Research and Development of Heat Pumps Using Nonazeotropic Mixture Refrigerants

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ABSTRACT

Although nearly a century has passed since the use of multicomponent refrigerants was first proposed, such refrigerants have achieved only extremely limited application. Further research and development will be needed before widespread use of nonazeotropic mixture refrigerants will be commercially attractive. This paper summarizes a workshop conducted to identify these research and development needs.

INTRODUCTION

The 1985 Annual Meeting of the American Society of Heating, Refrigerating, and Air-Conditioning Engineers (ASHRAE) included two symposia on "Advances in Nonazeotropic (Zeotropic) Mixture Refrigerants for Heat Pumps." These symposia provided an update on the state of the art of nonazeotropic mixture research. A one-day workshop was scheduled immediately following the ASHRAE meeting with the intent to:

- o Assess the status and potential of nonazeotropic mixture refrigerants,
- o Identify research and development needs associated with such refrigerants and the equipment in which they would be used, and
- o Encourage international cooperation and coordination in the conduct of such research.

Participation in the workshop was by invitation extended to the authors of the symposia papers, internationally recognized researchers in nonazeotropic mixtures, representatives of both refrigerant producers and heat pump manufacturers, utility representatives, and others selected from research organizations. A list of attendees is included as Appendix A. The workshop was held on 27 June 1985 at the Hawaiian Electric Company in Honolulu.

STATUS AND POTENTIAL OF NONAZEOTROPIC MIXTURES

Nonazeotropic refrigerant mixtures, used as a working medium in a refrigeration cycle, offer two generic characteristics not available from single-component fluids. These unique features are gliding-temperature phase-change processes in the heat exchangers (evaporator and condenser) and variable composition, and thus density, control possible through appropriate system design. The impact of these characteristics on thermodynamic performance (i.e., capacity and efficiency) of refrigeration, heat pump and air-conditioning systems depends largely upon the ingenuity of the designer. The theoretical and experimental studies reported to date

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make it clear that some hardware modifications to current systems will be necessary if significant improvement in performance is to be accomplished. The degree of improvement necessary for a given refrigerant mixture system to be attractive for application is both application specific and time dependent. Nonazeotropic mixtures are currently being researched for applications from residential-sized refrigerators (< 1 kW) to district heating heat pumps (> 25 MW). The degree of marginal benefit over current systems that a mixture system must offer to be cost effective to both the manufacturer and the consumer varies widely over such an application range. Common to all applications is the general lack of understanding of how mixture systems work and thus how they might be controlled for safe, efficient full-range operation. Also lacking is sufficient thermodymamic and transport property data for preliminary design and impact studies, let alone that required for detailed system design. Coupled with these problems is the situation that the state-of-the-art of systems design is not static; it is being improved as a result of many mechanical component and system improvements. It is therefore felt that a mixture system must offer performance improvements of the order of 20% or more over state-of-the-art single refrigerant systems to be acceptable for development.

The opportunities offered by nonazeotropic mixtures begin with the addition of a new dimension that can, at least theoretically, be superimposed upon almost any mechanical system, thus offering further potential for system performance improvement. Specifically, single component refrigerants undergo a phase change at constant temperature while refrigerant mixtures exhibit a "gliding" temperature. This phase-change gliding temperature attribute has been shown to improve the heat exchanger (i.e., condenser or evaporator) performance significantly by narrowing the log mean temperature difference between the refrigerant and the fluid being sensibly heated or sensibly cooled. This improvement is realized when the heat exchanger is designed to be counterflow. Another method of capitalizing on this gliding temperature attribute is to separate the working media into two or more streams of different compositions that serve multiple condensers and/or evaporators operating at different temperature levels. Conceptually at least, this type of application for a mixture will always show improved performance over what a single-component refrigerant system can offer. This benefit is of particular interest for such applications as domestic refrigerator/freezer boxes and industrial-sized food freezer/cooler systems.

The variable composition, and thus variable density, attribute provides an opportunity for independent control of a system's capacity. The inherent disadvantage of the vapor-compression cycle's loss of capacity with decreasing evaporator temperature (an inevitability since the vapor saturation densities of all pure components decrease with pressure) can be addressed by causing a shift toward the more dense component in the mixture. For the case of residential heat pumps, whose load increases with decreasing evaporator temperature, the opportunity to have the capacity paralleling the load demand is possible.

Utilization of these attributes within the vapor compression cycle alters the fundamental cycle itself. Recently a comprehensive study was done showing all the possible thermodynamic cycles that link the ends of the spectrum from the vapor compression cycle to the absorption cycle. Throughout this spectrum (except at the vapor-compression end point) a mixture is required as a working fluid. The vast majority of the cycles have remained unexplored. Many, on a preliminary basis, seem to offer thermodymamic advantages over current systems in a variety of applications. More importantly, many seem to offer improved performance for applications yet undeveloped, for example, multiple condenser applications with different temperature levels (e.g., space and water heating).

The future of mixtures as a refrigeration working media is unknown largely because it has not been adequately explored from either a materials capability or from cycle design/applications viewpoints. What is known, however, is that mixture systems offer an alternative (perhaps the only one) to the current vapor-compression and absorption development programs, which will inevitably reach cost-effectiveness limits. Mixtures offer this alternative by introducing new thermodynamic opportunities at a most fundamental level. The exploratory path ahead is undoubtedly long; the current refrigeration systems have had a long and intense developmental period and currently serve us well in many ways. However, the potential for performance improvements is unique and demands exploration.

PARTICIPANTS REPORTS

Five informal oral reports from four separate institutions were presented to the invited audience so as to keep fellow researchers informed on their respective current activities. A summary of these presentations follows:

George Alefeld, Technical University of Munich

Dr. Alefeld discussed the spectrum of possible thermodynamic cycles that link the vapor-compression cycle to the absorption cycle. he demonstrated that these two fundamental cycles can be elements of a large number of cycles that utilize mixtures as refrigerant working media. He illustrated that most of the cycles are essentially undeveloped and that some offer potential for improved performance in certain refrigeration applications. Moreover, his linkage of absorption and nonazeotropic systems suggests that mixture systems may be able to draw on the experience developed with absorption cycle research.

Reinhard Radermacher, University of Maryland and National Bureau of Standards

Dr. Radermacher presented an analysis of two refrigeration cycles, a single stage and a double stage, which utilize a solution pump between the evaporator and condenser to transmit some of the unevaporated liquid (biased with less volatile component) around the compressor. The theoretical model developed for this study incorporated component algorithms superimposed on an equation of state (Carnahan-Starling-DeSantis), which produced the property data. Results indicate that this type of two-stage cycle can achieve large temperature lifts with very reasonable pressure ratios.

Mark McLinden, National Bureau of Standards

Dr. McLinden presented thermodynamic rating characteristics (i.e., capacity and efficiency) for refrigerants in terms of reduced properties. Nomographs were presented for single-component refrigerants to assist in the selection of an optimum working fluid, for a given capacity requirement, in terms of the fluid's fundamental properties (e.g., critical point, etc.). Results for a specific heat pump application were presented for several refrigerant mixtures. The goal of this work is to devise a capacity/efficiency rating scheme for mixtures based on an ideal cycle (Lorentz) just as the single refrigerants are rated using their limiting ideal cycle (Carnot).

Horst Kruse, University of Hannover

Dr. Kruse discussed his studies on the effects of oil on the properties of mixtures. He demonstrated the need for the increased accuracy of the Carnahan-Starling-DeSantis equation of state over the Redlich-Kwong-Soave equation for the prediction of the thermodynamic properties of mixtures with oil. He also demonstrated that transport properties, particularly viscosity, which is needed for compressor lubrication assurance, still require empirically based relationships for prediction at sufficient accuracy. He has developed such relationships for mixtures with synthetic oils. Also, he showed that the already known empirical equations for mineral oils with a single refrigerant are not applicable for single refrigerants or mixtures with synthetic oils.

Thore Berntsson, Chalmers Institute of Technology

Dr. Berntsson presented the results of computer simulations of the performance of a large heat pump (for district heating) system with mixtures as the working media. These studies resulted in a double-peak profile on a performance-composition curve resulting from a matching of the heat exchanger temperature profiles. Also studied was a space heating application with a comparison of the two cases. This study found that the greater the temperature glide, the greater the advantage of the mixture performance over the single refrigerant working fluid.

RESEARCH AND DEVELOPMENT NEEDS

Based on the research already performed, as well as perceived opportunities and constraints, the following topics were identified as warranting further research.

Cycle Analysis

Experience to date has established that simple substitution of refrigerant mixtures into conventional equipment will not offer appreciable benefits, except to fill a gap in desired properties between available single-component refrigerants. Cycle analysis can be initiated at the theoretical level and progress through iterations of increasing complexity by the introduction of real-world nonidealities. Strong justification for cycle analyses lies in the opportunities for creativity and recognition of similarities to known systems.

Component and System Simulation

The combinations of candidate fluids, with virtually infinite composition proportions, result in an infinite number of candidate mixtures. Moreover, the conceivable number of cycle modifications and enhancements further expands the combinations to be screened and evaluated. Simulation, initially at a coarse screening level and progressing toward more precise analyses, can reduce the time and funds needed for experimental follow-on efforts.

Property Data

Only limited and not necessarily consistent data, are available for analyses of systems employing nonazeotropic mixtures. Specifically needed are:

GATE PROPERTY DATA

* Materials compatibility
* Health and safety
* Stability
* Cost and availability

THERMODYNAMIC DATA

* Vapor-liquid equilibria data for binary and ternary mixtures of common chlorofluorocarbon refrigerants and selected organic fluids
* Pressure-volume-temperature relations of such mixtures and the mixing coefficients needed to predict such state properties

THERMOPHYSICAL DATA

* Heat transfer coefficients for these mixtures
* Viscosity data for both the pure mixtures and for representative oil solutions

Note that accumulation of property data requires extensive support. Confining this effort to a tractable level, therefore, requires initial measurements of thermodynamic properties of an accuracy necessary for screening purposes only. Subsequently more accurate measurements of all properties need to be made only on specific mixtures that are designated as candidates for systems that will actually be developed.

Impact Studies

In parallel with the above efforts, examination and quantification of potential benefits of nonazeotropic mixtures are needed. Each of the proposed benefits of mixtures applications must be analyzed to determine inputed cost and efficiency sensitivities. Allowable cost increments will clearly vary by ownership. For consumer products, the performance of the mixtures machine must be sufficiently greater than the alternative unit so that the discounted savings during a consumer's planning horizon period will be from three to four times the manufacturer's incremental cost. This is because the installed price to a consumer is typically three to four times the manufacturer's cost. For commercial and industrial customers, allowable cost premiums may be greater. The result of these impact studies will be constraints or goals for subsequent engineering studies. Furthermore, such impact studies also enable the forecast of realistic performance improvement potential.

Development Studies

Based on screening via the cycle analyses and subsequent simulation and impact analyses, promising concepts should be developed. The precision of supporting property, component, and integration data must be refined as dictated by the innovation involved. Major component needs must be characterized to evaluate concerns unique to mixtures. The development studies must, therefore, progress from simulation and breadboard* analyses to engineering prototype** tests. The development studies should include component design and refinement where the components involved require innovation for success of the concepts studied. A necessary part of these design studies is examination of environmental and societal impacts of application. Included are gate properties (e.g., toxicity, corrosivity, flammability, availability, and disposability) of mixtures used as well as their materials' compatibility and stability in the envisioned application. These design studies are intended to establish concept feasibility and potential viability; further product development and production engineering are not included.

Field Tests

Actual field verification of cycle operation and evaluation of both prototypes and new products employing mixtures will be needed. Such tests can serve to validate existing models as well as to confirm claims made for commercialized products. Of particular importance is the measure of mixtures enhancement of the total system performance and identification of opportunities for integrated or multifunction applications.

System Modification and Optimization:

As a final research and development step prior to product engineering and market evaluation, efforts to improve emerging concepts and fluids selections are warranted, based on the above studies and tests, to enhance their attractiveness to potential manufacturers.

RESEARCH AGENDA FOR THE NEAR FUTURE

Time constraints for the workshop precluded a rigorous prioritization of research and development needs. Based on workshop discussions and through a summary review process, the following specific research and development topics were proposed for the near term:

1. Completion and validation of current efforts to develop equations of state for binary and ternary mixtures.

2. Integration of these equations of state into simulation models to enable development studies.

3. Theoretical cycle analyses, including absorption-compression cycles, to identify opportunities.

4. Screening of nonazeotropic mixture candidate fluids and absorption pairs suitable for absorption-compression cycles.

5. Collection of property data as needed for the above; sensitivity analyses based on these data to determine precision requirements for future data collection.

6. Laboratory tests of new concepts and fluids as they emerge (considerable attention has already focused on R22/R114, R12/R114 and R13B1/R152a mixtures; R23/R12 and R23/R22 are possible candidates warranting evaluation for increased capacity for low evaporator temperature applications).

7. Impact study identifying likely applications and quantifying the increase in performance as well as the return to the manufacturer and consumer.

*Breadboard: A laboratory working model affording access and easy substitution or adjustment of components to test concepts and modification sensitivities

**Prototype: A working model assembled to approximate a perceived device. An engineering prototype would incorporate the thermal or physical configuration of the device in order to test performance, interactions, and other physical attributes of the device. Subsequent marketing or production prototypes would also emulate packaging and machinery/assembly characteristics.

CONCLUSIONS

Several conclusions have been derived from the workshop discussions:

- o Nonazeotropic mixture refrigerants are not ready for commercialization. Demonstration of their practical utility will require at least several more years.
- o Research, both basic and applied, is needed to identify and establish the viability of specific nonazeotropic mixtures and associated cycle modifications. This research must develop the necessary data, design tools, and thermodynamic impact of selected cycles for specific applications.
- o Because of opportunities to exploit the advantages of gliding temperature evaportion and/or condensation (e.g., a Lorentz rather than a Carnot cycle), nonazeotropic mixture refrigerants may initially be found more attractive in heat pumps and refrigeration systems requiring high temperature glide. Such systems may include heat pump water heaters, community heat pump systems, industrial heat pumps, and multistage refrigeration systems.
- o Although nearly 100 years have passed since the use of refrigerant mixtures was first proposed, the full potential of nonazeotropic mixtures in refrigeration systems is still relatively unexplored. Opportunities for identification and development of appropriate mixtures and associated cycles exist, and more intensive research and development are needed and believed justified to evaluate their ultimate potential.
- o This workshop provided a useful forum for examination of nonazeotropic mixture refrigerant status. Moreover, this meeting afforded international leaders in this field an opportunity to meet and establish a basis for further communication and cooperation.
- o To date, test results with mixtures have shown only modest improvements over single component refrigerants. It is felt that this has been due to inadequate design changes to the hardware systems to fully capitalize on mixture attributes.
- o Commercialization of mixtures introduces a number of complexities in all stages of industry practice--from equipment design to field services--presenting additional cost elements beyond those directly attributable to the refrigerants themselves.

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APPENDIX

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