

AN ANALYTICAL SCREENING OF ALTERNATIVES FOR R-502 IN LOW-TEMPERATURE REFRIGERATING APPLICATIONS

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ABSTRACT

R-502 is used as the working fluid of low-temperature refrigerating systems with evaporating temperatures as low as -40°F (-40°C). It was selected as the refrigerant of choice for these applications because it is both nonflammable and nontoxic and has an acceptable compressor discharge temperature when used in a high-efficiency vapor-compression system. Replacement fluids are going to be needed for use in place of R-502, however, because of the provisions of the Montreal Protocol. R-502 is an azeotropic blend of R-22 and R-115, and R-115 is a chlorofluorocarbon (CFC) that is contributing to the destruction of stratospheric ozone. The provisions of the Montreal Protocol currently require a total phase-out of the production of all fully halogenated CFCs, including R-115, by the year 2000. Consequently, replacement fluids will be needed for new and existing equipment.

One alternative is to use R-22, but this requires major design and hardware changes in order to keep the compressor discharge temperature below the point where the lubricant begins to break down. This can be done with staged compression using liquid reinjection or other modifications to the compressor, but it is expensive, particularly for adapting existing equipment.

This study was initiated to identify other possible fluids that can be used either in new or retrofit applications for low-temperature refrigeration. It includes an evaluation of predicted cycle efficiency, system capacity, pressure ratio, fluid flammability, and compressor discharge temperature. Eight different chemical compounds are considered for use as pure refrigerants as well as components in binary and ternary mixtures: R-134a, R-134, R-125, R-143a, R-152a, R-32, R-124, and R-22. An exhaustive study of the composition of blends was performed to determine the mass fractions of each component in the mixtures that are most promising on the basis of efficiency, flammability, low discharge temperature, and acceptable capacity and pressure ratio. Several blends are identified for further laboratory and analytical evaluation.

INTRODUCTION

This project was initiated to identify refrigerants and mixtures of refrigerants that could be used as the working fluid in low-temperature refrigerating equipment in place of R-502. R-502 is used extensively in commercial refrigeration for display cases for fresh and frozen foods. It is an azeotropic blend of R-22 (48.8%) and R-115 (51.2%). R-115 is a chlorofluorocarbon (CFC) that is regulated by the Environmental Protection Agency (EPA) to keep the United States in accordance with the Montreal Protocol. As such, production of R-115 is restricted and will be gradually phased out by the year 2000. Consequently, a replacement fluid will be needed, either for maintaining existing equipment or for use in new systems, and this project was initiated to identify promising alternatives for further analytical and experimental analysis.

Few experimental data are available for many of the chemical compounds that could be used either alone or in mixtures as substitutes for R-502, so this work was structured as an analytical study based on a "corresponding states" equation of state and a relatively simple refrigeration cycle model. The Lee-Kesler-Plöcker (LKP) equation of state was chosen because

- computer subroutines were available (Kruse and Kauffeld 1989),
- few experimental data were required to add new compounds to the list of refrigerants available in the existing programs (e.g., molecular weight, critical temperature and pressure, and normal boiling point),
- correlations were available for calculating acentric factors for each refrigerant and interaction parameters for mixtures of refrigerants, and
- the calculations could be improved by making use of any available data on saturation temperatures and pressures to refine the choices of acentric factors and interaction parameters.

The CYCLE-7 model (Domanski and McLinden 1992; McLinden 1987) was chosen for the cycle calculations

because it provided an existing mechanism for computing system performance from refrigerant properties, secondary fluid temperatures (e.g., air temperatures entering the evaporator and condenser), and LMTD and pressure drops for each heat exchanger. This program was adapted to use the LKP routines, and new choices of refrigerants were added.

CYCLE MODEL

The cycle model that was used in these analyses was deliberately kept simple and did not account for many factors such as temperature or pressure drops in the suction, liquid, and discharge lines. The intent of this study is to evaluate many different combinations of refrigerants in binary and ternary mixtures in order to identify the most promising blends for further analytical and experimental evaluation. Compromises were consequently made to reduce the amount of computer time required for the calculations at the expense of the absolute accuracy of the results. That should not be a problem, however, since the final product of this study is a relative ranking of refrigerants and mixtures rather than precise system performance simulations. For want of a better name, the modified program has been called "CYCLE-10."

Some of the key points from CYCLE-10 are shown in the cycle diagram in Figure 1 on a pressure-enthalpy diagram for a hypothetical refrigerant. This figure indicates superheated vapor entering and leaving the compressor and entering the condenser (points 1, 2, and 3), subcooled liquid leaving the condenser (point 6), and saturated vapor leaving the evaporator (point 8). Point 2'' corresponds to an isentropic compression efficiency ($\eta_{isen} = 100\%$) and point 2' to the specified η_{isen} (56.5% in later calculations). The compressor input power is the mass flow rate, \dot{m}_r , times the enthalpy change between point 2' and point 1. The rate of compressor shell heat loss is assumed to be a specified fraction, η_{shell} , of the input power:

$$\dot{Q}_{shell} = \eta_{shell} \cdot \dot{m}_r \cdot (h_{2'} - h_1). \quad (1)$$

An iteration is performed to determine the compressor discharge temperature (the temperature at point 2) that corresponds to the refrigerant pressure and enthalpy. The evaporator capacity is computed from the enthalpy of the saturated vapor, h_8 , and the enthalpy at the evaporator inlet, h_7 . The system refrigerating efficiency is then given by

$$COP = \frac{h_8 - h_7}{h_{2'} - h_1}. \quad (2)$$

The operating temperatures, pressures, and enthalpies are calculated using the LKP equation of state and specified data for the

- overall LMTDs for the evaporator and condenser,
- liquid line and suction gas temperatures,

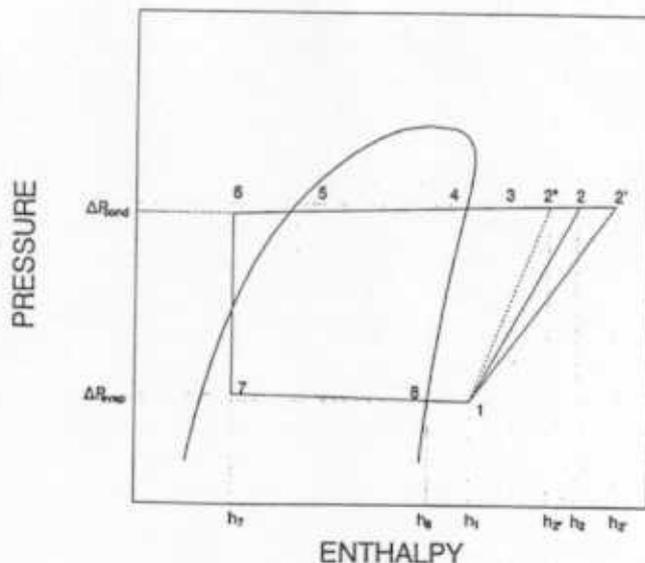


Figure 1 Cycle diagram used for low-temperature refrigeration system simulation.

- compressor isentropic efficiency and the fraction of the input energy rejected from the compressor shell, η_{comp} and η_{shell} , respectively, and
- source and sink conditions specified by inlet and outlet temperatures for the secondary fluid stream.

CYCLE-10 and measured field performance and compressor calorimeter data (Walker and Deming 1989) were used to determine input parameters for the screening analysis. A combined motor efficiency and compressor isentropic efficiency of 56.5% was calculated by taking the ratio of the measured calorimeter performance with the cycle COP computed from the ASHRAE tables for R-502 at the calorimeter test conditions. Data were available for the inlet water temperature and condensing pressure for baseline tests of field performance using a water-cooled condenser. The outlet water temperature and condenser LMTD were estimated by varying them during iterations with CYCLE-10 at the specified inlet water until the calculated condensing pressure matched the observed value. The rate of compressor shell heat loss, η_{shell} , was estimated to be 0.15 by adjusting it until the calculated compressor discharge temperature matched the observed value of 225°F. Validation of the CYCLE-10 model against field performance is summarized in Table 1.

LEE-KESLER-PLÖCKER EQUATION OF STATE

As mentioned earlier, the LKP equation of state is able to calculate fairly accurate thermodynamic properties from a very small amount of experimental data. The minimum amount of data required consists of the critical temperature and pressure (T_c and P_c), the molecular weight, the acentric factor (ω), and an analytical expression for the ideal gas heat capacity (C_p) as a function of the absolute temperature.

TABLE 1

Cycle-10 Modal Validation		
Parameter	Cycle-10	Field Test
Input Data:		
evaporator inlet air temperature	-15.2°F (-26.2°C)	N/A (N/A)
evaporator discharge air temperature	-20.0 (-28.9)	-20.0°F (-28.9°C)
condenser inlet air temperature	60.0 (15.6)	60.0 (15.6)
condenser discharge air temperature	65.0 (18.3)	N/A (N/A)
suction gas temperature	17.4 (-8.1)	17.4 (-8.1)
liquid line temperature	80.2 (26.8)	80.2 (26.8)
compressor efficiency	56.5% (56.5%)	56.5% (56.5%)
compressor shell heat loss	15.0 (15)	N/A (N/A)
Output Data:		
COP	1.16 (1.16)	1.05 (1.05)
evaporating temperature	-36.0°F (-37.8)	-33.0°F (-36.1)
condensing temperature	85.5°F (29.7)	N/A (N/A)
suction pressure	19.2 psia (132 kPa)	19.2 psia (132 kPa)
discharge pressure	191.9 psia (1.32 MPa)	191.9 psia (1.32 mPa)

Acentric Factors

The LKP equation of state computes thermodynamic properties of a fluid using the properties of a "simple" fluid and a "reference" fluid. The acentric factor, ω , is more or less a weighting factor used in combining the known values. The acentric factor can be calculated if the normal boiling point (T_b) is specified (Reid et al. 1987):

$$\omega = \frac{\left[-\ln P_c - 5.97214 + 6.09648 \times \theta^{-1} \right] + 1.28862 \times \ln \theta - 0.169347 \times \theta^6}{\left[15.2518 - 15.6875 \times \theta^{-1} \right] - 13.4721 \times \ln \theta + 0.43577 \times \theta^6} \quad (3)$$

where $\theta = T_b/T_c$ and P_c is the critical pressure (in atmospheres). This estimate can be improved if there are any measured data for saturation pressure, ($P_{sat,i}$), at known temperatures (T_i). Then a least-squares analysis can be performed to find ω_{min} , which minimizes the sum of the squares of the differences between the measured and calculated saturation pressure:

$$f(\omega) = \sum_{i=1}^N [P_{sat}(T_i) - P_{sat,calc}(T_i, \omega)]^2 \quad (4)$$

It is usually much easier to calculate ω_{min} "manually" than it is to set up a computer program to do it. This is done by making an initial guess for ω , calculating N saturation pressures (using a computer program), and computing the corresponding sum of the squares using the known saturation pressures. The process is repeated for a second guess for ω , a third, etc., until little improvement is found in the sum of squares.

Interaction Coefficients

One of the advantages of using a corresponding states method such as the LKP equation of state is that the

interaction coefficients for mixtures of refrigerants can be correlated with some of the fundamental properties of each component. Plöcker et al. (1978) presented data for experimentally determined interaction coefficients for 142 pair-wise mixtures of hydrocarbons, nitrogen, carbon dioxide, hydrogen, argon, oxygen, carbon monoxide, krypton, hydrogen sulfide, nitrous oxide, water, and ammonia. Figure 2 shows Plöcker's data (discrete points) for hydrocarbon-hydrocarbon mixtures plotted against the ratio of the products of the critical temperature (T_c) and critical volume (V_c) for the two components (i and j). This figure also contains a solid line indicating the least-squares polynomial fit to the data. Kruse and Kauffeld (1989) reduced the information in Figure 2 to a Fortran subroutine for use on computers and added information for interaction coefficients for several mixtures of halocarbon refrigerants.

Plöcker's data included interaction coefficients for mixtures of heavy hydrocarbons, so the correlation obtained from Kruse and Kauffeld was modified to be more

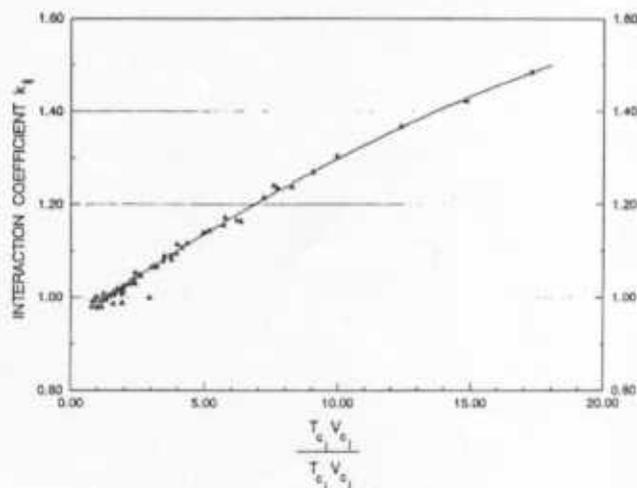


Figure 2 Binary interaction coefficients for hydrocarbon-hydrocarbon mixtures.

TABLE 2

Validation of Saturation Properties for R-12

Temperature		Liquid Enthalpy				Vapor Enthalpy					
		LKP		ASHRAE		% Δ	LKP		ASHRAE		% Δ
-100 F	200 K	152.08 Btu/lb	353.50 kJ/kg	152.24 Btu/lb	353.87 kJ/kg	0.10	230.79 Btu/lb	536.46 kJ/kg	231.05 Btu/lb	537.07 kJ/kg	0.11
-64	220	159.51	370.78	159.58	370.94	0.04	234.85	545.89	235.07	546.40	0.09
-28	240	167.14	388.51	167.08	388.36	-0.04	238.91	555.33	239.10	555.77	0.08
8	260	174.95	406.66	174.80	406.31	-0.09	242.89	564.58	243.07	565.01	0.08
44	280	182.97	425.30	182.82	424.95	-0.08	246.68	573.40	246.90	573.91	0.09
80	300	191.24	444.52	191.20	444.43	-0.02	250.18	581.52	250.47	582.21	0.12
116	320	199.86	464.56	200.01	464.91	0.08	253.21	588.58	253.60	589.49	0.15
152	340	209.01	485.84	209.39	486.71	0.18	255.51	593.93	255.98	595.02	0.18
188	360	219.16	509.42	219.77	510.84	0.28	256.44	596.07	256.92	597.20	0.19

appropriate for the methane- and ethane-based halocarbons used as refrigerants. The calculated binary interaction coefficients are now given by

$$k_{ij} = 0.97593011 + 0.00130196 \cdot \alpha + 0.00860429 \cdot \alpha^2 \quad (5)$$

where

$$\alpha = \frac{T_{c_i} \cdot V_{c_i}}{T_{c_j} \cdot V_{c_j}} \quad (6)$$

Specified interaction coefficients are still used for the binary mixtures for which they are known, and k_{ij} can be derived using a least-squares fit when saturation data are available for a mixture.

Validation

Extensive effort was put into validating the LKP calculations for pure refrigerants, azeotropes (e.g., R-502), and ternary mixtures using property values from public and private sources (private industry sources were required for some of the new refrigerants) (ASHRAE 1985; Bivens 1990; Hughes 1990). Table 2 shows some results for the enthalpies of saturated R-12 liquid and vapor and the percent difference between the reference value and that computed using the LKP equation of state (reference value - LKP value)/reference value).

The differences between the reference values and those from the LKP equation of state for other thermophysical properties (e.g., entropy, specific volume) of R-12 are of the same magnitude as the differences for the enthalpies in Table 2, as are the properties of the most commonly used refrigerants (e.g., R-11, R-22). Figures 3 and 4 show the percent deviations between published data and values calculated using the LKP equation of state for saturated properties for R-502 (an azeotropic mixture of R-22 and R-115) and a ternary blend of R-22, R-152a, and R-124. A comparison of COPs for three different application operating conditions is shown in Table 3 using both properties from ASHRAE publications and the LKP equation of state. Although the results from the LKP equation of state are not

as precise as property values computed from the Martin-Hau or Carnahan-Starling-Desantis equation of state, the LKP values are reasonable considering how little basic information is required to estimate values for each refrigerant. This makes it useful in identifying refrigerants or blends for more thorough experimental and analytical evaluation.

FLAMMABILITY INDEX

One of the presumptions at the outset of this project was that some refrigerant mixtures would need to be considered that contained one or more flammable components, although it was acknowledged that the mixture itself must be nonflammable. It was not possible to make a definitive statement on the flammability of refrigerants in this analysis, but it was possible to make the less precise statements that some proposed blends are probably flammable or nonflammable. The goal, consequently, was to identify refrigerants or mixtures of refrigerants that are probably nonflammable and would be good substitutes for R-502. Once a refrigerant or mixture is identified, then laboratory testing must be done to establish the limits of flammability as well as to verify its performance in a refrigeration system.

A fluorocarbon manufacturer provided an algorithm that estimates a flammability index of a pure compound from its constituent elements and for a mixture from the flammability indices of its components. Although company officials were willing to share the information, representatives requested the algorithm not be published, as it is still under development. Their method was modified so that a compound or mixture with a flammability index of less than 0 would probably be nonflammable, greater than 1 would be flammable, and between 0 and 1 would be of indeterminate flammability.

SCREENING ANALYSIS

The combined CYCLE-10 model and LKP subroutines were used to estimate the performance of mixtures of refrigerants in a freezer system at low-temperature refriger-

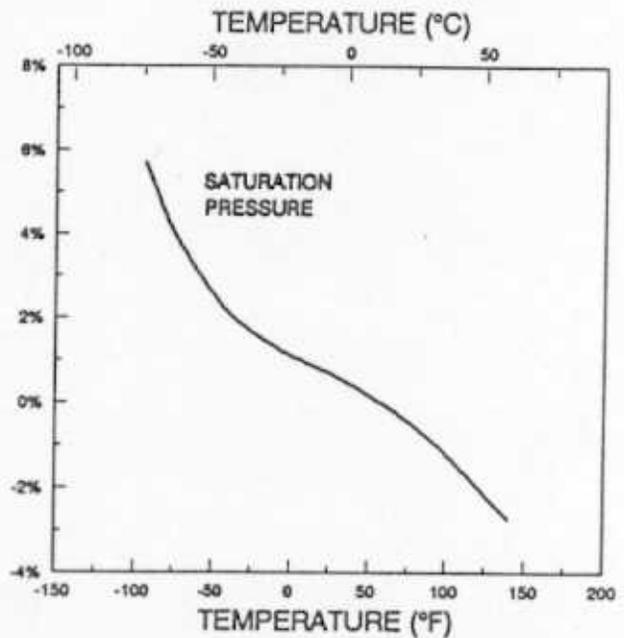
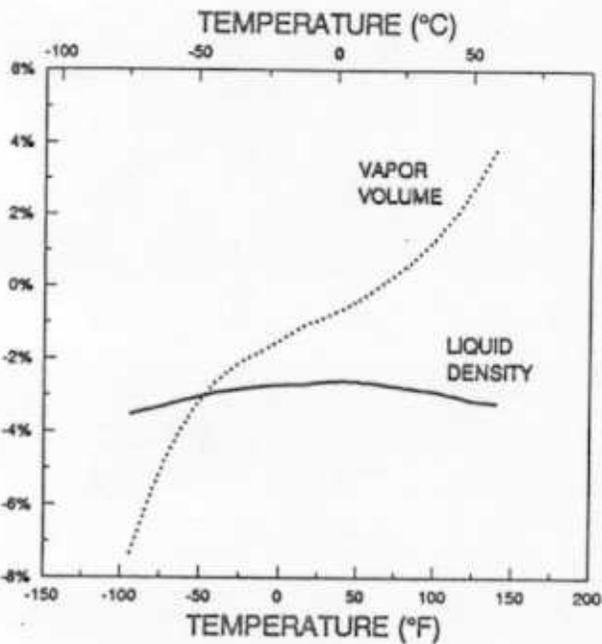
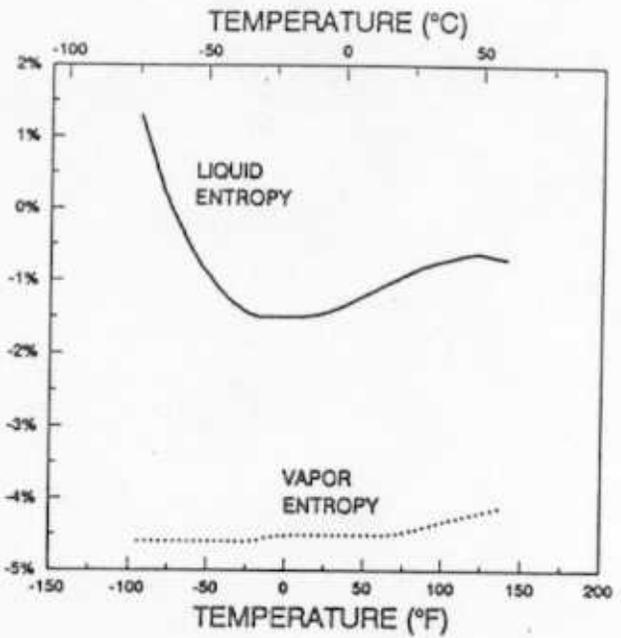
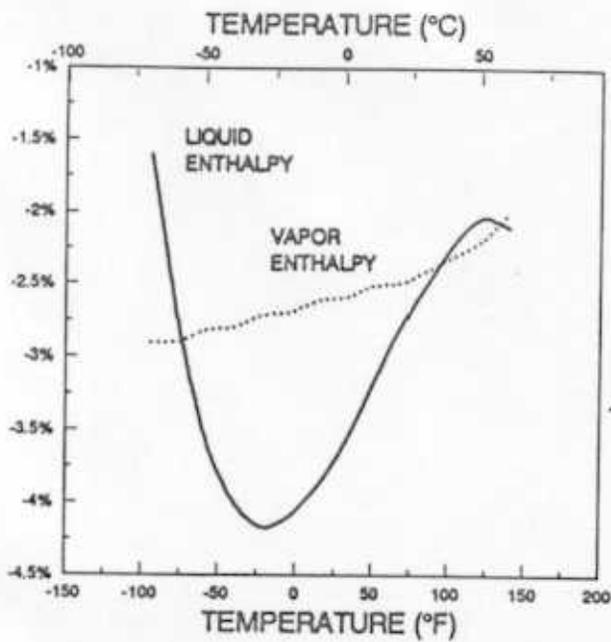


Figure 3 Percent deviation of saturation properties for a binary mixture, R-502, from ASHRAE publications and LKP equation of state ($100\% \times (\text{ASHRAE-LKP})/\text{ASHRAE}$).

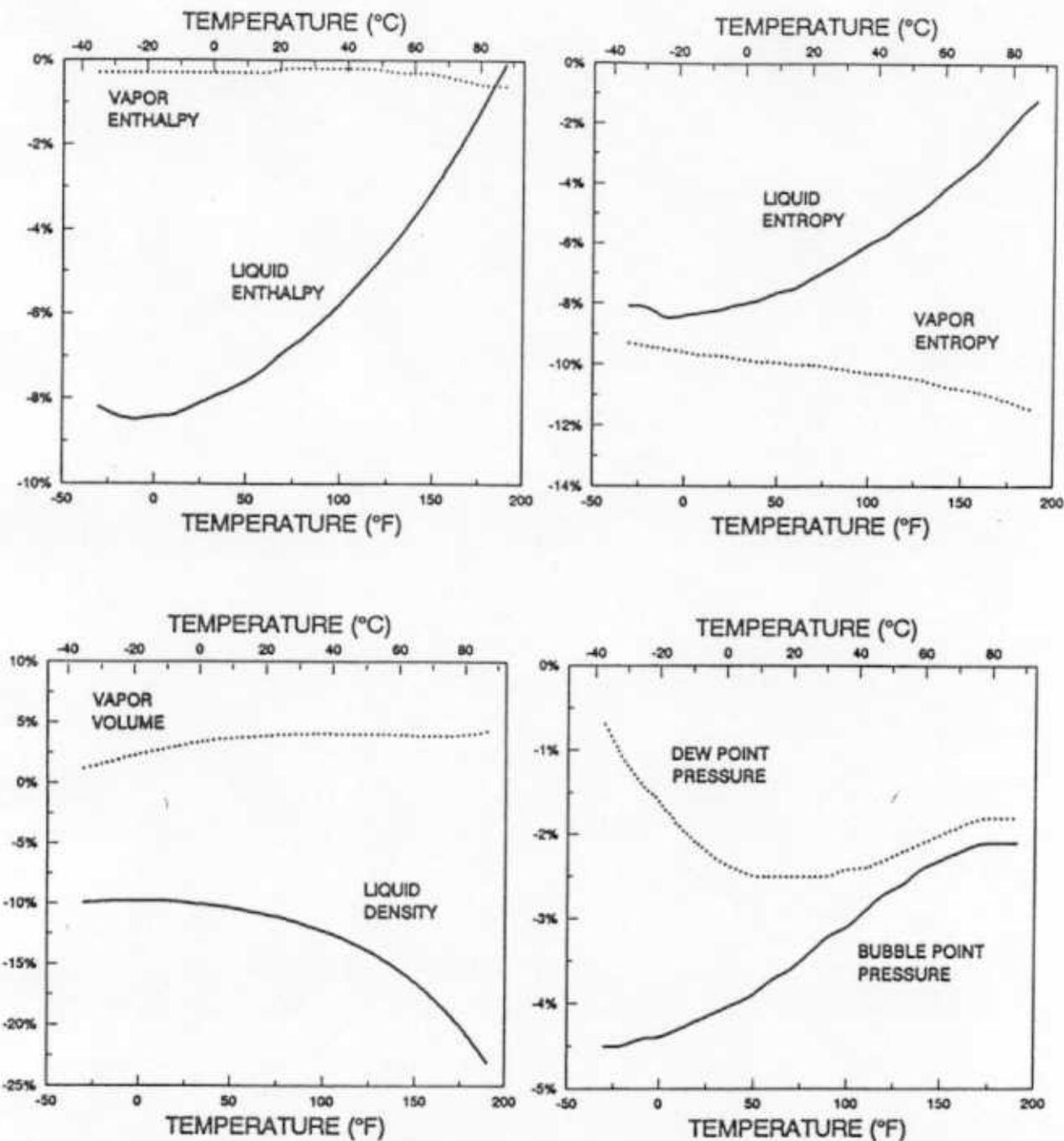


Figure 4 Percent deviation between property values from chemical manufacturer and saturation properties calculated using the LKP equation of state for a ternary blend of refrigerants ($100\% \times (\text{Manufacturer-LKP})/\text{Manufacturer}$).

TABLE 3

Comparison of Cycle Calculations Using ASHRAE Tables and LKP Equation of State							
Application	Refrigerant	Operating Conditions				Calculated Cycle COP	
		Condensing Temperature	Evaporating Temperature	Liquid Temperature	Return Gas Temperature	ASHRAE	LKP
Refrigerator Freezer	R-12	130°F (54.4°C)	-10°F (-23°C)	90°F (32.2°C)	90°F (32.2°C)	2.73	2.75
Air-Conditioner	R-22	110°F (43.3°C)	30°F (-1.1°C)	95°F (35.0°C)	50°F (10°C)	5.14	5.21
Commercial Refrigeration	R-502	105°F (40.6°C)	-40°F (-40°C)	100°F (37.8°C)	65°F (18.3°C)	1.98	2.02

ating conditions. Eight different refrigerants were used in the analysis—five nonflammable and three flammable. These are listed in Table 4. The decision to include R-125 in the candidate refrigerants presented a problem because of its relatively low critical temperature. Operating conditions had to be selected that were acceptable both in a practical sense (i.e., the condensing temperature had to be below the pseudo-critical temperature for the refrigerant or mixture) and in a computational sense (i.e., there were convergence and stability problems as the estimated condensing temperatures approached the critical temperature). Eventually two sets of operating conditions were selected for the screening analysis—one with an air-cooled condenser and one with a water-cooled condenser. The specified input data for the cycle calculations for these two cases are shown in Table 5.

The analysis was performed for pure refrigerants and mixtures of two or three components. No work was done on mixtures containing more than three components. There are 56 different combinations of the eight refrigerants listed in Table 5, taken three at a time, and each unique combination was evaluated with the mass fraction of each of the three components ranging from 100% to 0% in 10% steps. Figure 5 is a diagram illustrating the 66 different

mass fractions of each refrigerant evaluated for three hypothetical compounds—"a," "b," and "c." Besides noting the triangular nature of this diagram, it is worth mentioning that there is a constant mass fraction of compound "a" in each column, a constant percentage of "b" in each block of three rows, and constant values of "c" on the diagonals. Figure 6 shows the results of some of the calculations for R-22, R-125, and R-152a with the columns, rows, and diagonals labeled with the corresponding percentages of each compound and the intersection of "coordinate lines" labeled with the calculated refrigerating COP.

Figure 7 is an adaptation of the data in Figure 6, although in this case lines of constant COP have been drawn by interpolating between the data points in Figure 6 in order to show the dependence of COP on the fraction of each component in the mixture (note that the COPs have been "normalized" so they show 100% of the COP of R-502, 105%, etc.). In this case there is some curvature to the COP contours, although not much, and they go down as the concentration of R-125 increases. Similar contour plots can be drawn showing lines of constant pressure ratio, volumetric capacity, discharge temperature, and flammability.

TABLE 4

Refrigerants Used in R-502 Screening Analysis					
Refrigerant	Molecular Weight	Critical Temperature (°F)	Flammability Index	ODP (relative to R-11)	500 Year GWP (relative to CO ₂)
R-134a	102.03	214.0 (374.3°K)	-0.006	0	420
R-134	102.03	237.2 (387.1°K)	-0.006	0	420*
R-125	120.03	149.0 (338.1°K)	-1.35	0	860
R-124	136.475	252.5 (395.6°K)	-1.40	≤ 0.02	150
R-22	86.496	205.1 (369.3°K)	-1.486	0.02	510
R-152a	66.05	236.3 (386.6°K)	3.82	0	47
R-143a	84.041	163.7 (346.3°K)	1.58	0	1,000
R-32	52.023	173.2 (351.6°K)	1.38	0	47*

* estimated

Reference: IPCC 1990.

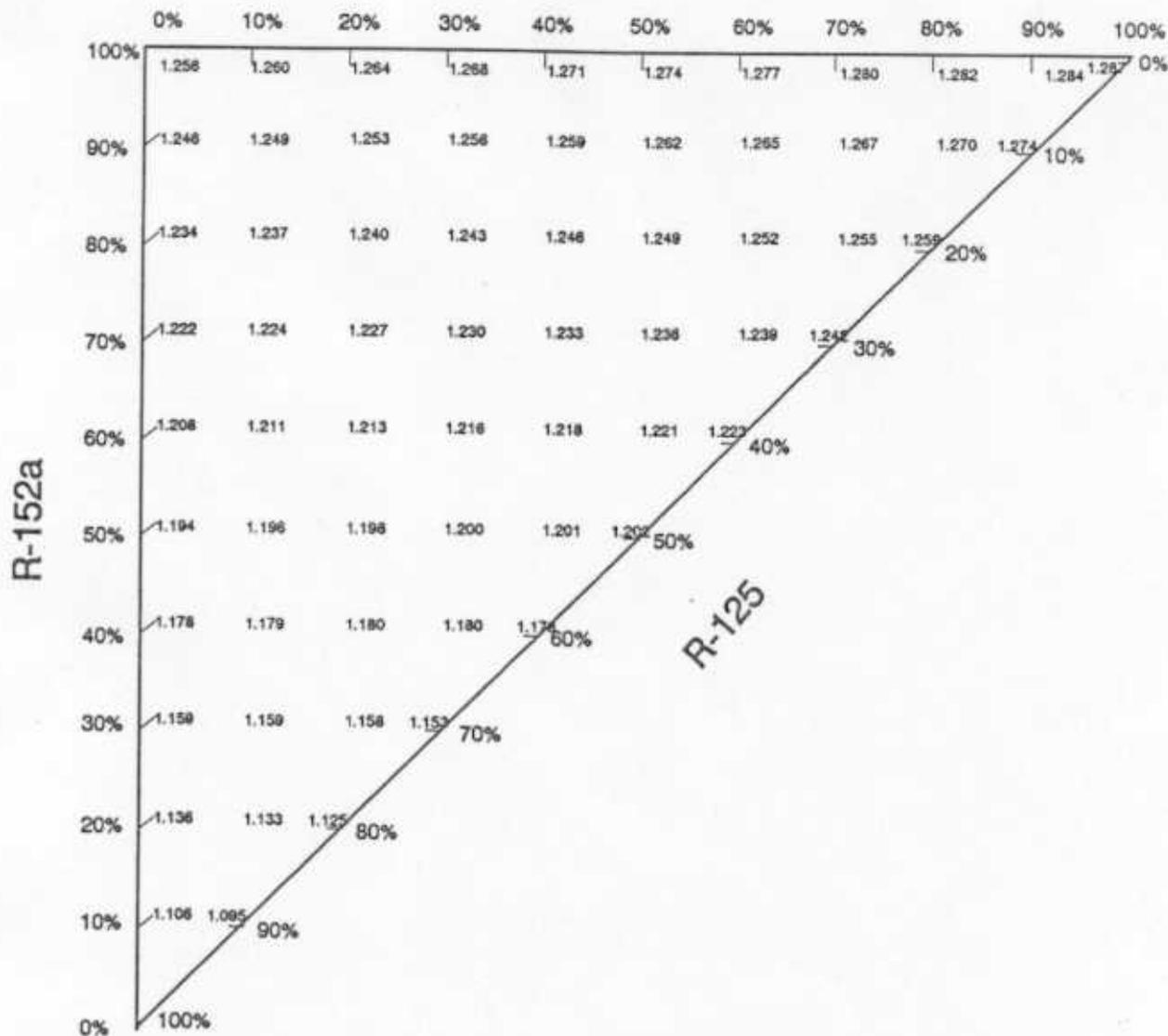
TABLE 5

Cycle-10 Operating Conditions		
	Air-Cooled Condenser	Water-Cooled Condenser
Evaporator:		
inlet air temperature	-15.2°F (-26.2°C)	-15.2°F (-26.2°C)
outlet air temperature	-20.0°F (-29.9°C)	-20.0°F (-28.9°C)
refrigerant-side ΔP	2.0 psia (13.8 kPa)	2.0 psia (13.8 kPa)
LMTD	18.0°F (10°C)	18.0°F (10°C)
Condenser:		
inlet air temperature	75.0°F (23.9°C)	60.0°F (15.6°C)
outlet air temperature	90.0°F (32.2°C)	65.0°F (18.3°C)
refrigerant-side ΔP	2.0 psia (13.8 kPa)	2.0 psia (13.8 kPa)
LMTD	21.6°F (-12.8°C)	16.0°F (8.9°C)
Liquid Line Temperature:	80.2°F (26.8°C)	80.2°F (26.8°C)
Suction Gas Temperature:	17.4°F (-8.1°C)	17.4°F (-8.1°C)
Compressor Efficiency:	56.5%	56.5%
% Input Power to Shell Heat Loss	15.0%	15.0%

0% a	10% a	20% a	30% a	40% a	50% a	60% a	70% a	80% a	90% a	100% a
0% b										
100% c	90% c	80% c	70% c	60% c	50% c	40% c	30% c	20% c	10% c	0% c
0% a	10% a	20% a	30% a	40% a	50% a	60% a	70% a	80% a	90% a	100% a
10% b										
90% c	80% c	70% c	60% c	50% c	40% c	30% c	20% c	10% c	0% c	0% c
0% a	10% a	20% a	30% a	40% a	50% a	60% a	70% a	80% a	90% a	100% a
20% b										
80% c	70% c	60% c	50% c	40% c	30% c	20% c	10% c	0% c	0% c	0% c
0% a	10% a	20% a	30% a	40% a	50% a	60% a	70% a	80% a	90% a	100% a
30% b										
70% c	60% c	50% c	40% c	30% c	20% c	10% c	0% c	0% c	0% c	0% c
0% a	10% a	20% a	30% a	40% a	50% a	60% a	70% a	80% a	90% a	100% a
40% b										
60% c	50% c	40% c	30% c	20% c	10% c	0% c	0% c	0% c	0% c	0% c
0% a	10% a	20% a	30% a	40% a	50% a	60% a	70% a	80% a	90% a	100% a
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50% c	40% c	30% c	20% c	10% c	0% c	0% c	0% c	0% c	0% c	0% c
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40% c	30% c	20% c	10% c	0% c	0% c	0% c	0% c	0% c	0% c	0% c
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20% c	10% c	0% c	0% c	0% c	0% c	0% c	0% c	0% c	0% c	0% c
0% a	10% a	20% a	30% a	40% a	50% a	60% a	70% a	80% a	90% a	100% a
90% b										
10% c	0% c	0% c	0% c	0% c	0% c	0% c	0% c	0% c	0% c	0% c
0% a	10% a	20% a	30% a	40% a	50% a	60% a	70% a	80% a	90% a	100% a
100% b										
0% c										

Figure 5 Mass fractions of components "a," "b," and "c" in R-502 screening analysis.

R-22



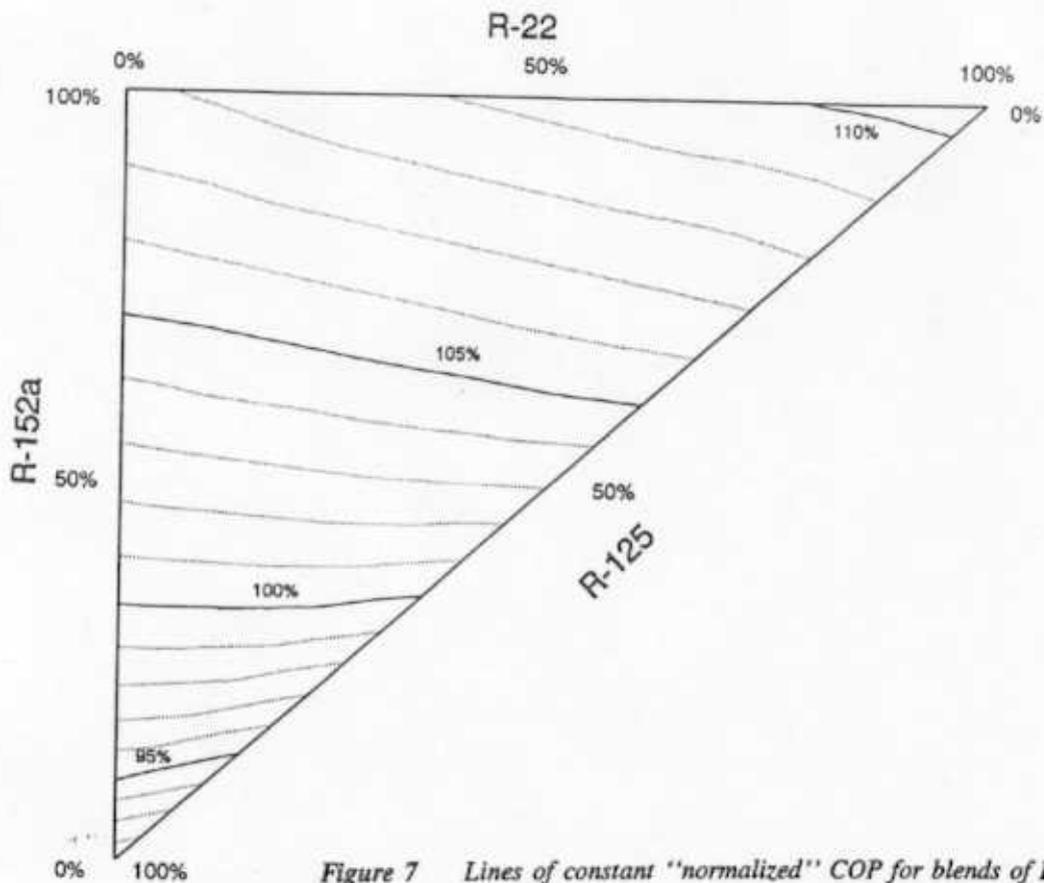


Figure 7 Lines of constant "normalized" COP for blends of R-125, R-22, and R-152a.

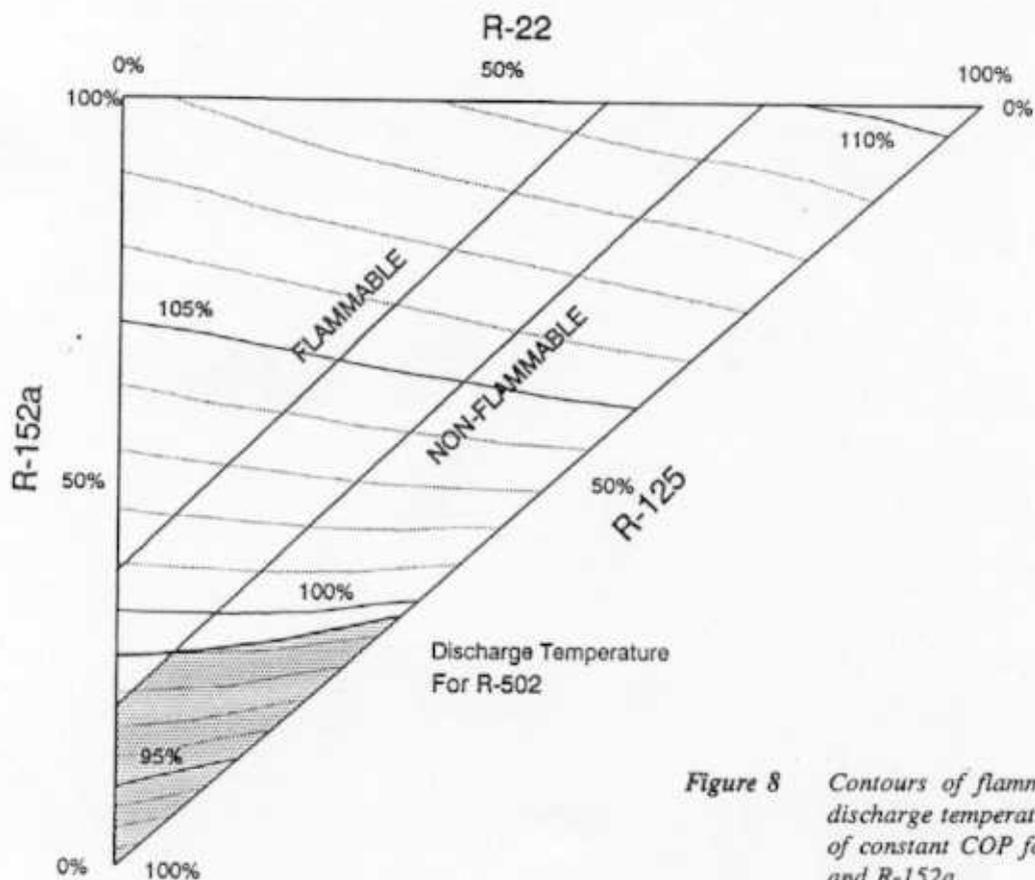


Figure 8 Contours of flammability index and 256°F discharge temperature superimposed on lines of constant COP for blends of R-125, R-22, and R-152a.

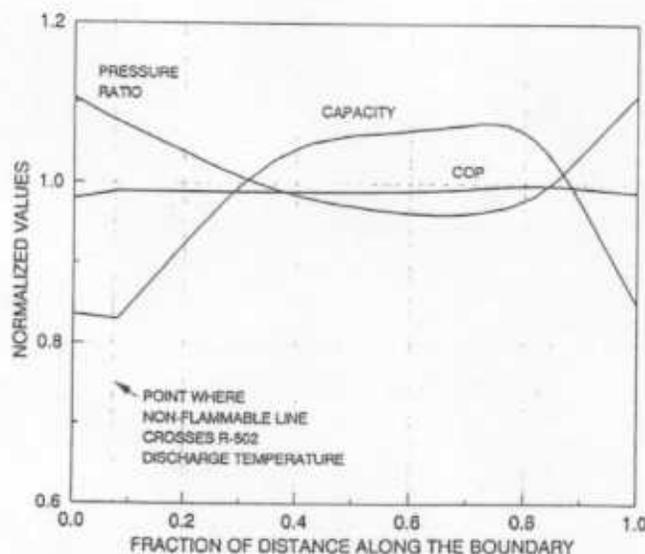


Figure 9 Normalized values of pressure ratio, COP, and volumetric capacity along the boundary of the feasible region for blends of R-125, R-22, and R-152a.

slightly from about 98% of the COP for R-502 to around 102% going up the flammability line until it meets the 256° line; it is fairly constant along the 256° line. Likewise, the pressure ratio starts at about 110% of the pressure ratio for R-502 and increases to about 115% before dropping off along the 256° line. The volumetric capacity drops slightly from 84% before increasing rapidly along the 256° line.

A high priority was placed on maintaining volumetric capacity in each of the cases evaluated. Consequently, the "best" point is a compromise between obtaining the highest COP (as a percentage of that for R-502) while at the same time having nearly the same volumetric capacity and "acceptable" pressure ratio. The mass fractions and coordinates used for locating the boundary in Figure 9 are listed in Table 6. The "distances" from one point to the next, shown in the fourth column, are computed using the standard "Euclidean norm" from plain geometry using the horizontal and vertical coordinates x and y :

$$d = \sqrt{(x_i - x_{i-1})^2 + (y_i - y_{i-1})^2} \quad (7)$$

The fifth column in Table 6 is the cumulative sum of the preceding distances in the fourth column, and the sixth column is the values for the cumulative sums for the distance of each point from the first point divided by the distance of the last point from the first point (0.355), the total distance. The data in the last four columns are what is used to create the plot in Figure 9. The corresponding data for flammability and discharge temperature are given in Table 7. In this case it can be seen from the tables and graph that the best composition is 69% R-125, 27% R-22, and 4% R-152a.

Results

Similar analyses were performed for each of the 56 combinations of refrigerants mentioned earlier for both the air-cooled condenser operating conditions and the water-cooled condenser conditions. These results are listed in Tables 8 and 9. The best of the results for air-cooled condensers are summarized in Table 10 and those for evaporative condensers in Table 11. These two tables give the composition of each promising mixture, the normalized COP, pressure ratio, and volumetric capacity; the ozone-depleting potential for the mixture (ODP); the global warming potential (GWP); and what has been identified as the azeotropic ΔT .

Pure compounds boil (evaporate) or condense at a constant temperature for any given pressure; the dew-point temperature and the bubble-point temperature are the same. Azeotropic mixtures are blends of two or more compounds that condense or evaporate at fixed temperatures like pure compounds. The columns labeled "Azeotropic ΔT " in Tables 10 and 11 show the difference between the dew-point and bubble-point temperatures across a range of pressures from 10 to 300 psia (68.9 to 2070 kPa). Calculations for R-502 across this same pressure range show differences between the dew-point and bubble-point temperatures of 0.01° to 0.19°F (0.00° to 0.11°C), essen-

TABLE 6

Coordinates and Data Values along the Boundary of the Feasible Region for Blends of R-125, R-22, and R-152a in Figure 8

Mass Fraction R-125	Mass Fraction R-22	Mass Fraction R-152a	Distance from Previous Point	Distance Along the Boundary	Fraction of the Distance Along the Boundary	Normalized Capacity	Normalized Pressure Ratio	Normalized COP
0.795	0.000	0.205	0.000	0.000	0.000	0.838	1.113	0.981
0.723	0.068	0.209	0.099	0.099	0.279	0.829	1.125	0.994
0.708	0.193	0.099	0.126	0.225	0.634	0.940	1.048	0.994
0.706	0.200	0.094	0.007	0.232	0.654	0.944	1.045	0.994
0.700	0.228	0.072	0.029	0.261	0.735	0.972	1.027	0.995
0.691	0.269	0.040	0.042	0.303	0.853	1.019	1.000	0.996
0.684	0.300	0.016	0.032	0.335	0.943	1.056	0.979	0.996
0.680	0.320	0.000	0.020	0.355	1.000	1.083	0.964	0.995

TABLE 7

Mass Fractions of R-125, R-22, and R-152a Used in Figure 9							
Mass Fraction R-125	Mass Fraction R-22	Mass Fraction R-152a	Flammability Index	Discharge Temperature (°F)	Normalized Capacity	Normalized Pressure Ratio	Normalized COP
0.795	0.000	0.205	0.000	248.9 (120.5°C)	0.838	1.113	0.981
0.723	0.068	0.209	0.000	256.0 (124.4°C)	0.829	1.125	0.994
0.708	0.193	0.099	0.000	256.0 (124.4°C)	0.940	1.048	0.994
0.706	0.200	0.094	-1.402	256.0 (124.4°C)	0.944	1.045	0.994
0.700	0.228	0.072	-0.815	256.0 (124.4°C)	0.972	1.027	0.995
0.691	0.269	0.040	-1.267	256.0 (124.4°C)	1.019	1.000	0.996
0.684	0.300	0.016		256.0 (124.4°C)	1.056	0.979	0.996
0.680	0.320	0.000		256.0 (124.4°C)	1.083	0.964	0.995

tially the same, so R-502 is an azeotropic mixture of R-22 and R-115.

The significance of azeotropes in refrigerating equipment is that if there are any leaks in the system, each of the components in the refrigerant mixture will escape at the same rate and the overall composition of the blend will remain the same. This requirement places another constraint on the screening analysis. Not only must the blend have a high COP, the same volumetric capacity, acceptable discharge temperature, and flammability, it must also have a small "azeotropic ΔT ." Although none of the blends listed in Tables 10 and 11 is a true azeotrope, several of them do have very small differences between their dew-point and bubble-point temperatures, and consequently these "near azeotropes" may be of interest.

Oil Return

An additional problem that must be addressed concerns the return of oil back to the compressor in a large refrigerating system. The velocity of the refrigerant, particularly the vapor in the suction risers, must be high enough that it sweeps the lubricant along and returns it to the compressor. The refrigerant velocities can be adjusted to some extent by the selection of pipe sizes, and this is perhaps more of a problem in the modification of an installed system than it is in new equipment. Although it has not been looked at yet, an evaluation of the refrigerant densities of the proposed alternatives should be made to determine how they compare with that of R-502 to see if there are significant differences that could affect oil return.

CONCLUSIONS

Several refrigerant mixtures have been identified that are promising alternatives to R-502 in both new and existing low-temperature refrigerating systems. This preliminary analytical evaluation shows that they should exhibit comparable properties with R-502 with regard to their operating efficiency, compressor discharge tempera-

ture, flammability, pressure ratio, and volumetric capacity. These conclusions are based only on calculations from the existing property data. Further work needs to be done, primarily in the laboratory, to support or refute the findings from this screening study. This work should be focused on R-32 and R-125, both as pure compounds and in binary mixtures with R-22 and in ternary blends with R-22, and either R-134a or R-134.

ACKNOWLEDGMENTS

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TABLE 8
Complete Results for Low-Temperature Refrigeration Using a Water-Cooled Condenser

Mixture Composition						Normalized Values		
First Component		Second Component		Third Component		Volumetric Capacity	Pressure Ratio	COP
R-32	13.8%	R-125	59.4%	R-143a	26.8%	122%	95%	98%
R-32	0.0%	R-125	67.4%	R-22	32.6%	108%	97%	100%
R-125	26.3%	R-143a	45.2%	R-22	28.5%	111%	95%	100%
R-32	9.3%	R-125	80.7%	R-152a	10.0%	102%	103%	99%
R-125	60.3%	R-22	29.5%	R-134a	10.2%	100%	100%	100%
R-143a	0.0%	R-22	0.0%	R-134a	100.0%	48%	149%	101%
R-125	70.3%	R-22	20.3%	R-152a	9.4%	85%	111%	99%
R-125	79.5%	R-143a	0.0%	R-152a	20.5%	90%	107%	96%
R-32	11.8%	R-125	66.5%	R-134a	21.7%	100%	106%	99%
R-32	13.7%	R-125	80.9%	R-134	5.4%	112%	100%	98%
R-125	43.0%	R-134a	57.0%	R-134	0.0%	67%	127%	97%
R-125	20.0%	R-134	13.3%	R-124	66.7%	31%	182%	98%
R-125	10.0%	R-134a	24.5%	R-124	65.5%	31%	183%	98%
R-125	65.4%	R-22	30.0%	R-124	4.6%	101%	101%	99%
R-134a	38.7%	R-134	0.0%	R-124	61.3%	31%	183%	98%
R-125	62.9%	R-22	30.1%	R-134	7.0%	100%	102%	99%
R-22	5.2%	R-134a	54.8%	R-134	40.0%	48%	149%	101%
R-22	0.8%	R-134	70.0%	R-124	29.2%	32%	182%	98%
R-22	2.0%	R-134a	80.0%	R-124	18.0%	48%	149%	101%
R-143a	100.0%	R-152a	0.0%	R-134	0.0%	48%	150%	101%
R-125	79.5%	R-152a	20.5%	R-134	0.0%	84%	111%	98%
R-134a	90.0%	R-152a	0.0%	R-134	10.0%	47%	147%	101%
R-125	50.8%	R-143a	36.2%	R-134a	13.0%	100%	97%	94%
R-125	71.5%	R-134a	10.0%	R-152a	18.5%	84%	111%	98%
R-143a	0.0%	R-134a	100.0%	R-134	0.0%	48%	149%	101%
R-32	0.0%	R-134a	100.0%	R-134	0.0%	48%	149%	101%
R-22		R-152a		R-134		no acceptable blends		
R-22		R-152a		R-124		no acceptable blends		
R-125	65.1%	R-152a	20.3%	R-124	14.6%	68%	125%	98%
R-134a	90.0%	R-152a	1.9%	R-124	8.1%	46%	145%	101%
R-22	1.3%	R-134a	98.7%	R-152a	0.0%	48%	149%	101%
R-152a	0.0%	R-134	70.0%	R-124	30.0%	32%	182%	98%
R-125	49.0%	R-143a	41.5%	R-124	9.5%	95%	100%	93%
R-143a	0.0%	R-22	0.0%	R-134	100.0%	32%	180%	98%
R-143a	40.9%	R-22	0.0%	R-124	59.1%	56%	140%	97%
R-143a	34.0%	R-134	0.0%	R-124	66.0%	43%	161%	96%
R-143a	34.0%	R-134a	0.0%	R-124	66.0%	40%	159%	97%
R-32		R-22		R-134		no acceptable blends		
R-32	0.0%	R-22	0.0%	R-134a	100.0%	48%	149%	101%
R-32		R-22		R-124		no acceptable blends		
R-32	13.5%	R-125	82.6%	R-124	3.9%	112%	100%	98%
R-32	0.0%	R-134	60.0%	R-124	40.0%	31%	182%	98%
R-32	0.0%	R-134a	80.0%	R-124	20.0%	48%	149%	101%
R-143a	0.0%	R-152a	0.0%	R-134	100.0%	32%	181%	98%
R-32	0.0%	R-152a	0.0%	R-134	100.0%	32%	181%	98%
R-32	0.0%	R-143a	0.0%	R-134	100.0%	32%	181%	98%
R-143a	0.0%	R-134a	100.0%	R-152a	0.0%	48%	150%	101%
R-32	0.0%	R-134a	100.0%	R-152a	0.0%	48%	149%	101%
R-32	0.0%	R-143a	0.0%	R-134a	100.0%	48%	149%	101%
R-143a	38.5%	R-152a	1.2%	R-124	60.3%	47%	153%	96%
R-32		R-22		R-152a		no acceptable blends		
R-143a		R-22		R-152a		no acceptable blends		
R-32	0.0%	R-143a	40.6%	R-124	59.4%	49%	151%	96%
R-32		R-152a		R-124		no acceptable blends		
R-32		R-143a		R-22		no acceptable blends		
R-32		R-143a		R-152a		no acceptable blends		

TABLE 9
Complete Results for Low-Temperature Refrigeration Using an Air-Cooled Condenser

Mixture Composition			Normalized Values		
First Component	Second Component	Third Component	Volumetric Capacity	Pressure Ratio	COP
R-32 14.6%	R-125 85.4%	R-143a 0.0%	119%	95%	98%
R-32 0.0%	R-125 68.0%	R-22 32.0%	108%	97%	100%
R-125 68.0%	R-143a 0.0%	R-22 32.0%	108%	97%	100%
R-32 8.3%	R-125 80.0%	R-152a 11.7%	100%	104%	99%
R-125 60.6%	R-22 28.6%	R-134a 10.8%	100%	99%	100%
R-143a 0.0%	R-22 0.0%	R-134a 100.0%	48%	157%	101%
R-125 68.0%	R-22 32.0%	R-152a 0.0%	106%	98%	100%
R-125 60.6%	R-143a 30.1%	R-152a 9.3%	97%	101%	96%
R-32 13.2%	R-125 76.8%	R-134a 10.0%	110%	100%	99%
R-32 13.4%	R-125 80.0%	R-134 6.6%	110%	100%	98%
R-125 89.2%	R-134a 0.0%	R-134 10.8%	94%	102%	94%
R-125 92.0%	R-134 0.0%	R-124 8.0%	91%	105%	93%
R-125 87.1%	R-134a 12.9%	R-124 0.0%	94%	103%	93%
R-125 66.2%	R-22 30.0%	R-124 3.8%	102%	100%	99%
R-134a 20.0%	R-134 8.9%	R-124 71.1%	36%	183%	99%
R-125 64.6%	R-22 30.0%	R-134 5.4%	102%	100%	99%
R-22 3.5%	R-134a 60.0%	R-134 36.5%	48%	157%	101%
R-22	R-134	R-124			
R-22 1.9%	R-134a 70.0%	R-124 28.1%	48%	157%	101%
R-134a 18.7%	R-152a 0.1%	R-134 81.2%	36%	182%	99%
R-125 66.3%	R-152a 17.1%	R-134 16.6%	73%	121%	98%
R-134a 18.7%	R-152a 0.1%	R-134 81.2%	36%	182%	99%
R-125 42.5%	R-143a 23.3%	R-134a 34.2%	87%	111%	96%
R-125 55.4%	R-134a 30.2%	R-152a 14.4%	73%	122%	99%
R-143a 10.0%	R-134a 8.5%	R-134 81.5%	36%	183%	99%
R-32 0.0%	R-134a 100.0%	R-134 0.0%	39%	176%	99%
R-22	R-152a	R-134	no acceptable blend		
R-22	R-152a	R-124	no acceptable blend		
R-143a	R-22	R-134	no acceptable blend		
R-143a 0.0%	R-22 0.0%	R-134a 100.0%	48%	157%	101%
R-143a 41.6%	R-22 4.6%	R-124 53.8%	53%	140%	98%
R-143a 16.0%	R-134 82.8%	R-124 1.2%	38%	180%	97%
R-143a 21.1%	R-134a 0.0%	R-124 78.9%	34%	190%	97%
R-143a	R-22	R-134	no acceptable blend		
R-143a 41.6%	R-22 4.6%	R-124 53.8%	53%	148%	98%
R-143a 20.0%	R-134 2.2%	R-124 77.8%	42%	171%	98%
R-143a 21.1%	R-134a 0.0%	R-124 78.9%	34%	190%	97%
R-32	R-22	R-134	no acceptable blend		
R-32 0.0%	R-22 0.0%	R-134a 100.0%	48%	157%	101%
R-32	R-22	R-124			
R-32 13.3%	R-125 82.2%	R-124 4.5%	110%	100%	98%
R-32	R-134	R-124	no acceptable blend		
R-32 0.7%	R-134a 70.0%	R-124 29.3%	48%	157%	101%
R-143a	R-152a	R-134	no acceptable blend		
R-32	R-152a	R-134	no acceptable blend		
R-32 0.0%	R-143a 100.0%	R-134	no acceptable blend		
R-32 0.0%	R-134a 100.0%	R-152a 0.0%	48%	157%	101%
R-32 0.0%	R-143a 0.0%	R-152a 0.0%	48%	157%	101%
R-143a 34.7%	R-152a 3.1%	R-134a 100.0%	48%	157%	101%
		R-124 62.2%	45%	158%	98%
R-32	R-22	R-152a	no acceptable blend		
R-143a	R-22	R-152a	no acceptable blend		
R-32 1.5%	R-143a 39.3%	R-124 59.2%	49%	154%	98%
R-32	R-152a	R-124	no acceptable blend		
R-32	R-143a	R-22	no acceptable blend		
R-32					
R-32	R-143a	R-152a	no acceptable blend		

TABLE 10
Detailed Results for the Most Promising Blends for Use with an Air-Cooled Condenser

Composition			Azeotropic ΔT	ODP	GWP	Normalized Values		
First Component	Second Component	Third Component				COP	Pressure Ratio	Volumetric Capacity
14.6% R-32	85.4% R-125	0.0% R-143a	0.2 - 0.7 °F (0.1-0.4°C)	0	740	0.98	0.95	1.25
68.0% R-125	32.0% R-22	0.0% R-32	0.3 - 0.7 °F (0.2-0.4°C)	0.02	750	1.00	0.97	1.08
60.6% R-125	28.6% R-22	10.8% R-134a	1.2 - 3.4 °F (0.7-1.9°C)	0.01	710	1.00	0.99	1.00
64.6% R-125	30.0% R-22	5.4% R-134	1.4 - 3.4 °F (0.8-1.9°C)	0.02	730	0.99	1.00	1.02
13.2% R-32	76.8% R-125	10.0% R-134a	1.7 - 2.8 °F (0.9-1.6°C)	0	710	0.99	1.00	1.10
66.2% R-125	30.0% R-22	3.8% R-124	1.8 - 4.2 °F (1.0-2.3°C)	0.01	730	0.99	1.00	1.02
13.4% R-32	80.0% R-125	6.6% R-134	2.1 - 3.7 °F (1.2-2.1°C)	0	720	0.98	1.00	1.10
13.3% R-32	82.2% R-125	4.5% R-124	2.6 - 4.7 °F (1.4-2.6°C)	0.01	720	0.98	1.00	1.10
8.3% R-32	80.0% R-125	11.7% R-152a	3.2 - 5.9 °F (1.8-3.3°C)	0	700	0.99	1.04	1.00

TABLE 11
Detailed Results for the Most Promising Blends for Use with a Water-Cooled Condenser

Composition			Azeotropic ΔT	ODP	GWP	Normalized Values		
First Component	Second Component	Third Component				COP	Pressure Ratio	Volumetric Capacity
13.8% R-32	59.4% R-125	26.8% R-143a	0.0 - 0.4°F (0.0-0.2°C)	0	790	0.98	0.95	1.22
67.4% R-125	32.6% R-22	0.0% R-32	0.3 - 0.7°F (0.2-0.4°C)	0.02	750	1.00	0.97	1.08
26.3% R-125	45.2% R-143a	28.5% R-22	0.3 - 0.7°F (0.2-0.4°C)	0.01	720	1.00	0.95	1.11
60.3% R-125	29.5% R-22	10.2% R-134a	1.2 - 3.2°F (0.7-1.8°C)	0.01	850	1.00	1.00	1.00
50.8% R-125	36.2% R-143a	13.0% R-134a	1.2 - 3.7°F (0.7-1.8°C)	0	850	0.94	0.97	1.00
62.9% R-125	30.1% R-22	7% R-134	1.7 - 4.2°F (0.9-2.3°C)	0.01	720	0.99	1.02	1.00
13.7% R-32	80.9% R-125	5.4% R-134	1.9 - 3.1°F (1.1-1.7°C)	0	720	0.98	1.00	1.12
65.4% R-125	30.0% R-22	4.6% R-124	2.1 - 5.0°F (1.2-2.8°C)	0.02	720	0.99	1.01	1.01
13.5% R-32	82.6% R-125	3.9% R-124	2.3 - 4.1°F (1.3-2.3°C)	0.00	720	0.98	1.00	1.12
9.3% R-32	80.7% R-125	10.0% R-152a	2.9 - 5.1°F (1.6-2.8°C)	0	700	0.99	1.03	1.02
11.8% R-32	66.5% R-125	21.7% R-134a	2.9 - 5.9°F (1.6-3.3°C)	0	670	0.99	1.06	1.00

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DISCUSSION

S.A. Klein, Professor, Department of Mechanical Engineering, University of Wisconsin, Madison: Please provide more details on the LKP model and how it handles nonidealities in the liquid phase.

Steven K. Fischer: The intricacies of how nonidealities are handled in the liquid phase of the LKP code are covered in a paper by Lee and Kesler (*AIChE J.* 1975, 21(3): 510) and Plöcker's doctoral dissertation from the University of

Berlin (1977). A detailed explanation of the mathematics is best left to a physical chemist, but the LKP code uses a fugacity value for the liquid phase that is represented in a similar manner to that used for the gas. A Pitzer accentric factor, ω , is used to quantify deviation functions relative to two reference fluids for reduced values of the liquid volumes in addition to enthalpies, entropies, etc. An English translation of Plöcker's dissertation is available from either myself or Jim Sand.