

Modelled performance of non-chlorinated substitutes for CFC11 and CFC12 in centrifugal chillers*

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A number of partially fluorinated alkanes and ethers were identified from earlier technical publications and from a joint Electric Power Research Institute/Environmental Protection Agency (EPRI/EPA) project as potential alternatives for chlorofluorocarbon (CFC) and hydrogen-containing CFC refrigerants. These larger molecules, by virtue of their more elaborate structure, have larger vapour phase heat capacities (C_p s) and larger molecular weights than currently used refrigerants, which result in decreased volumetric capacities and greater flash gas losses in simple cycle applications. The compounds were fitted to the Lee-Kessler-Plöcker and Carnahan-Starling-DeSantis equations of state, and refrigerant property routines based on these equations were used to simulate their performance in a single-stage centrifugal chiller as pure refrigerants and nearly azeotropic refrigerant mixtures. Consideration was given to the effects of acoustic velocity in the refrigerant, rotational mach numbers, the application of superheat prior to the compressor inlet to avoid 'wet isentropic compression', and liquid subcooling before isenthalpic expansion. Results indicate that several chlorine-free compounds give modelled chiller performance comparable to R11 and R123 and better than R12 and R134a. Blends of these refrigerants may be required to mitigate the inflammability of alternatives that show the best performance. Modifications to the basic chiller cycle - such as liquid subcooling and suction gas superheat - may offer unique advantages for more complicated, larger refrigerant molecules. An algorithm based on molecular bond energies and vapour phase C_p s was used to estimate the flammability of these alternatives and of blends made from them. Depending on desirable and permissible deviations from the currently used chiller operating conditions and on the acceptability of flammable refrigerant combinations, ideal coefficients of performance comparable to R11 and 5-10% better than R12 are indicated.

(Keywords: refrigerant; CFC; HCFC; R11; R12; R123; R134a; substitute; alkane; azeotropic mixture; performance; COP; modelling; equation of state; calculation)

Modélisation de la performance de substituts sans chlore du CFC11 et du CFC12, dans des groupes refroidisseurs centrifuges

On considère que plusieurs alcanes et éthers partiellement fluorés pourraient remplacer le CFC et HCFC. Ils ont été signalés dans des publications techniques antérieures ainsi que par l'Electric Power Research Institute et l'Agence américaine de la protection de l'environnement qui ont mis en oeuvre un projet de collaboration. Ces plus grandes molécules, grâce à leur structure plus élaborée, présentent des capacités thermiques en phase vapeur plus importantes (C_p) et un poids moléculaire plus élevé que les frigorigènes couramment utilisés, ce qui entraîne une diminution des capacités volumétriques et des pertes plus importantes en vapeur "instantanée" au cours d'applications en cycle simple. On a adapté les composés aux équations d'état de Lee-Kessler-Plöcker et Carnahan-Starling-DeSantis, et on a utilisé des logiciels sur les propriétés des frigorigènes, fondés sur ces équations, pour simuler leur performance dans un groupe refroidisseur centrifuge monoétage, d'abord à l'état pur puis en mélanges presque azéotropiques. On a considéré les effets de la vitesse acoustique dans le frigorigène, les nombres de Mach pour la rotation, l'application de la surchauffe avant l'entrée du compresseur, pour éviter la compression isentropique humide, et le sous-refroidissement du liquide avant la détente isenthalpique. Les résultats de simulation indiquent que plusieurs composés sans chlore présentent des performances similaires à celles du R11 et du R123 et meilleures que celles du R12 et du R134a. On pourrait mélanger ces frigorigènes dans le but d'atténuer l'inflammabilité de ceux qui présentent la meilleure performance. Des changements dans le cycle fondamental du refroidisseur, comme le sous-refroidissement du liquide et la surchauffe lors de l'aspiration, pourraient permettre l'utilisation de molécules plus compliquées et plus grandes. On a utilisé un algorithme fondé sur les énergies de lien moléculaire et sur la phase vapeur C_p pour évaluer l'inflammabilité de ces remplaçants et de leurs mélanges. En fonction des écarts souhaités et permis par rapport aux conditions de fonctionnement des groupes refroidisseurs couramment utilisés et de l'acceptabilité des combinaisons de frigorigènes inflammables, on indique des coefficients de performance idéaux semblables à ceux du R11 et meilleurs que ceux du R12 (de 5 à 10%).

(Mots clés: frigorigène; CFC; HCFC; R11; R12; R123; R134a; substitut; alkane; mélange azéotrope; performance; COP; modélisation; équation d'état; calcul)

Current scientific evidence indicates that stratospheric chlorine concentrations below two parts per billion will be necessary to reverse 'ozone hole' formations over the Earth's polar regions each spring and measurable decreases of stratospheric ozone at lower latitudes. This

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makes it unlikely that hydrogen-containing chlorofluorocarbon alternatives with non-zero ozone depletion potentials, no matter how small, will be accepted as refrigerants or blowing agents for foamed insulations in the long run. Pressure to eventually eliminate all high volume uses of chlorine-containing refrigerants provides a strong incentive to find hydrofluorocarbon or alternative chlorine-free compounds with pressure-volume-temperature ($p-v-t$) characteristics similar to R11, R123, R12 and R22 for new and existing large centrifugal chiller applications.

Centrifugal water chillers for the purpose of air conditioning represent one of the most efficient applications of electrical energy that we have today. There are roughly 70 000 centrifugal chillers in use in the USA and nearly 110 000 installed throughout the world¹. In the USA 80% of the vapour compression water chillers use R11 as the refrigerant primarily because of its high cycle efficiency, but also because R11 is easier to handle and store compared with R12 or R22, and R11 compressors operate at slower impeller speeds. Impellers for R11 machines can be driven directly from motors operating on 60 Hz electrical power rather than through a gear linkage to increase r.p.m.s.

The phase-out of R11 and R12 as a result of the Montreal Protocol², together with recent reports indicating a worsening of the stratospheric ozone depletion, and chronic toxicological effects of R123 have heightened efforts to find an efficient chlorine-free alternative which can be used instead of R11 or R123 in large direct-driven centrifugal chillers. In addition to the numerous environmental and chemical requirements of an acceptable alternative refrigerant for current centrifugal designs, the proposed alternative should have a high critical temperature, a low to moderate gas heat capacity (40–100 J mol⁻¹ K⁻¹ [10–24 Btu lb mol⁻¹ R⁻¹]) and a high critical pressure³. Given the limited number of chemical compounds that satisfy all of these requirements, some compromises in refrigerant properties or changes to the current chiller design may be required.

Several potentially useful fluorinated ethers and propanes were synthesized and partially characterized in a Joint Power Research Institute (EPRI)/Environmental Protection Agency (EPA) project aimed at finding new classes of organic compounds which could be used for chlorofluorocarbon (CFC) applications⁴⁻⁶. Physical property measurements that resulted from this project were used to fit the compounds to the Lee-Kessler-Plöcker (LKP) and Carnahan-Starling-DeSantis (CSD) equations of state (EOSs). Refrigerant property routines based on these equations were used to evaluate cycle performance in a chiller circuit from known or estimated temperatures and pressures. Other partially fluorinated ethanes and ethers suggested in earlier publications were also included in the study^{7,8}.

The modelled cycle performance of pure compounds and nearly azeotropic refrigerant mixtures (NEARMs) of these chlorine-free alternatives were compared with that for currently used refrigerants using appropriate computerized cycle simulations. The effects of several variations to standard single-stage chiller operating conditions were also modelled to illustrate differences between previously used refrigerants which have relatively simple molecular structures and these larger molecules.

Results indicate that several chlorine-free compounds have modelled performance comparable to R11 and R123 and better than R12 and R134a. Compounds showing the best performance are estimated to be flammable, so blends with non-flammable alternatives may be desirable. Performance improvements ranging from +5% to +10% over CFC12 are possible if cycle conditions are changed to suit the particular characteristics of these new compounds and mixtures of these new compounds.

Compounds modelled

The compounds that were screened for chiller performance are listed in Table 1. Structural formulas are given in addition to normal boiling points and critical temperatures to provide a correlation with assigned refrigerant numbers. A standardized method for designating propanes has been established by the American Society of Heating, Refrigerating, and Air-conditioning Engineers (ASHRAE)⁹, but no standard method has been adopted for ethers. The numerical designators given in Table 1 provide a convenient and efficient shorthand method for referring to these compounds in subsequent tables and results.

The system used in this table assigns an 'E' prefix for ethers. The numbering system is not definitive for methyl-ethyl-ethers because the position of the ether linkage in these molecules is not uniquely defined by either the number or the lower case suffix letters. The 'C' prefix is added for cyclic molecules and the 'EE' prefix refers to the two ether moieties in CF₃-O-CF₂-O-CF₃ (EE-218).

Whenever possible, boiling points and critical temperatures were taken from published or pre-publication data coming out of the laboratories at the University of Tennessee and Clemson University which synthesized these compounds. As part of their programmes, a minimum number of physical property measurements were made on the synthesized products⁴⁻⁶. For some compounds, critical properties were found in the Thermodynamics Research Centre *Thermodynamics Tables*¹⁰. If no experimentally measured physical property data were available, the required values were estimated using techniques outlined in Reid *et al.*¹¹.

Critical temperatures, pressures and volumes were estimated using the group contribution method of Joback which is described on pages 12–23 of reference 11. Average absolute percentage errors of 0.8%, 5.2% and 2.3% can be anticipated for critical temperatures, critical pressures and critical volumes, respectively, if this method is used for compounds whose normal boiling point is known.

Acentric factors which were needed for the LKP routines were estimated from Equation (1) using measured or estimated boiling points, critical temperatures and critical pressures:

$$\omega = \frac{3}{7} \left[\frac{T_b/T_c}{1 - T_b/T_c} \right] \times \log P_c - 1 \quad (1)$$

where: ω = acentric factor,
 T_b = normal boiling point (K),
 T_c = critical temperature (K),
 P_c = critical pressure (atmospheres).

Table 1 Chlorine-free CFC alternatives evaluated as CFC11 and CFC12 replacements in centrifugal chillers
 Table 1 *Substances sans chlore, pour le remplacement du CFC11 et du CFC12 dans des groupes refroidisseurs centrifuges*

Designation	Molecular formula	Normal boiling point (°C)	Critical temperature (°C)	Source of property information
E254cb	CHF ₂ -O-CF ₂ CH ₃	36.4	189.4	Reference 7
E245cb	CF ₃ -O-CF ₂ CH ₃	34.1	185.2	Reference 7
R152	CH ₂ FCH ₂ F	30.7	202.8	Reference 7
E143	CH ₂ F-O-CHF ₂	30.1	186.8	Reference 7
R254ca	CHF ₂ CF ₂ CH ₂ F	24.9	178.4	Reference 5
R245fa	CH ₃ CH ₂ CF ₂ H	15.3	157.5	Reference 5
R236ea	CF ₃ CHFCHF ₂	6.5	141.6	Reference 5
E134	CHF ₂ -O-CHF ₂	6.2	147.1	Reference 12
R236ca	CHF ₂ CF ₂ CHF ₂	5.0	138.9	Reference 5
R143	CH ₂ FCHF ₂	4.0	156.8	Reference 12
R236fa	CF ₃ CH ₂ CF ₂	-1.1	130.6	Reference 5
R236cb	CH ₂ FCF ₂ CF ₃	-1.4	130.1	Reference 5
E227ca	CF ₃ -O-CF ₂ CHF ₂	-3.1	114.7	Reference 6
EE218	CF ₃ -O-CF ₂ -O-CF ₃	-9.7	98.9	Reference 6
R227ea	CF ₃ CHFCF ₃	-15.2	103.5	Reference 5
R245cb	CH ₃ CF ₂ CF ₃	-18.3	106.9	Reference 5
R134	CHF ₂ CHF ₂	-19.8	118.9	Reference 12
E143a	CH ₃ -O-CF ₂	-23.8	104.9	Reference 5
R152a	CH ₂ CHF ₂	-25.0	113.5	Reference 12
R134a	CH ₂ FCF ₃	-26.2	101.2	Reference 12
CE216	CF ₂ -CF ₂ -CF ₂ -O	-29.1	88.4	Reference 6
E125	CF ₃ -O-CHF ₂	-34.6	80.7	Reference 5
R290	CH ₃ CH ₃	-42.1	96.7	Reference 12

Originally, the acentric factor was used to describe the eccentricity or non-sphericity of the molecule, but it is currently used to indicate the complexity of molecular geometry and the polarity of larger molecules.

Ideal gas heat capacities that were needed for both the LKP and CSD equation-of-state routines were obtained using the group contribution method worked out by Joback and described on pages 154–157 of reference 11. The four-term polynomial obtained from this method had to be converted to the corresponding three-term form required for the CSD routines using a standard statistical program.

Equation of state considerations

FORTRAN and BASIC computer codes based on several well established EOSs have been developed so that refrigerant *p-v-t* behaviour and thermodynamic properties can be calculated from known values. These codes can conveniently be used to model the performance of pure and mixed refrigerants in air conditioning and refrigeration cycles on a computer. Some routines, like those based on the Martin-Hou EOS, give very accurate results but require many coefficients and constants specific to the refrigerant being evaluated. Values for those coefficients and constants must be derived from extensive physical property measurements. In addition, these more elaborate EOS routines have not been fitted with the required mixing rules and algorithms to handle mixtures of refrigerants.

Several simpler (two- or three-term) EOS like the Redlich-Kwong-Soave (RKS), Peng-Robinson (PR), CSD and LKP have the necessary mixing rules and computational capabilities to simulate the characteristics of refrigerant mixtures. While these may not be as accurate as the Martin-Hou or Benedict-Webb-Rubin representations, they do not require as much physical property data to characterize a compound or as much computer-

run time for implementation. Most are accurate enough to prescreen candidates for relative comparisons.

Of the computer routines that encompass the newer refrigerant compounds and handle mixed refrigerants, the CSD code that was developed at, and is currently supported by, the National Institute of Standards and Technology (NIST)¹² and the LKP routines that were introduced by Dr Kruse's group at the University of Hannover and modified by Fischer and Sand¹³ at Oak Ridge National Laboratory, are most readily available.

An essential parameter for accurately calculating the thermodynamic properties of mixtures is an interaction coefficient (IC) which characterizes and quantifies the extent of ideality or non-ideality of the solutions formed by combinations of two or more compounds. The most reliable ICs are based on *p-v-t* data for known mixtures. Version 3.02 of REFPROP from NIST employs an algorithm to estimate this important parameter for molecules with known dipole moments and molecular volumes. Plöcker's refinement of the work of Lee and Kessler included a correlation he developed between the interaction coefficient and the critical temperatures and molar volumes¹⁴.

Some comparisons of refrigerant performance calculations based on an ideal cycle were made using thermodynamic refrigerant property values taken from ASHRAE tables and those calculated using CSD and LKP refrigerant property routines. These showed better agreement between the LKP results and the more generally accepted ASHRAE values. The $\pm 1-2\%$ accuracy obtainable with the simpler EOS – like the RKS, PR, CSD and LKP – was considered sufficiently precise for this screening work.

The CSD EOS is based on a 'hard sphere' theory of molecular structure, which is an adequate approximation for molecules like ammonia and ethers. The reduced property/corresponding state approach used in the LKP EOS seems to work better. Since one of the initial concerns for this research work was that the *p-v-t* and thermodynamic behaviour of ethers and other poorly

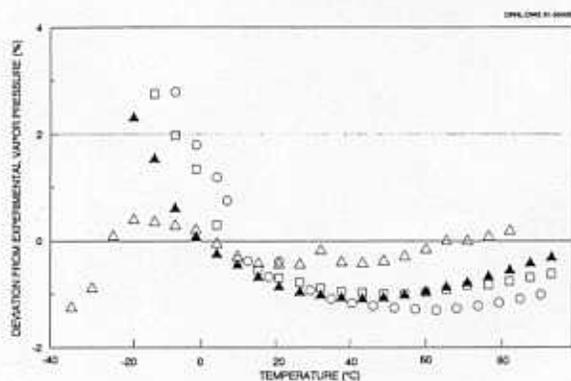


Figure 1 Deviations of vapour pressures calculated by LKP routines from experimental values – propanes from reference 5: ○ R245fa, □ R236ea, △ R227ea, ▲ R236fa

Figure 1 Écarts entre les pressions de vapeur calculées par les logiciels LKP et les valeurs expérimentales – propanes de la référence 5: ○ R245fa, □ R236ea, △ R227ea, ▲ R236fa

characterized compounds was to be estimated from a small amount of physical property data, the LKP routines were initially used.

As the modelling work progressed, it was necessary to determine the speed of sound in the compressor suction gas in order to evaluate the rotational mach number of the chiller impeller. Single-precision computer operation limited attempts to approximate the speed of sound based on numerical differentiation at two slightly different state points at the suction conditions. Since the CSD routines contained a subroutine which returned the velocity of sound from known conditions at the suction, the LKP routines were used to generate CSD EOS coefficients. The appropriate CSD routine was used to obtain values for the velocity of sound in the chiller modelling work, but all of the modelled predictions were ultimately obtained from the LKP routines and code.

An indication of how well the LKP property routines represent actual experimental p - v - t data was obtained by comparing the saturated vapour pressure measurements made on several of these compounds at the University of Tennessee and Clemson University, with those predicted by the LKP routines. Figure 1 shows the percentage deviation of vapour pressures calculated using the LKP routines from the experimental values reported for some of the partially fluorinated propanes being evaluated in this study. Figure 2 shows similar data for five of the fluorinated ethers being investigated. The worst deviations were near 4% for E125 in Figure 2, but generally errors of less than 2% were more common. A more extensive comparison of the results from the LKP routines with the refrigerant property values from other sources is given in reference 13. In the 4.0°C to 40°C region, important for chiller modelling, the deviation of calculated values from experimental values averaged less than 1%. This accuracy was considered acceptable for a screening exercise.

Chiller parameters modelled

A simple single-stage chiller model based on saturated refrigerant temperatures in the evaporator and condenser was developed using LKP and CSD refrigerant property routines to calculate

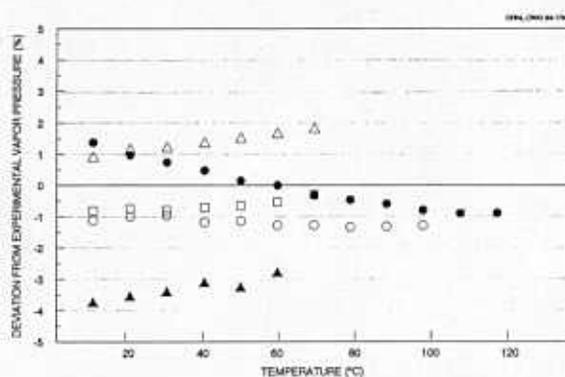


Figure 2 Deviations of vapour pressure calculated by LKP routines from experimental values – ethers from references 5 and 6: ● E227ca, ▲ E125, △ EE218, □ CE216, ○ E143a

Figure 2 Écarts entre les pressions de vapeur calculées par les logiciels LKP et les valeurs expérimentales – éthers des références 5 et 6: ● E227ca, ▲ E125, △ EE218, □ CE216, ○ E143a

1. condenser and evaporator pressures,
2. net refrigerating effect (Btu lb^{-1}),
3. isentropic compressor work (equivalent head),
4. ideal isentropic coefficient of performance (COP),
5. mass and volume flow rates per ton of refrigeration, and
6. sonic velocity at suction conditions.

All of these values could be readily calculated from the refrigerant property subroutines that were available, and results were compared with those given in previous publications listing the relative performance of alternative refrigerants^{15,16}.

When it was required, the model added just enough superheat in the evaporator to prevent formation of a two-phase refrigerant during isentropic compression; see Figure 3. Higher vapour phase heat capacity values inherent with larger refrigerant molecules result in a more severely slanted 'vapour dome' in pressure-enthalpy (Mollier) plots, so isentropic compression starting from saturated evaporator outlet conditions (1 on Figure 3) results in two-phase refrigerant, 'wet compression' at condensing pressures and temperatures. In these modelling studies, when 'wet compression' occurred, enough superheat was added in the evaporator, 1 to 1' in Figure 3, to give saturated vapour at the condenser inlet, 2'. The cooling effect of this superheat was added to the net refrigerating effect of the refrigerant and was included in the calculated COP. This benefits the cycle performance of these fluids, but was necessary to keep the results from this study comparable with those from previous studies^{17,18}. Larger molecules like the propanes and three-carbon ethers in this study are more likely to exhibit wet isentropic compression than simpler refrigerants containing one or two carbon atoms, like R11 and R123.¹⁹

Economizer operation in multi-stage chillers, or using flash gas to cool superheated refrigerant at staged levels of compression, may not be as advantageous for these compounds because loss of superheat during compression tends to result in two-phase refrigerant formation. Inefficiencies encountered in 'real' compressors and the practice of using refrigerant to cool the hermetic motor

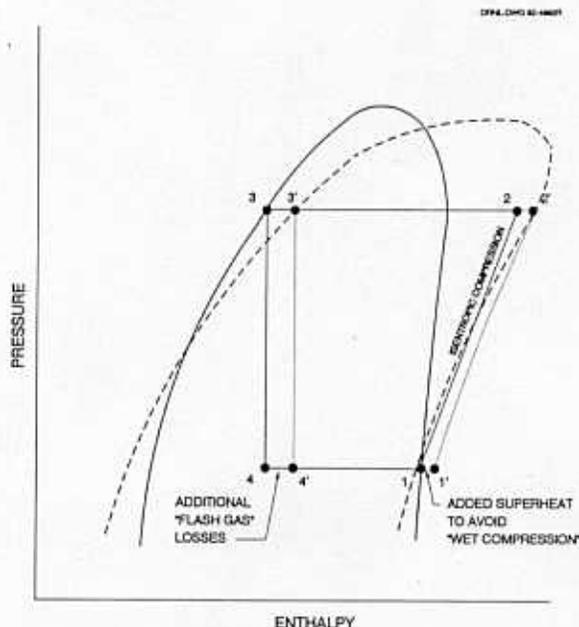


Figure 3 Effect of vapour heat capacity on the shape of the two-phase region of the pressure-enthalpy curve: — low C_p refrigerant (simple molecular structure), - - - high C_p refrigerant (complex molecular structure)

Figure 3 Effet de la capacité thermique de vapeur sur la forme de la région à deux phases de la courbe pression-enthalpie: — frigorigène avec C_p faible (structure moléculaire simple), - - - frigorigène avec C_p élevé (structure moléculaire complexe)

may add enough superheat to the suction gas to overcome this potential problem.

Other parameters, specific to the performance of centrifugal chillers, that were modelled in this study were

1. impeller tip speeds,
2. rotational mach numbers,
3. relative efficiencies due to rotational mach numbers, and
4. stage efficiency.

Typical values for a compressor head coefficient (0.59), tip flow coefficient (0.25) and mechanical efficiency (0.80) were assumed for these calculations.

The impeller tip speed (μ_{TS}) was calculated using Equation (2), which requires a value for the energy that must be added to the refrigerant by the compressor (equivalent head) and an assumed value for the compressor head coefficient (μ_{HC}).

$$\mu_{TS} = \sqrt{\frac{H \times g_0}{\mu_{HC}}} \quad (2)$$

where: μ_{TS} = impeller tip speed ($m\ s^{-1}$),
 H = equivalent head ($J\ m^{-1}$),
 g_0 = gravitational acceleration ($9.81\ m\ s^{-2}$),
 μ_{HC} = compressor head coefficient.

Typical values for the compressor head coefficient range from 0.550 to 0.590. The 0.590 value, which was used by Atwood and Murphy¹⁵, was assumed for this work.

The ratio of impeller tip speed to acoustic velocity in the refrigerant at the compressor suction is known as the rotational or machine mach number (M_0). Figure 4

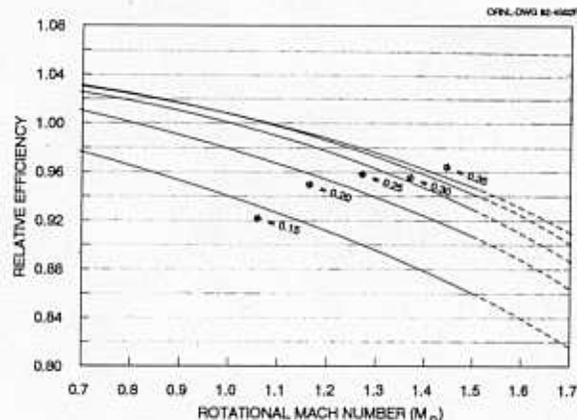


Figure 4 Relative chiller efficiency due to mach number (M_0), ϕ is the tip flow coefficient

Figure 4 Efficacité relative du groupe refroidisseur due au nombre de Mach (M_0), ϕ est le coefficient d'écoulement en bout d'aube

shows the relationship between the rotational mach number and the relative compressor efficiency that were taken from reference 15. To use this data, a value for the tip flow coefficient (ϕ) based on conditions of flow at the impeller tip must be selected. For the tip flow coefficient value of 0.25, which was used for this study, the polynomial correlation between relative efficiency and rotational mach numbers is described by Equation (3).

$$E_R = 1.045\ 62 - 2.053\ 18 \times 10^{-2} M_0 + 3.333\ 05 \times 10^{-4} M_0^2 - 2.531\ 68 \times 10^{-2} M_0^3 \quad (3)$$

where E_R = relative efficiency,
 M_0 = rotational mach number.

The single-stage efficiency value is the product of the relative efficiency due to rotational mach number and an assumed mechanical efficiency of 0.80. Isentropic or adiabatic efficiency is held at unity in Equation (4).

$$E_{stage} = E_{mechanical} \times E_R \quad (4)$$

where E_{stage} = stage efficiency,
 $E_{mechanical}$ = 0.80 (assumed),
 E_R = relative efficiency due to rotational mach number.

Chiller efficiencies in terms of kilowatts of electrical energy per unit (kilowatts or tons) of refrigeration were computed by factoring in all of these centrifugal specific parameters. This measure of efficiency, which is dependent on the characteristics of turbomachinery, could then be compared and contrasted with the calculated ideal isentropic COP that was totally dependent on the thermodynamic properties of the fluid.

The effects of transport properties like suction gas viscosity and liquid or vapour thermal conductivities were not modelled because these thermophysical properties were not available and their effect on chiller efficiency is much more complicated to evaluate.

Cycle conditions simulating a 37.8 °C (100 °F) condenser and 4.4 °C (40 °F) saturated evaporator that are fairly standard for a centrifugal water chiller were cho-

sen²⁰. No refrigerant subcooling or superheat was added unless superheating was necessary to avoid wet isentropic compression.

A flow chart diagram for this chiller model is shown in Figure 5. The only features that differentiate this code from a saturated heat exchanger model are a check to see if superheat is needed to avoid wet compression and the chiller specific calculations using the equations previously described.

Pure refrigerant and NEARM modelling results

Table 2 summarizes the ideal isentropic COP and kilowatts of electrical energy per kilowatt of cooling performance for fluorinated alkanes and fluorinated ethers which gave modelled results equal to or better than R134a. The COP values do not agree with the reciprocal of the kilowatt electricity/kilowatt cooling column because compressor and turbomachinery inefficiencies are factored into the latter values. More extensive tables for all of the compounds evaluated in this study that list all of the modelled parameters are available in reference 21. The results for R11, R123, R114 and R134a are also shown in Table 2 for comparison. Also tabulated are the amounts of superheat required over saturated evaporator conditions to avoid wet isentropic compression and rough estimates of atmospheric flammability based on summed bond energies and the molar heat capacity.

Only R152, E143 and R143 give COPs and kW t⁻¹ values that are comparable to R11. Very little physical property information was found for R152 and E143, so results for these two compounds are based primarily on estimated properties. Preliminary toxicological tests of R152 with male rats indicate an acute toxicity problem with this compound at concentrations as low as 25 parts per million in air²². Thermophysical and test loop data have become available for R143.^{11,23} All of these compounds are predicted to be flammable by the algorithm used to estimate flammability, but the validity of this technique is questionable as indicated by the results predicted for E134 in Table 2.

Under these modelling conditions, all of the other compounds in Table 2 show comparable or better performance than R134a, which is already being used to replace R12 in gear-driven centrifugal applications. The presence or absence of subcooling and superheat, as well as variations in the transport properties of the fluids, may change their relative rankings. As reported by McLinden, the incorporation of liquid line subcooling or liquid-to-suction line heat exchange into a simple Rankine model enhances the performance of refrigerants with more complex molecular structures more than that for relatively simpler refrigerant molecules¹⁹.

Table 2 also suggests the potential benefits of blending two or more refrigerants to make nearly azeotropic refrigerant mixtures (NEARMs) in which the superior cycle performance of one component is complemented by the non-flammability of the other(s). Unfortunately, no clearly non-flammable alternatives are available with boiling points near R152 and E143, but a non-flammable ether (E134) and several non-flammable propanes have boiling points (and vapour pressures) similar to R143.

Modelled chiller results for some flammable/non-flammable NEARM combinations of these alternatives

are shown in Table 3. As previously stated, no non-flammable, chlorine-free alternatives were found with a normal boiling point near R152, but several non-flammable NEARMs with uncertain flammability containing E143, R143 and E134 were modelled. No NEARM showed better performance than R11.

Conclusions and recommendations

Single-stage centrifugal chiller modelling work on several fluorinated 2- or 3-carbon alkanes and fluorinated ethers indicates that they are potential, chlorine-free alternatives for R11 and R123. The use of fluorinated ethers as CFC alternatives should be more thoroughly investigated.

Several of the newer compounds that give the best modelled performance are flammable. Blends of flammable and non-flammable refrigerants with similar vapour pressures can be used to make a non-flammable NEARM with a cycle performance intermediate between components of the blend. The flammability of fluorinated ethers should be more thoroughly characterized and evaluated so a method for predicting the combustibility of pure compounds and blends of compounds can be developed using molecular structures and known physical properties.

Problems with the use of flammable refrigerants in various applications have to be objectively evaluated against the potential environmental and energy efficiency gains. Modifications of the basic single-stage chiller cycle, such as deliberately adding subcooling or liquid-to-suction line heat exchange, will preferentially benefit the performance of refrigerants with more complex molecular structures and larger molecular heat capacities than currently used refrigerants. Also, applicability of these alternatives in multi-stage machines with interstage liquid flash cooling needs to be verified. These modifications will involve significant changes to the design and increases in the complexity of chillers.

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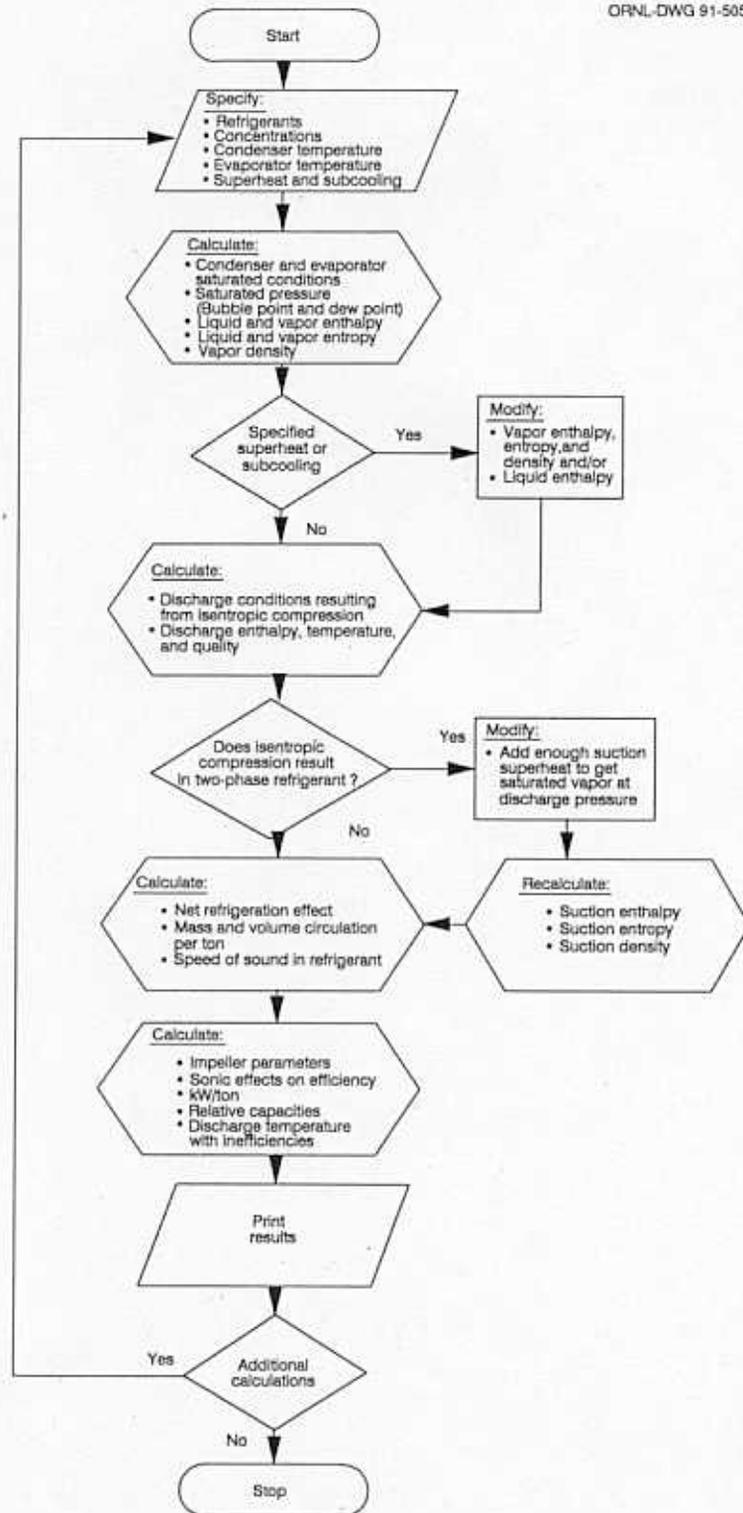


Figure 5 Pure and NEARM cycle model flow chart for chiller performance
 Figure 5. Organigramme sur la performance des groupes refroidisseurs avec des frigorigènes purs ou des mélanges presque azéotropiques

Table 2 Modelled performance results of chlorine-free alternatives in chillers – compounds with results comparable to or better than R134a (4.4 °C saturated evaporator, 37.8 °C saturated condenser, 0 °C superheat/subcooling)

Tableau 2 Résultats de la modélisation de la performance de substituts sans chlore pour les groupes refroidisseurs – mélanges donnant des résultats comparables ou supérieurs à ceux du R134a

Refrigerant	Formula	Normal boiling point (°C)	Modelled COP	kW electricity ^a per kW cooling	Superheat Added (°C)	Flammability indexing
E254cb	CHF ₂ OCF ₂ CH ₃	36.4	7.38	0.182	4.3	Flammable ^c
E245cb	CF ₃ O-CF ₂ CH ₃	34.1	7.33	0.183	6.5	Uncertain-to-flammable ^c
R152	CH ₂ FCH ₂ F	30.7	7.60	0.175	0.0	Flammable
E143	CHF ₂ O-CH ₂ F	30.1	7.50	0.178	0.0	Flammable ^c
R123 ^d	CHCl ₂ CF ₃	27.6	7.42	0.179	1.1	Non-flammable
R245ca	CHF ₂ CF ₂ CH ₂ F	24.9	7.33	0.182	3.9	Uncertain
R11	CCl ₃ F	23.8	7.54	0.174	0.0	Non-flammable
R245fa	CF ₃ CH ₂ CHF ₂	15.3	7.26	0.182	4.2	Uncertain
R236ea	CH ₂ CHFCHF ₂	6.5	7.14	0.185	6.5	Non-flammable
E134	CHF ₂ O-CHF ₂	6.2	7.32	0.180	0.0	Uncertain ^c
R236ca	CHF ₂ CF ₂ CHF ₂	5.0	7.11	0.185	6.7	Non-flammable
R143	CHF ₂ CH ₂ F	4.0	7.49	0.174	0.0	Flammable
R114	CClF ₂ CClF ₂	3.6	7.12	0.183	7.9	Non-flammable
R236fa	CF ₃ CH ₂ CF ₃	-1.1	7.04	0.186	7.2	Non-flammable
R236cb	CF ₂ CF ₂ CH ₂ F	-1.4	7.08	0.185	7.2	Non-flammable
R134	CHF ₂ CHF ₂	-19.8	7.17	0.180	1.4	Non-flammable
R152a	CHF ₂ CH ₃	-25.0	7.17	0.180	0.0	Flammable
R134a	CF ₃ CH ₂ F	-26.2	6.97	0.186	0.0	Non-flammable
R12	CCl ₂ F ₂	-29.8	7.06	0.181	0.0	Non-flammable

^a Enough superheat added to wet compression: cooling effect of superheat added to COP

^b To convert to kilowatts of electricity per ton (12 000 Btu h) of cooling multiply by 3.52

^c Validity of index for ethers uncertain

^d Currently used chlorine-containing refrigerants (in italics) are given for comparison

Table 3 Modelled performance results of chlorine-free NEARM alternatives in chillers – blends with results comparable to or better than R134a (4.4 °C saturated evaporator, 37.8 °C saturated condenser, 0 °C superheat/subcooling)

Tableau 3 Résultats de la modélisation de la performance des mélanges presque azéotropiques sans chlore pour les groupes refroidisseurs-mélanges donnant des résultats comparables ou supérieurs à ceux du R134a

NEARM	Composition (mass fractions)	Modelled COP	kW electricity per kW cooling ^a	Superheat added (°C)	Flammability index
R11 ^d	1.0	7.54	0.174	0.0	Non-flammable
E143/R245ca	0.21/0.79	7.32	0.182	1.9	Uncertain ^c
E143/R245ca	0.45/0.55	7.38	0.181	0.0	Uncertain ^c
R143/R236ea	0.11/0.89	7.19	0.183	4.9	Non-flammable
R143/R236ea	0.48/0.52	7.34	0.178	0.0	Uncertain
R143/E134	0.20/0.80	7.36	0.178	0.0	Non-flammable ^c
R114	1.0	7.12	0.183	7.9	Non-flammable
R143/R236ca	0.11/0.89	7.17	0.183	5.2	Non-flammable
R143/R236ca	0.48/0.52	7.33	0.178	0.0	Uncertain
R152a/R134	0.19/0.81	7.17	0.181	0.0	Uncertain
R12	1.0	7.06	0.181	0.0	Non-flammable

^a Enough superheat added to avoid wet compression; cooling effect of superheat added to COP

^b To convert to kilowatts of electricity per ton (12 000 Btu h⁻¹) of cooling multiply by 3.52

^c Validity of index for ethers uncertain

^d Currently used chlorine-containing refrigerants (in italics) are given for comparison

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