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REFRIGERANT MIXTURES AS HCFC-22 ALTERNATIVES

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SUMMARY

A recent international assessment of the atmospheric science has provided a basis to accelerate the chlorofluorocarbon (CFC) phase-out. In addition, the assessment provided a basis for advancing the phase-out schedule for long-lived hydrochlorofluorocarbons (HCFCs) such as chlorodifluoromethane (HCFC-22). The objective of this study was to identify potential alternatives to HCFC-22 and evaluate their performance in a room air conditioner. Computer model simulations of a theoretical refrigeration cycle suggested that a mixture of hydrofluorocarbons (HFCs) might perform the same as HCFC-22. The air conditioner test results indicate that mixtures may be used as alternatives to HCFC-22.

INTRODUCTION

HCFC-22 has been widely used in the air conditioning industry especially in residential unitary and central air conditioning systems for many years. In the United States approximately 5 million room air conditioners are sold each year, and most of them are used for residential service. /1/

Because HCFC-22 has been readily available, low cost, and less harmful to the environment than CFCs, it has become the alternative of choice for many new applications. For example, HCFC-22 is currently being used for some commercial and transport refrigeration applications which traditionally used R-502, new design industrial chillers which traditionally used CFC-11, and some stationary medium temperature applications which traditionally used CFC-12.

Recently, scientific information has indicated that ozone is being depleted over latitude bands that encompass the United States at faster rates than anticipated. /2/ This finding has increased concern over the potential long-term effects of certain long-lived HCFCs (such as HCFC-22) on atmospheric ozone concentrations.

Based on this new information, Du Pont Company Fluorochemicals announced intentions to discontinue sale of HCFC-22 for all but service applications by January 1, 2005 and for all applications by January 1, 2020.

Because HCFC-22 is used in a large variety of applications, more than one alternative may be needed to provide optimum performance for all applications. This study will focus on identifying possible HFC alternatives to HCFC-22 for use in residential cooling applications.

REFRIGERANT ALTERNATIVES CYCLE PERFORMANCE

A search was conducted to identify nonflammable compounds or mixtures which provided the same refrigeration capacity and energy efficiency as HCFC-22 at the ARI air conditioning and heat pump rating points. /3/ No single nonflammable compound was identified which provided the same theoretical capacity and energy efficiency as HCFC-22 (see figure I): HFC-134a was the only nonflammable refrigerant which offered a similar energy efficiency with about a 35% lower refrigeration capacity based on the same compressor displacement. Several HFC mixtures have been proposed as HCFC-22 alternatives based on model calculations (see figure II). /4/



A mixture of HFC-32 and HFC-134a offered the closest match in theoretical capacity and energy efficiency compared with HCFC-22 while having the potential to be nonflammable. The mixture of 32 weight% (wt%) HFC-32 and 68 wt% HFC-134a is a zeotropic mixture, having a bubble point/dew point temperature difference of 6 C (11 F) at a pressure of 620 kPa (90 psia).

Many questions have been raised concerning the use of zeotropic refrigerant mixtures such as HFC-32/HFC-134a for use in refrigeration equipment. In order to verify the model calculations and answer some of these concerns, we decided to compare the performance of this mixture in a room air conditioner designed to use HCFC-22.

AIR CONDITIONER AND INSTRUMENTATION

The air conditioner was rated by the manufacturer to have a cooling capacity of 4787 kcal/hr (19000 btu/hr). The unit was equipped with a rotary compressor, accumulator, and the evaporator and condenser each had three circuits.

The air conditioner was set up in an environmentally controlled chamber so that the dry and wet bulb temperatures could be held constant and/or adjusted during the experiments. /5/ The temperatures were varied over a wide operating range in order to study the effects on performance.

The air conditioner was not modified except to accommodate for the instrumentation necessary to take measurements. A schematic of the instrumentation is provided in Figure III.



Figure III

Several thermocouples and pressure transducers were installed for making measurements around the cycle. Using these measurements with our thermodynamic model allowed us to calculate the enthalpy at each point. A coriolis type mass flow meter was installed in the liquid line before the capillary tubes and several sample ports were added for liquid and vapor phase samples. These samples were later run on a gas chromatograph (GC) to check mixture composition.

A power meter was used to measure the volts and amperes drawn by the air conditioner. The power meter software calculated the watts drawn and applied a power factor to adjust for any distorted waveforms. The refrigeration capacity was calculated by taking the enthalpy difference across the evaporator times the mass flow rate. The energy efficiency ratio (E.E.R.) was calculated by dividing the refrigeration capacity by the total energy consumption. A data acquisition system was used to process the measurements.

The rotary compressor was charged with naphthenic mineral oil. The HFC refrigerants have little to no miscibility with mineral oil, but the oil was not changed in order to eliminate effects of different lubricants. Also, we wanted to determine if the air conditioner could operate during the test period with an immiscible refrigerant/lubricant combination.

TEST PROCEDURES

The first set of experiments were conducted to verify our measuring techniques. The system was evacuated with a two-stage vacuum pump and charged with 1100 grams of HCFC-22 (recommended nameplate charge size). The mass flow rate and capacity measurements were compared with the performance curves provided by the compressor manufacturer (see figures IV and V). The measurements agreed within +/- 4% for mass flow and +/- 5% for capacity. This small difference was probably due to the oil circulation through the mass flow meter. Based on this close agreement we had confidence in our measurement techniques and began evaluating the mixtures.



Figure IV



Figure V

The air conditioner was operated over a range of indoor and outdoor conditions and the steady-state performance measured at each condition.

To ensure there were no slow leaks which might alter performance measurements or change the mixture composition, the HCFC-22 charge was recovered in a cylinder cooled in a dry ice/acetone bath. The charge was weighed and over 98% was recovered.

A mixture of 32 wt% HFC-32 and 68 wt% HFC-134a was prepared in the lab by weight and composition checked with a gas chromatograph. The mixture was charged into the air conditioner liquid phase by inverting the cylinder which had a vapor only valve. The material was charged through the sample port at the inlet to the accumulator (see figure III). In order to determine the optimum charge size the mixture was added in small increments and the refrigeration capacity and E.E.R. plotted as a function of charge size. The optimum charge size for the HFC-32/HFC-134a mixture was 943 grams.

The air conditioner was operated at the same conditions as HCFC-22 and steady-state performance measured at each condition. To determine if the mixture composition changes around the cycle during operation, several samples were taken while the air conditioner was running. The refrigerant charge was recovered using the same method and the composition analyzed.

PERFORMANCE RESULTS

Figure VI provides a comparison of the experimental measurements between HCFC-22 and the HFC-32/HFC-134a mixture.

HCFC-22 and HFC-32/HFC-134a had an average capacity of 4938 and 4888 kcal/hr (19600 and 19400 btu/hr), respectively. HCFC-22 and HFC-32/HFC-134a both had an average E.E.R. of 3.0 (10.5 btu/hr/W). The average deviation in the capacity measurement was +/- 100 kcal/hr (400 btu/hr) and the E.E.R. deviation was +/- 0.05 (0.2 btu/hr/W). The compressor discharge line temperature was measured 10.2 cm (4 inches) from the compressor shell. The HFC-32/HFC-134a mixture had an average compressor discharge line temperature of about 9 C (16 F) lower than HCFC-22. The compression ratios for HCFC-22 and HFC-32/HFC-134a were 2.79 and 2.89, respectively.

The evaporator and condenser inlet and outlet pressures were measured and the overall pressure drop for both refrigerants calculated. The HFC-32/HFC-134a mixture had about the same percent pressure drop as HCFC-22 (3.8% versus 3.9% in the evaporator and 6.8% versus 6.4% in the condenser). The average evaporating and condensing temperatures were calculated by using the average pressures. Both HCFC-22 and HFC-32/HFC-134a had the same average evaporating and condensing temperatures of 9 C (48 F) and 48 C (118 F), respectively.

The mass flow rate for the HFC-32/HFC-134a mixture was about 10% lower than HCFC-22 because the suction gas density is about 10% lower (22.6 kg/m3 (1.41 lb/ft3) at 18.3 C (65 F) and 627 kPa (90.9 psia) versus 25.5 kg/m3 (1.59 lb/ft3) at 18.3 C (65 F) and 642 kPa (93.1 psia), respectively). The overall power consumption for the HFC-32/HFC-134a mixture was also slightly lower than HCFC-22.

	HCFC-22	HFC-32/HFC-1348
Capacity kcal/hr, (Btu/hr)	4938 (19600)	4888 (19400)
E.E.R. W/W, (Btu/hr/W)	3.0 (10.5)	3.0 (10.5)
Comp. Discharge Temp. C, (F)	96 (205)	87 (189)
euro talat Bree kPs (osia)	667 (96.8)	651 (94.4)
Outlet Pres kPa, (psia)	642 (93.1)	627 (90.9)
oned latet Pres kPa. (psia)	1890 (274.1)	1885 (273.4)
Outlet Pres kPa, (psia)	1772 (257.0)	1761 (255.4)
Compression Ratio	2.79	2.89
Mass Flow kg/hr, (lb/hr)	114.2 (251.6)	102.7 (226.1)
Power Consumption Watts	1864	1868

Figure VI

Figure VII and VIII are graphs of the evaporator and condenser temperature profiles. The temperature glide in the two-phase region can be seen with the HFC-32/HFC-134a mixture.

The exact temperature glides were difficult to determine from the limited number of thermocouples; however, the values seem to be near the calculated values of about 6 C (11 F) in the condenser and 5.5 C (10 F) in the evaporator.



Distance along Evaporator

---- HCFC-22 ---- HFC-32/HFC-134a

Figure VII



Distance along Condenser

--- HCFC-22 -+- HFC-32/HFC-134a

Figure VIII

Several refrigerant samples were taken while the air conditioner was in operation. The first set of samples were from the liquid line just before the mass flow meter with no refrigerant flashing in the accumulator (inactive). The second set of samples were taken at a low ambient condition with refrigerant flashing in the accumulator (active). We compared these samples with the initial refrigerant charged and within the accuracy of the GC method (+/- 0.3 wt%) did not see any composition charges in the liquid line samples (see Figure IX). Therefore, liquid in the accumulator (internal volume of 722 cc) had no effect on the circulating liquid composition.

Sample	Mixture Cor	nposition (wt%)
	HFC-32	HFC-134a
Initial Charge	32.2	67.8
Accumulator Inactive Liquid Line	32.1	67.9
Accumulator Active Liquid Line	32.2	67.8

Figure IX

FLAMMABILITY TESTING AND VAPOR/LIQUID MEASUREMENTS

The flammable limits for HFC-32 in HFC-134a were measured according to the ASTM 681 E test method. /6/ The liquid and vapor compositions for mixtures of HFC-32/HFC-134a were calculated at various temperatures to ensure that the flammable component HFC-32 did not exceed the flammability limit.

The maximum nonflammable HFC-32 concentration in HFC-134a at atmospheric pressure was about 56 wt% at room temperature and about 52 wt% at 80 C (176 F). The vapor composition of a cylinder containing 30 wt% HFC-32 and 70 wt% HFC-134a was calculated over a range of temperatures between -25 C (-13 F) and 40 C (104 F). The vapor composition was also calculated for a mixture containing 25 wt% HFC-32 and 75 wt% HFC-134a.





Figure X shows that at room temperature and above a mixture of 30 wt% HFC-32 and 70 wt% HFC-134a crosses the 80 C flammability boundary. At a temperature of about -20 C (-4 F) the same mixture crosses the room temperature boundary. A mixture containing 25 wt% HFC-32 and 75 wt% HFC-134a remained below both flammability boundaries. Therefore, mixtures of HFC-32 and HFC-134a which contain in excess of 25 wt% HFC-32 in the liquid phase may have a flammable vapor space under certain conditions.

Using the refrigeration cycle model, a mixture of 25 wt% HFC-32 and 75 wt% HFC-134a would have a capacity about 9% lower than HCFC-32 with the same energy efficiency. The lower capacity could be increased to HCFC-32 capacity mechanically by increasing the compressor displacement or chemically by adding HFC-125. A ternary mixture of 30 wt% HFC-32, 10 wt% HFC-125, and 60 wt% HFC-134a should provide the same capacity and energy efficiency as HCFC-32 based on model calculations. Adding small amounts of HFC-125 allows more HFC-32 to be added to HFC-134a because it lowers the HFC-32 concentration in the vapor space and acts as a better flammability suppressant. The ternary mixture remains below the flammability limits over the range of temperatures studied.

CONCLUSIONS

The objective of this study was to identify alternatives to HCFC-22 and evaluate their performance in a room air conditioner.

A mixture of 32 wt% HFC-32 and 68 wt% HFC-134a provided the same performance as HCFC-22 in a unmodified room air conditioner. The tests verified the cycle calculations which showed the mixture should have the same capacity, energy efficiency, and about a 9 C lower compressor discharge temperature compared with HCFC-22.

The tests proved that no major equipment changes may be necessary in order to switch from HCFC-22 to a zeotropic mixture such as HFC-32/HFC-134a in certain applications such as room air conditioners. The air conditioner operated with an immiscible refrigerant/lubricant combination with no apparent effects on performance for almost 1000 hours; however, polyol ester lubricants may be required for long-term acceptable compressor durability.

Refrigerant samples taken before and after operation suggest that zeotropic mixtures such as HFC-32/HFC-134a can be charged and recovered with no measurable composition changes. Also, no composition changes were detected during operation from samples taken at the liquid line.

Flammability tests and vapor/liquid composition measurements show that mixtures of HFC-32/HFC-134a which contain in excess of 25 wt% HFC-32 may be flammable under certain conditions.

A mixture of 25 wt% HFC-32 and 75 wt% HFC-134a would have about a 9% lower capacity with the same energy efficiency as HCFC-22. The lower capacity could be increased to HCFC-22' capacity by increasing the compressor displacement or by adding HFC-125. A ternary mixture of 30 wt% HFC-32, 10 wt% HFC-125, and 60 wt% HFC-134a may provide the same capacity and energy efficiency as HCFC-22, while remaining below the flammability limits over the range of temperatures studied. Based on cycle calculations and tests results, these mixtures as well as HFC-134a were nominated to the ARI task force which is investigating potential HCFC-22 alternatives. /7/ The next step is to verify the performance of the ternary mixture and test the mixtures in other applications such as unitary heat pumps.

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