

1990

Refrigerating Oils for Alternative Refrigerants

T. Kaimai

Kyodo Oil Technical Research Center Co.

Follow this and additional works at: <http://docs.lib.purdue.edu/iracc>

Kaimai, T., "Refrigerating Oils for Alternative Refrigerants" (1990). *International Refrigeration and Air Conditioning Conference*. Paper 101.

<http://docs.lib.purdue.edu/iracc/101>

This document has been made available through Purdue e-Pubs, a service of the Purdue University Libraries. Please contact epubs@purdue.edu for additional information.

Complete proceedings may be acquired in print and on CD-ROM directly from the Ray W. Herrick Laboratories at <https://engineering.purdue.edu/Herrick/Events/orderlit.html>

Performance Evaluation of Pure and Mixed Refrigerants in Domestic Refrigerators: Drop-in Replacement of R12

D.S. Jung and R. Radermacher
Department of Mechanical Engineering, University of Maryland
College Park, MD 20742

ABSTRACT

Computer simulation of domestic refrigerators charged with pure and mixed refrigerants is performed in an attempt to screen out the best substitutes for R12. No system modification was considered in pursuit of drop-in replacement. In simulating a steady-state thermal system, both successive substitution and Newton-Raphson methods are employed independently and yielded the same results without any significant difference in their performance. An extensive screening was carried out for 15 pure and 21 mixed refrigerants. Results indicate that no single pure fluids may be a drop-in replacement for R12 due to the mismatch of volumetric capacity even if a few fluids such as R22, R152a, R142b, R141b have a comparable COP to R12. Only R22/R142b and R32/R142b mixtures yielded an increase in COP up to 3% with the same capacity as that of R12. In the short run, these mixtures may be substituted for R12 solving the ozone layer depletion problem without significant enhancement in energy efficiency. To reduce the greenhouse effect as well, however, a major system modification might be necessary to increase energy efficiency.

1. Introduction

It has been well known that the stratospheric ozone layer acts as a shield against harmful ultraviolet (UV) solar radiation. During the past decade, researchers have discovered that chlorine released from synthetic chemicals called chlorofluorocarbons (CFCs) migrates to the stratosphere and destroys ozone molecules. The direct consequence of the depletion of the ozone layer is that more UV radiation is incident upon the earth's surface threatening lives of living creatures. An Environmental Protection Agency (EPA) report [1] indicates that each one percent depletion would increase exposure to UV radiation by up to 2 percent. Because of the long atmospheric lifetime of CFCs, as much as 120 years, the effort of restricting or banning the use of ozone depleting CFCs should be made immediately.

Recognizing that the ozone layer depletion is a global problem, 24 nations and the European Economic Community (EEC) signed the Montreal Protocol to regulate the production and trade of the ozone depleting substances. Fully halogenated CFCs, R11, R12, R113, R114, and R115 are covered by the Montreal Protocol as Group 1. Since 1930, these CFCs have been used in the field of refrigeration due to their favorable characteristics such as non-flammability, low toxicity, and non-aggressive behavior with other materials. As a supporting evidence, a study [2] indicates that 35 to 40% of the end use of CFCs is in refrigeration and air conditioning. In particular, R12 is now predominantly used for small refrigeration, air-conditioning, heat pumps, and marine applications.

One of the active means of resolving the ozone layer depletion problem might be developing or utilizing already developed ozone-safe refrigerants. McLinden and Didion [3] evaluated 860 industrial fluids in the search for the alternatives in the vapor compression system according to the requirements of refrigerants. A molecular approach was undertaken to tackle the problem more fundamentally and systematically. Their study revealed that there is little evidence to indicate that the alternatives will come from other than CFC family. By virtue of their stability, thermodynamic and health and safety characteristics, and familiarity to both manufactures and users, CFCs remain to be the clear choice.

Due to the extensive research during the past years, refrigerant manufacturers have come up with new fluids such as R134, R134a, R141b, R142b, R143a, R123, R124, and R125. At the present time, some of the new refrigerants are being tested for the replacement of R12 in refrigerators, which may take a few years to determine the overall performance of the new fluids including material compatibility in actual machines.

Among various refrigeration methods, the vapor compression method has been the most popular one due to its simplicity and reliability and hence been employed in small refrigeration applications.

Consequently, most of the technology and development associated with the vapor compression cycle has been related to the machines charged with R12. Even if modern machines operating under the vapor compression cycle are fairly energy efficient, energy efficiency might be further improved with creative design. There is other evidence [1] that these CFCs are also closely associated with the greenhouse effect responsible for the global warming of the earth. The imminent goal of resolving the ozone layer depletion as well as greenhouse effect can be accomplished by utilizing ozone-safe refrigerants and improving energy efficiency of the energy conversion devices simultaneously.

Recently, the use of nonazeotropic refrigerant mixtures (NARMs) as working fluids in heat pumps and domestic refrigerators has shown theoretical promise due to the additional degree of freedom, composition [4,5,6]. During evaporation at constant pressure, the saturation temperature changes, which is called a gliding temperature effect. When heat transfer fluids (HTFs) exchange heat with refrigerant in a counter-current flow mode, the thermodynamic irreversibility might be reduced by matching the temperature glide (refrigerant side) against the drop (HTF side) resulting in an increase in the coefficient of performance (COP). Several other advantages have been claimed for NARMs in refrigeration systems. Among these are capacity control and lower pressure ratio across the compressor.

Even if the use of NARMs is a thermodynamically sound idea, the success strongly depends on the operating conditions and applications. For instance, there are contradicting reports regarding the performance of NARMs in refrigerators among various researchers. Stoecker [7] employed an R12/R114 mixture in a pilot refrigerator unit and failed to obtain any increase in COP. Another study [8] reported that when an R22/R114 mixture was substituted for R12 in an actual two evaporator refrigerator unit, no significant change in performance was observed at all compositions. Kruse et al. [9], however, employed an R22/R142b mixture in an experimental unit and observed an increase in COP of 10% and 1.5% in the pull down and steady-state tests respectively.

Of special interest in the studies associated with mixtures is the method of comparing COPs of pure and mixed refrigerants. Both experimental and theoretical studies of the refrigerators with many prospect pure and mixed refrigerants may be taken to compare COPs. The former approach would be very costly and take at least a few years to complete to investigate various options and combinations. The latter approach, however, is less time consuming and cheaper to examine many options provided that proper simulation is done under reasonable assumptions. In order to be more cost effective, it is essential that proper refrigerant substitutes be identified before they are tested in actual refrigerators. From this view point, the latter approach of simulation must not be overlooked.

Even if a simulation approach is needed as the preliminary tool to screen out prospect refrigerant substitutes, there has been no realistic model available in the literature to investigate various refrigerants including NARMs. The purpose of this paper is (1) to address details of two methods of simulating steady-state thermal systems (successive substitution and Newton-Raphson's methods), (2) to compare the COPs of pure and mixed refrigerants, and (3) to suggest system modifications necessary to improve the performance. The task of replacing R12 with new fluids would be even more costly if it were accompanied by major system modifications. In this work, the focus will be limited to drop-in replacement of R12 by new fluids without involving any system modification

2. Previous works

Stoecker and Walukas [6] simulated single and two evaporator refrigerators with R12/R114 mixtures. The simulation was ideal in nature such that saturated liquid left the condenser while saturated vapor entered the compressor. The temperatures of heat transfer fluids (HTFs) entering and leaving evaporator and condenser were specified. With the requirement of constant cooling load in the evaporator, mass flow rate of HTF in evaporator was fixed while that of HTF in condenser varied to account for the different amount of condenser heat discharged. All heat exchangers were specified by the product of an overall heat transfer coefficient and an area (UA). The unknown state variables resulting from the steady state simulation were solved by employing the Newton-Raphson's (NR) method.

The results indicated that at 0.5 mass fraction of R114, the power requirement is 11.4 % less than that of a mixture at 0.01 mass fraction of R114. Because the computer program was designed for the mixture only, it failed to simulate for pure components. In the simulation of two evaporator

refrigerators, two thirds of the refrigeration load was assumed to be performed at low temperature evaporator (LTE) while the remainder at high temperature evaporator (HTE). The results showed a power saving of 12% at 0.5 mass fraction of R114. The major drawback of the simulation is the inability of investigating various pure and mixed refrigerants. This study, however, was the first in its kind and well demonstrated a general procedure for the simulation of steady-state thermal system.

Kruse et al. [9] reported the results of the simulation of a two-evaporator refrigerator with R22/R114 and R13B1/R114 mixtures. A similar approach as that of Stoecker and Walukas' [6] was taken in the simulation employing the NR method. The model employed the Redlich-Kwong-Soave (RKS) equation of state to compute properties needed and was limited to few mixtures. For R22/R114 mixtures, theoretically calculated improvement in COP is 18 to 20% at 0.4 mass fraction of R22 while for R13B1/R114 mixtures 20% increase in COP was obtained at 0.7 mass fraction of R13B1. Since the model was designed for a two evaporator refrigerator, the effect of other fluids as a 'drop-in replacement' of R12 can not be investigated. Furthermore, R114 and R13B1 are the regulated fluids under the Montreal Protocol.

McLinden and Radermacher [10] developed a program, CYCLE7, and presented the fair methods for comparing the performance of pure and mixed refrigerants in the vapor compression cycle. Even if CYCLE7 was designed for heat pump applications, it still can be used for calculating and comparing refrigeration COP and capacity. As with Stoecker and Walukas' model, saturated liquid and vapor were assumed to leave the condenser and enter the compressor. The compressor was assumed to operate isentropically. External HTF temperatures and Log-Mean-Temperature-Difference (LMTD) were specified in both condenser and evaporator. The unknowns were solved by a successive substitution (SS) method. All thermodynamic properties needed for the simulation were computed by Carhahan-Starling-DeSantis(CSD) equation of state developed by Morrison and McLinden [11]. The CSD equation state currently supports 17 pure refrigerants and their binary mixtures as long as an interaction parameter is available from experiments. Thanks to the versatility of the CSD equation of state, CYCLE7 is capable of simulating the ideal vapor compression cycle for most of the pure and mixed refrigerants.

Radermacher and Lavelle [12] used CYCLE7 to compare the performance of R22/R142b mixture against that of R12. The results showed increases of both COP and pressure ratio of up to 12 and 16% respectively and a decrease of capacity by 8% for an optimized mixture. The major drawback of CYCLE7 is that the effects of superheat, subcooling, and a suction line heat exchanger are not taken into consideration. Consequently, the performance might have been overestimated. In this paper, a rather more realistic simulation of a single evaporator refrigerator will be addressed with an emphasis given to the feasibility of refrigerant mixtures as a drop-in replacement for R12.

3. Cycle Simulation

3.1 Overall description of refrigerator cycle

Figures 1 and 2 show the schematic and temperature-entropy (T-s) diagrams of a typical domestic refrigerator charged with mixtures. Both refrigerant and air stream temperatures are illustrated with heat flows for reference. At state 7, two-phase refrigerant enters the evaporator. Due to the heat exchange with air stream, evaporation occurs and usually superheated vapor leaves the evaporator (State 1). During evaporation refrigerant temperature rises for mixtures (gliding temperature effect) while the temperature remains constant for pure components without consideration of pressure drop. According to the engineers at one of the major refrigerator manufacturing companies, the refrigerant vapor would reach close to the ambient temperature after further being heated by passing through the suction line heat exchanger (SLHX) and enter the compressor (State 2).

Presently, two types of condensers, natural and forced convection types, are available in the market. For medium to large capacity units, however, the forced convection type becomes predominant. Hence, a forced convection type condenser is assumed in the analysis. The condenser is assumed to be sized such that the subcooled liquid approaches the ambient temperature. Consequently, the vapor entering compressor, state 2, and liquid leaving the condenser, state 6, are at room temperature. In other words, the efficiency of the suction line heat exchanger is close to 1. Finally, expansion occurs through a capillary tube to complete the cycle.

In order to compare the performance of various fluids on a fair basis, it is reasonable to require of refrigerators that the net refrigeration effect, Q_{EVAP} , is constant regardless of the working fluids. This is accomplished by specifying air stream temperatures entering and leaving the evaporator, TS_7 and TS_1 , with a fixed mass flow rate, \dot{m}_E , generated by a fan in the freezer. As the compressor power, W_C , varies with working fluids, so does the coefficient of performance.

Since W_C differs with various fluids, the heat discharged through the condenser, Q_{COND} , which is the sum of Q_{EVAP} and W_C , also depends upon fluids. The air stream temperature entering the condenser, TS_6 , is assumed to be at ambient temperature. Since the volume flow rate of the air stream in the condenser side, \dot{m}_C , is fixed by another fan, the temperature of the air stream in the condenser side including TS_3 , TS_4 , and TS_5 in Figure 1, must change to satisfy the energy balance.

It is assumed that the compressor is a positive displacement machine with a constant volumetric flow rate and the nonideality of the compression process is accounted for by specifying an isentropic compressor efficiency, ϵ_C . According to one of the compressor manufacturers, ϵ_C is roughly 10 % of the energy efficiency ratio (EER) of the compressor which is obtained by compressor calorimetry. For small compressor units used in refrigerators, a typical EER is 4-6. Thus, ϵ_C is fixed to be 0.55 for all fluids in this study.

3.2 Heat Transfer Formulation of Heat Exchangers

A proper formulation of heat transfer in the evaporator and condenser is necessary to simulate the overall system performance. Both the evaporator and condenser are specified by the product of an overall heat transfer coefficient and an area (UA). Actual internal refrigerant side heat transfer areas for the evaporator and condenser were taken from a 18 cubic feet refrigerator manufactured by Whirlpool Corp. An Oak Ridge National Laboratory (ORNL) report [8] lists an actually measured UA value for evaporators and hence the U value was taken from the report. The U for the condenser, however, was assumed to equal the U of evaporator.

With given UA values, the heat transfer in the condenser and evaporator is treated as:

$$LMTD_E = (1-f_{supc})LMTD_{ipc} + f_{supc}LMTD_{supc} \quad (1)$$

$$LMTD_C = f_{subc}LMTD_{subc} + (1-f_{subc} - f_{supc})LMTD_{ipc} + f_{supc}LMTD_{supc} \quad (2)$$

$$Q_{EVAP} = U_E A_E LMTD_E \epsilon_{HX} \quad (3)$$

$$Q_{COND} = U_C A_C LMTD_C \epsilon_{HX} \quad (4)$$

where f_{supc} is the fraction of the total evaporator heat in the superheated vapor portion of the evaporator, f_{subc} and f_{supc} are the fractions of the total condenser heat in subcooled and superheated portions of the condenser, $LMTD_{ipc}$ and $LMTD_{supc}$ are the log mean temperature differences in the two-phase and superheated portions of the evaporator, $LMTD_{supc}$, $LMTD_{ipc}$, and $LMTD_{subc}$ are the log mean temperature differences in the superheated, two-phase, and subcooled portion of the condenser, and ϵ_{HX} is the heat exchanger correction factor to account for the effect of having cross or parallel flow heat exchanges in the condenser and evaporator.

Pressure drops in the condenser and evaporator are prorated according to the amount of heat transfer in subcooled, two-phase, and superheated regions as:

$$\begin{aligned} P_4 &= P_3 - \Delta P_C f_{supc} \\ P_5 &= P_3 - \Delta P_C (1-f_{subc} - f_{supc}) \\ P_6 &= P_3 - \Delta P_C \\ P_8 &= P_7 - \Delta P_E (1-f_{supc}) \\ P_1 &= P_7 - \Delta P_E \end{aligned} \quad (5)$$

No pressure drop is assumed in the suction line heat exchanger.

3.3 Steady-State Thermal System Modelling

Steady-state thermal system simulation has many applications in the design and optimization of chemical and power plant and HVAC equipment. Stoecker [13,14] presented a generalized program for steady state system simulation. In Ref [14], both successive substitution (SS) and simultaneous solution using Newton-Raphson technique (NR) methods are described to solve the unknown variables resulting from the simulation of steady state thermal systems. The interested reader is referred to references [13,14] for more general information about the SS and NR methods.

Considering that experimental approaches usually take longer time and are expensive, a proper simulation of a thermal system may be needed to investigate a variety of options in the system and to reduce the number of experiments. Despite the growing demand of a proper system simulation, detailed information of the SS and NR methods as they are applied to an actual system simulation is not readily available. In this paper, both SS and NR methods to simulate refrigerators will be described in detail.

3.3.1 Successive Substitution Method

The SS method involves a number of loops in which certain specified conditions such as an energy balance are to be satisfied to reach a converged solution. It starts with an inner most loop with an assumed trial value at one point. Other variables are solved with the assumed value. Unless this set of solutions satisfies a specified condition within the loop, the old guess is modified and substituted till a convergence is achieved. With this converged solution, it proceeds to the next loop to perform the similar task till a converged solution is achieved at the outer most loop.

The saturation temperature of liquid at point 5 is assumed and P_5 and H_5 are calculated. At point 6, H_6 is calculated with fixed T_6 and calculated P_6 by equation (5). Through the suction line heat exchanger, the amount of heat transferred, HX_{69} is assumed and hence H_9 is determined. With H_9 and P_9 , T_9 is determined. The temperature of refrigerant entering the evaporator, T_7 , is assumed. H_7 is the same as H_9 through an isenthalpic expansion process. P_7 is determined with T_7 and H_7 . At point 8, T_8 and H_8 are determined since P_8 is assumed to be known from equation (5). Since the degree of superheat is imposed, T_1 is known with P_1 .

At this stage, all variables in the evaporator side are determined. The log mean temperature difference in the evaporator, $LMTD_E$, is calculated and compared to the imposed value, DT_E which is determined by the specified amount of cooling load, Q_{EVAP} , and $U_E A_E$. If they are within a specified limit, the procedure is continued to the next loop starting from the state 2. Otherwise, T_7 is newly guessed and the procedure is repeated till $LMTD_E$ and DT_E are within a specified limit.

At state 2, with fixed T_2 and $P_2 = P_1$, H_2 and S_2 are determined. At state 3, P_3 and $S_3 = S_2$ are known and hence T_3 and H_3 are determined. At this point, of course, an isentropic compressor efficiency, ϵ_c is taken into account. With known P_4 , T_4 and H_4 are determined. At this stage, Q_{EVAP} , W_C , and Q_{COND} are calculated. If the energy balance of $Q_{EVAP} + W_C = Q_{COND}$ is not satisfied, then the procedure is repeated with $HX_{69} = H_2 - H_1$ to satisfy the energy balance in the heat exchanger. If the condition is met, then the log mean temperature difference in the condenser side, $LMTD_C$, is calculated.

The amount of heat transferred in the condenser is determined by equation (4) and compared with the sum of Q_{EVAP} and W_C . If they are within a specified limit, convergence is achieved and the simulation is done successfully. Otherwise, T_5 is newly guessed and the same procedure is repeated until the condition is satisfied. No serious problem of divergence has been observed with the SS method when it is applied to the simulation of refrigerators.

3.3.2 Simultaneous Solution (Newton-Raphson) Method

While the SS method involves a number of iterations within many internal loops to satisfy specified conditions to reach convergence, the NR method solves a set of nonlinear equations in a global manner. For a system without involving a chemical reaction, the Gibbs phase rule states that for binary mixtures either two or three properties are needed in a two or single phase condition respectively to fix the state of the system. For instance, at point 6 (single phase), three properties, T_6 , P_6 , and V_6 are to be known to determine H_6 needed for an energy balance while at point 7 (two-phase), $H_7 = H_9$ and P_7

are sufficient to determine other properties such as T_7 and quality. Table 1 lists the known (either fixed or assumed) and unknown variables at each state point.

The total number of independent variables in the simulation is 8 as in Table 2. Since all these variables are interrelated nonlinearly, a solution method for a set of nonlinear equations is needed. Even if there are a few algorithms available, the Newton-Raphson's method has been the most popular one and thus adopted in the study. The NR method requires initial guesses for all unknown variables so that the minimum number of properties as dictated by the phase rule is known to fix the state.

Since the states at each point are known (either fixed or assumed), all unknowns such as enthalpy are evaluated by the CSD equation of state. At each iteration level, the residuals listed in Table 2 are evaluated with thus calculated variables. Since the residuals may not be zero at first, the partial derivatives are calculated to obtain a new solution by solving the set of nonlinear equations simultaneously by a Gaussian elimination method. The change in the old and new solutions is checked against a convergence criterion. If convergence is not obtained, then the same procedure is repeated with a new solution till a convergence is achieved.

Overall, for the simulation of relatively simple thermal systems such as domestic refrigerators, both SS and NR methods were found to be satisfactory except that the execution time for the SS method took 20 to 25 % longer than that for the NR method. With the NR method, typical run times on a 80386/20 MHz PC with a 80387/20 MHz math-coprocessor were 20 and 40 seconds for pure and mixed refrigerants respectively.

4. Results and Discussion

A single evaporator refrigerator cycle (SERCLE) model has been applied to 15 pure refrigerants. Specified conditions are as follows; cooling load = 185 watts, air temperature entering and leaving the evaporator, $TS_1 = -11$, $TS_2 = -18$ °C, pressure drop in the evaporator and condenser, $\Delta P_E = 10$, $\Delta P_C = 15$ kPa, compressor efficiency and heat exchanger correction factor, $\epsilon_C = 0.55$, $\epsilon_{HX} = 0.8$, mass flow rate of air streams in the evaporator and condenser, $m_E = 0.026318$ kg/sec (40 CFM, density of air = 1.3947 kg/m³ at -20 °C) and $m_C = 0.05425$ kg/sec (100 CFM, density of air = 1.15 kg/m³ at 30 °C), ambient temperature, $T_{amb} = 32.22$ °C (90 °F), UA in the evaporator and condenser, $U_E A_E = 20$, $U_C A_C = 10$ (W/C).

Figure 3 illustrates the COP and percent increase (or decrease) of COP of each pure fluid as compared to that of R12 (ϕ_{R12}). The variation of COP among various refrigerants is less than 10% and only few refrigerants, i.e., R22, R141b, R142b, and R152a have slightly higher COP than R12 (Figure 3). It is no wonder why R12 and R22 have been the most popular refrigerants used in the vapor compression system. Considering the fact that the compressor is a constant volumetric flow rate device, the volumetric refrigeration capacity (kJ/m³) is expressed as the evaporator heat (kJ/kg) divided by the specific volume (m³/kg) of the vapor at the compressor inlet. The volumetric capacity is a measure of the compressor displacement volume as will be shown later.

Figure 4 shows the calculated volumetric capacities and pressure ratios across the compressor for various refrigerants. One can easily notice a distinct trend that the volumetric capacity and pressure ratio are a strong function of volatility; the more volatile a refrigerant is, the larger the volumetric capacity and the smaller the pressure ratio become.

The above finding leads to an interesting point; no single pure refrigerant can be a 'drop in replacement' of R12 unless major modifications are made in the compressor. For instance, even if R141b, R142b, R152a have higher COP than R12, their volumetric capacities are smaller than that of R12. Hence, in order to perform the same refrigeration duties, the compressor displacement volume should be increased with R141b, R142b, and R152a. The reverse is true with R22 and R32; a compressor with a smaller displacement volume is needed since the volumetric capacity is larger than that of R12.

Before considering binary mixtures as possible 'drop-in replacement' fluids, certain criteria have to be set to select best possible combination. With the same compressor, one of the requirements of any substitutes is that the volumetric capacity should be the same as that of R12. For a given binary

mixture, this requirement dictates that one component must be more volatile than R12 while the other be less volatile than R12, which is evident in Figure 4. For instance, the combination of R142b and R152a would always yield the smaller capacity than that of R12 since both components are less volatile than R12. On the other hand, R22 and R32 combination would always show the larger capacity due to their high vapor pressure.

A normal boiling point would be a useful parameter to select proper fluid pairs from the view point of vapor pressure. Fluids with higher normal boiling point are less volatile. Due to the requirement of the same volumetric capacity, the proper mixture should be composed of one component, more volatile than R12, and another, less volatile than R12.

Either predicted or experimentally observed increase in COP with binary mixtures largely comes from the well matching of the temperature glide and drop in refrigerant and air streams [10]. When temperatures are well matched, a fluid combination with a larger gliding temperature effect would yield a substantial increase in COP. A typical temperature drop or glide of air streams in the evaporator and condenser is less than 10 °C. Hence, another requirement of any possible combination of mixtures is that their gliding temperature be in the neighborhood of 10 °C in the evaporator and condenser to yield the maximum COP. With a temperature glide of only 10 °C, however, any significant increase in COP would not be expected [10].

Based on the above discussions, the possible binary mixture candidates may be selected as follows: The mixture would be a combination of one of R32, R125, R143a, and R22 as a more volatile component and one of R152a, R134a, R134, R142b, R141b, and R123 as a less volatile component.

It should also be considered that the COP of a mixture is in a sense a weighted value of pure components' COPs. Matching the temperature glide and drop in both streams is a necessary condition but not a sufficient one. In other words, for a binary mixture to yield any increase in COP, COPs of both pure components constituting a mixture should be reasonably high (ideally higher than R12). Otherwise, any gain expected by matching temperatures would be counter balanced by low COPs of pure components.

Since this study is concerned about the drop-in replacement of R12, COPs of pure components comprising a mixture should be comparable to that of R12 to warrant an increase in COP. Taking this into consideration, mixtures having one of R143a, R125, R123, R134, and R134a as a pure component would not be expected to yield any significant increase in COP. From the above consideration, what we are left with are R22 and R32 as more volatile components and R141b, R142b, and R152a as less volatile components.

Based upon the above reasoning, 21 mixtures were selected and the simulation was performed with SERCLE. For each mixture, overall composition varied from 0.0 to 1.0 mass fraction of the more volatile component in an interval of 0.1 mass fraction. The maximum COP (COP_{max}), percent increase of COP_{max} as compared to that of R12 (ϕ_{max}), and composition at which COP_{max} occurs (X_{max}), COP obtained at the composition where the volumetric capacity of mixture is the same as that of R12 (COP_{ve12}), percent increase of COP_{ve12} as compared to that of R12 (ϕ_{ve12}), and composition at which the volumetric capacity is the same as that of R12 (X_{ve12}) were determined and listed in Table 3.

Due to the small temperature drop of air stream in the evaporator, only small increase in COP was observed for all mixtures considered with the maximum increase in COP of only 5%. As explained above, in order to use the same compressor the volumetric capacity of a mixture should be the same as that of R12. When this is taken into consideration, the maximum percent increase in COP, ϕ_{ve12} , at compositions where the capacity is the same as that with R12 is just 2 to 3% obtained with R22/R142b and R32/R142b mixtures as listed in Table 3.

The results with mixtures also indicate that only a few pure fluids, i.e., R22, R32, R142b, and R152a can be constituents of the mixtures which may be substituted for R12. The requirement of having larger COP and keeping the capacity to that of R12 is satisfied only with the mixtures composed of these pure fluids.

Since the present study is concerned with the use of mixtures, it would be interesting to see how the results are affected by the gliding temperature difference in the evaporator and condenser, GTD_E and GTD_C respectively. Unlike the ideal Carnot cycle, evaporation occurs in the two-phase and superheated regions while condensation takes place in the subcooled, two-phase, and superheated regions as shown in the T-s diagram (see Figure 2). The evaporator superheat is usually less than 2% of the total evaporator heat. Thus, GTD_E is calculated to be the temperature difference between the saturated vapor and liquid (state points 8 and 7 in Figure 2) neglecting the superheat portion. In the condenser side, however, the typical values of superheat and subcooling are 40 and 7% of the total condenser heat. Hence, the GTD across only the two-phase region is not considered a proper one. The expression similar to equation (2) is used to calculate GTD_C :

$$GTD_C = f_{subc}GTD_{subc} + (1 - f_{subc} - f_{supc})GTD_{ipc} + f_{supc}GTD_{supc} \quad (6)$$

where GTD_{subc} , GTD_{ipc} , and GTD_{supc} are $(T_5 - T_6)$, $(T_4 - T_5)$, and $(T_3 - T_4)$ respectively.

Figure 5 illustrates the COP, GTD_E , GTD_C , and percent of condenser superheat for R32/R142b mixtures. The temperature differences of the air streams across the evaporator and condenser are 7 and 6 °C respectively. The expected gain in COP by matching the temperatures is not expected to take place in the condenser side of actual refrigerators because of the poor match of the temperatures; the GTD_C is an order of magnitude larger than the air stream temperature difference as shown in Figure 5. In the condenser side, the condenser superheat may be a used as a proper indicator for COP instead of GTD as discussed by McLinden and Radermacher [10]; the smaller the condenser superheat, the larger the COP.

For R32/R142b mixtures, the maximum COP ($\phi_{max} = 4.9\%$) occurs at 0.1 mass fraction of R32 where GTD_E (7.5 °C) is well matched with the temperature drop (7.0 °C) and the condenser superheat is the lowest as shown in Figure 5. Even if temperatures well match in the evaporator at 0.75 mass fraction R32 ($GTD_E = 7$ °C), the condenser superheat becomes larger and hence COP is degraded.

Since the mixtures do not seem to yield any significant increase in energy efficiency in an unmodified refrigerator due to a small temperature glide required, major system modifications might be necessary. For instance, refrigerators equipped with two evaporators using NARMs as working fluids as devised by Lorenz and Meutzner [15] may emerge as an alternative solution yielding higher COP due to a larger temperature glide. Proper design and analysis of such a system, however, may require a number of years to complete.

Thus, it may be of interest to seek for a simpler solution for increasing energy efficiency without involving major modification of the system. Even if today's evaporators and condensers are designed efficiently, there may be room for further improvement. In this regard, a simple numerical experiment is carried out by increasing the UA values used in the model with the other variable kept constant. In reality, this may be achieved either by increasing the heat exchanger area or constructing a more efficient heat exchangers using enhanced surfaces.

With increased UA values, the LMTDs in the condenser and evaporator would become smaller resulting in a lower pressure ratio across the compressor. Thus, the compressor work is reduced to yield an increase in COP. To verify this concept, few more runs were carried out with 1.5 times larger evaporator and condenser. As expected, pressure ratio becomes smaller as heat exchanger area is increased. Consequently, COP is increased up to 22-25% with pure and mixed refrigerants. The results, indeed, indicate that full attention has to be given to the heat exchangers in the spirit of seeking for a simpler solution for increasing energy efficiency.

5. Conclusion

The steady-state cycle simulation of domestic refrigerators was carried out in an attempt to select drop-in replacement fluids for R12. Special attention was given to the solution methods to solve the unknown variables resulting from the simulation. Both successive substitution (SS) and Newton-Raphson (NR) methods were described in detail to help other researchers utilize the technique to cope with the similar problems encountered in various thermal engineering fields. Both SS and NR methods are proven to be good for the simulation of a simple thermal system such as a refrigerator without disclosing any difference in their performance.

The simulation was performed with 15 pure refrigerants. The results indicate that no single pure CFC or HFC refrigerant available in the market would be a drop-in substitute for R12 unless major modifications such as the replacement of compressor are made in the system. Even if few fluids such as R22, R32, R152a, and R142b have the comparable COP as that of R12, none of them meets the requirement of the same volumetric capacity as that of R12.

The criteria for selecting proper refrigerant mixtures were discussed extensively. In order to warrant an increase in COP using a mixture, the gliding temperature of the mixture has to match the temperature drop in air stream (necessary condition) as well as the pure components must have at least comparable COP than R12 (sufficient condition).

Based on the selection criteria, 21 mixtures at various compositions were chosen for comparison. Due to the fact that the air stream temperature drop is small (less than 10 °C), no significant increase in COP was observed with all mixtures considered. Only R22/R142b and R32/R142b mixtures yielded the maximum increase of only 3% in COP. In conclusion, R22/R142b, R22/R152a, and R32/R142b can be drop-in replacement fluids for R12 in the short run without having significant increase in energy efficiency. Designing more efficient heat exchangers would increase COP significantly. In the long run, however, major system modifications may be necessary to increase energy efficiency aimed at reducing the greenhouse effect as well.

6. Acknowledgement

The support for this work by Pennwalt Corporation, US Environmental Protection Agency, and the University of Maryland, College of Engineering, is gratefully acknowledged. The authors thank M. McLinden and G. Morrison at US National Institute of Standards and Technology for the helpful discussions regarding thermodynamic properties of refrigerant mixtures.

7. References

1. EPA report, CFCs and Stratospheric Ozone, United States Environmental Protection Agency, Dec. 1987
2. T.G. Statt, Use of Chlorofluorocarbons in Refrigeration, Insulation, and Mobil Air Conditioning in the USA, Proc. of Int. Inst. Refrigeration, Purdue Conference on CFCs, Commissions B1, B2, E1 & E2, pp. 353-357, 1988
3. M.O. McLinden and D. Didion, Quest for alternatives, ASHRAE J., Vol. 29, 1987, pp. 32-42, 1987
4. W. Mulroy, M. Kauffeld, M. McLinden, and D. Didion, Experimental Evaluation of Two Refrigerant Mixtures in a Breadboard Air Conditioner, Proc. of Int. Inst. Refrigeration, Purdue Conference on CFCs, Commissions B1, B2, E1 & E2, pp. 27-34, 1988
5. H. Kruse, The Advantages of Non-Azeotropic Refrigerant Mixtures for Heat Pump Application, Int. J. Refrigeration, Vol. 4, pp. 119-125, 1981
6. W.F. Stoecker and D.J. Walukas, Conserving energy in Domestic Refrigerators through the Use of Refrigerant Mixtures, Int. J. Refrigeration, Vol. 4, pp. 201-208, 1981
7. W.F. Stoecker, Improving the Energy Effectiveness of Domestic Refrigerators by the Application of Refrigerant mixtures, ORNL report, ORNL/Sub-78/55463/1, 1978
8. ORNL report, An Evaluation of a Two-Evaporator Refrigerator-Freezer Using Nonazeotropic Refrigerant Mixtures, ORNL/Sub/82-47952/1
9. H. Kruse, Private discussion, ASHRAE seminar, Chicago, Jan., 1989
10. M.O. McLinden and R. Radermacher, Methods for Comparing the Performance of Pure and mixed Refrigerants in the Vapor Compression Cycle, Int. J. Refrigeration, Vol. 10, pp. 318-324
11. G. Morrison and M.O. McLinden, Application of a Hard Sphere Equation of State to Refrigerants and Refrigerant Mixtures, NBS Technical Note 1226, 1986, NBS, Gaithersburg, MD 20899
12. R. Radermacher and J. Lavelle, Comparison of Refrigerant 12 with the Blend of R-22/R-142b, pp. 25-30, Proceedings of ASME winter annual meeting, Chicago, Illinois, Nov. 1988
13. W.F. Stoecker, Design of Thermal Systems, 3rd edition, McGraw-Hill Book Comp., 1989
14. W.F. Stoecker, A Generalized Program for Steady-State system Simulation, ASHRAE Trans., Vol. 77, pp. 140-148, 1971

15. A. Lorenz and K. Meutzner, On Application of Non-Azeotropic Two Component Refrigerants in Domestic Refrigerators and Home Freezers, XIV Int. Congress of Refrigeration, Moscow, 1975

Table 1 Known and unknown variables at each state point

State point	Known (fixed)	known (assumed)	unknown
1	TS1	P1, T1=T8+DSH, V1	H1
2	T2=Tamb	P2, V2	H2, S2
3		P3, S3=S2, e _c	H3, T3, TS3
4		P4, X _v	H4, T4, TS4
5		P5, X _l	H5, T5, TS5
6	TS6=Tamb T6=TS6+0.1	P6, V6	H6
7	TS7	P7, H7=H9	T7, XQ7
8		P8, X _v	H8, T8, TS8
9		P9, T9, V9	H9

Table 2 Variables and residual equations for the Newton-Raphson method

Variables	Residuals	Description
VA(1)=m _{ref}	RE(1)=-Q _{EVAP} +U _e A _e LMTD _e e _{HX}	Heat transfer rate equation in evaporator
VA(2)=P ₂	RE(2)=-Q _{COND} +U _c A _c LMTD _c e _{HX}	Heat transfer rate equation in condenser
VA(3)=P ₃	RE(3)=- (H ₁ -H ₇) * f _{subc} + (H ₁ -H ₈)	Definition of f _{subc}
VA(4)=T ₃	RE(4)=- (H ₄ -H ₇) + (H ₂ -H ₁)	Energy balance in SLHX
VA(5)=TS ₃	RE(5)=-Q _{EVAP} +m _{ref} (H ₁ -H ₇)	Refrigerant energy balance in evaporator
VA(6)=TS ₂	RE(6)=- (H ₃ -H ₆) * f _{subc} + (H ₅ -H ₆)	Definition of f _{subc}
VA(7)=TS ₅	RE(7)=- (H ₃ -H ₆) * f _{subc} + (H ₅ -H ₆)	Definition of f _{subc}
VA(8)=TS ₈	RE(8)=-Q _{COND} +m _c C _{p,ref} * (TS ₃ -TS ₆)	Air stream energy balance

Table 3 Simulation results for various mixtures

Mixture	COP _{max}	φ _{max}	VC _{max}	X _{max}	COP _{vc12}	φ _{vc12}	X _{vc12}
R22/R152a	1.365	1.49	851	0.5	1.363	1.34	0.33
R22/R142b	1.393	3.70	706	0.3	1.383	2.82	0.57
R22/R134a	1.35	0.37	1115	0.8	1.333	-0.89	0.15
R22/R134	1.355	0.74	839	0.5	1.354	0.67	0.40
R22/R123	1.312	-2.45	168	0.2	1.275	-5.2	0.86
R32/R152a	1.379	2.52	1001	0.3	1.37	1.86	0.2
R32/R142b	1.411	4.9	544	0.1	1.39	3.34	0.27
R32/R134a	1.350	0.37	1170	0.3	1.34	-0.37	0.08
R32/R134	1.364	1.41	862	0.2	1.36	1.11	0.13
R125/R152a	1.358	0.96	671	0.0	1.356	0.82	0.2
R125/R142b	1.385	2.97	499	0.2	1.33	-1.11	0.55
R125/R141b	1.401	4.16	127	0.1	1.146	-14.7	0.9
R125/R134a	1.325	-1.48	715	0.0	1.324	-1.56	0.1
R125/R134	1.337	-0.59	670	0.2	1.33	-1.11	0.33
R125/R123	1.277	-5.05	100	0.1	1.11	-17.47	0.85
R143a/R152a	1.358	0.96	671	0.0	1.356	0.82	0.2
R143a/R142b	1.388	3.19	528	0.2	1.348	0.22	0.5
R143a/R141b	1.407	4.61	140	0.1	1.19	-11.5	0.85
R143a/R134a	1.326	-1.41	777	0.1	1.326	-1.41	0.1
R143a/R134	1.339	-0.44	694	0.2	1.335	-0.74	0.3
R143a/R123	1.293	-3.86	116	0.1	1.16	-13.75	0.85

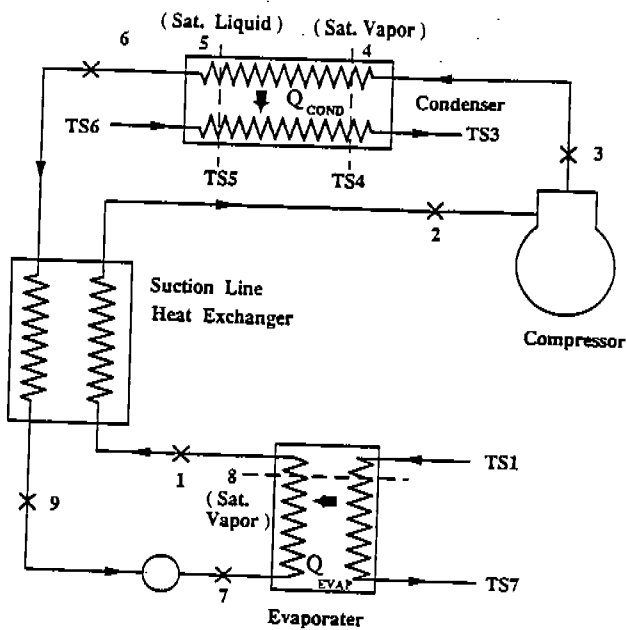


Figure 1. Schematic diagram of a single evaporator domestic refrigerator

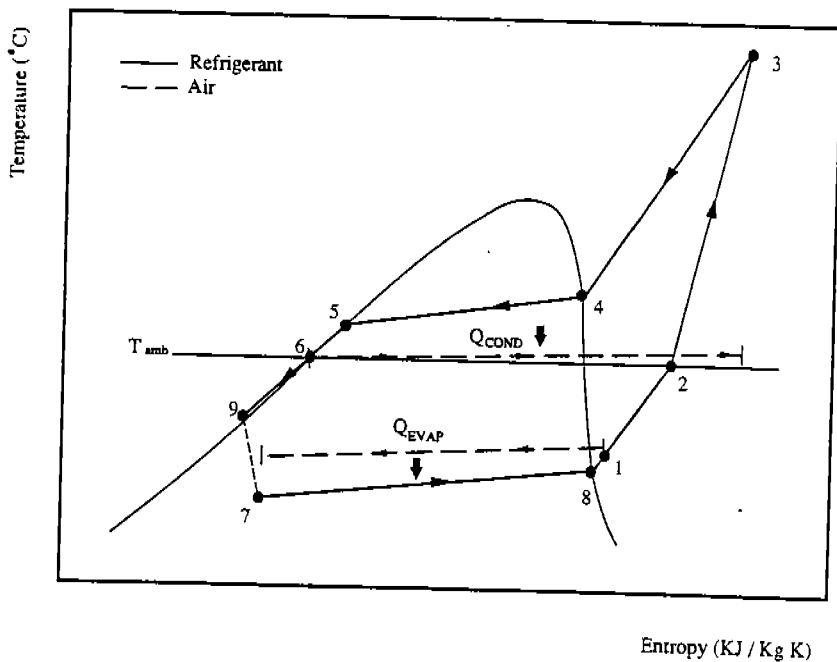


Figure 2. Temperature-entropy diagram of a single evaporator refrigerator

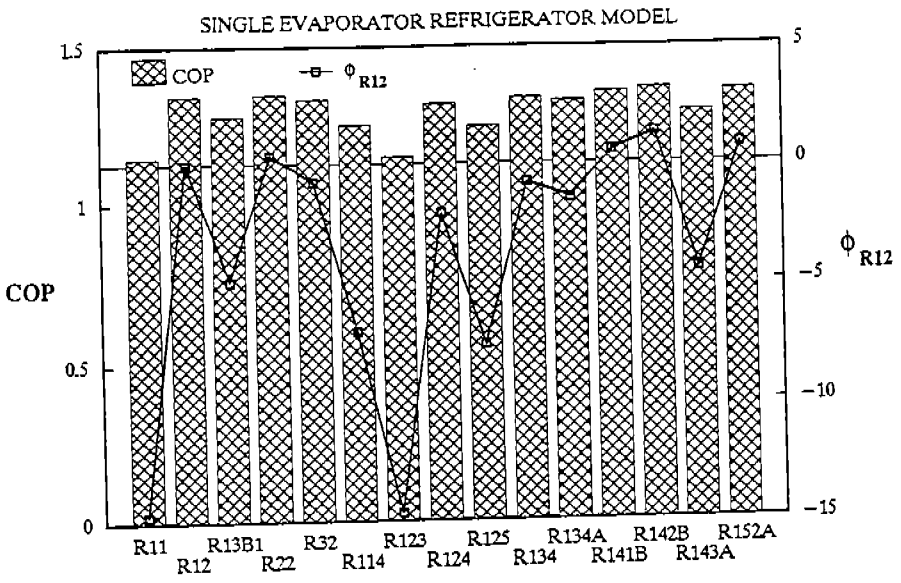


Figure 3. COP and percent increase in COP for various pure refrigerants

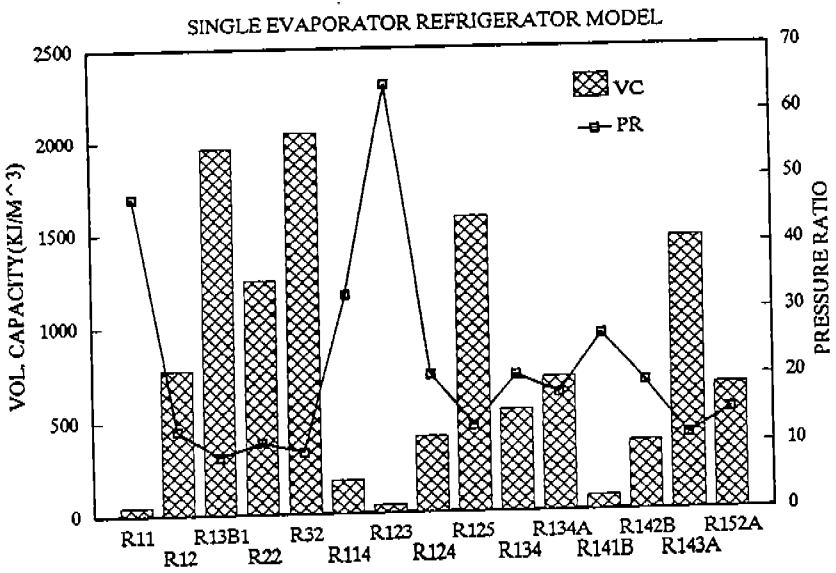


Figure 4. Volumetric capacity and pressure ratio for various pure refrigerants

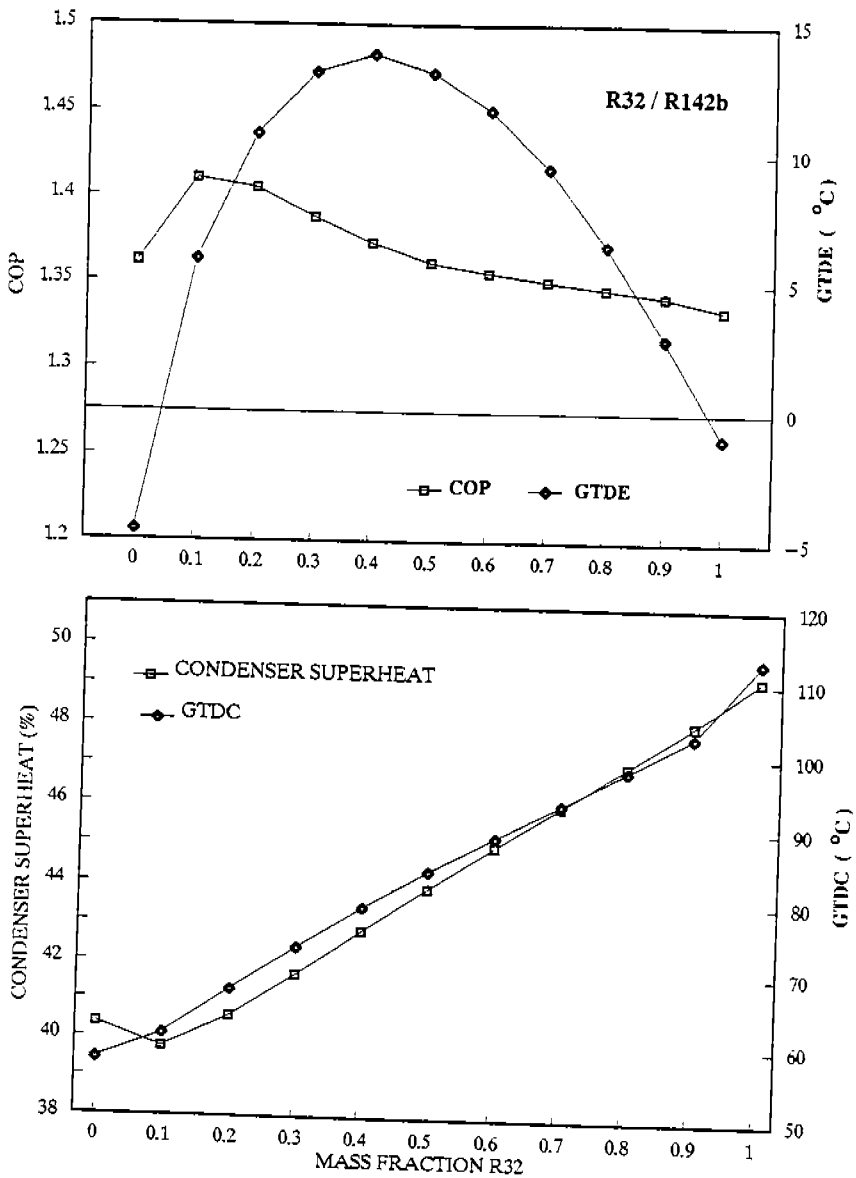


Figure 5. COP, $GTDE$, $GTDC$, and condenser superheat for R32/R142b mixture