Evaluation of self-decomposition for R-1132(E)-based refrigerant blends

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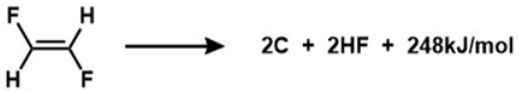
ABSTRACT

Refrigerants containing ethylene-based HFO are at risk of causing equipment failures due to self-decomposition reactions that result in increased temperature and pressure when external energy is applied. Therefore, it is crucial to elucidate the conditions under which these reactions occur. To date, evaluations of self-decomposition reactions have been conducted using discharges facilitated by dielectric breakdown as a form of energy, but challenges were present in inducing discharges at high gas pressures, similar to air conditioning operating conditions. This report describes the creation of a device capable of generating discharges even at high gas pressures, and evaluates the impact of discharge characteristics on self-decomposition reactions, as well as assessing mixed refrigerants containing R-1132(E).

Keywords: R-1132(E), Self-decomposition, R-474A, R-474B, R-479A

1. INTRODUCTION

The Kigali Amendment of 2016 mandated the phased reduction of HFCs on a CO2-equivalent basis. Currently, various applications are transitioning to refrigerants with lower global warming potential, and the demand for next-generation refrigerants that combine low GWP with energy efficiency is increasing in pursuit of achieving carbon neutrality by 2050. Since 2017, we have been developing new refrigerants and identified R-1132(E) after exploring various substances. Since 2018, we have participated in a NEDO-supported project aiming to develop a lower flammable refrigerant with GWP below 10 for direct expansion type air-conditioning equipment, conducting various safety evaluations and new refrigerant composition development. Since 2022, we have registered refrigerants such as R-1132(E) and its mixtures R-474A, R-474B, R-479A with the American Society of Heating, Refrigerating, and Air-Conditioning Engineers (ASHRAE). From 2023, we have been engaging in the NEDO-commissioned project "Development of Next-Generation Refrigerant and Refrigeration Air Conditioning Technology and Evaluation Methodology" as a subcontract from the Central Research Institute of Electric Power Industry, focusing on the commercialization of these ASHRAE-registered refrigerants. This project primarily advances efforts towards international standardization of self-decomposition reactions. R-1132(E), being an ethylene-based HFO, is known to undergo self-decomposition reactions involving pressure and temperature rise in the presence of an energy source under high temperature and pressure, similar to tetrafluoroethylene and trifluoroethylene (HFO-1123) (Scheme 1). To date, we have evaluated self-decomposition reactions against discharges utilizing dielectric breakdown as an energy source. This paper reports on the ISO evaluation method development led by NEDO Safety Group and the evaluation of self-decomposition reactions of mixed refrigerants containing R-1132(E) towards ISO international standardization.



Scheme 1 Self-decomposition of R-1132(E)

2. EFFORTS TOWARDS ISO STANDARDIZATION

2-1. TOWARDS THE DEVELOPMENT OF EVALUATION METHODS

To date, domestic businesses and universities have independently developed evaluation methods for self-decomposition reactions. For global dissemination of HFO refrigerants, international standardization of evaluation methods and safety classifications is expected to facilitate smooth deployment. Within the NEDO project's Group for Safety Evaluation, we are aiming to develop internationally recognized evaluation methods for self-decomposition reactions, with roles distributed for efficient exploration (Table 1). The Group for Safety Evaluation consists of four entities: the Central Research Institute of Electric Power Industry, Suwa University of Science, AGC Inc., and Daikin Industries, Ltd. The group focuses on (1) elucidating discharge phenomena in actual equipment, (2) proposing test methods, (3) determining test methods, and (4) evaluating registered refrigerants. Currently, the proposal of test methods (2) has been completed, and all entities are collaboratively working on (1) elucidation of discharge phenomena and (3) finalizing test methods.

Table 1 Task list for ISO International Standardization

Category	Subcategory	Item
(1) Analysis of discharge phenomenon in actual equipment	Energy quantitation	Inverter motor
		Non-Inverter motor
		Domestic/Foreign
(2) Proposal of test method	Method proposal	Proposal based on the TDG test
(3) Determination of test method	ILC exam.	Compare evaluations by using R-1132a
	Factor investigation	Energy density
		AC/DC
		Metal wire
		Structure
		Capacity
		L (Height) / D (Inner diameter) Ratio
		Comparison with Previous Research
(4) Evaluation of registered refrigerants	Evaluation	Evaluation of Refrigerants such as R-474A

Regarding international standardization, a task force was established in June 2024 to add a new "Stability Classification" as a refrigerant safety grade within ISO 817 (Refrigerants - Designation and safety classification). The aim is to finalize the standard addition by 2028, establishing three new classifications: α (sufficient stability for general use), β (sufficient stability under controlled conditions), and γ (unstable and must not be used). This will allow specifying safe mixed refrigerant compositions that are free from practical use issues related to the unique self-decomposition reaction of ethylene-based HFO refrigerants, facilitating global dissemination. As a method of classification evaluation, the Safety Group is currently proposing an evaluation method based on the stability test methods for flammable gases outlined in the United Nations Recommendations on the Transport of Dangerous Goods (TDG). The test conditions are shown in Table 2.

Table 2 Proposed test method for self-decomposition evaluation

Parameter		Value
Electrodes	Gap	[1.0±0.1 mm]
	Wire material	Ni
	Wire diameter	Φ 0.12 mm
Vessel	Shape	Cylindrical
	Volume	[>0.25 L]
	Diameter	[50±10 mm]
Ignition	Source	AC/DC
	Time	[max. 10 ms]
	Energy	25±5 J (10±2)
Refrigerant	Composition	WCF*
	Pressure	Saturated pressure (1.5±0.1 times)
	Temperature	150 ℃

*WCF(worst case formulation): The most easily decomposable composition, including refrigerant composition tolerance (±2.0%).

Based on the test conditions, the test apparatus designed by our company is shown in Figure 1. Electrodes are fixed in a pressure vessel using an insulator, with their tips placed at the designated position. Considering the typical operating range of high-pressure refrigerants like R-32 commonly used in air conditioners, the temperature and pressure for the test are set at approximately 65°C and 4 MPa. However, the maximum abnormal pressure is set at 1.5 times the saturation pressure at 65°C, based on the pressure resistance design of the compressor. We propose defining the classification α as those that do not undergo decomposition three times when evaluated under the same conditions. Moreover, once the proposed test apparatus is constructed, it will enable further exploration of these conditions.

In our setup shown in Figure 1, the electrodes are fixed in the pressure vessel using an insulator. When an electrical breakdown occurs at the tip of the electrodes, a self-decomposition reaction is triggered, associated with a rise in pressure and temperature, as known for ethylene-based HFOs like R-1132(E) under normal operating ranges of about 65°C and 4 MPa, commonly used in air conditioners. The Safety Group within the NEDO project proposes an international standardization of self-decomposition reaction evaluation methods for mixed refrigerants—based on the stability test methods of flammable gases as recommended by the United Nations Recommendations on the Transport of Dangerous Goods (TDG).

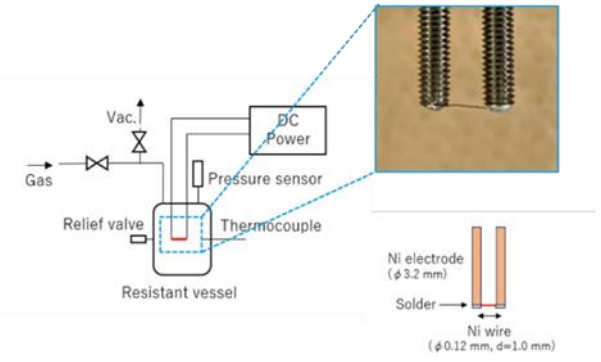


Fig. 1 Equipment of fusing wire and discharge method

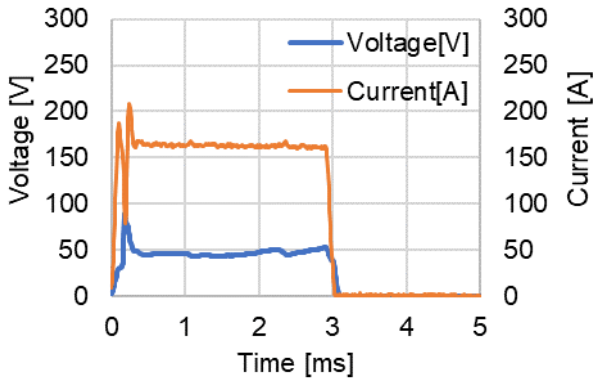


Fig. 2 Waveform of arc voltage and current

2-2. EVALUATION OF VESSEL DEPENDENCY

To achieve international standardization of the evaluation, it is essential to identify factors within the proposed evaluation methods and conditions that influence the judgement results, ensuring consistent results irrespective of the entity conducting the assessment. Therefore, it is necessary to test these factors by varying each parameter and assessing their impact. Within the Group for Safety Evaluation, such investigations are allocated as part of the item "(3) Determination of Test Methods."

This report focuses on one of the factor assessments handled by our company: the impact of test vessel dependency. Below, the test results under consistent conditions with those of the ILC testing, using different vessel capacities (38cc, 100cc, 500cc), are illustrated in Figure 3. No differences were observed in the results across the three tested conditions. From these results, it became evident that in a container with a height L and an internal diameter D, where L (height) to D (diameter) ratio is 1.2, the container's internal volume (cc) bears no dependency on the boundary pressure (MPa・A) at which decomposition propagation occurs, provided the volume is at least 38 cc.

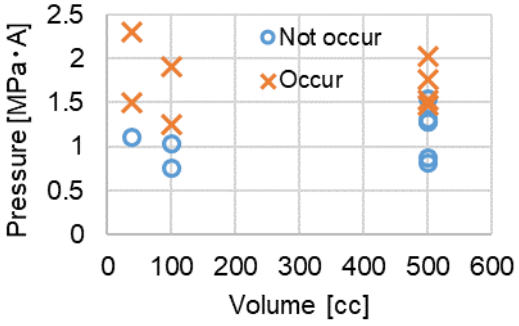


Fig. 3 Vessel dependency

2-3. EVALUATION RESULTS FOR R-474B (WCF COMPOSITION)

Among the R-1132(E) mixed refrigerants, R-474B, which has the highest concentration of R-1132(E), was evaluated using the test conditions proposed to ISO 817. The refrigerant composition used was R-474B with a WCF composition of R-1132(E)/R-1234yf at 33.5/66.5 mass%. The test conditions are shown in Table 3. Conducting the test with n = 3 trials confirmed that no self-decomposition reaction occurred. The temperature and pressure waveform obtained from the test is shown in Figure 4. A pressure increase of approximately 0.1 MPa was observed simultaneously with the occurrence of arc discharge. This pressure rise is considered to result from the thermal decomposition of the refrigerant in the arc discharge region. Furthermore, no temperature rise was observed.

Based on these results, it is considered that under the currently proposed test method, R-474B falls into the α classification (sufficient stability for general use). Given its lower concentration of R-1132(E), R-474A is also expected to be categorized similarly. R-479A will be evaluated similarly in the future. Additionally, the ILC test results and evaluation of the dependency on device parameters confirmed the soundness of the evaluation method. Once consensus is reached within the ISO task force, evaluations will be conducted again using this method to finalize refrigerant classification.

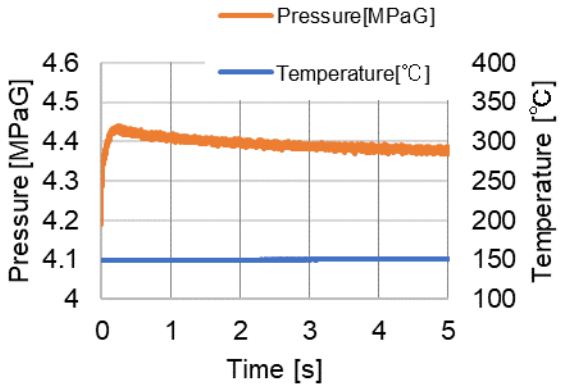


Fig. 4 Waveform of temperature and pressure

Table 3 Self-decomposition evaluation of R-474B

Parameter		Value
Ignition	Source	DC 200 V
	Time	<5 ms
	Energy	Apx. 25 J
Refrigerant	Composition	R-1132(E)/1234yf =33.5/66.5 mass%
	Pressure	4.4 MPa・A
	Temperature	150℃

3. EVALUATION OF R-1132(E) MIXED REFRIGERANTS

3-1. BOUNDARY FOR SELF-DECOMPOSITION REACTIONS IN R-1132(E)/R-1234YF MIXED REFRIGERANTS

The behavior of self-decomposition reactions under different test methods for R-1132(E)/R-1234yf mixed

refrigerants was confirmed. A previous test apparatus using the dielectric breakdown method is shown in Figure 5. This method involves creating a dielectric breakdown between electrodes by instantaneously applying high voltage, discharging the charge accumulated in a capacitor with adjustable discharge energy by varying the charging voltage. The test conditions are essentially the same as those currently proposed to ISO, with the modification that the test pressure is set arbitrarily and the energy expected in actual equipment is assumed to be 10 J. The determination of the presence of self-decomposition was similarly judged by whether the pressure increased to 1.3 times the initial pressure. Figure 6 shows results from the dielectric breakdown method in blue and those from the ISO proposed method in orange. Circles indicate no self-decomposition reaction, while crosses indicate its occurrence.

Previously, the dielectric breakdown method was only capable of measurements under conditions below 3 MPa・A, but the proposed method enables measurements above 3 MPa・A. The consistency with previous results using the dielectric breakdown method was confirmed by conducting tests with an R-1132(E)/R-1234yf = 70/30 mass% mixture, and consistency was observed. Moving forward, test points at other pressure ranges will be added to verify the impact of discharge characteristics on self-decomposition reactions.

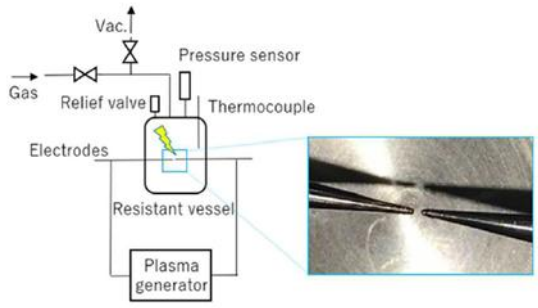


Fig. 5 Equipment of breakdown discharge method

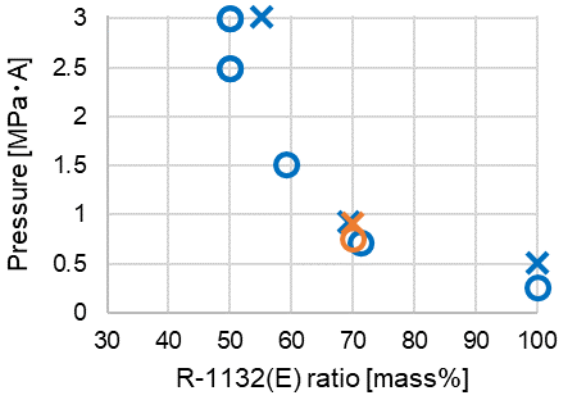


Fig. 6 Comparison of test methods

4. CONCLUSIONS

In the proposed evaluation method aimed at ISO international standardization, it was confirmed that the factor of container size, specifically at an L (height) to D (diameter) ratio of 1.2, does not affect the outcomes. Additionally, it was proven that mixed refrigerants R-474A and R-474B, including R-1132(E) with GWP below 10, determine the α classification under the proposed evaluation method. Furthermore, as a risk assessment for R-1132(E) mixed refrigerants, a device capable of discharging under high gas pressure was developed, and alignment with previous tests was verified in one condition. Moving forward, we aim to contribute to solving global environmental issues by internationally standardizing a new evaluation method for specific self-decomposition reactions of HFOs, facilitating the international adoption of next-generation ultra-low GWP HFO-based mixed refrigerants.

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