

Low GWP refrigerants for refrigeration and air conditioning systems in Japan

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The type of refrigerants used for air conditioning and refrigeration purposes have changed significantly over the years, for environmental reasons. In Japan, this conversion started early. There, legislation dealing with global warming has been in place since 1988, also affecting regulation on refrigerants, since they historically have a high global warming potential. Currently, the step is taken toward refrigerants with low global warming potential. Unfortunately, these types of refrigerants present a new kind of challenge: they are often flammable and combustible. This safety risk can be handled for some applications, but for others, more expertise and analysis are needed.

Introduction

Measures to counter global warming are needed to preserve the ozone layer and protect the global environment. As a result, the chlorofluorocarbons used as refrigerants in refrigeration and air-conditioning systems have changed significantly. Chlorine, identified as a substance that destroys the ozone layer, is found in certain chlorofluorocarbons (CFCs) such as refrigerants R11, R12, and R502 and in the hydrochlorofluorocarbon (HCFC) refrigerants R22, R123, etc. These refrigerants have therefore been replaced by for instance hydrofluorocarbon (HFC) refrigerants R410A, R404A, R134a, etc., none of which contain chlorine. These are now gradually being replaced by products with a low global warming potential (low-GWP products).

Except in the case of ammonia refrigerants, past refrigerant conversions – from CFC to HCFC, then to HFC – did not raise concerns regarding flammability. However, moving to even lower-GWP refrigerants tends to wea-

ken the chemical bonds between the atoms, increasing instability, which results in flammability. Finding ways to be able to use combustible refrigerants safely, while maintaining and improving energy-saving performance, is one of the largest challenges faced when converting refrigerants to combat global warming.

In Japan, the characteristics of flammable refrigerants have been clarified and risk assessments have been carried out for their use, in order to enact safety standards. In addition, the High Pressure Gas Safety Act which regulates safety standards for refrigeration and air-conditioning systems has been relaxed. International regulations such as ISO 5149, IEC 60336-2-40, and IEC 60336-2-89 have also been significantly revised. The movement to lower-GWP refrigerants in Japan to protect the global environment, the revisions to related laws and the current status of refrigerant conversion by product are detailed in Fig. 1.

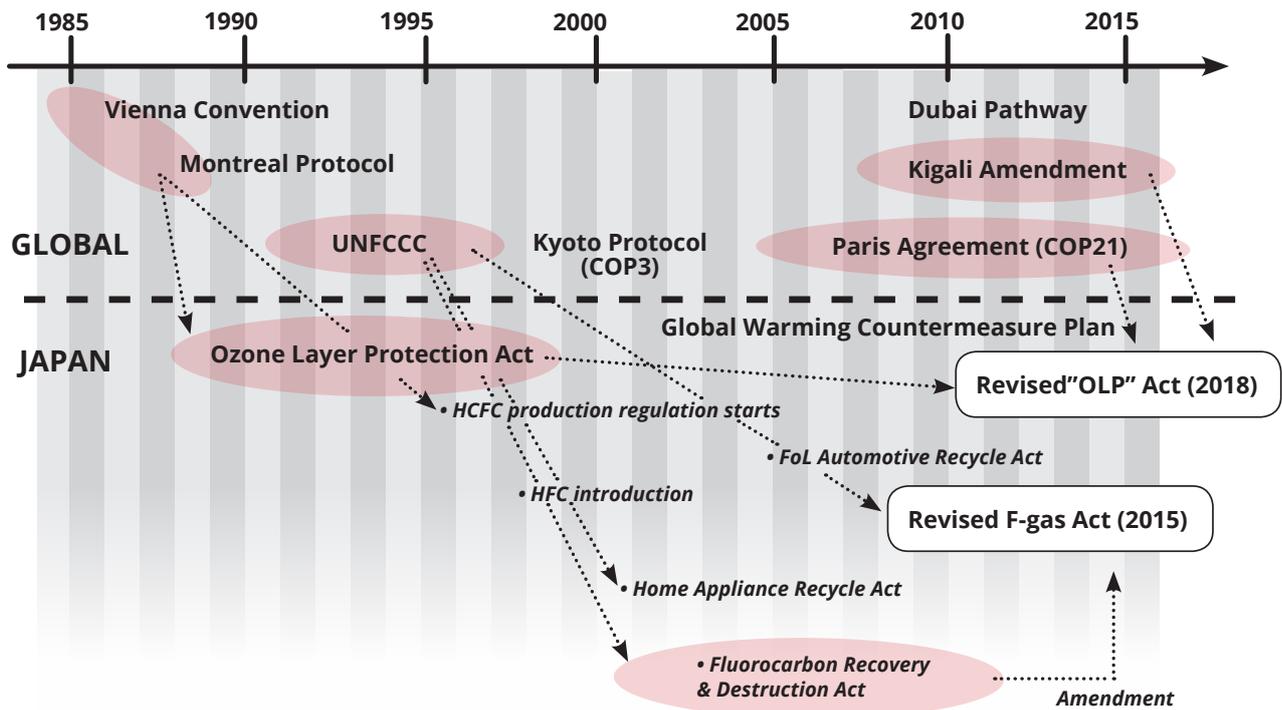


Fig. 1. Timeline of regulations and protocols (relationship between global and Japanese acts)

Refrigeration and air-conditioning refrigerant policy in Japan and worldwide – current status

The regulation of chlorofluorocarbons originated from the publication of an article by American researchers Rowland et al. in *Nature* in 1974 [1], which described the ozone depletion phenomenon caused by specified chlorofluorocarbons. Further efforts to control the use of chlorofluorocarbons in refrigeration and air-conditioning systems began with the Montreal Protocol of 1987 and continued with the enactment of global warming countermeasures based on the Kyoto Protocol of 1997.

Japan subsequently launched the Promotion of Measures to Cope with Global Warming in 1998. In 1999, the Energy Saving Law was revised and the Top Runner Program was enforced by this law. To encourage the recovery and destruction of refrigerants, the Fluorocarbon Recovery and Destruction Act and the Home Appliance Recycling Act were enacted in 2001, followed by the Automobile Recycling Act in 2002.

The control of chlorofluorocarbon refrigerants that was set out in a series of international agreements and protocols has thus been accompanied by improved Japanese laws and early refrigerant conversion (Fig. 1).

In April 2015, the Fluorocarbon Recovery and Destruction Act was renamed the Act on Rational Use and Proper Management of fluorocarbons (fluorocarbon Reduction Act), clarifying the shared responsibility for managing refrigerants throughout their life cycle. This includes the production, use, management, reuse and destruction of refrigerants. The Act required manufacturers of refrigeration and air-conditioning systems to market products suitable for refrigerants with an average GWP within the limits set for specific products (Table 1). Products specified in the fluorocarbon Reduction Act (products which use fluorocarbons with stipulated target values and target years) must be produced by refrigeration and air-conditioning manufacturers as low GWP equipment. The GWP of these products is to be reduced with a view to energy saving, safety and economic effi-

ciency. Target values and target years were therefore determined through discussions and approved by a national deliberative council.

In the international arena, the United Nations Climate Change Conference COP21 was held in Paris, France in December 2015. The resulting Paris Agreement set out an equitable and effective legal framework, effective from 2020 for all participating countries.

In response to the adoption of the Paris Agreement, Japan's Global Warming Prevention Headquarters drafted the Global Warming Countermeasures Plan. After being completed at the March 15, 2016 session of the Global Warming Prevention Headquarters, the Plan was adopted by the Cabinet on May 13, 2016. The Plan sets out a process for achieving a 26 % reduction in greenhouse gases by 2030 compared with fiscal year 2013, at the same time setting a goal of an 80 % reduction in greenhouse gas emissions by 2050.

The Kigali Amendment to the Montreal Protocol, adopted on October 14, 2016, introduced staged reductions (by CO₂ conversion) in the quantities of hydrofluorocarbons (HFC) produced and consumed. This will come into force on January 1, 2019 if it is approved by at least 20 countries. Through the Ozone Layer Protection Act amended on July 4, 2018, Japan has given a legal guarantee that it will regulate (allot) the production and consumption of ozone-depleting and global warming substances, which include specified fluorocarbons.

Noteworthy low-GWP refrigerants

Refrigerant conversion as a global warming countermeasure (rather than retrofitting or switching to refrigeration and air conditioning equipment newly designed and built for low GWP refrigerants) is a policy intended to minimize the GWP of fluorocarbons.

Low-GWP refrigerants include R32, R1234yf, and R1234ze(E), which are mildly flammable refrigerants (A2L: burning velocity of 10 cm/s or slower, a flammability

| Designated Products | Target GWP (Weighted Average GWP) | Target year |
|--|-----------------------------------|-------------|
| Residential A/Cs (mini-Split) | 750 | 2018 |
| Commercial A/Cs (Split/smaller than 6HP) | 750 | 2020 |
| Larger Commercial A/Cs (Split/exclude VRF) | 750 | 2023 |
| Centrifugal (Turbo) Chillers | 100 | 2025 |
| Mobile A/Cs | 150 | 2023 |
| Condensing unit & refrigerating unit | 1500 | 2025 |
| Cold storage warehouses | 100 | 2019 |
| Urethane foam | 100 | 2020 |
| Dust blowers | 10 | 2019 |

Two product categories will be added in April 2019

Table 1. Regulations relating to F-gases in Japan

| Refrigerant number | Safety class | Chemical formula or nominal composition of blends (mass-%) |
|--------------------|--------------|--|
| R-12 | A1 | CCl_2F_2 |
| R- 22 | A1 | CHClF_2 |
| R-123 | A1 | $\text{C}_2\text{HCl}_2\text{F}_3$ |
| R-13 11 | A1 | CF_3I (trifluoroiodomethane) |
| R-32 | A2L | CH_2F_2 |
| R-125 | A1 | CHF_2CF_3 |
| R-134a | A1 | CH_2FCF_3 |
| R-143a | A2L | CH_3CF_3 |
| R-245fa | B1 | $\text{CHF}_2\text{CH}_2\text{CF}_3$ |
| R-404A | A1 | R-125(44.0%) / R-143a(52.0%) / R-134a(4.0%) |
| R-407C | A1 | R-32(23.0%) / R-125(25.0%) / R-134a(52.0%) |
| R-407H | A1 | R-32(32.5%) / R-125(15.0%) / R-134a(52.5%) |
| R-407I | A1 | R-32(19.5%) / R-125(8.5%) / R-134a(72.0%) |
| R-410A | A1 | R-32(50.0%) / R-125(50.0%) |
| R-417A | A1 | R-600(3.4%) / R-125(46.6%) / R-134a(50.0%) |
| R-422D | A1 | R-600a(3.4%) / R-125(65.1%) / R-134a(31.5%) |
| R-427B | A1/A1 | R-32(20.6%) / R-125(25.6%) / R-143a(19.0%) / R-134a(34.8%) |
| R-444A | A2 L | R-32(12%) / R-125(5%) / R-1234ze(E)(83%) |
| R-445A | A2 L | R-744(6%) / R-134a(9%) / R-1234ze(E)(85%) |
| R-446A | A2 L | R-32(68%) / R-1234ze(E)(29%) / R-600(3%) |
| R-447A | A2 L | R-32(68%) / R-125(3.5%) / R-1234ze(E)(28.5%) |
| R-447B | A2 L | R-32(68%) / R-125(8%) / R-1234ze(E)(24%) |
| R-448A | A1 | R-32(26.0%) / R-125(26.0%) / R-134a(21.0%) / R-1234ze(E)(7.0%) / R-1234yf(20.0%) |
| R-449A | A1 | R-32(24.3%) / R-125(24.7%) / R-134a(25.7%) / R-1234yf(25.3%) |
| R-451A | A2L | R-1234yf(89.80%) / R-134a(10.20%) |
| R-451B | A2L | R-1234yf(88.80%) / R-134a(11.2%) |
| R-452A | A1 | R-32(11.0%) / R-125(59.0%) / R-1234yf(30.0%) |
| R-452B | A2 L | R-32(67.0%) / R-125(7.0%) / R-1234yf(26.0%) |
| R-454A | A2 L | R-32(35%) / R-1234yf(65%) |
| R-454B | A2 L | R-32(68.9%) / R-1234yf(31.1%) |
| R-454C | A2 L | R-32(21.5%) / R-1234yf(78.5%) |
| R-455A | A2 L | R-744(3.0%) / R-32(21.5%) / R-1234yf(75.5%) |
| R-457A | A2 L | R-32(18%) / R-1234yf(70%) / R-152a(12%) |
| R-459A | A2 L | R-32(68.0%) / R-1234yf(26.0%) / R-1234ze(E)(6.0%) |
| R-459B | A2 L | R-32(21.0%) / R-1234yf(69.0%) / R-1234ze(E)(10.0%) |
| R-460A | A1 | R-32(12.0%) / R-125(52.0%) / R-134a(14.0%) / R-1234ze(E)(22.0%) |
| R-460B | A1 | R-32(28.0%) / R-125(25.0%) / R-134a(20.0%) / R-1234ze(E)(27.0%) |
| R-463A | A1 | R-744(6.0%) / R-32(36.0%) / R-125(30.0%) / R-1234yf(14.0%) / R-134a(14.0%) |
| R-466A | A1 | R-32(49.0%) / R-125(11.5%) / R-1311(39.5%) |
| R-514A | B1 | R-1336mzz(Z)(74.7%) / R-1130(25.3%) |
| R-516A | A2L | R-1234yf(77.5%) / R-134a(8.5%) / R-152a(14.0%) |
| R-1224yd(Z) | A1 | cis- $\text{CHCl}=\text{CFCF}_3$ |
| R-1233zd | A1 | $\text{C}_3\text{H}_2\text{ClF}_3$ |
| R-1233zd(E) | A1 | |
| R-1234yf | A2L | $\text{CF}_3\text{CF}=\text{CH}_2$ |
| R-1234ze(E) | A2 L | $\text{CF}_3\text{CH}=\text{CHF}$ |
| R-1336mzz(E) | A1 | trans- $\text{CF}_3\text{CH}=\text{CHCF}_3$ |
| R-290 | A3 | $\text{CH}_3\text{CH}_2\text{CH}_3$ |
| R-600a | A3 | $\text{CH}(\text{CH}_3)_2\text{CH}_3$ |
| R-744 | A1 | CO_2 |

Table 2. List of conventional and alternative refrigerants

limit over 3.5 vol-% (or 0.10kg/m³) and heat of combustion lower than 19 MJ/kg). These, and many other refrigerants that are mixtures of these, are listed in ASHRAE Standard 34 (Table 2).

The listed refrigerants are composed of a mixture of R134a, R125, R152a, R290 (propane), R600 (isobutane), R744 (carbon dioxide), etc., based on R32, R1234yf, and R1234ze(E). Many refrigerants in refrigeration and air-conditioning systems, such as R410A, R134a, R404A, and others considered to be non-flammable, were classified in safety category A1 in ISO 817. If low-GWP refrigerants are to be used highly efficiently and safely in the future, it is imperative to evaluate mixed refrigerants that have been classified as A2L, A2, etc.

Introduction to lower-GWP products

Table 3 shows the status of refrigerant conversion for the major product categories in Japan. To the left of the arrows are refrigerants that are currently being used or that have been used previously. To the right of the arrow are refrigerants that have been introduced in order to lower GWP. A question mark (?) to the right of the arrow means that although a lower-GWP refrigerant is being sought, at this stage either there is no appropriate refrigerant or so many challenges still exist that it is impossible to specify an alternative.

For the most part, residential air-conditioners have been converted to R32. Small commercial air-conditioners are also being converted to R32. However, for VRF and other machines that require large quantities of refrigerant, the use of a low-GWP refrigerant that is flammable is not appropriate. Enacting and publicizing control standards to ensure safety is expected to take a significant time-frame to complete. For this reason, low-GWP machines of this type have made little headway in the market.

Residential water heaters, which are machines with a low water-heating capacity, have appeared on the market as R32 models, but residential-use heat pump-type water heaters known as “eco water heaters” use a carbon dioxide refrigerant. Commercial water heaters, on the other hand, use R410A and a carbon dioxide refrigerant. Systems requiring high-capacity water heating and systems that recover, reheat, and reuse hot water use R410A for the sake of system efficiency. Machines that use R454C (with a low GWP of 149) as an alternative refrigerant to replace R410A have also been launched. The reaction of the market will determine whether R454C becomes more mainstream.

For turbo chillers, low-pressure refrigerants (R1233ze(E), R1224yd(Z), R514A) and high-pressure refrigerants (R1234ze(E), R1234yf) have appeared and are already available on the market. Even after refrigerant conversion, there is only a slight decline in performance and no extensive changes to the design of the machines are required. It is assumed that conversion to these refrigerants will continue in the foreseeable future.

Chillers, on the other hand, are used over a wide range of temperatures and are equipped with many types of compressors. A variety of refrigerants match these

specifications, making it impossible to select and evaluate appropriate products.

As for refrigeration and cold storage equipment, products that use natural refrigerants such as carbon dioxide or isobutane are on the market, but only in extremely small numbers. For condensing units, machines using carbon dioxide refrigerant have been put on the market, but they do not ensure sufficient energy-saving performance in all usage ranges. They are often used in new systems because existing pipes cannot be used. For these reasons, many condensing units use fluorocarbon refrigerants; machines that use R448A, R449A, R407H, R463A, and other A1 refrigerants (i.e., refrigerants with a GWP of 1,500 or lower) have been released. However, no refrigerants with a GWP of less than 1,000 have appeared on the market. Refrigerants R448A and R449A have begun to be used as retrofit refrigerants in Europe, for example, but in Japan they are used in newly designed machines.

Refrigerants for automobile air-conditioners have been converted from R134a to R1234yf, but the spread of hybrid and electric automobiles has been accompanied by a reduction in the heat source used for heating, making it necessary to convert automobile air-conditioners to the heat pump model. As a result, automobile air-conditioners using carbon dioxide refrigerant are beginning to be used in some automobile models. Automobile air-conditioners could potentially be refrigerant-converted not only to fight global warming, but as a side effect of the trend towards the use of this kind of heat pump.

Domestic refrigerators and vending machines have already been converted to low-GWP refrigerants (R600a, carbon dioxide, R1234yf, etc.).

Outlook

Global warming countermeasures present huge challenges both within Japan and beyond. Improving energy-saving performance, converting to lower-GWP refrigerants and taking steps to prevent the leakage of refrigerants from equipment are all important areas for the refrigeration and air-conditioning industry to address.

The Paris Agreement and the Kigali Amendment require the use of HFCs to be reduced. Mildly flammable refrigerants that are slightly combustible (i.e., R32, R1234yf, R1234ze(E), and refrigerants that are mixtures of these) and carbon dioxide refrigerants that are higher pressure than fluorocarbons will often be used. Hydrocarbon refrigerants in the refrigeration and cold storage field will also be desirable as next-generation refrigerants. There are advantages and disadvantages to both that need to be considered. The number of refrigerants that must be handled more carefully than in the past, specifically to ensure safety, is rising.

For the refrigeration and air-conditioning industry to safely use flammable refrigerants with which it has little past experience, the safety risk must be evaluated and any dangers analyzed and mitigated. It is imperative that

| Product Category | Number of Units In fiscal year 2017 (x1,000) | Conventional Refrigerants → Alternatives |
|-----------------------------------|---|--|
| Residential A/Cs | 9,054.6 | R410A → R32 → ? |
| Commercial A/Cs | 827.1 | R410A → R32 (for small single split models) → ? |
| Gas engine-driven A/Cs | 28.7 | R410A → ? |
| Residential H/P Water heaters | 446.7 | CO ₂ (R744) / R32 |
| Commercial H/P Water heaters | | R410A → CO ₂ (R744) / R454C |
| Water Chilling Units | 12.2 | R410A / R407C / R404A / R134a → ? |
| Centrifugal (Turbo) Chillers | 0.266 | LP: R245fa → R1233zd(E) / R1224yd(Z) / R514A HP: R134a → R1234ze(E) / R1234yf |
| Commercial Built-in Ref. Cabinets | 184.8 | R404A / R410A / R134a → ? R600a / CO ₂ (R744) |
| Commercial Ref. Cabinets/split | 128.0 | R404A → R410A → R448A / R449A / R407H / R463A → ? CO ₂ (R744) |
| Condensing Units | 93.4 | |
| Refrigeration Units | 28.3 | R404A / R410A / R134a → ? |
| Automobile A/Cs | (4,700) | R134a → R1234yf (CO ₂ (R744)) |
| Vending Machines | (320) | R404A / R134a → R600a / CO ₂ (R744) / R1234yf |
| Domestic Refrigerators | (4,400) | R600a |

Table 3 Low-GWP alternatives and products

the industry collaborates with academic experts and regulatory authorities that are highly specialized and already possess this knowledge.

Using evaluation and analysis technologies to risk-assess mildly flammable refrigerants, along with safety evaluations and analyses carried out through industry/government/academic cooperation in Japan, could be a powerful force driving the conversion to low-GWP refrigerants. This is one way to counter global warming, which has now become a worldwide challenge.

References

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