[J. Res. Natl. Inst. Stand. Technol. 103, 000 (1998)]

Conference Report

REFRIGERANTS FOR THE 21ST CENTURY ASHRAE/NIST REFRIGERANTS CONFERENCE Gaithersburg, MD October 6-7, 1997

Report prepared by

Piotr A. Domanski

Building Environment Division, Building and Fire Research Laboratory, National Institute of Standards and Technology, Gaithersburg, MD 20899-0001

Available online: http://www.nist.gov/jres

1. Introduction

The "Refrigerants for the 21st Century" conference was the third refrigerants conference jointly organized by the American Society of Heating, Refrigerating and Air-Conditioning Engineers (ASHRAE) and the National Institute of Standards and Technology. The conferences in 1989 and 1993 covered technical issues related to the implementation of ozone-safe refrigerants. With global warming beginning to replace ozone depletion as the world's most significant environmental problem, the 1997 conference was related to both ozone depletion and global warming. The goal of the con-

ference was to review available air-conditioning and refrigeration technologies to assess their suitability for the years to come in view of the two global environmental problems.

The 2-day conference consisted of 16 comprehensive presentations; each day ended with a panel discussion. Table 1 contains the titles and authors of the papers presented. The topics included contemporary and future fluorochemicals, "natural" fluids, including hydrocarbons, carbon dioxide, and air, and secondary loop systems using ammonia and other chemicals. One hundred ninety professionals attended the conference. The purpose of this report is to summarize much of the material presented. For more in-depth information refer to the conference proceedings available from ASHRAE (http://www.ASHRAE.org).

2. Environmental Concerns: Ozone Depletion and Global Warming

After their introduction in 1930, chlorofluorocarbons (CFCs) and hydrochlorofluorocarbons (HCFCs) became the preferred refrigerants for most applications because of their favorable attributes, including safety and high efficiency. However, their recent implication in the ozone depletion phenomena resulted in a phaseout. The phase-out schedule was first formulated by the Montreal Protocol in 1987 and was made more stringent during follow-up international meetings. Predominant alternatives to CFCs and HCFCs came from the hydrofluorocarbon (HFC) family. Although most HFCs have a lower Global Warming Potential (GWP) than the fluids they are supposed to replace, some countries do not consider HFCs as the final solution because concerns about global warming have intensified. This raises the question: which refrigerant should the industry use in the future?

Volume 103, Number 5, September-October 1998 Journal of Research of the National Institute of Standards and Technology

Table 1. Papers presented at the ASHRAE/NIST Refrigerants Conference and included in the conference proceedings

Author	Affiliation	Title
Daniel L. Albritton	NOAA-Boulder, CO	Ozone Depletion and Global Warming
James M. Calm David Didion	Engineering Consultant-Great Falls, VA NIST-Gaithersburg, MD	Trade-Offs in Refrigerant Selections: Past, Present, and Future
Charles E. Bullock	Carrier Corporation—Syracuse, NY	Theoretical Performance of Carbon Dioxide in Subcritical and Transcritical Cycles
Jostein Pettersen	SINTEF-Trondheim, Norway	Experimental Results of Carbon Dioxide in Compression Systems
Pierre Weiss Jacques Gouguet	ELF Atochem-Levallois, France	Current and Projected Use of Refrigerants in Europe
Horst H. Kruse Thomas Tiedemann	University of Hannover-Germany	Experience with HC Refrigerants and Projections for Future Applications
Fred J. Keller Hongmei Liang Moshen Farzad	Carrier Corporation-Syracuse, NY	Assessment of Propane as a Refrigerant in Residential Air-Conditioning and Heat Pump Applications
Lee W. Burgett Michael D. Byars Kenneth J. Schultz	The Trane Company – La Crosse, WI	Absorption Systems: The Future, More That a Niche?
Paul M. de Larminat	York International—Corquefou Cedex, France	New Developments to Expand the Use of Ammonia
Predrag S. Hmjak	University of Illinois at Urbana—Champaign, IL	The Benefits and Penalties Associated with the Use of Secondary Loops
George R. Giles Richard G. Hunt George F. Stevenson	Normalair Garrett LtdYeovil, U.K.	Air as a Refrigerant for the 21st Century
James G. Crawford	The Trane Company-Tyler, TX	Heat Pump Technology on the Horizon
Keshav S. Sanvordenker	Consultant-Ann Arbor, MI	Status of CFC and HCFC Alternatives
H. Michael Hughes	AlliedSignal, IncBuffalo, NY	Contemporary Fluorocarbons
Donald B. Bivens Barbara H. Minor	Du Pont de Nemours & CoWilmington, DE	Fluoroethers and Other Next-Generation Fluids
Mark O. McLinden Eric W. Lemmon Richard T. Jacobsen	NIST – Boulder, CO NIST – Boulder, CO University of Idaho, Moscow, ID	Thermodynamic Properties for the Alternative Refrigerants

Daniel L. Albritton provided a status report on the current scientific understanding of ozone depletion and global warming. He considers the global warming problem to be more difficult to solve. Albritton commented that future generations may look upon the solving of the ozone depletion issue as an apprentice-ship for dealing with global warming. He pointed out that these two geophysical phenomena are not independent of each other although they are treated on the international scene by two different regulatory agreements: the Framework Convention for Climate Change and the Montreal Protocol.

Albritton presented a few key points from the 1995 scientific assessment by the Intergovernmental Panel on Climate Change (IPCC). He stressed the importance of understanding which facts concerning the climate system we know well and which facts we state with less confidence. For example, the principles of a natural

greenhouse effect are very well understood and are not disputed. Basic physics demonstrates that CO₂ and other greenhouse gases trap part of the infrared radiation emitted at the surface and warm the earth's climate.

Convincing data show that greenhouse gases caused by human activities are increasing in the atmosphere and are trapping more heat. It seems reasonable to predict that continued emissions will cause global climate change. This change may be very significant, altering temperature and rainfall patterns and affecting vegetation and the well being of living species. The issues are too complex to predict confidently local variations of climate and detailed effects. The important conclusion coming from the IPCC report is that global-average earth temperatures have increased over the past century, and the balance of evidence suggests a discernible human influence. The human-induced climate change occurs slowly and will be difficult to reverse.

3. Trade-Offs in Refrigerant Selection

Predicting to what degree climate change issues may affect refrigerant choices in the future is difficult. Well documented research shows that there are no refrigerant candidates that would satisfy all selection criteria (Calm and Didion).

The list of desired refrigerant properties is extensive. In addition to having good thermodynamic properties, an ideal refrigerant should be nonflammable, nontoxic, stable inside the system, and unstable in the atmosphere with harmless decomposition products. Practical considerations call for low cost and full compatibility with system materials including lubricants and machining fluids. The environmental criteria include the impact of the refrigerant on the stratospheric ozone layer and climate.

An "ideal" refrigerant does not exist, and the probability of finding one in the future is close to zero. This statement is supported by molecular screening of all elements and the developed understanding on how chemical composition determines properties of compounds. The list of elements for refrigerants identified by Midgley in 1930 consisted of carbon, nitrogen, oxygen, hydrogen, fluorine, sulfur, chlorine, and bromine. The concerns about the ozone layer narrowed this list by removing chlorine and bromine, and extensive research during the last decade has not expanded the list at all.

Therefore, selecting refrigerants for the 21st century is not about choosing between several ideal refrigerants waiting for implementation or looking for a compound that will satisfy this void. It is about screening a limited pool of refrigerants, each of which has its own well-documented demerit. Hence, the refrigerant selection process requires a careful analysis during which all fluid's adverse effects have to be properly weighted.

A refrigerant's contribution to climate change has a direct and indirect component. The direct component is a result of a refrigerant being a greenhouse gas. When released to the atmosphere, it traps part of the infrared radiation. The measure of the direct effect for a given gas is its GWP. It is a ratio of its heat trapping capability to that of the reference gas, commonly carbon dioxide. The indirect component is related to the carbon dioxide released in the process of producing electricity needed for operating the refrigeration system. The fuel or fuel mix used to generate electricity, the conversion rate, and other system effects impact the indirect effect. A refrigerant influences the indirect effect through its thermodynamic efficiency. For most refrigeration and airconditioning applications, the indirect component has the dominant effect on the global warming.

4. HFC and Other Carbon-Based Refrigerants

HFCs have become the predominant zero ozone depleting potential (ODP) alternatives for CFCs and HCFCs. The transition to HFCs has not occurred without difficulties, mainly because of lubricant compatibility problems. However, it still has been the most pragmatic move away from ozone-depleting fluids. When discussing the impact on earth's climate, the proponents of HFCs stress the importance of the system efficiency and the indirect effect on global warming. Because the direct effect is a result of the refrigerant's presence in the atmosphere, the key to environmentally acceptable use is to have minimal refrigerant escape from the system. If HFCs are contained in a system and their emissions are minimal, their direct contribution to climate change will be minimal as well (Sanvordenker).

Because other types of zero ODP refrigerants could be more preferable than HFCs, several organizations have investigated fluorinated ethers, alcohols, amines, and silicon and sulfur compounds. The evaluation criteria included thermodynamic performance, toxicity, flammability, stability, atmospheric lifetime, manufacturing feasibility, and cost. In most cases, the substances under consideration were large, more complex molecules requiring multi-step synthesis routes. For example, c-234fEbg and c-234fEab were the most promising substitutes for R-11 and R123. The thermodynamic performance of the majority of investigated fluids was worse than that of HFCs. Only 6 of 30 examined fluids had predicted performance within 5 % of the HFC they targeted to replace. None appeared to have a balance of refrigerant attributes to challenge HFCs in vapor compression equipment (Bivens and Minor).

5. Alternatives to HFCs Technology

More than half of the conference program was dedicated to other technologies than HFCs. Admittedly, none of these options are completely new. They are either widely applied in certain applications (e.g., ammonia or absorption) or they have been known since the pre-CFC times, i.e., before 1930, like carbon dioxide or hydrocarbons, and were discarded because of low efficiency or safety concerns. All concepts discussed in this category use refrigerants having a lower GWP than HFCs.

Ammonia has been used for over 100 years. It is a low-cost refrigerant with excellent thermodynamic properties and a zero GWP; however, it is toxic and flammable. Because of these properties and a strong odor, ammonia did not gain acceptance in direct cooling and is practically limited to applications in water and liquid chillers. The low cost of ammonia has been a strong factor for selecting it for large systems where refrigerant charge may be hundreds or thousands of kilograms. Such systems are typically used in food processing and industrial applications. Recent environmental concerns have promoted the use of ammonia in smaller capacity systems; however, ammonia's lack of compatibility with copper makes it a less attractive option for small machines.

Absorption is another well-established and centuryold technology. It has a long history of using environmentally safe refrigerants such as ammonia and water. In the United States, absorption systems are used mostly in large capacity applications. Availability of free waste heat or low gas rates favor the selection of an absorption system. In a free market with economics being the governing selection factor, absorption loses to electric-drive vapor compression. It appears that climate change concerns will not favor absorption systems because they tend to have a lower efficiency and higher indirect impact on climate change than their electric-drive competitor (Burgett et al.)

Propane was used as a refrigerant in the pre-CFCs era. Considering that a majority of the early refrigerants were either flammable, toxic, or both, propane's flammability was not so much a differentiating feature as it is now. The disappearance of propane-charged systems from the market was due to personal safety concerns. Current offerings of hydrocarbon-charged systems may be considered as a compromise between personal safety and environmental safety. Hydrocarbon proponents insist that the explosive behavior of propane and isobutane can be managed with reasonable precautionary efforts.

Hydrocarbons were re-introduced in refrigerators in Germany in 1993. Today, hydrocarbon-charged systems have almost 100 % market share of German refrigerator/freezer production (Kruse and Tiedemann). This success is not uniform in all of Europe; the marketing is mainly limited to Northern and Central European countries. Small systems using hydrocarbons have the potential of becoming more common; however, larger systems with larger refrigerant charges may have difficulties in gaining market acceptance because of the inherent risk of flammable fluids.

The short atmospheric live times of hydrocarbons make their GWPs close to zero, and their excellent thermophysical properties assure efficiencies that are comparable to those of HFCs. Because design changes necessary to mitigate safety risks associated with the use of flammable refrigerants add cost to the hydrocarbon-charged system, it is appropriate to consider the

possible efficiency improvement achieved when the same additional cost is applied to production of an HFC system. Consequently, both systems will have the same price tag and can be evaluated as to their direct and indirect impacts on climate change. A study presented at the conference (Keller et. al) showed that an example R410A split system redesigned to have the same cost as the propane system had a lower impact on climate change. The analysis for a window air-conditioner showed a propane system to be marginally better that the R410A system per unit of investment.

Carbon dioxide has several attractive properties and was also used before the advent of CFCs. Two CO2 handicaps, high pressure and low cycle efficiency, caused its demise when CFCs and HCFCs were introduced. These CO₂ handicaps still remain challenges today when application of CO₂ is revisited. Because of the low critical temperature, CO₂ operates in a transcritical cycle with supercritical gas cooling instead of gas condensing of the conventional vapor-compression cycle. An improvement in cycle efficiency can be achieved by matching the large temperature glide of the supercritical CO2 with the glide of the heat-transfer fluid. Cycle efficiency of carbon dioxide can also be considerably improved by reducing throttling losses through the use of an efficient expander (Bullock). Other features of carbon dioxide (e.g. compressor pressure ratio, heat transfer coefficient, and saturation temperature versus pressure relationship) are favorable for its application as a refrigerant and explain the intensive CO2 research effort undertaken in recent years in several countries (Pettersen).

Air deserves the name of a "natural refrigerant" more than any fluid. Air-cycle refrigeration, originally a 19th century invention, is most widely used in aerospace applications. Because of its low critical point, air does not undergo a phase change and remains as a gas throughout the refrigeration process for air-conditioning applications. In general, this results in higher energy use compared to a vapor compression cycle. Efficiency improvements may come from improved compressor design through the use of computational fluid dynamics in the design process (Giles et al.).

The trend to limit refrigerant emissions promotes the application of indirect refrigeration and air-conditioning using secondary loops. In such systems, the heat-transfer fluid is used to exchange heat between the air-conditioned/refrigerated space and the machine realizing the thermodynamic cycle. Some of the requirements for heat-transfer fluids are the same as for refrigerants. Heat-transfer fluids should be nontoxic, nonflammable, environmentally friendly, stable, and compatible with common engineering materials. High thermal conductivity, high specific heat, and low viscosity are the desired transport properties (Hrnjak).

The advantage of secondary loops is so significant for commercial large buildings that they are already predominantly used in such installations. Currently, supermarkets are drawing attention as a potentially new area for application of secondary loops. Secondary loops may pave the way to increased use of ammonia and hydrocarbons because secondary loop systems assure that the refrigerant will not be leaked to the conditioned/refrigerated area.

6. Concluding Comments

The conference provided a forum for presenting diverse views on possible responses to the ozone depletion and global warming problems. A consensus opinion was not developed, nor was one expected. The task of selecting "the best" refrigerant for the 21st century will be difficult because the merits of different refrigerants result from a complex combination of several attributes; the most important being ozone depletion potential, system efficiency, direct global warming, safety, and cost. Because these attributes may carry different weights in different application and countries, the merits of the considered refrigerants are viewed with a corresponding lack of uniformity. If refrigerant selection for the future is not affected by regulatory measures, it is safe to predict that HFCs will continue to be dominant for decades to come because of their high efficiency, personal safety, and the current strong position in the market. It is also certain that the search for new and the refinement of mature technologies will continue in an effort to produce environmentally friendly solutions for the years to come.