Risk Assessment of Mildly Flammable Refrigerants

2013 Progress Report

<u>Digest version</u>

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The Japan Society of Refrigerating and
Air Conditioning Engineers

1. Introduction

1.1 Trends in Refrigerant Regulation

The EU protocol 2006/40/EC for mobile air-conditioning refrigerants, effective from January 1, 2011, prohibits the release of new cars using refrigerants with a GWP over 150. Furthermore, starting from January 1, 2017, it prohibits the release of any new car using such refrigerants. In 2009, the automobile industry decided to replace the conventional refrigerant, R134a, with the low-GWP refrigerant, R1234yf. However, in April 2012, the EU Commission temporarily permitted the continued use of R134a owing to a supply shortage of R1234yf. The release of new model cars using refrigerants with a GWP over 150 has been prohibited since January 1, 2013.

The regulation regarding the use of stationary air conditioners is known as F-gas Regulation (EC) No. 842/2006. The present regulation focuses on reducing refrigerant leakage from air conditioners and requires proper management, instructional courses for operators, labeling of equipment containing F-gas, and reports by producers, importers, and exporters of F-gas. In November 2012, the EU Commission proposed to enhance the existing regulations. The new proposal aims to reduce the leakage of F-gas to two-thirds of the present level and prohibit the release of equipment using F-gas in fields where an environmentally friendly refrigerant has been developed. To achieve this, a phase-down schedule has been proposed that assumes that the annual amount of HFCs sold in the EU in 2015 has been reduced to one-fifth. In December 2013, the European Parliament and Council reached a trilogue agreement. The main points of the agreement are as follows:

- The “phase-down” schedule remains as initially proposed by the Commission;
- F-gases with GWPs above 2500 will be banned in stationary refrigeration systems from 2020, and those with GWPs above 750 will be banned in stationary air conditioners from 2025; and
- The issue of pricing or auctioning quotas is addressed through a review clause that empowers the Commission to assess a method for allocating quotas.

At the Conference of Parties, which aims to abolish practices that damage the ozone layer, three North American countries (US, Canada, and Mexico) submitted a proposal to revise the Montreal Protocol to restrict production and sales of HFCs. HFCs do not damage the ozone layer. The global warming issue was caused by the replacement of prohibited CFCs and HCFCs, which damage the ozone layer, with HFCs, which have high GWPs. The proposal suggests restricting the distribution of HFCs in the framework of the Montreal Protocol.

In Japan, the Global Environment Sub-Committee of the Central Environment Council and the Chemical and Biotechnology Sub-Committee of the Industrial Structure Council jointly created a task force and compiled an outline for the regulation of HFCs. Based on these discussions, the "Law on regulation of management and rational use of fluorocarbons" was established at the National Parliament on June 5, 2013. The name of the law was changed from the "Law for ensuring the implementation of the recovery and destruction of fluorocarbons concerning specific products." The new law requires following the replacement of high-GWP HFCs, refrigerant management and refrigerant recovery to reduce leakage of HFCs.

(1) Fluorocarbon manufacturers, through technology development and manufacturing of lower-GWP refrigerants, should reduce the environmental impact.

(2) Refrigeration and air-conditioning equipment manufacturers should achieve the goal of replacing high-GWP refrigerants with low-GWP refrigerants by the target year for each product sector.

(3) For users of commercial refrigeration and air-conditioning equipment, proper management, installation, inspection, and repair is required.

(4) For collection and destruction traders, a registration system of charging fluorocarbons for commercial refrigeration and air-conditioning equipment will be introduced, and a permit system for recovery of fluorocarbons will also be introduced.

1.2 Research Trends on the Safety of Mildly Flammable Refrigerants

The development of environmentally friendly refrigerants for room and package air conditioners is imperative to the growth of air-conditioning technology. The low-GWP refrigerants R1234yf and R32 are promising candidates for replacing conventional HFC refrigerants. However, these refrigerants are not very stable in air and are flammable. Therefore, it is essential to collect basic data about the flammability of low-GWP refrigerants and research their safety for practical use. The integration of basic information about refrigerant physical properties, cycle performance, life cycle climate performance (LCCP), flammability, and risk assessment will simplify their selection for practical use. These efforts are expected to contribute to the advancement of the global air-conditioning industry.

R1234yf and R32 are less flammable than propane and R152, and are therefore classified as mildly flammable refrigerants. In ASHRAE Standard 34, the rank 2L was set for mildly flammable refrigerants with burning heats lower than 19 MJ/kg and burning velocities lower than 10 cm/s. Together with ammonia, R1234yf and R32 are classified as 2L.

Rank 2L on ASHRAE Standard 34 changed the restriction on refrigerants regarding their flammability and allows for the practical use of low-flammability refrigerants. However, in Japan, only the classifications “non-flammable” and “flammable” are recognized in the High Pressure Gas Safety Act and the Ordinance on the Security of Safety at Refrigeration. With the objective of gathering essential data for the risk assessment of mildly flammable refrigerants, safety studies are being conducted by project teams from the Tokyo University of Science at Suwa, Kyusyu University, University of Tokyo, and the National Institute of Advanced Industrial Science and Technology. Since 2011, they have been sponsored by the project “Development on Highly Efficient and Non-Freon Air Conditioning Systems” of the New Energy and Industrial Technology Development Organization (NEDO).

In addition, a research committee was created by the Japan Society of Refrigerating and Air Conditioning Engineers to assess the risks associated with mildly flammable refrigerants. The Japan Refrigerating and Air Conditioning Industry Association and the Japan Automobile Manufacturers Association are presently undertaking risk assessments and the results are being discussed by the research committee. The 2013 activities of the committee to assess the risks associated with mildly flammable refrigerants are compiled in this report. The committee members would be pleased if this report is helpful for people working in associated fields.

2. Legal Issues with Mildly Flammable Refrigerant

2.1 Explanation of High Pressure Gas Safety Law and Legal Issues with Mildly Flammable Refrigerant

The present Refrigeration Safety Regulations recognize four classifications: inactive gases, active gases, toxic gases, and fluorocarbons other than inactive gases. The first three types of gases are defined by listing of those names and are demanded for an operation.

Because of the high probability that refrigerant gases with low global warming potential (GWP) will be needed in the future for a low-carbon society, after confirming the safety of a mildly flammable gas (A2L of ISO/FDIS 817), it seems that the correspondence which cooperated with foreign countries is also required. However, we are now having discussions with administrative authorities to clarify whether a mildly flammable gas can be used as an inactive gas (A1) to maintain the normal state of operation.

2.1.1 Outline of High Pressure Gas Safety Law

Some laws and regulations are already in place related to the appropriate pressures to maintain safety or prevent risks, and these depend on usage. Because these laws are binding, incorrect operation is accompanied by government punishment. Although the regulatory restrictions are based on the laws, they are basically arbitrary. We should operate without confusing the laws and regulations.

High Pressure Gas Safety Law widely regulates the manufacture, operation, maintenance of package air conditioners, chilling units, and turbo refrigerant (these are called refrigeration equipment), which are used to maintain a comfortable daily lifestyle and environment.

The decree regarding high pressure gases primarily consist of laws, government ordinances, ministerial ordinances, and ministerial notifications (described below). Based on the laws, the technical standards, application procedures, inspection procedures are specified in detail by ministerial ordinances. Government ordinances have specified exemptions to laws, permissions for production and storage, values that require notification reports, and high pressure gases that do not require notification reports on their sales. Ministerial ordinances are divided into several types, depending on the type of business category and object of the regulation, and the Refrigeration Safety Regulations are ministerial ordinances regarding refrigerant equipment.

Law	:High Pressure Gas Safety Law.
Government ordinance	:Order for Enforcement of High Pressure Gas Safety Law
Ministerial ordinance	:1. Refrigeration Safety Regulations–regulations on production, sale, etc. of refrigerant equipment.
	2. General High Pressure Gas Safety Regulations–regulations on production, sale, etc. of high-pressure gas equipment.
	3. Container Safety Regulations–regulations on cylinders that contain high-pressure gas.
Ministerial notification	:1. High Pressure Gas Safety Law enforcement ordinance-related notification.
	2. Location of production facility and notification defining the details of technical standards regarding structures, facilities, and production methods.

(b)Related Exemplified Standard and Operating Interpretation Internal regulations are defined for the interpretation, operation, and individual items related to the law, government ordinances, ministerial ordinances, and ministerial notifications. The related exemplified standard of the ministerial ordinances described above are included in these internal regulations. The standard regarding refrigerant equipment is called the related exemplified standard of the Refrigeration Safety Regulations. Specific examples regarding technical factors (pressure tests, airtight tests, materials, welding, etc.) of ministerial ordinance are indicated in the standard. The production and sale (including exports) of refrigerant equipment are regulated based on the laws (government ordinances, ministerial ordinances, ministerial notifications, etc.). These require attention because incorrect operation is accompanied by government punishment.

2.1.2 Daily Issues with Use of Mildly Flammable Refrigerant (example)

To use a room air conditioner, package air conditioner, or turbo refrigerating machine (hereafter called refrigeration apparatus), the treatment of three fundamental elements, “operation,” “charging,” and “recovery,” must be considered in daily action and these elements are difficult to understand. Moreover, regarding law and its response (notification report, etc.) to each operation, all parties are involved, especially the builders, producers, and users. Although the law for a refrigeration apparatus has been adapted from the Refrigeration Safety Regulations, it treats only “the act where a gas for refrigeration is compressed or liquefied to produce a high-pressure gas.” Other acts are regulated by other rules such as the General High Pressure Gas Safety Regulations. Charging a refrigerant gas is an act that produces a high-pressure gas. Therefore, the related law is based on the General High Pressure Gas Safety Regulations, and a notification report is required for every installation location. However, charging with an inactive fluorocarbon or the act of recovery performed with a recovery subsystem is excluded. Moreover, the act of charging a refrigeration apparatus during repair service is not only an act of producing, but also one of selling (whether with or without compensation) the high-pressure gas. Thus, it is necessary to follow the General High Pressure Gas Safety Regulations for commercial sales (or to include a type change notification for the high-pressure gas regarding sales). However, because an act that uses a small container (this is called a cylinder and the internal volume is less than 1 l) is excluded from the High Pressure Gas Safety Law, it is also exempted from the notification report on producing and selling a high-pressure gas. Moreover, when selling a class 1 refrigeration apparatus, a separate notification report on a high-pressure gas dealer is also needed, based on the Refrigeration Safety Regulations.

2.1.3 Legal Treatment of R1234yf, R1234ze(E), R32, and Others

Although “flammable gases,” “toxic gases,” and “inactive gases” are defined by the second article of the Refrigeration Safety Regulations, and each refrigerant name is listed, the definition standard is not clear. Of course, there is no definition for “mildly flammable.” At present, R1234yf, R1234ze(E), and R32 are listed neither as inactive gases nor as flammable gases. In this case, the easing of various regulations is not applied to R1234yf, R1234ze(E) and R32.

(b)Treatment by General High Pressure Gas Safety Regulations “Flammable gases,” “toxic gases,” and “inactive gases” are defined by the second article of the General High Pressure Gas Safety Regulations, and the names of these gases are listed for each category. In contrast to the Refrigeration Safety Regulations, fluorocarbons (except for flammable gases) are described under “inactive gases,” and gases (except for listed gases) with the following properties are described under “flammable gases.” (1) The lower limit for an explosion is less than 10%, and (2) the difference between the higher limit and lower limit for an explosion is more than 20%.

Figure 2.1.1 shows these types, along with where R1234yf, R1234ze(E), R32, and R717 would fall. The shaded and white parts indicate “flammable” and “non-flammable,” respectively. In ASHRAE, on the other hand, although R1234yf, R1234ze(E), R32, and R717 were defined as “2L” by “ASHRAE standard 34” in 2010, their treatment was not clearly defined.

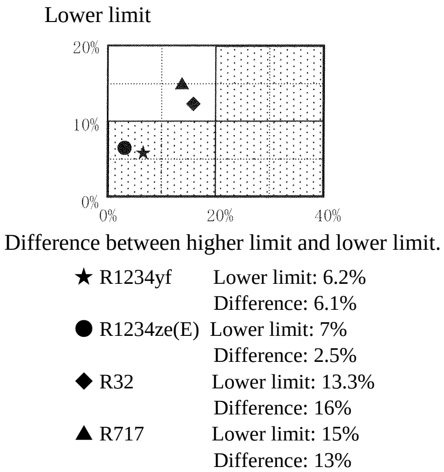


Fig. 2.1.1 Measurement results based on General High Pressure Gas Safety Regulations (JFMA, 2012)

In the recovery of R1234yf, R1234ze(E), and R32, because the fluorocarbon (only an inactive gas: High Pressure Gas Safety Law enforcement ordinances) in the recovery equipment is being contracted out by law, R32 corresponds to it. However, this requires attention because, when recovery equipment contains R1234yf and R1234ze(E), these are handled based on the General High Pressure Gas Safety Regulations.

2.1.4 Issues with High Pressure Gas Safety Law Regarding Mildly Flammable Refrigerant

(a)Revision of Listing Name Principle Although “flammable gases,” “toxic gases,” and “inactive gases” are defined by the second article of the Refrigeration Safety Regulations, and each refrigerant name is listed, the definition standard is not indicated. It is doubtful that

R413A which is classified as “A2” (mildly flammable) in “ASHRAE standard 34” (ASHRAE 34:2013) is listed as an inactive gas. Because the treatment of a new refrigerant gas (particularly a mildly flammable gas) or a mixed gas cannot presently be determined from the viewpoint of global warming prevention, these are handled on an individual basis by sending an inquiry to the Commercial Affairs Circulation Preservation Group High Pressure Gas Preservation Section, Ministry of Economy, Trade and Industry. The “flammable” number concepts of the Refrigeration Safety Regulations should be consistent with the General High Pressure Gas Safety Regulations.

(b)Recovery and Legislation of Refrigerant Gas That Is Not Treated As Inactive Gas Even when classified as flammable, gases should not be regulated uniformly. In particular, regarding a flammable gas close to an inactive gas (A2L of the mildly flammable gases), discussions are needed to ease the regulations. Moreover, it is necessary to inquire about the establishment of technical standards for the recovery subsystem.

(c)Easing Requirements for Specified Equipment Even though the refrigerant that can be used by a specified piece of equipment is limited to only an inactive fluorocarbon by a High Pressure Gas Safety Law enforcement ordinance-related notification, discussions are also expected in relation to the application range of fluorocarbons that are not flammable gases.

2.1.5 Issues with Mildly Flammable Refrigerants from Foreign Countries

From the safety administration perspective, it is desirable to clarify several issues, as follows. (1) If R32 is listed as an inactive gas, close attention must be given to foreign countries because they might interpret the listing differently. (2) We should clarify what is eased or changed by changing from A2 to A2L. (3) In legislation, explanations of the activities of many foreign countries are needed.

2.2 Situation for Overseas Laws, Standards, and Regulations: Current Global Trends Regarding Refrigerants

2.2.1 Trends in Japan

The Japanese government revised the current Law Concerning the Recovery and Destruction of Fluorocarbons and promulgated the new Act on June 12, 2013. Preparations, including governmental and ministerial ordinances, are underway toward full legal enforcement beginning on April 1, 2015. The following four countermeasures are being proposed as countermeasures spanning the entire fluorocarbon lifecycle from production to destruction, adding to the existing laws for fluorocarbon recovery and destruction.

(1) Promotion of low GWPs for products using fluorocarbons or non-fluorocarbons（conversion by manufacturers of equipment and products）
(2) Promotion of reuse of recovered refrigerant for actual phase-down of fluorocarbons (efforts by gas manufacturers)
(3) Prevention of fluorocarbon leaks when using commercial-use refrigeration and air conditioning equipment (refrigerant management by user)
(4) Charge by registered contractor and reuse by licensed contractor

2.2.2 Trends in Europe

The existing F-gas Regulation in Europe came into effect in 2007. A review for a revised proposal was scheduled in 2011. Although there was a slight delay, the European Parliament Environment Committee and EU Council reached an agreement on a revised proposal centering on an HFC phase-down to 21% by 2030. Parts of this agreement are shown as follows,

(1) Single split air-conditioning systems containing less than 3 kg of an F-gas with a GWP of 750 or greater are to be prohibited from January 1, 2025.
(2) Refrigerators and freezers for commercial use that contain an F-gas with a GWP of 2,500 or greater are to be prohibited from January 1, 2020.
(3) A pre-charge prohibition begins from January 1, 2017. However, equipment pre-charged with HFCs that are accounted for within the quota system may be placed on the market.
① A verifiable declaration of conformity is necessary.

After approval by the Committee of the European Parliament, this revised proposal will be submitted to a vote at the plenary session of the European Parliament (scheduled for March 11). Once approved by the EU Council, it will be promulgated and is expected to take effect from January 1, 2015.

2.2.3 Trends in United States

The trends in the United States include North American proposals to the Montreal Protocol conferences, CACC trends, ASHRAE standard trends, trends for the revision of UL standards, and SNAP trends. However, the AHRI refrigerant evaluation program "Low-GWP Alternative Refrigerant Evaluation Program" is primarily mentioned here. The following URL can confirm the details.

http://www.ahrinet.org/App_Content/ahri/files/RESEARCH/AREP_Final_Reports/

2.2.4 International Trends

Concerning HFC regulations, there are numerous global trends, and only a few of them are presented here.

(1) The G20 Summit was held in St. Petersburg, Russia, on September 5–6, 2013. HFC countermeasures were included in the item on climate change in the summit statement.

(2) On June 8, 2013, the United States and China agreed at a summit meeting to cooperate toward reductions in the manufacture and use of HFCs. This agreement stated that a global phase-down of HFCs could reduce carbon emissions by 90 Gt (CO_2 conversion) by 2050.

(3) The Twenty-Fifth Meeting of the Parties to the Montreal Protocol (MOP 25) was held in Bangkok on October 21–25, 2013. The North American proposals were also submitted in a continuation from the previous year.

(4) In international standards, the revised proposal for ISO5149 was passed after being voted on by each country. Concerning this revision, work has advanced toward the introduction of new safety classifications that include mildly flammable refrigerants. In ISO5149, the refrigerant charge amount is regulated based on the flammability. In addition, when a flammable refrigerant is used, explosion-proof electrical equipment is required in such places as mechanical rooms, but mildly flammable 2L refrigerants have been excluded from this requirement.

3. Progress at the University of Tokyo

To obtain information needed to assess the risks of using low-GWP refrigerants, we performed studies in the following areas.

1. Simulation of leakage of mildly flammable refrigerants
2. Thermal decomposition products of lower-GWP refrigerants
3. Risk of diesel combustion during pump-down of a heat pump

Simulation of leakage of mildly flammable refrigerants

Numerical simulations were conducted to examine the diffusion phenomena that occur when a refrigerant leaks from a room air conditioner (RAC), a variable refrigerant flow (VRF), or a chiller into a large space in which these are installed. Based on the simulation results, the refrigerant concentration distributions, the volumes and positions of the flammable regions, and their changes over time were examined. The commercial CFD program STAR-CD was used to simulate the refrigerant diffusion phenomena. Table 3.1 lists the leakage scenarios considered in this study.

Table 3.1 Leakage scenarios

case No.	Type	Refrigerant	Charged amount	Leakage velocity	Ventilation air flow	Air vent
1	wall-mounted indoor unit of RAC	R32	1.0 kg	125 g/min	0 m^3/h	exist
2				250 g/min	0 m^3/h	exist
3				1000 g/min	0 m^3/h	exist
4		R1234yf	1.4 kg	175 g/min	0 m^3/h	exist
5				350 g/min	0 m^3/h	exist
6				1400 g/min	0 m^3/h	exist
7		R290	0.2 kg	50 g/min	0 m^3/h	exist
8			0.5 kg	125 g/min	0 m^3/h	exist
9	floor-mounted indoor unit of RAC	R32	1.0 kg	250 g/min	0 m^3/h	exist
10		R1234yf	1.4 kg	350 g/min	0 m^3/h	exist
11	outdoor unit of RAC	R32	1.0 kg	250 g/min	0 m^3/h	(outdoor)
12		R1234yf	1.4 kg	350 g/min	0 m^3/h	(outdoor)
13	VRF	R32	26.3 kg	10 kg/h	0 m^3/h	none
14					0 m^3/h	exist
15					169 m^3/h	exist
16					0→169 m^3/h	exist

case No.	Type	Refrigerant	Charged amount	Leakage velocity	Ventilation air flow	Air vent
17	VRF	R32	26.3 kg	10→0 kg/h	0 m^3/h	exist
18		R1234yf	29.4 kg	10 kg/h	0 m^3/h	none
19					0 m^3/h	exist
20					169 m^3/h	exist
21					0→169 m^3/h	exist
22				10→0 kg/h	0 m^3/h	exist
23	water-cooled chiller	R32	23.4 kg	75 kg/h (burst leak)	0 m^3/h	exist
24				10 kg/h (rapid leak)	0 m^3/h	exist
25					545 m^3/h	exist
26		R1234yf	23.4 kg	70 kg/h (burst leak)	0 m^3/h	exist
27				9 kg/h (rapid leak)	0 m^3/h	exist
28					545 m^3/h	exist
29		R1234ze(E)	23.4 kg	54 kg/h (burst leak)	0 m^3/h	exist
30					545 m^3/h	exist
31				7 kg/h (rapid leak)	0 m^3/h	exist
32					545 m^3/h	exist

The simulation conducted in this study to examine leakage of refrigerants into a space yielded the following findings.

1. In the case of leakage from a wall-mounted indoor unit, combustion does not occur if an ignition source does not exist inside the indoor unit.
2. In the case of leakage from a floor-mounted indoor unit, safety regulations are required when flammable refrigerants are used in air conditioners.
3. In the case of leakage from a floor-mounted indoor unit or outdoor unit, the risk of combustion is higher with R1234yf than with R32.
4. In the case of leakage from an outdoor unit, the balcony with drains and undercuts are preferred for safety because an outdoor unit has a fan near the floor level, which may lead to spreading of the flammable region into entire balcony area.
5. In the case of leakage from a VRF, when the burning velocity is considered, the FVT is much smaller.
6. In the case of leakage from a water-cooled chiller, the ventilation air flow has a large effect on the FVT. When there is no ventilation air flow and the velocity of the refrigerant leakage is high, the FVT might increase after the refrigerant leaks out completely.

Thermal decomposition products of lower-GWP refrigerants

Experiments were carried out to quantify HF, the main toxic product of refrigerant decomposition, and to analyze other products of the thermal decomposition of refrigerants. There are two causes of HF generation from refrigerants: thermal decomposition by heating and combustion. An experimental apparatus for examining thermal decomposition was fabricated for use in this research.

The materials tested were mixtures of refrigerants (R32, R1234yf, and R134a) and air. An FT/IR-4200 (by JASCO), gas cell (temperature-controlled, 10-cm path length, by Harrick), and CaF2 windows were used to measure the concentrations of the refrigerants and products.

For R32, R1234yf, and R134a, the lower-limit temperatures of thermal decomposition and the amounts of products were measured in a manner that was relatively unaffected by the wall materials.

In the future, we plan to reduce the effect of soot, experiment with common wall materials such as SUS, and examine the reaction rates and mechanisms involved.

As one example of the results obtained, the concentration of HF versus the heater temperature is shown in Fig. 3.2. In this case, the tube was an Inconel 600 tube, the initial R1234yf concentration was 2.5 vol. %, the total flow rate was 200 ml/min, and the variable parameter was the absolute humidity [g/m^3].

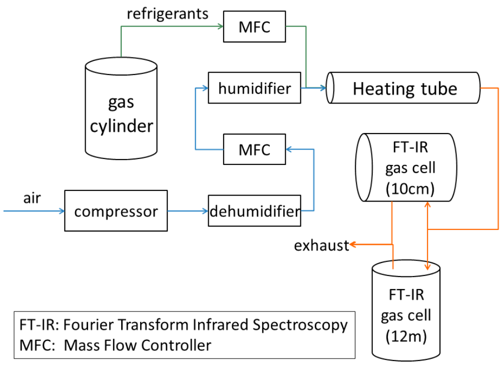


Fig. 3.1 Schematic diagram of experimental apparatus

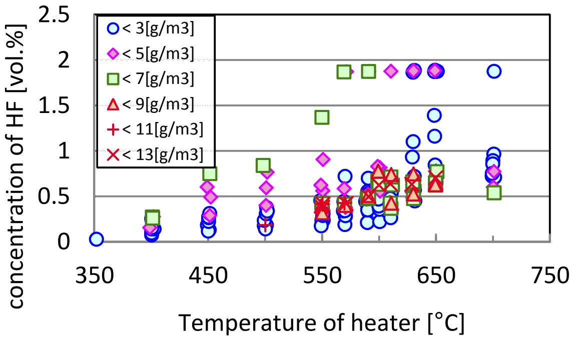


Fig. 3.2 Concentration of HF and heater temperature

(total 200 ml/min, 2.5 vol.% with air)

Risk of Diesel combustion during pump-down of the heat pump

This study also examined the risks of combustion of the different refrigerants considered using an experimental apparatus that reproduces diesel explosions. It is important to note that the result reported do not suggest that these refrigerants pose high risks of combustion. Rather, the apparatus and experimental conditions were designed to make it easy to induce diesel explosions. Fig. 3.3 shows the experimental apparatus, which consists of an air supply system, a refrigerant supply system, a temperature control system, a lubricant oil supply system, and a compressor (model engine) driven by a motor.

Fig. 3.4 shows a schematic diagram of the relationship of the maximum pressure at compression of a gaseous mixture of air, refrigerant, and lubricant oil to the concentration of the refrigerant. The concentration of the refrigerant is plotted on the horizontal axis, and the maximum pressure is plotted on the vertical axis. In the range of high refrigerant concentrations, no combustion occurred with any of the refrigerants, and the maximum pressure increased as the concentration of the refrigerant decreased. In the range of low refrigerant concentrations, self-ignition of the lubricant oil occurred first. If the refrigerant was one of high flammability, the maximum pressure would then be higher because of the combustion of the refrigerant itself. If the refrigerant was one of low flammability, on the other hand, the refrigerant itself would not combust and the maximum pressure would be low.

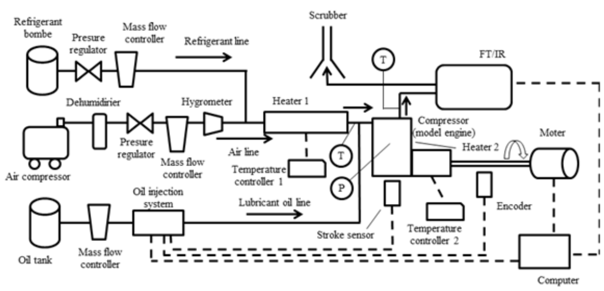


Fig. 3.3 Experimental apparatus

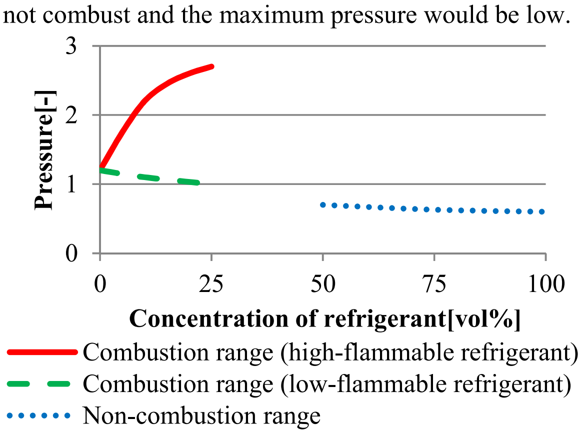


Fig. 3.4 Schematic diagram of the relationship between the maximum pressure and the concentration of refrigerant

4. Progress at Kyushu University

A part of the NEDO-funded research carried out this year is presented in this article. For the new low-GWP refrigerant, HFO-1234ze(Z), thermodynamic properties (i.e., critical parameters and $P\rho T$ property) and transport properties (i.e., thermal conductivity and viscosity) have been measured. On the basis of precise measurement results, an equation of state has been proposed, which was validated at temperatures from 273 to 430 K and pressures up to 6 MPa. The FLD file built in the proposed equation of state has been distributed by NIST, so that the properties of HFO-1234ze(Z) can be calculated using REFPROP 9.1. Additionally, the heat transfer characteristics of HFO-1234ze(Z) in a horizontal microfin tube and on a horizontal smooth tube have been clarified.

The thermodynamic properties of the selected low-GWP refrigerant mixture HFO-1234ze(E)/HFC-32/CO_2 have been precisely measured by a brief thermodynamic assessment. On the basis of the measurement results, the validation of the mixing model to predict the properties of the ternary mixture has been carried out. Using the verification results, the heat transfer characteristics of the refrigerant mixture in a horizontal microfin tube and a plated heat exchanger, as well as its cycle performance have been investigated.

5. Physical Hazard Evaluation of A2L Refrigerants Based on Several Conceivable Accident Scenarios

5.1 Introduction

At Tokyo University of Science, Suwa, a project titled "Evaluation of Combustion and Explosion Hazards and Risk Assessment on A2L Refrigerants for the Air-conditioning Systems" has been performed with the Research Institute for Safety and Sustainability (RISS), AIST. In this report, we describe the outline of the subject conducted by Tokyo University of Science, Suwa in FY2011-FY2013.

5.2 Details of physical Hazard Evaluation in Each Scenario

5.2.1 Scenario #1: Simultaneously used with a fossil-fuel heating system

Even if all the refrigerant contained inside a commercial room air conditioning system for an area of about 11 m2 leaked into the general living space (7.8 m2: approximately corresponding to the area of 4 pieces and half of a Tatami mat) where the heating system worked on, ignition and flame propagation did not occur. The generation ability of HF due to the thermal decomposition of A2L refrigerant was as much as that of the present refrigerant. When there were some flows inside the space, the HF concentration became greater.

5.2.2 Scenario #2: Service and maintenance situation

(1) Sub-scenario (a): We evaluated the physical hazard for a commercial portable gas lighter used in the space where the A2L refrigerant leaked and accumulated. When a piezo gas lighter was used, no ignition was confirmed. Although the ignition and small flame propagation near the outlet of a turbo lighter was confirmed, the flame quickly went out. However, significant pressure from the blast wave and temperature increases were not observed.

(2) Sub-scenario (b): We assumed that the A2L refrigerant leaked from a fracture or pinhole formed in the pipes or hoses from the factory for the service and maintenance. When the refrigerant was leaked from a 4 mmϕ pinhole for the simulation of a pipe breaking, the flammable zone was only formed near the outlet of the refrigerant. Even if the excess energy than the conceivable ignition source in actual situation was given to the refrigerant jet, the ignition and flame propagation to entire the refrigerant jet was not confirmed.

(3) Sub-scenario (c): We assumed that the A2L refrigerant leaked inside a device for the service and maintenance such as collection device. If there was no slit to diffuse the accumulated leaked refrigerant in the model collection device to the outside, the refrigerant was ignited and propagated to the entire refrigerant by an ignition source having a very large energy. However, generation of the ignition spark above the large energy is extremely low in the actual situation. If there is a slit of suitable width in the model collection device, accumulation of refrigerant could be controlled in a very short period of time and the ignition could be prevented.

5.2.3 Scenario #3: In situation that A2L refrigerant was installed to a VRF system

We focused on clarifying the properties of combustion behaviors originating from the combustion of A2L refrigerant and scale effect of these properties by a series of laboratory-scale experiments. For R1234yf, the influence of humidity on the combustion behavior was confirmed. In the present experiment, comparatively a larger blast wave pressure and temperature increase were observed for a 750 and 500 mm leak height. The scale of flame propagation and significant increases of these parameters depend on the amount of refrigerant that exceeded the LFL located above the ignition source. However, at most, the blast wave pressure only corresponds to the phenomena of a 10 mm thick acrylic board being slightly lifted.

6. Progress Report of Research Institute for Innovation in Sustainable Chemistry, AIST

The effects of temperature and humidity on the flammability of refrigerants are important. In general, the dependence of the flammability limits on the temperature can be explained by White's rule. The temperature dependences of the flammability limits for ammonia, R32, and R143a were found to basically agree with the values predicted by White's rule. On the other hand, the temperature dependences of the flammability limits for R1234yf and R1234ze(E) were considerably larger than those predicted by White's rule. With regard to humidity, the flammability limits of ammonia, R32, and R143a were found to not be greatly affected by the humidity of air. On the other hand, the flammable ranges of R1234yf and R1234ze(E), whose molecules contain more F-atoms than H-atoms, were found to be markedly dependent on the humidity.

The effect of relatively high humidity (i.e., up to 50% at 60 °C) on the flammability property was measured in air for R410A, R410B, R134a, and R125. Under this humidity condition, R410A, R410B, and R134a became flammable, whereas R125 did not.

Water vapor enhances the flammability property of compounds that have more F-atoms than H-atoms. There was concern over ammonia, which has enough hydrogen atoms. The flammability limits for binary mixtures of ammonia with R1234yf, 1234ze(E), R134a, and R125 were measured in dry air. The flammability limits of ammonia and R1234yf mixtures were found to be very different from the values predicted by Le Chatelier's equation. Similarly, the flammability limits of ammonia mixtures with each of R1234ze(E), R134a, and R125 were found to show characteristic behaviors. These behaviors could be explained by modifying Le Chatelier's equation.

The flammability limits, burning velocity, and quenching distance of R1234s became worse as the humidity of the air increases. This is because these compounds have a much higher F/H ratio than unity, and H_2O molecules supply H atoms to the reaction system. If they are used at the optimum humidity, their flammability will exceed that of ammonia. Similarly, care should be taken when R1234yf and R1234ze(E) are mixed with a compound having an F/H ratio of less than 1.0, such as ammonia. Such a mixture will show higher flammability than expected from the individual components.

Many blended refrigerants contain non-flammable components. To estimate the flammability of such refrigerants, the degree of non-flammability needs to be quantified. Thus, we recently introduced the concept of limiting methane concentration (LMC). LMC implicitly selects methane as a reference gas to estimate the degree of non-flammability. However, methane is not necessarily a good reference gas because there are many 2L and related compounds with excess F-atoms. This time, we selected R32 as the reference gas. In order to assess the suitability of R32 as a reference gas, we introduced the F2-number, which is the square of the normalized flammable range. The linearity between the F2-number and the mixing ratio was found to be good for nitrogen and carbon dioxide; fair for methane, R152a, R125, and R134a; and poor for R1234yf and R1234ze(E).

The thermal decomposition of refrigerants was investigated by using a flow reactor (Inconel, 12.7 mm outer diameter, 10.2 mm inner diameter, 44 cm length).

First, the effects of the R1234yf concentration and total flow rate on the thermal decomposition of R1234yf were studied. R1234yf was observed to decompose at a certain temperature, and the decomposition considerably increased at this temperature. At 7.8 vol% ($\varphi = 1.0$), R1234yf was observed to decompose at 600 °C or higher, and the decomposition temperature increased with decreasing R1234yf concentration when $\varphi < 1$. On the other hand, the decomposition temperature did not change when $\varphi > 1$. The major products were HF, COF_2, CO_2, and CO, and O_2 consumption and products such as HF increased with the R1234yf decomposition. The decomposition temperature was found to rise when the total flow rate was increased. No detectable differences were found between using a clean reactor and reactors that had been used in the previous experiments.

Second, the thermal decomposition of R1234ze(E) and R22 was studied at φ = 1 and a total flow rate of 100 cm^3/min. R1234ze(E) and R22 were observed to decompose at 550 and 450 °C or higher, respectively, if a clean reactor was used in the experiment. When a contaminated reactor was used, R1234ze(E) and R22 started to decompose at 150–250 °C below the temperature observed with a clean reactor.

The quenching distance and flame extinction diameter were measured to elucidate the ignition and quenching characteristics of 2L refrigerants. We also conducted a practical ignition test with a magnetic contactor connected to a high-voltage electric circuit. Based on the experimental results, we found the following.

First, 2L refrigerant compounds with $S_{u0,max}$ below 10 cm s^{-1} have E_{min} that is more than one order of magnitude greater than that of propane. E_{min} is greater than the spark energy from a human body.

Second, 2L refrigerants have a quenching distance more than three times larger than that of propane. Thus, electrical components will frequently generate sparks at gaps narrower than d_q of 2L refrigerants. In such cases, the conductive heat loss to electrodes will significantly increase the energy necessary for ignition of the 2L refrigerant. This may be one of the main reasons why R32 ignition occurred very rarely with a magnetic contactor whose spark energy was much greater than the E_{min} of R32.

Third, 2L refrigerants have a flame extinction diameter several times larger than that of propane. Even though there are small openings on the enclosure of potential igniters such as magnetic contactors and sockets, the flame of a 2L refrigerant cannot go through these openings, and such igniters will not become an ignition source for the refrigerant.

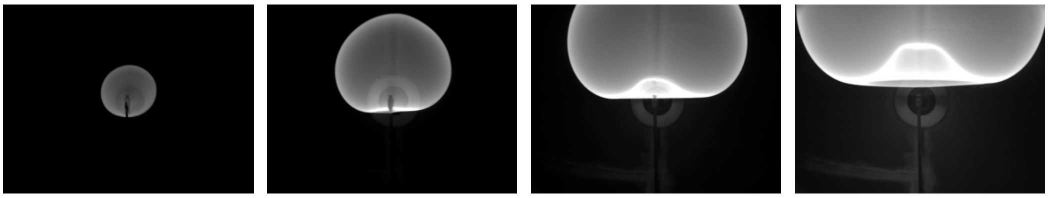
7. Physical Hazard Assessment on Explosion and Combustion of A2L Class Refrigerants

7.1 Combustion and explosion assessment for A2L/2L

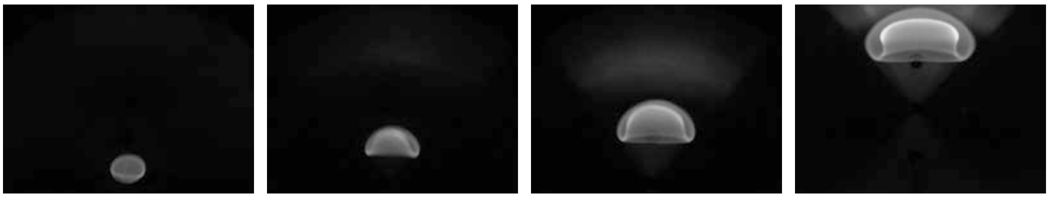
R32 and R1234yf are classified as A2L (ASHRAE, 2010) refrigerants, which are defined as having low toxicity and low flammability with a maximum burning velocity of ≤10 cm/s. A2L refrigerants have such low burning velocity that a lifted flame front due to buoyancy significantly affects their combustion behavior. In terms of safety, investigating the fundamental flammable properties of these alternative refrigerants is important. In this study, to observe and evaluate the effect of buoyancy on the flammable properties of R32 and R1234yf, a large-volume spherical vessel was prepared, and the flame propagation behaviors of R32 and R1234yf were observed using a high-speed video camera. The flame propagation velocity, burning velocity, maximum peak pressure, and deflagration index (i.e., constant that defines the maximum rate of pressure increase with time of combustion as defined by ISO 6184-2 (1985) and NFPA68 (2007)) were evaluated. In the current fiscal year, the flammability in the presence of moisture and elevated temperature was investigated owing to concern over summer, and the burning behavior upon ignition was also investigated. An evaluation scheme for the potential risk of combustion and explosion in actual situations will be considered from the experimentally obtained K_G values.

Experiment

The spherical vessel had a diameter of 1 m and volume of 0.524 m^3 and was equipped with a jacketed mantle heater that covered the entire surface area of the vessel to maintain the operating temperature. The burning behavior was observed with a high-speed video camera. Figure 7-1 (upper) shows example high-speed video images for the flame front propagation behaviors of R32 ϕ1.2. The flame expanded while slowly climbing upward. The shape of the flame front, which is the interface between the unburned and burned gas, was distorted under the influence of buoyancy and viscosity. For R1234yf ϕ1.35, no clear and smooth flame front was observed; the flame front was convoluted without symmetry and floated upward. Alternative compact elongated cylindrical vessels (10 cm in inner diameter and 20 cm in length) were prepared, and the flammable behavior at ignition was investigated. Figure 7-1 (bottom) shows the test result for the compact elongated vessel. A smooth and clear flame front was observed, and the relation between fluid dynamics from the high temperature produced by the burned gas and buoyancy and the slow burning velocity at the bottom of the flame resulted in the squeezed flame front shape. The flammability of the mixture gas in the closed vessel was affected by not only the fuel/air mixture ratio, initial pressure, and initial temperature but also the vessel size and shape, ignition source, and other factors. This result suggests that the small vessel volume and shape have an influence; it will be necessary to consider fluid dynamic behavior with regard to the flammability for scaled-up situations.



100 ms 200 ms 300 ms 400 ms



50 ms 100 ms 150 ms 200 ms

Fig. 7-1 Images of flame front propagation

(up: R32 ϕ1.2, large spherical vessel, bottom: R1234yf ϕ1.2, compact elongated vessel).

The effects of temperature and humidity on the flammability limits of some A2L/2L refrigerants have been reported; this is an important issue, especially with the hot and humid climate of Japan. Flammability tests were conducted under dry and wet conditions for R32 and for R1234yf. Research on the effect of buoyancy on the flammability behavior while considering humidity will continue to be conducted for R1234ze.

Deflagration index, K_G value

The deflagration index K_G is commonly used to estimate and design the explosion venting area of enclosures; it is described by

$$K_G = \left(\frac{dP}{dt}\right)_{max} \cdot V_{vessel}^{\frac{1}{3}}$$

where P is the pressure (100 kPa), t is the time (s), and V_{vessel} is the volume of the vessel (m^3). A larger K_G requires a larger venting area to prevent the enclosure from bursting. The deflagration indices for gases K_G of each refrigerant are summarized, along with other flammable properties. Table 7-2 lists P_{max} and K_G with other major gases in descending order of K_G. The table indicates that K_G values for R32 and R1234yf were considerably small and the same as or less than that 10 for ammonia, as given in NFPA68 (2007). Thereafter, the obtained fundamental flammability characteristics should be expanded for application to flammable behavior at actual scales; an evaluation scheme for the potential risk of combustion and explosion in actual situations will be considered.

Numerical simulation for combustion of A2L/2L

To apply refrigerants safely to air-conditioning equipment, the potential risk of combustion and explosion in actual situations should be evaluated. The relationship between the deflagration index and the influence on human and structures can be considered with the help of the concept of vent design using the K_G value. First, a non-reactive numerical simulation can be tested to reproduce the experimental results in the large spherical vessel; the effect of the reduced pressure rise (P_{red}) if an aperture exists in the vessel can then be evaluated. Then, the reduced effect due to the aperture in the actual room can be evaluated according to the design scheme described in NFPA68 (2007).

Table 7.1: Comparison of P_{max}, K_G, and other parameters with other gases.

Flammable Material	P_{max} (100 kPa)	K_G (100 kPa·m·s^{-1})	Burning velocity (cm·s^{-1})	Flammability limits(%)	Detonation limits(%)*3 Cofined tube	Unconfined	Autoignition Temperature (℃)*7
Acetylene	10.6 *1	1415 *1	166*2	2.5—80.0*3	4.2—50.0		305
Hydrogen	6.8 *1	550 *1	312*2	4.2—75.0*3	18.3—58.9		400
Ethylene			80*2	2.70—36.0*3	3.32—14.70		490
Diethyl ether	8.1 *1	115 *1	47*2				
Benzene			48*2	1.3—7.9*3	1.6-5.55		562
Ethane	7.8 *1	106 *1	47*2	3.0—12.4*3	2.87—12.20	4.0–9.2	515
Propane	7.9 *1	100 *1	46*2	2.1—9.5*3	2.57—7.37	3.0–7.0	450
Butane	8.0 *1	92 *1	45*2	1.8—8.4*3	1.98—6.18	2.5–5.2	405
Ethyl alcohol	7.0 *1	78 *1		3.3—19.0*3	5.1—9.8		
Methanol	7.5 *1	75 *1	56*2				
Methane	7.1 *1	55 *1	40*2				
Ammonia	5.4 *1	10 *1	7.2*4	15—28*5			651
R32	7.6 †	9 †	5†	13.3—29.3*6			
R1234yf	6.2 †	6 †	1†	6.2—12.3*6			

*1 Ref. (NFPA68, 2007), Table E.1 (0.005 ft^3 sphere; E = 10 J, normal condition). *2 Ref. (NFPA68, 2007), Table D.1.
*3 Ref. (Mannan, 2005), Detonation limits obtained for confined tube. *4 Ref. (ISO/DIS 817, 2010)
*5 Ref. (NFPA325,1994) *6 Ref. (JFMA, 2013)
*7 Ref. (Mannan, 2005), Table 16.4 † This work.

8. Efforts of the Japan Refrigeration and Air Conditioning Industry Association

8.1 Progress by Mini-Split Risk Assessment SWG

8.1.1 Outline of Mini-Split Risk Assessment SWG

The mini-split risk assessment SWG advanced the risk assessment of a 2.2–8 kW small business–use air conditioner, which is equivalent to a residential air conditioner. The risk assessment of a residential-use multi-split type air conditioner with two or more indoor units for one outdoor unit was also started last year. The SWG worked on the risk assessment of a floor-standing type small household air conditioner of 8 kW or less. In order to carry out the risk assessment of one-to-one air conditioners in stores of 3.6–25 kW, the mini-split risk assessment SWG (II) was formed. The SWG (II) promoted the risk assessment by collecting experts on the equipment.

8.1.2 Procedure with Risk Assessment

In the risk assessment, the existence of ignition sources and flammable regions as discussed by Yao et al. (2000) was evaluated to calculate the probability that they materialize simultaneously by fault tree analysis (FTA). The risk assessment techniques were taken from the handbook provided by the Ministry of Economy, Trade and Industry as much as possible. We referred to a risk map to judge the safety. Reports from Imamura et al. (2012), Takizawa (2011), and Goetzler et al. (1998) were used by the SWG to describe items assumed to be ignition sources. Low-voltage electrical equipment in Japanese homes almost never ignites. Burning tobacco that does not emit a flame does not cause ignition. Static electricity produced by humans in a living space almost never causes ignition. Based on the above considerations, the ignition sources of outdoor and indoor units of mini-split air conditioners using R32 or R1234y were assumed to be open flame in the risk assessment. For the leakage space, an indoor space with an air conditioner and dimensions of a 7 m^2 floor area and 2.4 m height was assumed; the installation position of the indoor wall-mounted type unit was at a height of 1.8 m from the floor, and the floor-standing type unit was set on the floor. To generate the flammable region, which is important in the risk assessment of a mildly flammable refrigerant, the values for R32 and R1234yf were obtained with the same technique used by Yao et al. (2000); the simulation was performed at the University of Tokyo. According to NITE, the probability of a major accident caused by a home appliance is 10^{-8} sets/year (1 million set base). In other words, a product with 1 million units distributed a year is considered safe if a fatal accident occurs only once in 100 years. The total number of mini-split air conditioners and residential air conditioners in Japan is about 100 million sets, so the target probability was $\leq 10^{-10}$ sets/year. Since the tolerance of the products was increased because they are handled by trained professionals except when used by customers, the target values of the other steps were set to 10 times this target probability.

8.1.3 Wall-Mounted Type Risk Assessment Results

The risk assessment reviewed recent findings. The FTA of smoking as a major ignition source was reviewed. Mildly flammable refrigerants such as R32 do not ignite from lit tobacco and piezoelectric lighters according to a report by the Tokyo University of Science (Suwa). The FTA was reviewed at each life cycle step—logistics, installation, use, service, and disposal—and the new findings were as described above. Table 8.1.1 presents the risk assessment results of the review.

Table 8.1.1 Risk assessment results of review

Risk: Ignition Probability			
Step	R290	R32	R1234yf
Logistics	9.2×10^{-11}–1.4×10^{-7}	4.1×10^{-12}	4.5×10^{-12}
Installation	3.7×10^{-9}–2.2×10^{-8}	2.7×10^{-10}	3.1×10^{-10}
Use (Indoor)	5.0×10^{-13}–9.5×10^{-9}	3.9×10^{-15}	4.3×10^{-15}
(Outdoor)	4.9×10^{-13}–9.3×10^{-9}	1.5×10^{-10}	2.1×10^{-10}

Service	2.8×10^{-7}–8.1×10^{-7}	3.2×10^{-10}	3.6×10^{-10}
disposal	4.1×10^{-7}–5.1×10^{-7}	3.6×10^{-11}	5.3×10^{-11}

The ignition probability of indoor units was considerably smaller than 10^{-10} units/year based on the risk assessment of small business–use air conditioners using R32 and R1234yf. These values were not considered to be of any concern. In contrast, the ignition probabilities of the outdoor unit were 1.5×10^{-10} and 2.1×10^{-10}, which are slightly higher than the target value of 10^{-10} units/year. These FTA values assumed a hazard degree of severity (IV) (i.e., fatality) in the matrix of the risk map. However, verification of the hazard severity or ignition in open space like outdoors is required. The ignition probabilities during the service and installation steps were less than 10^{-9} units/year, or less than the target value.

8.1.4 Risk Assessment Results of Floor-Standing Type Air Conditioners

In a risk assessment based on the FTA of floor-standing type air conditioners with a 1 kg charge, the SWG found that the tolerance value of the current situation with no counter-measures was 9.8×10^{-8}, which did not meet the target value. As the refrigerant R32 is generally heavier than air, it tends to accumulate more easily at lower heights. Since the specific height of ignition sources from the floor can be defined, we considered reassessing risks by dividing the air space by the height.

In order to reassess the volume of flammable space for floor-standing type air conditioners, the SWG calculated the height reached above the floor based on the floor space under the strictest condition (i.e., the total amount of leaked R32 refrigerant should create an air space with the lowest LFL possible. Table 8.1.2 presents the risk assessment results for floor-standing type air conditioners in residences. We then considered room sizes of 13–19 m^2, which were larger than the initial 7 m^2 assumed for floor-standing type air conditioners. By limiting the air conditioner installation space to more than 10 m^2, the allowable ignition probability during usage (i.e., 9.9×10^{-10}) can be met.

Table 8.1.2 Results of floor-standing residential air conditioner risk assessment

Risk: Ignition Probability		
Step	Representative model	R32
Logistics (for every storehouse)	Middle-size storehouse	3.6×10^{-11}
Installation	3.24 m^2 veranda	4.0×10^{-11}
Use (indoor)	9.9 m^2 room	9.9×10^{-10}
(outdoor)	3.24 m^2 veranda	8.6×10^{-11}
Service	3.24 m^2 veranda	2.6×10^{-10}
Disposal	3.24 m^2 veranda	2.5×10^{-11}

For floor-standing type air conditioners in residences, we found that, when 4 kg of refrigerant leaks from an air conditioner installed in a room space of up to 13 m^2, the allowable risk during usage can be met by using a fan or another similar method to disperse the refrigerant in the air. However, according to the current international specifications for air conditioners (IEC60335-2-40), the upper limit of refrigerant charge for a floor-standing type air conditioner installed in a 13 m^2 room is 3 kg; therefore, further examination to ensure safety is necessary.

8.1.5 Progress in Store Package Air Conditioner (Mini-Split Risk Assessment SWG (II))

The store package air conditioner (package air conditioner) has a large amount of refrigerant compared to home residential air conditioners and is often installed in the slightly wider spaces of schools, offices, and small- and medium-sized stores. In the first risk assessment of the store package air conditioner, model cases were used to calculate the ignition probability in each step of the life cycle, as presented in Table 8.1.3.

Table 8.1.3 First risk assessment result of store package air conditioner

Risk: Ignition Probability		
Step	Model and Case	R32
Logistics	Semi-fireproof warehouse	1.6×10^{-12}
Installation	3.6–14.0kW(2-6 HP) R32: maximum charge 4 kg Indoor: Office ceiling cassette Outdoor: On ground	2.3×10^{-9}
Use (Indoor)		5.0×10^{-11}
(Outdoor)		6.7×10^{-10}
Service		3.0×10^{-9}
disposal		2.5×10^{-9}

As shown in the table, the results of the first risk assessment showed that all life cycle steps met the allowable probability values. We then performed a second risk assessment for cases where the expected risk is large but the probability of occurrence is considered small. The store package air conditioner can have a maximum of 30 m piping for indoor and outdoor units with no additional refrigerant charge. We decided to add a local filling depending on the pipe length and greatly increase the charge. When the amount of refrigerant in the system is increased, the risk of refrigerant leakage increases. In addition, refrigerant that leaks from floor-standing type air conditioners tends to stay in the floor, so a flammable volume is easily generated. The risk assessment also considered ice thermal storage systems (25kW) with more than 8 kg of refrigerant to examine the most severe cases. We plan to continue developing safety measures as necessary.

8.1.6 Conclusion and Future Subject

The mini-split risk assessment SWG examined wall-mounted type mini-split air conditioners that used R1234yf and R32. The results did not confirm any problems. For R1234yf, the flammable concentration depends on the humidity. A risk assessment was also carried out on floor-standing type air conditioners using R32. The results confirmed limits on the installation space. The SWG found that, when multiple indoor units are installed to one outdoor unit for home use, the relationship between the installation space and amount of refrigerant is one of the most important issues. Consistency with international standards must also be considered and will be the subject of further study by another working group of the Japan Refrigeration and Air Conditioning Industry Association. A risk assessment was also performed for a one-to-one store air conditioner using R32. In each life cycle step, the assessed risk of a store air conditioner installed on the ceiling was below the target value. Based on the results, safety measures are unnecessary. SWG will continue with second and third risk assessments for store air conditioners.

To reducing the risk, the SWG issued a manual. The results for unexpected risks and physical hazards of generated chemical substances are detailed in the 2011 and 2012 progress reports of the Japan Society of Refrigerating and Air Conditioning Engineers.

The Tokyo University of Science (Suwa), University of Tokyo, and National Institute of Advanced Industrial Science and Technology participated in the mildly flammable refrigerant risk assessment study group to improve the accuracy of the FTA results. We revealed the severity of the risks. Based on the developments described above, we encourage the risk assessment of mini-split air conditioner to increase the accuracy of the results.

8.2 Progress of SWG for VRF System Risk Assessment

8.2.1 Introduction

The risk assessment of VRF systems using mildly flammable refrigerants (A2L) was divided into first and second assessments. The basic data necessary for creating a fault tree analysis (FTA) were investigated by estimating the probability of refrigerant leaks occurring in the market, evaluating each type of ignition source, and investigating methods for calculating the probability of fire. The probability of fire was determined for typical installation cases. In the second risk assessment, installation cases that are considered rare in the market but possessing high risk were evaluated, and safety measures were proposed to reduce risks. As mildly flammable refrigerants, both R32 and R1234yf were subject to investigation; however, this interim report only presents information concerning R32.

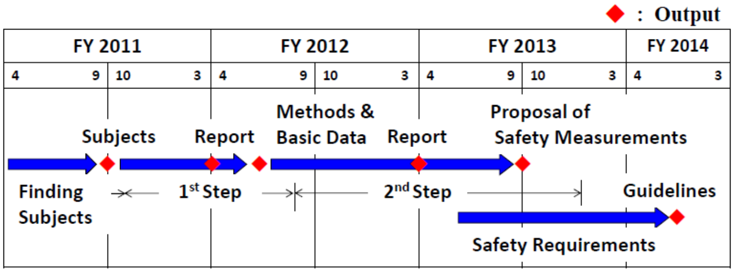


Fig. 1 Schedule of risk assessment

8.2.2 Main Features of Risk Assessment for VRF using R32

In order to appropriately evaluate the risks of R32 refrigerants for VRF systems, the following points were considered in the risk assessment.

(1) A computational fluid dynamics (CFD) technique was implemented to evaluate unsteady three-dimensional concentration fields. The refrigerant charge amount was varied from typical values to the maximum amount in the market. The volume of flammable space and its duration were studied for each installation case.

(2) Highly skilled service providers normally conduct installation, repairs, and maintenance for VRF; this lowers the occurrence of VRF operational error for VRF by one order of magnitude relative to residential air conditioners.

(3) To determine the ignition source range for mildly flammable refrigerant, we considered the results of the Risk Assessment Research Committee. They determined that R32 is not ignited by sparks from mechanical relays and nearby light switches, power outlets, or electric gas lighters for smoking.

(4) The calculation formula for the probability of fire was determined according to two triggers that cause a refrigerant to catch fire: activation of the ignition source in flammable space and generation of a flammable space in contact with open flame.

(5) The probability of a refrigerant leak was determined from the repair data of each company. The leaks were divided into three classes: slow, rapid, and burst. The probability of a slow leak was excluded except in special cases (i. e., completely sealed room or floor-standing unit) when calculating the probability of fire.

(6) Installation cases assumed to have a high risk were selected. Among indoor units, we identified cases of floor-standing units installed in small rooms of restaurants and ceiling cassette units installed at karaoke shops, where natural ventilation does not usually exist in order to prevent sound leakage. Ceiling space was also selected because ventilation is thought to be extremely limited. Among outdoor units, we selected cases of outdoor unit installation to each floor, to semi-underground structures, and to machinery rooms, where leaked refrigerant may accumulate.

(7) We set the allowable levels for the probability of fire and proposed safety measures for each installation case and life stage when these levels are exceeded.

(8) To investigate necessary changes to service port specifications, we considered the probability of fire occurring by improperly charging R32 refrigerant into R410A equipment when the specifications are unchanged. In this case of allowable risk, we made the allowable level one order of magnitude higher than the level for R32 equipment.

8.2.3 Results for Risk Assessment

Table 1 presents the risk assessment results. Even when measures were not enacted, the risks were within allowable levels for ceiling-installed units in offices provided that there was mechanical ventilation. VRF systems are most commonly applied in offices, and ceiling-installed indoor units comprise 95% of the installations. On the other hand, the risks exceeded the allowable values for floor-standing units in restaurants at the life-stage of use and repairs and for ceiling-installed units in karaoke shops at the life-stage of use. In addition, for outdoor units, the risks exceeded the allowable values under the conditions for semi-underground and machinery room installations excluding the life-stage of use. Tables 2 and 3 present the necessary safety measures for each installation case. With regard to the risk of improper charging, the risks were all within allowable values in the investigated life-stages of use, repair, and disposal.

Operator training is necessary for performing repairs and disposal in the presence of burners; carrying a refrigerant leak detection device is required when conducting installations, repairs, and disposal at installation sites prone to refrigerant accumulation such as semi-underground and machinery room installations.

Tables 4 and 5 present the main ignition sources and main causes of refrigerant leaks that affect the probability of fire the most in risk scenarios. Open flames of combustion-type heaters and gas stoves are the most common ignition sources during use, and brazing burners are the most common sources during work servicing such as installation, repair, and disposal. Enacting measures relating to indoor open flames and handling burners for work is very important.

Table 1: Results of R32 VRF risk assessment

Exponent values show probability of fire accident [times/year/unit] — allowable / not allowable

Installation Case (charge kg) <floor area m²*ceiling height m>		Life stage	Transport/ Storage		Installation		Using (indoor) Using (outdoor)		Repairing		Disposal (removal)	
		Allowable	< 1E-08				< 1E-10 (indoor) < 4E-09 (outdoor)		< 1E-08			
		Measure	N	Y	N	Y	N	Y	N	Y	N	Y
Indoor unit	Ceiling (26.3)	Office <40.6*2.7>	1.1E-15 ~ 2.7E-15	-	1.9E-09	-	3.5E-12*1)	-	8.7E-11	8.8E-12	2.9E-14	2.9E-15
	Floored (52.8)	Restaurant <9.7*2.5>			1.9E-09	-	3.8E-07	8.4E-11	1.2E-08	3.9E-11	3.4E-12	3.4E-13
	Ceiling (88.1)	Karaoke <4*2.4>			-		1.2E-06	0.0	-		-	
Outdoor unit	Typical (26.3)	-			1.9E-09	-	1.9E-11	-	1.4E-09	1.4E-10	2.4E-10	3.2E-11
	Each floor (26.3)	- <3.4*4.0>			1.9E-09	-	3.0E-09	-	3.1E-09	3.4E-10	1.0E-09	1.4E-10
	Semi-underground (26.3)	- <15.3*3.5>			1.1E-08	1.9E09	1.1E-07	2.5E-13	3.6E-07	2.1E-09	3.3E-08	4.8E-10
	Machinery room (26.3)	- <21.8*5>			1.1E-08	2.1E-09	3.2E-09*1)	-	8.6E-07	5.4E-09	2.2E-08	3.3E-10
Ceiling space (26.3)		- <38.4*0.8>	-				3.0E-10	3.0E-11	3.0E-09	3.0E-10	7.2E-11	1.1E-11
False charge		Allowable			Included in indoor unit		< 1E-11 (indoor) < 4E-10 (outdoor)		< 1E-09			
			-		-		8.7E-11 (Karaoke) 1.2E-14 (Outdoor)		6.0E-13		3.0E-14	

*1) With mechanical ventilation

Table 2: Indoor safety measures

Installation case		Using	Repairing
Floored	Restaurant	Mechanical Ventilation	Carrying leak detector +Education
Ceiling	Karaoke	Leak detection →Mechanical Ventilation	–

Table 3: Outdoor safety measures

Installation case	Installation	Using	Repairing	Disposal (Removal)
Semi-underground	Carrying leak detector	Mechanical Ventilation	Ventilation + Carrying leak detector +Education	Carrying leak detector +Education
Machinery room		Existing Mechanical Ventilation		

8.2.4 Future Development

In the future, we will evaluate the effect of natural ventilation as a safety measure for floor-standing units that are prone to refrigerant accumulation at floor level and proceed with the risk assessment for R1234yf. There is a plan to enact JRAIA safety guidelines in the autumn of fiscal 2014 to facilitate the safe use of mildly flammable refrigerants in VRF systems.

Table 4: Major ignition sources in risk assessment

Installation case		Life stage	Transport /Storage	Installa-tion	Using (indoor) Using (outdoor)	Repair-ing	Disposal (removal)
Indoor unit	Ceiling	Office	Smoking tool		Smoking tool Water heater	Brazing burner	Brazing burner
	Floored	Restaurant			Combustion heater Gas cooker		
	Ceiling	Karaoke					
Outdoor unit	Usual	-		Brazing burner	Boiler Gas/oil equipment	Brazing burner	Brazing burner
	Each floor	-					
	Semi-underground	-		Brazing burner + Boiler			
	Machinery room	-			Smoking tool		
Ceiling space		-			Fire of A/C Power failure	Brazing burner	Brazing burner

8.3 Progress of Chiller SWG: Chiller risk assessment and guideline establishment

8.3.1 INTRODUCTION

The heat-source system supplying hot or cold water to an air-conditioning system uses the hydrofluorocarbon (HFC) refrigerants R410A or R134a. Both refrigerants have a significant impact on global warming with a GWP exceeding 1000. Therefore, it is necessary to ultimately replace them with low GWP alternatives. Some refrigerants with a low GWP, such as R1234yf, R1234ze (E), and mixed refrigerants, have been evaluated in retrofit and performance tests. All of these low GWP refrigerants are mildly flammable. Risk assessments (RAs) of chillers, in which these two refrigerants and R32 were added, have focused on the ignition and burning characteristics of the refrigerants, and have been performed to evaluate security against fire accidents and burns.

The scope of these requirements mainly includes air-cooled heat pumps installed outdoors and water-cooled chillers installed in a machine room as a central air-conditioning heat source, with the exception of mobile facilities and those with a cooling capacity ranging from 7.5 to 17,500 kW.

The WG (chiller SWG), which consists of professional chiller engineers, was established by the Japan Refrigeration and Air Conditioning Industry Association (JRAIA) to perform RAs. Requirements for the chiller design and the condition of facilities that incorporate the measures and the actions defined by the RAs will be established as a JRAIA guideline (GL) in 2014. Progress toward this end is summarized in this report.

8.3.2 Prerequisite for performing risk assessments

Because the equipment has the same structure and applications as conventional equipment, the RAs[1,2] that have been performed are generally effective. The RAs have been performed in a manner that has improved their consistency and has focused on the differences in the flammability characteristics of refrigerants. In addition, we have referenced studies of the mini-split air conditioner and the multiple packaged air-conditioning unit system, for which RAs have been performed.

Risks were clarified using the FTA method and a numerical evaluation was performed by plotting a risk map (R-map) (Fig.5.4.1) based on the probability of occurrence and severity of harm of each probable ignition source and type of refrigerant leakage. The probability of occurrence and the severity of harm were based on the Risk Assessment Handbook.

In the study, risks were quantified using the risk-assessment list. Combinations of extracted ignition sources and causes of leakage were listed for each life stage of the equipment. A risk evaluation using the R-map and the evaluation of the hazard level of different areas using JISC60079-10 was conducted simultaneously. The treatment of the extracted risk was expanded to the GL.

↑ probability of occurrence of harm							
	Frequent	10 cases/units per year	13	24	27	29	30
	Probable	10^{-2}	12	20	23	26	28
	Occasional	1.06×10^{-3}	10	16	19	22	25
	Remote	1.06×10^{-4}	6	9	15	18	21
	Improbable	1.59×10^{-5}～7.94×10^{-6}	3	4	8	14	17
	Incredible	1.59×10^{-6}～7.94×10^{-7}	1	2	5	7	11
R-map (ISO/IEC Guide51 (JIS Z 8051))			0	I	II	III	IV
			None (No injury)	Negligible (Smoke generation of product・SCART)	Marginal: (Fire and ignition of product・Mild impairment)	Critical: (fire・Serious injury)	Catastrophic: (Death, Permanent fault, Fire(Fire of buildings))
			severity of harm →				

A region: 25～30 Intolerable
B region: 14～24 Acceptable (If the risk is as low as reasonably practicable.)
C region: 1～13 Acceptable

Fig.8.3.1 Risk assessment map

8.3.3 Analysis of the flammable space in the event of a refrigerant leak

For safety assessment the time that flammability persisted for and the volume of the flammable space were calculated when a refrigerant leaked. The results of the analysis are shown below.

a) Machine room

By considering that neither a flame from a match nor a large breaker was present as an ignition source at the point of leakage, the possibility of ignition was very low when an average machine room was designed based on the ISO5149 standard. From the results of the steady-state analysis, regardless of the refrigerant charge, there was no possibility that a flammable space could form. Therefore, it is considered that there should be no restrictions on refrigerant charge in the chiller GL.

However, a narrow machine room that is smaller than the average value of the machine room area (Fig.8.3.3) must also be considered. Because the level of ventilation is reduced and the amount of leakage over time is relatively large even if ventilation was provided at the same level as in an average machine room, there is a possibility that a flammable space could form. Therefore, it is necessary to add a consideration for a narrow machine room in the GL by assuming that the minimum floor area would be 1/3 of the floor area of the average machine room. To consider the risk when ventilation is stopped due to equipment failure or other factors, the risk of ignition was evaluated in consideration of the presence or absence of interlock action due to the formation of a flammable space and a sufficient refrigerant concentration.

b) Outdoor equipment

Because diffusion was fast, a small flammable space was formed near to the refrigerant leakage point at a height of 1.13 m. Because the velocity of the refrigerant was small and the ignition source was not in the immediate vicinity of the air heat exchanger, the possibility of ignition was very small. If the refrigerant leaks from a decorative panel on the outdoor equipment, it will accumulate at the bottom of the leakage point because the refrigerant is likely to have leaked from a slit in the bottom of the unit. The flammable space is formed for about 1 minute. Unlike leakage from the air heat exchanger, a flammable space was formed. Therefore, to assess the ignition risk, it is necessary to consider the probable existence of an ignition source.

Because this analysis was very rough, it is necessary to review the results and perform additional analysis.

8.3.4 Relationship between RA and GL

The probability of the presence of a flammable space and the ignition probability at each life stage were calculated (assuming there was no ventilation and that ignition sources always ignite). The results are shown in Table 8.3.2. The sum of the probability of occurrence of fires and burns is more than 10^{-6}. Therefore, it is necessary to take measures to reduce the probability to a level that is considered acceptable by society. This represents the standard for ventilation and the system of holding by it.

Table 8.3.2 Risk assessment results

Accident scenario	Life stage probability	Probabillity (cases/units per year)	Assessment
Logistics	0.0564	3.22x10−7 X Time × Volume	Safe
Installation	0.0564	5.01x10−7 X Time × Volume	Safe
Usage	0.7809	3.82x10−6 X Time × Volume	Nearly safe
Repair	0.2523	2.73x10−6 X Time × Volume	Nearly safe
Disposal	0.0565	1.38x10−6 X Time × Volume	Safe

8.3.5 Guideline planning taking IEC60079-10-1 into consideration

The GL is being prepared by suggesting measures to take against risks identified by the RA to KHKS 0302-3 and incorporating the necessary sections of ISO 5149-1, 3. The basic policy adopted in the GL is as follows:

- Only one slightly combustible refrigerant (A2L) is referred to as the target refrigerant and descriptions of the applications of other refrigerants will be deleted.
- The following measures should be adopted with reference to IEC60079 so that a machine room does not become a hazardous area even if a refrigerant leaks.

(1) Installation and inspection of ventilation devices (including backup with multiple devices as required).

(2) Refrigerant detector (including UPS and periodical inspection).

Note: The following is under debate in the SWG.

- Outdoor installation should be considered to be a non-hazardous area following an analysis.
- Electrical equipment should have a non-explosion- proof specification and conform to IEC/ISO.
- Specific values (twice or more/h ventilation, scope of a hazardous area) must be determined on the basis of the results of the analysis.
- Firearms are classified as either work firearms or other firearms (conforming to ISO) and must be considered in the risk assessment, with the exception of the construction period.

The following are the tasks required to establish the GL. The GL is described as a means for reducing the risk and will be established within 2014.

1) Rule of recovery after long-term suspension,
2) Rule of outdoor installation in consideration of IEC60079,
3) A method to consider spontaneous ignition temperature,
4) A rule to establish a refrigerant detector,
5) Control of refrigerant concentration (regulation of the amount of refrigerant filling, i.e., the filling amount regulation).

9. Deregulation Activities in Japan for the Introduction of Mobile Air Conditioning Refrigerant R1234yf

Background to R1234yf Introduction in Japan

Worldwide efforts to reduce greenhouse gases (GHGs) have resulted in a growing demand for mobile air conditioning refrigerants with low global warming potential (GWP). Since 2011, the European Union (EU) has banned the use of refrigerants with a GWP of greater than 150 in new-model vehicles (from 2017 onwards, the ban will apply to all new vehicles). Japanese automakers are taking the necessary steps for vehicles destined for the EU market.

Obstacles to R1234yf Introduction

A special ministerial approval scheme is currently in place in Japan to facilitate the approval of factory lines producing R1234yf-equipped vehicles based on the explosion-prevention measures taken. Because the number of these production lines is projected to increase in step with the growing number of vehicle models incorporating R1234yf, further deregulation of R1234yf is necessary.

With regard to after-sales servicing, operators of varying types and scale—including auto maintenance shop operators, auto body repair shop operators, and electrical equipment repair shop operators—are engaged in the retrieval/recharging of refrigerants for vehicles in need of repair or that were in accidents. For many of these operators, making the large investment necessitated by regulations governing R1234yf is difficult.

Activities of JAMA’s Vehicle Maintenance Subcommittee

In collaboration with the manufacturers of refrigerant retrieval/recharging equipment, refrigerant suppliers, auto maintenance shop associations and other stakeholders, JAMA has been carrying out activities aimed at resolving existing obstacles to the widespread use of R1234yf by 2014. One such activity was a study that used the risk assessment mapping method to assess risk by combining the “probability of injury” and “severity of injury” in a 6×5 matrix. Supported by the risk assessment mapping data, JAMA will petition the government to review its safety regulations in order to more accurately reflect the actual risks of R1234yf.

As a first step in its risk assessment study, JAMA conducted hearings with refrigerant retrieval/recharging equipment manufacturers and a survey of retrieval/recharging operators to more clearly identify the risks at maintenance work sites. In cooperation with the Japan Automobile Service Promotion Association, Japan Auto Body Repair Association, and Japan Automotive Electrical Equipment Service Association, the survey questionnaire was distributed to a representative selection of auto maintenance shops, in terms of business scale and services offered, across Japan.

Completed questionnaires were received from a total of 756 auto maintenance shops. The information provided by the 533 shops that performed their own retrieval/recharging operations was compiled into basic data on auto maintenance shops (number of workers, number of vehicles repaired, shop layout information, etc.) and workers’ on-the-job observations (on refrigerant leakage occurrence, ventilation conditions, the presence of ignition sources, etc.).

Based on the data obtained from the questionnaires on leakage-prone points, leakage amounts, and ignition source specifications, JAMA conducted an ignition test and leak simulation test; in both instances, worst-case R1234yf leakage conditions were assumed. The data obtained in these tests were used to calculate the probability and severity of injury caused by R1234yf leakage and map them for risk assessment.

Progress towards Deregulation

The results of the risk assessment activity described above were submitted in a report(5) to the Committee for the Study of R1234yf Retrieval/Recharging Equipment Standards and Implementation (chair: Professor Eiji Hihara of the University of Tokyo’s Graduate School of Frontier Sciences) by the High-Pressure Gas Safety Institute of Japan as part of its research work commissioned by Japan’s Ministry of Economy, Trade and Industry (METI).

The committee reviewed the assessment results with respect to the ignition risk of R1234yf and confirmed that the risk is within socially acceptable parameters. In addition, for deregulation purposes, the committee examined the risk reduction potential of double-layer safety measures such as the application of a well-ventilated structure to the retrieval/recharging equipment mainframe (with a fan and ventilation openings in two directions), elimination of static electricity, restricted refrigerant storage container capacity, and the introduction of user warning labels concerning R1234yf flammability.

The committee subsequently submitted to METI a report on R1234yf; this was then released to the public by METI in June 2013 with the comment that, given the proposed safety measures, the R1234yf retrieval/recharging equipment can be regarded as equally safe as the existing inert fluorocarbon retrieval/recharging equipment, which has been exempted from the High-Pressure Gas Safety Law.

In response to METI’s action, Japan’s Industrial Structure Council is scheduled to start discussing in March 2014 the possible exemption of R1234yf retrieval/recharging equipment from the High-Pressure Gas Safety Law.

As reported above, Japan has made great strides towards the deregulation of R1234yf retrieval/recharging equipment and the promotion of a low-GWP refrigerant beginning in 2014.