Simulation of a Leak/Recharge Process of Refrigerant Mixtures

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As alternatives to ozone-depleting refrigerants, zeotropic and near-azeotropic mixtures of nonflammable and flammable hydrofluorocarbon (HFC) refrigerants are being evaluated for use in most refrigeration/air conditioning machines that do not have flooded evaporators. Refrigerant leak from these systems is very important because a mixture composition may shift to a flammable range. After a recharging process, the mixture composition changes, as does the performance of the system. A model simulating isothermal and adiabatic leaks was presented by the authors in the first issue of this journal. This paper presents an isothermal or adiabatic leak simulation with a recharge process which is capable of simulating up to five cycles. Case studies of an isothermal leak of vapor and liquid phases, with a liquid or vapor recharge process were conducted for binary and ternary refrigerant mixtures at the specified overall composition of R-32/134a (30/70% by mass) and R-32/125/134a (23/25/52% by mass). Mass fraction changes in both vapor and liquid phases are presented. A theoretical machinery system performance change after each recharge was evaluated using another NIST simulation model. Changes in capacity and COP are presented.

INTRODUCTION

Development of an environmentally safe, single component fluid with similar saturation pressure has not been successful for HCFC-22 and R-502. Therefore, mixtures of two or more refrigerants are considered as alternatives to get a reasonable performance and desired properties. In a few special cases, the mixture forms an azeotrope. Otherwise, zeotropic mixtures are formed which have temperature and composition changes during evaporation or condensation processes. The development of refrigerant mixtures is inevitable, considering the limited number of pure refrigerants and the requirements which an alternative must meet. For the zeotropic mixtures, it is very important to predict the composition change under the leak conditions. Recently a study related to the leak process of refrigerant mixtures was done by Kim and Didion (1995), and the leak experiments of refrigerant mixtures were compared with the simulation results by Shiflett et al. (1992), and Kruse and Rinne 1992), but a generic model to describe leak and recharge situation is not known in the open literature.

In this paper, leak and recharge scenarios related to zeotropic mixtures are simulated. The objective of this study is an estimation of composition changes of the zeotropic mixtures in the leak and recharge process for vapor or liquid leak cases. The effect of composition change on the performance of refrigeration system is also dealt with. Two zeotropic refrigerant mixtures proposed as alternatives to R-22, namely, R-32/134a (30/70% by mass) (ASHRAE 1992) and R-32/125/134a (23/25/52% by mass) (Domanski and Didion 1993) were selected for sample calculations in this study.

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MODELING OF LEAK AND RECHARGE PROCESSES

During a leak process of a refrigerant mixture, refrigerant in a vapor or liquid phase escapes from the system. Inherently, the temperature of the fluid in the system decreases because the energy required for the vaporization is taken from the refrigerant remaining in the system and from the system wall. Two idealized cases of isothermal and adiabatic leaks are considered in this study. An Isothermal leak process represents a very slow leak situation in which the temperature of the system is maintained constant because of the heat transfer through the walls from the environment. In an adiabatic leak process, refrigerant leaks so quickly that no heat is transferred through the walls, and the temperature in the system decreases as the leak progresses. In the leak process of a refrigerant mixture, preferential evaporation makes the composition in the vapor phase different from that in the liquid phase. In order to model these leak situations, the following assumptions are made:

1. During the leak, only one phase (vapor or liquid) escapes from the system.
2. Refrigerant mixture inside the cylinder is in a vapor-liquid equilibrium state.
3. The leak process is either isothermal or adiabatic.
4. The escaping refrigerant has the same composition as the vapor inside the system during the vapor leak, or as the liquid during the liquid leak.

In recharging, the system is recharged with the refrigerant of the original composition. During recharge, refrigerant in either vapor or liquid phase from the charging cylinder can be put into the system. When the refrigerant from the charging cylinder is liquid, the composition change of the refrigerant mixture is negligible in comparison to when the refrigerant is vapor. In modeling the recharge process, liquid phase refrigerant in the charging cylinder is assumed to be put into the system, which is the recommended field practice for zeotropes. The amount of refrigerant mass added to the system is chosen to be the same as the mass which leaked out. After recharging, the temperature in the system is assumed equal to the initial temperature before the leak for the adiabatic leak process.

During the leak process, the overall mole fraction of the i-th component in the cylinder z_i is the sum of the mole fraction of the component i in both liquid and vapor phases.

$$z_i = x_i(1 - Q) + y_i Q \tag{1}$$

where Q is the overall molar quality defined by the molar fraction of the vapor phase in relation to the total number of moles in the system.

In the vapor or liquid leak, the number of moles of the escaped vapor is the same as the total number of moles released from the system. The remaining fluid in the system has an overall mole fraction z_i' for vapor leak:

$$z_i' = \frac{x_i(1 - Q) + y_i Q\left(1 - \frac{\varepsilon}{Q}\right)}{1 - \varepsilon} \tag{2}$$

and for liquid leak,

$$z_i' = \frac{x_i(1 - Q)\left(1 - \frac{\varepsilon}{1 - Q}\right) + y_i Q}{1 - \varepsilon} \tag{3}$$

where x_i and y_i are the mole fractions of the i-th component in liquid and vapor phase,

respectively, and ε is a fraction of the escaping moles with respect to the total number of moles in the system. Kim and Didion (1995) present other equations to describe the leak process.

The recharge process is modeled after a certain percentage of the original charge has leaked from the system. If the overall number of moles n^f exists in the system after the leak, and n^r mole with overall composition z^r is recharged into the system, the number of moles of the i-th component in the system after recharge n_i^a is

$$n_i^a = n_i^f + z_i^r n^r \tag{4}$$

The overall mole fraction of the i-th component in the system is

$$z_i^a = \frac{z_i^f + z_i^r \phi}{1 + \phi} \tag{5}$$

where $\phi = R/N^f$, and N^f is defined as the ratio of the final and the initial number of moles in the system. R is defined as the ratio of the recharged number of moles with respect to the initial number of moles. R can be rewritten as follows;

$$R = (1 - M^f)\frac{\overline{M}^i}{\overline{M}^r} \tag{6}$$

In Equation (6), M^f is defined as the ratio of the final and the initial mass in the system and $\overline{M}$ represents molecular mass.

The molar volume after recharging is represented by

$$v = \frac{v^i}{N^f + (1 - M^f)\dfrac{\overline{M}^i}{\overline{M}^r}} \tag{7}$$

The leak process is simulated in a quasi-steady manner by alternate steps of refrigerant escaping and the adjustment of internal refrigerant to thermodynamic equilibrium. The properties of refrigerant mixtures in the simulation are calculated by the REFPROP program (Gallagher et al. 1993).

LEAK/RECHARGE SIMULATION RESULTS

A schematic diagram of vapor and liquid leak/recharge systems is shown in Figures 1(a) and 1(b). During the leak process, vapor phase or liquid phase leaks out of the system, and after a user-specified amount of refrigerant has leaked, the system is recharged with the refrigerant of the original composition. In the recharging cylinder, it is assumed that the amount of liquid phase is much greater than that of vapor phase so that the composition of the recharging refrigerant remains uniform throughout the recharging cycles.

Leak/recharge Process of R-32/134a (30/70) Mixture

The leak and recharge path of R-32/134a mixture in the pressure-composition diagram is shown in Figure 2. This figure shows the pressure and the overall mass fraction change during two different isothermal vapor leak processes, one with an initial volumetric quality of 0 (i.e., full of liquid), and one with 0.85 (i.e., 15% volume of liquid in

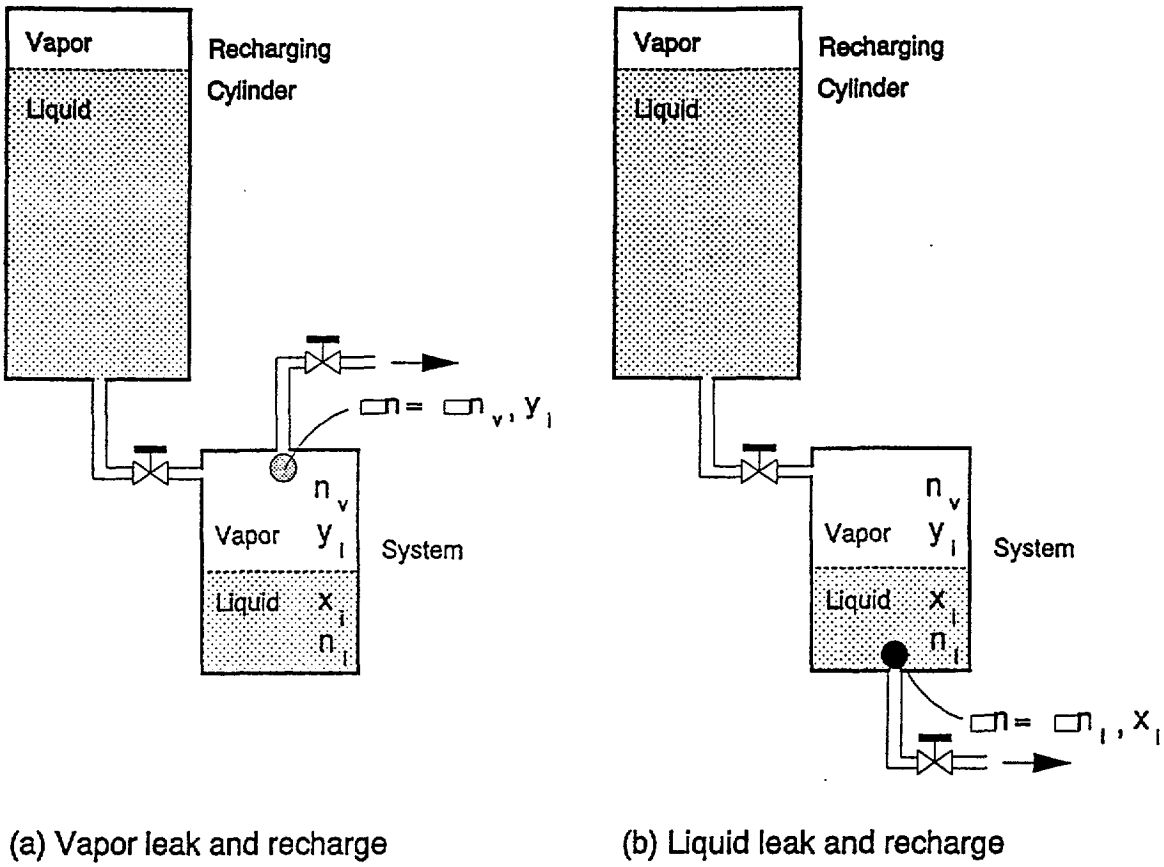

Figure 1. Schematic diagram of the leak and recharge system

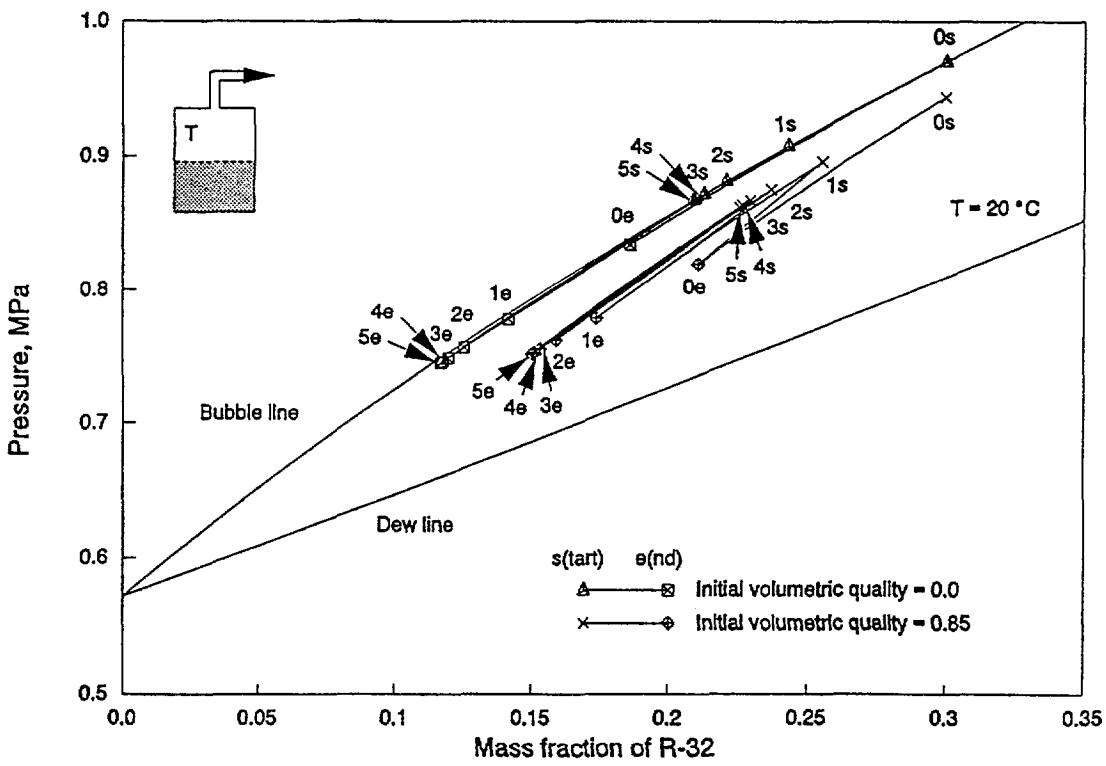

Figure 2. Pressure and overall mass fraction changes during isothermal vapor leak of R-32/134a mixture at 20°C for initial volumetric qualities of 0 and 0.85

(s and e represent starting and ending points of leak process, and numbers depict the number of recharges. System is recharged when 50% of refrigerant charge is leaked.)

the system). The bubble and dew lines at the constant temperature of 20°C are also shown. In Figure 2, 's' and 'e' represent the starting and ending points of each leak process, respectively, and the numbers indicate the state at the beginning of that particular recharge cycle. The path 0e – 1s represents the composition and pressure change during the first recharge process, and the path 0s – 0e – 1s – 1e represents the first two leak paths with one intermediate recharge. As the vapor phase leaks isothermally, the pressure decreases and the overall mass fraction of the more volatile component, R-32, decreases. It should be noted that the overall mass fraction just after the recharge (points marked with 's') approaches a constant value after several leak/recharge processes. This implies, with each succeeding recharge, that the escaping vapor approaches the same overall composition as that of the recharging liquid. This is because the mass fraction change is finite during the leak process and the system is recharged with the liquid phase of the same initial mass fraction. The overall mass fraction of the most volatile component, R-32, has its highest fraction initially, and the same is true for its mass fractions of the vapor and liquid phases. It is noteworthy that the fraction of R-32 decreases in the leak/recharge process because it is the only flammable component. The mole fractions x and y, obtained in the simulation are converted to mass fractions X and Y, and plotted in the various figures throughout this paper.

Temperature, pressure, and both liquid and vapor mass fractions are interrelated in the equilibrium state on which the leak/recharge simulation is based. Once temperature and pressure are given, vapor and liquid mass fractions are fixed for an equilibrium condition. In Figure 2, the mass fractions in the vapor and liquid phases are represented by the points at which the constant pressure line (horizontal line) touches dew and bubble lines, respectively. The mass fraction change during the isothermal vapor leak/recharge process for the R-32/134a mixture is shown in Figure 3 as a function of the number of recharges. In this figure, vertical step changes in mass fraction

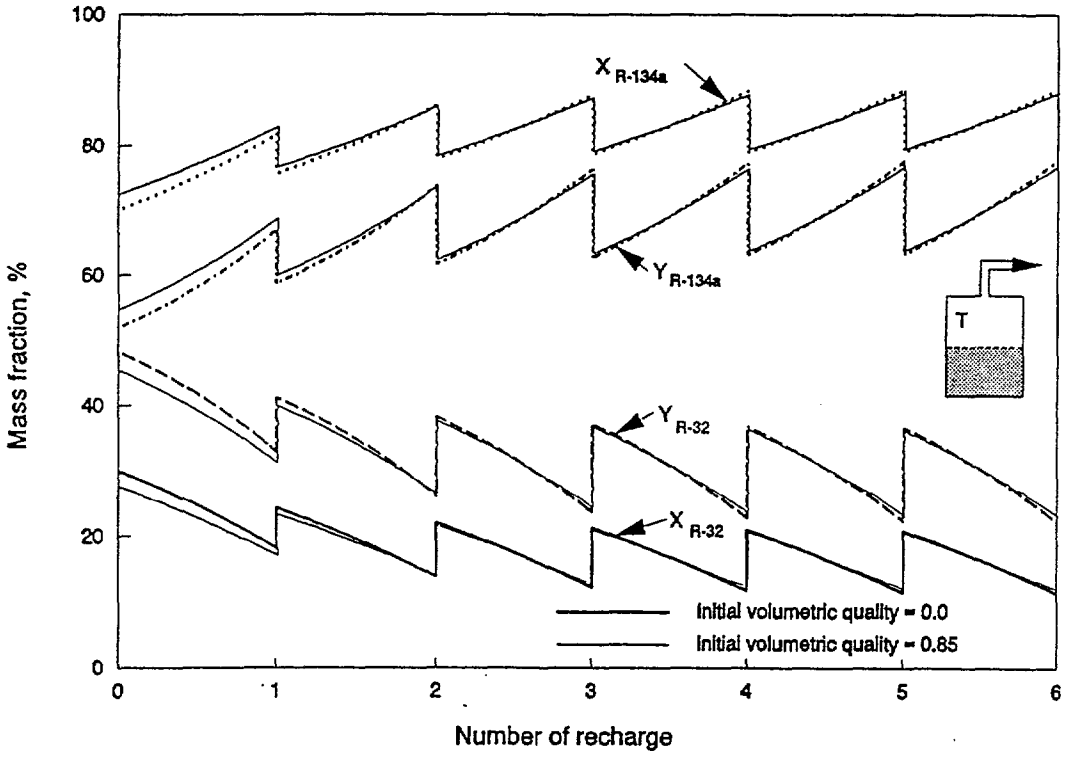

Figure 3. Mass fraction change during isothermal vapor leak/recharge process of R-32/134a mixture at 20°C as a function of number of recharges for two different initial volumetric qualities

(During each leak process, mass fraction change is plotted with respect to the leaked mass percentage. System is recharged when 50% of refrigerant charge is leaked.)

represent recharge process and between the steps are the isothermal leak paths with respect to the leaked mass fraction in percentage. In this simulation, the system is recharged with liquid refrigerant at 50% mass loss of the initial charge. For the case of initial volumetric quality of 0, the maximum change in mass fraction of vapor and liquid phases is represented. The simulation with initial volumetric quality of 0.85 represents a typical case of a heat pump system in which 15% of the internal volume is occupied by the liquid phase. The vapor, liquid, and overall mass fractions of the more volatile component (R-32) decrease during the isothermal vapor leak process because the mass fraction of R-32 in the leaking vapor phase is greater than that in the liquid phase. Because R-32 is the flammable component in this zeotropic refrigerant mixture (Richard and Shankland 1992), it is important for the leaking vapor and the remaining refrigerant mixture in the system to remain at a nonflammable composition and it should be noted that the initial charge has the highest percentage of the most volatile component during any isothermal vapor leak/recharge process.

The system pressure change during the isothermal vapor leak/recharge process is shown in Figure 4 as a function of the number of recharges. In Figure 4, both cases for initial volumetric quality 0 and 0.85 are shown, with vertical lines representing the mass fraction change during recharge process and other curves representing the leak paths. The pressure changes are derived from the data developed for Figure 2 by following the leak/recharge path. In the case for initial volumetric quality of 0.85, initial pressure is lower than that for the case of initial volumetric quality of 0, and the pressure decrease during the leak process is smaller because the overall amount of vapor which leaks out of the system is smaller. The pressure after each recharge approaches a constant value rather quickly because the mass fractions in the vapor and liquid phases reach constant values quickly at a given temperature.

In the isothermal leak and recharge process for the liquid phase leak of the R-32/134a mixture, the mass fraction changes for the initial volumetric quality of 0 are

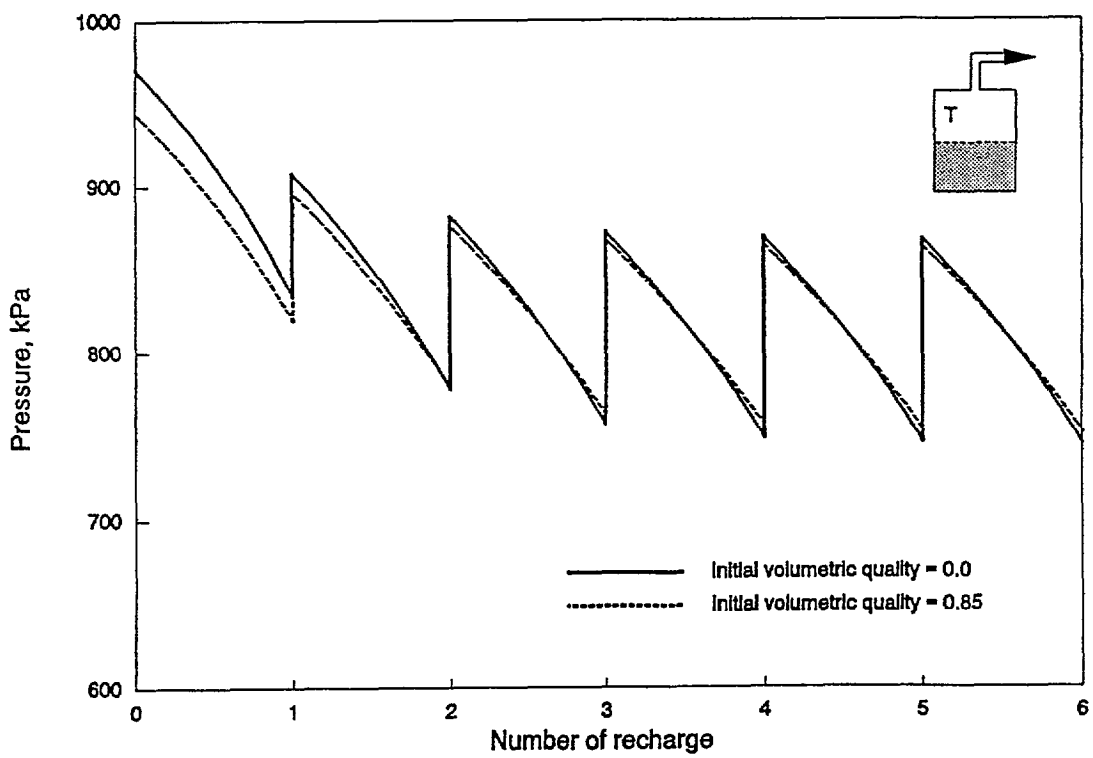

Figure 4. Pressure change during isothermal vapor leak/recharge process of R-32/134a mixture at 20°C

shown in Figure 5. Both the vapor and liquid mass fractions of the more volatile component ($Y_{R\text{-}32}$ and $X_{R\text{-}32}$) decrease only slightly during the leak process because both compositions in the vapor-liquid equilibrium decrease as the pressure decreases. Since each recharge operation replaces the leak mass with a liquid of virtually the same composition the mass fraction doesn't change much (less than 1%). After five recharges, both vapor and liquid phases have higher mass fractions of R-32, but only 0.2% variation from the initial refrigerant mixture. In the vapor leak, the mass fraction changes are greater due to the preferential evaporation of the more volatile component (R-32) from the liquid phase. During the liquid leak, only a small fraction of liquid must be vaporized to occupy the small volume of the escaping liquid and there is no severe change in the system. Therefore, the pressure decreases slightly and the mass fraction changes in both vapor and liquid phases are small.

In the adiabatic leak/recharge process, the refrigerant temperature decreases significantly because the escaping vapor evaporation energy taken from the liquid phase is not replaced by wall heat transfer, as shown in Figure 6. In this case, the refrigerant system was recharged after only 30% of the initial charge had leaked, because the temperature became too low for the property calculation. After recharge, it was assumed that the system has been restored to its original temperature of 20°C. The initial volumetric quality was chosen as 0, because this gives the maximum change in composition shift of any 30% leak and recharge process.

The mass fraction changes of each component in the vapor and liquid phases during the adiabatic vapor leak and recharge process of R-32/134a mixture are shown in Figure 7 as a function of number of recharges. In each leak process, the mass fraction in the liquid phase of the more volatile component (R-32), $X_{R\text{-}32}$, decreases, but the mass fraction in the vapor phase of this component, $Y_{R\text{-}32}$, increases. It is noteworthy that the highest mass fraction of the flammable component (R-32) is found in the vapor

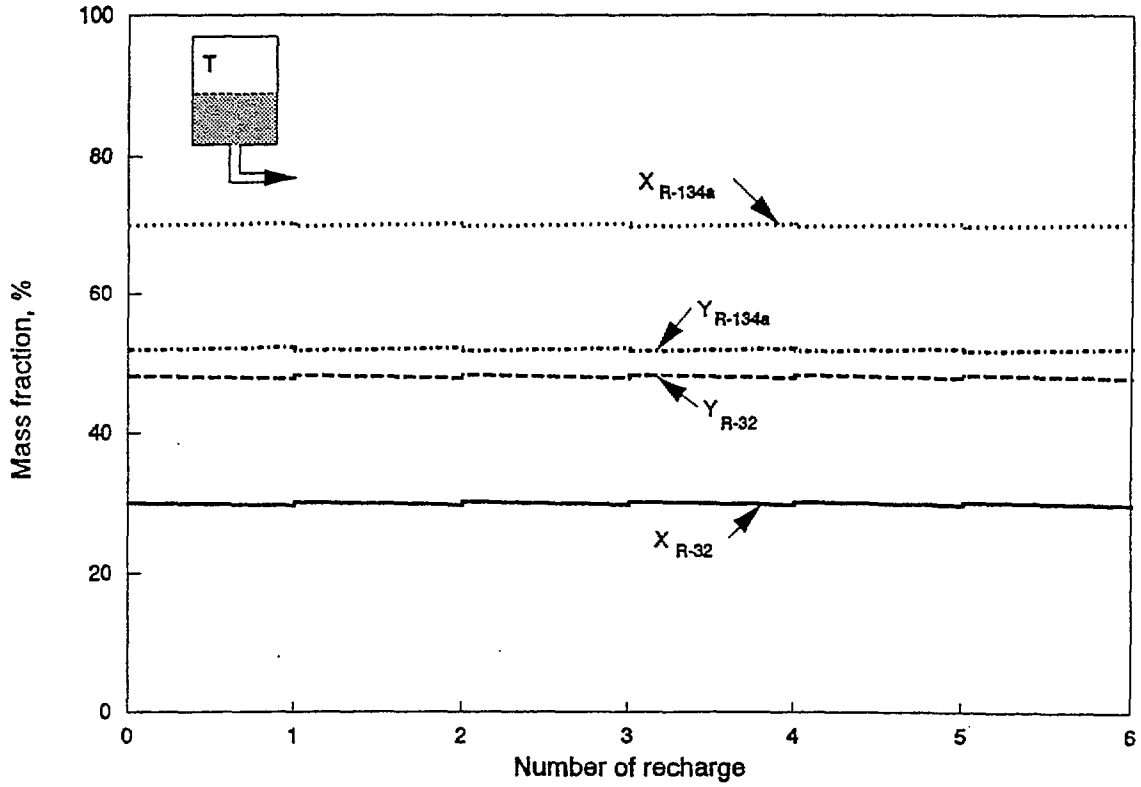

Figure 5. Mass fraction change during isothermal liquid leak/recharge process of R-32/134a mixture at 20°C as a function of number of recharges

(During each leak process, mass fraction change is plotted with respect to the leaked mass percentage. System is recharged when 50% of refrigerant charge is leaked.)

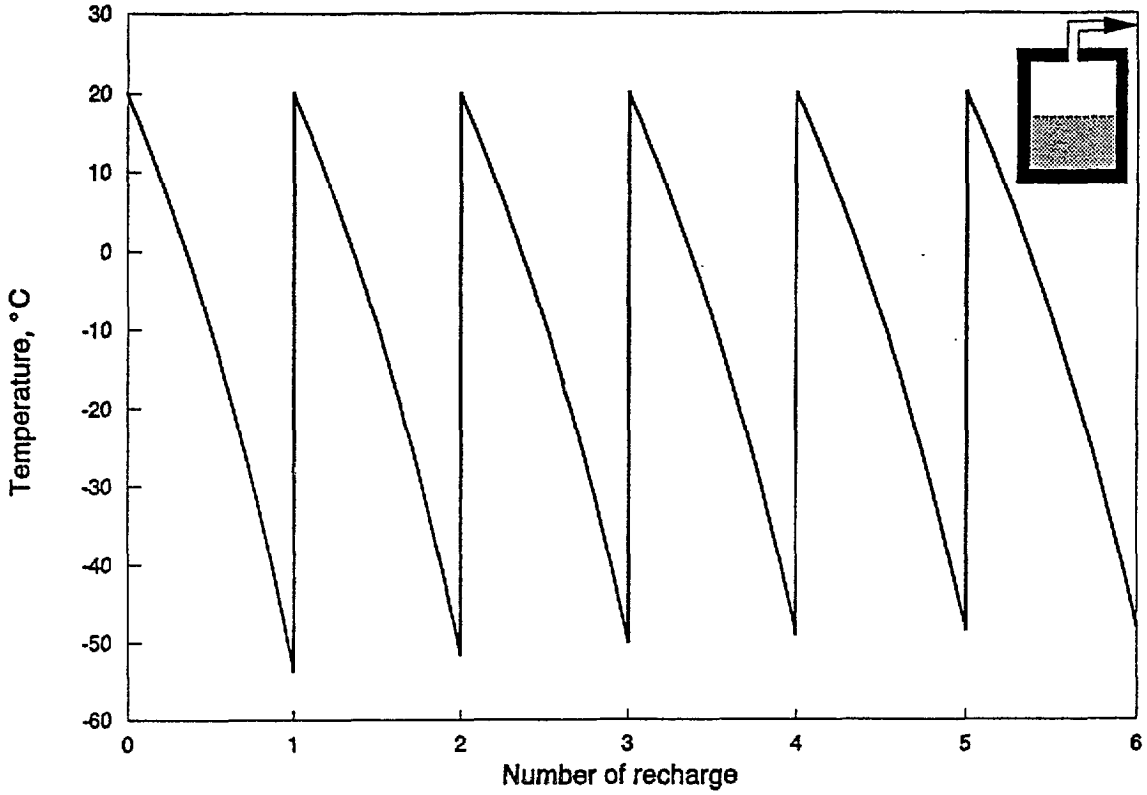

Figure 6. Temperature change during adiabatic leak/recharge process of R-32/134a mixture at initial temperature of 20°C and initial volumetric quality of 0

(After recharging, it is assumed that temperature is elevated to 20°C.)

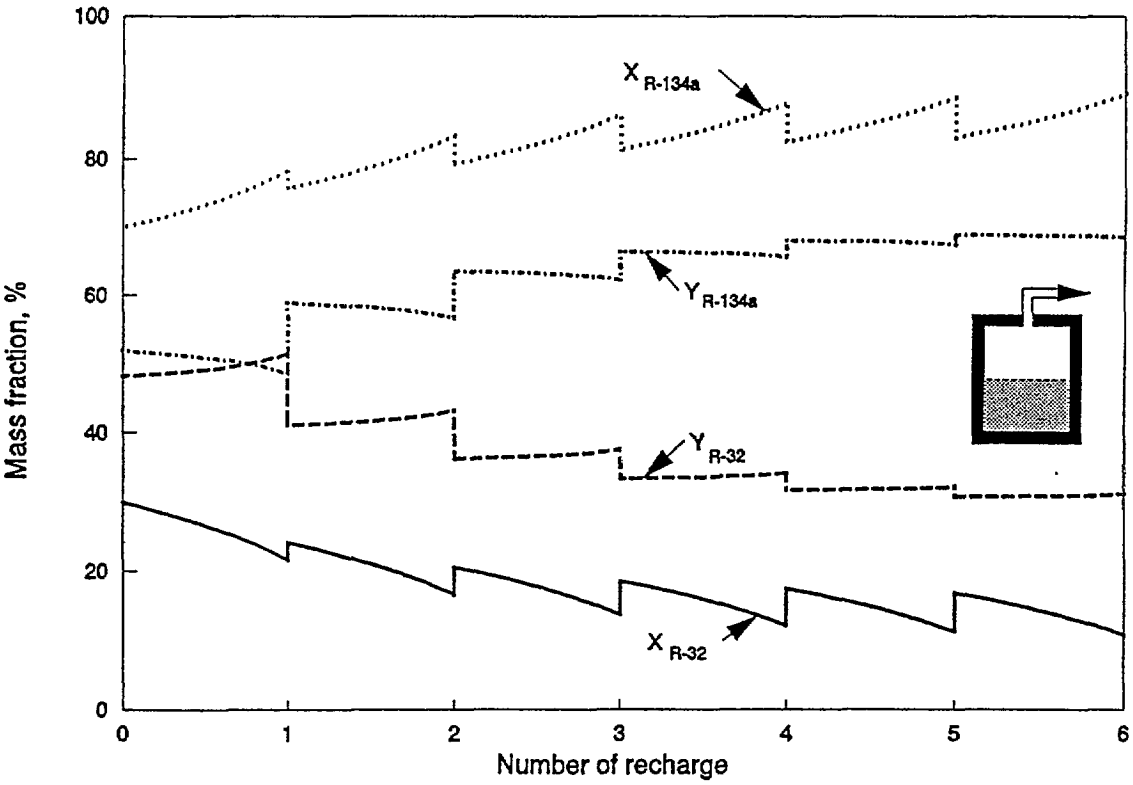

Figure 7. Mass fraction change during adiabatic vapor leak/recharge process of R-32/134a mixture as a function of number of recharges

(During each leak process, mass fraction change is plotted with respect to the leaked mass percentage. System is recharged when 30% of refrigerant charge is leaked.)

phase at the end of the first leak process. This is because the temperature drop influence on the equilibrium state is slightly more influential than the mass loss; see Figures 12 and 14 in Kim and Didion (1995). In the adiabatic leak/ recharge process, the mass fraction approaches a constant value more slowly than in the isothermal processes. Adiabatic liquid leak case is not considered because, as with the isothermal case, the composition shifting is quite small and, therefore, uninteresting.

Leak/recharge Process of R-32/125/134a (23/25/52) Mixture

For an R-32/125/134a mixture, an isothermal leak of 50% mass loss and recharge process, and an adiabatic leak with 30% mass loss and recharge process were examined. The mass fraction changes during the isothermal vapor leak/recharge process are shown in Figure 8 as a function of number of recharges, where vertical lines in the figure represent recharge process and other curves display leak process. Only the case for the initial volumetric quality of 0 is represented. The vapor and liquid mass fractions of the most volatile component (R-32) decrease and the least volatile component (R-134a) increase during the isothermal vapor leak process because the mass fraction of R-32 in the leaking vapor phase is greater, and that of R-134a is smaller, than that in the liquid phase. For the intermediate volatile component (R-125) in the ternary mixture, the mass fraction can be increased or decreased during the leak process depending on the thermodynamic vapor-liquid equilibrium of the mixture. In this study, the mass fractions of the intermediate volatile component in both vapor and liquid phases decreased during the leak process. The fraction of the flammable component, R-32, in the leaking vapor and the remaining refrigerant mixture in the system decreases during the leak.

During the adiabatic vapor leak and liquid recharge process, the initial volumetric quality was selected as 0. The mass fraction changes of each component in the vapor and liquid phases of R-32/125/134a mixture are shown in Figure 9. In each leak process, the mass fraction in the vapor phase of the most volatile component, R-32,

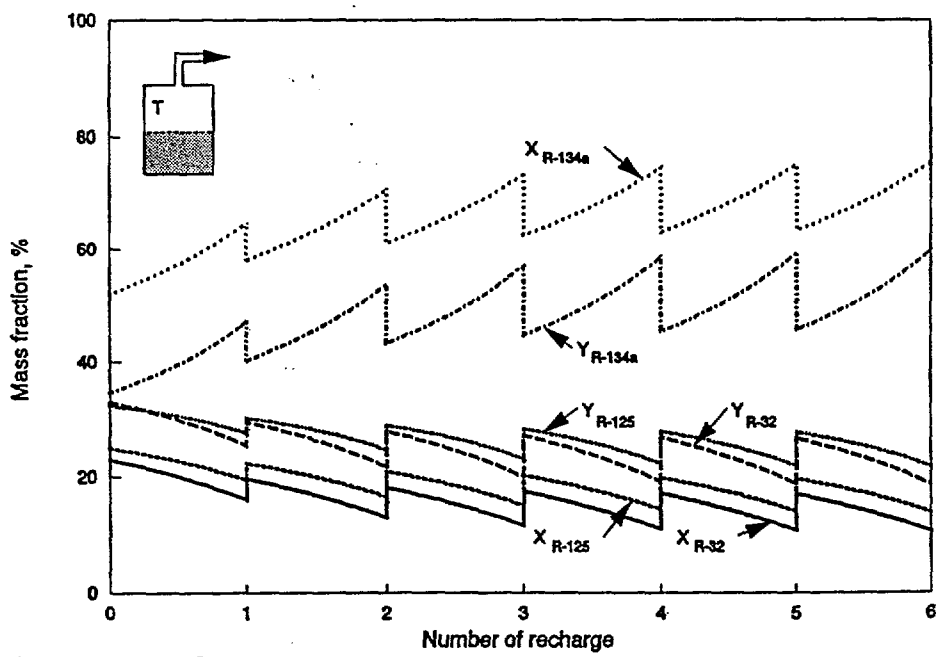

Figure 8. Mass fraction change during isothermal vapor leak/recharge process of R-32/125/134a mixture at 20°C as a function of number of recharges

(During each leak process, mass fraction change is plotted with respect to the leaked mass percentage. System is recharged when 50% of refrigerant charge is leaked.)

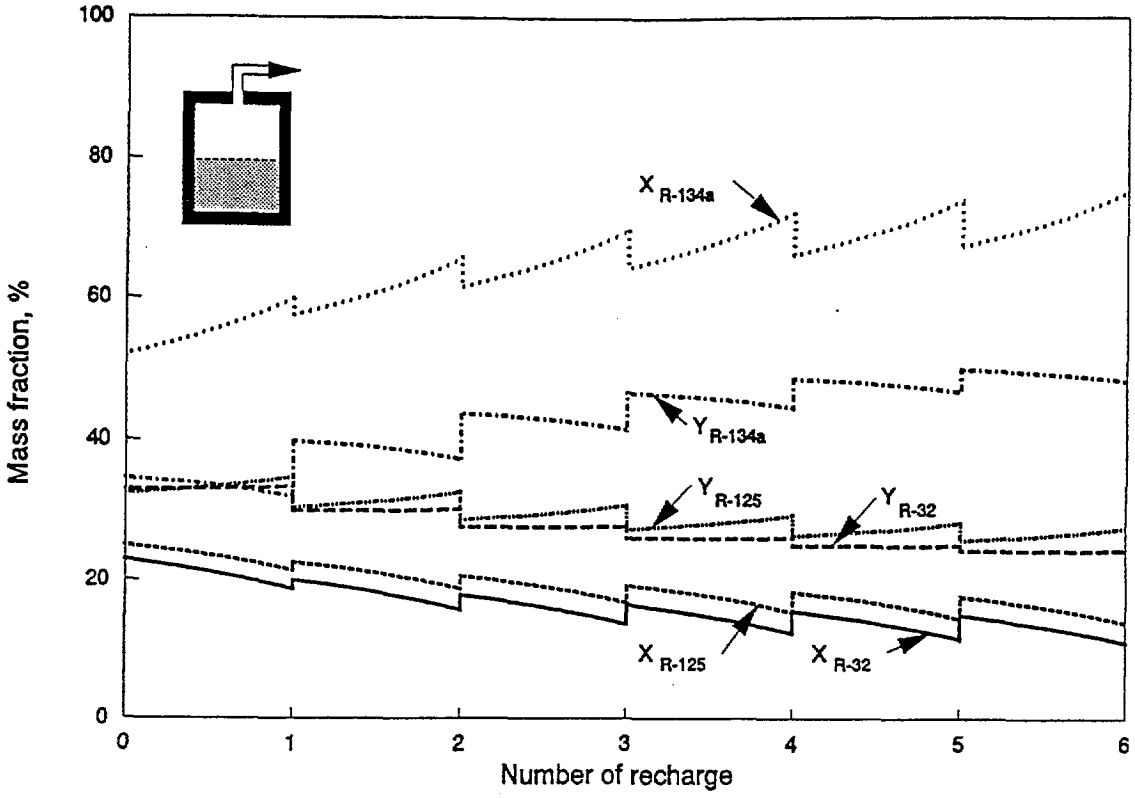

Figure 9. Mass fraction change during adiabatic vapor leak/recharge process of R-32/125/134a mixture as a function of number of recharges
(During each leak process, mass fraction change is plotted with respect to the leaked mass percentage. System is recharged when 30% of refrigerant charge is leaked.)

increased, but that in the liquid phase of R-32 decreased. When the mass fractions after each recharge are compared, the fractions of R-32 and R-125 are seen to decrease gradually and finally reach constant values.

SIMULATION OF CYCLE PERFORMANCE WITH LEAK/RECHARGE

Cycle performance change due to the composition change of refrigerant mixtures is described as a function of the overall composition change after each recharge. Both cooling capacity and coefficient of performance (COP) are obtained by using the program CYCLE11 (Domanski et al. 1994). The simulated vapor compression cycle is prescribed in terms of inlet and outlet temperatures of the external heat transfer fluids in the heat exchangers characterized by overall heat transfer coefficients. Thermodynamic properties of the refrigerants are calculated by the property calculation program (Gallagher et al. 1993). Typical data from R-22 heat pump laboratory tests were used as input including compressor speed, pressure drops through heat exchangers, condenser subcooling, evaporator superheating, etc. The temperatures of the heat transfer fluid entering and exiting the condenser were taken as 35.0°C and 43.2°C, and for evaporator, 26.7°C and 14.4°C, respectively.

The relative cooling capacity and coefficient of performance changes after each recharge with respect to those with the initial charge are shown in Figures 10 and 11 for R-32/134a and R-32/125/134a, respectively. The results from the leak/recharge simulations say that the mass fraction of R-32 decreased after each recharge, which means the density of the refrigerant mixture at the compressor inlet decreased since the saturation pressure of R-32 was higher than that of the other components. Also the latent heat of the refrigerant mixture decreased after each recharge. These two major factors give lower capacity with less fraction of R-32. The efficiency of lower capacity mixtures, however, was higher than that of the initial charge, as a result of lower heat

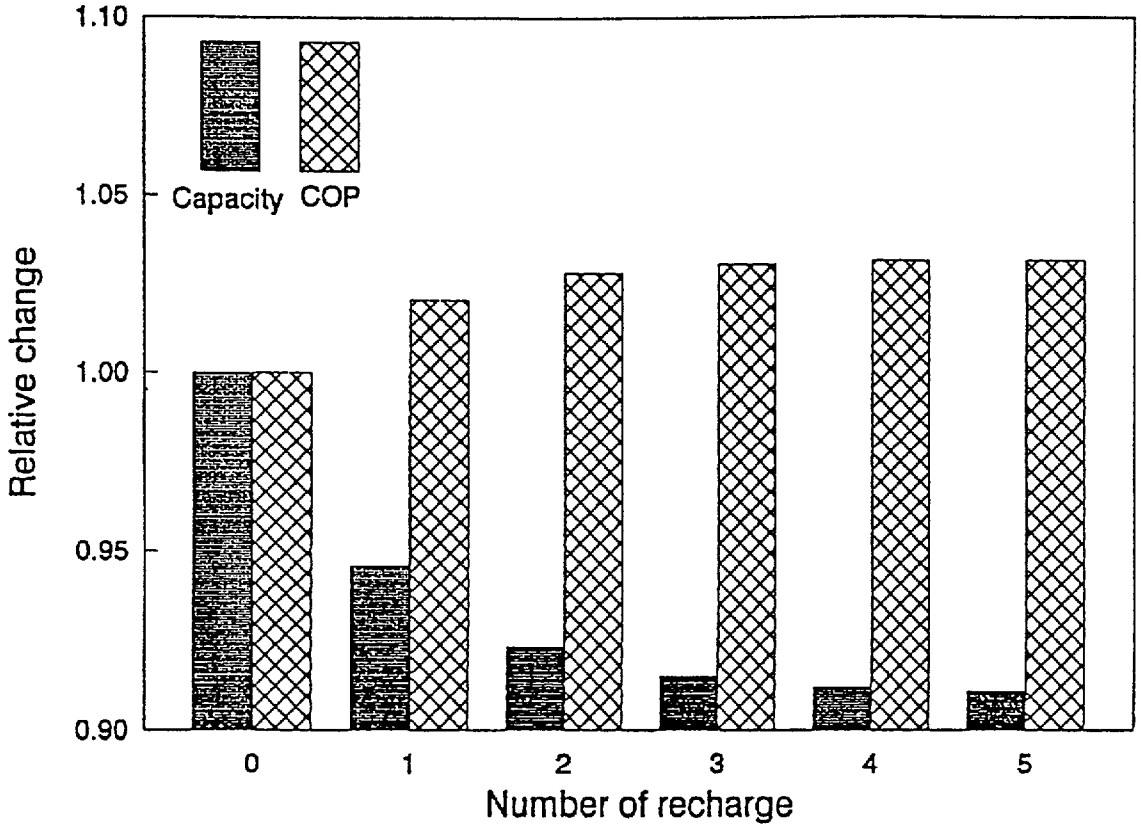

Figure 10. Relative change in capacity, coefficient of performance, with respect to those for initial charge during isothermal vapor leak of R-32/134a mixture
(Performance data are shown after each recharge process by the same mass of leaked refrigerant.)

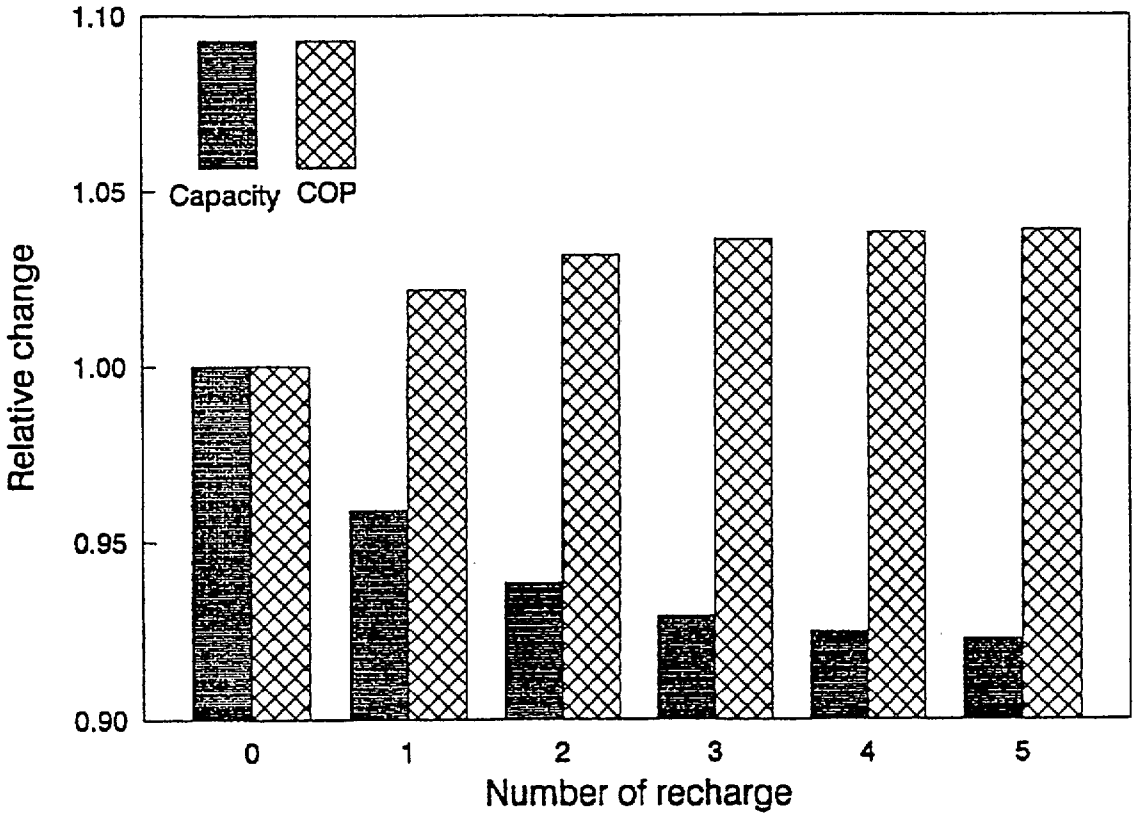

Figure 11. Relative change in capacity, coefficient of performance, with respect to those for initial charge during isothermal vapor leak of R-32/125/134a mixture
(Performance data are shown after each recharge process by the same mass of leaked refrigerant.)

fluxes and reduced refrigerant-to-heat source/sink temperature differences. The cooling capacity decrease after the fifth recharge of R-32/134a was about 8.9%, and the coefficient of performance increased around 3.2%. For the R-32/125/134a mixture, the capacity after the fifth recharge was about 7.7% less when compared with the capacity of initially charged refrigerant mixture, and the increase of the coefficient of performance was about 3.9%.

CONCLUDING REMARKS

In this paper, the leak/recharge process is described for isothermal and adiabatic leak conditions. Simulations were conducted for binary and ternary refrigerant mixtures; R-32/134a (30/70) and R-32/125/134a (23/25/52). The mass fraction change in the system was presented with respect to the mass percentage leaked and the number of recharge. During the isothermal leak, vapor and liquid mass fractions of the most volatile component decrease, and in the adiabatic leak process, the liquid mass fraction of this component decreased while the vapor mass fraction increased. Should a very slow leak occur (e.g., < 2%/hour) in an actual field condition, an isothermal leak process would be an accurate representation. Conversely, an adiabatic condition often assumed for rapid leaks would not be an accurate assumption for a bursting leak of very short duration since the escaping vapor would draw significant heat from the system walls. Therefore, the adiabatic assumption in the calculations only represents a theoretical limit of the final state of the mixture.

After each recharge of the same leaked mass of refrigerant, the compositions reached constant values for the leak/recharge process. The highest fraction of R-32, the flammable component in the mixture, was obtained in the vapor phase at the initial state for isothermal vapor leak/recharge process. For adiabatic leak/recharge processes, the highest fraction of R-32 was obtained at the end of the first leak of the mixtures evaluated. The simulated heat pump performance (capacity and coefficient of performance) significantly changed after each recharge compared with that of the original refrigerant mixture.

When the equation-of-state is based on careful measurements, the prediction of the thermodynamic properties of the equilibrium states can be done with excellent precision. Therefore, the precision of the predictions made here are dependent on simulating the mixtures with REFPROP. The weakest link is most probably the mixing coefficients. If they are measured values, one can expect precision of ± 0.01 to 0.02 mole fraction. If the mixing coefficients are just estimated, then a less precise value can be expected. The ultimate verification, however, would be a comparison with carefully measured composition from a slowly leaking container (for an isothermal process). Such an arrangement is possible when one is trying to qualify a refrigerant mixture for a safety rating under UL *Standard* 2182 (UL 1994). Data taken for the simple leak tests required for the worst-case fractionated composition determination could be used as a reference for comparison with the simulated results. If the difference between the two is satisfactory, the leak/recharge simulation might then be used to replace the rather lengthy (over 50 hours) five cycle leak/recharge tests that are currently required.

ACKNOWLEDGMENT

The authors thank Mr. Terry Statt, Project Manager at Electric Power and Research Institute and Mr. John Ryan of the U.S. Department of Energy for the sponsorship and Professor Sung Tack Ro, Director of Turbo and Power Machinery Research Center (TPMRC) of Seoul National University for the support of M.S. Kim's research at NIST. The authors appreciate helpful comments of Dr. Piotr A. Domanski at NIST.

NOMENCLATURE

M^f ratio of the final and initial number of moles
$\overline{M}$ molecular mass, kg/kmol

N^f ratio of the final and initial mass
n total number of moles, kmol
Q molar quality
R ratio of the recharged number of moles with respect to the initial number of moles
v molar volume, m^3/kmol
X liquid mass fraction
x liquid mole fraction
Y vapor mass fraction
y vapor mole fraction
z overall mole fraction
ε escaping fraction of the total moles
ϕ defined as $\phi = R/N^f$

Subscript

i i-th component

Superscript

$'$ property at the next step after a leak
a property after recharge
i initial state
f final state
r recharging refrigerant

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