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The History of NIST's Refrigerants Program: I. Zeotropic Mixture Cycles and Heat Transfer

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ABSTRACT

The refrigerants program at the National Institute of Standards and Technology (NIST) was initiated in 1981 by the Building and Fire Research Laboratory (BFRL), with the intent to determine if a zeotropic mixture, operating in a Lorenz cycle, could be found that would give superior performance to the traditional R-22 vapor compression cycle. From the very beginning it was necessary to establish a method for predicting both thermophysical properties of new refrigerants, as well as the properties of refrigerant mixtures, for incorporation into the existing NIST performance models. This thermophysical property data program eventually grew so large within the thermophysics division of NIST that it is described separately in part 2 of this paper. These models would then be used as the primary screening for promising mixtures. The heat pump facilities, both the breadboard apparatus and the production units, that were available from the energy conservation program of the 1970s, were adapted for counterflow heat exchange between the refrigerant and the secondary heat transfer fluid at the same time. In addition, the existing evaporative heat transfer rig was dedicated to mixture measurements. All of these projects were fully under way when the ozone crisis was officially announced in 1987 and when the NIST program goal was shifted to one of determining and evaluating alternatives to the CFCs that were in current use. Some of the more significant technical reports and journal papers are listed in this paper's references, as are the three database computer programs that were developed for public use.

INTRODUCTION

The refrigerants program of the National Institute of Standards and Technology (NIST)¹ began in 1981 as an outgrowth of the Building and Fire Research Laboratory (BFRL)²

thermal machinery group's research into methods of improving residential heat pump performance. For the previous five years, the group's main programmatic focus was on a U.S. Department of Energy (DOE) sponsored effort to develop performance test procedures for residential heating and cooling appliances. This work, in the form of draft standards documents, was completed, and the government/industry committee evaluations, used to fine-tune the work, were underway. It was therefore logical, with the group's newly developed expertise, that they initiate an in-house basic research program on residential equipment performance improvement, particularly because energy conservation was still a national priority. Heat pumps were selected from among all residential heating systems because their current production model performance was farthest from ideal, and they appeared to have the largest market growth. Coincidentally, at this time the relatively new industrial agency—The Electric Power Research Institute (EPRI)—was inviting proposals for advanced energy conservation concepts.

As group leader, I thought that an appropriate program would have to be both fundamental and practical—fundamental because it was in keeping with the laboratory's mission to lead the industry into new areas without competing with their own research organizations and practical because any success would have to be reasonably close to current system designs if the industry was to accept it. The idea of using refrigerant mixtures as a working fluid was not new. The original idea was conceived by Lorenz in 1894, and ever since Europeans had

1. Prior to 1988 NIST was known as the National Bureau of Standards (NBS).
2. Prior to 1988 BFRL was known as the Center for Building Technology.

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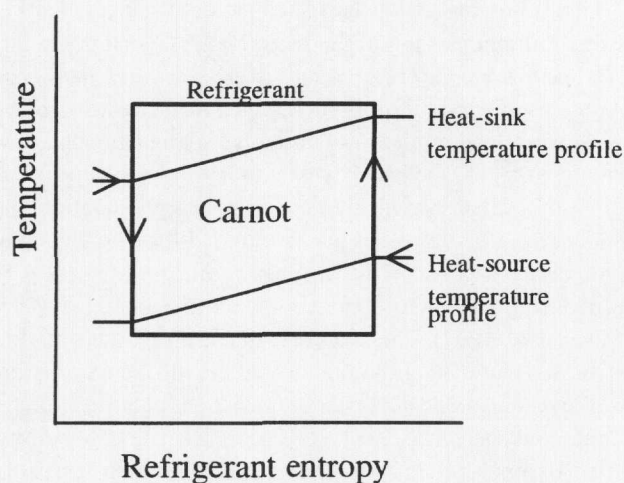


Figure 1a Carnot cycle.

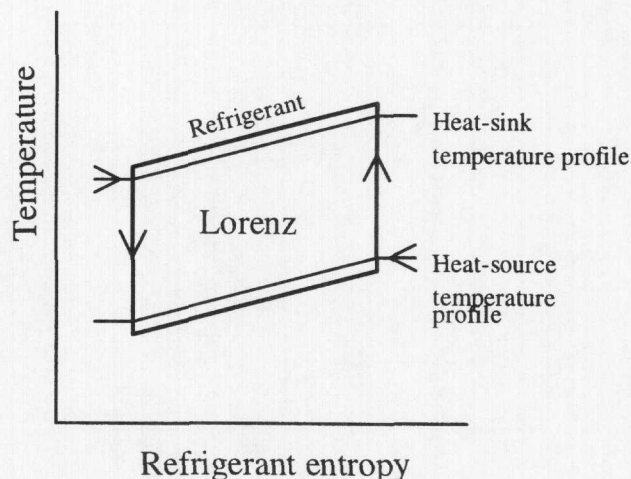


Figure 1b Lorenz cycle.

written about its theoretical advantages and performed an occasional experiment in one machine or another. Also at that time, General Electric was researching the use of mixtures in home refrigerators and DuPont was also exploring candidate zeotropic (a.k.a. nonazeotropic) mixtures with an appropriate temperature glide for use in air conditioners. However, there was no record of any systematic quantitative study as to the potential improvement that mixtures could have on refrigeration systems.

Figure 1 illustrates Lorenz's fundamental concept. Figure 1a represents the Carnot cycle, exchanging heat with external sensible fluids, where the areas between the temperature gradients are an approximate measure of the heat transfer irreversibilities. The approach temperatures (pinch-points) may be minimized by enlarging the heat exchanger; however, the average temperature differences are always greater than the minimum due to the differences in sensible and phase change fluid temperature gradients. Figure 1(b) represents the ideal Lorenz cycle, where the zeotropic refrigerant mixture's temperature glide matches the respective sensible fluids' gradients, and all the heat is transferred through a minimal temperature difference. The trade-off for this reduced thermodynamic irreversibility is a larger heat exchanger surface area. This is due to the heat being transferred through a smaller temperature difference. However, zeotropic mixtures were known to have smaller two-phase convection coefficients, which increased the temperature differences. Nevertheless, considering the stress on energy conservation at that time, these trade-offs seemed worthy of investigation.

Even at the proposal writing stage, it was obvious that the success of such a program would depend strongly on our knowledge of the thermodynamic properties of possible mixtures. For this reason, a physical chemist, Graham Morrison, from NIST's Thermophysics Division, was asked to join the program for the purpose of selecting an appropriate equation-of-state that could be used in the modification of the

group's vapor-compression cycle model. This model had been under development by Piotr Domanski for the DOE efficiency labeling program. The fact that this model was based on first principles as opposed to the industrial type, which is usually an empirically based component performance model, made it amendable to such a radical conversion. It was also obvious that a parallel study would have to be conducted into the heat transfer coefficient degradation that mixtures were known to have. This was because the possibility existed that the theoretical thermodynamic benefits that the Lorenz cycle would be offset by the poorer two-phase flow heat transfer of a zeotropic mixture.

The EPRI proposal constituted the initiation of the NIST refrigeration program. It stated that based on the NIST expertise in heat pump evaluation and thermodynamic equations-of-state, along with its laboratory facilities supporting both, we would begin to investigate the potential of the Lorenz concept for improving heat pump performance. It also stated that NIST would share equally in the funding of the effort. It is important to realize that NIST's impartiality toward this, or any project, allowed the approach to be one of determining the truth about the benefits of the Lorenz cycle. This meant that while outside sponsorship may have wanted to see benefits if continued funding was to be assured, the NIST definition of success had to do with the identification and quantification of the concept's trade-offs. The best way to achieve the NIST goal was take the most fundamental approach possible; that is, to attribute causes of system performance differences back to fluid and/or cycle properties wherever possible.

THE LORENZ CYCLE INVESTIGATION

Selecting a zeotropic mixture whose temperature glide (i.e., the difference between its dew and bubble points) can match the sensible fluid temperature gradient is the very essence of the merits of the Lorenz cycle's performance.

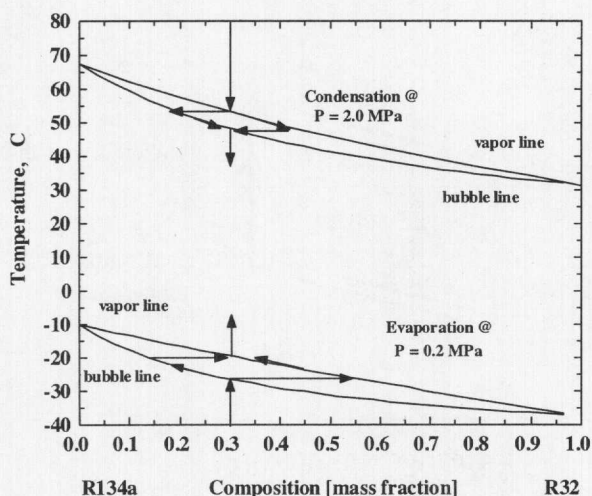


Figure 2 Phase diagram of a zeotropic mixture.

Figure 2 illustrates a typical zeotropic mixture phase diagram, which indicates a binary mixture's glide that might be ideally matched to the sensible fluids' gradient through as much of the heat exchanger as possible, as indicated in Figure 1(b). However, this concept has its hardware ramifications. In order to determine the maximum system performance benefits, it was necessary to construct heat exchangers that were grossly oversized and purely counterflow. These requirements virtually eliminate the possibility of using any single-phase gas (including air) as the secondary fluid in a practical system because of the excessive pressure drop it would have in a counterflow heat exchanger. In addition, the nature of binary zeotropes is such that the glide in the low-pressure evaporator is always greater than in the high-pressure condenser. The normal saturation pressure drop associated with any two-phase fluid in the direction of flow results in a superimposition of another (saturation) temperature gradient within the refrigerant flow. This saturation pressure/temperature gradient tends to decrease the mixture temperature glide in the evaporator and increase it in the condenser. It is quite difficult then to match both the sensible fluid gradients, so achieving an optimum performance rating of a given Lorenz cycle unit requires a compromise between the two heat exchangers' ideal temperature gradient matches. This usually means an average that favors the evaporator match since it is the evaporator performance that is most influential on the overall system performance.

This experimental work was done in the first of several newly constructed vapor compression rigs called breadboard heat pumps because the four thermally important components (i.e., evaporator, compressor, condenser, expansion device) were spread out so that instrumentation accuracy was not compromised. For example, an open compressor with a dynamometer imposed between it and the motor was used to ensure the mechanical work input was directly measured, rather than

hermetic compressor data corrected motor efficiency. Tests of different mixtures soon began to demonstrate that the binary zeotropes' temperature gradients were typically nonlinear. About this time, Mark McLinden, a chemical engineer, joined the group. He provided a quantitative explanation that the enthalpy of phase change was a function of composition, which of course was changing during the evaporation and condensation processes. It was also noted that the degree of nonlinearity was somewhat a function of the differences in normal boiling points of the components (Domanski 1995; Mulroy et al. 1994). The practical ramification of this nonlinearity was that a pinch-point between the refrigerant mixture and the secondary heat transfer of fluid in either the evaporator or the condenser was likely to occur. Heat transfer downstream of pinch points is insignificant. A solution to this problem was determined to be the employment of a third component whose normal boiling point was between the other two. However, our evaporative heat transfer work showed that zeotropic binary mixture's degradation was increased by the addition of a third component (see Figure 6 where R407C is a ternary composed of HCFC-32/125/134a). Thus, the benefit of linearizing zeotropic temperature gradients was somewhat mitigated by further reduction in the two-phase convection coefficient value.

In parallel with the above thermodynamic work, a two-phase heat transfer laboratory was created and developed for the specific purpose of explaining and quantifying the degradation of the zeotrope's heat transfer coefficient relative to the weighted average of the components' coefficients. Theory explained the qualitative process to be the occurrence of a lack of the higher pressure component at the two phase interface, whether it be at a nucleate bubble or the liquid-vapor boundary of annular flow. Thus, the heat transfer process is slowed by the superposition of a mass transfer process of the more volatile fluid through the less volatile fluid in order to change phase. Needs of the chemical process industry had brought about considerable data for hydrocarbons et al., but there was very little measured data for refrigerants. The work carried out by two sequential doctorate students (Ross et al. 1987; Jung et al. 1989) showed that the magnitude of the degradation could reach as much as 40% below the components' mass weighted average. This work also postulated that annular flow had a circumferential composition gradient as well as radial one. This was proven by a series of careful composition measurements of samples withdrawn from the annular flow's liquid layer, which is typically only 0.005 inch (0.13 mm) thick. Although the number of different mixtures measured was limited, it was concluded that the magnitude of the degradation may be a function of the difference in molecular size of the components (Morrison 1990). This evaporative flow work was taken over by a new full-time addition to the group, Mark Kedzierski, at about the time the entire program was to change its objective due to the advent of the ozone crisis. One of his first assignments was to review the past two-phase flow work

we had been doing and make qualitative conclusions (Kedzierski et al. 1992).

Early in the thermal machinery group's program, a third laboratory path was initiated. Zeotropic mixture drop-in tests were conducted in several commercial heat pumps. It was realized that it was unlikely that the full performance benefits could be seen in a unit, since the Lorenz cycle's smaller average temperature difference between the refrigerant and the secondary heat transfer fluid necessarily requires a larger heat exchanger surface. So the indoor coil was replaced with one that had several banks of coils to approximate a cross-counterflow condition between the zeotropic phase change glide and that of the moist airstream. The wide temperature glide of the original composition caused the coil temperature to drop below the airstream dew point and thus resulted in considerably more dehumidification than usual. However, the overall performance never came up to the original unit. In general, the cross-counterflow finned-tube heat exchanger, as the indoor coil, defeated the ability of the Lorenz cycle concept from exceeding the performance of the R-22 machine. This work did provide some practical estimates of component sizes that may be needed, particularly for cooling and dehumidification purposes.

Included in this phase of the program was an investigation to explore the possibility of improving performance through the use of multistage distillation (Rothfleisch 1995). An accumulator was modified to act as a distillation tower with a sump heater, to determine the degree of composition shift that is possible with a minimum of hardware changes. In general, with the R-32/134a mixture (30/70% mass fraction), it was possible to obtain a (06/94% mass fraction) composition with a subsequent decrease in capacity and an increase in efficiency that shifting toward the lower pressure component will bring. This implies that the heat pump could be operated on the higher pressure, higher volumetric capacity composition in the winter and the lower pressure, higher efficiency composition in the summer. This work was significant in that the additional hardware required for a heat pump that was already equipped with an accumulator was no bigger than the size of a man's fist. This demonstration proved the cost-effectiveness of developing a heat pump that could essentially operate on one composition in the cooling mode and a significantly different one in the heating mode.

In 1987, I postulated that zeotropic mixtures might be successful where the secondary heat transfer fluid was liquid, and true counterflow heat exchangers could be used without excessive pressure drop. Performance close to R-22 machines could be reached but probably not exceeded enough to cause manufacturers to take an interest (Didion 1987). However, once the existence of R-22 (an HCFC) was threatened due to the ozone crisis, this latter concept became a possibility. Finally in the mid-1990s, a complex laboratory system of heat pumps and secondary water loops was constructed, and tests on a variety of mixtures deemed as the best performers through simulation model studies were conducted (Payne et

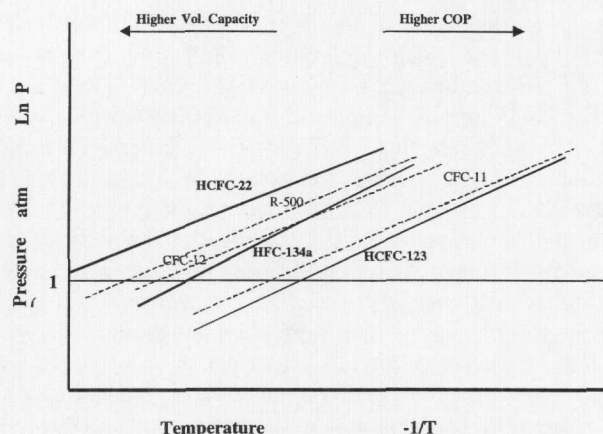


Figure 3 Vapor pressures of CFCs and their alternatives.

al. 1998). The motivation for this effort was not only the EPA schedule for the elimination of all HCFCs, including R-22, which was the primary working fluid for residential equipment, but also the growing threat of the elimination of many of the HFCs due to the global warming issue. The elimination of the HFCs would reduce the list of possible alternatives so much that once again flammable fluids would have to be considered. Although the 50/50% mass fraction composition of R-32/290 was determined to be the best performer, it only overcame about one-half of the performance deficit due to the additional heat exchangers for the secondary waterloops. It is, however, difficult to be certain about the potential of this concept based solely on tests of different fluids in the same apparatus. This is because optimum component sizing is unique for each fluid. Performance is influenced by the proper hardware size for the working fluid; thus, one of the fluids is necessarily operating in a wrongly sized system. Our later simulation study indicated that the practical benefits of the Lorenz cycle in comfort cooling and heating applications are limited because it cannot be effectively realized where the air-to-refrigerant heat exchangers are largely cross-flow (Marques and Domanski 1998).

THE ALTERNATIVE REFRIGERANTS PROGRAM

Not since the 1930s, when the halogens were introduced to the industry as a stable, safe (i.e., nonflammable and nontoxic), and efficient family of refrigerants, had such a widespread change in the industry's working fluids been proposed. This resulted from the acknowledgement that chlorine was degrading the earth's ozone layer. Very little was known about chlorine-free refrigerants because the CFCs were the most stable and the best performers. By the time that the ozone/refrigerant issue became public knowledge, the industry had already identified alternatives that had similar vapor pressures as the two most important CFCs—R-12 and R-11. Figure 3 illustrates the vapor pressure lines of R-134a (an HFC), which is an alternative for CFCs 500 and 12, and of

R-123 (an HCFC), which is the alternative for R-11. For each line, the uppermost point is the approximate critical point (CP) and the point at which the saturation line crosses the atmospheric pressure line is the approximate normal boiling point (NBP). Note there is an inherent trade-off between capacity and COP when selecting a refrigerant for a given application (Didion 1999a). Therefore, comparing HFC-134a to HCFC-123 results in a poorer COP. Comparing it to HCFC-22 (i.e., using an R-134a system for R-22 applications) will result in a lower volumetric capacity (i.e., the need for larger equipment) but higher efficiency. By 1987, NIST researchers were in a truly unique position in their refrigerant knowledge and database of how fluid properties affect the basic cycle performance. Realizing the need for the industry's engineers to understand the fundamentals of using different refrigerants, McLinden and Didion wrote a seminal paper discussing the halogen family refrigerants (1987). This paper also established NIST as an authority on the subject and paved the way for a decade of funding from a variety of government and industry organizations—"timing is everything." While it was true that we did not anticipate the ozone crisis when we began the refrigerant research program six years prior, the advantage of having the knowledge and experience in a field, before the multitude of research laboratories that ultimately became involved, cannot be overemphasized.

ASHRAE immediately recognized the impact of this ozone/refrigerants issue and offered to play an important central role, as did ARI, for interindustry communication. A series of special conferences were held with NIST and the Herrick Labs of Purdue University, in alternate years. The first was at NIST where the Building Environment Division hosted an invited speakers conference of 13 papers on the alternative refrigerants. It was titled "CFCS: Today's Options—Tomorrow's Solutions". It was subtitled "ASHRAE's 1989 CFC Technology Conference," indicating how intimately CFCs were intertwined with the very concept of a refrigerant. The second ASHRAE/NIST refrigerants conference in 1993 was "R-22/R-502 Alternatives." This subject was in response to the 1992 revisions to the Montreal Protocol, which called for the eventual phaseout of all HCFCs. The 1997 conference was entitled "Refrigerants for the 21st Century," and over half of the 16 invited papers were on natural refrigerants—ammonia, carbon dioxide, air, water, and hydrocarbons.

One of our most significant accomplishments during this phase of the program was that of Piotr Domanski's continuing modifications to the computer simulation model (CYCLE-11) to handle the ever-changing database that NIST's Thermophysics Division was developing in the form of what is now called REFPROP (Domanski and McLinden 1992). As these developments occurred, the model was given, unofficially, to selected industries. This enabled us to have a better understanding of their needs while not having the huge burden of support documentation and making it user-friendly in a Windows format. However, due to public request, a simplified version was developed in a Windows format and issued for sale through NIST's Standard Reference Database 49, CYCLE-D: NIST Vapor Compression Cycle Design Program (1995). This program enables the user to compare fundamen-

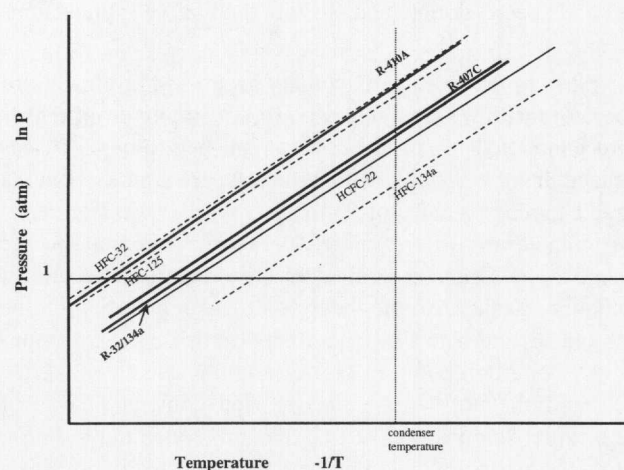


Figure 4 HCFC-22 alternatives and their components.

tal cycle performances among virtually any working fluid—single component or mixture—that is contained within REFPROP. It is limited, relative to CYCLE-11, in that it does not consider heat transfer to a secondary fluid in the evaporator and condenser. On the other hand, further developments to CYCLE-11 allowed simulations with counterflow, cross-flow, and parallel-flow heat exchangers, with consideration of the refrigerant circuitry design and its impact on pressure drop and heat transfer coefficient. Independent of this model, a standalone evaporator simulation model was developed to determine the heat transfer effectiveness and pressure drop for a multi-bank finned-tube heat exchanger on a tube-by-tube basis. It enables the designer to find the optimum refrigerant flow path through the heat exchanger for virtually any airflow distribution, uniform or nonuniform (Domanski 1999).

Numerous computer studies were conducted and published using a wide variety of mixtures (Domanski and Didion 1985; 1992, 1993, 1994, 1995; Pannock et al. 1992; Kim et al. 1996). Several of these studies led to experimental evaluations (Mulroy et al. 1988; Pannock et al. 1992; Kim et al. 1993, 1994; Rothfleisch and Didion 1991, 1993). This unique theoretical/experimental capability gave BFRL the ability to attract industrial guest workers, as well as university faculty and graduate students, to join us for terms of one to three years, which provided a variety of talents to support our permanent staff. By 1990 it was clear that all HCFCs, including R-22, would be eliminated eventually. This was the most significant event of the entire program for two reasons. At that time R-22 was the working fluid for about 80% of the machines in the industry and no single component refrigerant or azeotrope could be found that had similar properties. This meant that for the first time in history the industry would have to learn to deal with zeotropes on a production level. As a result, the industry searched for and developed several mixtures from which two types of zeotropes have emerged: one with a vapor pressure similar to R-22 and one of considerably higher vapor pressure. Figure 4 illustrates the relative magnitude of these fluids. The similar vapor pressure mixture

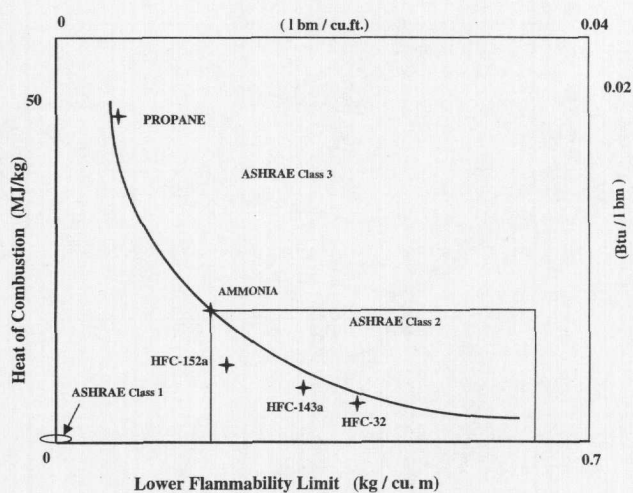


Figure 5 Flammability trends in refrigerants.

is the ternary zeotrope, designated as R-407C, whose composition is HFC-32/125/134a (23/25/52% mass fraction). It is intended as a "drop-in" for existing R-22 equipment or for new equipment where it may be competitive. In Figure 4, the alternative, which is of higher vapor pressure, is the binary near-azeotrope designated as R-410A, which is a composite of HFC-32/125 (50/50% mass fraction). Thermodynamically speaking, both are zeotropes (a.k.a., nonazeotropes), but the binary has a rather small maximum difference between the dew-point temperature and the bubble-point temperature and is thus distinguished by the jargon word "near-azeotrope" (that we at NIST invented for zeotropes whose composition shift under phase-change conditions is small). The refrigerant HFC-32 has unusually good thermal properties, and since HFC-410A has a relatively high percentage of it, the industry performance tests showed an efficiency similar to R-22, while allowing for a considerably smaller machine to provide the same capacity.

However, R-32 was one of the three flammable HFCs that was being introduced into different zeotropes. It was therefore necessary to mix nonflammable refrigerants with them such that the mixture was nonflammable under all feasible conditions. All of these developments were taking place at the same time ASHRAE was wrestling with how to determine flammability. Although there had been a longstanding test and rating methodology, the only flammable refrigerant in use was ammonia, so in a sense the methodology had never been taxed to this degree. The problem was that the test procedure, ASTM E681-85, was originally developed for hydrocarbons. With the new refrigerants being barely flammable (Figure 5), the ASTM test method was producing erratic results. ASHRAE SSPC34 had been formed to work on this issue. I followed Dr. McLinden to serve on this committee, and during the three years that these two zeotropes were being evaluated, I was chairman of the flammability subcommittee. During this period we set up a flammability test rig within BFRL and conducted tests on several mixtures so that we had a full under-

standing of the difficulties and weaknesses of the procedure. We added the innovation of recording the combustion process on videotape so that the flame spread of each test could be studied under slow-motion conditions and a permanent record attained. The procedure for zeotropic mixtures included a determination of the worst case (i.e., one with the highest percentage flammable component) composition that might occur in the field. A consensus of the committee decided that they could be met by a series of five slow leaks of 20% of the original quantity with subsequent recharges of the original composition. Establishing this composition experimentally turned out to be a procedure that took several days. Realizing REFPROP's ability to predict the composition of a mixture at any given thermodynamic state, I suggested that NIST develop a quasi-steady-state procedure to act as an alternative to the experimental procedure. The result was NIST Standard Reference Database 73 REFLEAK. This program can predict the composition change, for up to five recharge cycles, of any mixture that can be created in REFPROP, for either isothermal (slow) or adiabatic (fast) leaks (Kim and Didion 1995a; Didion 1995b; and Kim 1999b).

TWO-PHASE REFRIGERANT HEAT TRANSFER

From its inception, the challenge of the two-phase alternative refrigerant heat transfer program was to produce quality experimental data and fundamental understanding that would be useful to the U. S. refrigeration and air-conditioning industry in its time of (ozone) crisis. The main focus of the program was to fundamentally characterize pure refrigerant and refrigerant/lubricant mixture heat transfer. This was done for both tube-side and shell-side condensation and evaporation. Occasionally, single-phase work was done to support an immediate industrial need (Kedzierski and Kim 1996). That is to say, the program had a definite course, but it remained flexible enough to meet the changing needs of the refrigeration and air-conditioning industry. The research approach was derived from the philosophy of the thermal machinery group—make the research useful to as many companies as possible by keeping it fundamental and timely. The group also kept true to the NBS/NIST mission of being a premier measurement facility by working closely with other laboratories within NBS/NIST. For instance, the Statistical Engineering Division was consulted during both the experimental design stage and the data analysis stage to reduce the measurement uncertainties. Other laboratories, including physics, materials science and engineering, and manufacturing engineering, were essential to the success of the new and innovative aspects of the program.

One of the immediate needs of industry was the characterization of the performance of existing tube-side and shell-side passive heat transfer enhancements with the new refrigerants. Dr. Kedzierski, soon after his arrival, began simultaneous construction on a pool boiling and on a convective boiling/condensation rig to meet these needs. These were both significant undertakings due to the unique rig designs and consequently required several years to build. In the interim, an

existing quartz tube rig was modified and operated so that some experimental results could be made available to industry while construction was underway.

The test section of the quartz tube rig was a transparent tube fitted with thermocouples and a 3 mm wide heater strip along the bottom of the tube to measure the heat transfer coefficient. High-speed films, at 6000 frames per second, were taken of the low-quality refrigerant flowing in the tube with a 16 mm full-frame film camera. The films were projected on a large piece of trace paper to record the evolution of bubbles from the tube wall. Simultaneous heat transfer tests and films were made first with pure refrigerants to establish a baseline (Kedzierski 1990, 1993, 1994). We soon became quite familiar with the bubble parameters for pure refrigerants, which included diameter, volume, frequency, contact angle, and site density. This optical data gathering (i.e., bubble counting) was extremely tedious work but could be done carefully by undergraduate students with relatively little training. It provided employment to a long line of co-op students from the University of Maryland. (As soon as one went numb, he was replaced by another). Because of the familiarity with pure refrigerant observations, the films of refrigerant/lubricant mixtures surprised us. The refrigerant/lubricant boiling was dramatically different from the pure boiling. Rather than relatively large discrete bubbles characterized by pure refrigerants, the refrigerant/lubricant boiled in a misty cloud of micro bubbles. The lubricant caused the bubbles to be much smaller and more numerous than the pure refrigerant bubbles. The lubricant effect on bubble size, bubble frequency, and the site density were all quantified with the high-speed films.

The new convective rig differed from the previous electrically heated (constant heat flux) smooth tube rig; it was to have an isothermal wall. The new rig consisted of a 7 m micro-fin test tube section that was cooled by water flowing in an annulus that was formed by a concentric outer tube. One of the unique aspects of this rig was its ability to obtain local heat transfer data with fluid heating/cooling while maintaining low measurement uncertainties. Small measurement uncertainties were possible by careful calibration and placement of thermocouples and thermopiles and consideration and correction of measurement errors. One unlikely design feature that greatly assisted in the reduction of measurement uncertainties was the use of both counterflow and parallel flow measurements. The counterflow data had large uncertainties in the low quality region with low uncertainties in the high quality regions. The parallel flow data had the opposite/complementing characteristics. Measurements with low uncertainties were possible for all quality regions by combining the data from the two flow configurations. The data reduction also had the advantage of the latest beta version of REFROP, with the most up-to-date fluid properties of the new refrigerants. Fluid heating/cooling was done without interrupting the tube-side heat transfer by channeling the annulus water away from the test tube for water temperature measurements. The water-side temperature measurements were made with a "thermopile daisy" that was

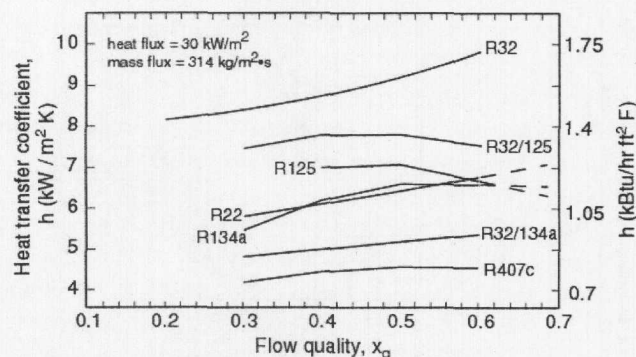


Figure 6 Measured evaporative heat transfer coefficients.

circumferentially fanned in the annulus (Kedzierski and Goncalves 1999). Wall temperature measurements permitted true local heat transfer measurements with fluid heating. The fluid heating aspect was important to industry because it matched the "true" heating boundary condition of the equipment.

Heat transfer measurements taken in the micro-tube convective boiling rig shown in Figure 6 illustrate the relative performance of the various refrigerants. The data are bracketed by the heat transfer performance of HCFC-32 and R-407C. The R-407C is a ternary mixture of HCFC-32, R-125, and R-134a that exhibits a lower heat transfer because it is a zeotropic mixture with degradations in heat transfer due to property effects and concentration gradients. The favorable transport properties of HCFC-32 (high liquid conductivity and low viscosity) are responsible for this refrigerant's performance. Because the HCFC-32/R-125 mixture (410A) is a near-azeotrope, it is a good replacement refrigerant having an approximately 20% larger heat transfer coefficient than R-22 (Kaul et al. 1996). Notice that the performance of the HCFC-32/R134a mixture is slightly better than that of R-407C. This difference is due to the greater mass fraction of HCFC-32 in the HCFC-32/R134a mixture (30% vs. 23%). In general, this group of mixtures experiences smaller concentration gradients with larger concentrations of HCFC-32 because HCFC-32 can easily diffuse through the less volatile components, which minimizes the concentration gradients, due to its relatively small molecular size. Larger concentrations of HCFC-32 also improve a mixture's heat transfer performance due to HCFC-32's favorable transport properties.

The uniqueness of the pool-boiling rig was that it was designed specifically to obtain measurements with low uncertainties with fluid heating (Kedzierski and Worthington 1993). Typically, shell side pool boiling heat transfer data are obtained via a Wilson plot technique (without wall temperature measurements) or via insertion of a cartridge heater in a tube with a single thermocouple to measure the wall temperature. The thermal machinery group's pool boiling rig had the advantage of fluid heating and 20 thermocouples to nonde-

structively measure the wall temperature and the heat flux. This was achieved by simplifying the test geometry by testing thick, flat plates rather than thin-walled, round tubes. Over the years, several important contributions were made with data from the pool-boiling rig. First, the performance of commercial tube surfaces was characterized with the new refrigerants R-123 and R-134a, with and without lubricants (Kedzierski 1995). Other studies were done to meet the needs of a chemical company that was interested in the performance-enhancing effects of additives for refrigerants (Kedzierski and Didion 1990, 2000). The quality of the data from the pool-boiling rig was such that it uncovered differences that were previously too small to be measured. For example, the rig had the unique capability of using either electric heating or fluid heating for the same test section independent of the data acquisition method. A comparison of several enhancements showed that the heat flux obtained by fluid heating can be as much as 30% greater than that obtained by electric heating (Kedzierski 1995). This casts a shadow on the use of electric heating as a valid test method for boiling. Another comparison study of two different types of boiling surfaces revealed a crossover in performance at low superheats. This data caused one company to change their tube specification for high-efficiency equipment that operated with low wall superheats. This was because the NIST study showed that a surface that had been shown to have less favorable performance at superheats above 4 K was shown to actually have a greater performance at superheats less than 2 K. High-speed films were also used to characterize the ebullition of various boiling enhancements. Data from the 16 mm films not only helped industry to redesign surfaces for the new refrigerants but also were indispensable in the understanding of the influence of lubricant on boiling.

It was clear that refrigerant/lubricant mixture heat transfer was an area where the industry needed design tools for evaporators. We parametrically investigated the influence of lubricant viscosity, miscibility, and composition with specially designed lubricant. A model was derived to predict the influence of each lubricant property on the heat transfer performance (Kedzierski 2001a). In general, it is possible to attain 100% enhancement relative to the pure refrigerant heat flux with a small quantity of high viscosity lubricant that is partially miscible in the refrigerant. The high viscosity increases the thickness of the thermal boundary layer, which in turn encourages an increase in bubble site density. Lubricant acts to reduce the bubble size but increase the site density. The amount of lubricant is proportional to these effects. Consequently, as more lubricant is added to a refrigerant, the bubble size becomes much too small for the effect of increased site density to cause an enhancement. The proximity of the bulk fluid temperature to the critical solution temperature (partial miscibility) may induce the formation of excess liquid films or drops that draw superheated liquid onto the bubble sides.

It is the thermal machinery group's view that the lubricant effect is governed by a layer of lubricant that accumulates on

the heat transfer surface. In an effort to build a better predictive model for refrigerant/lubricant interaction, we have recently developed a fluorescence measurement technique to measure the lubricant excess layer on the wall (Kedzierski 2001b, 1998). The technique has been used for what is believed to be the first measurements of a nonadiabatic excess layer on a boiling surface. The excess lubricant layer has been substantiated. This will greatly aid in the development of a better understanding of refrigerant/lubricant boiling.

SUMMARY

As part of the U.S. Department of Commerce, NIST programs should be supportive to the needs of American industry, particularly in the areas of technical data and measurement problems. Its research programs should complement—not compete—with parallel industry research, and they should, whenever possible, stem from a somewhat unique expertise. The refrigerants program met these criteria because we had a six-year head start with the exploratory heat pump performance studies. The importance of taking a fundamental approach (i.e., relating system performance to refrigerant properties) cannot be overemphasized. It provided us with the understanding of what trade-offs could be expected, based only on an alternative refrigerant's properties. It also gave us the flexibility to shift program goals and still utilize all our previous research.

As it turned out, no Lorenz cycle mixture could be found that would exceed the performance of the state-of-the-art R-22 vapor compression cycle, where cross-flow heat exchangers are used. However, other zeotropic mixture attributes that we explored remain undeveloped. An example is the addition of a simple distillation column that would allow for operation of a heat pump with high-efficiency composition in the summer and a high-capacity composition in the winter. Also, if the politics of the current global warming crisis dictate the elimination of HFCs, there exists a possibility that flammable zeotropic mixtures can come quite close to current performance, while safely isolating the flammable fluids to the outdoor system.

The directions in which product developments have progressed in response to the ozone problem—and will go in the future in response to the global warming issue—should be an industry decision. It is they, after all, who have to live with the consequences of product cost, safety, and performance. Thus, the role of NIST and other nonprofit research institutions is one of pure technical analysis—to objectively determine useful data and honestly report the inherent trade-offs that innovative system and component concepts present. All too often researchers report only the “good news” in hopes that their work will be put into practice. However, the more fundamental the approach, the more likely the results will be used, albeit not necessarily in the manner first intended. So it was with our early mixtures work. We were studying how to maximize the benefits of the zeotropic composition shift (Didion and Bivens 1990). When the refrigerant alternatives search

became necessary, it was our knowledge of how to minimize the impact of composition shift on system performance that was needed. As it turned out, when it became necessary for industry to replace the CFCs and HCFCs, they employed azeotropes, near-azeotropes, and even zeotropes for both new equipment and drop-in alternatives.

The NIST refrigerants program is by no means completed. At this time the thermodynamic performance of the so-called natural fluids are being studied in both simulation models and in laboratory systems (Brown and Domanski 2000). The impact of lubricant on refrigerant heat exchanger effectiveness is being measured by innovative techniques that provide data never before possible (Kedzierski 2000, 2001). The challenge offered by global warming is greater than that of ozone. This is because any refrigeration performance degradation is likely to do more indirect harm to the environment via the increased power plant emissions than will the refrigerant emissions. No evaluation of future alternatives can be complete without a thorough measurement and analysis of the alternative's in-situ field performance of a production hardware system.

This is a time when building fuel prices have doubled and are predicted to quadruple and when our most populated state is having "rolling blackouts" during its non-peak season. The current European trend to enact specification standards to ban HFCs as an environmentally harmful substance cannot lead to the optimum solution without consideration of the indirect power plant emissions. What the industry needs is more flexibility rather than less. NIST/BFRL has had a long tradition of advocating performance standards over specification standards. Now, with simultaneous energy and environmental crises facing our nation, innovative compromises have never been more important. The Total Environmental Warming Index (TEWI) is one such concept. Fundamental research in the thermal engineering field supporting such concepts is the likely path toward the best solution of our energy and environmental problems.

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DEDICATION

This paper is dedicated to Dr. Graham Morrison whose untimely death in 1993 left all the members of the refrigerants program with a deep personal and professional loss.

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