Alternative Refrigerants and Their Thermophysical Properties Research

Koichi Watanabe
Department of System Design Engineering
Faculty of Science and Technology
Keio University
Januarius V. Widiatmo
Department of System Design Engineering
Faculty of Science and Technology
Keio University
(On leave of absence from the Agency for the Assessment and Application of Technology
Jakarta 10340, Republic of Indonesia)

Contact Address:
3-14-1, Hiyoshi, Kohoku-ku, Yokohama 223-8522, Japan
Phone: 81-45-563-1141, Ext. 3127, Fax: 81-45-563-2778
E-mail: watanabe@sd.keio.ac.jp

Abstract

The alternative refrigerants to be covered by the present paper include HFC (hydrofluorocarbon) refrigerants and their mixtures, natural refrigerants such as hydrocarbons and carbon dioxide, and some new candidates such as HFEs (hydrofluoroethers), which all are non-ozone depleting substances. The authors aim to present an overview of the current state of the art with respect to several promising alternative refrigerants typically accepted in the refrigeration and air-conditioning industries in Japan. An emphasis will be given to the thermophysical properties research update that has significantly contributed to accelerate an adoption of binary and/or ternary HFC blends in various engineering applications. An important international collaboration through the IEA-Annex 18 project will be stressed so as to explain how the thermophysicists worldwide did contribute to achieve a successful landmark on thermodynamic property modeling of HFC refrigerants and their mixtures. Some essential features of other alternatives, such as hydrocarbons, carbon dioxide, and HFEs will also be discussed based on the general technical observations.

Keywords: alternative refrigerants, hydrofluoroethers, natural refrigerants, thermophysical properties.

INTRODUCTION

It should be emphasized that it has already passed a decade since the Montreal Protocol on Ozone Depleting Substances was agreed in 1987 and a quarter of century since the depletion of stratospheric ozone layer by means of chlorofluorocarbon (CFC) compounds was first suggested by Molina and Rowland [1]. During the last 10 years since the Montreal Protocol was originally ratified, several amendments to the Protocol have been agreed internationally so as to accelerate phaseout of CFC refrigerants and regulation timetable with respect to production and consumption of hydrochlorofluorocarbon (HCFC) refrigerants. In the developed nations, complete phaseout date for HCFCs is assigned being 2020, whereas CFCs and HCFCs are scheduled to be banned in 2010 and 2040, respectively, in the developing nations.

Under such an international regulation, a worldwide challenge to identify the optimum alternative refrigerants to replace R-22 as well as R-502 is one of the most urgent and crucial issues in this field. Chlorodifluoromethane ($CHClF_2$), R-22, is the major product among HCFCs and is being used almost exclusively as a refrigerant for air-conditioning and heat-pumping equipments which are currently manufactured ca. 2.7 million units annually worldwide. An azeotropic refrigerant R-502 [R-22/115 (48.8/51.2 wt%)] is another important refrigerant for commercial low-temperature applications and its substitution by environmentally-acceptable alternatives is also recognized essential.

It is well known that, among the chlorine-free halocarbons to be considered from the environmental viewpoint, there exists no single-component HFC (hydrofluorocarbon) refrigerant to replace both R-22 and R-502, partly because of the expected degradation of heat transfer and cycle performance and partly due to the reported flammability issue for some of the HFC compounds [2]. As a result, the industry has begun an intensive effort to adopt various zeotropes and, if possible, azeotropes among HFC refrigerants to serve as long-term refrigerants. It is needless to emphasize that reliable information about the thermophysical properties of HFC refrigerant mixtures plays an essential role not only in identifying the best possible selection among the promising candidates to replace conventional refrigerants, but also in designing and manufacturing environmentally-acceptable equipments with new refrigerant mixtures. In the present paper, therefore, the authors aim to discuss the recent progress in some basic research on thermophysical properties of binary and ternary HFC refrigerants. In addition, some essential features of other alternatives, such as hydrocarbons, carbon dioxide, and HFEs will also be discussed based on the general technical observations.

HFC REFRIGERANTS AND THEIR MIXTURES

Table 1 summarizes some basic thermodynamic properties of HFC compounds together with those for R-22 and R-502. It should be noted that chlorine-free HFC compounds exhibit zero ODP (ozone-depletion potential) but their impact on global warming in terms of GWP (global warming potential) will never be negligible, since their overall atmospheric lifetime becomes even longer than HCFC refrigerants although their stratospheric lifetime is expected to be reduced due to the existence of hydrogen atoms within the molecule. Additional drawbacks regarding HFC refrigerants include a reduction in their mutual solubility with lubricants and existing flammability with respect to some HFC compounds such as R-32, R-143a and R-152a.

Table 1 Some Basic Thermodynamic Properties of HFC Refrigerants

ASHRAE Designation	Chemical Formula	Molar Mass (kg/kmol)	Normal Boiling Point (K)	Critical Temperature (K)	Critical Pressure (MPa)	Critical Density (kg/m^3)
R-23	CHF_3	70.014	191.00	299.00	4.815	529
R-32	CH_2F_2	52.024	221.50	351.255	5.780	424
R-125	CHF_2CF_3	120.022	224.66	339.165	3.616	568
R-134a	CH_2FCF_3	102.031	247.07	374.110	4.052	511
R-143a	CH_3CF_3	84.041	225.92	345.860	3.764	434
R-152a	CH_3CHF_2	66.051	249.10	386.41	4.512	368
R-22	$CHClF_2$	86.468	232.33	370.30	4.988	513
R-502		111.63	227.84	355.37	4.065	567

Table 2 HFC Refrigerants Mixtures to Substitute R-22 and R-502

Replacement to	ASHRAE Designation	Composition (wt%)	Normal Boiling Point (K)	Temperature Glide (K)	
R-22 (Air Conditioner)	R-410A R-407C	R-32/125 (50/50) R-32/125/134a (23/25/52)	221.7 229.2	0.1 7.2	Near-Azeotrope Zeotrope
R-22 or R-502 (Low Temperature Refrigeration)	R-404A R-407A R-507A	R-125/134a/143a (44/4/52) R-32/125/134a (20/40/40) R-125/143a (50/50)	226.5 227.9 226.0	0.4 4.1 0.0	Near-Azeotrope Zeotrope Azeotrope

Generally speaking, chemical stability and atmospheric lifetime of compounds increase with increasing number of fluorine atoms since carbon-fluorine bonding posseses larger bond energy, and their toxicity will also be reduced. On the other hand, flammability increases with increasing number of hydrogen atoms and it should be noted that flammability appears, in general, for molecules with a ratio of hydrogen atoms to fluorine atoms being larger than unity. These facts suggest that some reconciliations are needed between environmental issues and safety issues in practical applications. Additional key-factors to be considered include some fundamental aspects with respect to cycle performance in terms of refrigeration capacity and coefficient of performance (COP) of the equipment.

Having analyzed these contradictory issues mentioned above, it is currently understood that some binary and/or ternary blends of HFC compounds including R-32, R-125. R-134a, and R-143a are promising candidates to replace R-22 and R-502, as shown in Table 2.

Basically R-32 and R-134a play an important role to constitute alternative HFC mixtures in which the flammability of R-32 is expected to be reduced by blending it with nonflammable R-125 and R-134a. It is also interesting to note that improvement in COP values may be expected by increasing the composition of R-134a and/or of R-32, whereas significant improvement in refrigerating capacity becomes feasible by increasing the composition of R-32 and/or of R-125. In other words, an increase in R-134a composition may provide improvement in COP but reduction in refrigerating capacity. In addition, the mixtures with greater percentage of R-32 composition will reduce load to the environment, since the GWP value for R-32 is considerably small among HFC compounds. Again, therefore, there exists no single solution to overcome mutually-opposing issues simultaneously and this fact reflects the existing "dilemma" in selecting the best substitute even among HFC refrigerant mixtures. It is believed, therefore, that the optimum compositions of respective HFC compounds should be determined on the basis of a general examination of adaptability in practical equipments with specified objectives.

In accord with a selection of alternative blends, a fractionation problem of HFC mixtures is another essential factor to be studied rather extensively. Namely, one should recognize an essential difference between zeotrope and azeotropic blends in terms of their significant difference in compositions both at vapor and liquid phase. More specifically, one of the major disadvantages of zeotropes for the industry is an issue on fractionation of the refrigerants during charging and leaking. Theoretically, composition of the refrigerant mixture can change significantly, if a leak occurs from the equipment under a vapor-liquid coexistence, and the system is recharged with the original composition a number of times. Therefore, for the last several years, a specific attention has been paid to zeotropes known as "near-azeotropes" or "zeotrope-like" blends which exhibit minimal temperature and composition change or glide during vapor-liquid phase change.

THERMOPHYSICAL PROPERTIES RESEARCH IN PROGRESS

GENERAL BACKGROUND It is essential to note that a reliable set of information about the thermophysical properties of selected working fluids plays a crucial role at any stage of R & D of thermal energy conversion systems. Without a set of reliable and quantitative thermophysical property data, the progress of technology would be impeded and industry would be condemned to a costly "trial and error" development of new equipment.

Thermophysical properties of fluids, in general, are classified into three different categories; thermodynamic or equilibrium properties, transport or non-equilibrium properties, and other miscellaneous properties. Thermodynamic properties, such as vapor pressures, *PVT* properties, specific heat capacities, enthalpies, speeds of sound, and surface tensions, are the macroscopic properties to be observed at the thermodynamic equilibrium condition of the fluid system, whereas the transport properties including viscosity, thermal conductivity and diffusion coefficient can be observed when the potential gradient in momentum, energy and mass transfer does exist in the fluid system, respectively.

THERMODYNAMIC PROPERTIES In meeting the urgent need for selecting the optimum HFC refrigerant mixture candidates to replace R-22, significant progress has been achieved recently on the principal thermodynamic properties of interest. It should be noted, however, that the accumulation of reliable experimental data on different properties in an extended range of temperatures, pressures and compositions is still not sufficient, both quantiatively and qualitatively, especially for ternary HFC mixtures. It is needless to emphasize the importance of studying the thermodynamic properties of single-component HFC refrigerants rather accurately and extensively in advance, since they are the constituents for the binary and/or ternary mixtures. In other words, a thermodynamic consistency in different equilibrium properties of refrigerant blends over an entire composition range is essential to understand the overall thermodynamic behavior of alternative mixtures.

Fortunately, accumulation of reliable experimental data on major thermodynamic properties of single-component HFC alternatives such as R-134a, R-32 and R-125 seems fairly satisfactory, whereas measured data for R-143a are still limited [3, 4]. The thermodynamic behavior of binary and/or ternary refrigerant mixtures is more complicate than that of pure fluids, even for the blends with specified composition. Namely, the vapor-pressure curve for zeotrope mixtures, for example, is never a single temperature-dependent curve but also depends on the composition and, moreover, provides two different pressure values, bubble-point pressure and dew-point pressure, at specified temperature and composition. Therefore, it is essential to reveal the so-called VLE (vapor-liquid equilibrium) properties along the vapor-liquid coexisting conditions in the case of mixtures. Among the existing research projects partially reported and partially on-going regarding the experimental studies of various thermodynamic properties of binary HFC mixtures to replace R-22, more than half of them are dealing with VLE properties, i.e., temperature dependence of bubble-point and/or dew-point pressures at different compositions. It should be emphasized that a complete understanding of the VLE properties for ternary refrigerants, such as the R-32/125/134a system, does require a thorough examination of the thermodynamic properties of the three different binary systems consisting the ternary blend. Therefore, additional accumulation of reliable experimental data on the binary R-125/134a system is definitely required. The number of properties of the ternary R-32/125/134a system studied has certainly been increasing quite recently. However, they are mainly concentrated on *PVTx* property measurements with respect to the ternary alternatives with specified compositions of industrial interest, but few reported data are available for the VLE properties.

Among various thermodynamic properties to be revealed for binary and/or ternary refrigerant mixtures, it is needless to stress the importance of *PVTx* property measurements: a relationship among pressure, P, volume, V, temperature, T, and composition, x. Based on the well-established theory in thermodynamics, we can develop the equation of state whenever some reliable sets of experimental *PVTx* property data are available at different compositions. Incorporated with additional information about the specific heat capacity data at the ideal-gas state, most of the essential thermodynamic property values including enthalpy, entropy and isobaric heat capacity can be derived analytically from the developed equation of state. However, in the case of refrigerant mixtures, we do need additional knowledge on the so-called mixing rules to be associated with the established equation of state.

Generally speaking, the availability of measured *PVTx* property data on promising alternative refrigerants seems fairly sufficient for the binary R-32/134a system, and the next-to best situation is observed for the binary R-32/125 system. At a glance, one may think that the availability of *PVTx* property data for the ternary R-32/125/134a system is rather sufficient, but this is far from being the case for the quantity of data to cover a wide range of entire fluid phases with different compositions. Specifically, the quality of reported data is still so limited that one should accumulate additional reliable *PVTx* property data in order to develop the models in terms of the thermodynamically consistent equations of state for this important ternary HFC mixture.

In addition to the measured information about the VLE and *PVTx* property data mentioned above, it is also worthwhile to have some additional experimental data on other essential thermodynamic properties including heat capacities and speeds of sound. Whenever the correlators endeavor to formulate the thermodynamic models to represent the experimental VLE and *PVTx* property data, one would face a significant difficulty, whether or not the developed models are accurate and reliable enough to be applied in various engineering applications. One of the best measures for examining such a criterion is to compare the developed models with experimental data on heat capacities, isobaric and/or isochoric, as well as speeds of sound.

As already mentioned, these thermodynamic properties can be derived analytically from the developed formulations in terms of the second partial differentials, either of the developed Helmholtz or Gibbs function, which defined the thermodynamic state surface by the models. Mathematically speaking, in general, the second differentials of the established three-dimensional surface provide the curvature of the surface, whereas the first differentials give the inclination of the surface. Therefore, it is not so easy for the correlators to develop the formulations so as to provide the accurate behavior of the second differentials, i.e., heat capacity and speed of sound. This is a very important reason why the correlators always ask the experimenters to produce reliable sets of measured data on isobaric and/or isochoric heat capacities, as well as speeds of sound in the entire fluid phase. On the other hand, precise measurements of heat capacities and speeds of sound were used to be very difficult and less accurate than other conventional thermodynamic property measurements, such as the vapor pressure and *PVTx* property measurements for single-component fluids. Fortunately, however, some significant progress has been achieved quite recently in improving the accuracy and precision of the experimental techniques with the aid of advanced computer technology and measuring devices for quick and reliable measurements of the caloric and acoustic properties mentioned above. It is also interesting to note that such significant progress in experimental thermophysics has been achieved in conjunction with the increasing demand for these thermodynamic property data for the alternative refrigerants. Good examples include the speed of sound measurements by means of a spherical resonator by a group of the present authors for gaseous alternative refrigerants [5-7] and their mixtures [8,9]. We have claimed an experimental uncertainty in speed of sound not greater than ± 0.01 % for the single-component and binary refrigerants, and as low as ± 0.02 % for the gaseous ternary refrigerant mixtures. Another example is the liquid-phase isochoric heat capacity measurements currently in progress at the NIST for the binary refrigerants which claim an estimated uncertainty of $\pm$ 2.0 %

One of the most comprehensive compilations of the thermodynamic properties of HFC refrigerants and their binary and ternary blends in entire range of compositions of the constituents has been published recently by a group of the present authors at Keio University [10]. This publication includes a complete set of formulations associated with the numerical tables of various thermodynamic property values at different temperatures, pressures and compositions. Two important thermodynamic charts, pressure-enthalpy and temperature-entropy diagrams, for these alternative refrigerants are also provided in this compilation.

TRANSPORT PROPERTIES Current status regarding the availability of experimental data on transport properties of HFC refrigerants and their mixtures is significantly different from that of thermodynamic properties discussed above. Despite of their essential importance in understanding some basic heat and mass transfer phenomena as well as in practical R & D of heat exchanger design, accumulation of reliable measured data on transport properties such as viscosity, thermal conductivity and thermal diffusivity is still far limited both quantitatively and qualitatively. Among HFC refrigerants and their mixtures of the present interest, it seems fair to mention that transport properties of R-134a and R-152a have been investigated to fairly extensive degree. Then the measured data for R-32 and R-125 seem to increase gradually quitely recently, whereas those for R-143a are less studied. In addition, the availability of transport property data for binary and ternary blends is far behind than that for single-component HFC refrigerants. It is also interesting to note that the availability of viscosity data is, in general, slightly better than that of thermal conductivity, although the covered range of temperatures, pressures, densities and compositions is still restricted so far.

Regarding the viscosity of R-134a, a comprehensive data survey including critical data evaluation and correlation has been published by Krauss et al. [11] in conjunction with an international collaboration under the auspices of IEA Annex-18 project. This earlier correlation is effective for the range of temperatures 290 – 430 K, pressures up to 30 MPa and densities up to 1400 kg/m^3 including the critical region and the correlation is expected to provide the viscosity values of R-134a within around 5 %. Since then, however, some additional sets of measured data have been available in the literature and some minor modification may become required so at to update this correlation. Similar compilation including correlation was also published with respect to R-152a by Krauss et al. [12]. This correlation for R-152a does cover the range of temperatures 240 – 440 K, pressures up to 20 MPa and densities up to 1050 kg/m^3 and expected reliability of the viscosity values reproduced by this correlation is reported being ± 0.3 %.

Regarding the viscosity of other important HFCs including R-32, R-125 and R-143a, an extensive compilation and evaluation of available data has been completed recently by Tanaka et al. [13] in conjunction with a publication program on thermophysical properties of these three HFC refrigerants at the Japan Society of Refrigerating and Air Conditioning Engineers (JSRAE, former JAR: Japanese Association of Refrigeration), Tokyo.

Regarding the viscosity data for binary and/or ternary HFC mixtures, the situation seems much worse since most of the reported data have been obtained only along a specified composition of the mixture. No measurements have been reported for compressed-liquid mixtures, whereas two independent measurements [14, 15] are available for saturated liquid mixtures. Only a single group [16-18] is currently challenging an oscillating-disk viscometry for the vapor-phase measurements at saturated and superheated vapor including atmospheric pressure of the binary R-125/134a, R-32/23 and R-32/134a systems.

Similarly to the availability of viscosity data, accumulation of thermal conductivity data is rather limited mostly for single-component HFC refrigerants since the thermal conductivity measurements for binary and/or ternary HFC mixtures seem just started quite recently. Regarding single-component HFC refrigerants, very comprehensive compilations and correlations have been published for R-134a [11] and for R-152a [12]. On the other hand, Yata [19] has recently completed a very extensive survey of thermal conductivity data for other HFC refrigerants including R-32, R-125 and R-143a.

Concerning HFC refrigerant mixtures, on the other hand, a limited number of investigations have been conducted at restricted compositions up to the present. It is also interesting to note that these recent thermal conductivity measurements for HFC refrigerant mixtures have been performed exclusively by applying the transient hot wire method.

IEA ANNEX-18 PROJECT

Despite of its essential importance, only about 40 research groups worldwide have contributed to accelerate the thermophysical properties research on alternative HFC refrigerants and their mixtures. Roughly a dozen of research groups among them have agreed to join an international research collaboration project entitled "Thermophysical Properties of the Environmentally Acceptable Refrigerants". This international project, officially called as the Annex-18 project, was established by the International Energy Agency (IEA) in March, 1990 and completed its 3 term, 9 years collaboration last March, 1999 with lots of successful and fruitful results in the field of thermophysical properties research on alternative refrigerants. The purpose of this Annex-18 was to bring together leading experts involved in this field of basic science to share results and coordinate efforts with the ultimate goal of arriving at internationally accepted formulations for the thermophysical properties of alternatives to the ozone-depleting refrigerants.

A total of 11 meetings of the Annex-18 were held at different member countries including Canada, Germany, Japan, Norway, Sweden, UK and USA (Austria joined only for the second term) during 1990 through 1999. Among the leading products through this Annex-18, one of the most important achievements was to designate the international standard equations of state for R-134a [20], R-123 [21], R-32 [22], R-125 [23] and R-143a [24] which all have been selected among the other proposed formulations throughout the extensive and careful evaluation and examination by the Annex-18. Concerning the thermodynamic modeling of the HFC refrigerant mixtures, on the other hand, the Annex-18 agreed not to select the international standard formulation in terms of the competition but to prepare the evaluation report [25] with respect to 5 proposed models from different research groups.

Throughout the IEA Annex-18 project, it is important to note that an extensive international collaboration among the participated experts has been accelerated by the exchange of information especially about the unpublished experimental thermophysical property data through the electronic network system operated at the University of Stuttgart, Stuttgart, Germany, where the thermophysical property database was originally established by German contribution to the Annex-18 project. Unlike to other IEA Annex projects, the Annex-18 was operated completely on the basis of voluntary collaboration of the experts worldwide associated with a task-sharing scope. The authors believe that this type of international collaboration is truly an ideal one so as to achieve the goals in basic field of science even for the coming 21st century.

NATURAL WORKING FLUIDS

It seems us that there exist two different aspects regarding an increasing concern worldwide about the so-called natural working fluids, which were used to be called as natural refrigerants. Namely, in developing nations, natural working fluids such as hydrocarbons are the substances easily available with modest cost in comparison with, for example, HFC refrigerants, although the safety issue typically on flammability of most hydrocarbons should be carefully considered. In developed nations, on the other hand, an increasing interest to natural working fluids comes from the unavoidable impact of HFCs on the global warming when they are released to the atmosphere. The Kyoto Protocol agreed at the 3rd Conference of the Parties on the Framework Convention of the Global Climate Change in Kyoto in 1997 has decided to categorize HFCs together with carbon dioxide and other gases being the controlled substances to be regulated internationally.

Historically speaking, it is well known that our earlier refrigerants in the cradle period of refrigeration technology back to the middle of the last century till the 1920's were such natural working fluids including water, ammonia (originally called as alkaline air), carbon dioxide and hydrocarbons. These substances available in the nature were then superceded by halocarbons, man-made organic substances synthesized in the early 1930's. Hence, in other words, a recent increasing concern about natural working fluids reflects our retrospect to the origin of refrigeration more than 150 years ago.

Table 3 Basic Requirements and Properties for Refrigerants

Essential Requirements	Chemical Stability Safety Issues ● Global Environmental Impact ● Safety in Operation and Maintenance Thermodynamic Properties
Requirements for Equipment Design	Solubility to Lubricants Materials Compatibility Water Content Transport Properties Static Dielectric Constant Energy Efficiency
Requirements for Application	Easy Leak-detection Easy Recycling Easy Handling (Serviceability for Maintenance) Cost Economy

Table 3 summarizes basic requirements and properties for refrigerants that one should examine so as to select the optimum candidate. Among various items tabulated, one of the most important criteria currently recognized is the safety issues that consist impact to the global environment as well as the operation and maintenance safety. As we have already overviewed in the preceding sections, HFC refrigerant mixtures are excellent except their global warming impact. To the contrary, most of natural working fluids possess negligible impact to the global environment but they have different disadvantages to be examined in comparison with HFC refrigerant mixtures.

Table 4 summarizes the reported global environmental impacts by different refrigerants including CFCs, HCFCs, HFCs, HFC mixtures, PFCs (perfluorocarbons), natural working fluids and HFEs (hydrofluoroethers). The promising HFC refrigerant blends such as R-410A, R-407C, R-404A and R-507A show almost equivalent or even higher GWP values than R-22 and R-502 that have to be substituted by these alternatives. On the other hand, it becomes clear from Table 4 that natural working fluids such as R-290 (propane), R-600a (isobutane) and R-717 (ammonia) have basically no impact to the environment as mentioned earlier. Similarly, some selected HFEs also exhibit excellent characteristics in this respect.

The pros and cons on the basis of general observation about several leading natural working fluids are discussed here. Water (R-718) is the oldest refrigerant ever applied in refrigeration and its fundamental thermodynamic properties are considered the origin of its disadvantage being a refrigerant. Namely, the normal boiling point temperature of R-718 is extremely high being 393.124 K (99.974 ℃) and its vapor pressures become too low at temperatures of engineering interest in refrigeration and air-conditioning. This fact leads to a disadvantage that one should design a compressor with larger dimensions associated with an extremely high pressure ratio, since the specific volume values of water vapor (steam) become large. A good news, however, is that some advanced technology in designing a very high-speed (ca. up to 15000 rpm) compressor become available to overcome the existing difficulty mentioned above.

Air (R-729) is naturally a safe working fluid and excellent except its extremely low theoretical refrigeration efficiency together with a possible noise problem. Several advanced challenges to apply either the Stirling cycle and/or Vuilleumier cycle with air and other environmentally safe gases are certainly the attractive options but still far from the practical feasibility in refrigeration.

Among the hydrocarbons, several candidates including propane (R-290), isobutanane (R-600a), n-butane (R-600) and their mixtures such as R-290/600a, R-290/600 and R-290/600/600a are attracting being environmentally benign refrigerants. They have, in general, excellent thermophysical properties and heat transfer characteristics

Table 4 Major Environmental Impacts of Refrigerants

Refrigerant	Chemical Formula	Atmospheric Lifetime (yrs.)	ODP	GWP
Carbon dioxide	CO_2	50 – 200	0	1
Methane	CH_4	12 ± 3	0	21
Nitric oxide	N_2O	120	0	310
CFC 11	CCl_3F	50 ± 5	1.0	4 000
CFC 12	CCl_2F_2	120	1.0	8 500
CFC 113	CCl_2FCClF_2	85	0.8	5 000
CFC 114	$CClF_2CClF_2$	300	1.0	9 300
CFC 115	$CClF_2CF_3$	1700	0.6	9 300
R-502	R-22/115 (48.8/51.2 wt%)		0.283	5 600
HCFC 22	$CHClF_2$	13.3	0.055	1 700
HCFC 123	$CHCl_2CF_3$	1.4	0.02	93
HCFC 124	$CHClFCF_3$	5.9	0.022	480
HCFC 141b	CH_3CCl_2F	9.4	0.11	630
HCFC 142b	CH_3CClF_2	19.5	0.065	2 000
HCFC 225ca	$CH_3CF_2CHCl_2$	2.5	0.25	170
HCFC 225cb	$CClF_2CF_2CHClF$	6.6	0.033	530
HFC 23	CHF_3	264	0	11 700
HFC 32	CH_2F_2	5.6	0	650
HFC 125	CHF_2CF_3	32.6	0	2 800
HFC 134a	CH_2FCF_3	14.6	0	1 300
HFC 143a	CH_3CF_3	48.3	0	3 800
HFC 152a	CH_3CHF_2	1.5	0	140
HFC 227ea	CF_3CHFCF_3	36.5	0	2 900
HFC 236fa	$CF_3CH_2CF_3$	209	0	6 300
HFC 245ca	$CH_2FCF_2CHF_2$	6.6	0	560
R-410A	R-32/125 (50/50 wt%)		0	1 900
R-407C	R-32/125/134a (23/25/52 wt%)		0	1 600
R-404A	R-125/134a/143a (44/4/52 wt%)		0	3 700
R-507A	R-125/143a (50/50 wt%)		0	3 800
PFC 14	CF_4	50 000	0	6 500
PFC 116	C_2F_6	10 000	0	9 200
PFC 218	C_3F_8	2 600	0	7 000
PFC C318	c-C_4F_8	3 200	0	8 700
sulfur hexafluoride	SF_6	3 200	0	23 900
R-290	C_3H_8 (propane)		0	negligible
R-600a	C_4H_{10} (isobutane)		0	negligible
R-717	NH_3 (ammonia)		0	negligible
HFE-143m	CF_3OCH_3	5.1	0	
HFE-245mc	$CF_3CF_2OCH_3$	6.5	0	622
HFE-347mcc	$CF_3CF_2CF_2OCH_3$	5.6	0	368

as a refrigerant. Their features include zero impact on global environment, low vapor-phase density and excellent miscibility even with conventional lubricants such as mineral oils, but their flammability is an exclusive issue of industrial concern especially in Japan and U.S.A. It is true, however, that their application to the household refrigerators with modest refrigerant charge in Germany has initiated to attract the industries in several European nations for their extensive applications to small-scale window-type air-conditioners, milk manufacturing plant and other heat pumping systems. To the contrary, however, in other industrialized nations including U.S.A. and Japan, a majority of refrigeration and air conditioning industry seems rather reluctant to apply them immediately in massive production of various home appliances. This is mainly due to the mortgage for flammability security essentially required to their products, and partly due to their enormous amount of investment already paid for the R & D of their products with new HFC refrigerant mixtures. In other words, it seems us fair to mention that the industry will go along with HFC mixtures as long as they are permitted by endorsing not to release them to the atmosphere and also by continuing to increase the energy efficiency of equipment so as to reduce the global warming impact. In any event, further assessment on the flammability issue of hydrocarbon refrigerants should be expanded, since their excellent characteristics as refrigerants have already been recognized in various sectors worldwide.

Regarding ammonia (R-717), it is needless to emphasize its historical and long-term achievements as an excellent refrigerant especially in large-scale commercial and/or industrial refrigeration systems. Toxicity, flammability and required higher superheat of this substance have been well known for the last many years and some new challenges are in progress so as to overcome these existing drawbacks; for example, by reducing the refrigerant charge to the minimum level of 35 g/kW and also by combining the ammonia unit with other secondary coolant system using carbon dioxide (R-744) in commercial applications. It is basically important that further technical R & D should be continued to apply this refrigerant to small-scale refrigeration systems by establishing to design the hermetic ammonia compressors.

Carbon dioxide (R-744) is definitely attracting most extensively in refrigeration industry in the last several years. Theoretical COP values of the vapor-compression system with R-744 are not always high as those with HFC refrigerants, when the refrigeration cycle conditions remain unchanged. This is simply due to the thermodynamic properties inherent to R-744, since, for example, the critical temperature is 304.2 K corresponding to extremely high critical pressure of 7.38 MPa among various refrigerants. In order to improve the COP values, therefore, it is essential to design the R-744 refrigeration cycle being a so-called transcritical cycle by which the condensing pressure exceeds the critical pressure and this fact leads to name the condensing unit as a gas cooler instead of a conventional condenser. Another advantage to apply R-744 includes its excellent heat transfer characteristics due to higher thermal conductivity and this leads to a possible design of compact heat exchangers. Higher operating pressure level of the R-744 system is certainly a challenge but, on the other hand, this may also lead to a compact compressor design with modest pressure ratio at the compressor.

The RACE (Refrigeration and Automotive Climate System under Environmental Aspects) project by the EUCAR (European Council for Automotive R & D) in EU nations was a strong incentive to leading manufacturers of the vehicle air-conditioner for their careful examination of the R-744 system. In addition, some challenges to apply R-744 even for domestic and commercial refrigeration and heat pumping equipment are in progress in several European nations and such a recent trend may reflect an increasing interest worldwide to the R-744 system.

Table 5 Overall Evaluation for Refrigerants

	Safety	Environ. Impact	Refrig. Capacity	Energy Efficiency	Cost Economy
HCFC	0	- -	0	0	0
HFC	0	-	0	0	0
HC	- -	+	0	0	-
R-729	+ +	+	+ (?)	- -	+
R-718	+ +	+ +	- -	0	+ (?)
R-717	- (-)	+ +	0	0	-
R-744	+ (+)	+	+ +	-	- (?)

Having summarized a sort of general observations mentioned above, an overall evaluation given in Table 5 is prepared [26] with respect to natural working fluids together with conventional HCFC and HFC refrigerants. The evaluated results summarized in Table 5 are naturally presented on a relative basis to the existing technology level (designated being 0) in various applications. It should be noted that a symbol (?) denotes the present evaluation completed with considerable uncertainties, but it seems reasonable to conclude that R-744 is the most promising alternative among the proposed natural working fluids for the forthcoming 21st century.

HYDROFLUOROETHERS (HFEs)

As one of the Japanese national research projects, the New Sunshine Project, a fairly extensive R & D project is in progress to develop the new generation alternatives to replace CFCs and HCFCs being used as refrigerants, blowing agents and cleaning agents. This R & D project is undertaken by the Research Institute of Innovative Technology for the Earth (RITE), Japan, and is supported by the New Energy and Industrial Technology Development Organization (NEDO), Japan.

As far as the new generation alternative refrigerants developed for the refrigeration technology sector by the RITE are concerned, several fluorinated ethers including those listed in Table 4 have been proposed. Among them, heptafluoropropyl methyl ether (HFE-347mcc) is expected to substitute R-11, heptafluoroethyl methyl ether (HFE-245mc) for R-114, and trifluorodimethyl ether (HFE-143m) for R-12, respectively. It is needless to emphasize that these new generation alternative refrigerants have no ODP values and may contribute to a considerable reduction in global warming, since their GWP values are far lower than those of the conventional refrigerants.

A group of the present authors have studied various fundamental thermodynamic properties of these new candidates [27-31] experimentally, since almost no single set of reliable measurements were available. Basically, the vapor pressures, *PVT* properties both in the compressed liquid and superheated vapor regions, and saturated liquid densities have been measured at Keio University for the first time. Currently, additional efforts to develop the thermodynamic property models to cover the entire fluid phase are also in progress.

CONCLUDING REMARKS

A general overview on the current state of the art regarding the non-ozone depleting refrigerants has been presented. Special emphasis, however, was given to the updated thermophysical properties research specifically on HFCs and their blended mixtures of industrial interest.

International task-sharing collaboration through the IEA-Annex-18 project and its fruitful achievement were discussed. Some of the recent observations about natural working fluids have also been summarized so as to provide the perspective on existing issues.

In developed nations, it is noteworthy to conclude that refrigeration and air conditioning industry is concentrating to commercialize their products with HFC refrigerant mixtures such as R-407C and R-410A for air-conditioners to substitute R-22, whereas R-404A, R-407A and/or R-507A to replace either R-502 or R-22 for commercial applications. However, it is definitely true that many industries worldwide are increasing their interest to natural working fluids significantly in the last several years. As an example, it seems us fair to mention that hydrocarbon refrigerants are now considered to belong to a family of "ordinary refrigerants", although they were used to be understood being "not-in-kind refrigerants" in the early 1990's. It is, therefore, expected that we should challenge to apply some of the promising candidates among natural working fluids on the basis of a principle to assign the right person to the right place in our future refrigeration technologies, although paying a full attention especially to the safety issues.

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