MODELED PERFORMANCE OF NON-CHLORINATED SUBSTITUTES FOR CFC-11 AND CFC-12 IN CENTRIFUGAL CHILLERS

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ABSTRACT

Current scientific evidence indicates that stratospheric chlorine concentrations below two parts-per-billion will be necessary to reverse and prevent "ozone hole" formations over the Earth's polar regions each spring. This makes it unlikely that HCFC alternatives with non-zero ozone depletion potentials (ODPs), no matter how small, will be accepted as refrigerants or blowing agents for foamed insulations for the long term. Pressure to eventually eliminate all high volume uses of chlorine containing refrigerants provides a strong incentive to find HFC or alternative, chlorine-free compounds with P-V-T characteristics similar to R-11 and R-123 for new and existing large centrifugal chiller applications.

Stable chlorine-free compounds with normal boiling points near CFC-11 and HCFC-123 are found in the fluorinated propane or butane or fluorinated ether families. These larger molecules have larger vapor phase heat capacities (Cp), molecular weights, and lower critical temperatures which thermodynamically decrease their volumetric capacity and coefficient of performance in simple cycle applications. Larger molar latent heats of vaporization caused by hydrogen bonding in the ethers may improve their net refrigerating effect (volumetric capacity) over CFC-11 and HCFC-123, however.

A number of fluorinated alkanes or fluorinated ethers that were identified in earlier technical publications or in joint EPRI/EPA project aimed at synthesizing and partially characterizing a third generation of CFC alternatives were fitted to the Lee-Kessler-Plöcker (LKP) and Carnahan-Starling-DeSantis (CSD) equations of state. Refrigerant property routines based on these equations were used to simulate the performance of a centrifugal chiller with pure refrigerants and nearly azeotropic refrigerant mixtures (NEARMs) of these alternatives. Consideration was given to the effects of acoustic velocity in the refrigerant, rotational mach numbers, the application of superheat to avoid "wet isentropic compression," and liquid subcooling before isenthalpic expansion.

The results indicate that there are several chlorine-free compounds that give modeled chiller performance comparable to CFC-11 and HCF-123 and better that CFC-12 and HFC-134a. Blends of these refrigerants may be required to mitigate the flammability of some of the alternatives which show the best performance, and modifications to the current chiller cycle such as liquid subcooling and suction gas superhead may offer unique advantages for more complicated, larger refrigerant molecules.

1. INTRODUCTION

Centrifugal water chillers represent one of the most efficient applications of electrical energy for the purpose of air conditioning we have today. There are roughly 50,000 centrifugal chillers in use in the United States and nearly 100,000 installed throughout the world.[1,2] Eighty percent of these water chillers use R-11 as the refrigerant because if its high cycle efficiency.

The phaseout of R-11 as a result of the Montreal Protocol and recent reports indicating a worsening of the stratospheric ozone depletion and some chronic toxicological effects of R-123 have heightened interest in finding a chlorine-free alternative which can be used instead of R-11 or R-123 in large, direct driven centrifugal chillers.

Several potentially useful fluorinated ethers and propanes were synthesized and partially characterized in a joint Electric Power Research Institute (EPRI)/Environmental Protection Agency (EPA) project aimed at finding new classes of organic compounds which could be used for CFC applications with fewer detrimental effects on the earth's stratospheric ozone layer. Physical property measurements made as a result of this project were used to fit these compounds to the Lee Kessler Plöcker (LKP) and Carnahan Starling DeSantis (CSD) equations of state (EOS). With these, cycle performance estimates can be made by calculating thermodynamic properties of the refrigerant at various state points in the circuit from known or estimated temperatures and pressures. Some other partially fluorinated ethanes and ethers suggested in earlier American Society for Heating, Refrigeration, and Air Conditioning Engineers (ASHRAE) publications were also included in the study.[3,4]

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 $mol^{-1}K^{-1}$) and a high critical pressure.[5] Given the limited number of chemical compounds which satisfy most of these requirements, some compromises in refrigerant properties or changes to the current chiller design may be required.

2. COMPOUNDS MODELED

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 because the standard method for assigning a refrigerant number to partially halogenated propanes is changing and no method has been adopted for ethers.[6] The numerical designators given in Table 1 are being used because they 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. The "C" prefix is added for cyclic molecules and the "EE" prefix refers to the two ether moieties in CF_3-O-CF_2-O-CF_3 (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 were synthesizing the compounds and performing physical property measurements on the synthesized products.[7,8] For some compounds, critical properties were obtained from the Thermodynamics Research Center (TRC) Thermodynamics Tables[9] or were estimated using techniques outlined in Reid, Prausnitz, and Poling.[10]

Table 1. Chlorine-Free CFC Alternatives Evaluated as CFC-11 and CFC-12 Replacements In Centrifugal Chillers

Designation	Molecular Formula	Normal Boiling Point (°F)	Critical Temperature (°F)	Source of Property Information
E-254cb	CHF_2-O-CF_2CH_3	97.6	373.0	ASHRAE Papers[1]
E-245cb	CF_3-O-CF_2CH_3	93.3	365.3	ASHRAE Papers[1]
R-152	CH_2FCH_2F	87.2	397.1	ASHRAE Papers[1]
E-143	CH_2F-O-CHF_2	86.1	368.3	ASHRAE Papers[1]
R-245ca	$CHF_2CF_2CH_2F$	78.8	345.8	EPA/EPRI Project
R-245fa	$CF_3CH_2CF_2H$	59.5	315.4	EPA/EPRI Project
R-236ea	$CF_3CHFCHF_2$	43.7	285.9	EPA/EPRI Project
R-143	CH_2FCHF_2	41.0	316.0	ASHRAE Papers[1]
R-236ca	$CHF_2CF_2CHF_2$	41.0	282.1	EPA/EPRI Project
E-134	CHF_2-O-CHF_2	40.4	308.2	ASHRAE Papers[1]
R-236cb	$CF_2FCF_2CF_3$	34.2	278.0	EPA/EPRI Project
R-236fa	$CF_3CH_2CF_3$	30.0	267.2	EPA/EPRI Project
E-227ca	CF_3-O-CF_2-CHF_2	24.5	238.4	EPA/EPRI Project
EE-218	CF_3-O-CF_2-O-CF_3	14.4	210.6	EPA/EPRI Project
R-227ea	CF_3CHFCF_3	4.6	218.2	EPA/EPRI Project
R-245cb	$CH_3CF_2CF_3$	-0.9	224.5	EPA/EPRI Project
E-143a	CH_3-O-CF_3	-11.5	220.7	EPA/EPRI Project
CE-216	CF_2-CF_2 CF_2-O	-20.4	191.6	EPA/EPRI Project
E-125	CF_3-O-CHF_2	-30.3	178.2	EPA/EPRI PRoject

1 Summarized in Vineyard, E., Sand, J., and Statt, T., "Selection of Ozone-Safe Nonazeotropic Refrigerant Mixtures for Capacity Modulation in Residential Heat Pumps," ASHRAE Trans. 95, 34-46, (1989).

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W. Kopo, "Beyond CFCs: Extending the Research for New Refrigerants", Proceedings of ASHRAE's 1989 CFC Technology Conference, NIST, Gaithersburg, MD, pp 39-46, Sept. 1989.

3. CHILLER PARAMETERS MODELED

A simple chiller model based on saturated refrigerant temperatures in the evaporator and condenser was developed using LKP and CSD refrigerant property routines to calculate condenser and evaporator pressures, net refrigerating effect (Btu/lb), isentropic compressor work (equivalent head), ideal isentropic coefficient of performance (COP), mass and volume flow rates per ton of refrigeration, and sonic velocity at suction conditions. When it was required, the model added just enough superheat in the evaporator to prevent formation of two-phase refrigerant during isentropic compression. The cooling effect of this superheat was added to the net refrigerating effect of the refrigerant and was included in the calculated COP. This was done to keep results from this study comparable with those from previous studies.[11, 12, 13, 14] Larger molecules with larger vapor phase heat capacities (C_p), like the propanes and three-carbon ethers in this study, exhibit "wet isentropic compression" more often than simpler one- and two-carbon refrigerants.[15]

Other parameters, specific to the performance of centrifugal chillers, that were modeled in this study were impeller tip speeds, rotational mach numbers, relative efficiencies due to rotational mach numbers, stage efficiencies, impeller revolutions per minute, and impeller pumping capacities. Typical values for a compressor head coefficient, tip flow coefficient, mechanical efficiency, impeller diameter, and pumping capacity factor were assumed for these calculations. Chiller efficiencies in terms of kilowatts per ton of refrigeration (kW/t) were computed factoring in all of these centrifugal specific parameters. This measure of efficiency, which is more dependent on the characteristics of turbomachinery, could then be compared and contrasted with the isentropic COP that was totally dependent on the thermodynamic properties of the fluid and assumed ideal, 100% efficient operation.

Transport properties like suction gas viscosity and liquid or vapor thermal conductivities were not modeled.

Cycle conditions simulating a 100°F condenser and a 40°F saturated evaporator which are fairly standard for a centrifugal water chiller were chosen.[16] No refrigerant subcooling or superheat was added unless superheating was necessary to avoid wet isentropic compression.

4. EQUATION OF STATE CONSIDERATIONS

Equations of State (EOS) are needed to estimate the enthalpy, entropy, and specific volume of the refrigerant as it circulates through a vapor compression cycle in a heat engine (refrigeration machine). Several simpler EOS have been reduced to computer subroutines which can conveniently be used on a personal computer to calculate the thermodynamic and pressure-volume-temperature (P-V-T) characteristics of refrigerants and/or mixtures of refrigerants in any refrigeration cycle. The Redlich-Kwong-Soave (RKS), Carnahan-Starling-DeSantis (CSD), Peng-Robinson, and Lee-Kessler-Plöcker (LKP) all fit this description. Each has advantages and disadvantages.[17, 18]

The LKP EOS was chosen initially for this work because it is a corresponding-states EOS which requires only the most fundamental data like the critical temperature, critical pressure, molecular weight, normal boiling point, acentric factor, and a temperature based correlation for the ideal gas heat capacity to simulate fluid behavior. The acentric factor which can be calculated from the normal boiling point and critical constants describes the non-ideality or complexity of molecules which results in nonsphericity and polarity. The CSD and RKS equations use a hard sphere model for simulating molecular interactions and require more extensive experimental (or estimated) P-V-T data to calculate EOS coefficients.[19] An additional advantage of the LKP EOS is that it contains an empirically based computer algorithm for estimating the interaction coefficient for mixtures of refrigerants.

The LKP EOS routines were tested by comparing vapor pressures and liquid densities calculated using these routines to experimentally measured values for some of the EPRI/EPA fluids which had been more extensively characterized in the laboratory. In most cases, calculated values differed by less than one or two percent from experimental data. Whenever possible, correlations between calculated and experimental results were improved by making small adjustments to the LKP dacentric factor.

The LKP code obtained from the University of Hannover did not contain a subroutine for calculating the speed of sound in refrigerant vapor. Since this is an important parameter for assessing refrigerant performance in centrifugal chillers, vapor pressures, liquid densities, and vapor densities calculated from the LKP routines were used to develop CSD coefficients so the appropriate CSD subroutine could be used to find the acoustic velocity in refrigerants at suction conditions.

5. RESULTS

Table 2 summarized the ideal isentropic COP and kilowatt per ton of refrigeration (kW/t) performance results for fluorinated alkanes and fluorinated ethers which gave modeled results equal to or better than R-134a. Results are also presented for R-11, R-123, R-114, and R-134a for comparison. Also tabulated in this table are rough estimates of atmospheric flammability based on summed bond energies and the molar heat capacity. These estimates seem pessimistic for the fluorinated ethers as indicated by the "Uncertain" designation for E-134.

Only R-152, E-143, and R-143 give COPs and kW/t values that are comparable to R-11. Very little physical property information was found for R-152 and E-143, so results for these two compounds are based primarily on estimated properties. Some experimental performance is available for R-143.[19] All of these compounds are probably flammable.

Under these modeling conditions, all of the other compounds in Table 2 show comparable or better performance than R-134a which is already being used to replace R-12 in gear-driven centrifugal applications. The presence or absence of subcooling and superheat as well as variations in the transport properties of the fluids could change their relative rankings. Incorporation of liquid line subcooling or liquid-to-suction line heat exchange into this simple model enhances the performance of refrigerants which have more complex molecular structures more than the relatively simpler molecules previously used.[15]

This table 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 complimented by the non-flammability of the other(s). Unfortunately, no clearly non-flammable alternatives are available with boiling points near R-152 and E-143, but a non-flammable ether (E-134) and several non-flammable propanes have boiling points (and vapor pressures) similar to R-143.

Table 2. Modeled Performance Results of Chlorine-Free CFC Alternatives In Chillers
- Compounds with results comparable to or better than R-134a -
- 40°F saturated evaporator, 100°F saturated condenser, 0°F superheat[1]/subcooling -

Refrigerant	Formula	Normal Boiling Point (°F)	Modeled COP	Kilowatt Per Ton	Flammability Index
E-254cb	CHF_2-O-CF_2CH_3	97.6	7.38	0.641	Flammable[2]
E-245cb	CF_3-O-CF_2CH_3	93.3	7.33	0.643	Uncertain-to-Flammable[2]
R-152	CH_2FCH_2F	87.2	7.60	0.615	Flammable
E-143	CHF_2-O-CH_2F	86.1	7.50	0.628	Flammable[2]
R-245ca	$CHF_2CF_2CH_2F$	78.1	7.33	0.639	Uncertain
R-11	CCl_3F	***74.9***	***7.54***	***0.614***	***Non-Flammable***
R-245fa	$CF_3CH_2CHF_2$	59.5	7.26	0.642	Uncertain
R-236ea	$CF_3CHFCHF_2$	43.7	7.14	0.650	Non-Flammable
R-236ca	$CHF_2CF_2CHF_2$	41.0	7.11	0.651	Non-Flammable
R-143	CHF_2CH_2F	41.0	7.49	0.611	Flammable
E-134	CHF_2-O-CHF_2	40.4	7.32	0.633	Uncertain[2]
R-114	$CClF_2CClF_2$	***38.5***	***7.12***	***0.645***	***Non-Flammable***
R-236cb	$CF_3CF_2CH_2F$	34.2	7.08	0.651	Non-Flammable
R-236fa	$CF_3CH_2CF_3$	30.0	7.04	0.654	Non-Flammable
R-134	CHF_2CHF_2	-3.5	6.97	0.651	Non-Flammable
R-152a	CHF_2CH_3	-13.0	7.17	0.633	Flammable
R-134a	CF_3CH_2F	***-15.7***	***6.97***	***0.653***	***Non-Flammable***

[1] Enough superheat added to avoud "wet compression", cooling effect of superheat added to COP.
[2] Validity of Index for Ethers uncertain

6. CONCLUSIONS

Centrifugal chiller modeling work on several fluorinated 2- and 3-carbon alkanes and fluorinated ethers indicate that they are potential, chlorine-free alternatives for R-11 and R-123. Use of fluorinated ethers as CFC alternatives should be more thoroughly investigated.

Several of the newer compounds which give the best modeled performance are flammable. Blends of flammable and non-flammable refrigerants with similar vapor 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 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 gains in energy efficiency.

Modifications of the basic chiller cycle such as deliberately adding subcooling or liquid-to-suction line heat exchange may preferentially benefit the performance of refrigerants with more complex molecular structures and larger molecular heat capacities. These modifications would involve significant changes to the design and substantial increases in the complexity of chillers because of the large volumes of refrigerant that must be circulated to achieve acceptable cooling capacities.

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