

1990

Optimum Refrigerants for Non-Ideal Cycles: An Analysis Employing Corresponding States

M. O. McLinden
NIST

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

McLinden, M. O., "Optimum Refrigerants for Non-Ideal Cycles: An Analysis Employing Corresponding States" (1990). *International Refrigeration and Air Conditioning Conference*. Paper 89.
<http://docs.lib.purdue.edu/iracc/89>

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>

OPTIMUM REFRIGERANTS FOR NON-IDEAL CYCLES: AN ANALYSIS EMPLOYING CORRESPONDING STATES¹

Mark O. McLinden
Thermophysics Division
National Institute of Standards and Technology
Boulder, Colorado 80303-3328 USA

ABSTRACT

The principle of corresponding states is used to evaluate the effects of the thermodynamic characteristics of the working fluid on the performance of refrigeration cycles. The desired characteristics, expressed in terms of the critical temperature and ideal gas heat capacity (C_p^o) using propane as the reference fluid, are examined for various departures from the theoretical (ideal) vapor compression cycle. These departures from the ideal cycle approximate a refrigerator.

Cycle performance and the resulting conclusions regarding the optimum refrigerant are strong functions of the assumptions made in modeling the cycle. The baseline cycle for the comparisons includes compressor efficiency and heat transfer limitations in the condenser and evaporator. For the baseline cycle, there are trade-offs between a high coefficient of performance (COP) and high volumetric refrigerating capacity; low values of C_p^o , corresponding to simple fluids such as the single-carbon CFCs, yield the highest COP. When simple representations for subcooling and/or heat exchange between the liquid and suction lines are added to the baseline cycle, the dependence of COP on the refrigerant critical temperature is greatly reduced, and the optimum C_p^o is much higher. These results indicate that modifications to the basic vapor compression cycle should be considered for more complex refrigerants such as the two-carbon HFCs and HCFCs.

INTRODUCTION

The working fluid used in refrigeration and heat pumping equipment has significant impacts on design and performance. For most applications, past practice restrains the choices to a very limited list. In the case of household refrigerators, for example, that list has for many years consisted of a single fluid--R12. The implication of R12 and other fully halogenated chlorofluorocarbons (CFCs) in stratospheric ozone depletion and greenhouse warming has resulted in the need to reexamine the requirements of a refrigerant in order to identify environmentally acceptable alternatives to the CFCs.

A refrigerant must satisfy many requirements, including the desirability of a nonflammable and nontoxic fluid and compatibility with common lubricants and materials of construction, as discussed by Threlkeld (1974) and McLinden and Didion (1987). This paper, however, will be restricted to the thermodynamic characteristics of refrigerants and, for this discussion, the 'optimum' refrigerant will be the fluid which yields the highest coefficient of performance (COP) and/or volumetric capacity.

The conventional approach for comparing the performance of refrigerants has been to either numerically simulate or experimentally test many different fluids in the

¹Contribution of the National Institute of Standards and Technology, not subject to copyright.

application of interest. With this approach there is always the possibility (or at least the nagging doubt) that the 'best' fluid has been overlooked. The principle of corresponding states, on the other hand, provides a way to examine fluid performance on a fundamental basis. This principle expresses the observation that, in reduced variables, the thermodynamic properties of many fluids are nearly identical. (A reduced property is the ratio of a quantity, such as density, to its critical value.)

The principle of corresponding states is a powerful tool that has been used in a variety of ways. It is the basis for the thermophysical properties prediction model developed by Ely and Huber (1990). In a refrigeration application, Bertinat (1986) has applied corresponding states to estimate the COP and capacity of the theoretical vapor compression cycle for a large number of fluids in terms of properties that could be related to the critical parameters of the refrigerant. Unterleutner *et al.* (1981) correlated the performance of 16 fluids in terms of reduced temperature, critical pressure, and four fluid categories. Angelino and Invernizzi (1988) rated the performance of fluids in terms of the ratio of the actual COP to the COP of the Carnot cycle operating over the same temperature difference; they showed that the reduced temperature of the evaporator, the reduced temperature lift between the evaporator and condenser, and a parameter related to the complexity of the fluid molecular structure are the main determinants of cycle performance.

The present work is an extension of an earlier thermodynamic evaluation of refrigerants using reduced properties (McLinden, 1988). This earlier evaluation (in contrast to those cited above which used corresponding states primarily to correlate the performance of many actual fluids) used reduced coordinates to define a fluid with properties characteristic of the whole family of halocarbon refrigerants. The calculation of cycle performance, also in terms of dimensionless variables, was then carried out for this 'characteristic' refrigerant. It concluded that there was a fundamental tradeoff between high COP and high capacity, and that small, simple molecules would be the best refrigerants. The present work extends the earlier evaluation by considering the effects of departures from the ideal (theoretical) vapor compression cycle; it also employs a more sophisticated and more correct property formulation. The present work will focus on refrigerators.

METHODS

Thermodynamic properties

To apply the principle of corresponding states to cycle analysis, the cycle conditions are non-dimensionalized by the critical parameters of a reference fluid. In this work, propane is used as the reference fluid. Although occasionally used as a refrigerant, propane is not the most obvious choice for the reference fluid. Propane, like most of the refrigerants, is a simple molecule; its normal boiling point (231.1 K, -42.1 °C) and critical temperature (369.85 K, 96.7 °C) are close to refrigerants such as R12, R22, and ammonia. The archetypical alternative refrigerant is R134a, and this highly polar halogenated ethane would be a better reference fluid for the entire class of alternative refrigerants. The exploration of the full range of possible cycle and fluid conditions can result in temperatures far outside the range normally experienced in equipment. Thus, it is more important for the reference fluid property formulation to be reliable over as wide a range as possible than for it to be of the utmost accuracy. While a wide-ranging

formulation for R134a is in preparation (Ely, 1990), the currently available formulation (McLinden *et al.*, 1989) is somewhat limited. The existence of extensive property data and the availability of an accurate, wide-ranging equation of state for its thermodynamic properties are the overriding reasons for choosing propane as the reference fluid.

The pressure-volume-temperature (PVT) properties of propane are expressed in terms of a modified Benedict-Webb-Rubin (MBWR) equation of state proposed by Jacobsen and Stewart (1973). It is of the form:

$$p = \frac{RT}{V} + \sum_{n=2}^9 \frac{a_n}{V^n} + \exp(-V_c^2/V^2) \sum_{n=10}^{15} \frac{a_n}{V^{2n-17}} \quad (1)$$

where the a_n are functions of temperature involving a total of 32 adjustable parameters. The MBWR formulation by Younglove and Ely (1987) accurately represents the properties of propane from 85 to 800 K, or a reduced temperature range of 0.23 to 2.16.

The temperature dependence of the ideal gas (zero pressure limit) heat capacity, C_p° , is required in addition to a PVT equation of state to completely express the thermodynamic properties of a fluid. In this work, C_p° is expressed as:

$$C_p^\circ = C_p^\circ(T_c) [1 + \lambda(T/T_c - 1)] \quad (2)$$

where $C_p^\circ(T_c)$ is the value of C_p° at the critical temperature, T_c , and the temperature dependence of a wide range of halogenated refrigerants is approximated by $\lambda = 0.56$ (McLinden, 1988). The ideal gas heat capacity is independent of the PVT behavior and is indicative of the molecular complexity of a substance. By using the generalized expression for C_p° (Eqn. 2) with varying values of $C_p^\circ(T_c)$, a wide range of hypothetical fluids can be simulated.

Reference cycle

The desirable thermodynamic characteristics of a refrigerant arise from the interaction with the refrigeration system in a particular application--i.e., there is no single 'best' refrigerant. Thus, to compare refrigerants, a reference cycle must be defined. There are many possible levels of detail for this reference cycle. The simplest is the Carnot cycle for which the COP depends only on the temperatures of the heat sink and heat source and not at all on fluid properties. This cycle would clearly be of no use in comparing fluids. The other extreme would be an experimental comparison in full-size equipment. At this level of detail the results would depend more on the detailed specifications of the equipment than on the properties of the fluid. A comparison might also be biased toward the established fluid for which the equipment had been optimized. A comparison using a highly detailed equipment simulation program would possess many of the drawbacks of an experimental comparison.

A middle approach is required. The next level of detail above the Carnot cycle is the theoretical vapor compression cycle. In this cycle, the refrigerant exits the condenser and evaporator as saturated liquid and vapor, respectively, and the reversible expansion engine of the Carnot cycle is replaced with an irreversible expansion at constant enthalpy. This cycle represents the theoretical limit of most actual refrigeration equipment. Its performance depends only on the thermodynamic properties of the working fluid and the condensing and evaporating temperatures.

The theoretical cycle can be modified to account for the non-idealities present in real equipment such as heat transfer limitations, compressor efficiency, condenser subcooling, and evaporator superheat. By expressing these deviations from the theoretical cycle in generic terms (e.g. an overall heat exchanger conductance rather than a detailed specification of the size, number, geometry, and spacing of the tubes and fins in a heat exchanger), fluid comparisons can apply to an entire class of equipment, such as domestic refrigerators, rather than to only a specific model of a particular manufacturer.

The reference cycle used in this work is depicted in Fig. 1. It includes simple models for the compressor and the heat transfer processes in the condenser and evaporator. Saturated refrigerant is assumed to exit the condenser and evaporator. Heat transfer between ambient and the liquid and suction lines is included; by appropriate choice of the ambient temperature, refrigerant subcooling and superheat may be approximated. Also included is a heat exchanger operating between the liquid and suction lines. This cycle is intended to approximate a domestic refrigerator.

Simulation model

A simulation model, written in FORTRAN, was developed to study the reference cycle discussed above. By appropriate choice of cycle parameters, simpler cycles, including the ideal vapor compression cycle, can be simulated. The model is similar to, and shares its roots with, the CYCLE11 model described by Domanski and McLinden (1990); it lacks the more detailed compressor model of CYCLE11 and treats subcooling, superheat, and the suction line/liquid line heat exchange slightly differently. The condenser and evaporator are specified in terms of an average effective temperature difference as described by Domanski and McLinden (1990). The other heat exchange processes are modeled with a heat exchanger effectiveness (see, for example, Kays and London 1958). The effectiveness factor concept was used because of the ease of 'turning off' a heat exchange by specifying a zero effectiveness.

The cycle is defined by specifying the temperatures of the external heat transfer fluids entering and leaving the condenser and evaporator, the ambient temperature, heat exchanger temperature differences or effectiveness factors, compressor efficiency, etc. Thermodynamic properties are supplied by a set of subroutines implementing the MBWR equation of state. Results are computed on an absolute basis and converted to a reduced basis by dividing by the critical parameters of the propane reference fluid.

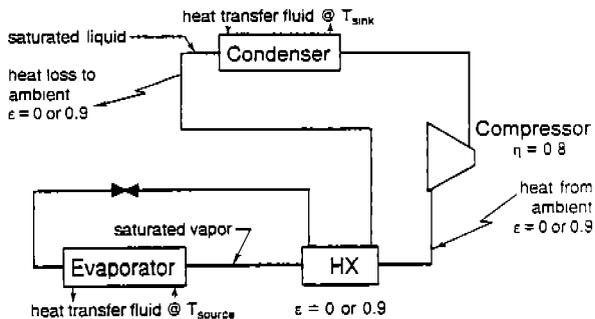


Figure 1. Refrigeration cycle simulated in this work.

RESULTS

For the simulations, cycle conditions are specified by the ratio of the heat sink temperature to the refrigerant critical temperature and a dimensionless temperature lift between the heat source and heat sink, $\zeta = (T_{\text{sink}} - T_{\text{source}})/T_{\text{sink}}$. For the reference fluid, and for refrigerants with the same reduced PVT behavior as the reference fluid, the performance depends only on the reduced temperature of the heat sink, the dimensionless temperature lift, and the ideal gas heat capacity. The simulations were carried out for $C_p^0(T_c)$ values of 50, 100 and 200 $\text{J mol}^{-1} \text{K}^{-1}$; this range of $C_p^0(T_c)$ encompasses virtually all of the present refrigerants, as well as all likely future refrigerants. Performance is expressed in terms of the coefficient of performance for refrigeration (COP_{refr} or simply COP); the volumetric refrigerating capacity (heat removed in the evaporator per unit volume of refrigerant vapor entering the compressor) is divided by the critical pressure to yield a dimensionless refrigerating capacity.

The baseline cycle for this work includes two nonidealities which are always present in actual equipment—compressor inefficiencies and heat transfer limitations. An effective average temperature difference of $0.04 \cdot T_{\text{sink}}$ for each heat exchanger and a compressor isentropic efficiency of 0.8 are assumed. The refrigerating COP and dimensionless refrigerating capacity for the reference fluid in the baseline cycle are given in Fig. 2. With changes in T_{sink}/T_c , the general trend is for COP to increase as capacity decreases and vice versa. The second factor to be examined is the effect of ideal gas heat capacity. For this cycle, low values of $C_p^0(T_c)$ yield the highest COP and capacity. These results are for a single temperature lift ($\zeta = 0.18$); as previously shown (McLinden, 1988), smaller temperature lifts will increase both COP and capacity.

Next, let us add subcooling and superheat in the liquid and suction lines, respectively, to the cycle with compressor and heat transfer inefficiencies. An effectiveness factor of 0.9 for heat transfer to an ambient temperature of $0.95 \cdot T_{\text{sink}}$ is assumed. (These parameters were chosen to approximate the conditions that a refrigerator might experience; i.e. for a T_{sink} of 308 K (35 °C), the ambient temperature would be 293 K (20 °C).) Heat transfer to the suction line (superheat) results in slightly lower COPs than the baseline cycle, as shown in Fig. 3. The refrigerating capacity is reduced by up to 16%; the trends in capacity are the same as those seen in Fig. 2 and are not shown.

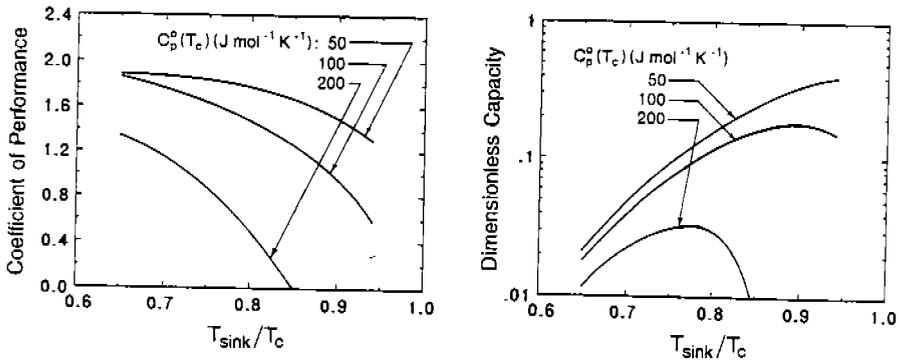


Figure 2. Coefficient of performance for refrigeration and dimensionless refrigerating capacity for the baseline cycle (cycle with compressor efficiency and heat transfer limitations).

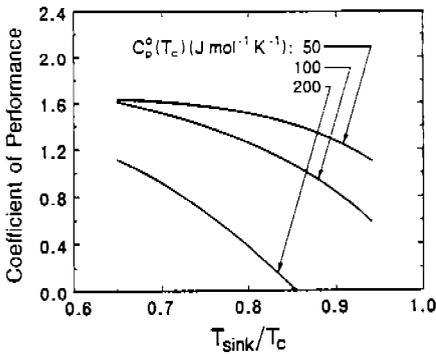


Figure 3. Coefficient of performance for baseline cycle plus vapor superheat.

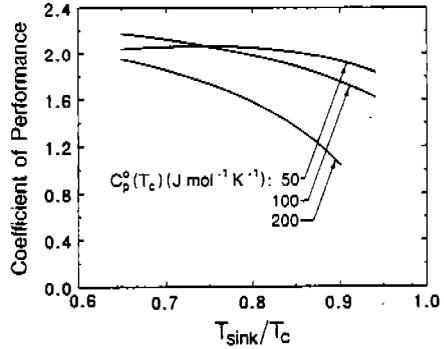


Figure 4. Coefficient of performance for baseline cycle plus liquid subcooling.

The effects of subcooling the liquid exiting the condenser are quite dramatic, as seen in Figure 4. The refrigerating COP is significantly higher than the baseline case, especially for sink temperatures approaching the refrigerant critical temperature. The result is a much weaker dependence of COP on critical temperature.

The results for adding heat exchange between the suction and liquid lines to the baseline cycle are shown as the dotted lines in Fig. 5. The increase in COP and the reduced dependence of COP on the critical temperature are even more pronounced than those for liquid subcooling. The refrigerating capacity is also significantly improved. The most striking result, however, is the effect of ideal gas heat capacity. With this heat exchange, the higher values of $C_p^o(T_c)$ (100 and 200 $\text{J mol}^{-1} \text{K}^{-1}$) yield the highest COPs; this trend is opposite that observed in the previous cases. The lower values of heat capacity still give a higher refrigerating capacity, but the variation with C_p^o is small.

Finally the effects of considering together all of the departures from the ideal cycle (heat transfer limitations, compressor efficiency, heat transfer to ambient, and intracycle heat exchange) are shown as the solid lines in Fig. 5. Both the coefficient of performance and the refrigerating capacity are the highest observed here.

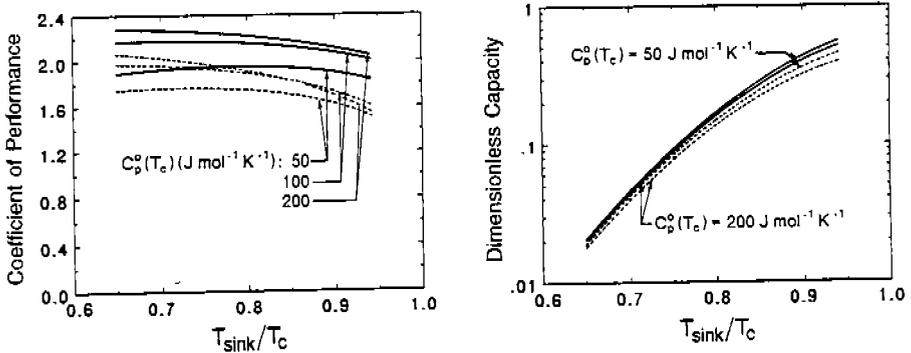


Figure 5. Coefficient of performance and dimensionless refrigerating capacity for the baseline cycle plus liquid line/ suction line heat exchange, (.....) and the cycle with all of the nonidealities considered here (—).

DISCUSSION

Effects of ideal gas heat capacity and departures from the ideal cycle

Perhaps the best way to understand the effects of the ideal gas heat capacity, as well as those of subcooling, superheat, and intracycle heat exchange, is to examine cycles on temperature-entropy diagrams. When the value of $(\partial S/\partial T)$ along the saturated vapor line is zero, the saturated vapor curve is vertical and the ideal (isentropic) compression process would both begin and end with saturated vapor. Lower values of C_p° result in a more negative value of $(\partial S/\partial T)_{\text{sat}}$ (as seen in the T-S diagram on the left hand side of Fig. 6 drawn for a $C_p^\circ(T_c)$ of $50 \text{ J mol}^{-1} \text{ K}^{-1}$). This will result in an ideal compression process extending into the superheated vapor region, as indicated by the dotted line. With higher values of C_p° , the two-phase region slumps over to the right so that an isentropic compression process starting with saturated vapor would terminate in the two-phase region. Practical considerations aside, this two-phase compression process avoids the COP penalty associated with superheating the refrigerant at the compressor discharge to a higher than needed temperature, and one might think that it would yield the highest COPs. But, C_p° also affects the liquid side of the two-phase region and, thus, the expansion process. Higher values of ideal gas heat capacity result in higher vapor qualities at the outlet of the isenthalpic expansion process, or in other words, a smaller fraction of the refrigerant entering the evaporator is liquid which can contribute a useful refrigeration effect by evaporating. With a sufficiently high C_p° and/or temperature lift, the refrigerant can flash completely to vapor in the expansion process, resulting in zero refrigeration effect (as was seen in Figs. 2 and 3 for $C_p^\circ(T_c) = 200 \text{ J mol}^{-1} \text{ K}^{-1}$).

The result of these offsetting effects on COP is an optimum value of $C_p^\circ(T_c)$ which varies with the reduced temperature of the heat sink and also the assumptions made in the cycle analysis. The optimal $C_p^\circ(T_c)$ were found by calculating COP for various values of $C_p^\circ(T_c)$, employing a simple Fibonacci search to locate the maximum. These optimal heat capacities are plotted in Fig. 7 along with the $C_p^\circ(T_c)$ for various fluids. (Note that in order to plot the optimal C_p° versus absolute (rather than reduced) temperature, specific cycle conditions must be chosen; here $T_{\text{sink}} = 308 \text{ K}$ (35°C) and the temperature lift of $\zeta = 0.18$ implies a source temperature of 253 K (-20°C). These conditions were chosen to approximate a domestic refrigerator.) For the baseline cycle, the values of $C_p^\circ(T_c)$ which yield the highest COP range from 35 to $70 \text{ J mol}^{-1} \text{ K}^{-1}$, depending on the refrigerant critical temperature. These fairly low values of C_p° correspond to moderate to high amounts of superheat upon compression.

Subcooling increases the refrigeration COP by reducing the amount of refrigerant that must be vaporized in the expansion process to cool the entire fluid stream from the condenser to evaporator temperatures. This process has a greater relative effect at high C_p° as seen in the expansion processes for the cycles drawn as dashed lines in Fig. 6. These reduced expansion losses can be traded off against compression superheat losses and thus the optimum value of $C_p^\circ(T_c)$ shifts slightly higher in Fig. 7. (This discussion is for refrigeration; the results for heat pumping will depend on whether the heat rejected in the subcooling process is at a useful temperature.)

Superheat at the compressor inlet, on the other hand, exacerbates the compression superheat losses as indicated by the right-hand portion of the cycles shown as dashed lines in Fig. 6. The effect of superheat is seen mainly on COP; the optimal $C_p^\circ(T_c)$ are only about $2 \text{ J mol}^{-1} \text{ K}^{-1}$ lower than the baseline cycle. The lower densities of

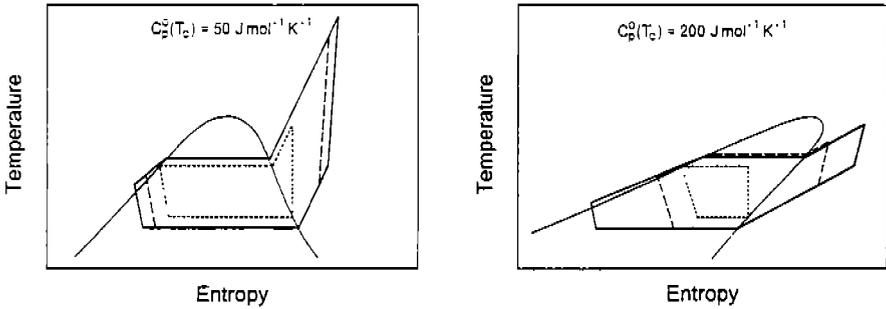


Figure 6. Simulated refrigeration cycles on temperature entropy coordinates drawn for fluids with $C_p^0(T_c)$ of 50 and 200 $\text{J mol}^{-1} \text{K}^{-1}$; (.....) theoretical vapor compression cycle; (-----) cycle with subcooling and superheat; (—) cycle with liquid line/suction line heat exchange.

superheated vapor, compared to saturated vapor at the same pressure, are the cause of the lower refrigerating capacities noted above.

Heat exchange between the suction and liquid lines combines the effects of subcooling and superheat as indicated by the cycles shown as solid lines in Fig. 6. The advantages seen with simple subcooling are enhanced with intracycle heat exchange since the liquid refrigerant exiting the condenser can be cooled to a much lower temperature (but not all the way to the evaporation temperature, even with perfect counter-flow heat exchange, since the vapor will always have a lower heat capacity than the liquid). The subcooling effects more than offset the penalties associated with superheat, resulting in the improved COPs compared to the baseline cycle seen in Fig. 4 and the substantially higher optimal $C_p^0(T_c)$ (ranging from 110 to 210 $\text{J mol}^{-1} \text{K}^{-1}$) seen in Fig. 7.

The final cycle combines compressor efficiency, heat transfer limitations, subcooling, superheat, and liquid line/suction line heat exchange. With heat exchange between the suction and liquid lines, heat transfer between the suction line and ambient has little effect (at least for the conditions simulated here) since the vapor is heated

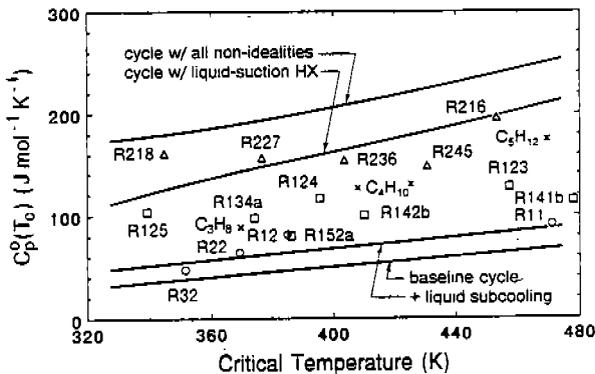


Figure 7. C_p^0 for a variety of refrigerants and other fluids as a function of critical temperature, and the optimal C_p^0 for the cycles simulated here plotted for a heat sink temperature of 35 °C.

nearly to the ambient temperature in the intracycle heat exchanger. The combination of ambient and intracycle heat exchange, on the other hand, has an additive effect on subcooling. Thus, not surprisingly, this combination yields the highest COPs relative to the baseline cycle and results in the highest values for the optimum $C_p^o(T_c)$ (Fig. 7).

Implications for fluid selection

The results presented above yield two different approaches to searching for optimum working fluids:

- (1) Given an application (i.e. specified source and sink temperatures) and cycle configuration (e.g. the presence or absence of an intracycle heat exchanger), what are the characteristics of the optimum refrigerant?
- (2) Given the characteristics of a refrigerant (i.e. critical temperature and ideal gas heat capacity), what cycle conditions and/or modifications to the basic vapor compression cycle will most favor a fluid with the given characteristics over other fluids?

In the present discussion, maximization of the refrigerating coefficient of performance will be assumed as the objective to be met by an 'optimum' fluid.

Let us consider both of these approaches by examining the range of available fluids plotted by their $C_p^o(T_c)$ in Fig. 7. The first observation to make is that nature is kind: there is considerable overlap between the optimal $C_p^o(T_c)$ and the $C_p^o(T_c)$ of real fluids. The general trend of $C_p^o(T_c)$ increasing with T_c is also the same for both real and optimum fluids. One is further struck by the close correspondence between the single-carbon halocarbons (such as R22, R12, and R11, plotted as circles) and the optimal $C_p^o(T_c)$ for the theoretical and baseline cycles. It is certainly no coincidence that such simple cycles employing such simple molecules as the working fluid dominate refrigeration and heat pumping applications today.

Most of the 'new' or 'alternative' refrigerants (such as R134a, R123, and R125, plotted as squares in Fig. 7) are ethane-based (two carbon) halocarbons. In moving to these more complex molecules, it is inevitable that the ideal gas heat capacity should increase. The $C_p^o(T_c)$ for these fluids lie above the optimum for simple cycles (those without intracycle heat exchange or subcooling). The fact that these new refrigerants are being tested and simulated in equipment using these simple cycles (i.e. cycles and equipment optimized for the low C_p^o , single-carbon CFCs) may explain, in part, the persistent reports that the 'new' refrigerants may result in lower COPs.

Faced with this realization, and the need to find alternatives to the fully halogenated CFCs, let us consider the two approaches presented above. There are certainly compelling reasons to find a fluid suitable for use in existing equipment. Thus we could take the first approach and consider re-opening the search for alternative refrigerants for use in simple cycles. Such cycles require fluids with low heat capacities for maximum energy efficiency, and this most likely implies single-carbon compounds. But among methane and its chlorine and fluorine derivatives, only R22 and R23 also satisfy the other prime attributes desired of a refrigerant--nonflammability, low toxicity, and short atmospheric lifetime (McLinden and Didion, 1987). The critical temperature of R23 (299 K, 26 °C) is, however, much too low for ordinary refrigeration applications. If one is willing to relax the requirement for a nonflammable fluid, R32 is also a

possibility. Thus, we must conclude that, apart from R22 and possibly R32, any new refrigerant will be a more complex molecule.

Let us then take the second approach and attempt to find a cycle that fits the fluids, in this case the two-carbon HFCs and HCFCs. It is clear from the above results that with higher values of $C_p^o(T_c)$ the COP is improved by subcooling the liquid refrigerant exiting the condenser and/or exchanging heat between the liquid and suction lines. This is also the conclusion reached by Angelino and Invernizzi (1988) for heat pump cycles employing more complex fluids (except that they used a 'parameter of molecular complexity' rather than ideal gas heat capacity). On a more fundamental level, the Achilles heel of the complex (high C_p^o) refrigerants is the large expansion loss as discussed above and also by Angelino and Invernizzi (1988). Both subcooling and liquid line/suction line heat exchange improve COP by reducing expansion losses. Thus, other means to reduce these losses should be considered. While an expansion engine might be the ultimate device for this purpose, its complexity will likely rule it out for the new refrigerants, just as it is not in common use with the CFCs. Other schemes, such as flash gas removal, do, however, bear reexamination.

The optimum C_p^o for some of the cycles (including the one which yielded the highest COP) lie above the C_p^o of the new HFCs and HCFCs. What of still more complex molecules, such as three-carbon halocarbons (plotted as triangles in Fig. 7) or the four- and five-carbon hydrocarbons (plotted as crosses)? While this analysis would seem to suggest these fluids, other factors favor as simple a molecule as possible. Larger molecules generally have poorer transport properties. The heat of vaporization on a molar basis is a function mainly of the normal boiling point temperature, and thus the higher molecular weight fluids will have lower heats of vaporization on a mass basis. In addition, more complex molecules are generally more difficult to manufacture and less stable.

Other considerations

This analysis has ignored a number of factors which may affect the results. The main omission has been to completely disregard the influence of refrigerant transport properties. Other non-idealities present in equipment, most notably pressure drops in the heat exchangers and piping, and the internal heat exchanges and other losses present in hermetic compressors, have not been considered. The present results were computed using propane as the reference fluid; another reference fluid (such as R134a) may behave differently in a refrigeration cycle. Finally, the present results are for refrigerators; other applications should be considered separately.

CONCLUSIONS

In this analysis, the principle of corresponding states has been used to consider the impact of refrigerant thermodynamic characteristics on the performance of the theoretical vapor compression cycle and deviations from the ideal cycle. The advantage of corresponding states is that the results are not restricted to one or a few fluids but rather encompass a wide range of fluid behavior. This has allowed the specification of the 'optimum' refrigerant in terms of critical temperature and ideal gas heat capacity.

Except for the simplest departures from the theoretical cycle (isentropic compressor efficiency and heat transfer limitations in the condenser and evaporator), the

results clearly refute the assumption, implicit in previous analyses, that the relative ranking of fluids in the theoretical cycle will be the same as in more realistic cycles. The simple cycles exhibit a pronounced trade-off between high COP and high refrigerating capacity and favor fluids with low $C_p^0(T_c)$ (35 - 70 J mol⁻¹ K⁻¹) such as the single-carbon CFCs. Cycles with liquid subcooling and/or heat exchange between the liquid and suction lines, on the other hand, can simultaneously achieve high capacity and efficiency with more complex fluids, those having a $C_p^0(T_c)$ of as high as 250 J mol⁻¹ K⁻¹.

While the results presented here are suggestive and clearly demonstrate the strength of the corresponding states approach, they must be considered preliminary and applied with caution. Not considered are several key factors affecting the cycle (i.e., heat exchanger pressure drops and details of the compression process) and fluid (i.e., transport properties and deviations from the reference fluid). Further work including these factors is planned. The present results do suggest that the two-carbon HFCs and HCFCs continue to be the most promising replacements to the CFCs, but one cannot rule out *a priori* more complex fluids. For fluids with two or more carbons, modifications to the basic vapor compression cycle may be required for maximum energy efficiency.

REFERENCES

- Angelino, G. and C. Invernizzi. 1988. General method for the thermodynamic evaluation of heat pump working fluids. *Int. J. Refrig.* 11 16-25.
- Bertinat, M.P. 1986. Fluids for high temperature heat pumps. *Int. J. Refrig.* 9 43-50.
- Domanski, P.A. and M.O. McLinden. 1990. A Simplified cycle simulation model for the performance rating of refrigerants and refrigerant mixtures. *Proc., ASHRAE-Purdue CFC Conference.*
- Ely, J.F. 1990. personal communication, National Institute of Standards and Technology, Boulder, Colorado, USA.
- Ely, J.F. and M.L. Huber. 1990. A predictive extended corresponding states model for pure and mixed refrigerants. *Proc., ASHRAE-Purdue CFC Conference.*
- Jacobsen, R.T. and R.B. Stewart. 1973. Thermodynamic properties of nitrogen including liquid and vapor phases from 63 K to 2000 K with pressures to 10,000 bar. *J. Phys. Chem. Ref. Dat.* 2 757-922.
- Kays, W.M. and A.L. London. 1958. *Compact Heat Exchangers.* New York: McGraw-Hill.
- McLinden, M.O. 1988. Thermodynamic evaluation of refrigerants in the vapour compression cycle using reduced properties. *Int. J. Refrig.* 11 134-143.
- McLinden, M.O. and D.A. Didion. 1987. CFCs: Quest for Alternatives. *ASHRAE Journal* 29 (12) 32-42.
- McLinden, M.O., J.S. Gallagher, L.A. Weber, G. Morrison, D. Ward, A.R.H. Goodwin, M.R. Moldover, J.W. Schmidt, H.B. Chae, T.J. Bruno, J.F. Ely, and M.L. Huber. 1989. Measurement and formulation of the thermodynamic properties of refrigerants 134a (1,1,1,2-tetrafluoroethane) and 123 (1,1-dichloro-2,2,2-trifluoroethane). *ASHRAE Trans.* 95 pt 2 263-283.
- Threlkeld, J.L. 1970. *Thermal Environmental Engineering,* 2nd ed. Englewood Cliffs, NJ: Prentice-Hall, Inc.
- Unterleutner, K., H. Huemer, and F. Moser. 1981. Search for optimal working fluids in high temperature heat pumps. *Proc. of the XVth IIR Cong.,* vol. II 483-490.
- Younglove, B.A. and J.F. Ely. 1987. Thermophysical properties of fluids. II. Methane, ethane, propane, isobutane and normal butane. *J. Phys. Chem. Ref. Dat.* 16 577-798.