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THE EFFECT OF A NONAZEOTROPIC BINARY REFRIGERANT MIXTURE
ON THE PERFORMANCE OF A SINGLE STAGE REFRIGERATION CYCLE

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1. INTRODUCTION

The use of nonazeotropic refrigerant mixtures in refrigeration and heat pump systems has received considerable attention in recent years. A sample of relevant publications is found in References /1/ and /2/. The purpose of this paper is to study the use of a nonazeotropic binary refrigerant mixture in a single stage refrigeration or heat pump system from a rigorous, fundamental viewpoint. Emphasis is placed on the operation of the two heat exchangers as this is where the main difference occurs between a system utilizing a refrigerant mixture and one which uses a simple substance.

2. THEORETICAL CYCLE ANALYSIS

Consider a refrigeration or heat pump cycle which is used exclusively to transfer energy from a single phase heat transfer fluid at a low temperature to a second single phase heat transfer fluid at a higher temperature. An example is an air to air heat pump. Assume the two heat transfer fluid inlet temperatures to be fixed at T_L and T_H respectively and the heat transfer rate from the low temperature heat transfer fluid to be fixed at Q_L . A schematic diagram of this system with the thermodynamic boundaries used in the following analysis is shown in Figure 1.

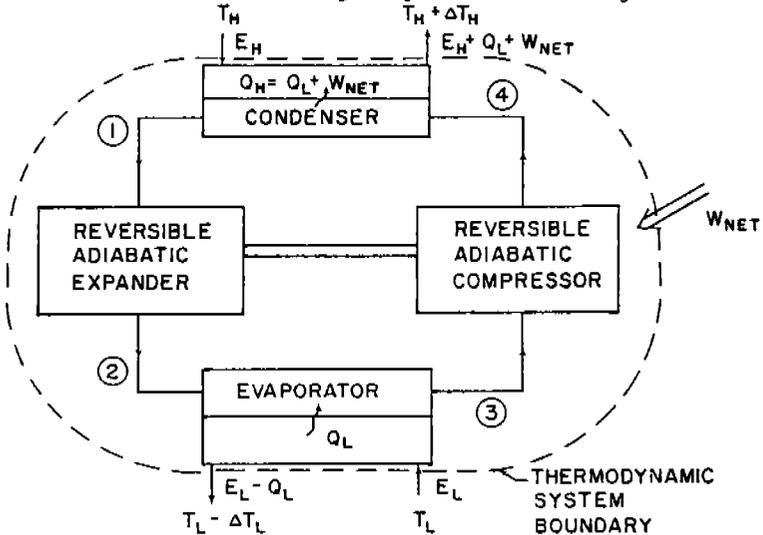


Fig. 1. Schematic diagram of a single stage vapor compression refrigeration machine illustrating the location of the thermodynamic system boundary used in the present analysis.

The minimum power required to transfer the heat Q_L from T_L to T_H occurs when a reversible cycle is used. This could take the form of a Stirling cycle, Ericsson cycle, Carnot cycle or any other completely reversible cycle. We will limit our discussion to a Carnot cycle as it is a reasonable model for a single stage mechanical vapor compression refrigeration cycle.

The Carnot cycle is shown schematically on a T-S coordinate diagram in Figure 2a. The solid lines indicate the refrigerant process lines. The dotted lines indicate the heat transfer fluid process lines. The energy content of the entering and exiting heat transfer fluid streams is indicated as are the areas representing the cycle refrigerating load and net power requirement.

If the working fluid is a simple substance which undergoes a phase change during the heat transfer, the pressure drop must be zero within each heat exchanger. The

pumping power is also zero for each of the two external heat transfer fluids which indicates no pressure drop on the other side of the heat exchangers. The temperature difference between the refrigerant and each heat transfer fluid is zero which indicates reversible heat transfer. Therefore the cycle has no irreversibilities within the system boundary as defined on Figure 1. The heat transfer fluid leaving each heat exchanger is at the same temperature as the surrounding fluid so any heat transfer between the fluid streams and the surrounding fluid is also reversible. Therefore there are no external irreversibilities outside the system boundary shown in Figure 1.

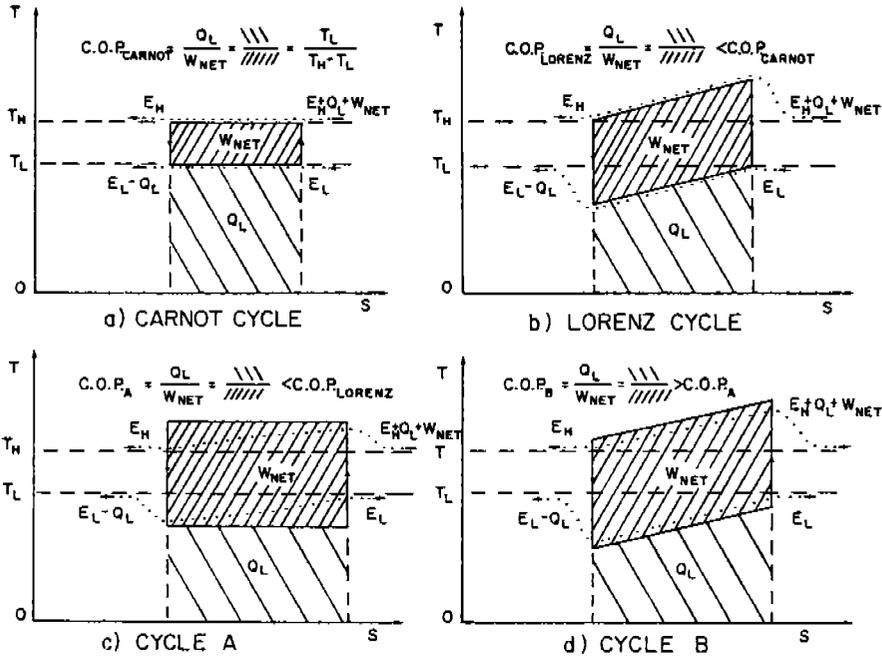


Fig. 2. Temperature-entropy diagrams of four refrigeration cycles with the same load, Q_L , operating between the same temperature levels, T_H and T_L .

Thus the Carnot cycle is indeed completely reversible and exhibits the minimum power requirement for the given load and temperature levels. However the Carnot cycle is not very practical. The product of the heat exchanger heat transfer coefficient times surface area (UA) must equal infinity for the temperature difference to be zero in a system of finite capacity. Also, the heat transfer rate divided by the heat transfer fluid capacity rate (Q/C) must be zero for each heat exchanger as the heat transfer fluid is assumed to be single phase and does not change in temperature. The refrigerating capacity of the system is finite which indicates that either 1) the heat transfer fluids have infinite specific heat capacity or 2) their mass flow rates are infinite.

A cycle that overcomes part of the limitation of the Carnot cycle has been termed the Lorenz cycle. In this cycle, the constant temperature restriction during the heat transfer processes is relaxed. This allows the use of heat transfer fluids with finite specific heat capacities and finite mass flow rates. This cycle is shown on T-S coordinates on Figure 2b. In order to allow the heat transfer fluids to change temperature during the heat transfer processes without introducing heat transfer irreversibility, the refrigerant must match the temperature of the heat transfer fluids in the heat exchangers as shown on the figure. A binary refrigerant mixture undergoing phase change can approximate this condition when the phase changes occur at constant pressure. However the heat transfer fluid capacity rates (C) of the refrigerant and the heat transfer fluid must be equal in each heat exchanger. This cycle has no internal irreversibilities similar to the Carnot cycle. However it does have external irreversibilities due to the temperature difference between the two heat transfer fluids when they leave the heat exchangers and the surrounding fluid. This irreversibility is termed thermal irreversibility.

The irreversibilities require additional power to overcome so the C.O.P. of this cycle is lower than the Carnot cycle for the same load Q_L and temperature levels T_L and $T_H/3$. Although the requirement of infinite heat transfer fluid capacity rate has been relaxed, this cycle still suffers from the restriction that the heat exchanger heat transfer coefficient times surface area (UA) is infinitely large.

Cycle A shown on Figure 2c is a cycle in which both of the limitations on the Carnot cycle have been removed. The heat transfer fluids have finite capacity rates and the heat exchangers have finite thermal resistance. The refrigerant experiences a Carnot cycle as in Figure 2a. However in Cycle A, the heat transfer within the heat exchangers is irreversible due to the finite temperature difference between the refrigerant and the heat transfer fluids. The external irreversible heat transfer with the heat transfer fluids is also present. Therefore this cycle has more irreversibility than the Lorenz cycle and has a lower C.O.P.

If one wishes to use a variable temperature in the refrigerant during the heat transfer process, Cycle A shown in Figure 2c changes to Cycle B shown in Figure 2d. One can approximate this cycle by using a nonazeotropic binary mixture as the refrigerant and maintaining thermodynamic equilibrium and constant pressure during the phase change heat transfer processes. This cycle has all the irreversibilities described for Cycle A.

The following discussion is a comparison of the C.O.P. between Cycle A and Cycle B described above. These two cycles have the same refrigeration load and operate between the same temperature levels. Consider each to have the same overall heat transfer coefficient times surface area (UA) and heat transfer fluid mass flow rate in the corresponding heat exchangers. Therefore these two cycles are identical except that in Cycle A the refrigerant exchanges heat isothermally whereas in Cycle B the refrigerant changes temperature during the heat transfer processes. Thus this comparison illustrates the difference between using a simple substance as the refrigerant and using a nonazeotropic binary mixture in the same system under the same operating conditions. The cycle with the lowest total irreversibility is the cycle with the largest C.O.P. In the analysis here the refrigerant and the two heat transfer fluids are assumed to have negligible viscosity so the only irreversibilities are due to heat transfer. A list of equations for computing irreversibilities in typical refrigeration systems is given in /3/.

The compressor and expander are completely reversible so the only internal irreversibilities arise in the heat exchangers. The only external irreversibilities are due to the irreversible heat transfer with the two heat transfer fluids. These irreversibilities can be computed together for each heat exchanger to minimize the effort. Therefore the total irreversibility of each cycle can be written as

$$I_{\text{Total}} = I_C + I_E \quad (1)$$

Considering the low temperature heat exchanger first for Cycle A, termed the evaporator, with a constant temperature and pressure phase change

$$I_E = \Delta S_{\text{Refrigerant}} + \Delta S_{\text{H. T. Fluid}} \quad (2a)$$

$$= Q_L/T_E - Q_L/T_L \quad (2b)$$

The heat transfer rate can be written in terms of a log mean temperature difference $LMTD_E$ as

$$Q_L = (UA)_E LMTD_E = (\dot{m} c_p \Delta T_L)_{\text{H.T. Fluid}} \quad (3)$$

so the evaporator total irreversibility becomes

$$I_E = Q_L(1/(T_L - \Delta T_E) - 1/T_L), \quad \Delta T_E = \Delta T_L / (1 - \exp(-\Delta T_L / LMTD_E)) \quad (4)$$

Similarly for the condenser, introducing the condenser log mean temperature difference, $LMTD_C$, and the energy balance, $Q_H = Q_L + W_{\text{net}}$, gives

$$I_C = \Delta S_{\text{Refrigerant}} + \Delta S_{\text{H. T. Fluid}} = -Q_H/T_C + Q_H/T_H \quad (5)$$

$$= (Q_L + W_{\text{net}})(1/T_H - 1/(T_H + \Delta T_C)), \quad \Delta T_C = \Delta T_H / (1 - \exp(-\Delta T_H / LMTD_C)) \quad (6)$$

Consider next the irreversibilities associated with Cycle B where the refrigerant changes temperature during the heat transfer processes. Equation (2a) is a valid expression for the irreversibilities in the evaporator. However the entropy change of the refrigerant is not as simple to determine as in Cycle A where the temperature of the refrigerant remained constant. The refrigerant entropy change can be calculated using either of the following equations which are equivalent

$$\Delta S_{\text{Refrigerant}} = m \int \frac{dh}{T} \quad (7a)$$

$$\Delta S_{\text{Refrigerant}} = \int \frac{\partial Q_L}{T} \quad (7b)$$

If one considers the use of a nonazeotropic binary mixture undergoing a constant pressure, variable temperature phase change, the enthalpy change can be written

$$dh = C_p dT \quad (8)$$

where

$$C_p = \text{constant} = \left. \frac{\partial h}{\partial T} \right|_p \quad (9)$$

Substituting Equations (8) and (9) into (7a) or (7b) and integrating across the heat exchanger, the refrigerant entropy change becomes

$$\Delta S_{\text{Refrigerant}} = \dot{m} C_p \ln(T_3/T_2) \quad (10)$$

This can be written in terms of the specified load as

$$Q_L = \dot{m} C_p (T_3 - T_2) = (UA)_E \text{ LMTDE } F_E = (\dot{m} C_p \Delta T_L)_{\text{H.T. Fluid}} \quad (11)$$

$$\Delta S_{\text{Refrigerant}} = \frac{Q_L \ln(T_3/T_2)}{T_3 - T_2} \quad (12)$$

The entropy change of the low temperature heat transfer fluid due to the irreversible heat transfer with T_L is the same as for Cycle A. The total irreversibility associated with the evaporator in Cycle B then becomes

$$I_E = Q_L \left[\frac{\ln(T_3/T_2)}{T_3 - T_2} - \frac{1}{T_L} \right] \quad (13)$$

Using a similar approach for the condenser, the total irreversibility associated with the other heat exchanger becomes

$$I_C = (Q_L + W_{\text{net}}) \left[\frac{1}{T_H} - \frac{\ln(T_1/T_4)}{T_1 - T_4} \right] \quad (14)$$

One can show that the net power required for a given load on a refrigeration or heat pump cycle operating between two fixed temperature levels can be written as /3/.

$$W_{\text{net}} = W_{\text{Carnot}} + I_{\text{Total}} T_H, \text{ C.O.P.} = Q_L / W_{\text{net}} \quad (15)$$

where

$$W_{\text{Carnot}} = Q_L (T_H - T_L) / T_L, \text{ C.O.P. Carnot} = T_L / (T_H - T_L) \quad (16)$$

The only irreversibilities in the cycles considered here are associated with the two heat exchangers so the net power required can be written

$$W_{\text{net}} = \frac{Q_L (T_H - T_L)}{T_L} + (I_C + I_E) T_H \quad (17)$$

Evaluating Equation (17) for Cycle A with fixed working fluid temperatures during the heat transfer processes results in

$$\text{C.O.P.}_A = \frac{T_H}{T_H + \Delta T_C} \left/ \left[\frac{T_H - T_L}{T_L} + \left(\frac{T_H}{T_L - \Delta T_E} - \frac{T_H}{T_L} \right) + \left(1 - \frac{T_H}{T_H + \Delta T_C} \right) \right] \right. \quad (18)$$

Note that when $\Delta T_C = \Delta T_E = 0$, Cycle A shown on Figure 2c becomes equal to the Carnot cycle shown on Figure 2a and Equation (18) reduces to Equation (16). Evaluating Equation (17) for Cycle B with the variable temperature working fluid during the heat transfer processes results in

$$\text{C.O.P.}_B = \frac{T_H \ln(T_1/T_4)}{T_1 - T_4} \left/ \left[\frac{T_H - T_L}{T_L} + \left(\frac{T_H \ln(T_3/T_2)}{T_3 - T_2} - \frac{T_H}{T_L} \right) + \left(1 - \frac{T_H \ln(T_1/T_4)}{T_1 - T_4} \right) \right] \right. \quad (19)$$

If the temperature change of the refrigerant in Cycle B equals the heat transfer fluid temperature change through each heat exchanger and the heat exchangers are purely counterflow, $T_2 = T_L - \Delta T_L - \text{LMTD}_E$, $T_3 = T_L - \text{LMTD}_E$, $T_1 = T_H + \text{LMTD}_C$ and $T_4 = T_H + \Delta T_H + \text{LMTD}_C$. Under these conditions, Equations (18) and (19) can be written solely in terms of T_H , T_L , ΔT_H , ΔT_L , LMTD_C and LMTD_E . If the refrigerant temperature change differs from the heat transfer fluid temperature change, T_2 or T_3 and T_1 or T_4 must be known. The two remaining unknown refrigerant temperatures can be computed from the following equations:

$$\text{LMTD}_E = \frac{T_3 - T_2 - \Delta T_L}{\ln \left(\frac{T_L - T_2 - \Delta T_L}{T_L - T_3} \right)}, \quad \text{LMTD}_C = \frac{T_1 - T_4 + \Delta T_H}{\ln \left(\frac{T_1 - T_H}{T_4 - T_H - \Delta T_H} \right)} \quad (20)$$

It can be shown that $\text{C.O.P.}_B > \text{C.O.P.}_A$ whenever the same values of T_H , T_L , ΔT_H , ΔT_L , LMTD_C and LMTD_E are assumed for the two cycles. For example, if the refrigerant and heat transfer fluid temperature changes are equal, $\Delta T_H = \Delta T_L = 10\text{K}$, $T_H = 300\text{K}$, $T_L = 250\text{K}$, and $\text{LMTD}_C = \text{LMTD}_E = 5\text{K}$, then $\Delta T_C = \Delta T_E = 11.57\text{K}$, $T_1 = 305\text{K}$, $T_2 = 235\text{K}$, $T_3 = 245\text{K}$ and $T_4 = 315\text{K}$. The cycle performance values become $\text{C.O.P.}_A = 3.26$, $\text{C.O.P.}_B = 3.43$ which indicates that the C.O.P. of Cycle B is 5% larger than for Cycle A. Approximately two-thirds of the cycle irreversibility is associated with the evaporator, the remaining one-third is with the condenser. If the refrigerant temperature change does not match the heat transfer fluid temperature change, Cycle B continues to show improved performance over Cycle A but the improvement is less than for the matching case. If the values in the example above are used again except T_2 is set at 237K and T_4 at 313K, T_3 and T_1 are computed from Equation (20) to be 242.263K and 307.737K respectively and the C.O.P. for Cycle B changes to 3.39, a 4% improvement over Cycle A. The difference in C.O.P. between the two cycles is generally less than 10%.

Some data have been presented that show the phase change heat transfer coefficient to be lower in a nonazeotropic mixture than in a pure substance /1/ which would make $U_B < U_A$. The heat exchangers may not be strictly counterflow which gives a log mean temperature correction factor, F_B , less than 1.0. Both these factors will increase the values for LMTD_C and LMTD_E for Cycle B when Q_L , T_H , T_L , ΔT_H and ΔT_L are the same for both cycles. Cycle B will have a C.O.P. greater than for Cycle A (3.26) when $\text{LMTD}_C = \text{LMTD}_E < 6.56\text{K}$. Therefore in the example illustrated here, Cycle B will have a superior performance to Cycle A only when $U_B F_B / U_A \geq 0.76$.

3. THEORETICAL SINGLE STAGE MECHANICAL VAPOR COMPRESSION REFRIGERATION CYCLE

A theoretical single stage refrigeration cycle has a reversible, adiabatic compression process that begins with saturated vapor and lies entirely in the

superheated vapor region. The reversible, adiabatic expander is replaced by an adiabatic throttling device with fluid entering at the saturated liquid state. The heat transfer processes are similar to those described in the previous section.

Consider two theoretical single stage cycles, one using a pure substance as the refrigerant, the other using a nonazeotropic binary mixture. Each cycle has the same load on the evaporator, $Q_L = 3.52$ kW and operates between the same heat transfer fluid temperature levels, $T_L = 245$ K and $T_H = 302$ K. The log mean temperature difference in the evaporator and in the condenser is the same for each cycle, $LMTD_E = 9.938$ K and $LMTD_C = 11.058$ K. Each cycle has saturated vapor leaving the evaporator and saturated liquid leaving the condenser.

In the present example, a 50% mixture of R-12 and R-22 is used as the mixture and pure R-12 and R-22 as the pure refrigerant. The mixture properties were obtained from /4/ and the R-12 and R-22 properties from /5/.

Results of the performance of the three cycles operating under the conditions given above are shown in Table 1.

The results show that the C.O.P. from three cycles are within 6% of each other. The mixture has the lowest C.O.P. which does not agree with the previous results. The discrepancy could be caused by the property values used for the mixture. These are not well documented or easy to apply and may have contributed to the difference.

Table 1. Performance of three ideal theoretical single stage mechanical vapor compression refrigeration cycles, $T_H = 302$ K, $T_L = 245$ K, $\Delta T_E = 9.938$ K, $\Delta T_C = 11.058$ K

	50%/50%	R12	R22
	R12/R22		
Q_L (kW)	3.52	3.52	3.52
Q_H (kW)	5.42	5.34	5.33
W_{Comp} (kW)	1.90	1.82	1.81
C.O.P.	1.85	1.93	1.95
I_{Total} (KW/k)	0.0036	0.0033	0.0033

4. CONCLUSIONS

The analysis above is valid for any two-phase mixture region and any refrigerants selected. The results indicate that a nonazeotropic refrigerant mixture can provide a larger theoretical cycle C.O.P. than the exact same system operating under the same conditions using a simple substance as the refrigerant. The performance difference is generally less than 10%. The nonazeotropic mixture system will exhibit inferior performance if the overall heat transfer coefficient ratio times log mean temperature correction factor is less than some prescribed amount. An example of a theoretical single stage system showed the mixture cycle to have a lower C.O.P. However this could be attributed to inaccurate thermodynamic properties.

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L'effet d'un Mélange Réfrigérant Binaire Nonazeotropique
sur le Rendement d'un Cycle de Réfrigération Simple

Nous présente une analyse thermodynamique fondamentale rigoureuse d'un réfrigération simple ou d'un cycle de pompe thermique, qui fonctionne entièrement dans une région de mélange diphasé. La seule différence entre un cycle qui utilise une matière pure comme réfrigérant et celui qui utilise un mélange binaire se trouve dans l'opération de deux échangeurs thermiques extérieurs. Les résultats numériques montrent que le cycle que utilise la matière pure a un C.O.P. supérieur à celui qui utilise le mélange binaire, quand tous les deux fonctionnent avec la même charge réfrigérante et aux même niveau de température extérieure. Un exemple d'un cycle qui utilise R12 pur, R22 pur ou un mélange 50/50 de R12 et de R22 illustre le fait que le rendement (C.O.P.) théorique du cycle (avec le mélange) est presque la même qu' avec chaque matière pure.

EFFECT OF A NONAZEOTROPIC BINARY REFRIGERANT
MIXTURE ON THE PERFORMANCE OF A SINGLE-STAGE
REFRIGERATION CYCLE

This paper shows a fundamental thermodynamic analysis of a single-stage refrigeration system of a heat pump cycle, that works in a region of binary mixture. The only difference between a cycle using a simple substance as refrigerant and a cycle using a binary mixture is to be found in the operation of two external thermic heat exchangers. Numerical results evidence that the cycle that uses a pure substance has a lower C.O.P. than the one which uses a binary mixture when both use the same refrigerant quantity, and both external temperatures are the same. An example of a cycle that uses either a pure R12, a pure R22 or a mixture of 50% of R12 and 50% of R22 shows that the theoretical performance of the cycle (C.O.P.) with the mixture is lower than with every pure substance.