

# Performance Evaluation of Two Azeotropic Refrigerant Mixtures of HFC-134a With R-290 (Propane) and R-600a (Isobutane)

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*The reduction in chlorofluorocarbon (CFC) and hydrochlorofluorocarbon (HCFC) production and the scheduled phase-out of these ozone-depleting refrigerants require the development and determination of environmentally safe refrigerants for use in heat pumps, water chillers, air conditioners, and refrigerators. This paper presents a performance evaluation of a generic heat pump with two azeotropic refrigerant mixtures of HFC-134a (1,1,1,2-tetrafluoroethane) with R-290 (propane) and R-600a (isobutane); R-290/134a (45/55 by mass percentage) and R-134a/600a (80/20 by mass percentage). The performance characteristics of the azeotropes were compared with pure CFC-12, HFC-134a, HCFC-22, and R-290 at the high temperature cooling and heating conditions including those using liquid-line/suction-line heat exchange. The coefficient of performance of R-290/134a is lower than that of HCFC-22 and R-290, and R-134a/600a shows higher coefficient of performance than CFC-12 and HFC-134a. The capacity for R-290/134a is higher than that for HCFC-22 and R-290, and R-134a/600a exhibits higher system capacity than CFC-12 and HFC-134a. Experimental results show that the discharge temperatures of the studied azeotropic mixtures are lower than those of the pure refrigerants, CFC-12 and HCFC-22.*

## 1 Introduction

In the search for alternative refrigerants, emphasis has been put on finding safe (i.e., nonflammable and nontoxic), chlorine-free, single-component fluids with saturation pressures similar to those of the refrigerants which are replaced. The most successful, to date, has been the development of HFC-134a as an alternative to CFC-12. However, even this alternative has its limitations if it is intended as a "drop-in" for existing CFC-12 machines. Most significant is the lack of mineral oil solubility with this or any other chlorine-free refrigerant. Although ester-based lubricants have been developed recently, in the drop-in application (i.e., one in which an alternative would be used in existing equipment originally designed for a CFC), a thorough flushing of the mineral oil would be necessary, which may prove difficult if not impractical in many cases. Also, this ethane-based alternative refrigerant has, inherently, a lower evaporator vapor pressure and a less steep liquid saturation pressure curve on a pressure-enthalpy diagram than the methane-based CFC-12. Theoretically, this implies more flash gas during the expansion process and a lower suction gas density, thus a loss in capacity relative to CFC-12. The HCFC-22 alternative search has been far more difficult, with no known single component fluid having a reasonably

close saturation pressure curve. As a result, mixing of two or more components to obtain all the desired working fluid properties has become important. Several zeotropic mixtures of compositions resulting in vapor pressures similar to HCFC-22 are the only possible drop-ins known at the present time (Domanski and Didion, 1993). These are being evaluated by industry rather reluctantly because of the inherent complexity of maintaining the design composition in the field during leakage and partial recharging operations.

Among the different types of mixtures, azeotropes are preferred because they retain both vapor and liquid at the same composition throughout the phase change; consequently, they are no different from single-component refrigerants for all practical purposes. However, virtually all of the halogenated hydrocarbon azeotropic pairs have been identified (Morrison and McLinden, 1993), and so it is interesting to explore halogenated hydrocarbon and hydrocarbon pairs to determine if any of their azeotropes can match the performance of the fluids slated for elimination. Such a search has a high likelihood of success because azeotropes are most likely to exist between molecules with large differences in polarity.

Hydrocarbons are natural refrigerants which are environmentally safe and will not have to be recycled. Incorporating a hydrocarbon within an azeotrope is also likely to offer the additional advantage of making the mixture soluble with mineral oil. Thus, if this type of azeotrope has a similar performance to the refrigerant it is replacing, it could act as a true

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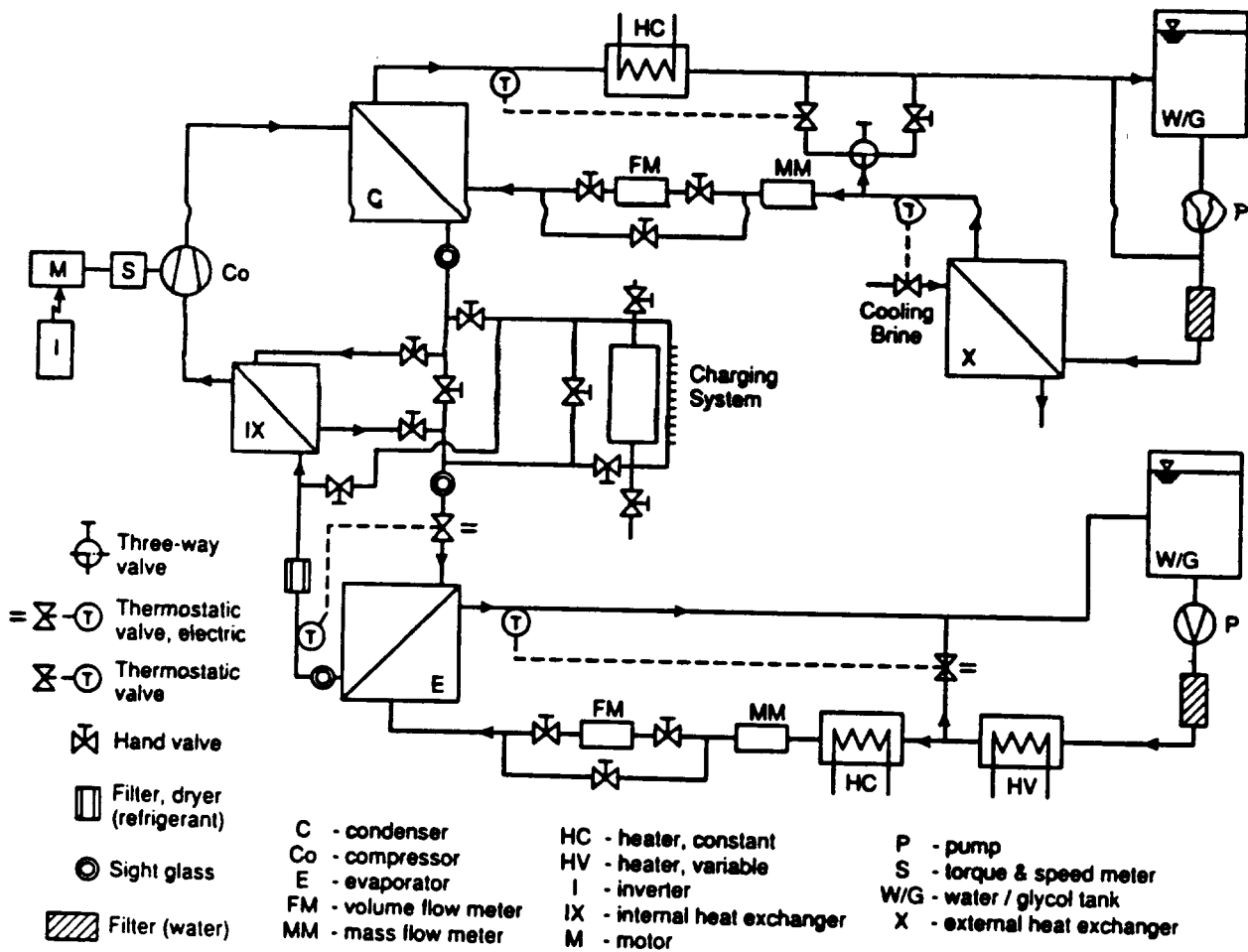


Fig. 1 Schematic diagram of the mini-breadboard heat pump test rig

drop-in. Of course, the disadvantage of using a high percentage of hydrocarbon in any mixture is that it is likely to be flammable. Although current practice does not include the use of flammable refrigerants for residential or commercial applications, many industrial applications do. Furthermore, the presence of the halogen atoms will certainly mitigate the flammability hazards, by reducing the combustion energy and flammability limits, compared with the pure hydrocarbons.

The quantification of the relative performance factors, particularly coefficient of performance (COP) and capacity of two such azeotropes, is the subject of this paper.

## 2 Laboratory Performance Evaluation

The experimental mini-breadboard heat pump test setup was comprised of compressor, condenser, expansion device, and evaporator, as shown in Fig. 1, and is described in detail by Pannock and Didion (1992). A reciprocating open compressor was driven by a variable-speed motor and a shaft torque meter was installed between the compressor and the motor. The condenser and the evaporator were tube-in-tube, concentric-type, counterflow heat exchangers. The refrigerant flowed inside the inner tube of the heat exchangers and a water/ethylene glycol mixture was pumped through the annulus. As an expansion

device, a manually adjusted needle valve was used in the system to control the flow rate of refrigerant and the pressure levels. A liquid-line/suction-line heat exchanger was installed so that the refrigerant could flow either to the expansion device directly or through this heat exchanger to the expansion device. The liquid-line/suction-line heat exchanger was used to subcool the condensed liquid refrigerant by superheating the low-temperature refrigerant vapor leaving the evaporator.

The test conditions in this study are based upon the high-temperature cooling or heating conditions described in ASHRAE standard 116 (ASHRAE, 1983). For the high-temperature cooling condition, the inlet temperatures of the heat transfer fluids (HTF) were chosen as in the ASHRAE standard and the choice of outlet temperatures of the heat transfer fluids were based on previous experiments (Pannock and Didion, 1992). These temperatures are shown in Table 1. For the high-temperature heating condition, inlet temperatures were chosen as in the ASHRAE standard and outlet temperatures were obtained based on the same flow rates of the heat transfer fluids as used in the high-temperature cooling tests. The heating mode tests were conducted with reversed heat transfer fluid flow rates; that is, the evaporator flow rate for the heating condition was the same as the condenser flow rate for the cooling condition, and the condenser flow rate for the heating

## Nomenclature

COP = coefficient of performance =  $\dot{Q}/\dot{W}$   
 $\dot{Q}$  = transferred heat per unit time (W)  
 $\dot{W}$  = compressor power (W)

## Subscripts

$h$  = heat pumping  
 $r$  = refrigeration

**Table 1 High-temperature cooling and heating conditions**

Position	High Temperature Cooling Condition (°C)	High Temperature Heating Condition (°C)
Condenser Inlet	35.0	21.1
Condenser Outlet	43.2*	VFRE
Evaporator Inlet	26.7	8.3
Evaporator Outlet	14.4*	VFRC

VFRC : Volume flow rate of heat transfer fluid in condenser  
 VFRE : Volume flow rate of heat transfer fluid in evaporator  
 \* : Selected value

**Table 2 Mini-breadboard heat pump test results (high-temperature cooling condition)**

Refrigerant	HCFC-22		R-290		R-290/134a	
	NO	YES	NO	YES	NO	YES
Composition					44.1/55.9	43.2/56.8
Cooling COP	4.733	4.786	5.130	5.277	4.425	4.713
Cooling capacity, W	2743.3	2799.3	2469.2	2512.7	2757.3	2926.2
Compressor speed, rpm	1000.2	1000.4	1001.0	1000.2	1000.2	999.9
Compressor power, W	579.6	584.9	481.3	489.4	623.1	620.9
Evap. HTF inlet T, °C	26.7	26.7	26.7	26.7	26.7	26.7
Evap. HTF outlet T, °C	14.4	14.4	14.4	14.4	14.4	14.4
Cond. HTF inlet T, °C	35.0	35.1	35.0	35.0	35.0	35.0
Cond. HTF outlet T, °C	43.2	43.2	43.2	43.3	43.1	43.2
Comp. suction P, bar	6.72	6.74	6.59	6.61	7.84	7.85
Comp. discharge P, bar	17.34	17.39	15.49	15.35	19.15	18.94
Discharge P/suction P	2.581	2.578	2.351	2.321	2.443	2.413
Comp. discharge T, °C	79.9	89.6	64.0	73.2	65.4	73.9
Cond. subcool, °C	2.1	2.3	2.7	2.5	2.4	2.2
Evap. superheat, °C	14.3	14.6	13.4	13.6	14.1	14.0
Cond. P drop, bar	0.47	0.39	0.18	0.26	0.38	0.40
Evap. P drop, bar	0.53	0.48	0.28	0.25	0.49	0.44
Refrigerant	CFC-12		HFC-134a		R-134a/600a	
LSHX	NO	YES	NO	YES	NO	YES
Composition					81.1/18.9	82.4/17.6
Cooling COP	4.259	4.533	4.369	4.690	4.406	4.748
Cooling capacity, W	1657.0	1755.0	1807.7	1899.7	1926.1	2078.1
Compressor speed, rpm	1006.2	1003.6	1002.2	1001.1	1002.5	1000.6
Compressor power, W	389.1	387.2	413.8	405.0	437.2	437.7
Evap. HTF inlet T, °C	26.7	26.7	26.7	26.7	26.7	26.7
Evap. HTF outlet T, °C	14.3	14.4	14.4	14.4	14.3	14.4
Cond. HTF inlet T, °C	35.1	35.0	35.0	35.0	35.0	35.0
Cond. HTF outlet T, °C	43.3	43.2	43.2	43.2	43.1	43.2
Comp. suction P, bar	4.16	4.20	4.11	4.14	4.88	4.89
Comp. discharge P, bar	10.97	10.97	11.44	11.38	12.69	12.82
Discharge P/suction P	2.637	2.610	2.785	2.751	2.601	2.618
Comp. discharge T, °C	67.1	78.3	65.2	73.0	61.6	70.5
Cond. subcool, °C	1.7	3.0	2.0	3.4	2.5	2.3
Evap. superheat, °C	13.2	13.2	13.7	13.8	12.7	12.9
Cond. P drop, bar	0.32	0.30	0.32	0.31	0.31	0.40
Evap. P drop, bar	0.38	0.37	0.36	0.31	0.39	0.33

condition was the evaporator flow rate for the cooling condition.

In order to obtain comparable test data, condenser subcooling was adjusted as close to the saturation as possible, which ranged from 1.7 to 4.6 °C in practice, as shown in Tables 2 and 3. Also, evaporator superheating was maintained at 14 °C for the cooling tests and 8 °C for the heating tests. To obtain these conditions, the expansion valve opening as well as the refrigerant charge were adjusted. The compressor speed was kept constant at 1000 rpm for all tests in order to simulate relative drop-in performance in a constant speed compressor system. The operating conditions and test results are given in Tables 2 and 3 for the high-temperature cooling and heating conditions, respectively.

The refrigerant mixture composition was measured by extracting a small amount of vapor from the compressor discharge line during steady-state operation. The sample was evaluated with a gas chromatograph.

### 3 Performance Test Results and Discussion

**3.1 Thermodynamic Properties.** The search for azeotropes among the multitude of possible candidates from two

**Table 3 Mini-breadboard heat pump test results (high-temperature heating condition)**

Refrigerant	HCFC-22		R-290		R-290/134a	
	NO	YES	NO	YES	NO	YES
Composition					44.3/55.7	44.0/56.0
Heating COP	5.335	5.414	5.625	5.825	5.100	5.341
Heating capacity, W	2404.1	2406.8	2168.7	2226.7	2482.4	2572.0
Compressor speed, rpm	1001.5	1000.5	1000.7	1000.5	1000.3	1001.2
Compressor power, W	450.6	444.6	385.6	382.3	486.7	481.5
Evap. HTF inlet T, °C	8.3	8.3	8.3	8.3	8.3	8.3
Evap. HTF outlet T, °C	3.1	3.0	3.0	2.9	3.1	2.9
Cond. HTF inlet T, °C	21.1	21.1	21.1	21.1	21.1	21.1
Cond. HTF outlet T, °C	31.9	31.7	31.9	31.7	32.2	31.9
Comp. suction P, bar	4.76	4.78	4.73	4.74	5.63	5.63
Comp. discharge P, bar	12.90	12.74	11.61	11.48	14.58	14.19
Discharge P/suction P	2.710	2.663	2.455	2.420	2.588	2.519
Comp. discharge T, °C	68.9	78.2	52.8	63.4	52.2	63.1
Cond. subcool, °C	2.3	2.3	2.8	2.8	2.9	2.5
Evap. superheat, °C	8.4	8.3	7.9	7.9	8.2	8.4
Cond. P drop, bar	0.35	0.33	0.25	0.24	0.31	0.33
Evap. P drop, bar	0.37	0.30	0.19	0.17	0.34	0.31
Refrigerant	CFC-12		HFC-134a		R-134a/600a	
LSHX	NO	YES	NO	YES	NO	YES
Composition					81.2/18.8	81.5/18.5
Heating COP	4.755	5.004	4.844	5.114	4.972	5.315
Heating capacity, W	1464.6	1514.1	1556.1	1570.7	1697.1	1746.9
Compressor speed, rpm	1003.3	1003.3	1002.0	1002.5	1001.9	1000.8
Compressor power, W	308.0	302.6	321.2	307.2	341.3	328.7
Evap. HTF inlet T, °C	8.3	8.3	8.3	8.3	8.3	8.3
Evap. HTF outlet T, °C	3.0	3.2	3.2	3.0	3.2	3.0
Cond. HTF inlet T, °C	21.1	21.1	21.1	21.1	21.1	21.1
Cond. HTF outlet T, °C	31.9	31.8	31.8	31.3	32.0	31.5
Comp. suction P, bar	2.94	2.98	2.82	2.83	3.43	3.41
Comp. discharge P, bar	7.99	8.00	8.16	8.11	9.39	9.24
Discharge P/suction P	2.714	2.683	2.899	2.867	2.738	2.713
Comp. discharge T, °C	58.4	68.6	54.8	62.5	50.9	59.7
Cond. subcool, °C	4.1	4.6	3.1	2.1	3.8	2.5
Evap. superheat, °C	8.4	8.1	8.0	7.9	7.7	7.8
Cond. P drop, bar	0.25	0.23	0.26	0.25	0.23	0.24
Evap. P drop, bar	0.28	0.27	0.21	0.20	0.27	0.24

different chemical families and the various possible compositions, of each of the candidates selected, quickly becomes unwieldy. Therefore, several ground rules for selection must be established even if only binary pairs are to be considered, as was the case here. First, only simple molecules were considered so as to keep the specific heat relatively close to that of the CFC; otherwise, the amount of flash gas and superheat in the fluid's basic vapor compression cycle will render for performance so low in COP that the system will be noncompetitive (McLinden and Didion, 1987). Both fluids to be matched together should have reasonably close or slightly higher normal boiling points (NBP) to the CFC. This is because when azeotropes do occur in these fluids, they are usually high-pressure (i.e., low-temperature) azeotropes. An acceptable drop-in candidate should have a vapor pressure as close as possible to that of the CFC to achieve a similar capacity in the same machine. Using these simple rules and the thermodynamic property program (Gallagher et al., 1991), it was possible to determine the candidate binaries and the compositions at which they form azeotropes.

Figure 2 presents bubble and dew point pressures with respect to composition for the R-290/134a mixture at several different temperatures. In Fig. 2, a maximum in pressure for each constant temperature curve, that is, a point higher in pressure than either of the two pure fluids of which the mixture is comprised, is observed. It is also observed that at the maximum, the point of azeotropic composition, the dew and bubble lines touch and are tangent. At this point, the compositions of the vapor and liquid phases are identical; that defines the azeotrope (Morrison and McLinden, 1993). For the temperature range of refrigerating, air conditioning, and heat pumping applications, the azeotropic point is approximately 45 percent pro-

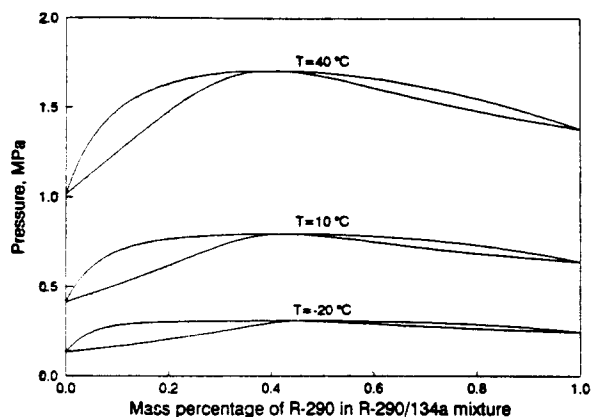


Fig. 2 Pressure with respect to composition diagram of the R-290/134a mixture

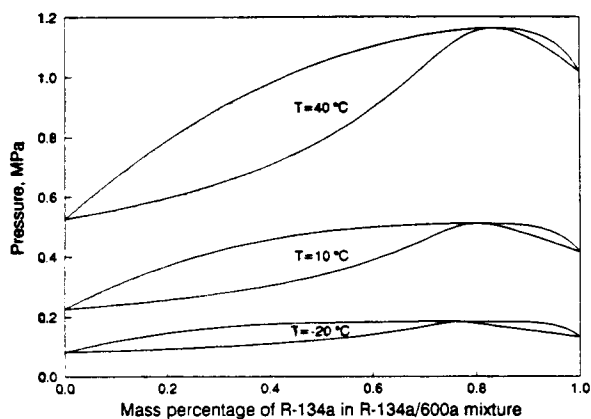


Fig. 3 Pressure with respect to composition diagram of the R-134a/600a mixture

pane by weight. As the temperature increases, the azeotropic composition shifts to the lean R-290, i.e., rich HFC-134a direction, which means the azeotropic composition changes as the pressure or temperature changes; but it is regarded as a near-azeotrope (Didion and Bivens, 1990) for engineering applications.

Figure 3 shows the bubble and dew point pressures with respect to composition for the R-134a/600a mixture at several different temperatures. Each constant temperature curve displays a pressure maximum. For each temperature considered, the azeotropic composition is approximately 80 percent HFC-134a by weight. As the temperature increases, the azeotropic composition shifts to the rich HFC-134a direction.

The compositions of the azeotropes in this study were determined by measuring the saturation pressures at known temperatures, two-phase densities, and compositions near the azeotropic point (maximum pressure being at the azeotropic point). The binary interaction coefficients regressed from this data were then used in the property calculation program (Gallagher et al., 1991).

The saturation pressure curves of the refrigerants are shown in Fig. 4. As indicated in the previous figures, these fluids form high-pressure azeotropes; thus the saturation pressure of R-290/134a is higher than that of either HCFC-22 or R-290, and the saturation pressure of R-134a/600a is higher than that of CFC-12, HFC-134a, or R-600a. Theoretically, a higher saturation pressure implies a working fluid with a higher volumetric capacity. This trend was reflected in the test results (see Figs. 8 and 9).

**3.2 High-Temperature Cooling Test Results.** In this test, the inlet temperature of the heat transfer fluid entering the condenser was maintained at 35.0 °C, and that entering the

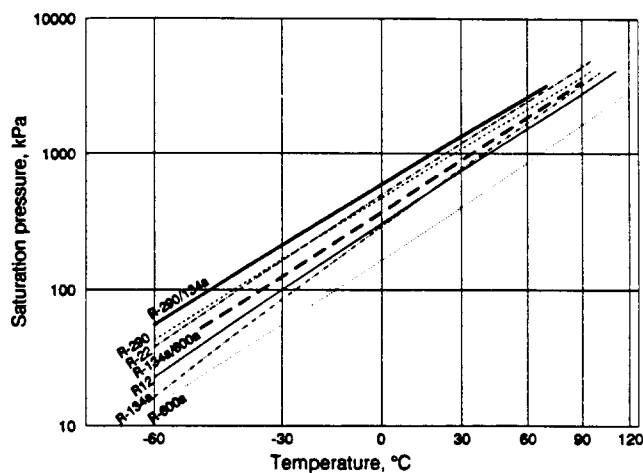


Fig. 4 Saturation pressure curves for several refrigerants

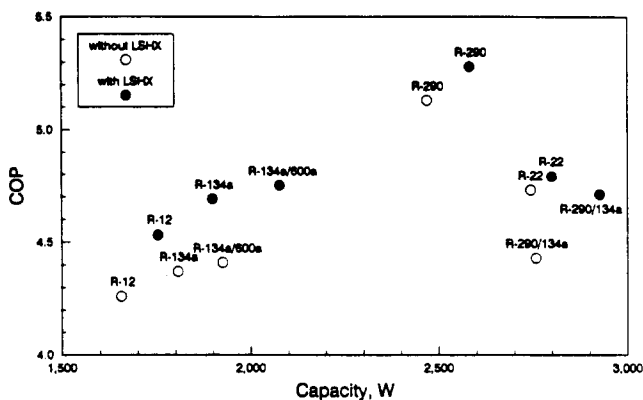


Fig. 5 Cooling COP with respect to cooling capacity at the high-temperature cooling condition (by experiment)

evaporator was kept at 26.7 °C. The outlet temperatures, chosen based on the previous experiment (Pannock and Didion, 1992), were 43.2 °C and 14.4 °C, respectively. The test results for all fluids are presented in Fig. 5. The cooling capacity is the amount of heat ( $Q_c$ ) that is removed from the water/ethylene glycol stream within the evaporator per unit time. The cooling capacity was calculated by measuring the temperature difference across the evaporator and the mass flow rate of secondary heat transfer fluid. The coefficient of performance (COP) is defined as the capacity ( $Q_c$ ) divided by the actual shaft work input to the compressor per unit time ( $W$ ). Detailed test data are presented in Table 2.

It is reasonable to categorize the fluids into two capacity groups for comparison, of which the first is HCFC-22 and its replacements, R-290 and R-290/134a, and the second is CFC-12 and its replacements, HFC-134a and R-134a/600a.

The cooling capacity of R-290/134a is greater than that of HCFC-22 or R-290 as would be expected of a higher pressure refrigerant. The cooling capacity is closely related to the product of the density of the vapor entering the compressor and the latent heat at the evaporator pressure, which is the greatest for R-290/134a. The cooling capacity of R-134a/600a is greater than that of CFC-12 or HFC-134a.

The coefficient of performance for R-290/134a is smaller than that for HCFC-22 and R-290, which is mainly due to the increased compression work per unit time as shown in Table 2. The work required in compression per unit time is closely related to suction pressure, volume flow rate of suction gas, pressure ratio, etc., among which suction pressure is a dominant factor at the test condition in this study. In spite of the increased cooling capacity, the COP is smaller for R-290/134a mixture. For R-134a/600a, the coefficient of performance is greater than that for CFC-12 and HFC-134a.

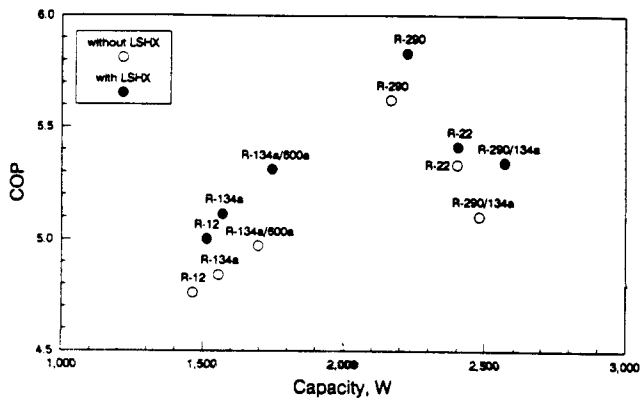


Fig. 6 Heating COP with respect to heating capacity at the high-temperature heating condition (by experiment)

The discharge temperature and pressure are important factors because they influence lubricant life and system design. As shown in Table 2, the discharge temperature of R-290/134a is lower than that of HCFC-22 and slightly higher than that of R-290. R-134a/600a shows lower discharge temperature than CFC-12 and HFC-134a. Since the suction temperature is almost the same for all tests, the discharge temperature is largely a function of the specific heat of the vapor. For example, the specific heat of R-290/134a is larger than that of HCFC-22, so the discharge temperature is lower, which is a desirable condition.

The discharge pressure of R-290/134a is higher than that of HCFC-22 and R-290, and R-134a/600a shows slightly higher discharge pressure than CFC-12 and HFC-134a. Because the condensing temperature is almost the same for all tests, the discharge pressure is primarily related to saturation pressure (Fig. 4). Because the saturation pressure of R-290/134a is higher than that of HCFC-22 and R-290, and that of R-134a/600a is higher than that of CFC-12 and HFC-134a, the discharge pressures are higher for these azeotropic mixtures. The discharge pressures for all cases were lower than the commercial design pressure limit of approximately 2.6 MPa.

**3.3 High-Temperature Heating Test Results.** In this test, the inlet temperature of heat transfer fluid into the condenser is maintained at 21.1 °C and that into the evaporator is kept at 8.3 °C. In this heating mode test, the outlet temperatures are determined by reversing the heat transfer fluid flow rates between condenser and evaporator; that is, the evaporator flow rate for the heating condition is the same as the condenser flow rate for the cooling condition and vice versa. The main reason for doing this is that the flow rates of indoor and outdoor units in commercial heat pumps typically do not change when the operating mode (cooling or heating) is changed. Detailed test results are shown in Table 3.

The coefficient of performance for R-290/134a is lower than that for HCFC-22 and R-290, as is also shown in Fig. 6. For R-134a/600a, the coefficient of performance is higher than that for CFC-12 and HFC-134a.

The discharge temperature shown in Table 3 presents a similar pattern to the previous test condition. The discharge temperature of R-290/134a is lower than that for HCFC-22 and slightly higher than that for R-290. The discharge temperature of R-134a/600a is lower than that of CFC-12 and HFC-134a. Because the suction temperatures are almost the same for all tests of the same test condition, a higher discharge temperature is obtained for refrigerants with a lower vapor specific heat as is the case.

The discharge pressure of R-290/134a is higher than that of HCFC-22 and R-290, and that of R-134a/600a is slightly higher than that of CFC-12 and HFC-134a, as shown in Table 3. All the discharge pressures of this test condition are lower than those of the previous high-temperature cooling tests.

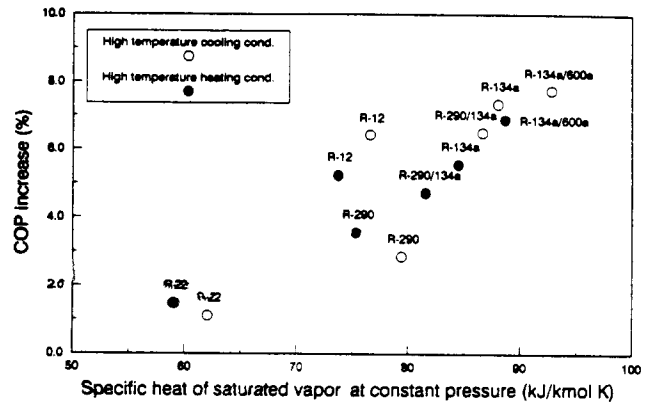


Fig. 7 COP increase versus specific heat of saturated vapor at constant pressure when liquid-line/suction-line heat exchange is applied

**3.4 Liquid-Line/Suction-Line Heat Exchange.** The high-temperature cooling and heating test results with liquid-line/suction-line heat exchange (LSHX) are shown in Figs. 5 and 6. The LSHX subcools the liquid from the condenser with the suction vapor from the evaporator. The benefit of LSHX depends on both operating conditions and refrigerant properties (Domanski et al., 1992); it is an advantage when the vapor specific heat is high and the lost work of expansion is comparatively large. All the test conditions with LSHX are maintained the same as the previous cases without LSHX.

The application of LSHX increases cooling or heating capacity in both high-temperature cooling and heating tests, but the magnitude of the increase is different for the different fluids in this study. For the R-290/134a mixture, the vapor specific heat is greater than that of HCFC-22 or R-290; thus, the increase in cooling or heating capacity is greater than that of HCFC-22 or R-290 at both test conditions. For R-134a/600a, which has a greater vapor specific heat than CFC-12 and HFC-134a, the capacity increase at the high-temperature cooling condition is greater than that of CFC-12 or HFC-134a, but almost the same as that of CFC-12 at the high-temperature heating test. The COP increase of R-290/134a is greater than that of HCFC-22 or R-290 for both the high-temperature cooling and heating tests. For the R-134a/600a mixture, the increase in COP is significant compared with CFC-12 and HFC-134a. The COP increase with respect to specific heat of the saturated vapor at constant pressure is shown in Fig. 7. As shown in Fig. 7, COP increase is almost proportional to the specific heat of the vapor phase, which corresponds with the simulated result in the reference (Domanski et al., 1992).

The discharge temperature is higher for all tests with LSHX, which is expected when any refrigerant's superheat is increased. The results show that the highest discharge temperature is obtained for HCFC-22 in every case, which is a result of its having the lowest vapor specific heat. The discharge temperatures for other refrigerants are lower than that of HCFC-22 because they are more complex molecules, and, therefore, have a higher specific heat. The discharge pressure is almost the same for all tests with LSHX as for those without LSHX. As shown in Tables 2 and 3, the average difference between the two cases is less than 2.5 percent for all test conditions.

**3.5 Performance Simulation.** Cycle performances were also simulated on the computer using the program CYCLE11 (Domanski and McLinden, 1990). This computer model simulates a vapor compression cycle that takes the thermodynamic deviations from the ideal cycle into account. The simulated cycle is prescribed in terms of inlet and outlet temperatures of the external heat transfer fluids with the heat exchangers generalized by an average effective temperature difference. An isenthalpic expansion process is assumed. The program also

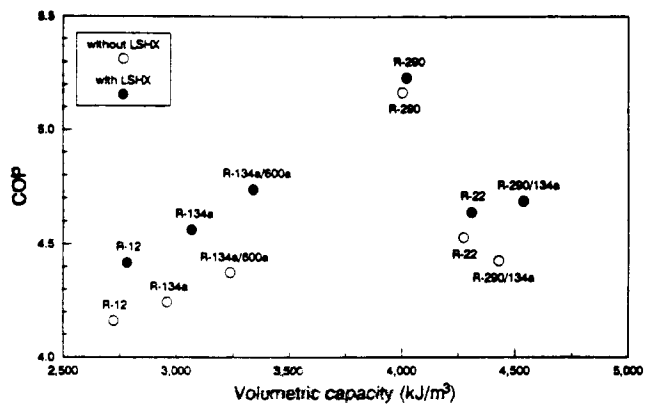


Fig. 8 Simulated cooling COP with respect to volumetric capacity at the high-temperature cooling condition

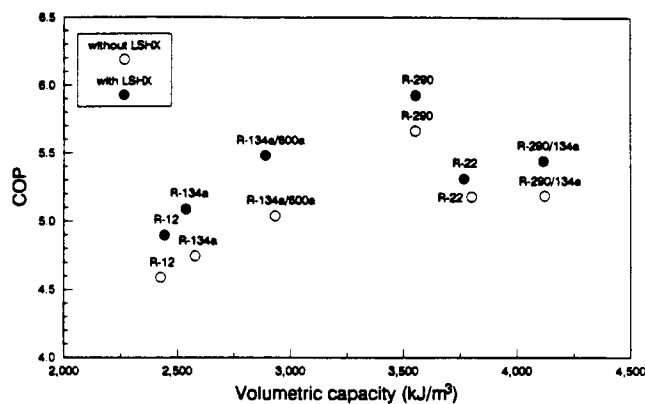


Fig. 9 Simulated heating COP with respect to volumetric capacity at the high-temperature heating condition

includes a rudimentary model of a compressor and a representation of a liquid-line/suction-line heat exchange. Thermodynamic properties of the refrigerants are calculated using the property program (Gallagher et al., 1991). Experimental data were used as input to simulate cycle performance including compressor speed, pressure drops through heat exchangers, condenser subcooling, evaporator superheating, compressor polytropic efficiency, and overall compression efficiency. The temperatures of the heat transfer fluid entering and exiting the heat exchangers were taken from Table 1.

The predicted coefficient of performance with respect to volumetric capacity at the high-temperature cooling condition is shown in Fig. 8 and that at the high-temperature heating condition is presented in Fig. 9. Assuming that volumetric flow rates for different refrigerants are almost the same in the constant compressor speed test, the simulated volumetric capacity corresponds to the capacity in the experiment. Compared with the experimental results of Figs. 5 and 6, the capacities and the coefficients of performance are well predicted by CYCLE11. The simulated results for the cases using a liquid-line/suction-line heat exchanger show a similar pattern. Compared with the pure refrigerants, the azeotropes in this study produce comparable volumetric capacity. The coefficient of performance for R-290/134a is predicted slightly lower than that of HCFC-22, and the COP of R-134a/600a is higher than that of CFC-12 or HFC-134a when LSHX is not used. By applying LSHX, slightly higher volumetric capacities and COPs are predicted.

Tests for this study have been performed using a constant compressor speed criterion instead of the constant heat flux criterion used in most previous NIST heat pump studies. In a practical sense, the constant compressor speed test answers the drop-in question of performance change in a system as a result of changing only the refrigerant. Typically, constant heat flux tests are performed with the capacity maintained constant by varying the compressor speed; hence, they evaluate the effect on system performance of two component changes: refrigerant and compressor speed. Constant compressor speed tests overstate the efficiency of low volumetric capacity refrigerants as a result of lower heat flux and commensurately reduced refrigerant-to-heat sink temperature difference. Constant heat flux tests tend to understate the efficiency of low volumetric capacity refrigerants as a result of increased refrigerant pressure drop (particularly on the low pressure side) with increased compressor speed. The comparisons in this study are made in two capacity groups, one near CFC-12 and the other near HCFC-22. It is felt that the capacity range in each group is sufficiently small that test results by either criterion would be comparable since the two test criteria are identical when comparing refrigerants of identical volumetric capacity. However, in interpreting the results, it is well to be alert to this bias in

favor of low-capacity refrigerants when comparisons are made among more widely disparate refrigerants.

A final point should be made regarding the R-290 test results relative to HCFC-22. Although the coefficient of performance of R-290 is less than that of HCFC-22 in a simplified computer simulation which generally ignores heat transfer, irreversibility, etc., the laboratory tests in this study show the opposite results. We should note that the experimental data were used in simulating cycle performance in this study, and all of the tests were conducted with the constant compressor speed criteria. The capacity of R-290 is lower than that of HCFC-22; thus, the heat exchanger loading decreases and so does the average temperature difference in the heat exchanger. The liquid viscosity of R-290 is approximately 65 percent and the vapor density is approximately 41 percent of HCFC-22 in the test range; so R-290 has a significantly smaller pressure drop (about half of HCFC-22) in the heat exchangers and the liquid thermal conductivity of R-290 is approximately 10 percent higher than that of HCFC-22. Therefore, the overall heat transfer coefficient for R-290 is higher than that for R-22 and the effective average temperature difference in the heat exchanger for R-290 is lower. These factors result in higher COP values than the simplified simulation results.

Although system performance is influenced by design optimization for a specific working fluid, the tests were conducted in the same test rig and the same test conditions. Therefore, a different system may give slightly different results, but the major conclusions will not change.

#### 4 Flammability Measurements

Flammability tests were performed to determine the flammability limits of the azeotropic mixtures in this study. The flammability test apparatus is described in ASTM-E681 (ASTM, 1992). It is desirable that refrigerants be nonflammable; however, recent studies suggest that pure propane (R-290) has several merits as a refrigerant (Kramer, 1991), and, of course, ammonia has been widely used in industrial applications throughout the history of refrigeration. Investigations into the use of propane in domestic refrigerators have included energy consumption tests, combustion tests, fire tests, etc., (James and Missenden, 1992). The conclusion is that a refrigerator with propane is capable of similar performance to one with CFC-12 without design changes, and the explosion and fire risks are small. Many industrial applications of heat pumps have traditionally used hydrocarbons as refrigerants, particularly where other flammable materials are present and experienced personnel are available. Nevertheless, a minimization of flammability is always desirable with all other characteristics being equal.

The main concept of our study of flammability is to add

nonflammable HFC-134a to flammable hydrocarbons to reduce the flammability of the hydrocarbon and retain the thermodynamic and practical advantages. In this study, the compositions of the mixtures were sought out so as to have azeotropic behavior and the flammability tests are done for those specific compositions.

The flammability limits were determined by visual observation of all the recorded flammability tests on videotapes. In this study, the flammability limits of flammable mixtures are represented by the composition range where the flame propagates horizontally outward from the ignition source after being mixed with air and ignited. The flammability limits of R-290/134a (45/55 by mass percentage) are found to be 2.9–11.0 percent by volume in a refrigerant/air mixture. Those of R-134a/600a (80/20 by mass percentage) are 3.9–13.3 percent by volume in a refrigerant/air mixture. These results may be compared to the results for pure hydrocarbons R-290 and R-600a, where the limits are 2.1–9.6 percent and 1.7–9.7 percent by volume, respectively, (Richard and Shankland, 1992). It is noteworthy that the lower limit is higher for both mixtures than that for pure hydrocarbons. Although the azeotropic mixtures remain flammable, they are less flammable than their pure hydrocarbon compounds. It is well known that the presence of a halogen compound may show flame inhibition characteristics (Biordi et al., 1973; Ho et al., 1992). One might also reason that the presence of a relatively high specific heat nonflammable halogen will reduce the combustion energy of the hydrocarbon. While suppressing flammability, a drawback to the addition of halogen compounds is their tendency to produce toxic combustion products.

The heat of combustion can be calculated if the chemical equations describing the combustion process are known. Unfortunately, the combustion processes of HFC refrigerants are seldom known, and it was therefore difficult to predict the final combustion products in this study. But from the chemical features of the refrigerant mixture and the visual observation of flame propagation and flame intensity in this study, the released heat of combustion of the mixture seems less than that of pure hydrocarbons.

## 5 Concluding Remarks

In this paper, heat pump performance tests were conducted for two azeotropic refrigerant mixtures of HFC-134a (1,1,1,2-tetrafluoroethane) with R-290 (propane) and R-600a (isobutane): R-290/134a (45/55 by mass percentage) and R-134a/600a (80/20 by mass percentage). The performance characteristics of R-290/134a were compared with those of pure HCFC-22 and R-290, and those of R-134a/600a were compared with those of CFC-12 and HFC-134a at the high-temperature cooling and heating test conditions, including those cases using liquid-line/suction-line heat exchange.

The cooling or heating capacity of R-290/134a is greater than that of HCFC-22 and R-290. The capacity of R-134a/600a is also greater than that of CFC-12 or HFC-134a. The coefficient of performance for R-290/134a is lower than that for HCFC-22 and R-290, and R-134a/600a shows higher COP than CFC-12 and HFC-134a. Results show that the discharge temperature of R-290/134a is lower than that of HCFC-22 and slightly higher than that of R-290. The discharge temperature of R-134a/600a is lower than that of CFC-12 and HFC-134a. R-290/134a mixture has a higher discharge pressure than

HCFC-22 and R-290, and R-134a/600a has a slightly higher discharge pressure than CFC-12 and HFC-134a.

Even though the coefficient of performance of R-290/134a is slightly lower than that of HCFC-22 and R-290, because of its greater capacity and reduced flammability compared with R-290, R-290/134a can be possible substitute for HCFC-22. As regards the R-134a/600a mixture, it can be a possible substitute for CFC-12 because of its higher capacity and coefficient of performance.

Although the simulation required a careful application of the model because it generally ignores irreversibilities, by using experimental data judiciously, as model input, the different systems (i.e., working fluids) were more accurately simulated to account for friction, heat transfer, etc.

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