REFRIGERANT SELECTION IN ROOM AIR CONDITIONING INDUSTRY FOR SUSTAINABLE DEVELOPMENT

A Thesis

by

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ABSTRACT

History shows us that refrigerant choice was never easy, with an evolvement from natural refrigerants to synthesized refrigerants, and maybe back to natural ones. Pursuing alternative substance or technology with zero ozone depleting potential (ODP) once was the priority concern of governments and manufacturers and was regarded as a long-term solution and the best way to protect the environment since the Montreal Protocol has been enforced to phase out all ozone depleting refrigerants that have been commonly used in air-conditioning. While the consequence of Climate Change issue is better known today, this argument will be challenged because of future sustainability concerns, and to be more precisely, refrigerant selections anticipate the need to mitigate greenhouse effect as well.

Manufacturers have commercialized more than 50 new refrigerants (including blends) in the last decade, and they are examining additional candidates. There is no general rule governing the selection of refrigerants. But basically refrigerants are examined according to some classic criteria in thermodynamic properties, technological and economic aspects and safety and environmental factors. Many relevant research and programs are conducted and most of their concentrate on one indicator such as energy efficiency or flammability of refrigerants, or in a given appliance under some specific standards, without careful consideration of regional differences such as local climatic conditions, local regulations and standards and “cultural” criteria associated with professions, applications, customs and user training levels. Unfortunately no current

refrigerants are ideal. Furthermore, future discovery of ideal refrigerant is extremely unlikely. Thus, from the perspective of different countries, how to make an informed choice from the existing imperfect candidates remains a tough challenge.

In this paper, methodologies were demonstrated to evaluate some typical refrigerants based on their performance in safety issues, environmental protection, and economic efficiency, with thermodynamic property and technology innovation incorporated from a whole country's perspective. Aiming at providing suggestions and recommendations to the national room air conditioning industry associations and also international manufacturers, the differences of local climatic conditions, technical gap, customer's use habit and environmental awareness among countries and regions are taken into consideration. Meanwhile case study of China and Japan utilizing this methodology are analyzed and compared. Additionally weighting methodology and its distance-to-target principle were also introduced briefly, as well as their important application in refrigerant selection.

The results of the research showed:

- In safety aspect, specific hazards from refrigerant always fall into two categories: toxicity and flammability, and their corresponding indicators TLV-TWA and HOC were chosen. Based on classification standard involving these indicators, the refrigerants currently being widely used in air conditioning industry are all categorized into group A1, with the properties of non-flammability and low toxicity, except R717. The HC alternatives, particularly R290, which attract the attention of air conditioning and refrigeration industry recently, are proven to have higher flammability and accidents occurred due to their high flammability. China and Japan have showed different acceptance on the flammable refrigerants which may lead to the different refrigerant selection in the future. On one side China believes the bright future of R290 and its risk management, while on the other hand Japan's lowest requirement in flammability is A/B2L. Further risk assessment is needed if flammable refrigerants are utilized in the processed of production, transportation, operation, after sales service and disposal. Moreover special training is suggested to be provided to the services suppliers and corresponding requirements are recommended to deliver the after sales services of air conditioners.

- In Environmental protection aspect, Ozone depletion and global warming are the main impacts caused by refrigerants. Consequently ODP and TEWI are carefully examined and then integrated into a whole environmental indicator by utilizing weighting methodology. TEWIs in average for a whole country when using different refrigerants vary a lot. In different cases, based on many factors such as total ownership of RAC, level of technology, energy structure, use habit and local climate conditions, the best or worst performers may change. In general, Japan has a smaller TEWI value when using the same refrigerant in the similar air conditioning system, mainly due to the technical gap and favorable local climatic conditions and energy structure. In terms of Environmental indicator, there exist great differences among

countries for the same refrigerant. Despite the higher absolute value of TEWI and ODs emission by a Chinese room air conditioning system, the relative value of environmental impact to a whole country that it causes is still limited due to its much larger territory area and huger population than Japan. This difference may affect the sensitivity of the national industry to environmental sector and may even lead to the final different choice in refrigerants. Basically the second generation refrigerants have a much higher value for Environmental indicators than others due to high ODP while the natural refrigerants perform well in ozone depletion impact, but differ in global warming impact due to efficiency differences.

- In economic efficiency aspect, price is the first concern. Basically the more complicated the chemical structure of refrigerant is, the more expensive it is. The availability also influences the selection process. Consequently the natural refrigerants keep a favorable position other than those synthesized refrigerants in HFCs. HFO1234yf has a much higher cost, including refrigerant price, production cost, handling cost and patent fees than the ones being used. Additional cost is required for flammable refrigerants when taking safety measures in application and handling.

Keywords: Refrigerant Selection, Safety Issues, Environmental Protection, Economic Efficiency, Local Climatic Conditions, TEWI, Environmental Indicator, Weighting Methodology.

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DEDICATION

Effort, dedication, and commitment were fundamental elements for the completion of my master research. However what is more important was the kind support from my beloved family and friends for their loving considerations and great confidence in me. Today I dedicate this professional achievement to them because without their support and understanding, I would never be able to achieve my goal.

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LIST OF ABBREVIATIONS

ACGIH	American Conference of Government and Industrial Hygienists
AHRI	the Air-Conditioning, Heating, and Refrigeration Institute
ASHRAE	American Society of Heating, Refrigerating and Air-Conditioning Engineers
CFC	Chlorofluorocarbon
COP	Coefficient of Performance
DE	Direct Emission
EPA	Environmental Protection Agency
GWP	Global Warming Impact
HC	Hydrocarbon
HCFC	Hydrochlorofluorocarbon
HFC	Hydrofluorocarbon
HOC	the Heat of Combustion
HPMP	HCFC Phase-out Management Plans
IE	Indirect Emission
JRAIA	the Japan Refrigeration and Air Conditioning Industry Association
LCCP	Life Cycle Climate Performance
LFL	the Lower Flammability Limit
ODP	Ozone Depletion Potential

LIST OF ABBREVIATIONS (Continued)

ODS	Ozone Depletion Substance
OSHA	Occupational Safety and Health Administration
PFC	Perfluorocarbons
SNAP	Clean Air Act and Significant New Alternatives Policy
TEWI	Total Equivalent Warming Impact
TLV-TWA	Threshold Limit Value - Time Weighted Average
WEEL	Workplace Environmental Exposure Limit

1 INTRODUCTION

Refrigerant selection has become one of the most important challenges in recent years because some important practical issues of air-conditioning system such as energy saving performance, the system design, size, initial and operating costs, safety, and reliability etc. depend very much on the type of refrigerant selected for a given application. Additionally, various refrigerants used have a close relation with several environmental issues such as ozone layer depletion and global warming. An informed choice will contribute to sustainable future, particularly in the energy issue. However this target seems rather difficult to accomplish and many challenges are waiting to be overcome.

1.1 Definition of Refrigerants

According to the American Society of Heating, Refrigerating and Air-Conditioning Engineers (ASHRAE), refrigerant is defined as the vital working fluid in refrigeration, air-conditioning, and heat pumping systems, which absorbs heat from one area, such as an air-conditioned space, and rejects it into another, such as outdoors, usually through evaporation and condensation processes, respectively.

1.2 Types of Refrigerants

Refrigerants are classified into the following five categories: HaloCarbons, Azeotropic Refrigerants, Zeotropic Refrigerants, Inorganic Refrigerants, Hydrocarbon Refrigerants, and each as its characteristics and famous examples shown in the Table 1.

Table 1 Types of Refrigerants

Types of refrigerants	Characteristics	Examples
HaloCarbons	Synthetically produced and developed as the Freon family of refrigerants. High ODP and GWP	CFC’s: R11, R12, HCFC’s : R22, R123 HFC’s : R134a, R404a, R407C, R410a
Azeotropic Refrigerants	A stable mixture of two or several refrigerants whose vapour and liquid phases retain identical compositions over a wide range of temperatures.	R-500 : R12/R152 (73.8%, 26.2%) R-503 : R23 and R13 (40.1%, 59.9%)
Zeotropic Refrigerants	A mixture whose composition in liquid phase differs to that in vapour phase and will not boil at constant temperatures unlike azeotropic refrigerants. Relatively high GWP	R404a : R125/143a/134a (44%,52%,4%) R407c : R32/125/134a (23%, 25%, 52%) R410a : R32/125 (50%, 50%)
Inorganic Refrigerants	Zero ODP and zero/low GWP, some are poisonous	carbon dioxide, water, ammonia, air, sulphur dioxide
Hydrocarbon Refrigerants	Zero ODP and low GWP, some are flammable	R170, Ethane, C_2H_6 R290 , Propane C_3H_3 R600, Butane, C_4H_{10}

Each type has its own advantages and disadvantages and is dominating or used to dominate in some field or at some time based on special needs as the history of refrigerant evolved.

1.3 History of Refrigerant Choice

History shows us that refrigerant choice was never easy. Figure 1 depicts the progression of refrigerants from their advent through four generations.

1.3.1 1830-1930 Natural Refrigerants Replace Ice

Before CFCs were invented, refrigerants were toxic, flammable, or both. When mechanical refrigeration became available in the 1920s, entrepreneurs rapidly commercialized systems with a wide variety of refrigerants, including carbon dioxide, water, ammonia, isobutene, sulfur dioxide and methyl chloride (carbon dioxide, water, ammonia, isobutene have recently been “rediscovered” and designed by proponents as “natural refrigerants”). Mechanical refrigeration was vastly superior to ice, which was increasingly contaminated and did not always assure safe temperatures for food refrigeration. However, leaks of the most common refrigerants of the 1920s-sulfur dioxide and ammonia-typically required rapid evacuation of homes and buildings. People who came into contact with these substances suffered from vomiting, burning eyes, and painful breathing. Accidents with sulfur dioxide and ammonia rarely resulted in death, but those ones with methyl chloride refrigerant were frequently fatal.

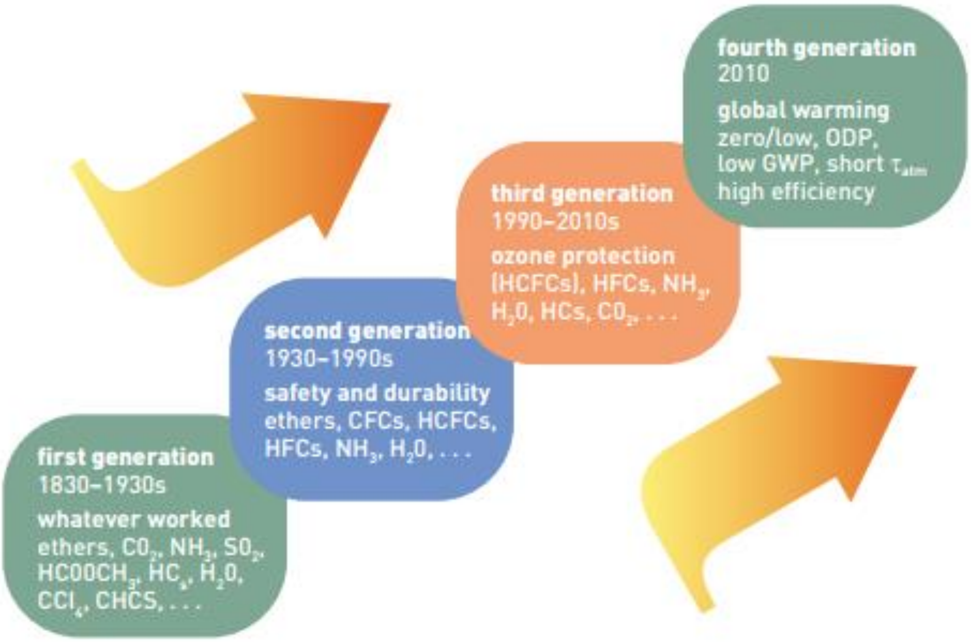


Figure 1 Progression of Refrigerants

1.3.2 1930-1985 CFCs and HCFCs Replace Natural Refrigerants

In 1928, Thomas Midgley, working with Albert Henne and Robert McNary at General Motors Research Laboratory, invented CFCs (Kauffman, 1989). CFCs proved to be non-flammable, non-explosive, non-corrosive, low toxicity, and odourless chemicals with vapor pressures and heats of vaporization that made them very good refrigerants. General Motors patented the family of CFCs and formed a joint stock company with DuPond to manufacture and market them (Andersen Sarma, 2002).

CFCs and HCFCs rapidly replaced natural refrigerants in many applications. CFCs-12 soon became the dominant refrigerant in most small appliance applications. In the 1950s, HCFC-22 was applied in commercial refrigeration (particularly as an ingredient in R-502), and CFC-11 was applied in centrifugal chillers (Cagin and Dray 1993, Anderson & Sarma, 2002).

Natural refrigerants continued to be used in certain applications, but CFCs and HCFCs captured much of the global refrigeration and air conditioning markets. Ammonia continued to be used in cold storage, ice making, and ice rinks and hydrocarbons continued to be used in industrial refrigeration, particularly at oil and chemical works (Anderson & Sarma, 2002). CFC and HCFCs refrigerants captured the rest of the market and sales increased with expanding global population, wealth and consumerism. Because they were relatively inexpensive, near-absolute containment was not a design priority for equipment manufacturers or users.

Until the early 1970s, CFCs and HCFCs were considered perfect in every known way because neither stratospheric ozone depletion nor global warming were understood or anticipated. Refrigeration and air-conditioning equipment manufacturers and their customers came to think of CFCs and HCFCs as “wonder gases”. Refrigerants were typically vented at service to avoid any risk of damage to equipment from refrigerants contaminated with air, acid, water or metal filings. Reliability was the only incentive manufacturers had to encourage refrigerant containment (Cagin and Dray 1993, Anderson & Sarma, 2002)

Then in 1974, Mario Molina and F. Sherwood Rowland- building on the work of many scientists including Paul Crutzen who shared their 1995 Nobel Price- warned that CFCs deplete the stratospheric ozone layer that protects life on earth from harmful ultraviolet radiation. In the next two decades the Molina- Rowland hypothesis was scientifically verified; the 1987 Montreal Protocol singed, ratified, and entered into force; and CFCs, HCFCs and other ODs production was scheduled to be halted in developed countries and finally in developing countries.

1.3.3 1985-1995: HFCs Replace CFCs and HCFCs

When Montreal Protocol was firstly agreed in 1987, there was no time to wait for new technology. Stratospheric ozone layer depletion threatened life on earth with skin cancer, cataracts, suppression of the immune system, destruction of agricultural and natural ecosystems and other unimaginable consequences. ODs replacements had to be found immediately. Hydrocarbon natural refrigerants were quickly proposed to replace CFCs, but the typical leak rates and service venting practices would have been unsafe. Additionally, no one knew how quickly technology could be implemented to mitigate flammability.

Other natural refrigerants were proposed, but they required further study and technological innovation. Meanwhile, the fluorocarbon chemical industry and their refrigerant customers moved quickly to the market existing HCFC-22 and HCFC-142b to replace HCFCs, to commercialize HFC-134a to replace CFC-12, and to commercialize HCFC-123 to replace CFC-11. HFC-134a and HCFC-123 had been identified decades earlier and patented in the 1970s. New chemicals, including HCFC-225, HFC-143a and HFC-124, replace ODs in applications other than refrigeration. By the time Gustav Lorentzen and colleagues filed their first modern patent for the carbon dioxide system in 1989 (granted in 1993), this technology was too late to capture any market for the CFC phase-out (Lorentzen and pattersen, 1993).

Major industry support hastened the transition from CFC to HFC refrigerants. The mobile air conditioning (MAC) sector was first in 1988 to agree to recover and recycle refrigerants and was the first in 1990 to announce plans to replace CFC-12 with HFC-134a. The early MAC commitment to HFC-134a gave the chemical manufacturers the confidence to invest in full scale production, even before the toxicity testing and the government approval was completed. HFC-134a was quickly embraced by other refrigeration and air conditioning applications because it was similar to CFC-12, non-flammable, non-toxic, proven compatible with specific lubricants, competitively priced and widely available. Coca-Cola, the world’s largest customer for refrigerator cases and vending machines, also made an early worldwide commitment to HFC-134a, which encouraged their suppliers in both developed and developing countries to take ozone layer protection seriously and to move quickly with the CFC-12 phase-out.

1.3.4 1995 and Continuing: Natural Refrigerant Stage a Come-Back

Natural refrigerants staged a cone-back in 1990s. In 1992, Greenpeace inspired European government, industry and customer for the use of hydrocarbons in domestic refrigerators (Greenpeace, 2006). Within one year a hydrocarbon domestic refrigerator was introduced in Germany, and it rapidly penetrated and expanded across the market. Soon hydrocarbon refrigerators gained market dominance in Europe and penetrated markets in Asia, including Japan. Meanwhile, suppliers of equipment using ammonia as a natural refrigerant recaptured the market from HCFC cold storage and food freezing, They also made limited progress in applying ammonia to commercial refrigeration and air conditioning using secondary loops for safety. At the same time, European researchers with the help of European vehicle manufacturers—particularly the German automobile manufacturers—pursued carbon dioxide for use in mobile air conditioners.

Despite their comeback, natural refrigerants still faced stiff competition at the turn of the millennium, although companies in developed countries had halted the use of CFC refrigerants in new equipment by 2000, there was still plenty of CFC refrigerant around. Refrigerant stockpiles and recycling provided an ample CFC supply for service of CFC equipment, as did a conspicuous illegal trade in Europe and North America. Some equipment was retrofit from CFCs to HCFCs, but new equipment provided energy saving which made retrofit financially and environmentally unattractive by comparison. In Australia and elsewhere, some MACs were retrofit to use hydrocarbon despite the opposition of vehicle manufacturers and service associations (and despite the findings by US EPA that CFC MAC systems are unsuitable for retrofit to hydrocarbon because of high leak rates potentially unreliable aging parts and the absence of systems to mitigate fire risks.) HCFC refrigerants

> were also pervasive in 2000 because Montreal Protocol controls on HCFC were years away and most countries had not scheduled aggressive early phase-out.
>
> Today natural refrigerants compete favorably against fluorocarbon refrigerants in an increasing variety of applications and systems. Hydrocarbon natural refrigerants are competitive in systems with relatively small charges but only in a very small number of systems with large charges. Ammonia is increasingly competitive in industrial and commercial refrigeration, nut has not significantly penetrated air conditioning applications, In Japan, there is considerable success with carbon dioxide heat-pump water heaters in markets where the only water heating competition is electric resistance.

This part reviewed the history of refrigerant selection, identifying lessons learned in refrigerant selection. One important lesson is the significance of safety issue and environmental impacts of refrigerants should be given enough attention in the evaluation process. Moreover, how to balance from different sectors or impacts, for example global warming and ozone depletion, is also a huge challenge. The Parties to the Montreal and Kyoto Protocols need to rethink their considerations and coordinate their actions. Reconsiderations by the Parties to the Montreal Protocol and by regional and national environmental authorities is particularly important for those cases where a refrigerant scheduled for Montreal Protocol phase-out environmentally outperforms alternatives in modern systems. So far, the most suspicious example of this is that HCFC-123 often demonstrates better Life Circle Climate Performance in commercially available building air conditioning chillers than HFCs and natural refrigerant alternatives.

1.4 Possible Future Refrigerants

On one side, manufacturers and researchers are endeavoring to explore new alternative refrigerants. However considering the influences of chemical composition on the behavior of refrigerants, the possibility of finding an ideal refrigerant, particularly with the exhausting searches performed to date, is practically zero. Those waiting for a perfect solution will be disappointed. Based on the existing simple refrigerants, from an engineering perspective, each element of added complexity increases costs, refrigerant charge amount, the potential for leaks, and thermodynamic irreversibility. Each addition also reduces the system's reliability. Hence, simple refrigerant molecules have an inherent advantage to reach higher efficiencies at lower costs and with lower system risk of environmental harm. Conversely, elimination of the simple molecules implies higher system costs and higher risks.

Another lesson from the repeated searches for new refrigerants is that the number of suitable elements that can be combined at the molecular level is small. Figure 2 below returns to the elements identified by Midgley and his cohorts as well as subsequent research.

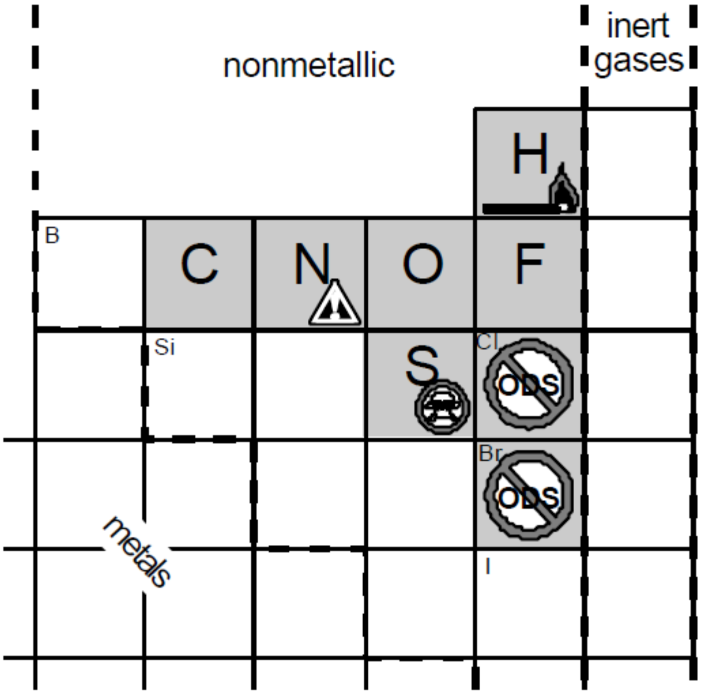


Figure 2 Candidate Elements of Refrigerants

Examinations of these options suggest that increasing the content of:

- carbon increases the molecule size, generally increasing the normal boiling point and molar heat capacities, making large molecules unsuitable;
- nitrogen makes the resulting compound more reactive, generally increasing toxicity and decreasing stability;
- oxygen reduces the atmospheric stability, and therefore ODP and GWP, but also may increase flammability, reactivity, and toxicity;
- sulfur generally increases toxicity and may decrease stability;
- hydrogen generally decreases atmospheric lifetime, and therefore ODP and GWP, but also increases flammability especially when the number of hydrogen atoms exceeds the number of connected halogen atoms;

- fluorine attached to carbon increases the GWP, particularly in perfluorinated molecules;
- chlorine increases lubricant miscibility, but also the ODP and, generally, the toxicity;
- bromine rapidly increases the ODP, but greatly diminishes flammability, and total fraction of attached halogens increases atmospheric lifetime, particularly for perhalogenated compounds, and therefore ODP and GWP.

1.5 Recent Projects on Refrigerant Assessment

Confronted such challenges, many institutions and manufacturers are developing projects on evaluating the existing and potential future refrigerants, and achieved some progress. While some research is concentrating on the evaluation by single indicator such as Global Warming Impact (GWP) - conducted by Intergovernmental Panel on Climate Change-, and Coefficient Of Performance (COP), some national and international projects are endeavoring to analyze from many aspects at the same time, some of which would be introduced as follows.

1.5.1 HCFC Phase-out Management Plans

In 2007, the Parties to the Montreal Protocol agreed to accelerate the phase-out of HCFCs (initially targeted for 2040) largely because of the substantive climate benefits this would bring about. Parties operating under the Montreal Protocol's Article 5(1) (mostly developing countries) may receive financial assistance from the Multilateral Fund for the implementation of the Montreal Protocol (MLF) to formulate their overarching strategy and prepare HCFC Phase-out Management Plans (HPMPs).

One of their country assistance is assessment and demonstration of HCFC alternative technologies by providing technical support and information with respect to alternative technologies and substances, taking into consideration, inter alia, ozone, climate benefits and energy efficiency; facilitating engagement of industrial and commercial enterprises in discussions related to alternative technology developments/assessments; assessing new low carbon technologies for use in developing countries; and promoting South-South cooperation.

In the assistance units, some projects involving potential refrigerants evaluation and relative new technology development are being funded. For example, with its financial and technical help, Media, a famous air conditioning manufacturer in China has completed the world's first refrigerant R290 split-type air conditioner demonstration production line, and the performance of R290 was carefully evaluated.

Since the assessment of refrigerants is not the only focus of this project, the evaluation methodology has not been developed fully and systematically in this project. However, its attempt and trial on new technologies and new refrigerants extend the study subjects, hence contributing to the future refrigerant selection.

1.5.2 Clean Air Act and Significant New Alternatives Policy (SNAP) Program

Started from 1963, the Clean Air Act is the law that defines EPA's responsibilities for protecting and improving the nation's air quality and the stratospheric ozone layer. In Section 612(c) of the Clean Air Act, the Agency is authorized to identify and publish lists of acceptable and unacceptable substitutes for class I or class II ozone-depleting substances, which are often used as refrigerants.

The Significant New Alternatives Policy (SNAP) Program is EPA's program to evaluate and regulate substitutes for the ozone-depleting chemicals that are being phased out under the stratospheric ozone protection provisions of the Clean Air Act (CAA). The purpose of the program is to allow a safe, smooth transition away from ozone-depleting compounds by identifying substitutes that offer lower overall risks to human health and the environment. According to SNAP, refrigerants are now classified as Acceptable, Acceptable subject to use conditions, Acceptable subject to narrowed use limits, Unacceptable, Pending alternatives, based on their human health harm and environmental risks. EPA's evaluation of each substitute in an end-use is based on the following types of information and analyses.

- Atmospheric effects

  The SNAP program considers the ozone depletion potential and 100-year integrated global warming potential of compounds to assess atmospheric effects.

- Exposure assessments-

  Exposure assessments are used to estimate concentration levels of substitutes to which workers, consumers, the general population, and environmental receptors may be exposed over a determined period of time. These assessments are based on personal monitoring data or area sampling data if available.

  - Releases in the workplace and in homes
  - Releases to ambient air and surface water
  - Releases from the management of solid wastes

- Toxicity data-

  Toxicity data is used to assess the possible health and environmental effects for exposure to substitutes. The Occupational Safety and Health Administration (OSHA) or EPA approves wide health based criteria that is available for a substitute such as:

  - Permissible Exposure Limits (PELs for occupational exposure)
  - Inhalation reference concentrations (RfCs for noncarcinogenic effects on the general population)
  - Cancer slope factors (for carcinogenic risk to members of the general population)

  If OSHA has not issued a PEL for a compound, EPA also considers Workplace Environmental Exposure Limits set by the American

Industrial Hygiene Association or Threshold Limit Values set by the American Conference of Governmental Industrial Hygienists. If limits for occupational exposure or exposure to the general population are not already established, then EPA derives these values following the Agency's peer reviewed guidelines.

Exposure information is combined with this toxicity information to explore any basis for concern. Toxicity data is used with existing EPA guidelines to develop health-based criteria for interim use in these risk characterizations.

- Flammability

  Flammability is examined as a safety concern for workers and consumers. EPA assesses flammability risk using data on:

  - Flash point and flammability limits (e.g. OSHA flammability/ combustibility classifications)
  - Data on testing of blends with flammable components
  - Test data on flammability in consumer applications conducted by independent laboratories

- Other environmental impacts-

  The SNAP program also examines other potential environmental impacts such as eco-toxicity and local air quality impacts. A compound that is likely to be discharged to water may be evaluated for impacts on aquatic life. Some substitutes are volatile organic compounds (VOCs), which are chemicals that increase stratospheric air pollution by contributing to ground-level ozone formation. In addition, EPA notes whenever a potential substitute is considered a hazardous air pollutant or hazardous waste.

The SNAP Program is fully supported and reinforced by EPA, providing the careful and detailed analysis of some ozone depletion substances (ODs) that are being phased out under the Clean Air Act (CAA). It reviews substitutes in eight sectors including some refrigerants, but considering that only a small part of refrigerants are ODs, the number of refrigerants being studied in SNAP Program is still quite limited. Moreover, even though the refrigerants are well classified into five categories as long as some criteria are satisfied, it does not compare those who perform well particularly with the HFCs or HCs.

1.5.3 Low GWP Alternative Refrigerant Evaluation Program

In response to environmental concerns raised by the use of high global warming potential (GWP) refrigerants, the Air-Conditioning, Heating, and Refrigeration Institute (AHRI) has launched an industry-wide cooperative research program to identify and evaluate promising alternative refrigerants since March 2011.

The program will consist of compressor calorimeter testing, system drop-in testing, soft-optimized system testing, and heat transfer testing. All tests other than heat transfer coefficient measurements are expected to be performed at participating companies' laboratories, using their own resources, at their own expense. Participating companies will include U.S. and international manufacturers. The heat transfer coefficient measurements will be contracted out on a competitive basis to universities and private research laboratories. The intent of the program is to help industry select the most promising refrigerants, understand technical challenges, and identify the research needed to use these refrigerants.

Basically this program is giving great attention on technical aspect based on practical experiments, but it is still on its initial stage.

1.6 Current Situation in Refrigerant Selection

1.6.1 Current Choice by Different Countries

Faced with the difficulty, every country made its own choice based on its technical level, environmental awareness, and the targets to achieve according to Kyoto Protocol on the phase out plan of HCFC and some HFC.

The table below shows the current choices by different countries.

Table 2 Currently Applied Refrigerants in Different Countries

Country	Current Main Choice
European Union	HFC 410A
Japan	HFC 410A; HFC 404a
The United States	HCFC 22 ; HFC 407c
China	HCFC 22 ; HFC 134a

Japan and EU are at the forefront in refrigerant policy and regulation and are still active in searching for the alternative refrigerants such as HFO-1234yf. On the other hand, China’s leading air conditioner companies have shifted their attention to R290 to reduce costs and increase competitiveness. But due to the flammability of HC290, more testing process is required.

1.6.2 Some potential Alternative Refrigerants

From the existing candidates, some alternative refrigerants are worthy of more detailed comment as follows.

- Ammonia

  Excellent environmental credentials, 0 ODP and 0 GWP; highly toxic, Flammable, highly noxious smell; extensively used in industrial refrigeration, food processing; only recently found limited usage in air conditioning applications.

- Hydrocarbons

  Excellent environmental credentials, 0 ODP and nearly 0 GWP; flammable and explosiveness; previously only used in large industrial refrigeration systems and recently, in domestic refrigerators; unsuitable for the majority of commercial air conditioning systems

- HFC 407c

  A ternary blend of HFC32, HFC 125 and HFC 134a; a zeotropic blend with a range or glide of approximately 5°C; no chlorine content, no ODP, and only a modest direct GWP; serves as an HFC refrigerant replacement for R-22 in various air-conditioning applications, as well as in most refrigeration systems.

- HFC 134a

  Good thermo physical properties and favorable heat transfer characteristics; low operating pressures, suitable for use in heat pumps and air cooled applications; widely used as a refrigerant in centrifugal chillers and automobile air conditioning; will be soon halted in EU.

- HFC410A

  A blend of HFC 32 and HFC125; a near azeotrope blend with no significant glide ; a very high refrigeration effect and operating pressures; good heat transfer ; successfully commercialized in the air conditioning, rapidly replacing HFC407C in split systems, mini chillers and some packaged units.

- HFC 404A

  A nearly azeotropic blend HFC 143a, HFC 125 and HFC134a; very high direct GWP.

- HFO 1234yf

  A fluorinated hydrocarbon; slightly flammable; lower lifetime greenhouse gas emissions; dramatically shorter atmospheric lifetime; compatibility with current automotive A/C systems; superior cooling efficiency; best ease of adoption; safety for mobile applications; proposed as a replacement for HFC134a in automobile air conditioners, developed to help automakers meet European regulations that go into effect in 2011 requiring that all new car platforms for sale in Europe use a refrigerant in its AC system with a GWP below 150.

- CO_2

  Naturally available, safe, 0 ODP and nearly 1 GWP with best thermo-physical and transport properties after ammonia; low critical point and high pressures in appliances.

2 METHODOLOGY

As mentioned before, up to now, there is no perfect alternative candidate and future discovery of ideal refrigerant is unlikely allowing for candidate elements. How to make an informed choice from the existing imperfect candidates for sustainable future remains a tough but significant challenge. Refrigerants are basically examined according to many criteria such as thermodynamic properties, safety and economic aspect, among which their environmental performance has been and will be given great attention. The previous studies were often concentrating on one aspect such as environmental performance or safety issue, or the several refrigerants in a specific and given appliances. In this paper, the assessment of refrigerants is based on their performance in safety issues, environmental protection, and economic efficiency, with thermodynamic property and technology innovation incorporated. Aiming at providing suggestions and recommendations to the national air conditioning industry associations and also international manufacturers, the differences of local climatic conditions, technical gap, customer’s use habit and environmental awareness among countries and regions are taken into consideration. Meanwhile case study of China and Japan utilizing this methodology are analyzed and compared.

2.1 Safety Issue

Refrigerant safety is straightforward: If the refrigerant stays contained in the cylinder or in the system then it presents little danger to people. The hazard occurs when the refrigerant comes out of the container or system, often quickly and unexpectedly. Basically injuries can be avoided if regular safety checks are performed. However depending on the types of refrigerants, each refrigerant has its own risk to cause dangerous incidents and that potential should be carefully evaluated and tested. Specific hazards from refrigerant fall into two categories: toxicity and combustion/flammability.

2.1.1 Toxicity

Most refrigerants have undergone extensive toxicity testing before being released for general refrigeration or air conditioning use. Testing generally involves a range of exposure levels and times to determine any possible effects on test animals.

- Short term exposures at high concentrations indicate any acute hazards such as irritation, sensitization of the heart or adrenaline and lethal concentration (LC_{50} is the amount which kills half the animals in a short amount of time).
- Tests that expose animals for longer periods of time, such as 90 days to two years, are designed to indicate chronic problems. These can include mutagenicity (changes to cells), reproductive problems, effects on organs or carcinogenicity (cancer-causing).

Exposure levels are values given to refrigerants to indicate how much of the chemical a person can regularly be exposed to without adverse effects. All toxicity test results are considered when setting this level. The first value is the occupational exposure limit, namely the Threshold

Limit Value - Time Weighted Average (TLV-TWA), which is the maximum allowable concentration of chemical a person can be exposed to repeatedly for 8 hours a day, 40 hours a week, without adverse health effects. Set by The American Conference of Government and Industrial Hygienists (ACGIH), it is an indication of chronic (long-term, repeat exposure) toxicity of the refrigerant. The values are based on the best available information from industrial experience and experimental testing.

The maximum value for any chemical is 1,000 ppm, though many refrigerants have shown no effects in toxicity testing at values much higher than that. Other organizations and chemical producers have similar exposure level indexes based on the same criteria. These are the Workplace Environmental Exposure Limit (WEEL) set by the American Industrial Hygiene Association (AIHA); Permissible Exposure Limit (PEL) set by OSHA; and Acceptable Exposure Limit (AEL) used by DuPont.

There is also the Short Term Exposure Limit (STEL), which is based on a 15-minute exposure time in any given day as well as the value Immediately Dangerous to Life or Health (IDLH). These are used to give guidance for machinery room requirements, ventilation and alarms in an emergency or escape situations, or in circumstances where short releases of refrigerant are expected, which could include refrigerant transfers or servicing large equipment.

Toxicity data is usually summarized in great detail on Material Safety Data Sheets (MSDS). The toxicity of refrigerants is well classified based on those indicators introduced above such as TLV-TWA in many related regulations or standards. According to Program for Alternative Fluorocarbon Environmental Toxicity, in the case of refrigerants, the indicator of TLV-TWA is more appropriate because it has stricter requirements and covers more toxic and harmful objects. In ANSI / ASHRAE 34(U.S.), EN 378(EU) and GB/T 7778(China) Standards for refrigerants, refrigerants are regarded low toxic and classified in Group A when its TLV-TWA is more than 0.04% (V/V). For those whose TLV-TWA is less than 0.04% (V/V), they are viewed as high Toxic and classified in Group B. This methodology of classification is most widely adopted in measuring the toxicity of refrigerants.

2.1.2 Flammability

Flammability is another key parameter in evaluating the safety level of a refrigerant. Flammable refrigerants present an immediate danger when released into the air. The refrigerant can combine with air at atmospheric pressure and ignite, causing a flame and possibly an explosion to occur. Because of the obvious hazards, the use of flammable refrigerants is restricted to environments that have proper ventilation, well airtight equipment.

Basically some indicators are often used to assess the flammability level of refrigerants.

- The lower flammability limit (LFL) is the lowest concentration at which the refrigerant burns in air under prescribed test conditions. It is an indication of flammability. It is typically given as a percentage by volume. The test is based at 77°F and 14.7 psia. To convert from a volume percentage to a density the percentage should be multiplied by 0.0000257*(molecular mass) to obtain lb/ft^3. The actual test method is described in Concentration Limits of Flammability of Chemicals, ANSI/ASTM Standard E681-85, American Society of Testing and Materials, Philadelphia, Pa., 1984.
- The heat of combustion (HOC) is an indicator of how much energy the refrigerant releases when it burns in air, assuming complete reaction to the most stable products in their vapor state. Negative values indicate endothermic reactions (those that require heat to proceed) while positive values indicate exothermic reactions (those that liberate heat).
- Burning Velocity is the function of the flammable gas concentration in the total mixture with air and can be measured at concentrations ranging from the lower propagation limit (LPL) of the flame to the upper propagation limit (UPL). The burning velocity reaches a maximum in the vicinity of the stoichiometric concentration. So

the ranking is based on the maximum BV of a given refrigerant. Several methods of BV measurement are available and each of them presents its own advantages and drawbacks. The most well known are for the non-stationary flame methods: the tube method, the bubble method, the spherical bomb, and for the stationary ones: the burner and the flat flame methods.

Similar to the toxicity assessment, the flammability level of refrigerants is also emphasized in some famous regulations and standards, such as ANSI / ASHRAE 34(U.S.) and EN 378(EU). In ASHRAE 34, three categories: 1, 2, and 3 and one optional subclass: 2L have been created based on lower flammability limit (LFL) testing, heat of combustion (HOC), and the optional burning velocity measurement.

- 1: is not flammable at 101 kPa and 21°C
- 2: LFL > 0.1 kg/m^3 at 101 kPa and 21°C and HOC < 19 MJ / kg
- 2L(optional): LFL > 0.1 kg/m^3 at 101 kPa and 21°C and HOC < 19 MJ / kg, with a maximum burning velocity(BV) of≤10 cm/s when tested at 23 °C and 101.3 kPa
- 3: LFL < 01 kg/m^3 at 101 kPa and 21°C and HOC >19 MJ / kg

In most cases, refrigerants are categorized into these three classes: higher flammability, lower flammability (including both 2 and 2L) and no flam Propagation, with the methodology introduced in ANSI / ASHRAE.

2.1.3 Relevant Standards

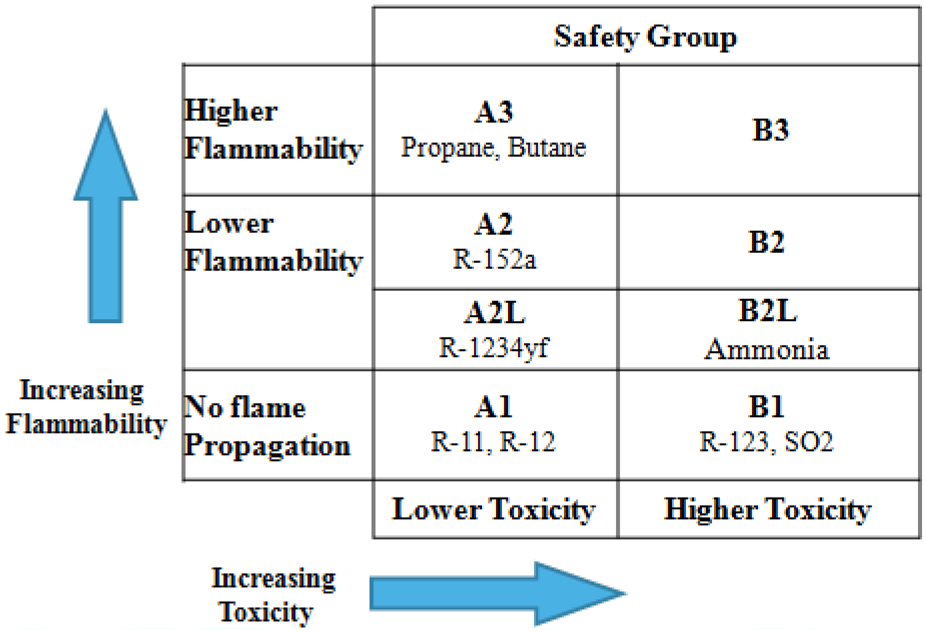
As mentioned before, some countries or organizations have made their own security requirements and classification criteria, which is of great help to evaluate the refrigerants in safety perspective. Although these regulations and criteria have some differences, basically they are complying with the same principles. Table 3 shows the details of some important relevant standards.

Table 3 Important Relevant Standards on Refrigerants

Country or Region	Standards	Safety Groups
	ISO 5149 Cooling and Heating Mechanical Refrigeration System's Security Requirements	Level 1: no major harm to human health, non-flammable; Level 2: toxic or corrosive, LfLv $\geq$ 3.5%; Level 3: , LfLv $\leq$ 3.5%;
U.S.	ANSI / ASHRAE 34 The Number of Signs and Refrigerant Security Classification	Toxicity Category Grade A:non-toxic, TLV-TWA $\geq 400*10^{-6}$; Grade B:non-toxic, TLV-TWA $\leq 400*10^{-6}$; Flammability Classification Level 1: non-flammable; Level 2: HOC < 19MJ/kg, LFLw$\geq$ 0.1kg/m^3; Level 2L: same as Level 2+ maximum BV$\leq$ 10cm/s Level 3: HOC$\geq$19MJ/kg,LFLw < 0.1kg/m^3
EU	EN 378 Refrigeration and Heat Pump Systems - Safety and Environmental Requirements	Flammability Classification same as that of ISO5149. Toxicity Category basically the same flammability classification of ANSI / ASHRAE 34
Japan	Security Regulation for General High-Pressure Gas	Flammable refrigerant: LfLv ＜3.5% or (UFLv-LFLv) $\geq$ 20%; Non-flammable refrigerant: the rest
China	GB/T 7778 Number Designation and Security Classification of Refrigerants	basically the same flammability classification of ANSI / ASHRAE 34

Among these, ANSI / ASHRAE 34 “The Number of Signs and

Refrigerant Security Classification” is accepted most widely. This classification consists of Toxicity Category and Flammability classification at the same time. The capital letter corresponds to toxicity and the digit to flammability, shown as Figure 3.



	Safety Group	
Higher Flammability	**A3** Propane, Butane	**B3**
Lower Flammability	**A2** R-152a	**B2**
	A2L R-1234yf	**B2L** Ammonia
No flame Propagation	**A1** R-11, R-12	**B1** R-123, SO2
	Lower Toxicity	**Higher Toxicity**

Figure 3 Safety Classification of Refrigerants

This methodology of classification combines both toxicity and flammability as a whole indicator to evaluate the safety performance of refrigerants, and will be adopted in this research. Blends whether zeotropic or azeotropic, with flammability and/or toxicity characteristics which may change as the composition changes during fractionation, shall be assigned a safety group classification based on the worst case of fractionation.

2.2 Environmental Protection

Chlorofluorocarbons (CFCs) and hydrochlorofluorocarbons (HCFCs) can affect both stratospheric ozone and climate change, whereas hydrofluorocarbons (HFCs) can affect climate change. Ozone depletion and global warming are major environmental concerns with serious implications for the future development of the air conditioning industries.

2.2.1 Ozone Depletion Impact

The stratospheric ozone layer filters out the UV-B portion of the sun’s ultraviolet (UV) radiation. Overexposure to this radiation increases the risk of skin cancer, cataracts, and impaired immune systems. It also can damage sensitive crops, reduce crop yields, and stress marine phytoplankton (and thus human food supplies from the oceans). In addition, exposure to UV radiation degrades plastics and wood. Stratospheric ozone depletion has been linked to the presence of chlorine and bromine in the stratosphere. Chemicals with long atmospheric lifetimes can migrate to the stratosphere, where the molecules break down from interaction with ultraviolet light or through chemical reaction. Chemicals such as CFCs and HCFCs release chlorine, which reacts with stratospheric ozone, thus thinning the ozone layer.

According to McQuay International, the second largest air conditioning, heating, ventilating and refrigeration company in the world, by 2002, about 27% of the CFCs in the atmosphere are from refrigerant emissions. HCFC refrigerant emissions account for 83% of the total HCFCs found in the atmosphere. As of 1996, refrigerants were responsible for 28% of the anthropogenic ozone depletion. Refrigerants over the next century will be responsible for 24% of the anthropogenic ozone depletion.

In 1987 the Montreal Protocol on Substances That Deplete the Ozone Layer was ratified, forcing abandonment of these ozone-depleting substances (ODSs). Thanks to these efforts, the concentrations of CFCs, HCFCs and other ODs both in the atmosphere and the stratosphere had peaked and are now slowing declining.   The ozone layer is expected to return to pre-industrial levels by the middle of this century. Refrigerants have been and will continue to be a major factor in ozone depletion.

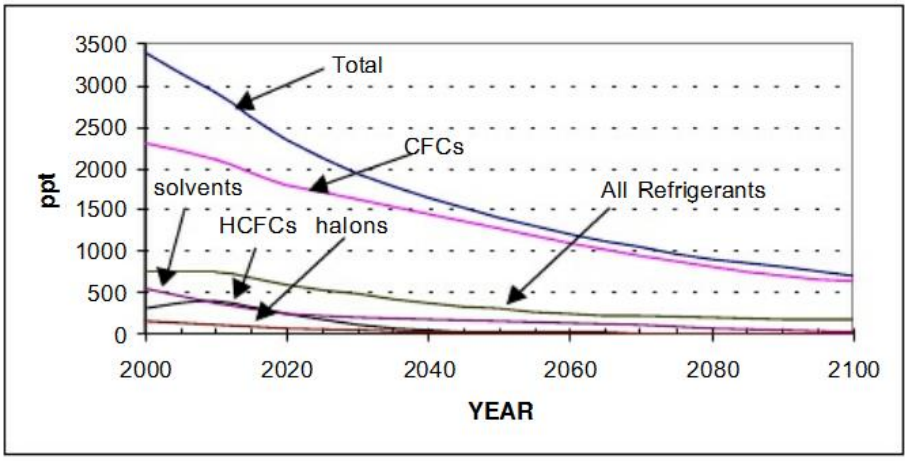


Figure 4 Ozone Depletion Capacity Based on Global Adherence to the Montreal Protocol

To assess a material’s ability to deplete stratospheric ozone, Ozone Depletion Potential (ODP) is most widely used. Firstly proposed by Wuebbles in 1983, it was defined as the ratio of global loss of ozone due to given substance over the global loss of ozone due to CFC-11 of the same mass.

ODP can be estimated from the structure of a given substance. Chlorofluorocarbons (CFCs) have ODPs roughly equal to 1. Brominated substances have usually higher ODPs in range 5 - 15, because of more aggressive bromine reaction with ozone. Hydrochlorofluorocarbons (HCFCs) have ODPs mostly in range 0.005-0.2 due to the presence of the hydrogen which causes them to react readily in the troposphere, therefore reducing their chance to reach the stratosphere. Hydrofluorocarbons (HFCs) have no chlorine content, so their ODP is essentially zero. The ODPs for blends are mass-weighted averages.

The table below shows the ODP values of some refrigerants.

Table 4 ODP of Some Refrigerants

Refrigerants	CFC -11	HCFC -142b	HFC -410a	HCFC -22	HFC -32	R -290	R -717
ODP	1.0	0.043	0	0.034	0	0	0

2.2.2 Global Warming Impact

Another environmental issue that was also partly caused by refrigerants is global warming. Global warming, sometimes referred to as climate change is a serious challenge caused by the Greenhouse Gases (GHGs). Many substances are greenhouse gases, including methane, nitrous oxide, chlorofluorocarbons (CFCs), hydrochlorofluorocarbons (HCFCs), Hydrofluorocarbons (HFCs), perfluorocarbons (PFCs), sulfur hexafluoride (SF_6) and carbon dioxide (CO_2). CFCs, HCFCs and HFCs represent most of the substances used for refrigerants in the world today. Much of the electrical power used to operate air conditioning systems comes from the burning of fossil fuels, which emit CO_2, also a greenhouse gas.

Refrigerants affect global warming in two ways. The first way is when released directly into the atmosphere. This part of impact is usually expressed by the Global Warming Potential (GWP) of refrigerants, which compares the abilities of different greenhouse gases to trap heat in the atmosphere, relative to CO2. Most of the refrigerants in use today have some level of GWP. Some are very high. The good news is the actual amount of refrigerants released to the atmosphere is very small (especially when compared to CO_2 emissions) and so the overall direct effect is limited. Over the period 2000-2100, CFC, HCFC and HFC refrigerant manufacture and emissions will account for only 3% of the total climate forcing due to long-lived anthropogenic greenhouse gases.

The second way refrigerants affect global warming is indirect and deals with system efficiency. In many cases the energy used to operate an air conditioning system comes from the burning of fossil fuels. The carbon dioxide released in this process affects climate change. The more efficient the air conditioning system, the less carbon dioxide released.

Total Equivalent Warming Impact (TEWI) helps to assess the climate-change impact fairly, as a life-cycle approach, it accounts for both the direct and indirect effects in evaluating global warming. TEWI highlights the importance of careful consideration of overall system efficiency over the life of the product. Its calculation method is shown as follows:

$$\mathrm{TEWI} = \mathrm{GWP} \times \mathrm{L} \times \mathrm{n} + \mathrm{GWP} \times \mathrm{m} \times (1 - \alpha) + \mathrm{n} \times \mathrm{E} \times \beta \qquad (1)$$

Where, L - leakage rate per year (kg);

n - system operating time (year);

m - the refrigerant charge (kg);

α - recycling factor;

E - energy consumption per year by thermal power(kW·h);

β - CO2-emission/ per (kW·h).

Figure 5 shows the Stella model of TEWI for a country.

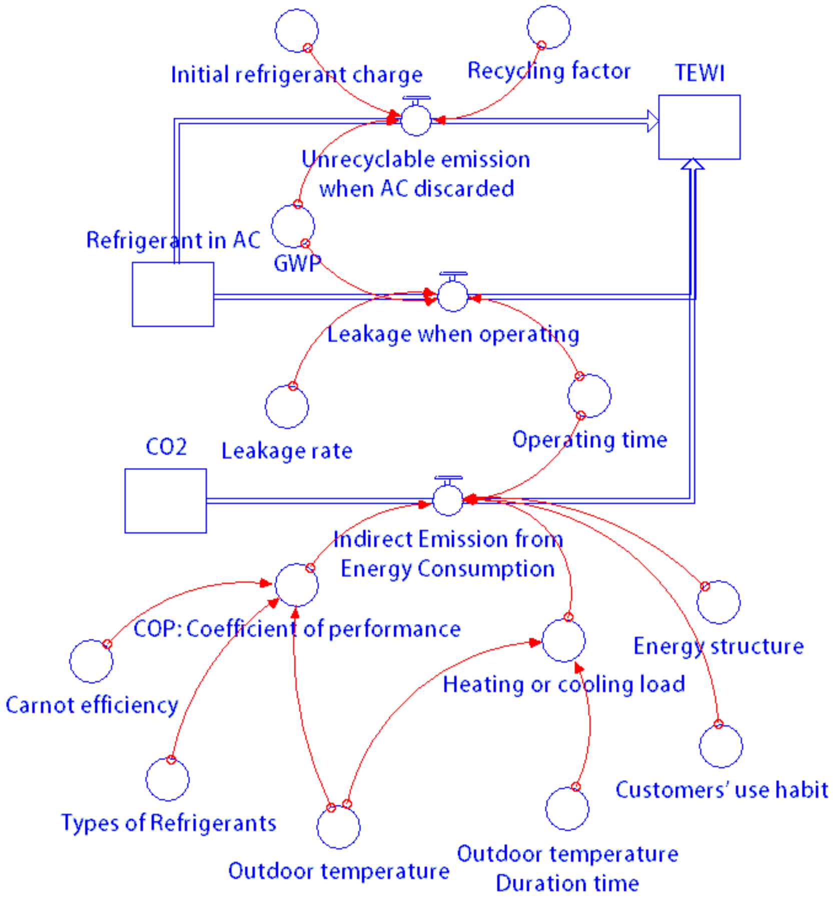


Figure 5 Stella Model of TEWI for a country

In the stella model, three parts of CO_2 emission contribute to TEWI. The first part is the direct emission of the unrecyclable refrigerant omitting into the atmosphere when the air conditioner is discarded. The second part is direct emission of the leakage of refrigerants while AC system is operating. The third part is the indirect emission due to energy consumption. To calculate TEWI, many parameters and situations should be taken into consideration. Some are relatively easy to acquire, such as GWP , while others are quite difficult, particularly in the case of COP. In principle, energy efficiency depends very much on the type of refrigerant selected, which results in great differences on energy consumption (E).

Meanwhile, the outdoor temperature and its duration time also affect it by imposing an influence on determining coefficient of performance (COP) and heating or cooling load in the following ways which are stated in Room Air Conditioners, Japan Industrial Standard C 9612,2005:

Cooling: $$\mathrm{BL_c(t)} = \Phi_{\mathrm{cr}} \times \frac{(\mathrm{t}-23)}{(33-23)} \qquad (2)$$

Heating: $$\mathrm{BL_h(t)} = \frac{1.25\times\Phi_{\mathrm{hr}}\times 0.82\times(17-\mathrm{t})}{17} \qquad (3)$$

Where, $BL_c(t)$ - cooling load when the outdoor temperature is t ℃;

$BL_h(t)$ - heating load when the outdoor temperature is t ℃;

Φ_{cr} - rated cooling capacity (w);

Φ_{hr} - rated heating capacity (w);

t - the outdoor temperature.

In this research, the heating and cooling load are assumed to be 3.6 kW and 2.8 kW respectively, which are the common parameters of a representative room air conditioner in Japan and China. Hence the loads for a conventional room using typical residential air conditioner are shown in graph 6.

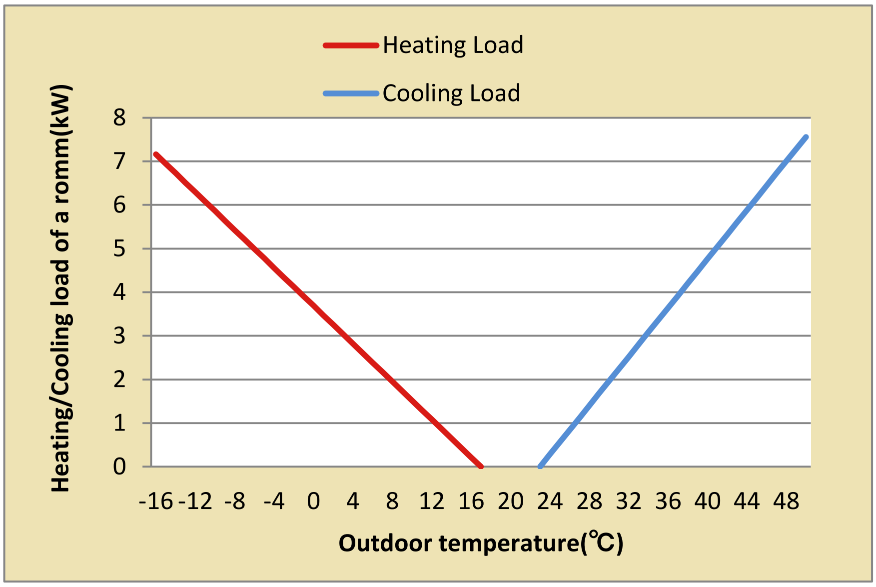


Figure 6 Heating/Cooling Loads for A Conventional Room Using Typical Residential Air Conditioner

The thermodynamic efficiency of an air conditioning system varies a lot with its operating temperature. As for the case of COP, when the recommended indoor temperature is set, the outdoor temperature is an important determinant. Figure 7 shows the working process of air conditioner where the basic principles are that liquids (refrigerants) absorb heat when changed from liquid to gas and gases (refrigerants) give off heat when changed from gas to liquid.

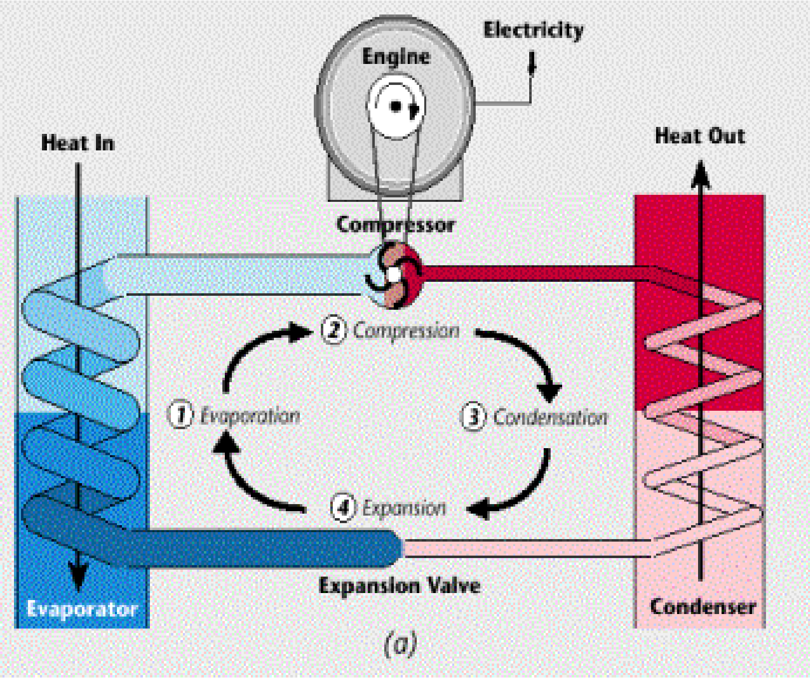


Figure 7 Air Conditioning System

For an air conditioning system to operate with economy, the refrigerant must be used repeatedly. For this reason, all air conditioners use the same cycle of compression, condensation, expansion, and evaporation in a closed circuit. The same refrigerant is used to move the heat from one area, to cool this area, and to expel this heat in another area.

- The refrigerant comes into the compressor as a low-pressure gas, it is compressed and then moves out of the compressor as a high-pressure gas.

- The gas then flows to the condenser. Here the gas condenses to a liquid, and gives off its heat to the outside air.

- The liquid then moves to the expansion valve under high pressure. This valve restricts the flow of the fluid, and lowers its pressure as it leaves the expansion valve.

- The low-pressure liquid then moves to the evaporator, where heat from the inside air is absorbed and changes it from a liquid to a gas.

- As a hot low-pressure gas, the refrigerant moves to the compressor where the entire cycle is repeated.

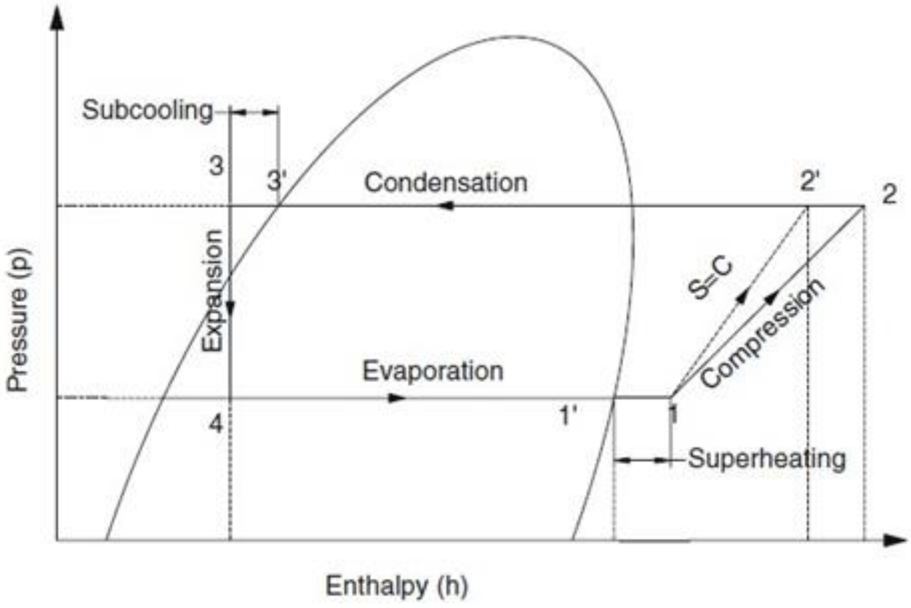


Figure 8 Carnot Cycle

Figure 8 shows the thermodynamic principles of air conditioner called “Carnot Cycle” in which the states of four points including the temperatures, pressures and enthalpy are determined, COPs could be figured out.

Cooling: $$\mathrm{COP_c} = \frac{h_1 - h_4}{h_2 - h_1} \quad (4)$$

Heating: $$\mathrm{COP_h} = \frac{h_2 - h_3}{h_2 - h_1} \quad (5)$$

Where, $\mathrm{COP_c}$- coefficient of performance for cooling process;

$\mathrm{COP_h}$- coefficient of performance for heating process.

To calculate COP under different outdoor temperatures, refrigerant parameters from Refprop are applied. Refprop (Reference Fluid Thermodynamic and Transport Properties Database), published by the National Institute of Standards and Technology (NIST), is a database software used in science research. Its program uses equations for the thermodynamic and transport properties of refrigerants to calculate the state points of the fluid or mixture. These equations are the most accurate equations available worldwide.

By quantitative analysis using programming, based on the assumption of 5℃ temperature difference between evaporating/ condensing temperature and outdoor/ indoor temperature respectively and 80% compression coefficient, and also if the outdoor temperatures in a specific area is acquired, the ideal COPs under different outdoor temperatures are accessible.

Then by using the equation below, E'(the energy consumption/year) by an air conditioning system in a specific area can be figured out.

$$E' = \sum_{q}^{t=14} \frac{BL_h(t)}{COP_t} + \sum_{t=24}^{j} \frac{BL_c(t)}{COP_t} \quad (6)$$

Where, E' - the energy consumption/year;

COP_t - coefficient of performance of air conditioning system by a refrigerant when the outdoor temperature is t ℃;

$BL_c(t)$ - cooling load when the outdoor temperature is t ℃;

$BL_h(t)$ - heating load when the outdoor temperature is t ℃;

$$E = \alpha \times E' \tag{7}$$

E - energy consumption per year by thermal power (kW·h);

α - percentage of thermal power accounting for in total power supply.

It should be noted that the E' acquired from the equation is based on the ideal conditions and cannot present the real situation. To solve this problem, the Carnot Efficiency is introduced and applied. Carnot Efficiency is the gap between practical COP and ideal COP, and regarded as the same in a country’s case resulting from the technical level. Hence the estimated practical energy consumption by room air conditioners could be achieved if Carnot Efficiency is known. In this process, Annual Performance Factor (APF) is a useful tool, which takes into account not only power consumption at rated time but also load conditions such as buildings where air conditioners are used and purpose of use, outside air temperature while cooling or heating, and efficiency of the air conditioner depending on the differing capacities of inverter devices, thus making it possible to evaluate energy consumption performance against utilization. APF is defined as follows which is also stated in Room Air Conditioners, Japan Industrial Standard C 9612,2005:

$$\mathrm{APF} = \frac{\text{Heating Season Total Load+Cooling Season Total Load}}{\text{Heating Season Total Energy+Cooling Season Total Energy}}$$

$$= \frac{Total\ Load}{E'} \qquad (8)$$

On the basis of the equation, the ideal APF could be figured out and then compared with the actual ones of products widely used in one country, the Carnot Efficiency of one country can be available. Hence the estimated practical energy consumption by room air conditioners could be figured out.

When evaluating TEWI from the national perspective, different local climate conditions and climatic regionalization should be taken into consideration. In each region, the outdoor temperature and its duration time at a certain time are regarded as the same. Consequently, TEWI in average for a whole country could be defined as below:

$$\text{TEWI in average} = \mathrm{GWP} \times \mathrm{L} \times \mathrm{n} + \mathrm{GWP} \times \mathrm{m} \times (1-\alpha)$$

$$+ \frac{\mathrm{n}\times\beta\times\left\{\sum_{\mathrm{m}=1}^{\mathrm{n}}\left(\mathrm{N_m}\times\sum_{\mathrm{q}}^{\mathrm{t}=14}\frac{\mathrm{BL_h(t)}}{\mathrm{COP_t}}\right)+\sum_{\mathrm{m}=1}^{\mathrm{n}}\left(\mathrm{N_m}\times\sum_{\mathrm{t}=24}^{\mathrm{j}}\frac{\mathrm{BL_c(t)}}{\mathrm{COP_t}}\right)\right\}}{\left(\sum_{\mathrm{m}=1}^{\mathrm{n}}\mathrm{N_m}\right)\times\gamma} \qquad (9)$$

Where, $\mathrm{N_m}$ - the number of RAC in region m;

COP_t - coefficient of performance of air conditioning system by a refrigerant when the outdoor temperature is t ℃;

$BL_c(t)$ - cooling load when the outdoor temperature is t ℃;

$BL_h(t)$ - heating load when the outdoor temperature is t ℃;

γ - Carnot Efficiency.

It should be noted that there are other mechanical methods for evaluating global warming, such as Life Cycle Assessment (LCA) and Life Cycle Climate Performance (LCCP), which even include the production and transportation processes of refrigerants compared with TEWI. However, since the processes differ from case to case and the access to relevant data is lacking, these indicators are not adopted.

2.2.3 Weighting Methodology and Environmental Indicator

To assess the environmental performance of refrigerants from a holistic perspective, weighting methodology is proposed to integrate the two relatively independent impacts into one single indicator. In the previous study, weighting methodology is usually used in the Life Cycle assessment of products in different environmental impacts such as greenhouse effect, acidification and eutrophication. Weighting is the process of converting indicator results of different impact categories by using numerical factors based on value-choices. And in the case of environmental impact, it evidently reflects not only scientific influence, but also the social value, and political views.

Weighting factor for a particular type of environmental pollution may be determined by one or more principles as below:

- The social evaluation (expressed in financial terms) of damage to the environment.

- The prevention costs for preventing or combating the relevant environmental impact by technical means.
- The energy consumption that is necessary to prevent or combat the environmental impact by technical means.
- Avoiding the use of weighting factors by using only one environmental effect, in this case energy consumption, as a measure of the total environmental pollution.
- The evaluation of experts (for example, a group of respondents in a panel) who express the relative seriousness of an effect by assigning a weight to the effect or impact.
- The degree by which a target level is exceeded. The greater the gap between the current environmental impact and a target level, the higher the rating given to the seriousness of the impact. In most situations, the target levels are derived from annual load targets as set by national environmental protection agencies, laws and regulations.

Among these principles, the last one is most widely used and adopted in weighting methodology such as Eco-Indicator 95/99. And based on it, here is the equation how to calculate the indicator value

$$\mathrm{I} = \mathrm{F_i} \times \mathrm{W_i} \times \frac{\mathrm{E_i}}{\mathrm{N_i}} \qquad (10)$$

Where, I - indicator value;

F_i - weighting factor or the reduction factor.

W_i - subjective weighting factor, aiming at making corrections in the event that the distance-to-target principle does not sufficiently represent the seriousness of an effect. Here in this paper, it is assumed as 1, which means the seriousness could be fully expressed by the distance-to-target principle.

Ei - contribution of a product life cycle to an effect i such as ODP and TEWI.

N_i - Normalization value, referring to the total characterized impact indicator result calculated on the basis of an inventory of all the society's activities in some given area and over a reference period of time. The scope of this assessment is the whole country.

By this means, if weighting factor, normalization value and the contribution of environmental indicator, such as TEWI or ODP are acquired, the normalized indicator values can be obtained, which can be added up directly to display the environmental performance of refrigerants from a holistic perspective.

2.3 Economic Efficiency

2.3.1 Cost and Availability

The first indicator for economic efficiency is obviously the refrigerant price. For manufacturers and customers they prefer to choosing the cheaper refrigerants if similar safety and environmental performances are shown. However the price differs from case to case due to the differences in production and transportation processes. Additionally the market of raw materials and relevant policies will also impose a huge influence on the price.

2011 started with significant price rises for refrigerants. This trend is expected to continue through the year with talk of increases by as much as 50% or more.

The causes are complex. All manufacturers and wholesale outlets are affected worldwide. These price hikes are a result of increased raw material costs, higher demand and limited production of key components. Demand is exceeding product availability for many refrigerants. At present stock availability from the manufacturers is only given at the time of ordering. Standing or forward orders are generally not being accepted. Bulk pricing is only given at time of acceptance of an order.

Key causes are:

- R-125 production does not meet global demand.
- Demand for HFC refrigerants is much higher than expected.
- Due to European F-Gas regulation preventing R-22 usage.
- Due to U.S usage replacing R22 at higher than forecast rates.
- Due to faster than anticipated recovery of the A/C manufacturing

after the global financial Crisis.

- R134a usage higher than forecast.
- R22 import quotas and a gross reduction in manufactured volume
- Raw material costs increasing (e.g. chloroform).

Such a broad array of issues has resulted in most common refrigerants being affected. There is no chance of an early recovery from this situation and the prognosis is that prices will continue to rise in 2012 and availability will remain very tight.

R-125 production affects most R-400 refrigerants. This includes R-402A, R-404A, R-407C, R-408A, and R-410A. It also affects R-507. All of these refrigerants contain some R-125 in their blend. Add to this R-22 and R-134a (due to manufacturing constraints) and rising raw material costs implies all common refrigerants will be affected.

The consequences of all of these factors has lead to a worldwide instability in pricing and availability of refrigerants

To compare the refrigerants on the same basis, all the refrigerant products are from DuPont and Honeywell, these two most famous refrigerants suppliers and if different prices appear, average price will be the final price for the refrigerant.

There are other cost that should be taken into consideration, such as costs for safety, handing. But unlike price, these costs are quite difficult to acquire. But according to some projects aiming at developing new technologies on refrigerants, some important implications should be noticed.

3 RESULTS

3.1 Safety Issue

As introduced in the methodology part, the refrigerants are classified according to the ANIS/ASHRAE 34, and the table below shows some results of alternative refrigerants.

Table 5 Classification of Some Refrigerants

Classification	Denomination	Composition or chemical formula (mass percentage)	Safety classification
INORGANIC COMPOUND			
R717	ammonia	NH3	B2L
R718	water	H2O	A1
R744	carbon dioxide	CO2	A1
ORGANIC COMPOUND			
R170	ethane	CH3CH3	A3
R290	propane	CH3CH2CH3	A3
R600a	isobutane	CH(CH3)2CH3	A3
Halocarbons			
Chlorofluorocarbons (CFCs) and Bromofluorocarbons (BFCs)			
R11	trichlorofluorometha	CCl3F	A1
R12	dichlorodifluorometh	CCl2F2	A1
Hydrochlorofluorocarbures (HCFC)			
R22	chlorodifluoromethan	CHClF2	A1
R141b	1,1-dichloro-1-fluor	CH3CCl2F	A2
R142b	1-chloro-1,1-difluor	CH3CClF2	A2
Hydrofluorocarbons (HFCs)			
R32	difluoromethane	CH2F2	A2L
R125	pentafluoroethane	CHF2CF3	A1
R134a	1,1,1,2-tetrafluoroe	CH2FCF3	A1
R143a	1,1,1-trifluoroethan	CH3CF3	A2L
R152a	1,1-difluoroethane	CH3CHF2	A2
Hydrofluoroolefin (HFOs)			
R1234yf	2,3,3,3-Tetrafluorop	CH2=CFCF3	A2L
R1234ze	1,3,3,3-Tetrafluorop	CHF=CHCF3	A1
Azeotropic mixtures			
R502		R22/R115 (48.8/51.	A1
R507		R125/R143a (50/50)	A1
Zeotropic mixtures			
R404A		R125/R143a/R134a (44/52/4)	A1
R407C		R32/R125/R134a (23/25/52)	A1
R410A		R32/R125 (50/50)	A1

The refrigerants currently being widely used in air conditioning industry, such as R-22, R-410A, R134a, and R407C are all categorized into group A1, with the properties of non-flammability and low toxicity. CFC and the blends refrigerants also perform well in the safety aspect. Some refrigerants from the other groups of halocarbons, namely HCFC, HFC and HFO, can be combustible, but limited to the lower level. It is noticeable that the three examples from HC group are with higher flammability which means risk of fire and explosion incidents should be seriously considered.

In table 5, all the candidates listed have low toxicity except R-717(Ammonia), showing low toxicity is one of the main concerns in the selection of alternative refrigerants.

3.2 Environmental Protection

3.2.1 Case Study of Japan

Aiming at obtaining the average TEWI in a certain air condition system special for a country, many factors should be taken into consideration, such as the climatic regionalization, the local climatic conditions including the outdoor temperature and its duration time, energy structure of the country, customers' use habit and also some technical parameters related to the national technological level in air condition and refrigeration industry. Relevant parameters are compiled from open literature data, displayed in Table 7. Ten year lifetimes are assumed for Japanese representative room air conditioner, while the initial charge, recycling factor, leakage rate and rated capability are all based on the common situation in Japan. The thermal power ratio and CO_2 emission rate numbers given in Table 7 are taken from the “Energy Report 2010” published by the Japanese Ministry of Economy, Trade and Industry, which provides the most recent data.

Table 6 Relevant Parameters for Average TEWI for Japan

Relevant Parameters	Values
Rated cooling capability	2.8kW
Rated heating capability	3.6kW
Equipment lifetime	10 years
initial refrigerant charge	2.5lbs
recycling factor	30%
leakage rate	2%
thermal power ratio	61.70%
CO_2 kg/kWh emission rate by thermal power	0.634 kg/kWh

According to JIS B 8616-2006, Japan is divided into 5 regions based on its local climate conditions, shown as Figure 9.

In each region, the local climate conditions are viewed as the same, meaning that at a certain time the outdoor temperatures in one region is regarded as the same and so is the duration time for a certain outdoor temperature.

Figure 9 Climatic regionalization of Japan

The outdoor temperature and its duration time in each region in Japan are as follows:

Table 7 Operation Time for Cooling

Outdoor temperature(℃)	Operation time for cooling(hr)				
	Region 1	Region 2	Region 3	Region 4	Region 5
24	196	137	153	77	187
25	225	126	150	67	188
26	225	116	160	56	172
27	240	102	196	34	168
28	181	50	122	29	176
29	122	53	94	15	154
30	93	33	72	10	157
31	92	14	48	12	147
32	35	8	25	3	73
33	11	4	5	0	34
34	6	2	2	0	22
35	4	0	0	0	6

Table 8 Operation Time for Heating

Outdoor temperature(℃)	Operation time for heating(hr)				
	Region 1	Region 2	Region 3	Region 4	Region 5
-16	1	0	0	0	0
-15	1	0	0	0	0
-14	2	0	0	0	0
-13	3	0	0	0	0
-12	3	0	0	0	0
-11	5	0	0	0	0
-10	14	0	0	0	0
-9	13	0	0	0	0
-8	38	0	0	0	0
-7	42	0	0	0	0
-6	67	1	0	0	0
-5	84	4	0	0	0
-4	99	9	2	0	2
-3	123	16	19	0	19
-2	87	31	67	0	3
-1	110	92	82	4	2
0	134	114	129	15	12
1	153	167	154	33	19
2	150	151	110	68	28
3	102	167	102	119	49
4	99	180	127	169	64
5	87	158	140	169	73
6	71	175	143	234	90
7	59	157	141	276	140
8	71	146	171	289	126
9	71	126	166	245	110
10	47	113	128	241	133
11	0	92	164	269	134
12	0	87	148	209	115
13	0	101	123	192	121
14	0	74	95	151	130

By adopting the equations (2) and (3) in the methodology part, the heating/cooling load under different outdoor temperature can be figured out. Combined with the coefficient of performance (COP_t) acquired from the programming listed in the Appendix, the energy consumption/year ($E^{'}$) when using different refrigerants in different regions can be worked out. To get the average value, the numbers of room air conditioners (RAC) in each region, displayed in Table 8, are estimated based on the ownership of RAC per household and the numbers of households in each region.

Table 9 Number of RAC in Each Region of Japan

Region	Prefectures or Cities covered	Number of RAC(unit)
1	Hokkaido	3878517
2	Aomori, Akita, Iwate	2220187
3	Yamagata, Miyagi, Niigata, Fukushima, Ishikawa, Toyama, Nagano, Gunma, Tochigi, Ibaraki, Fukui, Gifu Shiga	13738429
4	Kyoto, Aichi, Mie, Shizuoka, Yamanashi, Saitama, Kanagawa, Tokyo, Chiba, Nara, Osaka, Wakayama, Hyogo, Tottori, Okayama, Shimane, Hiroshima, Kagawa, Tokushima, Kochi, Ehime, Yamaguchi, Fukuoka, Oita, Saga, Nagasaki, Kumamoto	60549957
5	Miyazaki, Kagoshima, Okinawa	2735331
Total	Japan	83122421

On a basis of all the data, by using equation (6), ideal APF (Annual Performance Factor) when applying different refrigerants in Japan is calculated and compared with the actual ones. The typical room air conditioners selected in Japan are popular products from Daikin, Panasonic, Mitsubishi and Toshiba with 2.8kW rated cooling capacity. With average practical APF of 6.225 for R410A, the Carnot Efficiency for Japan is 0.550.

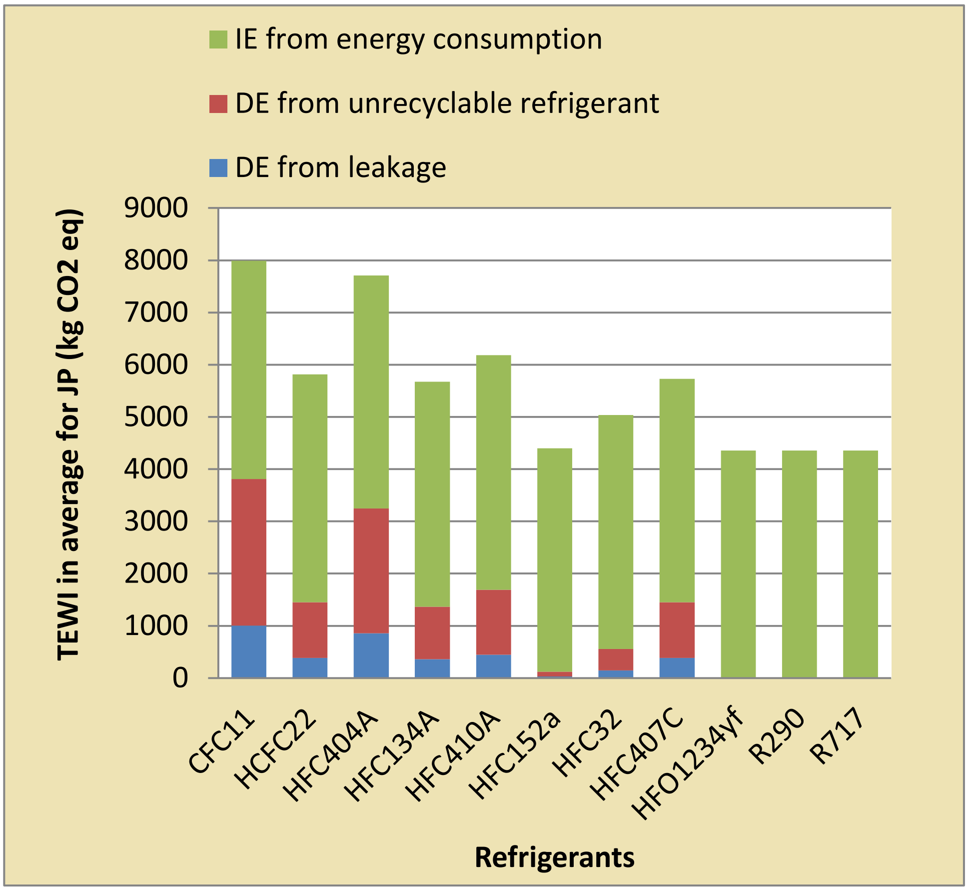


Figure 10 TEWI in average for RAC in Japan by different refrigerants

The average TEWIs of a room air conditioner in Japan by some typical are calculated based on the methodology introduced in Chapter 2. Figure 10 shows that TEWI for Japan when using different refrigerants varies a lot. Within the given samples, the highest one is 1.84 times of the lowest, with a gap of 3637.5 kg of CO_2. The best performance is given by HFO1234yf while the worst is CFC11, due to its high GWP of 4460. As for the indirect emission resulting from energy consumption, there exists some differences due to the efficiency difference of refrigerants. The direct emission also varies a lot because of the GWP difference of refrigerant. Direct TEWI accounts for less than 40% of the total in the example of CFC-11, where this ratio is the highest. Compared to the direct emission, the indirect one from energy consumption should be given priority, implying that those refrigerants with higher COP have great potential.

The customer’s use habit will affect the result to some extent. For example, after the Fukushima Nuclear Accident, due to the shortage of energy supply, in the following summer, the indoor temperature was suggested to be set at 28℃ instead of 27℃, and the TEWI would reduce 0.67% to 2.96% based on this model. Also a change in national or regional energy structure will cause a significant change in TEWI. Confronted with the challenge of careful reconsideration in nuclear power utilization, in a short term, more oil, LNG and coal, which belongs to the traditional power supply will be consumed to substitute for the loss by nuclear power, and this will increase the indirect emission caused by the air conditioning and TEWI. If the ratio of thermal power supply increases by 10% on the current basis, the TEWI will increase by 8.5% to 16.2%, with a net increase of 677.3 to 723.1 kg CO2. However in long term, renewable energy is taken as a central pillar in Japan's energy policy instead of thermal power, which was and is being emphasized by the Japanese government, and TEWI is expected to be lowered consequently. In addition, historical data from Energy Information Administration (EIA) and other sources indicate that carbon emissions from fossil-fueled power plants are falling gradually as a result of technology development and improvement, lowering TEWI in the future. The breakdown of TEWI in average for Japan gave more details. The energy consumption for heating is much bigger than that for cooling, with the lowest 2.29 times and the highest 21.6 times. Take HFC410A as an example shown in Figure 11.

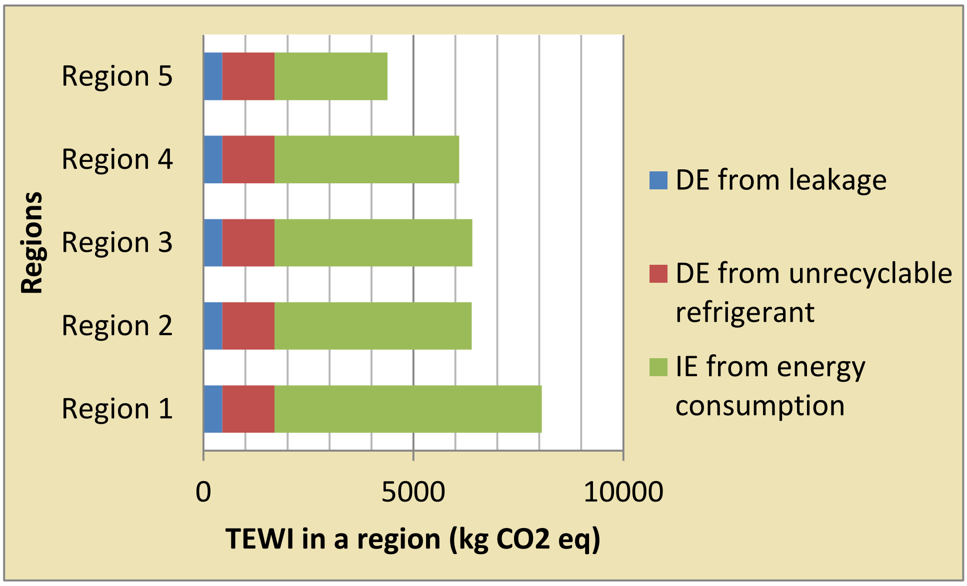


Figure 11 TEWI in Different Regions by HFC410A Refrigerant

From Region 1 to Region 5, the average temperature is getting higher, and evidently the TEWI value is getting smaller since the indirect emission is decreasing, implying in the cold areas, the COP which affects the indirect emission significantly should be paid enough attention when selecting refrigerants.

3.2.2 Case Study of China

In the case of China, the situation is much more complicate due to its complex and variable natural conditions and imbalanced economic growth.

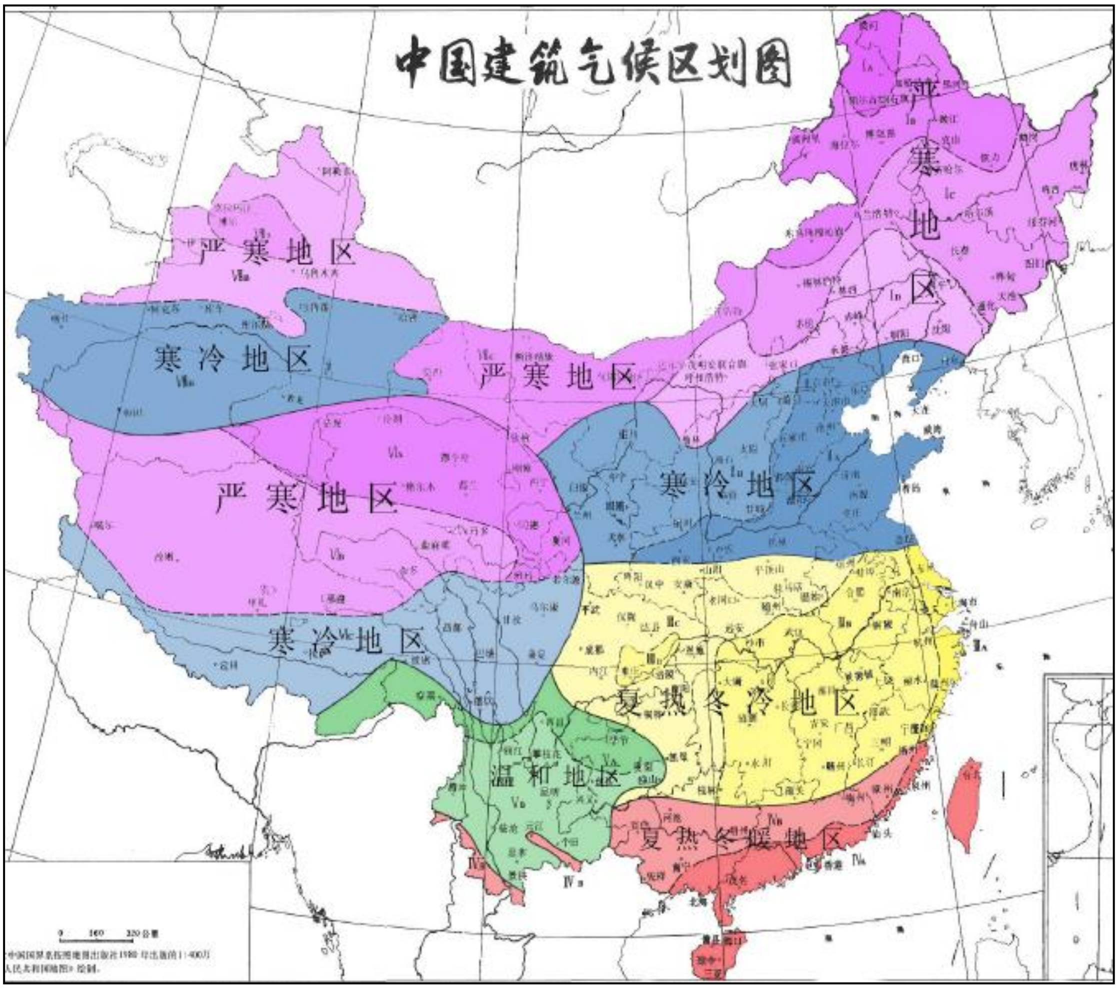


Figure 12 Climatic Regionalization of China

According to Chinese standard of climatic regionalization for architecture 50178-93, China is divided into 5 main regions showed in 5 colors, and to be more accurate, 20 areas in details. Climate conditions are quite different between areas. Detailed information is shown in Figure 12.

Unlike the case of Japan, the boundary of each region does not comply with that of a province or a city, resulting in difficulties in estimating the numbers of room air conditioners in each region. Assumption of uniform distribution of households in every province, including both urban and rural households is made. Based on some important data about each province in China, such as the ownership of RAC per urban/ rural household, number of households and total population by urban and rural residence displayed in Appendix, by utilizing Photoshop to divide and calculate the proportion of the area in a region accounting for certain provinces or cities involved in, combined with ownership of RAC per household in each province, the approximation of the number of room air conditioners in a region can be acquired, shown in table 10.

Table 10 Number of RAC in Each Region of China

Region	Provinces or municipalities (partly) covered	Number of RAC(unit)
Ⅰ $_A$	Heilongjiang, Inner Mongolia	66828
Ⅰ $_B$	Heilongjiang, Inner Mongolia	316909
Ⅰ $_C$	Heilongjiang, Jilin, Inner Mongolia	736568
Ⅰ $_D$	Jilin, Liaoning, Inner Mongolia, Hebei, Shaanxi	4420163
Ⅱ $_A$	Liaoning, Beijing, Tianjin, Hebei, Jiangsu, Anhui, Shandong, Henan, Shaanxi	58883717
Ⅱ $_B$	Inner Mongolia, Hebei, Shaanxi, Gansu, Ningxia	5116755
Ⅲ $_A$	Shanghai, Jiangsu, Zhejiang, Fujian,	28665407
Ⅲ $_B$	Jiangsu, Zhejiang, Anhui, Fujian, Jiangxi, Henan, Hubei, Hunan, Guangdong, Guangxi, Chongqing	77728710
Ⅲ $_C$	Anhui, Henan, Hubei, Hunan, Guangxi, Sichuan, Guizhou, Shaanxi, Gansu	23844915
Ⅳ $_A$	Fujian, Guangdong, Guangxi, Hainan, HongKong, Macao, Taiwan	32930880
Ⅳ $_B$	Fujian, Guangdong, Guangxi, Yunnan	23440908
Ⅴ $_A$	Sichuan, Guizhou, Yunnan, Tibet	919531
Ⅴ $_B$	Guangxi, Sichuan, Guizhou, Yunnan, Gansu	1033893
Ⅵ $_A$	Sichuan, Qinghai, Xinjiang	208702

Table 10 Number of RAC in Each Region of China (Continued)

Region	Provinces or municipalities (partly) covered	Number of RAC(unit)
Ⅵ B	Sichuan, Tibet, Qinghai, Xinjiang	140044
Ⅵ C	Sichuan, Yunnan, Tibet, Gansu, Qinghai	4977177
Ⅶ A	Xinjiang	14871
Ⅶ B	Xinjiang	92093
Ⅶ C	Inner Mongolia, Gansu, Xinjiang	180576
Ⅶ D	Gansu, Xinjiang	156783
Total	China	263875429

Similar to the case of Japan, in each region, the local climate conditions are regarded as the same. The outdoor temperature and its duration time in the 20 climatic regions in China are displayed in the Appendix. Other parameters are set as follows:

Table 11 Relevant Parameters for Average TEWI for China

Relevant Parameters	Values
Rated cooling capability	2.8kW
Rated heating capability	3.6kW
Equipment Lifetime	10 years
initial refrigerant charge	2.5lbs
recycling factor	0%
leakage rate	2%
thermal power ratio	75.6%
CO_2 kg/kWh emission rate by thermal power	0.800 kg/kWh

In China, Media and Gree are chosen as typical representatives and market shares of frequency conversion and fixed frequency air conditioning are also analyzed. The Carnot Efficiency for China is 0.353.

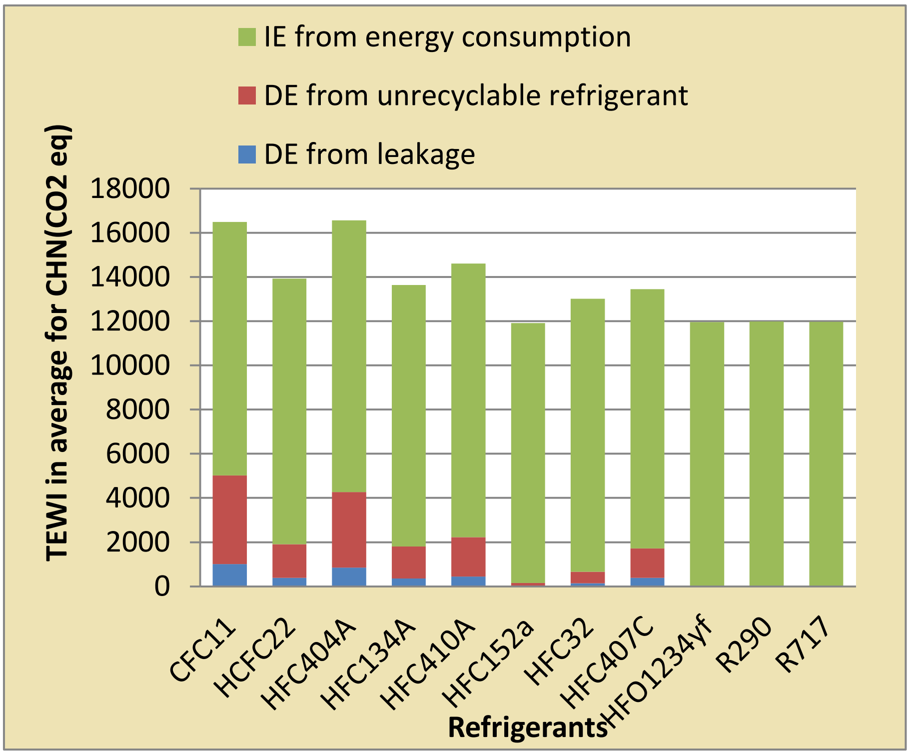


Figure 13 TEWI in Average for RAC in China by Different Refrigerants

Similar to Japan's case, the TEWI for China could be calculated and some similar conclusions could be drawn. However, according to the results in Figure 12, HFC152a performs the best while HFC404A is the worst.

The differences among regions are even more obvious. In 12 regions namely Ⅰ$_A$, Ⅰ$_B$, Ⅰ$_C$, Ⅰ$_D$, Ⅱ$_A$, Ⅱ$_B$, Ⅵ$_A$, Ⅵ$_B$, Ⅶ$_A$, Ⅶ$_B$, Ⅶ$_C$, Ⅶ$_D$, central heating is provided and TEWI includes the indirect CO$_2$ emission only resulting from cooling process. Moreover Climate conditions are quite different. For example, in Ⅰ$_A$ area, the lowest and highest air temperature is - 48 ℃and 33℃ respectively, while in III$_B$, they are - 4 ℃ and 39℃, which leads to the huge differences in TEWI in a region.

3.2.3 Comparison between Japan and China

In both cases, although some similar conclusions could be drawn, great differences exist among cases due to some significant factors, which may lead to affect decision-making process in refrigerant selection in the future.

When the same refrigerant is applied, TEWI of China is 2.06 to 2.75 times larger than that of Japan.

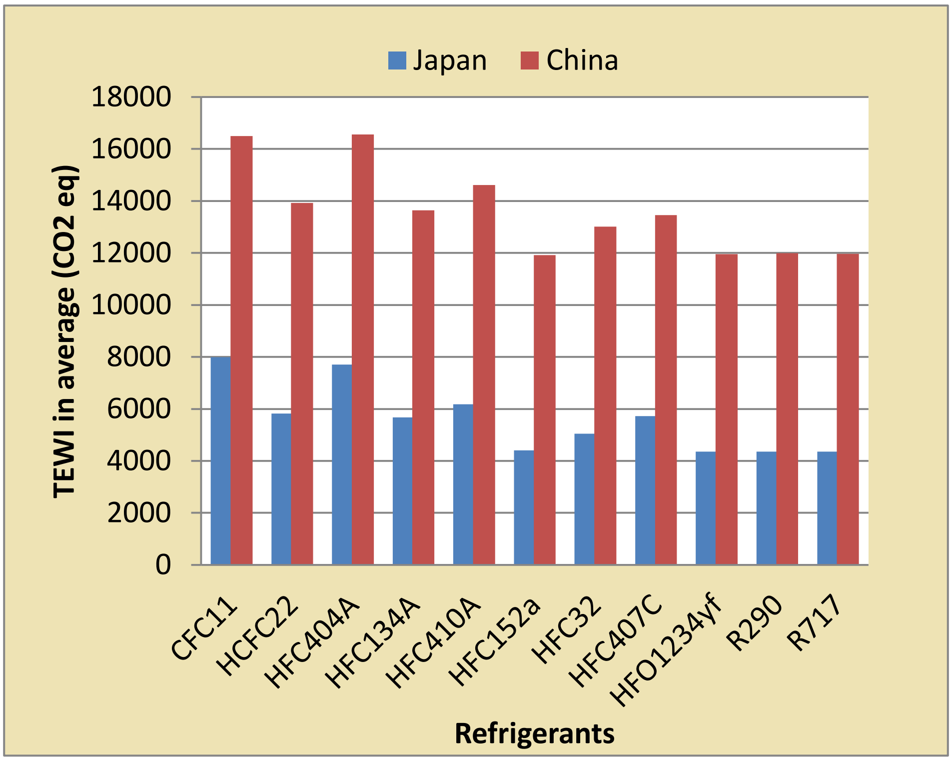


Figure 14 Comparison of Average TEWI by Different Refrigerants between China and Japan

This great difference is caused mainly by four reasons. Firstly, due to the technical gap and standard differences, the Carnot Efficiency for China is approximately 0.643 times of that for Japan, which leads to the different result. Secondly, the difference in CO_2 intensity for thermal power generation also helps further widens the gap. Compared with

China, Japan has advantages in technology and stricter requirement, with a lower CO_2 emission rate. The third cause is the difference in temperature and duration. From the national perspective, China has more extremely cold or hot hours than Japan, and during these periods, the efficiency of refrigerants would drop evidently while heating/cooling loads are raised, which means more energy would be consumed, thus resulting in a higher TEWI. Finally the energy structure also affects the results. In the indirect emission sector, only the thermal power produces the CO_2 emission, which means the less the thermal power accounts for in the energy structure, the lower TEWI for a country might be. Compared with 80.3% in China, Japan is 61.7%. These differences mainly affect the indirect emission resulting from the energy consumption, sequentially influencing TEWI, which is evident from Figure 15. It should be also noticeable that there is a fact that narrows the gap. In China, in winter, some areas are extremely cold and central heating is provided by the government. Among the 20 areas, about 12 are given this privilege and heating by air conditioners is unnecessary, in this way, TEWI for China is lowered.

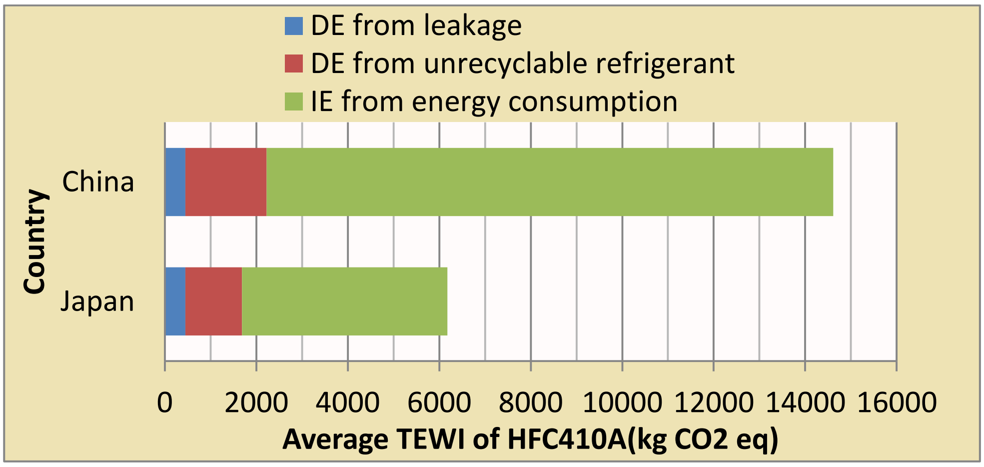


Figure 15 Comparison of average TEWI by HCF-410A refrigerant between China and Japan

Additionally, from Japan to China, both the best and worst performers change.

To assess the environmental impact from the holistic viewpoint, utilizing the weighting methodology introduced in Chapter 2, the total environmental indicator is calculated, shown in the Table 12.

Table 12 Environmental Indicator of Refrigerants for Japan and China

Indicator value(*10^{-3})	I_{ODP}		I_{GWP}		$I_{ENV.}$		Ranking	
Country	Japan	China	Japan	China	Japan	China	Japan	China
CFC11	3055.754	84.962	9.323	1.316	3065.077	86.278	11	11
HCFC22	103.896	2.889	6.787	1.111	110.683	4.000	10	10
HFC404A	0.000	0.000	8.994	1.322	8.994	1.322	9	9
HFC134A	0.000	0.000	6.622	1.089	6.622	1.089	6	7
HFC410A	0.000	0.000	7.210	1.166	7.210	1.166	8	8
HFC152a	0.000	0.000	5.133	0.952	5.133	0.952	4	1
HFC32	0.000	0.000	5.879	1.038	5.879	1.038	5	5
HFC407C	0.000	0.000	6.683	1.074	6.683	1.074	7	6
HFO1234yf	0.000	0.000	5.080	0.954	5.080	0.954	3	2
R290	0.000	0.000	5.086	0.957	5.086	0.957	2	4
R717	0.000	0.000	5.085	0.955	5.085	0.955	1	3

From the results here, obviously indicators value of same refrigerant for

Japan is 5.3 to 35.6 times of those for China, implying that a room air conditioner utilizing different refrigerants in the processes of operation and abandon impose more severe consequences of impairment of the local environment in the scope of Japan than that in China. Despite the higher absolute value of TEWI and ODs emission by a Chinese room air conditioning system, the relative value of environmental impact to a whole country that it causes is still limited due to its much larger territory area and huger population than Japan. This difference may affect the sensitivity of the national industry to environmental sector and may even lead to the final different choice in refrigerants. In both cases, we can see that CFC11 and HCFC22, these two typical second generation refrigerants have much higher Environmental Indicator value, which indicates the impossibility of these refrigerants to be reused. The current widely applied HFC410A in Japan and E.U. does not perform as well as some natural refrigerants. HFC group displays generally in both cases, except HFC152a. Natural refrigerants such as R717 and R290 are quite outstanding in environmental aspect. The best performers also change, but just remaining little advantage over the followers.

3.3 Economic Efficiency

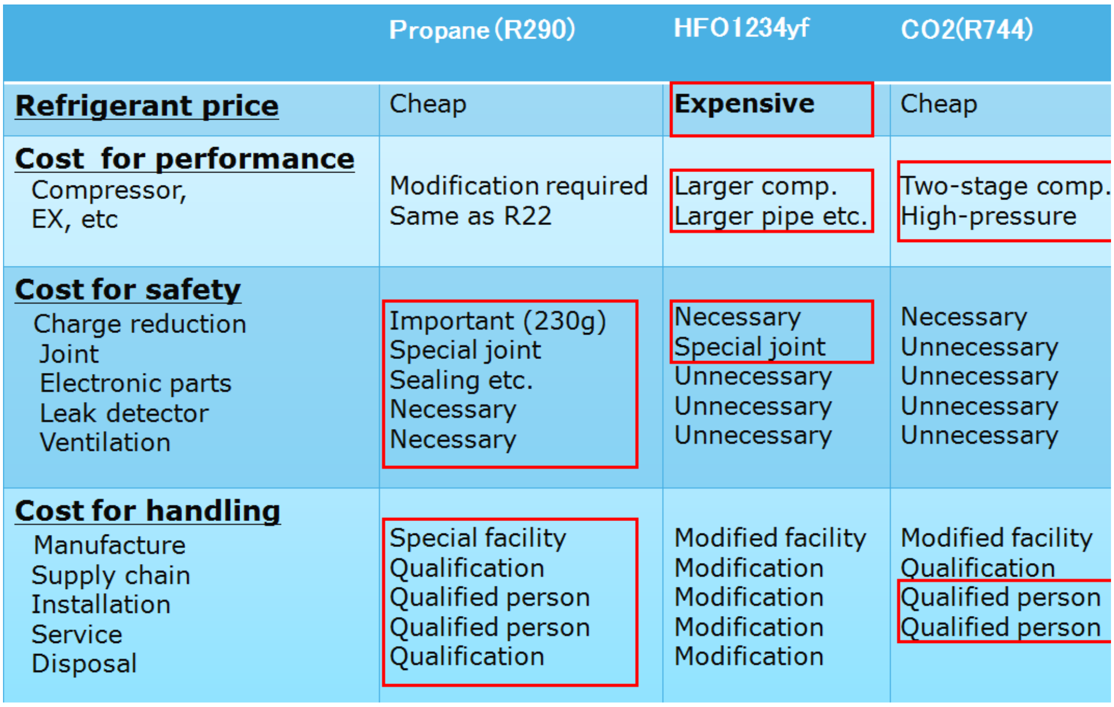
Table 12 shows the estimated price for some typical refrigerants. It should be noticeable that the data were collected from various sources such as E-commercial platform Alibaba and Amazon, as well as some agencies, mainly focusing on the products of DuPont and Honeywell. The data varies a lot and still the database is small. Consequently uncertainty relating to the prices is therefore fairly large.

Table 13 Estimated Prices for Some Typical Refrigerants

Refrigerants	Estimated Price(RMB/Ton)
CFC11	20000
HCFC22	33186
HFC404A	68833
HFC134A	71953
HFC410A	48673
HFC152a	26000
HFC32	22500
HFO1234yf	321000
R744	600
R290	7240
R717	4100

The price of HFO1234yf, a newly introduced refrigerant is much more expensive than the others, while some natural refrigerants present their advantages to others with complex chemical structures in price.

As for the other cost which should also be taken into consideration, such as costs for safety and handing, some important implications are shown in Figure 16. In the case of R290 which is with high flammability, it requires additional cost when taking safety measures in application and handling.



	Propane (R290)	HFO1234yf	CO2(R744)
Refrigerant price	Cheap	**Expensive**	Cheap
Cost for performance Compressor, EX, etc	Modification required Same as R22	Larger comp. Larger pipe etc.	Two-stage comp. High-pressure
Cost for safety Charge reduction Joint Electronic parts Leak detector Ventilation	Important (230g) Special joint Sealing etc. Necessary Necessary	Necessary Special joint Unnecessary Unnecessary Unnecessary	Necessary Unnecessary Unnecessary Unnecessary Unnecessary
Cost for handling Manufacture Supply chain Installation Service Disposal	Special facility Qualification Qualified person Qualified person Qualification	Modified facility Modification Modification Modification Modification	Modified facility Qualification Qualified person Qualified person

Figure 16 Additional Costs for Propane, HFO1234yf and CO_2 as Refrigerants

Besides those costs, the patent fee of refrigerant application can't be ignored either. In order to utilize the refrigerant, the manufacturers have to pay amount of money to the patent owner. Basically speaking, it accounts for 1 to 2% of the whole selling price of a room air conditioner system.

Table 14 Relevant Patents

Refrigerants	Patent owner	Types of business	Note
R 410A	DuPont Honeywell Daikin	U.S chemical company U.S chemical company Japanese manufacturers(AC)	Expired in Nov. 2011
R1234yf	DuPont Honeywell	U.S chemical company U.S chemical company	In the process of research and test
R290	Gree	Chinese manufacturers(AC)	In the process of research and test

4 DISCUSSION

4.1 Limitation of Indicators

Although the indicators presenting the properties and performance are well evaluated and selected, some details cannot be fully articulated and there still exists some limitations.

For TEWI which measures the global warming impact caused by the refrigerants, it leaves out the CO_2 emission during the processes of manufacture, transportation, distribution and destruction of the refrigerants accounting for less than 5% of TEWI in most cases. Instead the indicator Life Cycle Climate Performance (LCCP) contains all these missing emissions and thus can tell the whole story in greater details. Unfortunately these processes are different from case by case and accurate values are not available. Consequently TEWI is adopted as the greenhouse impact indicator on a basis that rough estimation of leaf out CO_2 emission indicated much smaller value than above.

The adoption of weighting methodology and its sequent environmental indicator may be also controversial because in this paper the subjective weighting factor was assumed as 1.0, ensuring the results completely objective without individual subjective opinion. Based on the national target and regulation in future plans, such as Montreal Protocol, the weighting factor or reduction factor (current level/target level) could be figured out. In the cases of Japan and China, it is 2.500 and 1.538 respectively for ozone depletion impact and 1.328 and 0.658 for global warming impact. Obviously Japan set stricter targets in environmental sector as a developed country than China. Both of the countries take ozone depletion impact more serious. China's weighting factor of global warming is even below 1.0 because China promised to cut its "carbon intensity" or CO_2 emission per unit of gross domestic product (GDP) by 40 to 45 percent below 2005 levels by 2020. According to Academician Ding, provided the continuing economic growth in China, the estimated CO_2 emission in 2020 is 12530 billion tons, with an actual increase of4289 billion tons on the baseline of 2010. This will lead to the indifference in global warming impact in China.

Table 15 Weighting Factor/Reduction Factor of Japan and China

	Weighting factor/Reduction factor		
	Ozone depletion impact	Global warming impact	Ratio (Ozone depletion/Global warming)
Japan	2.500	1.328	1.88
China	1.538	0.658	2.34

In addition, the weighting methodology is based on nationwide scope, which takes these two environmental impacts as local problems. If think globally, the weighting factors and normalization values are viewed as the same, and that will lead to different results. The environmental indicator of China will be higher than that of Japan, indicating more severe consequences of impairment to the global environment. However, since each country tend to make its own choice on proper refrigerants on account of their local conditions and values, the national scope seems more appropriate.

4.2 Balance between Safety, Environmental Impacts and Costs

Consideration on the flammable refrigerants, particularly those with lower flammability is ongoing with the belief that lean flammable substances can be used if properly handled. Since 1995 researches have been carried out in Japan, Europe, and the U.S. for flammability classification of refrigerants. This classification is of importance in order to mitigate flammability risks in a rational manner, which includes both the lower flammability limit (the likelihood of the risk-event) and the heat of combustion (the severity of the impacts).

Actually sometimes accidents happen due to the application of flammable refrigerants, such as the two pictures showed here. The left one occurred in a New Zealand supermarket and caused large fire while the right one in China with a tragedy of death and injury.

Propane (R290)
explosion in a New Zealand supermarket.

Source: EFCTC newsletter

Air Condition Sudden Explosion in China
< 1 killed , 2 seriously injured >

Source: HEA.CN newsletter

Figure 17 & 18 Accidents Caused by the Application of Flammable refrigerants

According to the Japan Japan Refrigeration and Air Conditioning Industry Association, there used to be 49- 97 estimated incidents/year in Japan with R290 room air conditioners, shown as Figure 18.

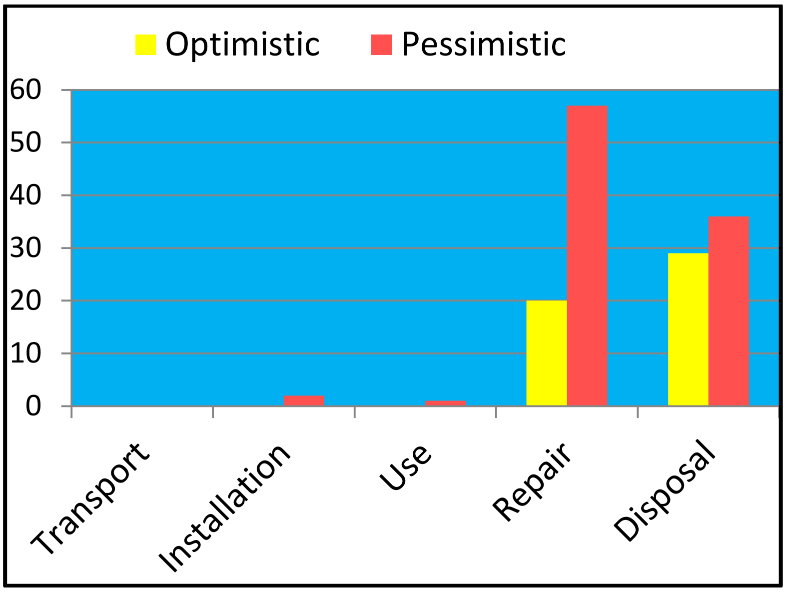


Figure 19 Estimated Incidents/ Year in Japan with R290 Room Air Conditioners

Source: Risk assessment work on HC refrigerant carried out by JRAIA Non Fluorocarbon Refrigerant WG in 1999-2000.

The accidents usually happen during repair and disposal processes, during which time no power is supplied for the unit and measures such as forced fan operation cannot work. Once the leakage of flammable refrigerant occurs by accident and the concentration accumulates to the lower flammability limit, explosion and fire may be caused. Since the room air conditioners are equipped in almost each home, these processes are beyond the control of manufacturers. Instead some service suppliers who are lacking the professionalism in air conditioning and refrigerants are delivering repair and disposal services, increasing the risk considerably. To solve these problems, on one side, special trainings can be provided by the industrial association or relevant departments to the services suppliers and corresponding requirement should be compulsory to conduct the services of air conditioners. Or the air conditioner manufacturers could deliver all the after-sale services by themselves, ensuring the safe and professional services.

Fortunately compared with the package or central air conditioning system used in commercial or industrial sectors, the room air conditioner always has smaller capability between 2 kW and 10.5 kW and thus contains smaller amount of refrigerants. For example, a room air conditioner with R-22 as its refrigerant is charged between 0.5 and 2 kg of refrigerant, with an average of 0.75 kg. It means that compared with those in commercial or industrial sectors, air conditioners in residential sector has less risk and more flammable refrigerants could be utilized on the premise of carefully tests and evaluation. Up to now, China and Japan have showed different acceptance on the flammable refrigerants. Hydrocarbon refrigerants, represented by R290, is somewhat embraced by China and some European countries such as Germany, yet is questioned and challenged by Japan. The Chinese air-conditioning system manufacturer Gree Electric Appliances is one of the companies developing technology equipment to use propane to replace R22 and HFC-410A in new systems. Japan air conditioning industry believes even the little risk on fire or explosion may cause severe consequences, thus essentially sidelining by now, with a persistence of at least A2L /B2L level.

The excellent performance of R290 in the respects of environmental protection and price, which can be analyzed from the Results, is the main attraction to China. Additionally, China also has received technical assistance and funding to develop R290 technology from UNEP and the Multilateral Fund in an effort on HCFC phase-out target, which saves the costs apparently.

Japan prefers HFC32 and HFO1234yf at this moment despite the higher price cost, approximately 3.0 and 44.3 times of that of R290. Costs including price will be reduced as the technology gradually matures. Moreover, compared with China, the Japanese manufacturers retain their advantage on relevant patents.

Based on the Results, HFO1234yf gives an excellent performance in environmental protection while HFC32 perform fairly, and both of them are classified into A2L safety group, the lowest requirement in safety in Japan. As for R290 and R152a, they are out of the consideration due to underperforming in flammability.

5 CONCLUSIONS

Refrigerants perform quite differently in safety issue, environmental protection and economic efficiency aspects partly due to their properties. However the environment and local conditions where they are applying also have a huge impact on their performance. In this paper, indicators to evaluate refrigerants in each aspect were carefully selected and their values are calculated.

In safety aspect, the refrigerants currently being widely used in air conditioning industry are all categorized into group A1, with the properties of non-flammability and low toxicity, except R717. The HC alternatives, particularly R290, which attract the attention of air conditioning and refrigeration industry recently, are proven to have higher flammability and accidents happened due to the application of high flammable refrigerants. China and Japan have showed different acceptance on the flammable refrigerants which may lead to the different refrigerant selection in the future. Further risk assessment is necessary to use flammable refrigerants for production, transporting, operation, after sales servicing in field and disposal. Moreover special training is suggested to be provided to the services suppliers and corresponding requirement are recommended to deliver the services of air conditioners.

In Environmental protection aspect, Ozone depletion and global warming are the main impacts caused by refrigerants. As a result, ODP and TEWI are carefully examined and then integrated into a whole environmental indicator by utilizing weighting methodology. TEWIs in average for a whole country when using different refrigerants vary a lot. In different cases, based on many factors such as total ownership of RAC, level of technology, energy structure, use habit and local climate conditions, the best or worst performers may change. In general, Japan has a smaller TEWI value when using the same refrigerant in the similar air conditioning system, mainly due to the technical gap and favorable local climatic conditions and energy structure. In terms of Environmental indicator, there exist great differences among countries for the same refrigerant. Despite the higher absolute value of TEWI and ODs emission by a Chinese room air conditioning system, the relative value of environmental impact to a whole country that it causes is still limited due to its much larger territory area and huger population than Japan. This difference may affect the sensitivity of the national industry to environmental sector and may even lead to the final different choice in refrigerants. Basically the second generation refrigerants have a much higher value for Environmental indicators than others due to high ODP while the natural refrigerants perform well in ozone depletion impact, but differ in global warming impact due to efficiency differences.

Moreover, the change of user’s habit and future energy policy will also affect their performance in environmental aspect by changing the indirect emission of CO_2 resulting from the energy consumption which accounting for the most of the TEWI. The decrease of thermal power ratio in the energy structure will diminish the importance of the influence by the refrigerants.

In economic efficiency aspect, HFO1234yf has a much higher cost, including refrigerant price, production cost, handling cost and patent fees than the ones being used, while some natural refrigerants present their advantages to others with complex chemical structures in price. Additional cost is required for flammable refrigerants when taking safety measures in application and handling.

REFERENCES

American Society of Heating, Refrigerating, and Air-Conditioning Engineers (ASHRAE). 1997. *Designation and Safety Classification of Refrigerants, ANSI/ASHRAE Standard 34-1997*, Atlanta, GA.

ARI. 1996. S*tatistical Profile of the Air Conditioning, Refrigeration, and Heating Industry.* Air Conditioning and Refrigeration Institute, 4301 North Fairfax Drive, Arlington, VA, USA.

Beggs, C. 1996. A method for estimating the time-of-day carbon dioxide emissions per kWh of delivered electrical energy in England and Wales. *Buildings Service Engineering Residential Technology*, 17(3): 127-134.

Bhatia. 2006. *Selection Tips for Environmentally Safe Refrigerants*. Houston: Decatur Professional Development, LLC.

Calm J.M., and Didion, D.A.1998. Trade-offs in Refrigerant Selections – Past, Present, and Future. *International Journal of Refrigeration*, 21(4): 308–321.

Chris Begert. 2006. *Heat Pumps and Environmental Performance-Assessing the potential of ground-source of heat pump.* Sydney: Alternative Technology Association.

Douglas, J. 1996. *Evaluation of Propane as an Alternative to HCFC-22 in Residential Applications.* Proceedings of the 1996 International Refrigeration Conference at Purdue, West Lafayette, 13-18.

EPA. 1993. *Space Conditioning: The Next Frontier*, EPA 430-R-93-004, April, F-1

Feldman, S. 1995. *Energy Consumption and TEWI Comparison of R-410A and HCFC-22 in a Residential Heat Pump.* Proceedings of the International CFC and Halon Alternative Conference, Washington, D. C. 359-368.

Fischer, S. 1991. Fischer, S., et al. 1991. *Energy and Global Warming Impacts of CFC Alternative Technologies*. AFEAS and DOE.

Fischer, S. 1993. Screening Analysis for Chlorine-Free Alternative Refrigerants to Replace R-22 in Air Conditioning Applications, *ASHRAE Transactions*, 99(2): 627-636.

Fischer, S. 1994. Energy and Global Warming Impacts of Not In-Kind and Next Generation CFC and HCFC Alternatives, AFEAS and DOE

Haruo Onishi，Ryuzaburo Yajima， and Shotaro Ito. 2004. *LCCP OF SOME HVAC & R APPLICATIONS In Japan*. Earth Technologies Forum.

J. M. Calm. 1998. *Property, Safety, and Environmental Data for Alternative Refrigerants.* Proceedings of the Earth Technologies Forum, Washington, DC, 26-28.

James M. Calm, and Glenn C. Hourahan. 2001. Refrigerant Data Summary. *Engineered Systems*, 18(11):74-88.

James M. Calm. 2008. The next generation of refrigerants – Historical review, considerations, and outlook. *International Journal of Refrigeration,* 31(2): 1123-1133.

John T. McMullan. 2002. Refrigeration and the Environment-Issues and Strategies for the Future. *International Journal of Refrigeration,* 25(3): 89-99.

Katar na Heikkilä.2004. Environmental Impact Assessment Using a Weighting Method for Alternative Air-conditioning Systems. *Building and Environment*: 39(10): 1133–1140.

Lakeman J A. 1995. *Climate change 1995- the science of climate change.* Cambridge: Cambridge University Press.

Mark Goedkoop of PRe Consultants. 1995. *Final report for Eco-indicator 95.* Netherlands: Netherlands agency for energy and the environment and Naitonal Institute of Public Health and Environmental Protection.

Ministry of Internal Affairs and Communications, Japan. 2010. Population Census of Japan, Preliminary Counts of the Population and Households, Statistics Bureau. Tokyo: Ministry of Internal Affairs and Communications, Japan.

National Bureau of Statistics of China. 2010. *China statistical 2010 yearbook*. Bejing: National Bureau of Statistics of China.

National Electrical Manufacturing Association of Japan. 2005. *Room Air Conditioners, Japan Industrial Standard C 9612,2005.* Tokyo: Japanese Industrial Standards Press

Philip CH Yu. 2008. Refrigerant Selection for Sustainable Future. ASHARE JOURNAL,2007-2008: 25-30.

R. D. Vocke, Jr. Atomic Weights of the Elements 1999. *Pure and Applied Chemistry,* 71(8):1593-1607 and errata 71(9):1809.

REFERENCES (Continued)

Stephen O. Andersen, and Kristen Taddonio. 2006. US Refrigerant Regulation and Voluntary Program to Protect the Climate and its Fragile Ozone Layer. *Second International Symposium on Natural Refrigerant*, 4-13.

Tetsuro Kishimoto, and Sugawara Sakuo. 2009. *Standards Labeling System for Air-conditioning Equipment in US, Europe and Japan*, the Japan Refrigeration and Air Conditioning Industry Association (JRAIA)

The EPA website. [Online].2012. *Available: http://www.epa.gov/ozone/science/ods/index.html*

The EPA website. [Online]. 2012. *Available: http://www.epa.gov/ozone/snap/refrigerants/safety.html*

The wikipedia website. [Online]. 2012. *Available: http://en.wikipedia.org /wiki/Ozone_depletion_potential*

UNEP. 1987. *Montreal Protocol on Substances that Deplete the Ozone Layer, United Nationals Environmental Programme (UNEP).* Montreal: Secretariat for the Vienna Convention for the Protection of the Ozone Layer & the Montreal Protocol on Substances that Deplete the Ozone Layer.

UNEP. 2000. *Handbook for the International Treaties for the Protection of the Ozone Layer (Fifth Edition),* UNEP Ozone Secretariat, Nairobi, Kenya.

World Meteorological Organization (WMO). 2003. *Scientific Assessment of Ozone Depletion: Report of the Montreal Protocol Scientific Assessment Panel.* Switzerland: World Meteorological Organization

Working groups of Intergovernmental Panel on Climate Change (IPCC). 2007. *Technical summary on climate change* [R]: 15- 80.

Yitai Ma, and Qingsong An. 2009. Evaluation Criterion of Refrigerant Environmental Performance Based on Natural Degree. *HV&AC*: 39(5): 35-51.

Yunho Hwang, and Dae-Hyun Jin. 2004. *Comparison of Hydrocarbon R-290 and Two HFC Blends R404A and R410A for Low Temperature Refrigeration Application.* Global Refrigerant Environmental Evaluation Network Program

Zhang, C. Zhu, J. K. O. Sin, and P. K. T. Mok. 1999. A novel ultrathin elevated channel low-temperature poly-Si TFT. *IEEE Electron Device Lett.*, 20: 569–571.

APPENDIX A

Ideal COP for the Heating Process

Outdoor temperature(℃)	R11	HCFC22	HFC134A	R152A	HFC404A	HCF407C	HFC410A	R32	HFO1234yf	R290	R717
-35	3.4023	3.2326	3.2145	3.2884	3.0637	2.9999	3.1296	3.1434	3.1108	3.2053	3.1760
-34	3.4597	3.2874	3.2702	3.3443	3.1176	3.0597	3.1826	3.1965	3.1661	3.2602	3.2315
-33	3.5190	3.3439	3.3277	3.4020	3.1733	3.1213	3.2374	3.2514	3.2233	3.3170	3.2888
-32	3.5802	3.4024	3.3872	3.4617	3.2308	3.1849	3.2941	3.3082	3.2825	3.3756	3.3479
-31	3.6435	3.4628	3.4487	3.5234	3.2904	3.2506	3.3526	3.3668	3.3436	3.4363	3.4091
-30	3.7089	3.5253	3.5123	3.5871	3.3520	3.3186	3.4132	3.4275	3.4070	3.4990	3.4723
-29	3.7766	3.5900	3.5781	3.6531	3.4158	3.3888	3.4759	3.4903	3.4725	3.5639	3.5377
-28	3.8466	3.6569	3.6463	3.7215	3.4819	3.4615	3.5409	3.5553	3.5404	3.6312	3.6055
-27	3.9192	3.7263	3.7170	3.7923	3.5504	3.5367	3.6082	3.6227	3.6109	3.7009	3.6756
-26	3.9943	3.7982	3.7903	3.8656	3.6214	3.6146	3.6780	3.6925	3.6839	3.7731	3.7484
-25	4.0722	3.8728	3.8663	3.9417	3.6952	3.6953	3.7504	3.7650	3.7597	3.8480	3.8238
-24	4.1531	3.9502	3.9452	4.0207	3.7717	3.7790	3.8256	3.8402	3.8384	3.9258	3.9021
-23	4.2370	4.0306	4.0271	4.1027	3.8513	3.8659	3.9036	3.9183	3.9202	4.0067	3.9834
-22	4.3242	4.1141	4.1124	4.1880	3.9340	3.9561	3.9848	3.9996	4.0052	4.0907	4.0678
-21	4.4148	4.2010	4.2010	4.2766	4.0201	4.0499	4.0692	4.0840	4.0937	4.1780	4.1557
-20	4.5091	4.2914	4.2933	4.3689	4.1098	4.1474	4.1571	4.1720	4.1859	4.2690	4.2471
-19	4.6073	4.3856	4.3894	4.4650	4.2032	4.2489	4.2487	4.2636	4.2819	4.3637	4.3423
-18	4.7096	4.4838	4.4896	4.5652	4.3006	4.3546	4.3442	4.3591	4.3820	4.4625	4.4415
-17	4.8163	4.5862	4.5942	4.6697	4.4023	4.4648	4.4438	4.4587	4.4866	4.5656	4.5450
-16	4.9277	4.6932	4.7034	4.7788	4.5085	4.5797	4.5479	4.5628	4.5957	4.6732	4.6531

APPENDIX A (continued)

Ideal COP for the Heating Process

Outdoor temperature(℃)	R11	HCFC22	HFC134A	R152A	HFC404A	HCF407C	HFC410A	R32	HFO1234yf	R290	R717
-15	5.0440	4.8049	4.8175	4.8928	4.6195	4.6998	4.6567	4.6716	4.7099	4.7857	4.7660
-14	5.1657	4.9219	4.9370	5.0121	4.7357	4.8253	4.7705	4.7855	4.8294	4.9034	4.8842
-13	5.2931	5.0444	5.0621	5.1371	4.8575	4.9567	4.8898	4.9047	4.9546	5.0267	5.0079
-12	5.4267	5.1727	5.1932	5.2680	4.9852	5.0943	5.0148	5.0298	5.0859	5.1560	5.1375
-11	5.5667	5.3075	5.3309	5.4055	5.1192	5.2386	5.1461	5.1610	5.2237	5.2917	5.2736
-10	5.7138	5.4490	5.4756	5.5498	5.2601	5.3900	5.2840	5.2989	5.3685	5.4342	5.4165
-9	5.8685	5.5979	5.6277	5.7017	5.4083	5.5493	5.4291	5.4440	5.5209	5.5842	5.5668
-8	6.0314	5.7548	5.7880	5.8616	5.5645	5.7168	5.5820	5.5968	5.6815	5.7421	5.7252
-7	6.2032	5.9202	5.9571	6.0303	5.7292	5.8934	5.7432	5.7581	5.8509	5.9088	5.8921
-6	6.3845	6.0949	6.1357	6.2085	5.9033	6.0798	5.9136	5.9284	6.0298	6.0847	6.0684
-5	6.5762	6.2796	6.3246	6.3969	6.0874	6.2769	6.0938	6.1086	6.2192	6.2709	6.2549
-4	6.7793	6.4754	6.5248	6.5965	6.2826	6.4854	6.2848	6.2995	6.4198	6.4681	6.4524
-3	6.9947	6.6831	6.7372	6.8083	6.4897	6.7066	6.4875	6.5022	6.6328	6.6774	6.6620
-2	7.2236	6.9039	6.9630	7.0334	6.7100	6.9416	6.7031	6.7176	6.8592	6.8999	6.8848
-1	7.4674	7.1391	7.2035	7.2732	6.9446	7.1916	6.9327	6.9472	7.1004	7.1369	7.1220
0	7.7275	7.3901	7.4602	7.5291	7.1951	7.4584	7.1777	7.1922	7.3579	7.3898	7.3751
1	8.0055	7.6585	7.7348	7.8027	7.4630	7.7434	7.4399	7.4543	7.6333	7.6603	7.6459
2	8.3035	7.9463	8.0291	8.0960	7.7502	8.0488	7.7210	7.7353	7.9285	7.9503	7.9360
3	8.6236	8.2555	8.3453	8.4112	8.0589	8.3767	8.0231	8.0373	8.2459	8.2618	8.2478
4	8.9684	8.5886	8.6861	8.7507	8.3916	8.7298	8.3486	8.3627	8.5878	8.5976	8.5836

APPENDIX A (continued)

Ideal COP for the Heating Process

Outdoor temperature(℃)	R11	HCFC22	HFC134A	R152A	HFC404A	HCF407C	HFC410A	R32	HFO1234yf	R290	R717
5	9.3409	8.9485	9.0542	9.1176	8.7511	9.1111	8.7004	8.7144	8.9573	8.9603	8.9465
6	9.7444	9.3386	9.4533	9.5151	9.1408	9.5240	9.0817	9.0957	9.3578	9.3534	9.3397
7	10.1831	9.7627	9.8872	9.9474	9.5646	9.9729	9.4965	9.5103	9.7934	9.7809	9.7672
8	10.6618	10.2256	10.3607	10.4191	10.0272	10.4624	9.9492	9.9630	10.2688	10.2475	10.2338
9	11.1862	10.7328	10.8796	10.9359	10.5342	10.9985	10.4453	10.4590	10.7897	10.7586	10.7449
10	11.7630	11.2909	11.4506	11.5045	11.0921	11.5880	10.9914	11.0049	11.3630	11.3211	11.3073
11	12.4007	11.9080	12.0818	12.1332	11.7090	12.2396	11.5952	11.6086	11.9969	11.9430	11.9291
12	13.1093	12.5938	12.7835	12.8320	12.3947	12.9634	12.2665	12.2798	12.7015	12.6342	12.6202
13	13.9013	13.3606	13.5679	13.6132	13.1615	13.7722	13.0171	13.0303	13.4892	13.4070	13.3927
14	14.7925	14.2235	14.4507	14.4922	14.0245	14.6820	13.8619	13.8750	14.3758	14.2767	14.2621

APPENDIX B

Ideal COP for the Cooling Process

Outdoor temperature(℃)	R11	HCFC22	HFC134A	R152A	HFC404A	HCF407C	HFC410A	R32	HFO1234yf	R290	R717
24	33.7356	32.4169	33.1252	33.1076	32.1120	33.8648	31.5406	31.6077	33.1138	32.6162	32.6882
25	29.4448	28.2411	28.8567	28.8626	27.9169	29.4748	27.4311	27.5055	28.8216	28.4070	28.4955
26	26.1069	24.9921	25.5352	25.5600	24.6512	26.0582	24.2328	24.3137	25.4812	25.1316	25.2344
27	23.4361	22.3918	22.8767	22.9170	22.0362	23.3229	21.6723	21.7591	22.8070	22.5097	22.6256
28	21.2505	20.2634	20.7003	20.7537	19.8943	21.0832	19.5755	19.6680	20.6174	20.3632	20.4910
29	19.4288	18.4888	18.8854	18.9501	18.1072	19.2150	17.8266	17.9244	18.7910	18.5731	18.7121
30	17.8869	16.9863	17.3486	17.4233	16.5929	17.6327	16.3452	16.4480	17.2442	17.0572	17.2068
31	16.5650	15.6977	16.0303	16.1140	15.2930	16.2749	15.0739	15.1817	15.9169	15.7567	15.9165
32	15.4190	14.5802	14.8868	14.9785	14.1645	15.0968	13.9707	14.0834	14.7653	14.6286	14.7982
33	14.4159	13.6016	13.8853	13.9844	13.1753	14.0645	13.0041	13.1216	13.7564	13.6404	13.8196
34	13.5305	12.7374	13.0008	13.1066	12.3007	13.1524	12.1499	12.2721	12.8650	12.7675	12.9561
35	12.7432	11.9686	12.2136	12.3258	11.5216	12.3403	11.3893	11.5163	12.0714	11.9906	12.1885
36	12.0385	11.2801	11.5085	11.6266	10.8229	11.6126	10.7076	10.8392	11.3603	11.2946	11.5016
37	11.4041	10.6597	10.8731	10.9968	10.1924	10.9564	10.0928	10.2292	10.7192	10.6673	10.8833
38	10.8298	10.0979	10.2974	10.4265	9.6205	10.3615	9.5355	9.6765	10.1381	10.0989	10.3239
39	10.3074	9.5865	9.7733	9.9075	9.0990	9.8197	9.0276	9.1734	9.6089	9.5814	9.8152
40	9.8303	9.1190	9.2941	9.4332	8.6213	9.3238	8.5629	8.7133	9.1247	9.1080	9.3507
41	9.3926	8.6899	8.8540	8.9979	8.1820	8.8682	8.1357	8.2910	8.6798	8.6733	8.9248
42	8.9898	8.2946	8.4485	8.5970	7.7763	8.4480	7.7416	7.9017	8.2697	8.2727	8.5330
43	8.6177	7.9292	8.0735	8.2264	7.4004	8.0585	7.3768	7.5417	7.8901	7.9020	8.1712

APPENDIX B (continued)

Ideal COP for the Cooling Process

Outdoor temperature(℃)	R11	HCFC22	HFC134A	R152A	HFC404A	HCF407C	HFC410A	R32	HFO1234yf	R290	R717
44	8.2730	7.5903	7.7256	7.8829	7.0510	7.6975	7.0379	7.2078	7.5378	7.5581	7.8361
45	7.9527	7.2750	7.4019	7.5635	6.7250	7.3613	6.7222	6.8970	7.2098	7.2381	7.5249
46	7.6543	6.9810	7.0999	7.2657	6.4202	7.0473	6.4271	6.6070	6.9035	6.9394	7.2351
47	7.3756	6.7061	6.8174	6.9873	6.1342	6.7532	6.1507	6.3358	6.6168	6.6599	6.9645
48	7.1147	6.4484	6.5524	6.7265	5.8653	6.4772	5.8911	6.0813	6.3477	6.3977	6.7113
49	6.8699	6.2063	6.3034	6.4816	5.6118	6.2174	5.6467	5.8422	6.0947	6.1513	6.4739
50	6.6398	5.9784	6.0689	6.2511	5.3723	5.9724	5.4160	5.6169	5.8561	5.9191	6.2508

APPENDIX C

Heating Load for a Representative Room

Outdoor temperature(℃)	Heating load(kW)	Outdoor temperature(℃)	Heating load(kW)
-16	7.1629	1	3.4729
-15	6.9459	2	3.2559
-14	6.7288	3	3.0388
-13	6.5118	4	2.8218
-12	6.2947	5	2.6047
-11	6.0776	6	2.3876
-10	5.8606	7	2.1706
-9	5.6435	8	1.9535
-8	5.4265	9	1.7365
-7	5.2094	10	1.5194
-6	4.9924	11	1.3024
-5	4.7753	12	1.0853
-4	4.5582	13	0.8682
-3	4.3412	14	0.6512
-2	4.1241	15	0.4341
-1	3.9071	16	0.2171
0	3.6900	17	0.0000

Note: Rated heating capability of air conditioner is 3.6kW.

Source: The loads were calculated according to Japan Industrial Standard C 9612, 2005.

APPENDIX D

Cooling Load for a Representative Room

Outdoor temperature(℃)	Cooling load(kW)	Outdoor temperature(℃)	Cooling load(kW)
24	0.2800	38	4.2000
25	0.5600	39	4.4800
26	0.8400	40	4.7600
27	1.1200	41	5.0400
28	1.4000	42	5.3200
29	1.6800	43	5.6000
30	1.9600	44	5.8800
31	2.2400	45	6.1600
32	2.5200	46	6.4400
33	2.8000	47	6.7200
34	3.0800	48	7.0000
35	3.3600	49	7.2800
36	3.6400	50	7.5600
37	3.9200		

Note: Rated cooling capability of air conditioner is 2.8kW.

Source: The loads were calculated according to Japan Industrial Standard C 9612, 2005.

APPENDIX E

Number of Households and Air Conditioners in Each Prefecture of Japan

Prefecture	Number of households	Number of air conditioners	Prefecture	Number of households	Number of air conditioners
Hokkaido	2,424,073	3878517	Shiga-ken	517,236	827578
Aomori-ken	513,311	821298	Kyoto-fu	1,122,634	1796214
Iwate-ken	483,971	774354	Osaka-fu	3,832,319	6131710
Miyagi-ken	901,254	1442006	Hyogo-ken	2,254,880	3607808
Akita-ken	390,335	624536	Nara-ken	523,280	837248
Yamagata-ken	388,670	621872	Wakayama-ken	393,750	630000
Fukushima-ken	720,587	1152939	Tottori-ken	211,832	338931
Ibaraki-ken	1,088,848	1742157	Shimane-ken	262,108	419373
Tochigi-ken	745,045	1192072	Okayama-ken	754,067	1206507
Gumma-ken	755,297	1208475	Hiroshima-ken	1,184,606	1895370
Saitama-ken	2,842,662	4548259	Yamaguchi-ken	597,195	955512
Chiba-ken	2,515,220	4024352	Tokushima-ken	302,144	483430
Tokyo-to	6,403,219	10245150	Kagawa-ken	390,334	624534
Kanagawa-ken	3,843,424	6149478	Ehime-ken	590,782	945251
Niigata-ken	838,922	1342275	Kochi-ken	321,671	514674
Toyama-ken	383,323	613317	Fukuoka-ken	2,110,880	3377408
Ishikawa-ken	440,995	705592	Saga-ken	294,854	471766
Fukui-ken	275,424	440678	Nagasaki-ken	558,439	893502
Yamanashi-ken	327,642	524227	Kumamoto-ken	688,106	1100970
Nagano-ken	794,362	1270979	Oita-ken	481,957	771131
Gifu-ken	736,555	1178488	Miyazaki-ken	460,277	736443
Shizuoka-ken	1,398,550	2237680	Kagoshima-ken	729,330	1166928
Aichi-ken	2,933,464	4693542	Okinawa-ken	519,975	831960
Mie-ken	703,704	1125926			

Source: 2010 Population Census of Japan, Preliminary Counts of the Population and Households, Statistics Bureau, Ministry of Internal Affairs and Communications, Japan

APPENDIX F

Number of Households and Ownership of Air Conditioners Per 100 Households in Each Province of China

Province	Family Households (10000 Households)	Proportion of urban households (%)	Urban households	Rural households
Beijing	668	85.00	162.68	86.53
Tianjin	366.1848	78.01	129.92	55.50
Hebei	2039.5118	43.00	84.51	8.50
Shanxi	1033.02	45.99	33.78	3.90
Inner Mongolia	817.6128	53.40	10.23	0.63
Liaoning	1499.4046	60.35	29.73	1.01
Jilin	900.1598	53.32	6.22	0.06
Heilongjiang	1295.991	55.50	7.92	0.58
Shanghai	825.116	88.60	196.04	134.83
Jiangsu	2439.3386	55.60	163.80	39.59
Zhejiang	1885.37	57.90	180.05	76.52
Anhui	1830.8	42.10	110.31	19.26
Fujian	1120.6844	51.40	175.36	26.98
Jiangxi	1149.7043	43.18	101.99	6.20
Shandong	3010.5	48.32	95.04	12.64
Henan	2592.6993	37.70	112.81	15.05
Hubei	1669.8928	46.00	112.47	12.45
Hunan	1863.186	43.20	102.81	7.32
Guangdong	2774.7417	63.40	196.21	30.98
Guangxi	1315.14	39.20	106.34	2.81
Hainan	222.4884	49.13	66.52	1.25
Chongqing	974.49	51.59	151.13	10.11
Sichuan	2580.2326	38.70	98.38	5.18
Guizhou	1038.9579	29.89	17.49	0.98
Yunnan	1235.5	34.00	1.50	0.25
Tibet	67.0835	23.80	6.22	----
Shaanxi	1071.8565	43.50	100.57	4.41
Gansu	690.0389	32.65	5.28	0.28
Qinghai	152.904	41.90	1.28	0.33

APPENDIX F (Continued)

Number of Households and Ownership of Air Conditioners Per 100 Households in Each Province of China

Province	Family Households (10000 Households)	Proportion of urban households (%)	Urban households	Rural households
Ningxia	184.207	46.10	10.47	0.17
Xinjiang	639.8569	39.85	11.22	0.65

Source: China statistical yearbook 2010, National Bureau of Statistics of China

APPENDIX G

Proportion of Provinces in Each Region of China (%)

Province	Ⅰ$_A$	Ⅰ$_B$	Ⅰ$_C$	Ⅰ$_D$	Ⅱ$_A$	Ⅱ$_B$	Ⅲ$_A$	Ⅲ$_B$	Ⅲ$_C$	Ⅳ$_A$	Ⅳ$_B$	Ⅴ$_A$	Ⅴ$_B$	Ⅵ$_A$	Ⅵ$_B$	Ⅵ$_C$	Ⅶ$_A$	Ⅶ$_B$	Ⅶ$_C$	Ⅶ$_D$
Beijing	6.7	33.6	59.7	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Tianjin	0.0	0.0	93.0	7.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Hebei	0.0	0.0	0.0	64.4	35.6	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Shanxi	5.1	21.6	16.2	22.6	0.0	7.4	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	27.1	0.0
Inner Mongolia	0.0	0.0	0.0	0.0	100.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Liaoning	0.0	0.0	0.0	0.0	100.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Jilin	0.0	0.0	0.0	21.6	65.1	13.3	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Heilongjiang	0.0	0.0	0.0	7.5	11.6	80.9	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Shanghai	0.0	0.0	0.0	0.0	0.0	0.0	100.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Jiangsu	0.0	0.0	0.0	0.0	35.5	0.0	23.6	40.9	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Zhejiang	0.0	0.0	0.0	0.0	0.0	0.0	28.6	71.4	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Anhui	0.0	0.0	0.0	0.0	10.2	0.0	0.0	73.6	16.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Fujian	0.0	0.0	0.0	0.0	0.0	0.0	5.3	56.5	0.0	13.5	24.7	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Jiangxi	0.0	0.0	0.0	0.0	0.0	0.0	0.0	100.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Shandong	0.0	0.0	0.0	0.0	100.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Henan	0.0	0.0	0.0	0.0	52.6	0.0	0.0	1.3	46.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Hubei	0.0	0.0	0.0	0.0	0.0	0.0	0.0	50.2	49.8	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Hunan	0.0	0.0	0.0	0.0	0.0	0.0	0.0	78.1	21.9	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Guangdong	0.0	0.0	0.0	0.0	0.0	0.0	0.0	9.6	0.0	49.2	41.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Guangxi	0.0	0.0	0.0	0.0	0.0	0.0	0.0	7.6	8.9	13.9	67.2	0.0	2.4	0.0	0.0	0.0	0.0	0.0	0.0	0.0

APPENDIX G (Continued)

Proportion of Provinces in Each Region of China (%)

Province	Ⅰ A	Ⅰ B	Ⅰ C	Ⅰ D	Ⅱ A	Ⅱ B	Ⅲ A	Ⅲ B	Ⅲ C	Ⅳ A	Ⅳ B	Ⅴ A	Ⅴ B	Ⅵ A	Ⅵ B	Ⅵ C	Ⅶ A	Ⅶ B	Ⅶ C	Ⅶ D
Hainan	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	100.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Chongqing	0.0	0.0	0.0	0.0	0.0	0.0	0.0	100.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Sichuan	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	41.5	0.0	0.0	6.4	6.1	1.4	0.9	43.7	0.0	0.0	0.0	0.0
Guizhou	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	49.9	0.0	0.0	29.5	20.5	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Yunnan	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	4.5	11.4	80.5	0.0	0.0	3.5	0.0	0.0	0.0	0.0
Tibet	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	8.0	0.0	0.0	51.5	40.5	0.0	0.0	0.0	0.0
Shaanxi	0.0	0.0	0.0	7.3	19.6	40.0	0.0	0.0	33.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Gansu	0.0	0.0	0.0	0.0	0.0	39.3	0.0	0.0	5.2	0.0	0.0	0.0	0.0	17.4	0.0	0.7	0.0	0.0	33.5	3.9
Qinghai	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	57.1	39.2	3.7	0.0	0.0	0.0	0.0
Ningxia	0.0	0.0	0.0	0.0	0.0	100.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Xinjiang	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	6.2	8.3	0.0	4.9	30.4	0.2	50.0
Taiwan	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	100.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Hongkong	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	100.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Macao	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	100.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0

Source: Based on Chinese standard of climatic regionalization for architecture 50178-93, utilizing Photoshop to estimate the area of each part.

APPENDIX H

TEWI by Different Refrigerants in Each Region of Japan

	TEWI (kg CO2 eq)				
Refrigerants	Region 1	Region 2	Region 3	Region 4	Region 5
R11	9719.34	8244.17	8191.90	7903.11	6306.75
HCFC22	7631.86	6082.05	6028.33	5724.28	4062.05
HFC134A	7491.66	5943.84	5888.28	5580.79	3937.84
R152a	6183.89	4661.48	4607.58	4307.83	2674.78
HCF32	6904.95	5310.19	5255.75	4942.92	3238.44
HFC404A	9602.47	7987.78	7931.39	7610.01	5915.18
R407A	7592.96	6008.35	5949.53	5627.67	3997.58
HFC410A	8051.67	6386.22	6398.27	6084.87	4379.32
HFO1234yf	6217.14	4631.84	4573.75	4254.92	2595.98
R290	6183.33	4626.26	4571.63	4264.29	2604.86
R717	6193.69	4629.85	4573.21	4262.57	2598.13

Notes: Calculated based on methodology introduced in the paper.

APPENDIX I

TEWI by Different Refrigerants in Each Region of China

	TEWI (kg CO2 eq)									
Region	R11	HCFC22	HFC134A	HFC152a	HFC32	HFC404A	HFC407C	HFC410A	HFO1234yf	R290	R717
Ⅰ$_{A}$	5341.82	2253.07	2132.85	489.52	1008.37	4621.26	2048.02	2573.77	338.65	341.72	336.25
Ⅰ$_{B}$	5101.58	2000.36	1885.99	243.40	748.45	4364.11	1805.53	2312.51	90.69	90.75	87.00
Ⅰ$_{C}$	5675.88	2603.41	2476.38	831.93	1370.23	4979.42	2385.60	2937.58	683.85	691.01	682.99
Ⅰ$_{D}$	6151.93	3103.78	2966.26	1320.07	1886.42	5490.56	2867.15	3456.70	1176.26	1189.15	1177.29
Ⅱ$_{A}$	7298.46	4314.40	4151.87	2499.16	3138.62	6734.55	4035.42	4718.37	2370.77	2395.48	2370.75
Ⅱ$_{B}$	6123.54	3074.27	2937.38	1291.17	1856.17	5460.82	2838.93	3426.41	1147.40	1159.84	1148.00
Ⅲ$_{A}$	21241.59	18865.56	18530.61	16780.73	18078.47	21608.05	18323.51	19681.77	16901.62	16925.96	16924.37
Ⅲ$_{B}$	24134.53	21921.92	21534.99	19760.73	21239.98	24762.58	21302.03	22866.61	19939.75	19976.96	19947.37
Ⅲ$_{C}$	17659.99	15112.00	14819.72	13102.29	14216.07	17749.90	14618.33	15807.02	13142.16	13174.26	13174.38
Ⅳ$_{A}$	11051.94	8235.54	8001.95	6337.57	7168.94	10722.26	7823.07	8760.25	6240.27	6300.38	6265.78
Ⅳ$_{B}$	13059.64	10347.22	10080.01	8400.90	9347.66	12892.27	9881.17	10950.62	8339.54	8407.81	8361.13
Ⅴ$_{A}$	19636.73	17172.43	16868.30	15129.81	16328.70	19865.78	16676.03	17920.06	15223.32	15237.16	15249.63
Ⅴ$_{B}$	15028.62	12354.54	12109.18	10405.18	11377.02	14932.22	11942.61	12956.89	10411.24	10425.46	10435.92
Ⅵ$_{A}$	5243.30	2149.04	2031.54	388.54	901.67	4515.64	1948.47	2466.49	236.86	238.72	234.00
Ⅵ$_{B}$	5017.50	1912.50	1800.00	157.50	658.13	4275.00	1721.25	2221.88	4.50	3.38	1.34
Ⅵ$_{C}$	48410.15	47288.98	46765.85	44698.68	47280.43	50909.64	46782.86	48941.38	45615.83	45390.94	45486.22
Ⅶ$_{A}$	9459.47	6620.30	6411.99	4736.47	5538.07	9137.51	6275.13	7147.24	4660.20	4698.35	4632.38
Ⅶ$_{B}$	6560.45	3538.89	3392.64	1742.52	2338.71	5942.66	3289.21	3914.05	1607.72	1623.48	1604.53
Ⅶ$_{C}$	8450.62	5547.89	5361.12	3694.53	4424.56	8025.14	5235.75	6021.72	3597.68	3628.12	3578.81

APPENDIX I (Continued)

TEWI by Different Refrigerants in Each Region of China

	TEWI (kg CO2 eq)										
Region	R11	HCFC22	HFC134A	HFC152a	HFC32	HFC404A	HFC407C	HFC410A	HFO1234yf	R290	R717
Ⅶ$_{D}$	13891.04	11369.50	11069.23	9337.22	10492.07	14120.20	10902.45	12174.26	9389.34	9446.82	9278.31

Notes: Calculated based on methodology introduced in the paper.