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DECARBONISATION THROUGH INNOVATION

Development for revision of ISO 817 - Evaluation method of self-decomposition reactivity of next-generation refrigerants -

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Abstract

HydroFluoroOlefin (HFO) refrigerants are attracting significant attention as next-generation refrigerants due to their exceptionally low Global Warming Potential (GWP) and superior thermal properties. However, certain ethylene-based HFOs exhibit self-decomposition reactivity, which poses potential risks of compressor rupture if such reactions occur inside the refrigeration cycle. Comprehensive safety evaluations are necessary for practical application, yet ISO 817 (Refrigerants - Designation and safety classification) currently specifies only flammability and toxicity, not self-decomposition reactivity (refrigerant stability). Conventional refrigerants used so far do not exhibit self-decomposition reactivity, and there is no standardized evaluation method for the reaction. In this report, developments to revise ISO 817 to include refrigerant stability classification are discussed.
Self-decomposition reaction occurs when energy, such as an electric spark, is applied to the refrigerant in high-pressure and high-temperature environments. Therefore, for evaluation, the refrigerant to be tested is sealed in a reaction vessel at high pressure and high temperature, and energy is applied by an ignition source inside the vessel. The ignition source is particularly important, and previous research has shown that reactivity changes depending on the type of ignition source. For international standardization, reproducibility and simplicity of testing are also required. Additionally, controlling the amount of energy input to the refrigerant is an important aspect. After investigating existing standards and similar tests, the Fusing Wire and Discharge Method was developed for those reasons. In this method, a fine metal wire (Fusing Wire) is placed between electrodes spaced about 1mm apart, and voltage is applied. When current flows, the Fusing Wire heats up and melts due to Joule heat, causing arc discharge between the electrodes. The phenomenon of melting and discharge was investigated under different gas types, gas pressures, and temperature conditions using this method. Furthermore, the self-decomposition reactivity of next-generation HFO refrigerants was evaluated.

Keywords: Low-GWP refrigerant, Safety, HFO refrigerants, Self-decomposition reaction, Standardization

1. Introduction

The Montreal Protocol, adopted in 1987, regulates substances that are likely to destroy the ozone layer. Chlorofluorocarbons (CFCs), which had been widely used as refrigerants, have already been completely phased out. Their substitutes, hydrochlorofluorocarbons (HCFCs), are also scheduled for complete phase-out by 2020 in developed countries and by 2030 in developing countries [1]. Hydrofluorocarbons (HFCs) have been used as alternatives to HCFCs; however, in response to recent concerns about global warming, the Kigali Amendment was adopted in 2016. Under this amendment, the reduction of HFCs in terms of CO_2-equivalent emissions was mandated. Developed countries, including Japan, are required to reduce HFC emissions by 70%

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by 2029, 80% by 2034, and 85% by 2036, compared to the baseline years of 2011–2013. Developing countries are also required to achieve an 80% or 85% reduction by the 2040s. In order to achieve these targets and mitigate global warming, a rapid transition to low-environmental-impact refrigerants is urgently needed.

In Japan, more than 90% (in terms of CO_2-equivalent) of HFCs are used for refrigeration applications. Of these, approximately 60% are used for air conditioning and nearly 40% for refrigeration and freezing [2]. Therefore, refrigerant conversion in these sectors is particularly important. On the other hand, since refrigeration and air conditioning equipment are closely linked to people's daily lives, the refrigerant itself must be safe. In Japan, the mainstream air conditioning systems are direct expansion systems, such as residential split-type air conditioners and commercial multi-type air conditioners. In these systems, the indoor unit (serving as an evaporator or condenser) is installed indoors, allowing the generated heat to be directly released into the target space. Since the refrigerant can directly heat or cool the indoor space, these systems are highly efficient and do not require energy for transporting a secondary medium, resulting in energy savings. However, because refrigerant piping is routed indoors, the safety of the refrigerant itself is required. For example, if a refrigerant leak occurs, the leaked refrigerant could reach the occupied space. Therefore, safety measures and risk management, including flammability and toxicity, are necessary. Given the above background, it is necessary to develop and transition refrigerants with consideration of S+3E, which includes not only environmental performance (Environment), energy efficiency (Energy), and economic feasibility (Economic), but also safety (Safety) [3].

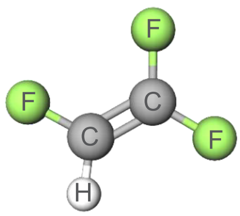
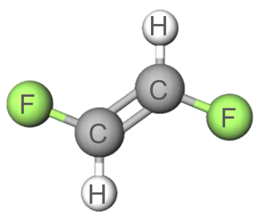
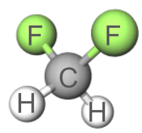
This paper presents an investigation into the safety of next-generation refrigerants, particularly initiatives aimed at the revision of ISO 817.

2. Next-Generation HFO Refrigerants and Self-Decomposition Reactions

Hydrofluoroolefin (HFO) refrigerants are attracting attention as next-generation refrigerants. These substances contain a carbon–carbon double bond in their molecular structure and generally exhibit extremely low global warming potential (GWP) and relatively low flammability. An example of an HFO refrigerant is R1234yf (molecular formula: $C_3H_2F_4$), which has a GWP of less than 1, indicating excellent environmental performance. R1234yf has become widely used as a replacement for R134a in automotive air conditioning systems, and many R1234yf-based blends with other refrigerants have also been proposed and put into practical use. However, because R1234yf has low latent heat of vaporization and low saturation pressure, its performance is limited when it is used as a single-component refrigerant in air conditioning or refrigeration equipment.

As next-generation HFO refrigerants for air conditioning and refrigeration applications, HFO-1123 (CF_2＝CHF) and R1132(E) (CHF=CHF) are attracting attention. Both are ethylene-based refrigerants with two carbons connected by a double bond, and both have excellent environmental performance with a GWP of less than 1. Their thermophysical properties are similar to those of R32, making them promising alternative refrigerants for indoor air conditioning, electric vehicle air conditioning, and refrigeration applications.

Table 1. HFO-1123 and R1132(E)

	HFO-1123	R1132(E)	R32
Chemical formula	CF_2＝CHF	CHF=CHF	CH_2F_2
Normal Boiling Point	-59*	-52.5	-51.7
GWP	<1	<1	675
			

*: referred to [4]

On the other hand, there are safety concerns regarding the self-decomposition reaction of HFO-1123 and R1132(E). A self-decomposition reaction is a chemical reaction in which two or more molecules react with each other under external energy input, resulting in the formation of two or more different products.

The chemical reaction equations for HFO-1123 and R1132(E) are shown in Eqs. (1)(2), respectively. Due to the exothermic reaction, the temperature and pressure may increase.

$$\mathrm{HFO-1123:}\quad \mathrm{CF_2 = CHF \rightarrow \frac{1}{2}\,CF_4 + \frac{3}{2}\,C + HF} \qquad \Delta H = -250\ \mathrm{kJ/mol} \tag{1}$$

$$\mathrm{R1132(E):}\quad \mathrm{CHF = CHF \rightarrow 2C + 2HF} \qquad \Delta H = -248\ \mathrm{kJ/mol} \tag{2}$$

A self-decomposition reaction is triggered when the following three factors are present simultaneously (Fig. 1):

- High composition of HFO-1123 or R1132(E)
- High-temperature and high-pressure conditions
- Energy input from an ignition source.

In particular, since high temperature and high pressure conditions are required, the reaction is unlikely to occur if the refrigerant leaks from the refrigeration cycle into the atmosphere and reaches atmospheric pressure. On the other hand, unlike combustion, oxygen is not required for the reaction, so it can also occur inside the refrigeration cycle. In particular, there is concern about the risk of accidents in which energy is supplied to the refrigerant due to abnormal compressor operation. Risk assessments are conducted by examining the energy that can be generated inside the compressor and the temperature and pressure conditions during equipment malfunctions [5]. It is important to conduct safety evaluations related to self-decomposition reactions and to promote their practical application.

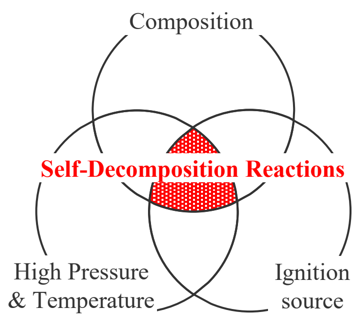


Figure 1. Factors causing self-decomposition reactions.

3. ISO 817 and Ongoing Discussions on Stability Classification

3.1. Safety classification of refrigerants

The safety classification of refrigerants is specified in ISO 817:2024 (Refrigerants — Designation and Safety Classification) and is based on flammability and toxicity [6].

As for flammability, refrigerants are classified into four categories: 1, 2L, 2, and 3 as shown in Table 2. If no flame propagation occurs at 60°C and 101.3 kPa, the refrigerant is classified as Class 1. If flame propagation is observed, the refrigerant is classified based on its LFL (Lower Flammable Limit), HOC (Heat of Combustion), and BV (Maximum Burning Velocity). The test method for determining the LFL is specified in ASTM E681 (Standard Test Method for Concentration Limits of Flammability of Chemicals (Vapors and Gases)), in which an electric discharge is applied to the refrigerant in a glass flask [7]. The burning velocity is determined according to ISO/PAS 24499 (Method of test for burning velocity measurement of A2L flammable gases) or other credible method. ISO/PAS 24499 specifies the vertical glass tube method for measuring burning velocity [8].

Table 2. Flammability classification

Class		Flame propagation*	LFL**	HOC***	BV_{max}****
Class 1	No Flame Propagation	No			
Class 2L	Lower flammability	Yes	>3.5vol%	and <19000kJ/kg	and ≤10cm/s
Class 2	Flammable	Yes	>3.5vol%	and <19000kJ/kg	
Class 3	Higher flammability	Yes	≤3.5vol%	or ≥19000kJ/kg	

*: tested in air at 60 °C and 101,3 kPa
**LFL: lower flammability limit
***HOC: heat of combustion
****BV_{max}: maximum burning velocity

For toxicity, refrigerants are classified into two classes (A and B) as described below. Class A indicates lower toxicity, while Class B indicates higher toxicity.

Table 3. Toxicity classification

Class	Mortality TCF*	TCF* • of cardiac sensitization • and of anaesthetic or central nervous system • and of other escape impairing and permanent injury	OEL**
Class A	≥2500ppm	and ≥ 10000 ppm	and ≥ 150 ppm
Class B	<2500ppm	or <10000ppm	or < 150ppm

*TCF: toxic concentration factor

**OEL: occupational exposure limit

In the previous version revised in 2014, toxicity classification was based solely on chronic toxicity using the OEL (Occupational Exposure Limit). Refrigerants with OEL ≥ 400 ppm were classified as Class A, while those with OEL < 400 ppm were classified as Class B [9]. In the 2024 revision,

- the criteria for classification based on OEL were relaxed, and
- acute toxicity was newly included as an additional criterion.

As a result, the toxicity classification of some refrigerants has been revised.

As described above, the safety classification of refrigerants is defined by both flammability and toxicity, and their combination yields designations such as A1 or B2.

3.2. Additional revision for stability classification

As described above, the safety classification of refrigerants is based on flammability and toxicity; however, conventional classifications do not address stability issues such as self-decomposition reactions. In response to the emergence of refrigerants such as HFO-1123 and R1132(E), which exhibit excellent environmental performance and favorable thermophysical properties but have the potential to undergo self-decomposition reactions, TF3 (Refrigerant Stability Classification) was established within ISO/TC86/SC8 in June 2024. Efforts have begun to revise ISO 817 to include a refrigerant stability classification. Fig. 2 shows the organizational structure under TC86 [10].

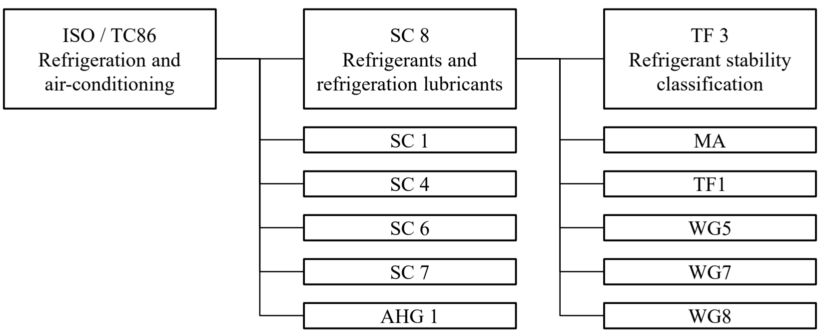


Figure 2. ISO/TC86 and TF3.

Within TF3, the following key topics are under discussion for establishing a refrigerant stability classification:

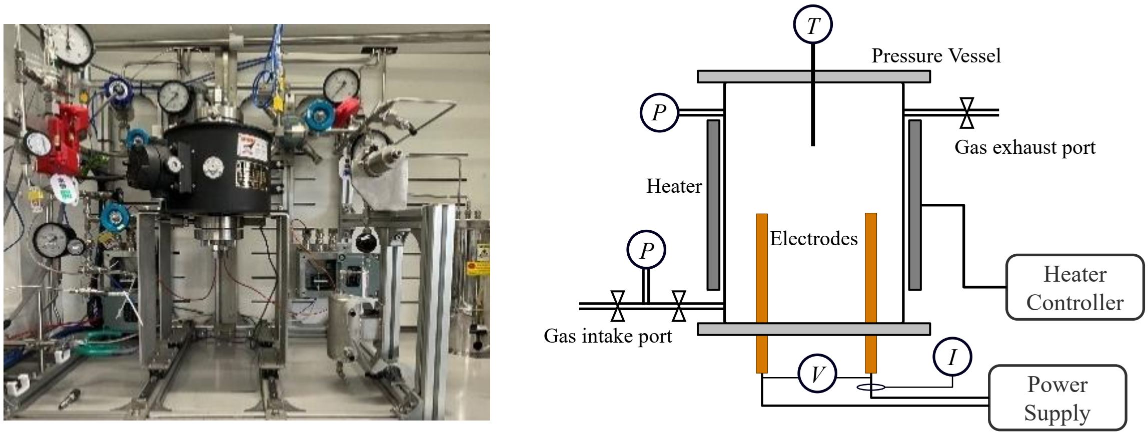
- Definition of refrigerant stability classes. The following three categories are under consideration:
  - Class α – Stable
  - Class β – Stable under controlled conditions
  - Class γ – Instable
- Test apparatus
- Test conditions

As of November 2025, it is also being discussed to establish a new working group (WG) to replace TF3, which will lead the revision work, and to specify the test method in a new International Standard (IS) separate from ISO 817. To date, no established method exists for evaluating the self-decomposition reactivity of refrigerants, making it necessary to develop both the test apparatus and evaluation methodology. The next section describes efforts toward the development of an evaluation method.

4. Development of evaluation methods for self-decomposition reactions

4.1. Various evaluation methods for self-decomposition reactions

As mentioned above, since self-decomposition reactions occur under high temperature and high pressure conditions, their evaluation is also conducted under similar conditions. Fig. 3 shows the appearance and schematic diagram of the apparatus used to evaluate self-decomposition reactions. An electrode rod is inserted into a pressure vessel capable of withstanding pressures up to 50 MPa. Electrodes are attached to the tip of the rod, allowing current to be supplied from an external power source and thereby delivering energy to the refrigerant. Heaters are installed around the vessel, allowing the temperature to be raised up to 150°C. The apparatus is equipped with a pressure gauge and thermometer to monitor the refrigerant, and the propagation of the self-decomposition reaction is assessed by measuring pressure changes.



(a) Appearance (b) Schematic diagram

Figure 3. Self-decomposition reaction evaluation apparatus.

For standardization, it is necessary to specify the configuration of the test apparatus as well as experimental conditions such as temperature, pressure, and the amount of energy supplied to the refrigerant. Among these, the ignition method is particularly important because it provides the energy required to initiate the reaction. Various methods have been devised to date.

4.1.1. Melting method

A metal wire with a diameter of less than 1mm is placed between the electrodes, and when current is passed through it, the wire heats up and eventually reaches its melting point and fuses. During this process, energy is supplied to the refrigerant, which can initiate the reaction [11]. The amount of energy input basically depends on the volume of the metal wire. Most of the input power is consumed in heating and melting the metal, making it difficult to determine the amount of heat actually transferred to the refrigerant.

4.1.2. Discharge method (Movable electrode)

The electrode is constructed by suspending a bolt from a metal plate. When current is applied with the bolt tip in contact with the plate, electrical repulsion causes the electrode to move, creating a small gap in which an arc discharge occurs [12]. The amount of energy input is controlled by the current value and the duration of current flow. This method enables easy generation of arc discharge. On the other hand, because the energy input also depends on bolt movement, it may depend on factors such as the force with which the metal plate presses against the bolt.

4.1.3. Discharge method (Spiral electrode)

Two copper spiral electrodes are partially overlapped to form the electrode structure. When current is applied, the electrodes repel each other electrically, creating a small gap where an arc voltage is generated [13]. The amount of energy input is controlled by the current value and the duration of current flow. This method enables easy generation of arc discharge; however, the amount of energy input requires adjustment of the spiral electrodes.

4.1.4. Discharge method (Electrical breakdown)

Needle-shaped electrodes are positioned facing each other. A high voltage of 40 kV is momentarily applied to induce dielectric breakdown, releasing the energy stored in a capacitor as an arc discharge. The amount of energy input is controlled by the charge of the capacitor [14]. The energy input can be easily controlled. However, a high-voltage power supply is required, and conducting tests in refrigerant atmospheres at pressures exceeding 3 MPa is challenging.

4.1.5. Heat spot method

This method involves passing current through a metal wire for a specified duration to create a localized heat source by Joule heating [14]. The temperature of the heat source is estimated based on the resistance characteristics of the metal wire. The amount of energy transferred to the refrigerant must be estimated separately.

4.2. Proposed Method: Fusing wire and discharge method

As mentioned above, various evaluation methods have been developed. For an evaluation method to be internationally standardized, the following requirements are considered important:

- High reproducibility: Tests should yield consistent results when repeated or performed by different operators.
- Low complexity: Tests should be simple and easy to implement.
- Controllable energy input: Energy delivered to the refrigerant should be quantifiable and adjustable.

Based on the third requirement, it is preferable to use arc discharge to supply energy to the refrigerant, since the amount of energy can be directly calculated from the measured current and voltage. However, fluorocarbon gases are highly insulating, so especially under high-pressure conditions, it is technically challenging to form an arc discharge. If the arc discharge becomes unstable, the amount of energy supplied will also fluctuate. Therefore, an additional requirement is necessary for international standardization.

- Stable discharge under high-pressure refrigerant conditions

Based on these requirements, the Fusing Wire and Discharge Method is considered a promising test method for international standardization. Fig. 4 shows a schematic diagram of this method. The outline of the test procedure is as follows:

- A fine metal wire (fusing wire) is positioned between electrodes set a few millimeters apart.
- When current is applied through the wire, its temperature rises due to Joule heating, eventually reaching the melting point and causing the wire to fuse.
- An arc discharge then occurs between the electrodes, supplying the energy that triggers the self-decomposition reaction in the refrigerant.

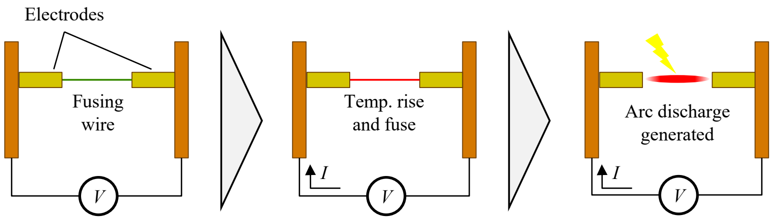


Figure 4. Fusing wire and discharge method.

Fig. 5 shows the electrodes used in the fusing wire and discharge method installed in the test apparatus shown in Fig. 3. Two copper electrodes with a diameter of 3 mm are arranged horizontally, facing each other with a 1 mm gap, and a fusing wire (nickel wire with a diameter of 0.1 mm) is soldered between them. In this method, the metal vapor generated from the fusing wire promotes arc discharge formation even in high-pressure refrigerant atmospheres. This technique, in which a metal wire is placed between electrodes to generate a discharge, has already been standardized in international standards such as EN 1839 (Determination of the explosion limits and the limiting oxygen concentration (LOC) for flammable gases and vapours) [15] and TDG (United Nations Recommendations on the Transport of Dangerous Goods) [16]. It is also widely used in other fields, including electric power equipment [17] and explosion testing [18]. However, for testing self-decomposition reactions, it is necessary to develop and adapt the method for this specific purpose, since the target gases are high-pressure fluorocarbons, which make discharge generation difficult, and the required energy levels are different.

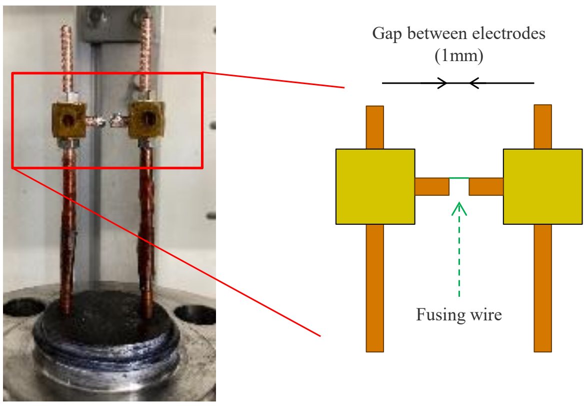


Figure 5. Electrodes of fusing wire and discharge method.

4.3. Efforts Toward the Establishment of an Evaluation Method

Here, efforts toward the establishment of an evaluation method are introduced.

4.3.1. Considerations for Energy Control

The amount of energy supplied by arc discharge is calculated as the time integral of the product of current and voltage. Fig. 6 shows the current and voltage changes in the Fusing Wire and Discharge method. The test conditions are an electrode gap of 2.5 mm, with the test conducted in air at room temperature. In this figure, the fusing wire melts at t_{fus}, and arc discharge occurs from that point until t_{arc}. The amount of energy supplied is expressed as the time integral of current and voltage, as shown in Eq. (3). The energy consumed up to t_{fus} is only a small fraction of the total, and the energy supplied by the arc discharge between t_{fus} and t_{arc} is dominant. Therefore, quantification and control of the energy supplied by arc discharge are important.

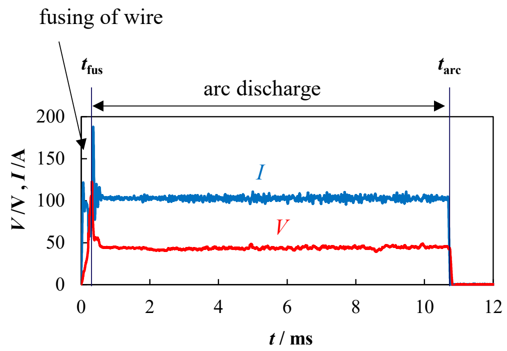


Figure 6. Change in voltage and current.

$$E = \int_0^{t_{arc}} IVdt \tag{3}$$

In general, the arc voltage during arc discharge is determined by the electrode geometry, type of gas, and conditions such as temperature and pressure, rather than by the power supply. Furthermore, when a stabilized power supply is used, the current and time duration are specified by the power supply. Therefore, prediction and control of the arc voltage are necessary for controlling the input energy.

Fig. 7 shows the arc voltage when the electrode distance (L) was varied [19]. The horizontal axis represents the electrode distance, and the vertical axis represents the arc voltage. Tests were conducted with R32 and N_2 (and air) at pressures of 0.1 MPa and 0.7 MPa. A nickel wire with a diameter of 0.1 mm was used as the fusing wire. As shown in Fig. 7, it was found that the arc voltage increases linearly with the electrode distance. The intercept value was approximately 20 V and remained nearly constant under all experimental conditions. The slope was larger for R32 than for N2, and the slope increased with higher pressure.

Fig. 8 shows the arc voltage when the gas density was varied [19]. The horizontal axis represents gas (R32) density, and the vertical axis represents arc voltage. In all cases, the electrode gap was 1 mm, and a nickel wire with a diameter of 0.1 mm was used. The experimental results obtained at different temperatures and pressures are organized by gas density. Arc voltage increased with gas density. Furthermore, under these conditions, temperature dependence was small, and arc voltage increased in proportion to the square root of gas density.

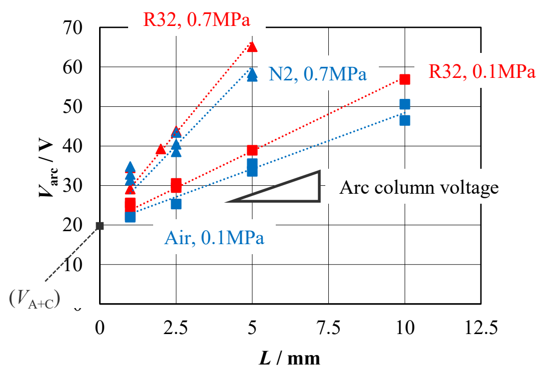


Figure 7. Relationship between arc voltage and electrode distance [19].

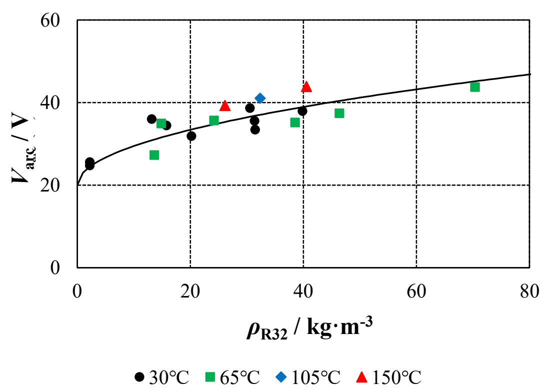


Figure 8. Relationship between gas density and arc voltage [19].

These results indicate that arc voltage and input energy can be predicted from electrode gap and gas density. In particular, as the electrode distance increases, the arc voltage also increases, which leads to greater arc instability and makes discharge more difficult. Therefore, from this perspective, the electrode distance should be short. For the fusing wire, using a thinner wire reduces the energy consumed in fusing, allowing for more accurate identification of the energy supplied to the refrigerant. Considering workability, the electrode distance of 1 mm and the fusing wire diameter of 0.1 mm were considered appropriate. Table 4 shows the conditions for the test method deemed suitable based on these tests, along with the relevant conditions in the TDG method and EN 1839.

Table 4. Comparison with existing standards.

	Method for self-decomposition reaction evaluation	TDG	EN 1839
Diameter of electrodes	3mm	-	-
Distance between electrodes	1mm	3-6mm	4-6mm
Material of thin wire	Ni	Ni	NiCr
Diameter of thin wire	0.1mm	0.12mm	0.05-0.2mm

4.3.2. Interlaboratory Comparison Test

An interlaboratory comparison (ILC) test was performed to validate the test method. Central Research Institute of Electric Power Industry (CRIEPI), AGC, and Daikin Industries — participants in the NEDO project "Development of High-Efficiency Refrigeration and Air-Conditioning Technologies for the Practical Use of Next-Generation Low-GWP Refrigerants" in Japan [20] — performed tests under identical conditions using the Fusing Wire and Discharge Method, and the results were compared [21]. The tests were conducted at 150°C, and R1132a was used as the refrigerant. R1132a (CH_2=CF_2) is an ethylene-based refrigerant and is known to undergo self-decomposition reactions, similarly to the previously mentioned two refrigerants. The initial pressure was varied to investigate the presence or absence of reaction propagation, and the following parameters were compared:

- Upper Bound Pressure (UBP): the highest initial pressure at which no reaction propagation occurred
- Lower Bound Pressure (LBP): the lowest initial pressure at which reaction propagation occurred
- Reaction Boundary Pressure (RBP): (UBP + LBP) ÷ 2

The results are shown in Fig. 9. Considering the range between UBP and LBP, the results from all three organizations were within ±5% of the average value. These results show that the test method and conditions described in this paper can provide consistent results across different laboratories.

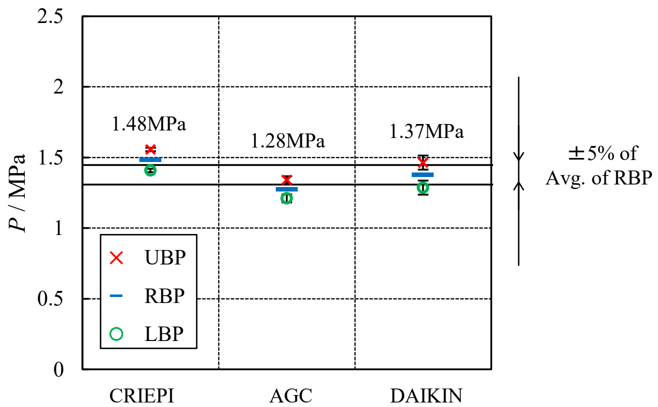


Figure 9. Result of interlaboratory comparison test [21].

Based on these results, Table 5 compares the characteristics of different ignition methods. The Fusing Wire and Discharge Method exhibits excellent characteristics with respect to the requirements for international standardization described earlier. Comparisons of reaction boundaries using different ignition methods, as well as dependencies on other experimental conditions, have also been investigated [22][23]. Various efforts are underway to evaluate the safety of self-decomposition reactions.

Table 5. Comparison of Ignition Methods for International Standardization

Methods	High reproducibility	Low complexity	Controllable energy input	Stable discharge
Fusing Wire and Discharge method (Proposed method)	Validated by ILC. Consistent results obtained.	Similar methods are already standardized internationally. A low-voltage power supply is available.	The amount of energy is controlled by current value and discharge duration. Easily estimated from the measured current and voltage.	Arc discharge can be easily generated even in a high-pressure refrigerant atmosphere.
Melting method	Just manage the diameter and length of the metal wire.	Simple	Difficult to estimate the amount of energy supplied to the refrigerant.	-
Discharge method (Movable electrode)	Adjustment related to the movement of the electrodes is required.	Adjustment related to the movement of the electrodes is required.	The amount of energy is controlled by current value and discharge duration. Easily estimated from the measured current and voltage.	Arc discharge can be easily generated even in a high-pressure refrigerant atmosphere.
Discharge method (Spiral electrode)	Adjustment related to the movement of the electrodes is required.	Adjustment related to the movement of the electrodes is required.	The amount of energy is controlled by current value and discharge duration. Easily estimated from the measured current and voltage.	Arc discharge can be easily generated even in a high-pressure refrigerant atmosphere.
Discharge method (Electrical breakdown)	Just requires matching the electrode gap and power supply settings	Power supply generating high voltage is required	Accurately controlled by the charging capacity of the capacitor	Difficult under high-pressure refrigerant atmospheres
Heat spot method	Just requires controlling the energization time and current value	Necessary to estimate in advance the relationship between the current value and temperature.	Needs to be estimated separately	-

5. Conclusion

In this paper, the trends in the revision of ISO 817 related to self-decomposition reactions and the efforts toward this revision were presented. HFO-1123 and R1132(E) are attracting attention as next-generation refrigerants with excellent environmental performance and thermophysical properties; however, safety concerns remain regarding self-decomposition reactions. Safety evaluation through international standardization is essential for their practical application and widespread use. The current ISO 817 specifies the safety classification of refrigerants based on flammability and toxicity. In June 2024, ISO/TC86/SC8/TF3 (Refrigerant Stability Classification) was established, and work is underway to add a refrigerant stability classification to ISO 817. The development of test methods is progressing, and among them, the Fusing Wire and Discharge Method is considered promising for ignition methods with regard to the requirements for standardization such as high reproducibility and low testing complexity. To apply the method to refrigerant evaluation, the electrode parameters and input energy were examined. The interlaboratory comparison (ILC) showed that the reaction boundary pressure was reproduced within ±5%, supporting the robustness of the proposed method for international standardization. Through these studies, proposals for test conditions and evaluations of test validity are being advanced.

Acknowledgements

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