DEVELOPMENT OF EVALUATION METHOD FOR SELF-DECOMPOSITION REACTIONS OF NEXT-GENERATION REFRIGERANTS

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ABSTRACT

Hydrofluoroolefin (HFO) refrigerants have attracted significant attention as next-generation refrigerants due to their low GWP and favorable thermophysical properties. However, there is a safety concern related to their self-decomposition reactivity. For their practical implementation, comprehensive safety assessments and the standardization of evaluation method of reactivity are necessary. This study presents the development of a method for evaluating self-decomposition reactions of the next-generation refrigerants. A test apparatus was constructed, consisting of a reaction vessel capable of withstanding high temperature and pressure, along with an ignition source to apply energy to the refrigerant. As the ignition source, a fusing wire and discharge method was developed and adopted to reliably generate discharges with high reproducibility under high-pressure fluorocarbon conditions. Interlaboratory comparison tests were conducted, and the results confirmed the validity of the evaluation method.

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

1. INTRODUCTION

Following the Kigali Amendment to the Montreal Protocol adopted in 2016, countries have been working to reduce the consumption of hydrofluorocarbon (HFC) refrigerants. In developed countries, including Japan, mandatory reduction targets have been set at 70% by 2029, 80% by 2034, and 85% by 2036 relative to the baseline year. While the transition to low-GWP (Global Warming Potential) refrigerants is progressing across various application sectors, it has been relatively slow in residential and commercial air conditioning, as well as in small-scale commercial refrigeration and freezing systems. Consequently, there is a strong demand for refrigerants that can simultaneously deal with challenges related to safety, energy efficiency, and environmental performance.

To meet this demand, the New Energy and Industrial Technology Development Organization (NEDO) launched the project "Development of High-Efficiency Refrigeration and Air-Conditioning Technologies for the Practical Use of Next-Generation Low-GWP Refrigerants" in 2023 [1]. The project focuses on residential and commercial air conditioning and commercial refrigeration and freezing systems. The aim is to promptly identify feasible Hydrofluoroolefin (HFO)-based refrigerants The project is organized into four groups: Group for Refrigerant Property Evaluation, Group for Equipment Component Technologies, Group for Safety Evaluation, Group for System Performance Evaluation. This paper reports on the activities of the Group for Safety Evaluation.

HFO refrigerants have attracted significant attention as next-generation alternatives. These refrigerants contain carbon–carbon double bonds within their molecular structure, which reduce molecular stability and shorten atmospheric lifetime, resulting in extremely low GWP. In the air-conditioning and refrigeration sectors, HFO-1123 ($CHF=CF_2$) and R1132(E) (CHF=CHF trans.) are considered promising candidates. Both are ethylene-based HFO refrigerants and exhibit excellent low-GWP characteristics and favourable thermophysical properties. The blended refrigerants incorporating R1234yf or R32 have been proposed [2,3].

However, the reduced molecular stability associated with carbon - carbon double bonds raises safety concerns. In general, there is a trade-off between GWP and flammability; with lower GWP often correlating with higher flammability. For HFO-1123 and R1132(E), an additional safety concern arises from a self-decomposition reaction. It is a chemical process in which two or more molecules react with each other and break down into two or more different products when external energy is supplied. This reaction is also referred to as a disproportionation reaction. The chemical equations for the self-decomposition of each refrigerant are shown in Eqs. (1) and (2). For these refrigerants, the reaction is exothermic, and both pressure and temperature can increase significantly.

$$\mathrm{CF_2 = CHF \rightarrow \frac{1}{2}\,CF_4 + \frac{3}{2}\,C + HF + 250kJ/mol} \quad (1)$$

$$\mathrm{CHF = CHF \rightarrow 2C + 2HF + 248kJ/mol} \quad (2)$$

Self-decomposition reactions may occur under the following conditions: (1) high ethylene-based HFO composition, (2) high pressure and temperature, and (3) the presence of energy from an ignition source. When the HFO refrigerants are used in actual systems, there is a safety risk that self-decomposition reactions could occur if the compressor reaches high-pressure and high-temperature conditions due to an abnormality, and an energy source, such as a layer short circuit, is introduced [4]. Furthermore, unlike combustion, this reaction does not require oxygen, posing a new safety risk that can occur even without refrigerant leakage from the system.
Against this background, the NEDO Group for Safety Evaluation, comprising Central Research Institute of Electric Power Industry (CRIEPI), AGC Inc. (AGC), Daikin Industries, Ltd. (DAIKIN), and Suwa University of Science, is conducting research and development on the safety evaluation of self-decomposition reactions in next-generation refrigerants. The main activities are as follows:

- Investigation of factors that induce self-decomposition reactions inside compressors and the amount of energy involved.
- Development of evaluation methods for self-decomposition reactions.
- International standardization and revision of standards related to self-decomposition reactions.
- Risk assessment for the use of next-generation refrigerants in actual equipment.

This paper reports on the development and international standardization of evaluation methods for self-decomposition reactions of refrigerants. In particular, it describes a fusing wire and discharge method developed as an evaluation technique and presents the results of an interlaboratory comparison test conducted to verify the validity of this method.

2. SAFETY CLASSIFICATION STANDARD

The safety of refrigerants is currently defined by flammability and toxicity in international standards [5,6]. However, stability with respect to self-decomposition reactions is not regulated. To deal with the growing need for the safe implementation of next-generation refrigerants, ISO established a task force (ISO / TC86 / SC8 / TF3) in June 2024 to develop refrigerant stability classifications. Discussions on classification schemes and evaluation methods are ongoing. The NEDO Group for Safety Evaluation is working on the development of evaluation methods for self-decomposition reactions.

3. OVERVIEW OF FUSING WIRE AND DISCHARGE METHOD

Since self-decomposition reactions can occur under high pressure and temperature conditions, evaluations must also be conducted under such conditions. The refrigerant to be tested is charged into a pressure vessel, and its temperature and pressure are controlled to specified values. Subsequently, energy is applied using an ignition source installed inside the vessel, and the presence of reaction propagation is determined based on the pressure change. In this evaluation method, the type of ignition source and the amount of energy applied are particularly critical factors.
Various ignition devices have been developed. A discharge device that creates a small gap by electrically repelling movable electrodes through current flow was developed and used for tests on HFO-1123 [7]. Spiral electrodes to generate discharge were also used for HFO-1123 evaluation [8]. A discharge device utilizing needle-shaped electrodes and applying a momentary high voltage via a boost circuit to induce dielectric breakdown was developed and evaluated for R1132(E) [9]. A fine wire melting method was also used [10]. These methods differ in characteristics such as their ability to accurately reproduce phenomena occurring inside compressors or the ease of energy control. However, challenges remain such as discrepancies in evaluation results among methods and the high complexity.
In this study, the following characteristics were considered essential for the ignition source for international standardization:

- High reproducibility
- Low testing complexity
- Ability to control and adjust the energy applied to the refrigerant
- Stable discharge even under high-pressure refrigerant conditions

Based on these considerations, the "Fusing Wire and Discharge Method" was identified as a promising approach. Fig. 1 shows a schematic diagram of this method. The outline of the test procedure is as follows:

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

Experimental evaluations have been conducted to evaluate and predict the amount of energy applied to the refrigerant using this method [11].

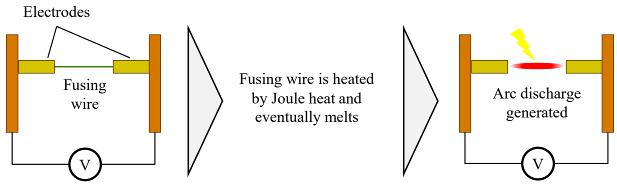


Fig.1 Fusing wire and discharge method

4. INTERLABORATORY COMPARISON

An interlaboratory comparison test was conducted to verify the validity of the evaluation method. In this test, three organizations performed experiments under identical conditions using the same refrigerant, and the resulting reaction boundary pressures were compared.

EXPERIMENTAL SETUP

As mentioned earlier, the self-decomposition reaction is a phenomenon that occurs when energy is applied under high-temperature and high-pressure conditions. Therefore, the evaluation method is designed to reproduce such an environment. Fig. 2 shows a schematic diagram of the evaluation apparatus. Here, the apparatus of CRIEPI is described as an example. The apparatus is used to perform the fusing wire and discharge method. Copper electrodes were horizontally placed, with a fusing wire positioned between them and fixed with solder. These electrodes are housed in a pressure vessel. The refrigerant was sealed in a pressure vessel and heated to reach the required temperature and pressure. A stabilized power supply (NF Corporation, DP090S) was used to apply voltage to the electrodes. The current limit, applied voltage, and application time were set at the power supply. The pressure and temperature of the refrigerant inside the pressure vessel were measured using a pressure gauge (Nagano Keiki, KJ16, accuracy ±0.5% F.S.) and a thermometer (K type thermocouple, accuracy ±1.35℃), respectively. The current and voltage were measured using an ammeter (Hioki, CT6876, accuracy ±0.04% F.S.) and a voltmeter (Keyence, NR-HV04, accuracy ±0.4V).

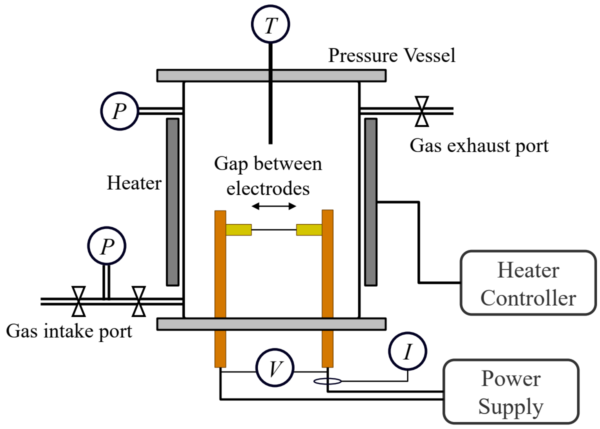
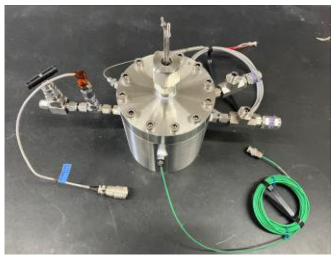


Fig.2 Schematic diagram of test apparatus

Table 1 shows the external views of the test apparatus, the dimensions of the reaction vessels, and the appearance of the ignition electrodes for the three organizations. All setups employed the fusing wire and discharge method for the ignition source shown in Fig. 1. Although the dimensions and external configurations of the apparatus differ, their basic structures are same as shown in Fig. 2.

Table 1 Experimental Apparatus

	CRIEPI	AGC	DAIKIN
Overview			
Size of pressure vessel (Inner diameter, height, volume)	φ40mm, 250mm, 314cm^3	φ72mm, 171.3mm, 650cm^3	φ82.5mm, 95mm, 500cm^3
Ignition source (Fusing wire and discharge method)			

EXPERIMENTAL CONDITIONS

Table 2 lists the experimental conditions. The refrigerant used was R1132a (CH_2=CF_2), which is considered a promising low-GWP alternative to low-temperature refrigerants such as R23 [12]. Similar to HFO-1123 and R1132(E), it is an ethylene-based refrigerant and has been reported to cause self-decomposition reactions [13]. Based on previous studies on compressor failure scenarios, the test temperature was set to 150 °C, and the input energy (E) was set to 25 J. The input energy was calculated as the time integral of the product of current and voltage using Eq. (3). The electrode gap was set to 1 mm. A nickel wire with a diameter of 0.1mm was used as a fusing wire. For each condition, allowable tolerances were defined as shown in Table 2, and any results that did not meet these tolerances were excluded from the analysis.

Table 2 Experimental Conditions

Parameter	Value
Refrigerant	R1132a
Initial temperature (T_0)	150±5°C
Initial pressure (P_0)	(Varied)
Input energy (E)	25±5J
Gap between electrodes	1±0.1mm
Fusing wire material	Nickel
Fusing wire diameter	0.1mm

$$E = \int_0^t IV dt \tag{3}$$

EXPERIMENTAL PROCEDURE

For each test, after charging the refrigerant, the pressure vessel was heated to achieve the specified temperature and pressure. Energy was then applied through the ignition source inside the vessel. When the reaction propagated, the internal temperature and pressure increased. Up to three tests were conducted at the same initial pressure (P_0), and the presence or absence of reaction propagation under each condition was determined as follows:

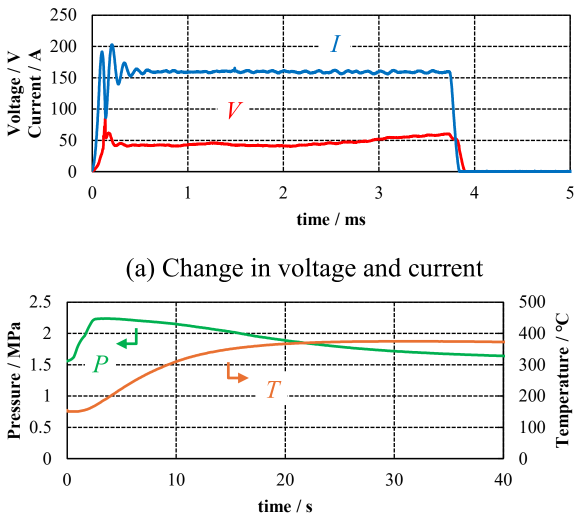
- Reaction propagation: If the pressure increased by more than 30% of the initial pressure in at least one of the tests, the condition was judged as "reaction propagation observed."
- No reaction propagation: If none of the tests showed a pressure increase of more than 30% of the initial pressure, the condition was judged as "no reaction propagation."

Among the tests judged as "reaction propagation", the lowest measured initial pressure was defined as the Upper Bound Pressure (UBP). Among the tests judged as "no reaction propagation", the highest average value of the measured initial pressure was defined as the Lower Bound Pressure (LBP). Tests are repeated with varying the initial pressure. The average of UBP and LBP was defined as the Reaction Boundary Pressure (RBP).

EXPERIMENTAL RESULTS

Fig. 3 shows the changes in the current and the voltage of the ignition source (Fig. 3(a)) and the temperature and pressure inside the vessel (Fig. 3(b)) under conditions where reaction propagation occurred (initial pressure: 1.56 MPa). In Fig. 3(a), the current remained nearly constant at the set value of the power supply (maximum 160 A). The arc voltage is determined by the refrigerant properties and the test pressure and temperature, and was approximately 50 V under these conditions. The input energy was controlled to 25 J by adjusting the discharge duration.

In Fig. 3(b), the pressure increased to a maximum of 2.24 MPa and then gradually decreased, while the temperature rose to approximately 400 °C. Since the ratio of the maximum pressure to the initial pressure (pressure ratio) was 1.44, exceeding 1.3, this condition was judged as reaction propagation.

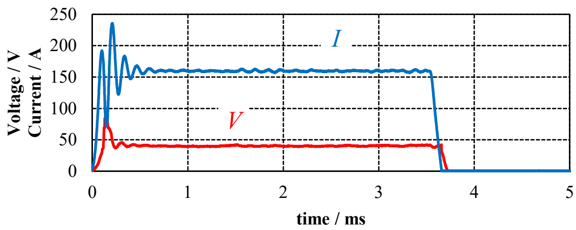


(a) Change in voltage and current

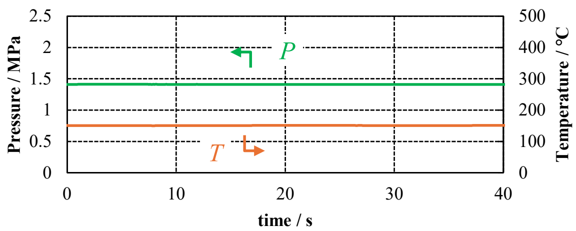
(b) Change in pressure and temperature

Fig.3 Results under "reaction propagation" condition (P_0 = 1.56MPa)

Fig. 4 shows the changes in the current and the voltage of the ignition source (Fig. 4(a)) and the temperature and pressure inside the vessel (Fig. 4(b)) under conditions where no reaction propagation occurred (initial pressure: 1.41 MPa). In Fig. 4(b), the pressure remained nearly constant, resulting in a pressure ratio of 1.00. This condition was judged as no reaction propagation.



(a) Change in voltage and current



(b) Change in pressure and temperature

Fig.4 Results under “no reaction propagation” condition (P_0 = 1.40MPa)

Fig. 5 summarizes the experimental results. Here, only the measurement data obtained by CRIEPI are included as example. The horizontal axis represents the input energy, and the vertical axis represents the initial pressure. Open circles indicate conditions where no reaction propagation occurred, while crosses indicate conditions where propagation was observed. In the present tests, the maximum and minimum input energies were 27.2 J and 22.2 J, respectively. All of them were in the target range of 25 ± 5 J. The results show that the fusing wire and discharge method enabled highly reproducible input energy. Based on these results, the reaction boundary pressure was determined as follows:

- LBP = 1.41 MPa
- UBP = 1.56 MPa
- RBP = 1.48 MPa.

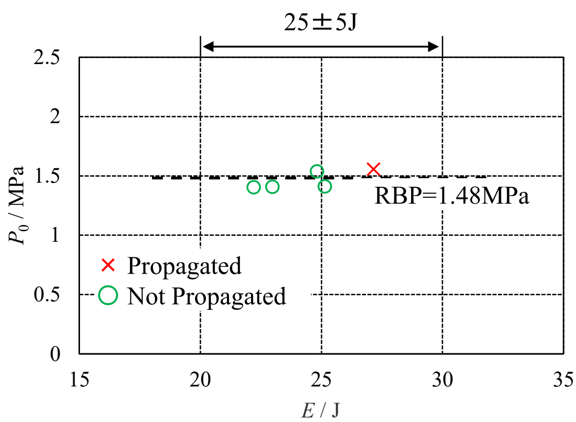


Fig.5 Experimental results

Fig. 6 compares the results obtained by the three organizations. The UBP, RBP, and LBP for each organization are shown, with measurement uncertainties for UBP and LBP included to account for pressure gauge accuracy. The RBPs obtained by the three organizations were 1.48 MPa, 1.28 MPa, and 1.38 MPa, respectively, with an average of 1.38 MPa. 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.

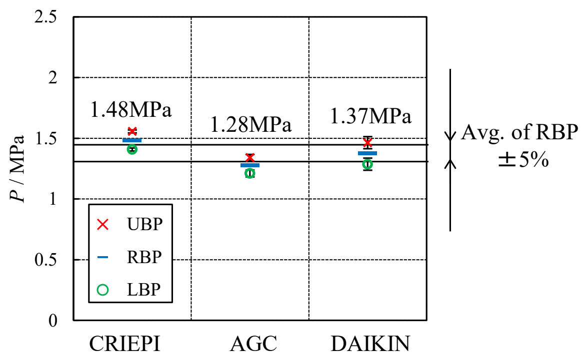


Fig.6 Comparison of results obtained by three organizations

5. CONCLUSION

This paper introduced the NEDO Group for Safety Evaluation and its efforts to develop evaluation methods for self-decomposition reactions, aiming at the practical application of next-generation low-GWP refrigerants. While HFO-based refrigerants such as HFO-1123 and R1132(E) have attracted attention as next-generation candidates, safety concerns related to self-decomposition reactions remain. To address these issues, the Group for Safety Evaluation is conducting studies on the factors that trigger self-decomposition reactions and developing evaluation methods for these reactions.

To enable reproducible discharges even under high-pressure fluorocarbon atmospheres, a fusing wire and discharge method was adopted. An interlaboratory comparison test was conducted to assess the validity of this method. The results confirmed that, by appropriately controlling experimental parameters, energy could be applied to the refrigerant with high reproducibility, and consistent reaction boundary pressures were obtained across laboratories. These results show the validity of the evaluation method.

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NOMENCLATURE

E	: Input energy, J
I	: Current, A
LBP	: Lower Bound Pressure, MPa
P	: Pressure, MPa
RBP	: Reaction Boundary Pressure, MPa
T	: Temperature, ℃
UBP	: Upper Bound Pressure, MPa
V	: Voltage, V
Subscript	
0	: Initial

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