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COP IMPROVEMENT OF REFRIGERATOR/FREEZERS, AIR-CONDITIONERS, AND HEAT PUMPS USING NONAZEOTROPIC REFRIGERANT MIXTURES

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ABSTRACT

With the February, 1992 announcement by President Bush to move the deadline for outlawing CFC (chloro-fluoro-carbon) refrigerants from the year 2000 to the year 1996, the refrigeration and air-conditioning industries have been accelerating their efforts to find alternative refrigerants. Many of the alternative refrigerants being evaluated require synthetic lubricants, are less efficient, and have toxicity problems. One option to developing new, alternative refrigerants is to combine existing non-CFC refrigerants to form a nonazeotropic mixture, with the concentration optimized for the given application so that system COP (Coefficient Of Performance) may be maintained or even improved. This paper will discuss the dilemma that industry is facing regarding CFC phase-out and the problems associated with CFC alternatives presently under development. A definition of nonazeotropic mixtures will be provided, and the characteristics and COP benefits of nonazeotropic refrigerant mixtures will be explained using thermodynamic principles. Limitations and disadvantages of nonazeotropic mixtures will be discussed, and example systems using such mixtures will be reviewed.

INTRODUCTION

Nearly 100 years have passed since the idea of using refrigerant mixtures was first proposed, however, the full potential of nonazeotropic mixtures in refrigeration systems is relatively unexplored [1]. Renewed interest in nonazeotropic refrigerant mixtures has developed in the last 15 to 20 years, but their use is limited mainly to the laboratory. With the sense of urgency being placed on the industry to come up with safe, efficient, and reliable alternatives to CFCs, an increased effort to develop their commercial potential is warranted.

The need to examine nonazeotropic refrigerant mixtures will be discussed as follows. First, the dilemma facing designers of refrigerator/freezers, air-conditioners, and heat pumps will be reviewed. Second, the uncertainties of the alternative refrigerants currently being developed to replace CFCs will be discussed. Third, the term "nonazeotropic" will be defined, and the characteristics and inherent benefits of nonazeotropic refrigerant mixtures will be described. The limitations and disadvantages of nonazeotropic refrigerant mixtures will also be identified. Next, research that has been conducted with nonazeotropic refrigerant mixtures, including a prototype heat pump developed for the Marshall Space Flight Center, will be explained. Finally, conclusions and recommendations will be discussed.

THE DILEMMA

Due to their ozone-depletion potential (ODP), CFC refrigerants R-11 and R-12 will be among the Group I refrigerants un-available beginning in 1996 [2,3]. Other CFC refrigerants in the accelerated ban include R-114, R-115, and R-500, but the remainder of this discussion will focus on the replacement of the two most common CFCs, R-11 and R-12.

The challenge of replacing R-11 and R-12 presents a great dilemma to manufacturers of home refrigerator/freezers since R-12 is a very popular working fluid for this application and R-11 is a common blowing agent used for refrigerator/freezer insulation [4]. In addition, home refrigerator/freezer manufacturers will be required to improve the efficiency of systems presently using these refrigerants by an average of 25% by 1993

(relative to 1990 standards) and possibly another 25% by 1998 [5]. The air-conditioning and commercial refrigeration industries also rely heavily on both R-11 and R-12 as working fluids [6]. The next section discusses the success of achieving these new goals with some existing alternative refrigerants.

ALTERNATIVE REFRIGERANTS

R-134a is becoming widely accepted as the replacement for R-12 in domestic refrigerator/freezer and automotive air-conditioning applications [7,8,9] and also as the replacement for medium pressure chillers which currently use either R-12 or R-500 [10]. R-123 is considered one of the leading candidates to replace R-11 in low pressure centrifugal chillers [10]. Unfortunately, these alternatives cannot simply be used as drop-ins for the CFCs they must replace; system enhancement, refurbishing, or component replacement is often necessary. Many challenges must be addressed before alternative refrigerants can be used on a full-scale basis.

First, R-134a is not compatible with the mineral oils commonly used for compressor lubrication [11]. There are a number of synthetic candidates being evaluated for use with R-134a, but none have been totally proven.

The refrigeration capacity and coefficient of performance (COP) of alternative refrigerants must also be established. Numerous investigations have been conducted to determine the capacity and performance of alternatives relative to their CFC counter-parts. A comparison of R-134a with R-12 in a residential heat pump [12] showed that approximately the same heating output was achieved with R-134a, but the COP of the system was approximately 15% less with R-134a than with R-12. Another series of tests [13] conducted at ARI (Air-Conditioning and Refrigeration Institute) Heat Pump Rating Conditions showed that R-134a exhibits a 6-11% increase in COP for moderate and warm rating conditions, while R-134a has a nearly identical COP to that of R-12 for a cold rating condition. In a test conducted for a household refrigerator/freezer [9], R-134a was shown to consume approximately 8% more power than R-12 and require more run-time, resulting in an energy consumption 45% greater than R-12. Tests conducted with R-123 indicate a 0 to 18% reduction in capacity compared to R-11 and a 0 to 15% reduction in COP [10]. These seemingly contradictory results indicate that more tests need to be conducted to establish the performance and capacity of alternative refrigerants. There is agreement, however, that systems need to be optimized for the replacement refrigerants to achieve adequate efficiency and capacity. This is due in part to different specific volumes at the compressor inlet, requiring compressor re-sizing.

The compatibility of alternative refrigerants with seals, bushings, gaskets, and other components is also still under investigation. R-123 may present some problems with elastomers made of Buta N or commonly used neoprenes, while R-134a has shown excellent material compatibility [10].

Toxicity is another major issue. The Southern Building Code Congress International (SBCCI) requires either ventilation, or a refrigerant detector and an alarm that sounds at a level of 10 parts per million (ppm) for R-123 [14,15]. There is less concern with the toxicity of R-134a, although it too requires either ventilation or detection because of its ability to displace oxygen [14,15]. Tests are presently being conducted to determine the carcinogenic effects of R-123, R-134a, and other refrigerants, with results expected by the end of 1992 [16].

The above discussion shows that much work has been done and is still being done to develop and test CFC pure-refrigerant alternatives. These alternatives have a lot of potential, but their total acceptance has not been established. Following is a discussion of another option, nonazeotropic refrigerant mixtures using existing non-CFC refrigerants.

NONAZEOTROPIC REFRIGERANT MIXTURES

Definition and Characteristics

The word "nonazeotropic" comes from the root word "zeotrope" with the double negative "non" and "a" as a prefix. Zeotrope is derived from the Greek words "zeo" (to boil) and "trope" (to change). Perhaps the easiest way to understand a nonazeotropic refrigerant mixture (NARM) is to examine an azeotropic mixture (normally

labeled an "azeotrope"). An azeotrope, as illustrated in Figure 1, is made up of two or more refrigerants and occurs only at a particular composition. An azeotrope behaves as a pure refrigerant, undergoing no temperature change during condensation and evaporation (single negative "a" with "zeo", to boil, and "trope", to change; i.e., no change during boiling). The thermodynamic properties of an azeotrope are different than those of its two constituent fluids. Common azeotrope refrigerants are R-500 (73.8% R-12 and 26.2% R-152a) and R-502 (48.8% R-22 and 51.2% R-115).

A nonazeotropic refrigerant mixture is made up of two (or more) refrigerants of different volatility [17] and does not act as a pure fluid. When these two refrigerants are used in a vapor-compression cycle, the mixture changes composition as it boils or condenses. As a result of this change in composition, a temperature variation occurs during a constant pressure phase-change process. The magnitude of this temperature variation or "temperature glide" is a function of the properties and relative composition of the mixture constituents. The two-phase region with the bubble- and dew-point lines for a typical nonazeotropic refrigerant mixture is illustrated in Figure 2.

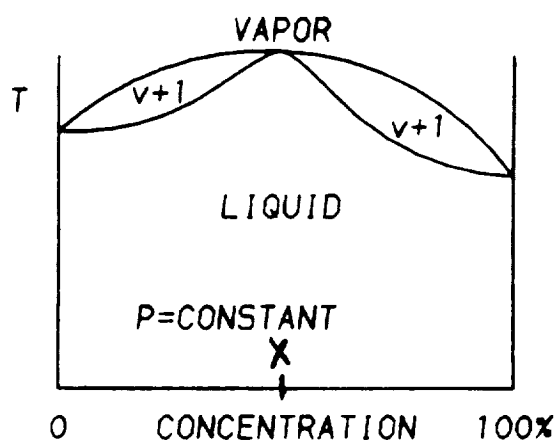


Figure 1. Two-phase Region for a Binary Mixture with an Azeotrope Occurring at Composition X.

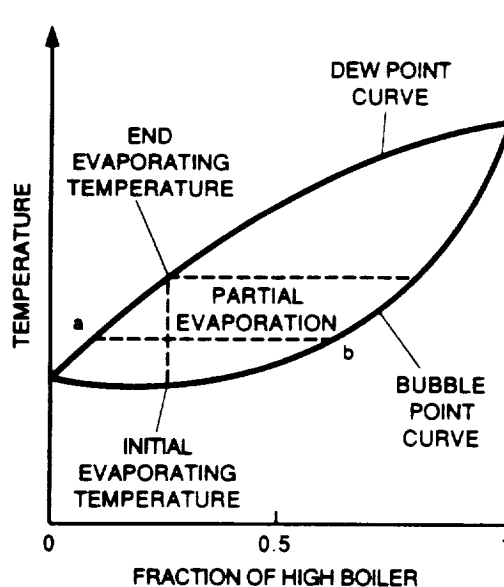


Figure 2. Two-phase Region for a Binary Mixture with no Azeotrope.

As liquid is vaporized during the evaporation process, the more volatile component (the refrigerant with the lower boiling point) will vaporize more rapidly than the less volatile component (high boiler). Therefore, the remaining liquid will be enriched with the less volatile component. From Figure 2, it is seen that as the liquid becomes more enriched with the less volatile component, the bubble point temperature increases. The bulk refrigerant temperature will rise as evaporation continues and will be at the temperature lying on the dew-point line at the completion of evaporation. Assuming that equilibrium exists at all points between the liquid and vapor phases, the concentration of the components in the two phases will be different. The points labeled (a) and (b) demonstrate this phenomena, marking the relative mass fractions in the two phases at some point along the length of the evaporator. The less volatile component is always more concentrated in the liquid phase than in the vapor phase.

COP Benefits

The potential benefit of a nonazeotropic refrigerant is illustrated in Figures 3 and 4. The arrows in Figure 4 indicate the flow direction in the heat exchanger. Also note that the same line nomenclature is used in Figure 4 as in Figure 3 (the solid lines represent pure refrigerant, etc.). It can be seen that using the nonazeotropic

refrigerant mixture can reduce heat pump irreversibility and therefore, increase efficiency. The temperature of pure refrigerants is constant in the two-phase region. If the heat source or heat sink temperature varies throughout the heat exchanger, as is the case with a chilled water system or a hot-water heat pump, the irreversibilities associated with the heat transfer can be large. By utilizing the correct nonazeotropic mixture, the temperature difference between the refrigerant and the heat source/sink can be reduced, thereby minimizing the irreversibility produced during heat transfer.

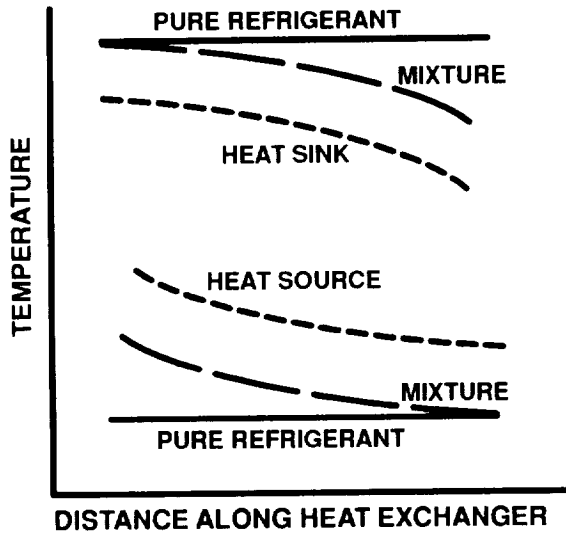


Figure 3. Temperature Variation Along Length of Condenser and Evaporator.

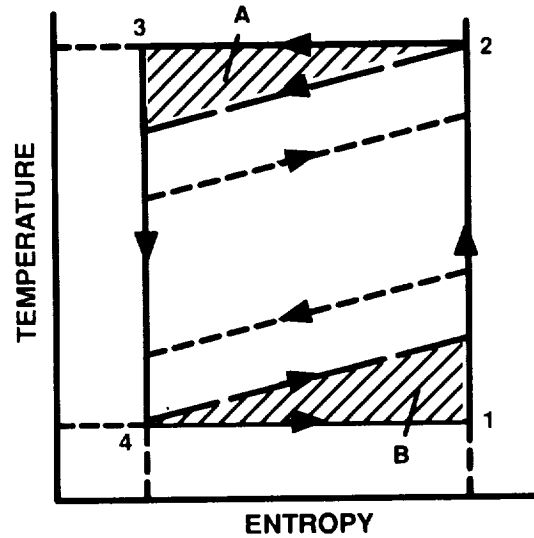


Figure 4. T-s Diagram of Counter-Flow Mixed Refrigerant Heat Transfer.

Assuming that the cycles for the pure refrigerant and the nonazeotropic mixture can perform the same duty, the ideal COP can be calculated for each cycle from the areas shown in Figure 4. The ideal (or carnot) COP of a heat pump using a pure refrigerant is simply the heat rejected by the condenser, Q_c , divided by the work of the compressor, W . For the pure refrigerant case, Q_c is the area below the condensation line, 2 to 3. The work W for the pure refrigerant is represented by the area enclosed by the points 1, 2, 3, and 4. Therefore, the ideal COP for a cycle with an isothermal phase change (pure refrigerant) is calculated as shown in equation 1. Areas A and B represent the difference in irreversibility between the two cycles. The ideal COP for a cycle with a non-isothermal phase change (nonazeotropic mixture) is calculated as shown in equation 2. It can be proven mathematically that the COP calculation in equation 2 is always greater than the COP calculation in equation 1.

$$COP = \frac{Q_c}{W} \quad (1)$$

$$COP = \frac{Q_c - A}{W - A - B} \quad (2)$$

Similar logic can be applied to a refrigeration or air-conditioning system. Equations 3 and 4 represent the ideal COP for each cycle as calculated from Figure 4. In these equations, Q_c is the heat absorbed by the evaporator for the pure refrigerant case, and is represented by the area below the evaporation line, 4 to 1. Inspection of equations 3 and 4 shows that the ideal COP of a cooling system operating with a nonazeotropic mixture is also always higher.

$$COP = \frac{Q_c}{W} \quad (3)$$

$$COP = \frac{Q_c + B}{W - A - B} \quad (4)$$

The potential increase in COP is the greatest in applications where the heat sink and heat source temperatures are approximately equal and of relatively large magnitude. The minimum requirements to achieve these performance improvements are: the selection of a mixture that yields the desired temperature change in both heat exchangers, a counter-flow heat exchanger that takes advantage of the temperature glide of the refrigerant, and minimized degradation of the heat transfer process. The magnitude of the phase change temperature glide is related to the differences in the normal boiling points of the mixture constituents.

Limitations and Disadvantages

Nonazeotropic mixtures should be selected for a specific operating condition, i.e., a heat source/sink temperature glide that remains constant. Any great variation from the design point could cause a decrease in COP, to the point where using the nonazeotropic mixture is less efficient than using a pure refrigerant.

Counter-flow or near counter-flow heat exchangers are necessary for both the condenser and evaporator to achieve benefits from nonazeotropic refrigerant mixtures. This is because a constant temperature difference between the refrigerant and the heat source/sink is necessary to minimize irreversibility in the condenser and evaporator. Ideally, the temperature glides of the condenser and evaporator must be similar in magnitude and slope.

Generally, nonazeotropic refrigerant mixtures exhibit lower heat transfer coefficients in the condenser and evaporator [18]. This is due partly to the concentration differences between the liquid and the liquid-vapor interface. Diffusion from areas of greater concentration to areas of lesser concentration tends to slow down the condensation (or evaporation) process.

When analyzing cycles for the pure refrigerant and the nonazeotropic mixture that perform the same duty, the heat exchange area of the condenser and evaporator must be greater for the nonazeotropic refrigerant mixture than for the pure refrigerant system. This is partly due to a reduction in log-mean-temperature-difference (LMTD) for the nonazeotropic system and also due to the reduced heat transfer coefficients.

Another disadvantage of nonazeotropic refrigerants is the added degree of complexity should a leak occur in the system. The more volatile constituent will leak first, leaving a higher concentration of the less volatile constituent. The entire system may need to be evacuated so that the correct mixture concentration may be re-established. This situation may become dangerous if a flammable refrigerant is mixed with a non-flammable refrigerant. When separation occurs, the flammable refrigerant may once again be a fire hazard.

TEST SYSTEMS USING NONAZEOTROPIC REFRIGERANTS

Automotive Air Conditioning

Tests on an automotive air-conditioning system were conducted to determine the feasibility of replacing ozone-depleting R-12 with a near-azeotrope blend of three refrigerants [8]. A near-azeotrope refrigerant is a mixture with a composition close to the azeotrope composition, acting nearly identical to a pure refrigerant (as does an azeotrope). The tests showed that the blend had a refrigeration capacity and COP slightly better than R-12. The blend also exhibited slightly better stability with compressor lubricants relative to R-12. The conclusions of the tests were that refrigerant mixtures show potential for use in automotive air-conditioning systems, although compressor replacement or modification is necessary.

Domestic Refrigerator/Freezer

A domestic refrigerator/freezer was tested using a nonazeotropic mixture of R-22 and R-142b [19]. Energy consumption was measured for a full day while the refrigerator maintained average temperatures of 5° F and 38° F (-15° C and 3.3° C) in the freezer and food compartments. To obtain the best performance with the nonazeotropic mixture, the condenser and evaporator were modified to achieve a cross-counter-current heat transfer arrangement. The local flow arrangement of an individual pass in this configuration remained cross-flow as in normal air-to-refrigerant heat exchangers. However, the overall flow arrangement became counter-current, therefore utilizing the advantages of the nonazeotropic mixture.

Results of the tests indicated a 3% increase in performance for a mixture containing 52% mass fraction of R-22 and 48% R-142b. The compressor was not modified or replaced for these tests, however, a synthetic lubricant was deemed necessary to achieve similar or better performance compared to R-12. Analysis indicated that an additional 5% increase in performance was possible by optimizing the motor and compressor design for the refrigerant mixture.

Air-to-Air Heat Pump

A mixture of R-22/R-152a showed a 5.5% COP increase relative to pure R-22 for a 3-1/2 ton high-efficiency (by 1985 standards) split heat pump [20]. This COP increase, verified using DOE test procedures, was obtained without changing the cross-flow heat exchanger configuration of the original heat pump design. There was a capacity decrease (7.9%) along with the COP increase, however, analysis predicted an 8% seasonal savings using the mixture. The performance increase was attributed to thermodynamic property variations. Further COP increases could be realized by employing a counter-flow heat exchanger or a cross-counter-current heat exchanger similar to the one referenced in the previous section. Even though the particular mixture tested may prove impractical due to the flammability of R-152a, the tests demonstrate the feasibility of nonazeotropic mixtures to improve the COP of air-to-air heat pump systems.

Water-to-Water Heat Pump

A prototype heat pump employing a nonazeotropic mixture of R-11¹ and R-22 was developed for the NASA Marshall Space Flight Center under a Phase II SBIR (Small Business Innovation Research) Contract. The prototype heat pump was developed to demonstrate the feasibility of using a nonazeotropic heat pump for crew hygiene² water heating on Space Station *Freedom* [21].

Figure 5 is a schematic diagram showing that the condenser side of the heat pump serves as the water heater (heat sink) while the evaporator side picks up waste heat from the thermal control system (TCS) of the space station (heat source). The hygiene water requires heating from 70° F to 145° F (21.1° C to 62.8° C) while the TCS water reaches 110° F (43.3° C) and is cooled to 50° F (10° C). The large temperature gradient required for the hygiene water system and the flexibility to adjust the TCS water temperature gradient make hygiene water heating on the space station an ideal application for a nonazeotropic heat pump.

To compare the performance of a nonazeotropic fluid to that of a pure fluid such as R-12, a theoretical analysis of the heat pump was performed from the thermodynamic properties of the two working fluids. The heat pump cycle for R-12 is shown in the T-s diagram of Figure 6 with a 45° F (7.2° C) saturated evaporator temperature

1. During the SBIR contract, NASA did not require the contractor to consider CFC phase-out. Therefore, R-11 was an acceptable refrigerant candidate, and contract objectives were met.

2. When the nonazeotropic heat pump contract was initiated, the hygiene water system was separate from the potable water system. Since then, the two systems have been combined.

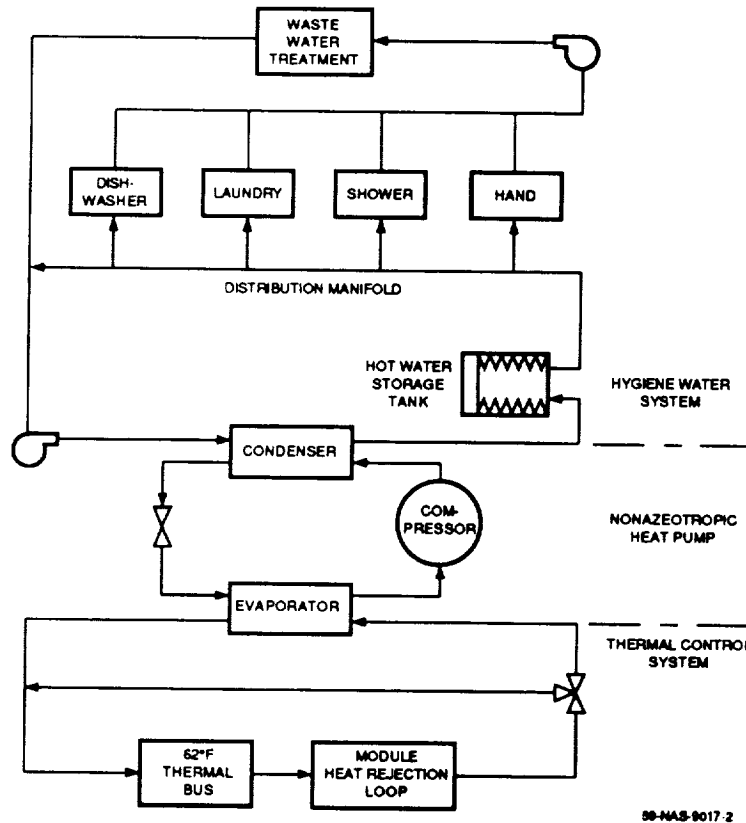
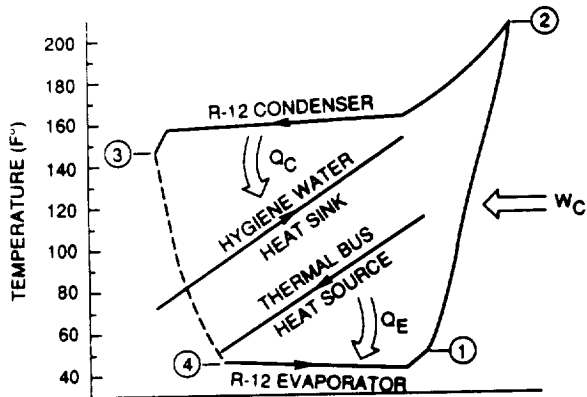


Figure 5. Water Heating Concept using a Nonazeotropic Heat Pump to Transfer Waste Heat from the Thermal Control System to the Hygiene Water System.

and a 150° F (65.6° F) saturated condenser temperature. The analysis assumed a 70% isentropic compressor efficiency, a 3 psi drop through each heat exchanger, 10° F (5.6° C) of condenser sub-cooling, and 5° F (2.8° C) of evaporator super-heat. In producing 3075 Btu/hr (900 W) of water heating, the R-12 heat pump consumes 263 W of power with a COP of 3.44.

A similar analysis was performed using the same heat sink and source for a mixture of R-22 and R-11. The T-s diagram of Figure 7 displays the results. The same compressor efficiency, heat exchanger pressure drop, condenser sub-cooling, and evaporator super-heat were assumed as in the R-12 case. The refrigerant mixture enters the evaporator at 45° F (7.2° C), similar to the R-12 cycle, however, the refrigerant mixture increases in temperature as it boils until it reaches 105° F (40.6° C) at the evaporator outlet. The condensing process begins at 150° F (65.6° C) as with the R-12 system, but the temperature glide of the refrigerant mixture results in 75° F (23.9° C) liquid at the condenser outlet. The nonazeotropic heat pump cycle produces the same amount of heating as the R-12 cycle, 3075 Btu/hr (900 W), while consuming only 102 W at a COP of 8.83. This dramatic theoretical COP increase is a direct result of the reduction in irreversibilities by using the nonazeotropic refrigerant mixture.

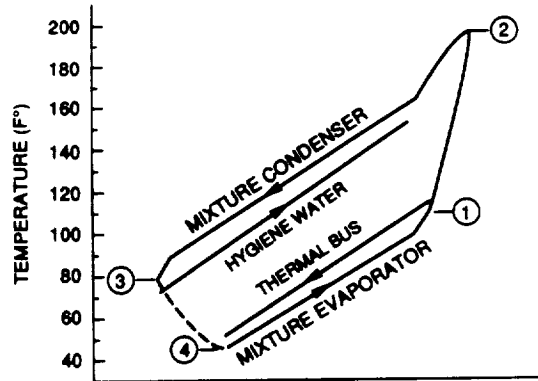
Some of the reduction in irreversibility can be attributed to a reduction in compression ratio. Note from Figures 6 and 7 the differences in system pressures between the two cycles, especially compressor discharge pressure (state point 2). The two theoretical compression ratios are 4.7 for the R-12 cycle and 2.2 for the mixture cycle. The reduced compression ratio not only allows significant power savings, but also increases compressor life.



	T	P	h
1	46.9	53.4	82.4
2	192.7	249.3	99.5
3	139.0	246.3	40.9
4	45.0	56.4	40.9

CONDENSER HEAT REJECTION 3075 BTU/HR
 EVAPORATOR HEAT ABSORPTION 2178 BTU/HR
 COMPRESSOR WORK 897 BTU/HR
 COMPRESSOR POWER CONSUMPTION 263 WATTS
 COEFFICIENT OF PERFORMANCE 3.44

Figure 6. R-12 Heat Pump Cycle.



	T	P	h
1	105.1	36.2	108.1
2	182.3	79.4	118.5
3	75.0	76.4	26.5
4	45.0	39.2	26.5

CONDENSER HEAT REJECTION 3075 BTU/HR
 EVAPORATOR HEAT ABSORPTION 2727 BTU/HR
 COMPRESSOR WORK 348 BTU/HR
 COMPRESSOR POWER CONSUMPTION 102 WATTS
 COEFFICIENT OF PERFORMANCE 8.83

Figure 7. Nonazeotropic Heat Pump Cycle.

Recall from the previous section that in order to accomplish the same amount of water heating with the nonazeotropic heat pump cycle described, a counter-flow heat exchanger with more area than that of the R-12 cycle is necessary. Prototype testing of the nonazeotropic heat pump resulted in measured COPs ranging from 70% to 90% of predicted values.

CONCLUSIONS

This paper presents reasons to continue investigation of nonazeotropic refrigerant mixtures. Due to CFC phase-out and higher efficiency standards, refrigeration and air-conditioning equipment designers face a dilemma. Uncertainties and problems associated with one possible solution, development of CFC alternatives, were reviewed. Another option, development of nonazeotropic mixtures using existing non-CFC refrigerants, was discussed, including definitions, characteristics, benefits, disadvantages, and limitations. Finally, tests of systems employing nonazeotropic mixtures were presented.

RECOMMENDATIONS

Because of the urgency to replace CFC refrigerants, it is recommended that the government and industrial sectors continue development of systems employing non-CFC nonazeotropic mixtures to the point of commercial and domestic application. It is suggested that this effort be conducted in parallel with the present effort to develop

pure-refrigerant CFC alternatives. Possible non-CFC refrigerant combinations were not addressed in this paper. Reference 22, which contains a systematic approach for selecting ozone-safe refrigerants, is a good starting point for nonazeotropic mixture selection.

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