ASHRAE Position Document on

Natural Refrigerants

Approved by ASHRAE Board of Directors
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American Society of Heating, Refrigerating and Air-Conditioning Engineers, Inc.

1791 Tullie Circle, NE • Atlanta, Georgia 30329-2305
404-636-8400 • fax: 404-321-5478 • www.ashrae.org

COMMITTEE ROSTER

The ASHRAE Position Document on Natural Refrigerants was developed by the Society's Natural Refrigerants Position Document Committee. Their current affiliations are listed below.

Zahid Ayub, Chair
Isotherm Inc.
Arlington, TX

Donald A. Siller
Electro Motion Refrigeration
O Fallon, MO

Cynthia Gage
United States Environmental Protection Agency
Research Triangle Park, NC

Doug Reindl
University of Wisconsin
Madison, WI

Norbert Mueller
Michigan State University
East Lansing, MI

Julian DeBullet
McQuay International
Front Royal, VA

Andrew Pearson
Star Refrigeration
Glasgow, United Kingdom

Risto Ciconkov
Skopje University
Skopje, Macedonia

Executive Summary:

Driven by international agreements such as the Montreal and Kyoto protocols (UNEP 1999 and United Nations 1998) as well as a desire for a higher degree of sustainability, there is a renewed interest in increasing the application of natural refrigerants. The class of refrigerants commonly referred to as “natural refrigerants” offers the potential to improve the environmental performance of refrigeration systems. Because of its alignment with sustainability initiatives, ASHRAE supports research, assessment, and strategic growth in the use of natural refrigerants such as ammonia, carbon dioxide, hydrocarbons, air and water in refrigeration systems and technologies.

Taking a leadership role means ASHRAE and its members will continue to extend the scope of refrigeration and air conditioning technology by conducting research, disseminating knowledge, developing standards and guidelines, and promoting the responsible use of sustainable refrigerants. Several technical committees within ASHRAE are committed to achieve this goal. Limited research has been undertaken within a few ASHRAE technical committees during the past decade with most efforts focused on ammonia and carbon dioxide.

In light of the current global scenario, ASHRAE’s response to the demand for environmental sustainability is to promote the development of systems which use natural refrigerants safely, economically and efficiently.

1.0 Issues

Refrigerants play a vital role in society by their use in systems to preserve food and produce ice, to condition space for human welfare and controlled environments, and to support industrial processes. As world economies grow the application of refrigeration and air conditioning systems also grows, which leads to a proliferation in refrigerant production by virtue of the “banked” refrigerant existing in deployed equipment and a greater quantity of refrigerant needed for servicing and maintenance. Both of these factors result in a greater potential for refrigerant emissions to the environment with the potential adverse impacts. At the same time as the need for refrigerants is growing, the world’s societies are becoming more concerned about the environmental consequences of the refrigerants being used and the systems which use them. Through the Montreal Protocol, the world developed an unprecedented response for the environmental problem of stratospheric ozone depletion by phasing out the manufacture and the eventual use of ozone depleting refrigerants. The primary substitutes for these refrigerants are hydrofluorocarbons (HFCs) but they are greenhouse gases which have been implicated in global climate change. Consequently, options for the reduction of greenhouse gas emissions are now under investigation.

In the search for alternatives which have low Global Warming Potential (GWP) and reduced likelihood of other environmental impacts, natural refrigerants are gaining increased interest. Natural refrigerants are substances that can be found naturally occurring in the environment. Natural refrigerants include ammonia, carbon dioxide, hydrocarbons, water, and air. Some of the natural refrigerants have been used in the market place for many decades although at varying degrees of application. Although environmentally superior, natural refrigerants are not free of other concerns, such as corrosion, toxicity, high pressures, flammability, or in some cases lower operating efficiencies.

Selection of the correct refrigerant for an application requires careful review of such criteria as capital cost, operating cost (including energy and maintenance), equipment size and location, operating temperatures/pressures, facility staff capability and local, national, and international regulations.

The American Society of Heating, Refrigerating, and Air-conditioning Engineers (ASHRAE) is an international leader in the field of refrigeration and air conditioning. Through its mission to advance the arts and sciences of heating, ventilating, air conditioning and refrigerating to serve humanity and promote a sustainable world, ASHRAE and its members are uniquely qualified to contribute to the correct advancement of natural refrigerants.

2.0 Background:

Natural refrigerants include a range of organic and inorganic compounds suitable for use in a variety of refrigeration and air conditioning system applications and presenting a variety of issues and challenges. Thus the successful application of these refrigerants will vary depending on the compound. A useful definition is "Natural refrigerants occur in nature's biological and chemical cycles without human intervention. These materials include ammonia, carbon dioxide, natural hydrocarbons, water and air."

The advantages of natural refrigerants have led to a significant increase in their use in recent years in applications traditionally served by fluorocarbons. For ammonia and hydrocarbons, a major goal of current development is to decrease the refrigerant charge in refrigerating systems in order to address safety concerns. Through careful design, it is often possible to reduce the required quantity of refrigerants in systems by the application of design techniques such as plate heat exchangers and dry expansion evaporators – both of which are already common in a number of applications.

Another way to decrease the refrigerant charge is the use of indirect refrigeration systems with secondary coolants. In these systems the refrigerant is limited to the machine room, and the secondary coolants circulate in the occupied spaces. In addition to traditional secondary coolants, such as glycols and salt brines, new coolants appeared on the market, and particularly beneficial results have been reported with CO_2 as a secondary coolant. These alternatives tradeoff environmental benefits of reduced refrigerant charge with lower system operating efficiency due to the presence of a secondary working fluid.

Another common issue for several of the natural refrigerants is the need to advance the development of system components which can cost effectively achieve desired energy and performance efficiencies.

2.1 Ammonia – R-717

Ammonia is the most important of the natural refrigerants because of its longstanding and widespread use in food and beverage processing and preservation, and because of its growing adoption in HVAC chillers, thermal storage systems, process cooling and air conditioning, district cooling systems, supermarkets, and convenience stores. Since the middle of the nineteenth century there have been many changes in types of refrigerants, but ammonia is unique because it has seen continued use over this 150 year period.

Ammonia has Ozone Depletion Potential (ODP) and GWP equal to zero. It has inherently high refrigeration system energy performance, excellent thermodynamic properties, and high heat transfer coefficients. In a vapor state it is lighter than air. It is easily detected by smell, or by a variety of electrochemical and electronic sensors, and is readily available at a relatively low price. Less than 2 % of all ammonia commercially produced in the world is used as a refrigerant; however, ammonia enjoys low cost due to the large volume of production for use as a fertilizer.

The primary disadvantage of ammonia is its toxic effect at higher concentrations (i.e. = above 300 ppm); however, this risk is somewhat mitigated by its pungent smell alerting humans of its presence since even at lower concentrations (5 ppm) it is self-alarming in the event of a leak. Ammonia is classified in ASHRAE Standard 34 as having "lower flammability " in air when its concentration ranges between 16 % and 28 % (by weight); and it is not compatible with copper and copper alloys.

In some jurisdictions, ammonia refrigerating systems are subject to legal regulations and standards because of personnel safety considerations. These do not necessarily present additional barriers because legal regulations, proper maintenance and training of personnel are required for other refrigerants as well. Furthermore, the use of fluorocarbon refrigerants is discouraged in many countries with imposition of environmental legislation and taxes, and uncertainty concerning the Kyoto Protocol consideration. If the regulations and standards are applied in practice, and if suitable training for maintenance personnel is provided, then danger from ammonia use is no different from that of most other refrigerants.

Ammonia provides useful cooling across the range of temperatures, from air conditioning to low temperature applications. Some air conditioning systems with ammonia chillers have recently been installed in commercial and public buildings. These units are currently more expensive than fluorocarbon-based chillers, but the price difference is expected to reduce as production volumes increase. A semi-hermetic ammonia compressor is already on the market and will be applied in chillers and in factory-packaged refrigeration units which are used commonly in ice plants and smaller food processing and storage facilities. In order to reduce the potential for ammonia leakage, compact refrigerating units are built, fully sealed and tested in factories, and can be supplied with a charge of less than 50 kg of ammonia for 1000 kW cooling capacity. Lastly, in large industrial systems where there is a need for low temperatures (-30 to -50 ^{o}C) ammonia has been used in cascade refrigerating systems with CO_2.

Absorption chillers with ammonia/water mixture are suitable and cost effective for some specific applications, especially using a waste heat, in Combined Chilling, Heat and Power (CCHP) systems and district cooling.

2.2 Carbon dioxide – R-744

Like ammonia, carbon dioxide was also used in the mid- to late-nineteenth century, particularly on board ships and in shops and theatres where the smell of ammonia was not acceptable. However, as ammonia system safety and efficiency improved at the beginning of the twentieth century carbon dioxide systems became less common. With the introduction of fluorocarbons in the 1930s carbon dioxide fell out of use by the 1950s. The low toxicity, non-flammability, zero ozone depletion potential and low global warming potential have attracted the attention of system designers beginning in the early 1990s when alternatives to chlorofluorocarbons (CFCs) were being sought. Since then, carbon dioxide has found widespread acceptance in the full range of vapor-compression systems, from low temperature freezers to high temperature heat pumps. It has also been widely used as a secondary refrigerant, offering significant improvements in efficiency compared with traditional water, glycol or brine systems.

One major difference between carbon dioxide and other refrigerants is in its pressure/temperature characteristic because the pressures experienced are approximately ten times higher than those in ammonia or R-404A systems. This high pressure requires special equipment designs, but it also offers many advantages over other refrigerants. The high pressure results in high gas density, which allows a far greater refrigerating effect to be achieved from a given compressor. It also produces very small reductions in saturation temperature for a given pressure drop allowing higher mass flux in evaporators and suction pipes without efficiency penalties. This effect is particularly noticeable at low temperatures (-30 to -50 ^{o}C), which is why carbon dioxide systems perform so well under these conditions. Exceptionally good system performance has been noted in low temperature plate freezers and multi-chamber blast freezers where improvements in efficiency and reductions in freezing time have been reported.

When the pressure is raised above the critical point (7.3773 MPa) it is not possible to condense carbon dioxide. Under these conditions heat rejection is achieved by cooling the very dense gas which results in a temperature glide effect. This has been used to great advantage in water-heating heat pumps for a range of applications from domestic to industrial. These trans-critical heat pumps are particularly efficient when the incoming water is low temperature, for example from the cold water supply. They are less effective over a small temperature range, for example in central heating systems.

The unusual fluid properties of carbon dioxide, including its high density and low critical point, make it particularly well suited for cooling very dense heat loads, such as those found in Information Technology applications like blade servers and trader rooms. The optimal temperature for transferring heat to carbon dioxide is 14 ^{o}C, which happens to be exactly the evaporating temperature required for IT cooling in order to avoid dehumidification. In comparison the optimum temperature for R-134a is 77 ^{o}C, and at 14 ^{o}C the heat transfer capability of R-134a is only one-sixth of carbon dioxide.

Carbon dioxide is proposed as a good alternative for car air conditioning. The German Association of the Automotive Industry (VDA 2007) has confirmed the joint decision of the German car industry to choose carbon dioxide for the next-generation of mobile air conditioning by 2011.

Today there are many trans-critical carbon dioxide systems in supermarkets. For about 90 % of the year the Coefficient of Performance (COP) of systems with carbon dioxide is higher than in HFC systems. This is the reason that it is an attractive choice for beverage cabinets and vending machines.

The carbon dioxide used as a refrigerant is generally of industrial or scientific grade, and is typically recovered from the waste streams of industrial processes. The embedded energy required to reclaim, clean, liquefy and transport carbon dioxide is estimated to have a carbon equivalent of 1 kg CO_{2eq} per kg. In contrast the ammonia production process has a carbon equivalent of 2 kg CO_{2eq} per kg and for fluorocarbons this is typically about 9 kg CO_{2eq} per kg.

2.3 Hydrocarbons

In nature, hydrocarbon refrigerants are constituents of oil and natural gas. Hydrocarbon refrigerants have excellent environmental, thermodynamic, and thermo-physical properties, however they are highly flammable. As a result of these factors, hydrocarbons are the molecular basis for the halocarbon refrigerants wherein some or all of the hydrogen atoms have been replaced by halogens such as chlorine, fluorine, and bromine which reduce flammability but can cause unwelcome effects on the environment.

Hydrocarbon refrigerants provide a range of boiling points with applicability from cryogenics to air conditioning. In the past hydrocarbon refrigerants have had limited applications primarily within the petrochemical industry to provide industrial chilling and process refrigeration. With the phase out of the CFCs, hydrocarbon refrigerants are entering into new arenas. One of the first uses has been as a small quantity constituent in halocarbon blends to provide enhanced thermo-physical properties, such as oil miscibility. For the last decade in the European and Asian countries, the commercial market for systems using hydrocarbon refrigerants has been growing as a result of concerns about the environmental consequences of the halocarbon refrigerants. Examples of commercially available equipment using hydrocarbon refrigerants are:

- systems with small charges including domestic refrigerator/freezers and portable air conditioners,
- stand-alone commercial refrigeration systems including beverage and ice-cream machines,
- as the primary refrigerant in centralized indirect systems for supermarket refrigeration,
- transport refrigeration systems for trucks, and
- chillers in the range 1kW – 150 kW (0.3 – 40 tons of refrigeration)

The hydrocarbons most commonly used as refrigerants are:

Methane	R-50
Ethane	R-170
Propane	R-290
Butane	R-600
Isobutane	R-600a
Ethylene	R-1150
Propylene	R-1270

2.4 Water- R-718

Water is another natural refrigerant with a renewed interest because it is non-toxic, non-flammable low cost, and abundant. Water is widely used as a refrigerant in higher temperature lithium bromide – water (LiBR-H_2O) absorption chillers where water is the refrigerant and lithium bromide is used as an absorbent. The challenge for absorption chillers is that even a double- effect absorption cycle only has a COP (Coefficient of Performance) slightly greater than 1. As a comparison electric drive centrifugal chillers have a COP greater than 5.

It is far less common to find water in use within a vapor compression refrigeration system, although it does have one particularly noteworthy attribute – its thermo-physical properties enable it to achieve a high coefficient of performance. R-718 systems present a number of technological characteristics that have, to date, limited their growth into the industry. First, the operating pressures for water-based refrigeration systems are extremely low – approaching a near perfect vacuum making their continued operation free of contaminants (air) difficult. Second, the density of water vapor is extremely low; thereby, necessitating compressors capable of processing extremely high volume flow rates. Lastly, water is inherently limited to refrigeration applications for high temperature only. However, developments at the proto-type level in the vapor compression-based R-718 systems continues and is paving way for the introduction of chillers in large sizes that could become a significant part of the chiller and ice-water markets.

2.5 Other

In addition to carbon dioxide, air and some of its constituents are used as refrigerants in niche industrial applications. As with carbon dioxide, pressure and efficiency considerations are important criteria for selection. Liquid nitrogen in direct contact freezing is not considered to be a natural refrigerant because the embedded energy required for the production and transport of the liquid is so high.

Recommendations:

Through its Strategic Plan, ASHRAE has recognized that the advancement of sustainable building design and operations is critical to the protection of our global environment and to society. Expanding the safe and efficient application of natural refrigerants supports this move towards sustainability and continues ASHRAE's legacy as an international leader in the field of refrigeration and air conditioning.

ASHRAE holds a strong position that:

- the use of natural refrigerants helps to meet growing HVAC&R demands in a sustainable manner
- there are still research needs in order to achieve this in a safe, cost-effective, and environmentally beneficial manner
- projects must be assessed in a rational, fact-based, systematic manner to ensure that environmentally beneficial technologies are not rejected on the basis of false information or irrational fears.

ASHRAE recommends that further research be conducted on

- safety, energy efficiency, costs and environmental impact for all refrigerants using a consistent and comprehensive methodology
- the development of systems and components which can ensure the safe application of natural refrigerants without compromising energy efficiency
- the behavior of natural refrigerants in operating systems
- the role of natural refrigerants in achieving sustainability

ASHRAE is committed to

- the application of natural refrigerants
- the development of strategic relationships to advance natural refrigerants
- the consideration of natural refrigerants in existing and new guidelines, codes and standards
- the provision of guidance and education to policy makers and the public
- the creation and dissemination of methods and tools for environmental assessment of refrigeration systems
- the publication of technical information highlighting best practices from a safety, reliability and efficiency standpoint
- the promotion of authoritative information on natural refrigerants through seminars and publications

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ASHRAE Standard 34 - Designation and Safety Classification of Refrigerants

ASHRAE Position Document: Ozone Depleting Substances

ASHRAE Position Document: Climate Change

ASHRAE Position Document: Ammonia as a Refrigerant