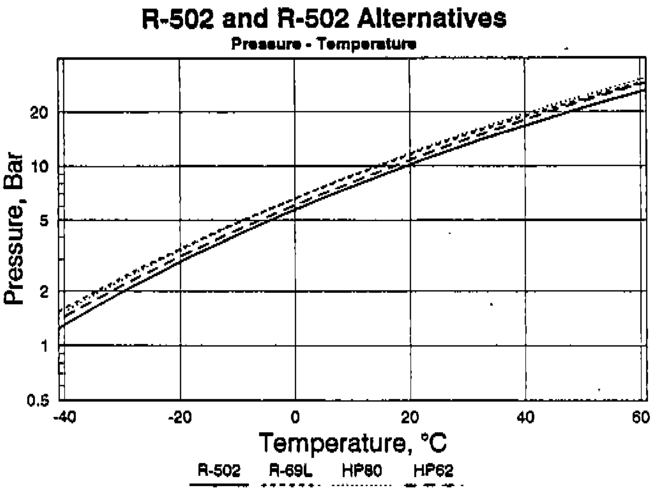

Figure B. Saturation Vapor Pressure of R-502 and R-502 Alternatives as a Function of Temperature.

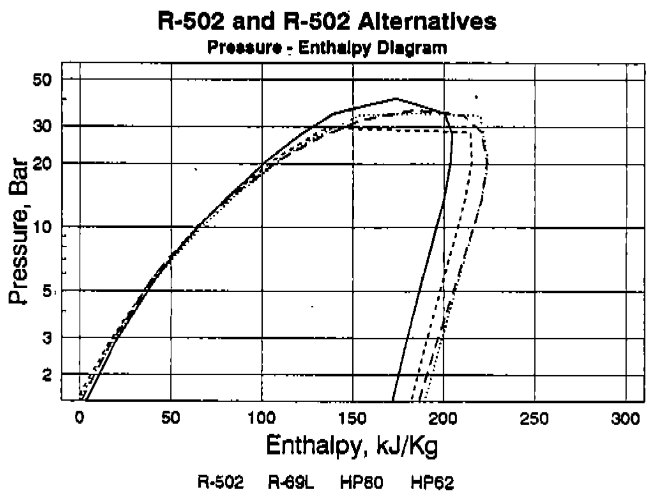

Figure C. Pressure-Enthalpy Diagram for R-502 and R-502 Alternatives.

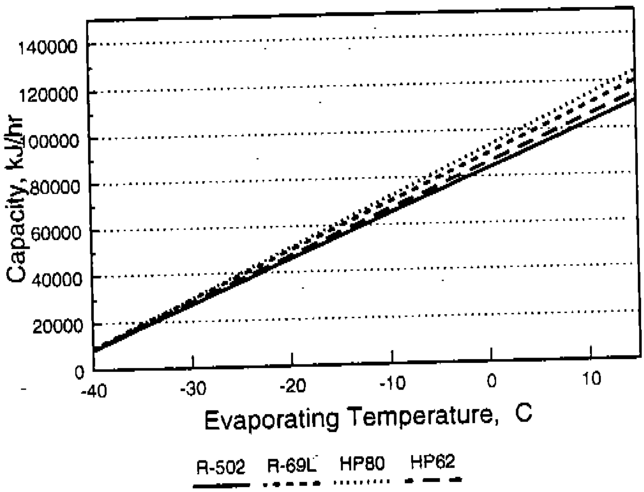

Figure D. Theoretical Capacity of R-502 and R-502 Alternatives at Various Evaporating Temperature. Condensing Temperature is 43.3 C. Compressor Displacement is 25 cubic meters per hour.

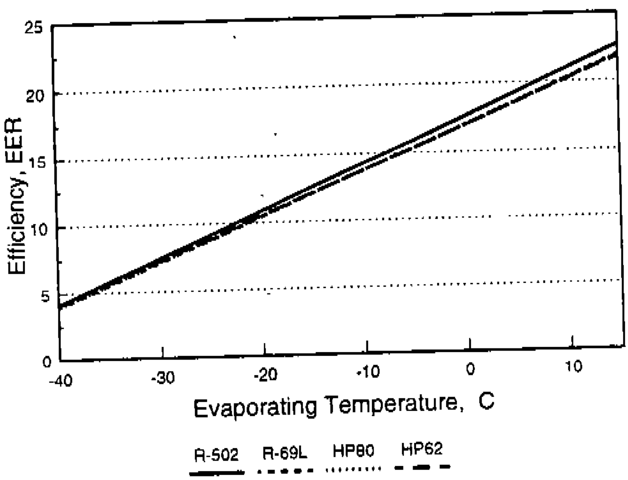

Figure E. Theoretical Efficiency of R-502 and R-502 Alternatives at Various Evaporating Temperatures. Condensing Temperature is 43.3 C.

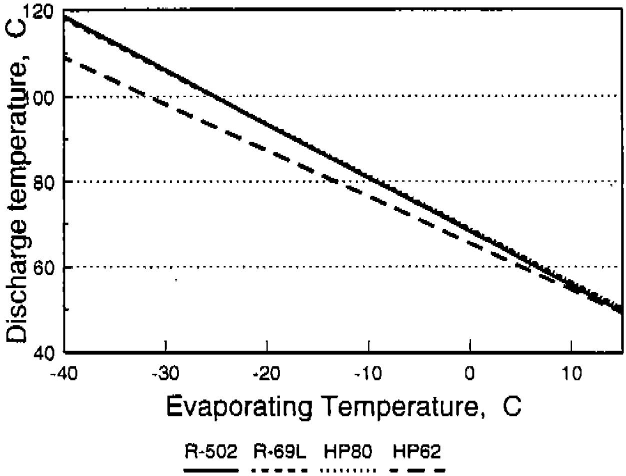

Figure F. Theoretical Discharge Temperature of R-502 and R-502 Alternatives at Various Evaporating Temperatures. Condensing Temperature is 43.3 C.

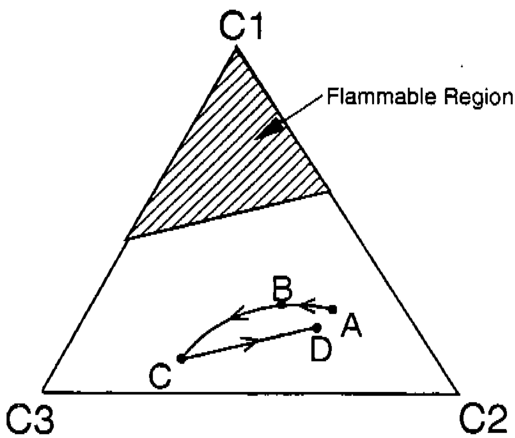

Figure G. Schematic Illustration of Leak Scenario in a Ternary Near-azeotrope with One Flammable Component.