



Development of Refrigeration and Air-Conditioning Technologies for
Practical Use of Next-Generation Low-GWP Refrigerants

Volume 2

Group for Refrigerant Property Evaluation

Evaluation of the Properties of Low-GWP Refrigerant Mixtures

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1. Overview of Research and Development and Outcomes

1.1 Overview

From the perspective of ozone layer protection, hydrofluorocarbons (HFCs) are currently used worldwide as chlorine-free alternative refrigerants in refrigeration and air-conditioning equipment. They have replaced specified fluorocarbons such as chlorofluorocarbons (CFCs) and hydrochlorofluorocarbons (HCFCs), whose phase-out was mandated under the Montreal Protocol. However, in recent years, extreme weather events associated with global warming have become a critical concern, and HFCs have been designated as gases subject to emission reductions under the Kyoto Protocol and Paris Agreement because of their high greenhouse effect. Moreover, because completely preventing refrigerant leakage during equipment operation and disposal is extremely difficult, the transition to next-generation refrigerants with substantially lower global-warming impacts is considered one of the most effective countermeasures.

Under the Kigali Amendment to the Montreal Protocol, adopted in October 2016 to mandate the phasedown of HFC production and consumption, Japan, as a developed country, is required to reduce HFC production and consumption by 85% by 2036 relative to the 2011–2013 baseline. This target cannot be achieved through continued reliance on existing refrigerants. In addition, the declaration of carbon neutrality by 2050, announced by the Prime Minister in October 2020, has created an urgent necessity to develop next-generation refrigerants with extremely low global warming potential (GWP), as well as refrigeration and air-conditioning equipment compatible with such refrigerants.

Against this background, previous New Energy and Industrial Technology Development Organization (NEDO) projects in the refrigeration and air-conditioning field have promoted refrigerant transition through several initiatives. The “Development of High-Efficiency Non-Fluorocarbon Air-Conditioning Equipment Technology” project (FY2011–FY2015) addressed technology development for commercial air-conditioning equipment and related applications. The “Development of Technology for Small- and Medium-Capacity Air-Conditioning Equipment Using High-Efficiency, Low-GWP Refrigerants” project (FY2016–FY2017) developed fundamental elemental technologies for low-greenhouse-effect refrigerants and compatible residential air-conditioning equipment while also improving system efficiency. Subsequently, the “Development of Next-Generation Refrigerant/Refrigeration and Air-Conditioning Technologies and Evaluation Methods Capable of Achieving Energy Savings and Low Greenhouse Effects” project (FY2018–FY2022) developed and evaluated next-generation refrigerants for small- and medium-scale refrigeration and air-conditioning equipment, including commercial refrigeration, cold-storage equipment, and residential air conditioners. The project also established safety and risk assessment methods and advanced application technologies. Although these projects achieved their respective objectives, the transition to new refrigerants has progressed more rapidly than originally anticipated. Therefore, the identification of new green refrigerants, development of corresponding components, and evaluation of system-level performance have become increasingly urgent. Under these circumstances, identifying suitable next-generation candidates as conventional single-component refrigerants is extremely difficult, making refrigerant mixtures a necessary option.

Compared with single-component refrigerants, refrigerant mixtures present several technical challenges in heat exchangers. These include reductions in refrigeration-cycle performance resulting from temperature glide during condensation and evaporation, as well as deterioration of heat-transfer performance caused by mass-transfer resistance. For compressors, refrigeration oils suitable for low-GWP refrigerant mixtures should be developed and evaluated, and both lubrication characteristics within compressors and the compression characteristics of zeotropic refrigerant mixtures should be clarified. Furthermore, issues related to system-level performance evaluation, safety, and economic feasibility must be promptly identified and addressed, particularly because these mixtures have not previously been used in practical applications. For these challenges to be overcome and commercialization achieved according to the approaching Kigali Amendment milestones, coordinated research and development across the entire technology chain must be conducted

with careful consideration of the required implementation timeline.

Based on this, the research and development sub-item “Evaluation of Thermophysical Properties, Safety, and Environmental Impacts of Low-GWP Refrigerant mixtures; Development of Elemental Technologies for Compatible Equipment; and Performance Evaluation of Systems” aims to achieve heat-pump air conditioners compatible with low-GWP refrigerants through an integrated approach, as shown in Figure 1.1-1. The scope extends from the “selection of candidate refrigerant mixtures” (Refrigeration A-1 and A-2) through “performance evaluation of refrigerant mixtures” (Refrigeration B-1 and C-1), “evaluation of component equipment” (Equipment A-1, A-2, A-3, B-1, C-1, C-2, and C-3), and “system performance evaluation” (Refrigeration D-1 and D-2) to “environmental impact assessment” (Refrigeration E-1).

This research and development project, “Characterization of Low-GWP Refrigerant Mixtures,” is responsible for the parts corresponding to “selection of candidate refrigerant mixtures” (Refrigeration A-1 and A-2), “performance evaluation of refrigerant mixtures” (Refrigeration B-1 and C-1), “system performance evaluation” (Refrigeration D-1 and D-2), and “environmental impact assessment” (Refrigeration E-1) shown in Figure 1.1-1.

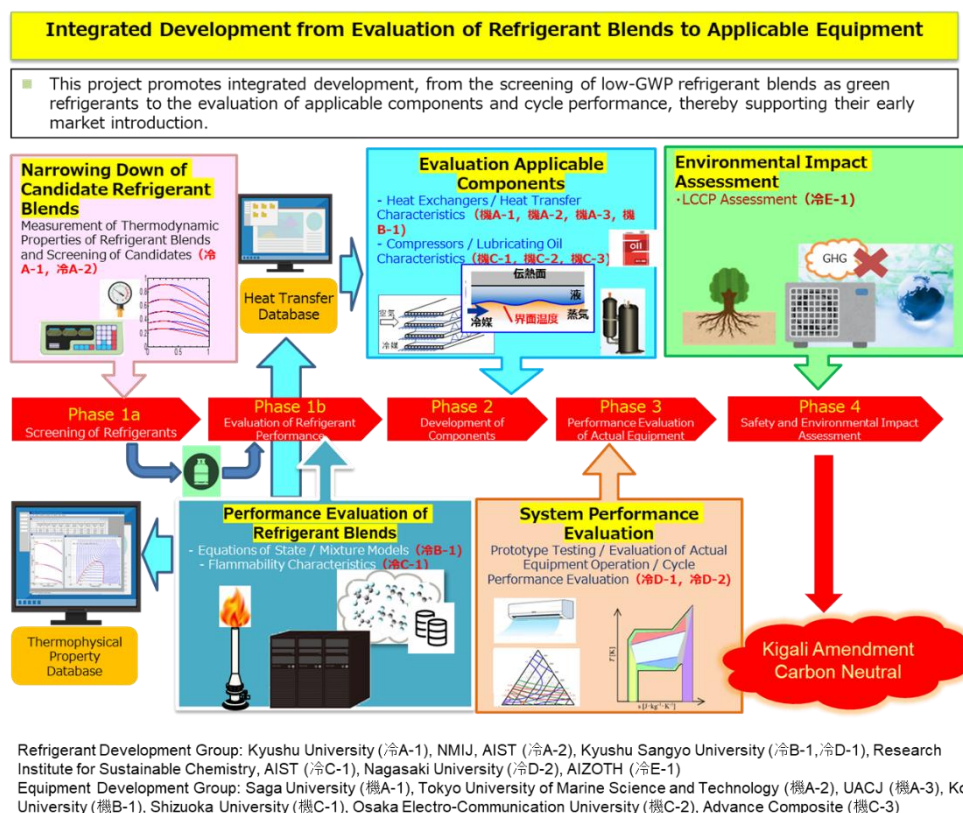


Figure 1.1-1 Workflow of the development of the next-generation refrigeration systems

First, in the “selection of candidate refrigerant mixtures” (Refrigeration A-1 and A-2) and “performance evaluation of refrigerant mixtures” (Refrigeration B-1 and C-1), low-GWP refrigerant-mixture candidates will be screened, and highly accurate thermophysical property data will be obtained for selected binary and ternary mixtures. Subsequently, equations of state and mixture models will be developed and incorporated into REFPROP, the thermophysical property calculation software provided by the National Institute of Standards and Technology (NIST), U.S. Department of Commerce. This process will enable the timely selection of target next-generation green refrigerants. In previous NEDO projects, refrigerant candidates were primarily selected based on GWP, thermophysical properties, heat-transfer characteristics, and cycle performance. In the present project, additional factors such as flammability and other safety characteristics, commercialization timing, refrigerant availability, and ASHRAE Standard 34 certification status will be treated as

important criteria. The resulting information will provide reliable foundational data for subsequent research and development activities, including the “evaluation of component equipment” (Equipment A-1, A-2, A-3, B-1, C-1, C-2, and C-3).

In “system performance evaluation” (Refrigeration D-1 and D-2), refrigerant mixtures selected through Refrigeration A-1, A-2, B-1, and C-1 will be evaluated as complete refrigeration-cycle systems incorporating the advanced heat exchangers, compressors, and refrigeration oils developed under Equipment A-1, A-2, A-3, B-1, C-1, C-2, and C-3. Hence, a refrigeration-cycle model test apparatus must be newly fabricated so that system performance can be flexibly evaluated while individual components, such as heat exchangers and compressors, are replaced as development progresses. Cycle performance will be evaluated while sequentially feeding back the results obtained in Refrigeration A-1, A-2, B-1, and C-1, and the resulting outcomes will be verified. The information obtained will also support more advanced system performance evaluation, simulation studies, and the development of actual equipment. At this stage, REFPROP, incorporating the equations of state and mixture models developed through Refrigeration B-1 and C-1, should function as the common thermophysical property calculation platform. Even when discrepancies occur between actual equipment tests and simulations conducted under other commissioned or subsidized projects, development time can be reduced if a collaborative environment is established in which the causes can be rapidly identified and fed back into the development process.

In “environmental impact assessment” (Refrigeration E-1), life cycle climate performance (LCCP) evaluation will be conducted with commercialization in view, and the marketability of products using new refrigerants will be examined from the perspectives of business development and productivity. Specifically, an LCCP evaluation method will be developed for air-conditioning equipment compatible with low-GWP refrigerant mixtures, a life cycle assessment (LCA) will be performed, and the environmental impact per unit of equipment will be evaluated. In addition, future demand for such equipment will be estimated. By integrating LCA results with demand projections, the future nationwide environmental impacts associated with the diffusion of air-conditioning equipment using low-GWP refrigerant mixtures will be assessed. The results will be fed back to the participating research institutions and companies to support the formulation of research strategies. Furthermore, AI-based analytical tools will be developed and applied to Refrigeration A-1, A-2, B-1, C-1, D-1, and D-2 and Equipment A-1, A-2, A-3, B-1, C-1, C-2, and C-3, thereby contributing to more efficient research and development.

1.2 Project Content and Outcomes

1.2.1 Project Content

The research and development items in “Characterization of Low-GWP Refrigerant Mixtures” consist of the following seven items.

Refrigeration A-1: Acquisition of thermophysical property data for low-GWP refrigerant mixtures and selection of candidate refrigerants

Refrigeration A-2: Acquisition of speed-of-sound data for low-GWP refrigerant mixtures

Refrigeration B-1: Development of equations of state and mixture models for low-GWP refrigerant mixtures

Refrigeration C-1: Evaluation of safety characteristics contributing to the selection of low-GWP refrigerant mixtures

Refrigeration D-1: Evaluation of cycle characteristics of low-GWP refrigerant mixtures and performance evaluation using a refrigeration-cycle model test apparatus

Refrigeration D-2: Analysis of losses within cycle components for low-GWP refrigerant mixtures

Refrigeration E-1: Development of LCCP evaluation methods and AI analysis for air-conditioning equipment compatible with low-GWP refrigerant mixtures

To promote the research and development activities, committees comprising external experts will convene several times

each year to facilitate continued technical discussion. The results obtained will also be presented in a timely manner at domestic academic societies, international conferences, and NEDO special lecture events, thereby supporting broad dissemination of the project outcomes.

In implementing the research and development items from Refrigeration A-1, A-2, B-1, C-1, D-1, D-2, and E-1, the project will collaborate not only with institutions participating in the sub-item “Evaluation of Thermophysical Properties, Safety, and Environmental Impacts of Low-GWP Refrigerant Mixtures; Development of Elemental Technologies for Compatible Equipment; and Performance Evaluation of Systems,” but also with other commissioned and subsidized project participants, the Japan Refrigeration and Air Conditioning Industry Association, and relevant domestic and international stakeholders. Through these collaborations, the project will take the necessary measures to maximize its outcomes.

1.2.2 Coordination with Other Project Plans

This research and development item, “Characterization of Low-GWP Refrigerant Mixtures,” corresponds to Refrigeration A-1, A-2, B-1, C-1, D-1, D-2, and E-1 in Figure 1. Thermophysical property data, equations of state and mixture models, flammability data, and other information on refrigerant mixtures narrowed down through “selection of candidate refrigerant mixtures” (Refrigeration A-1 and A-2) and “performance evaluation of refrigerant mixtures” (Refrigeration B-1 and C-1) will be used to develop advanced heat exchangers, compressors, and refrigeration oils under “evaluation of component equipment” (Equipment A-1, A-2, A-3, B-1, C-1, C-2, and C-3). In the integrated refrigeration-cycle performance evaluation under “system performance evaluation” (D-1 and D-2), cycle evaluation will be conducted by combining the data obtained in Refrigeration A-1, A-2, B-1, and C-1 with the applicable equipment developed in Equipment A-1, A-2, A-3, B-1, C-1, C-2, and C-3. Furthermore, a series of datasets obtained through Refrigeration A-1, A-2, B-1, C-1, D-1, and D-2 that contribute to environmental impact assessment and related analyses will be provided to “environmental impact assessment” (Refrigeration E-1).

1.2.3 Contribution to International Standards and Standardization

As outcomes of the above initiatives, by the end of FY2025, one or more mixture models will be made publicly available through REFPROP, and the registration of the released mixture models will be proposed to the ISO 17584 revision committee. In addition, for the flammability of candidate refrigerant mixtures, at least one set of data sufficient to support registration applications to ASHRAE Standard 34 and ISO 817 will be obtained. Furthermore, by the end of FY2027, three or more mixture models will be made publicly available through REFPROP.

2. Acquisition of Thermophysical Property Data for Low-GWP Refrigerant Mixtures and Narrowing Down of Candidate Refrigerants (Kyushu University)

2.1 Initial Selection of Candidate Refrigerants

The search for next-generation refrigerants begins with screening multiple candidates from a broad range of substances. The objective of this project is defined based on Japan's obligations under the Kigali Amendment to the Montreal Protocol, which require an 85% reduction in the production and consumption of HFCs relative to the baseline by 2036, and the national commitment to achieve carbon neutrality by 2050. Under these conditions, next-generation green refrigerants should be proposed while assigning the highest priority to minimizing the GWP. Therefore, appropriate selection of screening criteria is critical to the progress of the entire project, particularly given the limited time available for development and implementation.

Refrigerants used in refrigeration cycles for residential air conditioners, refrigerators, and related equipment transfer heat through phase changes during evaporation and condensation. Consequently, they must not only exist as fluids but also undergo phase change within temperature ranges appropriate for the equipment in which they are used. Therefore, refrigerant applications cover a wide range of temperature levels, from medical and cryogenic refrigeration equipment operating at approximately $-100\text{ }^{\circ}\text{C}$ to refrigerators and air conditioners operating near room temperature, as well as heat-pump systems that utilize medium- and high-temperature waste heat for energy conservation. Refrigerants suitable for each temperature range are required. Because most currently used refrigerants are high-GWP substances, replacing them with low-GWP alternatives is also essential. Under these conditions, fundamental thermophysical property information, including normal boiling points and critical constants, is used for initial screening.

In addition, safety has become a central issue in the evaluation of candidate refrigerants. Although the term "safety" is used broadly, the relevant evaluation criteria include flammability, toxicity, and self-decomposition reactions, and candidate refrigerants must be acceptable from both equipment-safety and human-safety perspectives. Additionally, note that safety evaluation is addressed in detail by other research groups within the overall project.

Considering these, this study used the results reported by McLinden et al. (2017, 2020) as reliable reference information for the first-stage screening of refrigerants. McLinden et al., researchers at the National Institute of Standards and Technology (NIST), specialize in thermophysical properties and are internationally recognized experts in refrigerant property research. Their studies have been published in peer-reviewed journals and have received an award from the International Institute of Refrigeration, indicating their high reliability. In addition, they develop and maintain REFPROP (Lemmon et al., 2018), which is widely considered the international standard database for refrigerant thermophysical properties, and have exchanged refrigerant-property information with Japanese researchers involved in this study for many years. They also operate a system for collecting highly accurate and reliable thermophysical property data from published literature through direct links to underlying databases. Based on their screening, 29 substances were initially selected. Referring to those results and considering accumulated experimental property data and experience among refrigerant-property researchers in Japan, including our group, we conducted a second-stage screening and selected the following 13 low-GWP refrigerants as candidates for room air conditioners.

(1) Hydrofluoroolefin (HFO) refrigerants (HFOs):

R-1132a, HFO-1123, R-1132(E), R-1234yf, R-1234ze(E), HFO-1243zf

(2) HFC refrigerants (HFCs):

R-32, R-152a

(3) Hydrocarbons (HCs):

R-290, R-1270, RE-170

(4) Others:

R-131I(CF₃I), R-744(CO₂)

Considering thermodynamic properties, safety, economic feasibility, and performance from multiple perspectives, no single-component substance can presently be identified as an optimal next-generation refrigerant candidate. Accordingly, all 13 refrigerants listed above were considered potential components of refrigerant mixtures.

Table 2.1-1 Thermophysical properties of HFO-1123 and R-1132(E)

	R-32	R-410A	HFO-1123	R-1132(E)
M (kg·kmol ⁻¹)	52.024	72.585	82.025	64.035
T_b (K)	221.50	221.75	211.90	220.50
T_c (K)	351.26	344.49	331.73	348.82
P_c (kPa)	5782	4901	4549	5174
ρ_c (kg·m ⁻³)	424	459	504	435
P_s at 298.15 K	1690	1657	2123	1657
GWP (AR4)	675	2088	0.0054	0.0056
ASHRAE safety code	A2L	A1	B2	B2 (A2) *

(*) As of January 2026, it is classified as B2 under ASHRAE standards but as A2 under ISO 817.

Among these 13 refrigerants, HFO-1123 and R-1132(E) are domestically developed refrigerants that were advanced in previous NEDO projects. Table 2.1-1 summarizes representative thermophysical property data for HFO-1123 and R-1132(E), together with corresponding data for R-410A and R-32, which are currently the dominant refrigerants for room air conditioners. HFO-1123 (CF₂=CHF, trifluoroethene; CAS No. 359-11-5) is an HFO refrigerant with a normal boiling point of 221.90 K (= -61.25 °C), which falls within the temperature range suitable for air-conditioning refrigerants, and its thermophysical properties are relatively similar to those of R-410A. R-1132(E) (CHF=CHF(E), trans-1,2-difluoroethene; CAS No. 1630-78-0) has a normal boiling point of 220.50 K (= -52.65 °C), and both its normal boiling point and critical parameters are close to those of R-32. In addition, the saturated vapor pressure of R-1132(E) at 298.15 K is nearly identical to that of R-32. Because both are ethylene-based HFO refrigerants, their GWP values are 1 or less, satisfying the highest-priority condition of this study. From a thermodynamic perspective, they could potentially be used as drop-in refrigerants under the temperature and pressure conditions of currently used room air conditioners. However, both refrigerants raise concerns regarding self-decomposition reactions, and manufacturers developing them consider their use as single-component refrigerants to be difficult. Therefore, binary, ternary, or higher-order refrigerant mixtures containing these HFO refrigerants must be considered.

Therefore, the initial objective of this project was to narrow down multiple candidate next-generation green refrigerants for room air conditioners by examining binary and ternary refrigerant mixtures containing either HFO-1123 or R-1132(E) as the first-component. In this screening, the minimum numerical criterion for a “low” GWP was set at 150 or less, consistent with the current F-gas regulation, whereas mixtures with GWP values as close to 1 as possible were treated as the preferred candidates. Because application in indoor room air conditioners is assumed, human safety was also established as an essential screening condition.

After the first-component refrigerant has been selected, low-GWP refrigerants must be identified as candidates for the second and third components of the refrigerant mixture. The GWP of these candidate refrigerants should be as low as possible, making HFO refrigerants strong candidates. Among available HFOs, R-1234yf and R-1234ze(E), which are already commercially available, are expected to have high priority. Among HFCs, R-32 (GWP = 675) and R-152a (GWP = 138), which have relatively low GWP values, were also considered priority candidates. In addition, despite remaining safety concerns, natural refrigerants such as propane (R-290) and carbon dioxide (R-744), which are being examined as next-generation refrigerants in Europe and Asia, were included as candidate components. Subsequently, thermodynamic property measurements were conducted for selected combinations of these refrigerants.

The refrigerant mixtures and component compositions measured by our group as of March 2026 are summarized in Table 2.1-2 for binary mixtures and in Table 2.1-3 for ternary mixtures. Measurements of additional refrigerant mixture combinations not listed in these tables are ongoing.

Table 2.1-2 Binary refrigerant mixtures measured at Kyushu University (as of March 2026).

binary mixture	Composition [mass%]	PvT	Saturated density	critical point	critical locus	VLE
R-1132(E)/1234yf	23/77 (R-474A)	✓	N/A	N/A	✓	✓
	30/70	✓	✓	✓		
	50/50	✓	✓	✓		
	70/30	✓	✓	✓		
R-1132(E)/32	20/80	✓	✓	✓	✓	✓
	50/50	✓	✓	✓		
	80/20	✓	✓	✓		
R-32/1234yf	7/93	✓	N/A	N/A	✓	✓
	10/90	N/A	✓	✓		
	20/80	✓	✓	✓		
	21.5/78.5 (R454C)	✓	N/A	N/A		
	43/57	✓	N/A	N/A		
	50/50	✓	✓	✓		
HFO-1123/1234yf	30/70	✓	✓	✓	✓	✓
	50/50	✓	✓	✓		
HFO-1123/32	40/60	✓	✓	✓	✓	✓
	60/40	✓	✓	✓		
R-1132(E)/290	60/40	✓	✓	✓	✓	✓
	80/20	✓	N/A	N/A		
HFO-1123/290	65/35	✓	✓	✓	✓	✓
	80/20	✓	✓	✓		
R-1132(E)/744	90/10	✓	N/A	N/A	N/A	N/A
	60/40	✓	N/A	N/A		

(*) A check mark indicates that the measurement has been completed, whereas “N/A” indicates that the measurement has not yet been conducted.

Table 2.1-3 Ternary refrigerant mixtures measured at Kyushu University (as of March 2026)

Ternary mixture	Composition [mass%]	PvT	Saturated density	Critical point	Critical locus	VLE
R-32/1132(E)/1234yf	10/30/60	✓	✓	✓	N/A	✓
	21.5/28.0/50.5 (R-479A)	✓	✓	✓		
	22.0/19.5/58.5	✓	✓	✓		
	44/23/33 (R-479B)	✓	N/A	N/A		
R-32/1123/1234yf	10/40/50	✓	✓	✓	N/A	✓
	21.5/40.0/38.5	✓	✓	✓		

2.2 Apparatuses to Measure Thermodynamic Properties

2.2.1 *PVT*-Property Measurement Apparatus

Figure 2.2-1 shows a schematic of the *PVT*-property measurement apparatus used in this study. Details of the apparatus and measurement procedure have been reported previously (Kobayashi et al., 2011; Higashi et al., 2015). A refrigerant-mixture sample prepared in advance at the target composition and density is charged into a stainless-steel pressure vessel (A), which constitutes the main part of the apparatus. The vessel is directly connected to a high-precision pressure transducer (B) and immersed in a liquid thermostatic bath containing silicone oil as the heat-transfer medium. The bath temperature is controlled at the target temperature with fluctuations maintained within ± 3 mK. When thermal equilibrium is reached, additional time is allowed until the pressure stabilizes; the pressure recorded after the variation decreases to within ± 1 kPa is used as the measured pressure. The *PVT* properties, representing the relationship among pressure, density (the reciprocal of specific volume), and temperature, are then determined from the charged mass of the sample and thermally corrected internal volume of the pressure vessel. Temperature is measured using a $25\ \Omega$ standard platinum resistance thermometer (D) and an AC thermometer bridge (E) and is calculated according to the International Temperature Scale of 1990 (ITS-90). Pressure is determined from the calibrated reading of the high-precision pressure transducer (B) with zero-point correction under a vacuum. Although measurement uncertainty varies slightly depending on refrigerant type and temperature range, the uncertainties were estimated to be within 5 mK for temperature, 1 kPa for pressure, and 0.15% for density. The composition of the refrigerant mixture was calculated from the mass ratio of the charged components using an electronic balance with a resolution of 1 mg, and its uncertainty was estimated to be within 0.0005 in mass fraction.

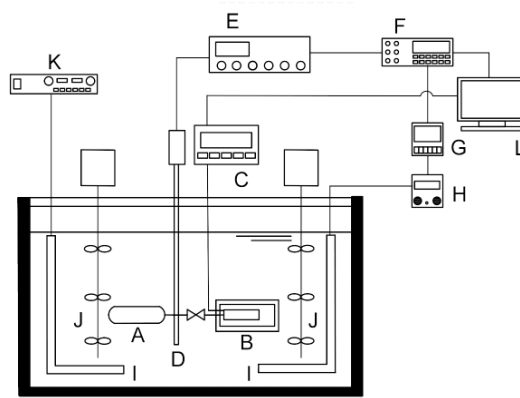


Figure 2.2-1 *PVT* measurement apparatus

A: Pressure vessel, B: Pressure transducer, C: Pressure indicator,
D: 25 Ω Platinum resistance thermometer, E: AC Thermometer bridge,
F: Digital multi-meter, G: PID controller, H: Voltage converter,
I: Heater, J: Stirrer, K: DC Power supply, L: Computer

2.2.2 Measurement Apparatus for Saturated Density and Critical Point

Figure 2.2-2 shows a schematic of the apparatus used to measure saturated densities and critical points. The apparatus determines saturated densities and critical constants through a direct visual observation of meniscus disappearance (Okazaki et al., 1983; Higashi, 1994). It consists of three cylindrical pressure vessels: a sample supply vessel (A), used for initial sample charging; an expansion vessel (B), used to adjust the density inside the system; and an optical cell (C), equipped with a Pyrex viewing window for observing the meniscus. For measurements of refrigerant mixtures, these vessels are mounted on a rocking stage that enables internal mixing. The combination of the three vessels allows up to eight measurement points to be obtained from a single sample charge while maintaining density uncertainty within the target range. This method is particularly effective for refrigerant mixtures, for which sample preparation is difficult, and for newly developed refrigerants for which only limited sample quantities are available. Temperature is measured using a 25 Ω standard platinum resistance thermometer (D), and density is calculated from the charged sample mass and the internal volumes of the three pressure vessels. Because this apparatus is not equipped with a pressure measurement system, the critical pressure is measured using the *PVT* apparatus shown in Figure 2.2-1. The measurement accuracy is within 10 mK for temperature and 0.15%–0.2% for density.

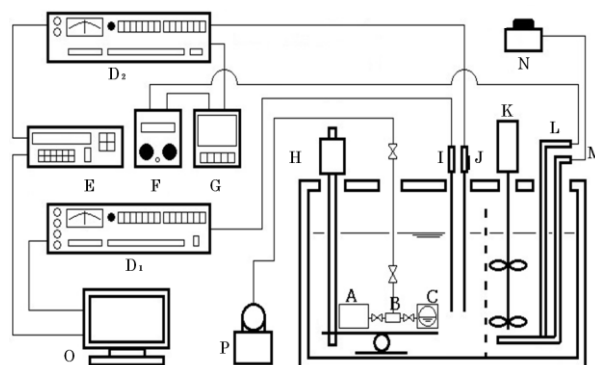


Figure 2.2-2 Saturated densities and critical point measurement apparatus

A: Supplying vessel, B: Expansion vessel, C: Optical cell,
D₁, D₂: Thermometer bridge, E: Digital multi-meter, F: Voltage converter,
G: PID Controller, H: Rocking stage, I, J: 25 Ω Platinum resistance thermometer,
K: Stirrer, L: 300 W Heater, M: 1.5 kW Heater, N: Voltage transformer,
O: Computer, P: Vacuum pump

2.2.3 Vapor-Liquid Equilibrium Property Measurement Apparatus

In this study, vapor–liquid equilibrium was measured using the circulation method (Yamada et al., 2020). The sample cell (A) has an internal volume of approximately 163 cm³ and is equipped with an observation window that enables visual confirmation of the gas–liquid interface. A quartz-crystal precision pressure sensor (B) is directly connected to the sample cell to enable direct measurement of the internal pressure. After the target temperature is stabilized using heaters (H and I), a thermostatic bath (W), and PID controllers (F and J), the temperature is measured using a 100 Ω standard platinum resistance thermometer (E). Vapor- and liquid-phase samples are circulated and mixed inside the sample cell using a circulation pump (V), collected separately from each phase, and analyzed for composition using a thermal conductivity detector (TCD) gas chromatograph (Q). The measurement uncertainties for temperature, pressure, and composition were estimated to be 10 mK, 2 kPa, and 0.0005 in mass fraction, respectively.

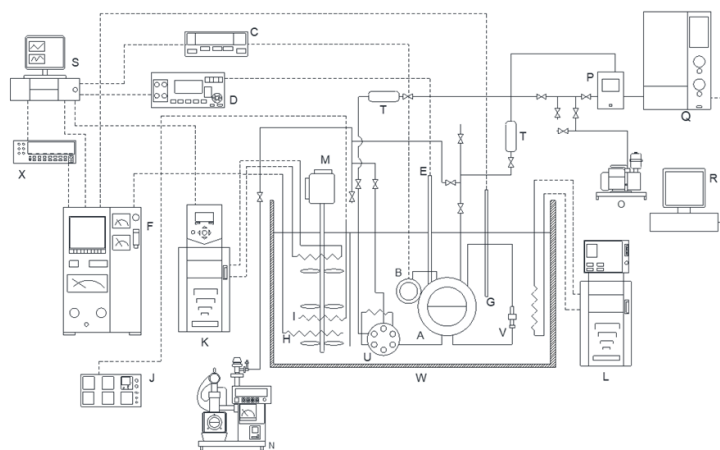


Figure 2.2-3 Vapor–liquid equilibrium measurement apparatus

A: Equilibrium cell; B: Pressure transducer; C: Digital pressure indicator;
D: Thermometer bridge; E: 100 Ω standard platinum resistance thermometer;
F: Temperature controller; G: 100 Ω platinum resistance thermometer; H: Main heater;
I: Sub heater; J: Temperature controller; K, L: Circulation bath; M: Stirrer;
N, O: molecular pump; P: Auto gas sampler; Q: Gas chromatograph; R, S: Computers;
T: Sample cylinder; U: Hexagon valve; V: Magnetic circulation pump
W: Thermostatic bath; X: AC/DC converter

2.3 Measurement Results

2.3.1 PVT_x Measurements of R-32/1234yf

Among the ternary refrigerant mixtures that have already received ASHRAE R numbers, the R-32/1234yf system is the most widely used binary mixture. This binary system is registered as part of the R-454 series, and equipment using R-454B (68.9 mass% R-32) and R-454C (21.5 mass% R-32) has begun to enter the market. However, thermophysical property data for R-32/1234yf mixtures remain limited, and additional data are required. In this study, in addition to the PVT_x data previously reported by the present authors (Kobayashi et al., 2011), PVT_x measurements were conducted. Subsequently, two sets of mixing parameters were evaluated: the parameters for the R-32/1234yf system used in REFPROP 10.0 (Akasaka model; Akasaka, 2013) and those developed by incorporating recent experimental data (Bell model; Bell, 2023). The following section compares the measured PVT_x data with calculations obtained using these two parameter sets. Numerical data are omitted from this report because the timing of their publication must be carefully considered; the data will be published sequentially in English-language journals when appropriate.

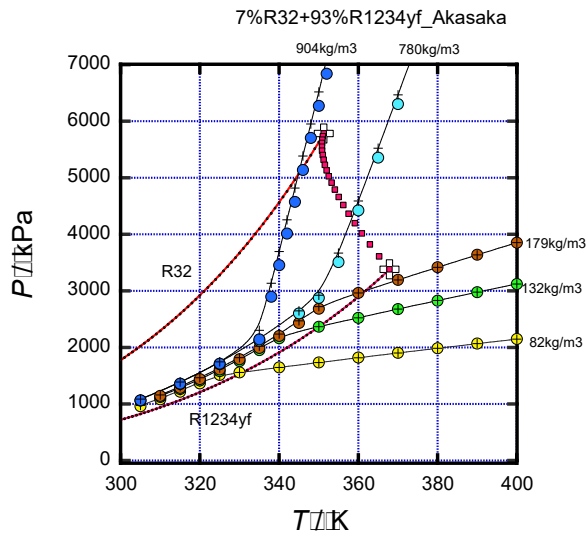


Figure 2.3-1 PVT_x data plots for R-32/1234yf (7/93). The line is drawn using the Akasaka mixing model.

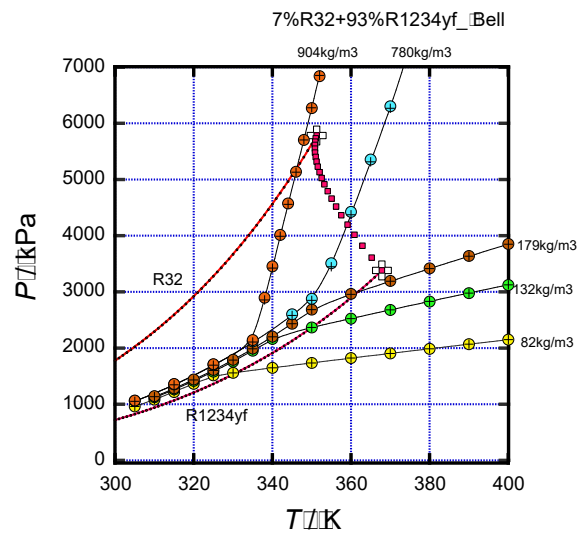


Figure 2.3-2 PVT_x data plots for R-32/1234yf (7/93). The line is drawn using the Bell mixing model.

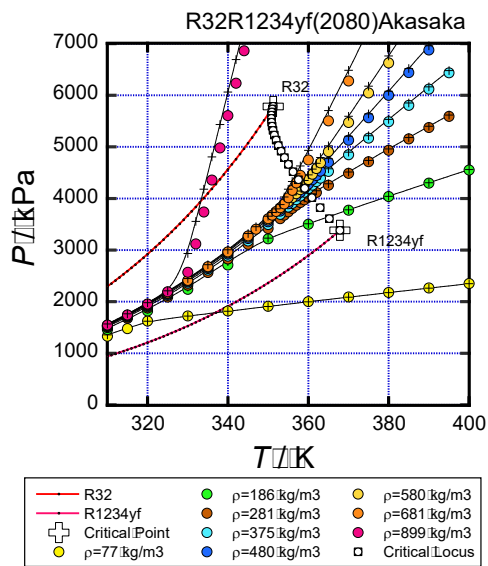


Figure 2.3-3 PVT_x data plots for R-32/1234yf (20/80). The line is drawn using the Akasaka mixing model.

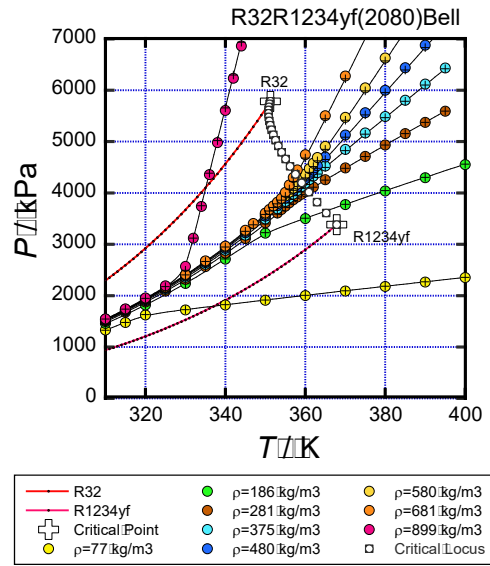


Figure 2.3-4 PVT_x data plots for R-32/1234yf (20/80). The line is drawn using the Bell mixing model.

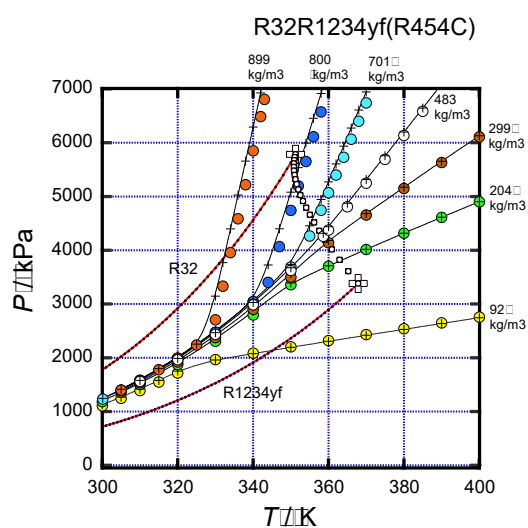


Figure 2.3-5 PVT_x data plots for R-32/1234yf (21.5/78.5). The line is drawn using the Akasaka mixing model.

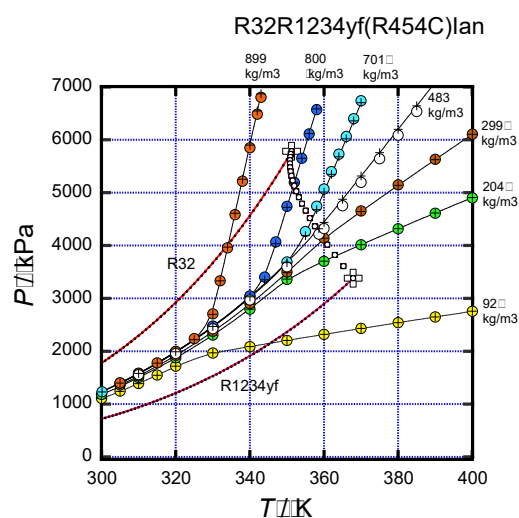


Figure 2.3-6 PVT_x data plots for R-32/1234yf (21.5/78.5). The line is drawn using the Bell mixing model.

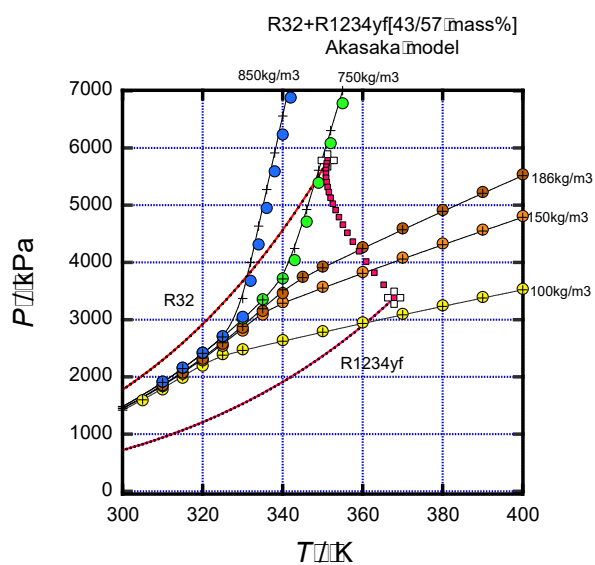


Figure 2.3-7 PVT_x data plots for R-32/1234yf (43/57). The line is drawn using the Akasaka mixing model.

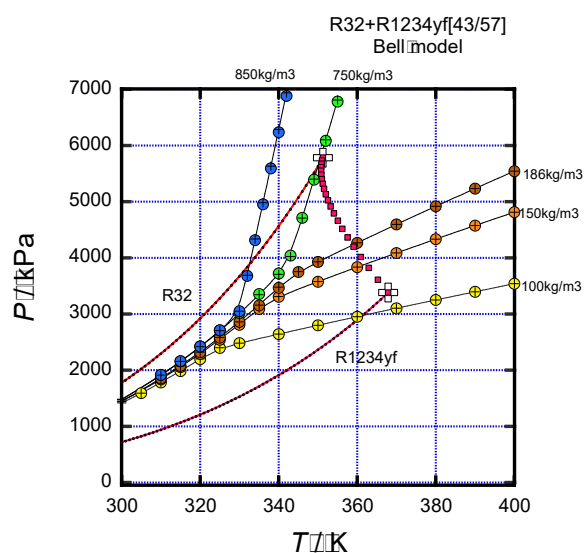


Figure 2.3-8 PVT_x data plots for R-32/1234yf (43/57). The line is drawn using the Bell mixing model.

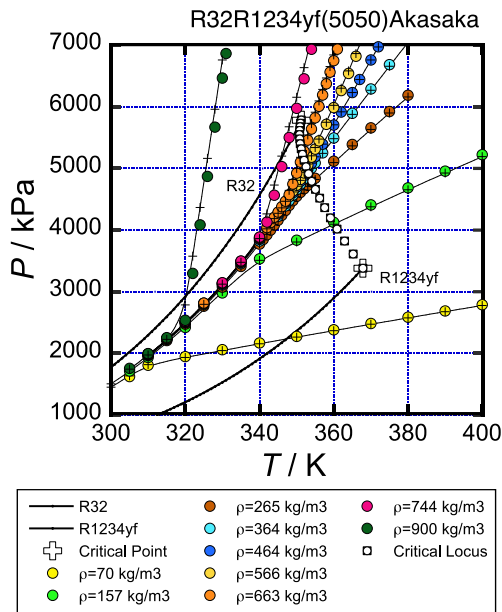


Figure 2.3-9 PVT_x data plots for R-32/1234yf (50/50). The line is drawn using the Akasaka mixing model.

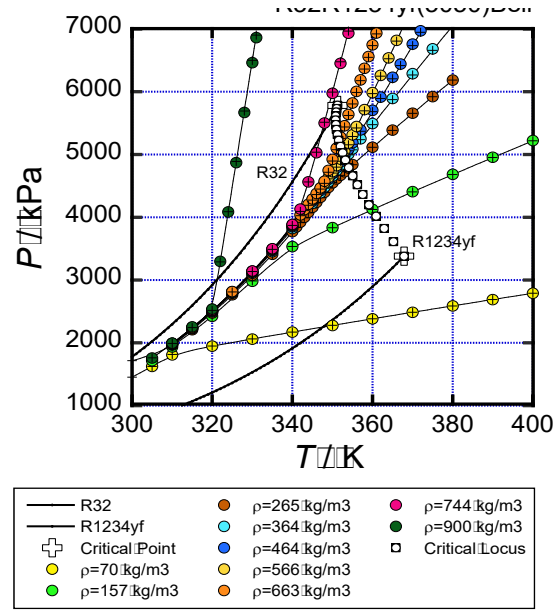


Figure 2.3-10 PVT_x data plots for R-32/1234yf (50/50). The line is drawn using the Bell mixing model.

Figures 2.3-1 to 2.3-10 compare the present PVT_x measurement results for five compositions of R-32/1234yf (7, 20, 21.5, 43, and 50 mass% R-32) with calculations based on the Akasaka mixing model (Akasaka, 2013), which is implemented in the original version of REFPROP 10.0 (Lemmon et al., 2018), and with calculations based on the Bell mixing model (Bell, 2023). In these figures, circles denote the present experimental data, whereas plus symbols and the connecting lines denote REFPROP 10.0 calculation results. Agreement between the circles and isochoric lines indicates good consistency between the experimental and calculated results.

For R-32/1234yf calculated using the original 2018 release of REFPROP 10.0 with the Akasaka mixing model (Akasaka, 2013), the calculation accuracy in the superheated vapor region (low-density region) is generally satisfactory. However, in the compressed-liquid (high-density) region, the deviation between experimental and calculated values increases with increasing density. The experimental densities in the compressed-liquid region also tend to be lower than the calculated densities, raising concerns regarding possible discrepancies in saturated-liquid-density (bubble-point-density) calculations. In contrast, the Bell mixing model (Bell, 2023), which was developed using recent experimental data, reproduces the experimental results well over a wide density range, except near the critical point. These results indicate that the decisive factor is not necessarily the equation-of-state framework itself, but rather whether reliable measured data are incorporated into the parameter fitting. Note that REFPROP 10.0 displays a warning message before calculations for refrigerant mixtures that are not yet fully characterized.

The pressure and density deviations corresponding to Figures 2.3-1 to 2.3-10 are summarized in Tables 2.3-1 to 2.3-5. Overall, the results confirm that the calculation accuracy for the R-32/1234yf mixture can be substantially improved by using the Bell mixing model, which represents the more recent parameter set. Therefore, when REFPROP 10.0 is used to calculate the properties of R-32/1234yf and ternary refrigerant mixtures containing R-32/1234yf, use of the Bell mixing model is strongly recommended.

Table 2.3-1 Summary of the pressure and density deviations for R-32/1234yf (7/93) between present experimental data and REFPROP 10.0 calculations. Two mixing models are adopted in REFPROP 10.0: Akasaka and Bell mixing models.

R-32/1234yf (7/93): Akasaka mixing model				R-32/1234yf (7/93): Bell mixing model			
	All data	1-phase data	1-phase data		All data	1-phase data	1-phase data
ρ (kg/m ³)	Δ PAAD (%)	Δ PAAD (%)	Δ rAAD (%)	ρ (kg/m ³)	Δ PAAD (%)	Δ PAAD (%)	Δ rAAD (%)
82	0.52	0.15	0.20	82	0.06	0.01	0.02
132	0.81	0.04	0.06	132	0.16	0.08	0.12
179	1.00	0.04	0.07	179	0.24	0.26	0.30
780	2.50	3.36	1.12	780	0.95	1.09	0.32
904	4.49	5.12	0.56	904	0.71	0.47	0.04
Average (%)	1.86	1.74	0.40	Average (%)	0.42	0.38	0.16

Table 2.3-2 Summary of the pressure and density deviations for R-32/1234yf (20/80) between present experimental data and REFPROP 10.0 calculations. Two mixing models are adopted in REFPROP 10.0: Akasaka and Bell mixing models.

R-32/1234yf (20/80): Akasaka mixing model				R-32/1234yf (20/80): Bell mixing model			
	All data	1-phase data	1-phase data		All data	1-phase data	1-phase data
ρ (kg/m ³)	Δ PAAD (%)	Δ PAAD (%)	$\Delta\rho$ AAD (%)	ρ (kg/m ³)	Δ PAAD (%)	Δ PAAD (%)	$\Delta\rho$ AAD (%)
77	0.53	0.17	0.22	77	0.20	0.22	0.29
186	0.93	0.22	0.45	186	0.21	0.20	0.41
281	1.21	0.64	2.14	281	0.35	0.08	0.31
375	1.33	0.80	2.49	375	0.54	0.38	1.15
480	1.42	1.37	8.41	480	0.74	0.88	4.89
580	1.64	2.10	6.30	580	0.89	1.21	2.93
681	2.22	3.60	3.88	681	0.88	1.39	1.15
899	6.51	9.19	0.97	899	0.78	0.67	0.09
Average (%)	1.97	2.26	3.11	Average (%)	0.57	0.63	1.40

Table 2.3-3 Summary of the pressure and density deviations for R-32/1234yf (21.5/78.5) between present experimental data and REFPROP 10.0 calculations. Two mixing models are adopted in REFPROP 10.0: Akasaka and Bell mixing models.

R-32/1234yf (21.5/78.5): Akasaka mixing model				R-32/1234yf (21.5/78.5): Bell mixing model			
	All data	1-phase data	1-phase data		All data	1-phase data	1-phase data
ρ (kg/m ³)	Δ PAAD (%)	Δ PAAD (%)	$\Delta\rho$ AAD (%)	ρ (kg/m ³)	Δ PAAD (%)	Δ PAAD (%)	$\Delta\rho$ AAD (%)
92	0.99	0.45	0.62	92	0.16	0.03	0.04
204	0.95	0.06	0.12	204	0.14	0.06	0.12
299	1.11	0.44	1.11	299	0.25	0.14	0.39
701	2.53	3.60	2.62	701	0.79	1.03	0.65
800	4.21	6.43	1.76	800	0.42	0.47	0.10
899	5.88	8.96	0.97	899	0.52	0.58	0.06
Average (%)	3.43	4.86	1.62	Average (%)	0.38	0.39	0.23

Table 2.3-4 Summary of the pressure and density deviations for R-32/1234yf (43/57) between present experimental data and REFPROP 10.0 calculations. Two mixing models are adopted in REFPROP 10.0: Akasaka and Bell mixing models.

R-32/1234yf (43/57): Akasaka mixing model				R-32/1234yf (43/57): Bell mixing model			
	All data	1-phase data	1-phase data		All data	1-phase data	1-phase data
ρ (kg/m ³)	Δ PAAD (%)	Δ PAAD (%)	$\Delta\rho$ AAD (%)	ρ (kg/m ³)	Δ PAAD (%)	Δ PAAD (%)	$\Delta\rho$ AAD (%)
100	0.75	0.64	0.95	100	0.06	0.02	0.04
150	0.73	0.58	0.96	150	0.11	0.03	0.06
186	0.60	0.49	0.97	186	0.09	0.05	0.12
750	1.93	3.93	1.51	750	0.28	0.28	0.10
850	4.34	5.98	0.85	850	0.41	0.6	0.08
Average (%)	1.67	2.32	1.05	Average (%)	0.19	0.20	0.08

Table 2.3-5 Summary of the pressure and density deviations for R-32/1234yf (50/50) between present experimental data and REFPROP 10.0 calculations. Two mixing models are adopted in REFPROP 10.0: Akasaka and Bell mixing models.

R-32/1234yf (50/50): Akasaka mixing model				R-32/1234yf (50/50): Bell mixing model			
	All data	1-phase data	1-phase data		All data	1-phase data	1-phase data
ρ (kg/m ³)	Δ PAAD (%)	Δ PAAD (%)	$\Delta\rho$ AAD (%)	ρ (kg/m ³)	Δ PAAD (%)	Δ PAAD (%)	$\Delta\rho$ AAD (%)
70	0.55	0.55	0.71	70	0.05	0.03	0.04
157	0.58	0.68	1.24	157	0.08	0.06	0.11
265	0.31	0.38	1.35	265	0.12	0.04	0.14
364	0.29	0.30	1.13	364	0.26	0.32	1.48
464	0.22	0.05	0.11	464	0.36	0.38	1.66
566	0.52	0.55	1.58	566	0.33	0.36	1.21
663	1.06	1.47	1.40	663	0.32	0.35	0.33
744	2.06	3.03	1.16	744	0.31	0.36	0.13
900	4.52	6.03	0.47	900	0.38	0.41	0.41
Average (%)	1.12	1.45	1.02	Average (%)	0.24	0.26	0.61

2.3.2 PVT_x Measurements of R-1132(E)/1234yf

The ultimate objective of this project is to identify new refrigerant mixtures with GWP values of 10 or less. The GWPs of currently used refrigerant mixtures are calculated by weighting the GWP values of the individual components according to their mass fractions. Consequently, a prerequisite for achieving a blended GWP of 10 or less is that each component refrigerant should itself have a GWP of 10 or less. Under this condition, HFC refrigerants cannot be included as components, and the remaining candidates are mixtures composed of HFO refrigerants or mixtures of HFO refrigerants with low-GWP substances such as hydrocarbons or carbon dioxide. In this study, thermodynamic property measurements were conducted for the binary and ternary systems listed in Tables 2.1-2 and 2.1-3. Owing to space limitations, representative binary and ternary mixtures composed primarily of HFO refrigerants are discussed.

The thermodynamic property results for the R-1132(E)/1234yf system are first presented, beginning with the PVT_x properties. PVT_x measurements were conducted for four compositions: 70, 50, 30, and 23 mass% R-1132(E). The R-1132(E)/1234yf blend with a composition of 23/77 has already been assigned the ASHRAE designation R-474A. The results for these four compositions are shown in Figures 2.3-11 to 2.3-14. In these figures, circles represent the present experimental data, whereas plus symbols and the connecting lines represent REFPROP 10.0 calculation results. Because R-1132(E) is not registered as a pure refrigerant in REFPROP 10.0 (Lemmon et al., 2018), official calculations for this blend are not currently available. The calculations shown here were performed using the equation of state for R-1132(E) and the mixture model for R-1132(E)/1234yf tentatively developed by Kyushu Sangyo University within this project, based in part on the present measurements. Figure 2.3-14 also shows the critical locus, i.e., the composition dependence of the critical point, determined in this study.

The calculation results obtained using the mixture model for R-1132(E)/1234yf developed in this project show relatively good reproducibility because the model parameters were determined using the present measured data. Except near the critical density, density deviations for both superheated vapor and compressed-liquid data remain within 0.5%. Pressure deviations in the compressed-liquid region are somewhat larger; however, this tendency is characteristic of the compressed-liquid region, where accurate evaluation is inherently difficult. These results indicate that, provided that the equations of state for the pure components describe the properties with sufficient accuracy and an experimentally based mixture model is available, REFPROP 10.0 can be expected to achieve a high level of accuracy.

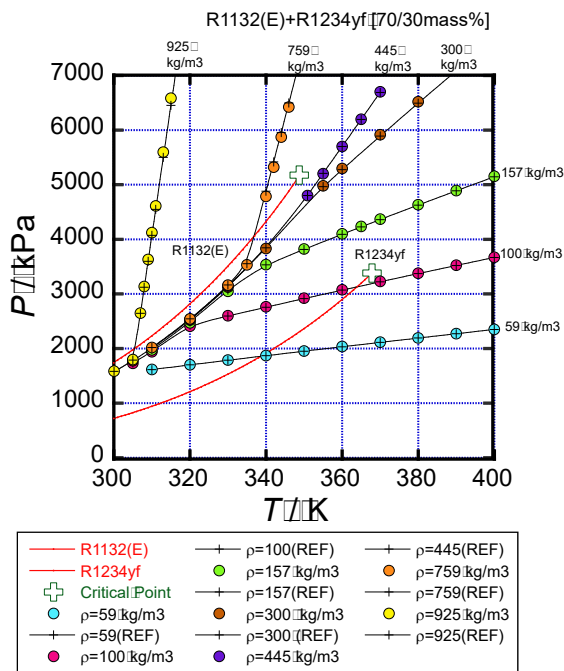


Figure 2.3-11 PVT_x data plots for R-1132(E)/1234yf (70/30).

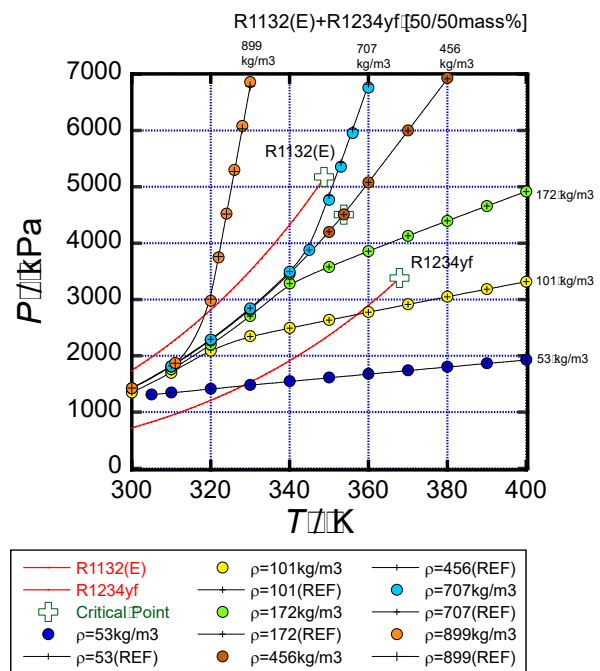


Figure 2.3-12 PVT_x data plots for R-1132(E)/1234yf (50/50).

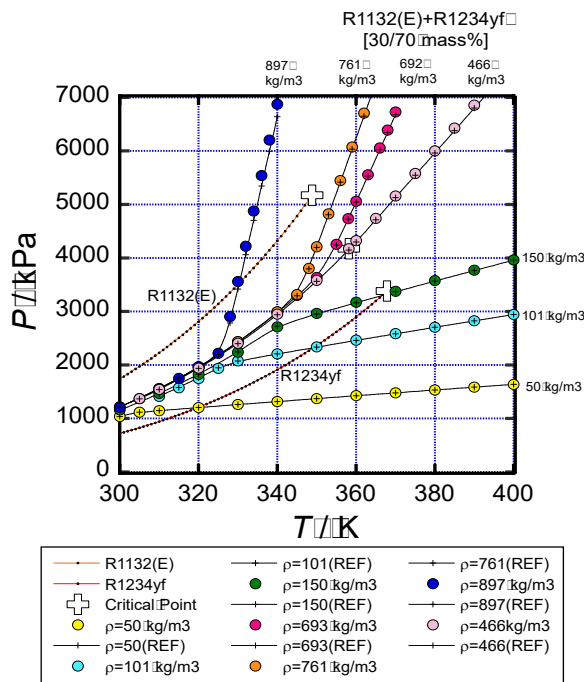


Figure 2.3-13 *PVT* data plots for R-1132(E)/1234yf (30/70).

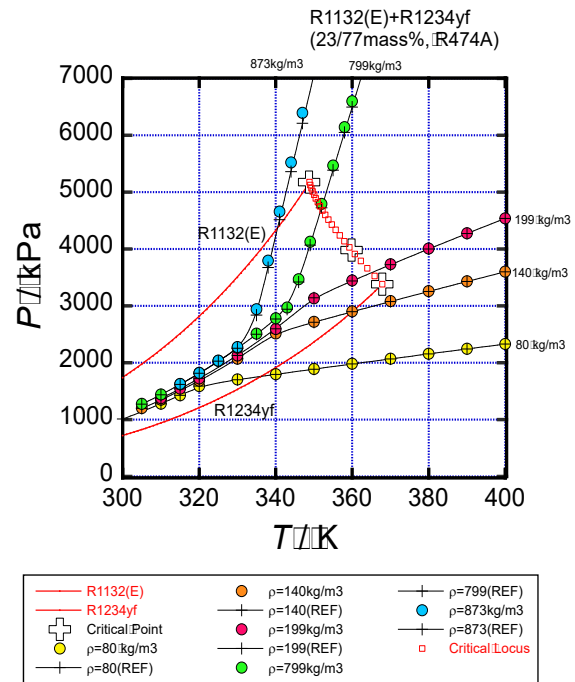


Figure 2.3-14 *PVT* data plots for R-1132(E)/1234yf (23/77) [R-474A].

2.3.3 Measurements of Saturated Density and Critical Points of R-1132(E)/1234yf

Figure 2.3-15 shows the measured saturated densities and critical points of R-1132(E)/1234yf. Measurements were conducted at three compositions—70, 50, and 30 mass% R-1132(E). In addition to saturated-density values under vapor–liquid equilibrium, determined by observing meniscus disappearance, the figure includes saturated-density points slightly away from the critical point. These points were obtained from the transition between two-phase and single-phase regions along isochoric lines in the *PVT_x* measurements. Table 2.3-6 lists the critical temperatures and densities for each composition, determined from the meniscus disappearance position and the intensity of critical opalescence, together with the critical pressures measured using the *PVT* apparatus based on the obtained critical-temperature and critical-density information. Experimental determination of critical constants for refrigerant mixtures is rare worldwide; therefore, these results represent the first experimentally obtained critical-point data for this mixture and constitute part of the limited set of measured critical-point data available for refrigerant mixtures. Table 2.3-6 also provides correlations that reproduce the measured critical constants, and Figures 2.3-16 to 2.3-18 show the corresponding critical loci, indicating the composition dependence of the critical constants.

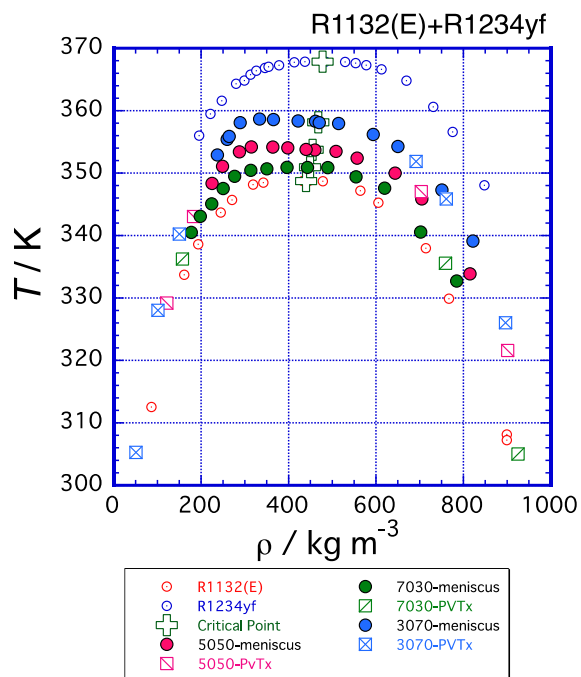


Figure 2.3-15 Experimental data plots of vapor–liquid coexistence curve for R-1132(E)/1234yf in the critical region.

Table 2.3-6 Critical parameters and their correlations proposed for R-1132(E)/1234yf mixtures.

Experimental Data	T_c / K	P_c / kPa	$\rho_c / \text{kg m}^{-3}$	$V_c / \text{cm}^3 \text{mol}^{-1}$
R1234yf	367.85	3382	478	238.6
30mass% R1132(E)	358.13	4172	466	198.3
50mass% R1132(E)	353.73	4510	455	180.3
70mass% R1132(E)	350.89	4800	448	164.6
R1132(E)	348.82	5175	438	146.2

$$T_{cm} = \theta_1 T_{c1} + \theta_2 T_{c2} + 2\theta_1 \theta_2 \Delta_T$$

$$P_{cm} = \theta_1 P_{c1} + \theta_2 P_{c2} + 2\theta_1 \theta_2 \Delta_P \quad \theta_i = \frac{x_i V_{ci}^{2/3}}{\sum x_j V_{cj}^{2/3}}$$

$$V_{cm} = \theta_1 V_{c1} + \theta_2 V_{c2} + 2\theta_1 \theta_2 \Delta_V$$

$$\rho_{cm} = 1000 \frac{M_m}{V_{cm}}$$

For R1132(E)+R1234yf blend

Δ_T	Δ_P	Δ_V
-6.87 K	258 kPa	-13.9 cm³/mol

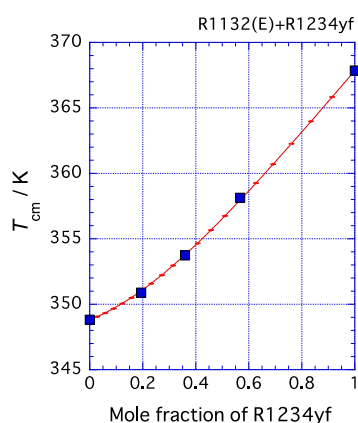


Figure 2.3-16
Composition dependence of critical temperatures for R-1132(E)/1234yf mixtures.

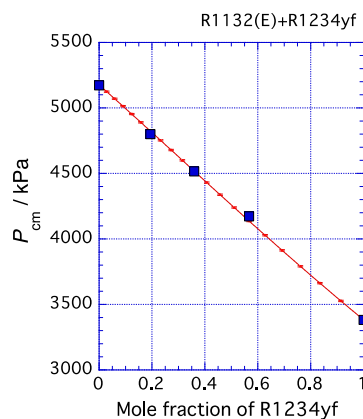


Figure 2.3-17
Composition dependence of critical pressures for R-1132(E)/1234yf mixtures.

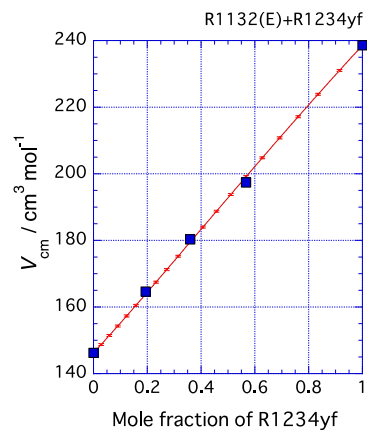


Figure 2.3-18
Composition dependence of critical molar volumes for R-1132(E)/1234yf mixtures.

2.3.4 Vapor-Liquid Equilibrium Property Measurements of R-1132(E)/1234yf

For refrigerant mixtures, vapor–liquid equilibrium properties, which describe the liquid- and vapor-phase compositions in the two-phase region, constitute important thermophysical information in addition to the thermodynamic properties typically considered for single-component refrigerants. The vapor–liquid equilibrium properties of R-1132(E)/1234yf measured in this study are presented as isothermal data on a P - x diagram in Figure 2.3-19. The vapor–liquid equilibrium cell used in this study samples small quantities of refrigerant for gas chromatographic analysis while circulating and stirring the sample. Generally, using a larger sample amount reduces fluctuations in composition and pressure caused by sampling. However, because R-1132(E) has not yet reached plant-scale production, measurements with smaller sample quantities are desirable. Therefore, in this study, refrigerant-mixture samples used in the PVT_x and critical-point measurements were recovered and reused.

For this mixture system, four samples with different compositions were recovered, recharged, and measured from 263.17 to 323.15 K at 10 K intervals. In Figure 2.3-19, the solid and dashed lines represent the boiling-point curve (saturated liquid line) and dew-point curve (saturated vapor line), respectively. These curves were obtained by optimizing the binary interaction parameter k_{ij} in the Peng–Robinson cubic equation of state to 0.026 based on the experimental data. The optimized Peng–Robinson equation reproduces the measured values well, indicating that it is sufficiently applicable to calculating vapor–liquid equilibrium properties for this system.

The thermodynamic state properties of R-1132(E)/1234yf obtained in Sections 2.3.2 to 2.3.4 will be provided to the equation-of-state development group at Kyushu Sangyo University, where mixture parameters will be determined for subsequent implementation in REFPROP. This procedure will be applied to all refrigerant mixtures under consideration, and the resulting data will serve as foundational information for the research activities conducted by all groups in this project.

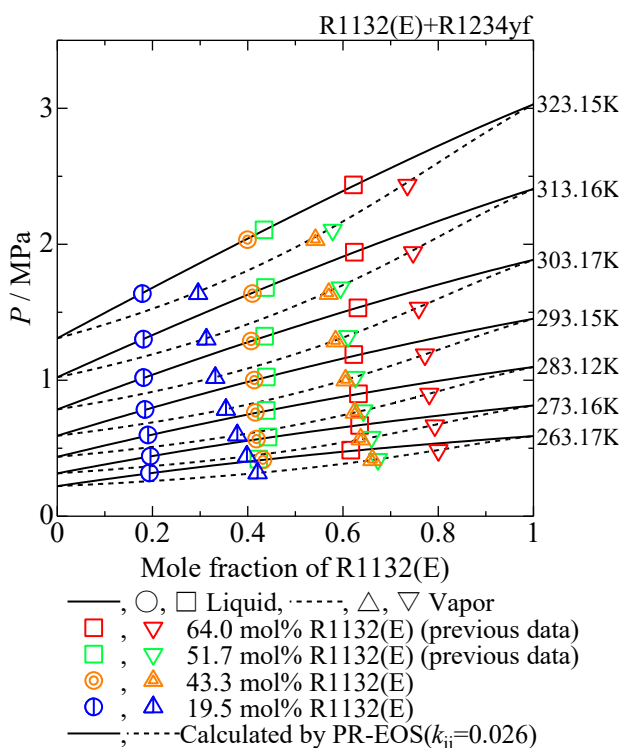


Figure 2.3-19 Vapor–liquid equilibrium for R-1132(E)/1234yf mixtures.

2.3.5 PVT_x Measurements of Ternary Refrigerant Mixtures

For ternary refrigerant mixtures, R-32/1132(E)/1234yf and R-32/1123/1234yf were selected as the initial candidate systems for the reasons described above. In selecting the experimental compositions, priority was given to safety and global-warming mitigation rather than to performance evaluation. The first condition was set as the maximum composition expected not to affect the self-decomposition reactions of R-1132(E) and HFO-1123. The R-32 composition, corresponding to an HFC component, was then determined using the GWP as a criterion. Specifically, the selected compositions included 21.5 mass% R-32, corresponding to a GWP of 150; 10 mass% R-32, corresponding to a GWP of approximately 70, or approximately half of 150; and 44 mass% R-32, corresponding to a GWP of 300, which is twice 150 and was selected from the perspective of prioritizing energy performance. This report presents PVT_x property data for the ternary mixtures shown in Figures 2.3-21 to 2.3-25: R-32/1132(E)/1234yf (21.5/28.0/50.5) [R-479A], R-32/1132(E)/1234yf (44/23/33) [R-479B], R-32/1132(E)/1234yf (10/30/60), and R-32/1123/1234yf (10/40/50), respectively. As noted earlier, both the Akasaka and Bell models are available for the R-32/1234yf binary system; therefore, comparisons are presented to examine the differences between these two models. The agreement between measured data points and REFPROP calculation results, shown by solid lines, provides a qualitative indication of reproducibility, which is reasonable even for ternary systems. With further accumulation of binary-mixture data, we expect that the thermodynamic properties of a wide variety of ternary refrigerant mixtures can be predicted with improved accuracy. However, currently, REFPROP cannot directly incorporate measured data for ternary mixtures into its mixture models; thus, experimental data for ternary mixtures can be used only to evaluate the reliability of calculations. Therefore, future research and development on optimization methods for equations of state and mixture models for multicomponent systems will be increasingly important.

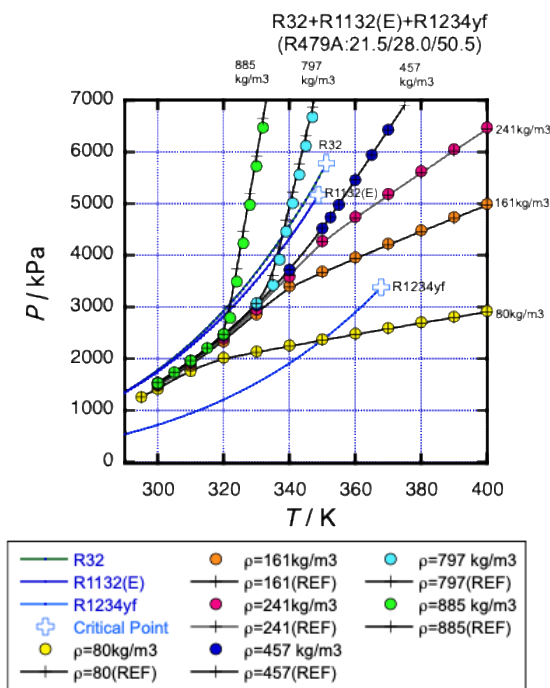


Figure 2.3-20

PVT_x data plots for R-32/1132(E)/1234yf (21.5/28.0/50.5) [R-479A]. The line was calculated using the R-32/1234yf Akasaka mixing model.

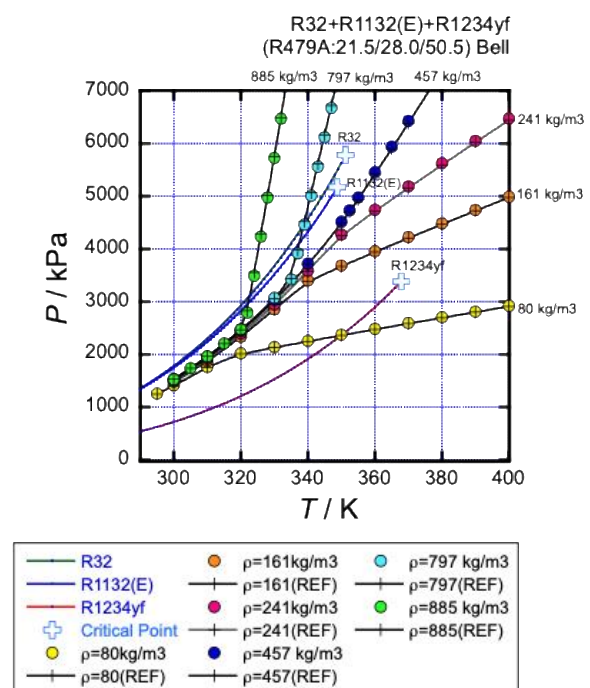


Figure 2.3-21

PVT_x data plots for R-32/1132(E)/1234yf (21.5/28.0/50.5) [R-479A]. The line was calculated using the R-32/1234yf Bell mixing model.

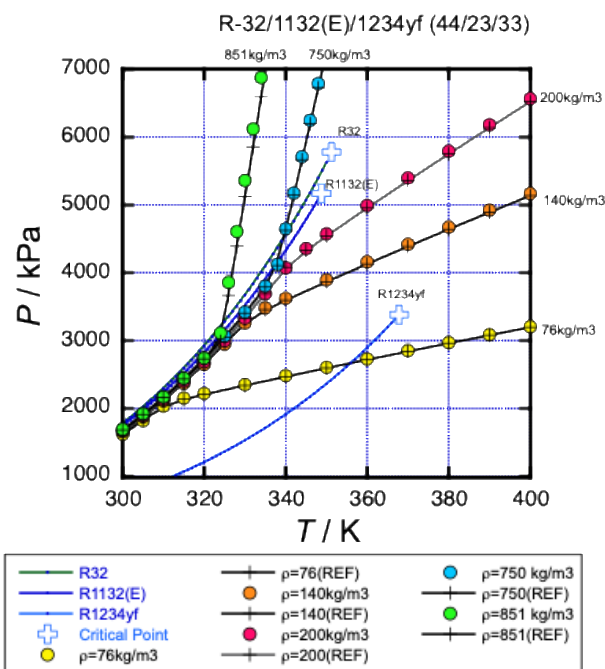


Figure 2.3-22

PVTx data plots for R-32/1132(E)/1234yf (44/23/33) [R-479B].

The line was calculated using the R-32/1234yf Akasaka mixing model.

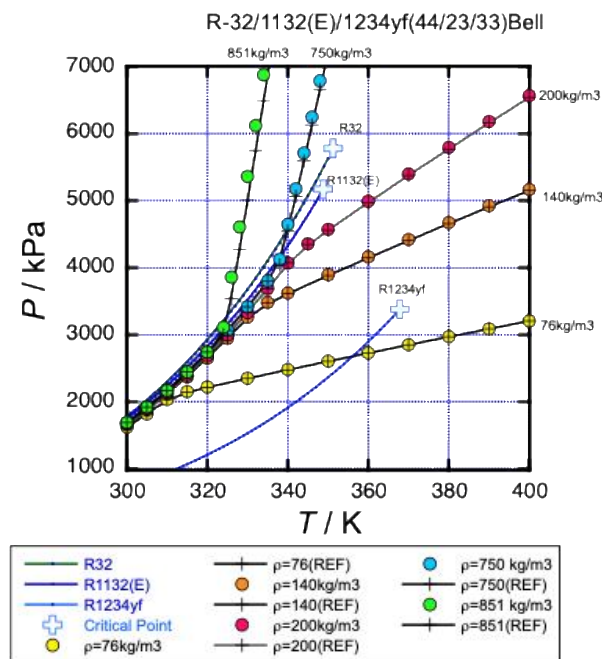


Figure 2.3-23

PVTx data plots for R-32/1132(E)/1234yf (44/23/33) [R-479B].

The line was calculated using the R-32/1234yf Bell mixing model.

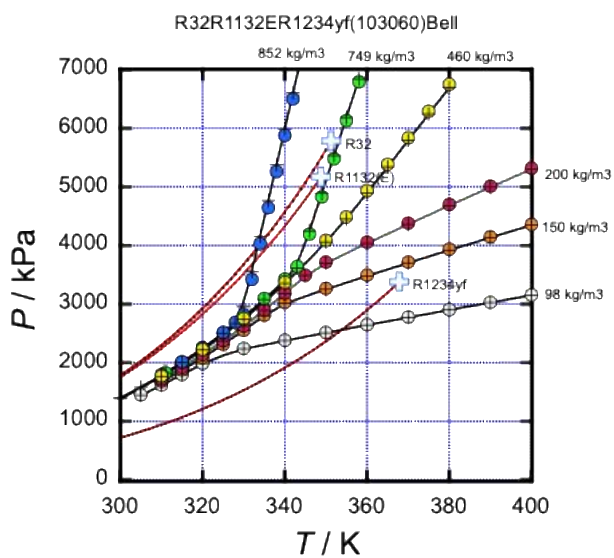


Figure 2.3-24

PVTx data plots for R-32/1132(E)/1234yf (10/30/60). The line was calculated using the R-32/1234yf Bell mixing model.

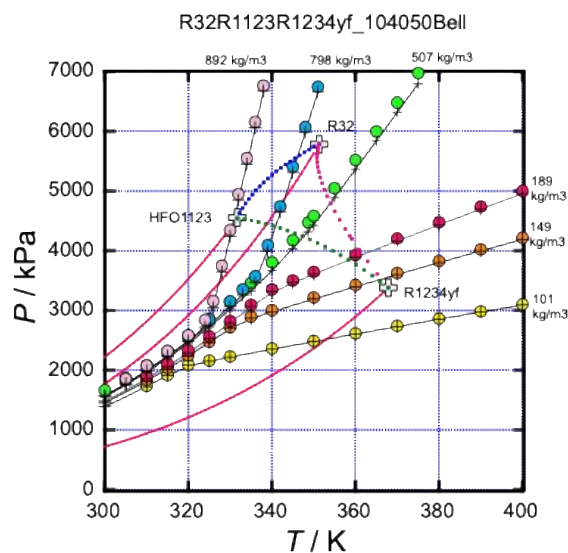


Figure 2.3-25

PVTx data plots for R-32/1123/1234yf (10/40/50). The line was calculated using the R-32/1234yf Bell mixing model.

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3. Acquisition of Speed-of-Sound Data for Low-GWP Refrigerant mixtures

(Research Institute for Engineering Measurement, National Institute of

Advanced Industrial Science and Technology)

For highly accurate thermodynamic equations of state to be developed for refrigerants, the coefficients of temperature- and density-dependent equations should be determined based on thermodynamic theory with high precision. This requires measured values of various thermodynamic properties obtained by differentiating the equations with respect to temperature and density. The Research Institute for Engineering Measurement at the National Institute of Advanced Industrial Science and Technology has been acquiring speed-of-sound data required for the development of equations of state and mixture models for binary and ternary refrigerant mixtures primarily composed of HFO-1123 or R-1132(E). The speed-of-sound is a thermodynamic property closely related to molecular thermal energy and contributes to improving the calculation accuracy of enthalpy, entropy, and other properties that are essential for refrigerant equations of state.

3.1 Measurement Method for Speed of Sound and Density in the Gas Phase

Figure 3.1-1 shows a schematic of the cylindrical resonator developed by the Research Institute for Engineering Measurement at the National Institute of Advanced Industrial Science and Technology for the gas-phase speed-of-sound measurements (Kano, 2021). The resonator is created from oxygen-free copper, which has high thermal and electrical conductivity, and contains a cylindrical cavity approximately 50 mm long and 24 mm in diameter. For minimal deformation of the resonator geometry due to sample pressure, the resonator is housed in an SUS316 pressure vessel such that the pressures inside and outside the cavity are equalized. The sample gas is introduced into the pressure vessel from the top through piping and charged into the cavity through a sample inlet on the side of the resonator. During acoustic resonance measurements, this sample inlet can be closed by a valve mechanism for the cavity to approximate an ideal cylindrical geometry.

Acoustic resonance is measured using two condenser microphones mounted on the central axis at both ends of the cylindrical cavity. Because the microphones are fabricated primarily from metallic materials, they can be used in fluorocarbon refrigerants, which exhibit high solubility in resin materials. However, electronic components such as preamplifiers, which amplify microphone signals, cannot be placed in the refrigerant environment. Therefore, the preamplifiers and transmitter adapters are installed outside the thermostatic bath at room temperature and are connected to the microphones inside the pressure vessel through hermetic feedthroughs and triaxial cables. A frequency response analyzer (FRA), capable of measuring the amplitude and phase vector components of acoustic signals over frequencies from several kilohertz to several tens of kilohertz, is used to measure the acoustic resonance frequency characteristics. The output signal from the analyzer is amplified by a driving amplifier and applied to the transmitting microphone, whereas the signal from the receiving microphone is amplified by a power module and input to the analyzer. Acoustic resonance frequency characteristics are obtained by sweeping the output frequency.

The acoustic resonance frequency f_{ac}^l of the longitudinal resonance mode in the cylindrical resonator and the speed-of-sound w in the sample gas are related as follows (Kano et al., 2020).

$$w = \frac{2L_0(1 + \chi p)}{l} (f_{ac}^l + \Delta f_{ac}^l) \quad (3.1-1)$$

Here, L_0 denotes the cavity length under vacuum, χ denotes the elastic compliance of the resonator material, l denotes the acoustic resonance mode order, and Δf_{ac}^l denotes the perturbation-theory correction term for the acoustic

resonance frequency. The value of L_0 can be determined from microwave resonance frequency measurements conducted at the same temperature as the acoustic resonance measurements. This capability to achieve absolute gas-phase speed-of-sound measurements is a key feature of the present apparatus. Details of the microwave resonance frequency measurements are described below.

As shown in Figure 3.1-2, the cylindrical resonator is precisely temperature-controlled within ± 3 mK in a liquid thermostatic bath. The temperature is measured using a standard platinum resistance thermometer calibrated according to ITS-90 and a precision thermometer bridge, and sample-gas pressure is directly measured using a quartz-crystal oscillation type pressure sensor. The expanded uncertainty of the gas-phase speed-of-sound measurements using the present apparatus is approximately 0.04 % at a 95 % confidence level. The validity of the measurement method has been confirmed using argon, for which reliable gas-phase speed-of-sound data are available (Kano, 2021).

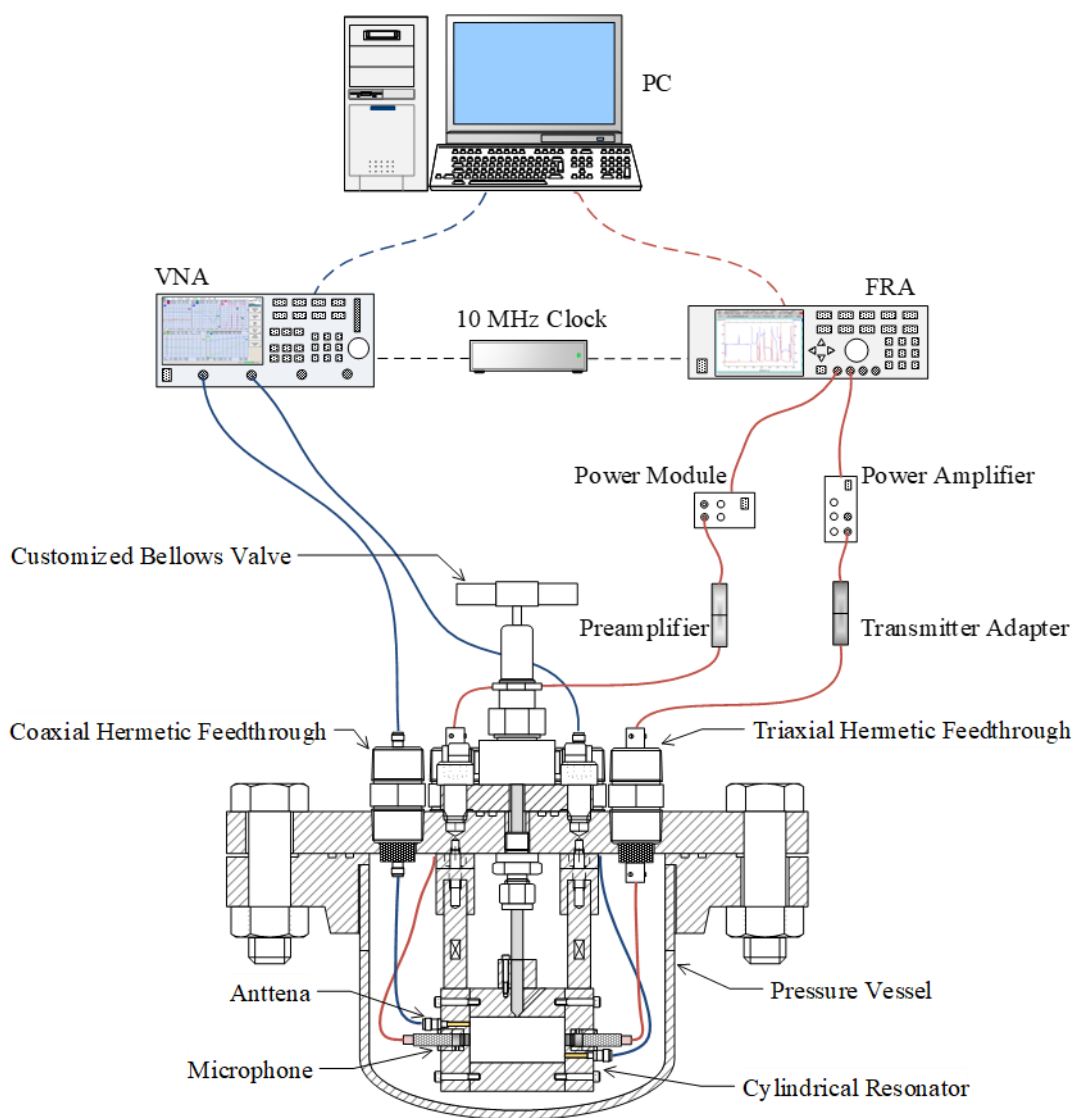


Figure 3.1-1 Cylindrical acoustic-microwave resonator for measuring the speed-of-sound and density in the gas phase (Kano, 2021)

The speed-of-sound in the gas phase can be represented by the following acoustic-virial equation (Kano, 2023a).

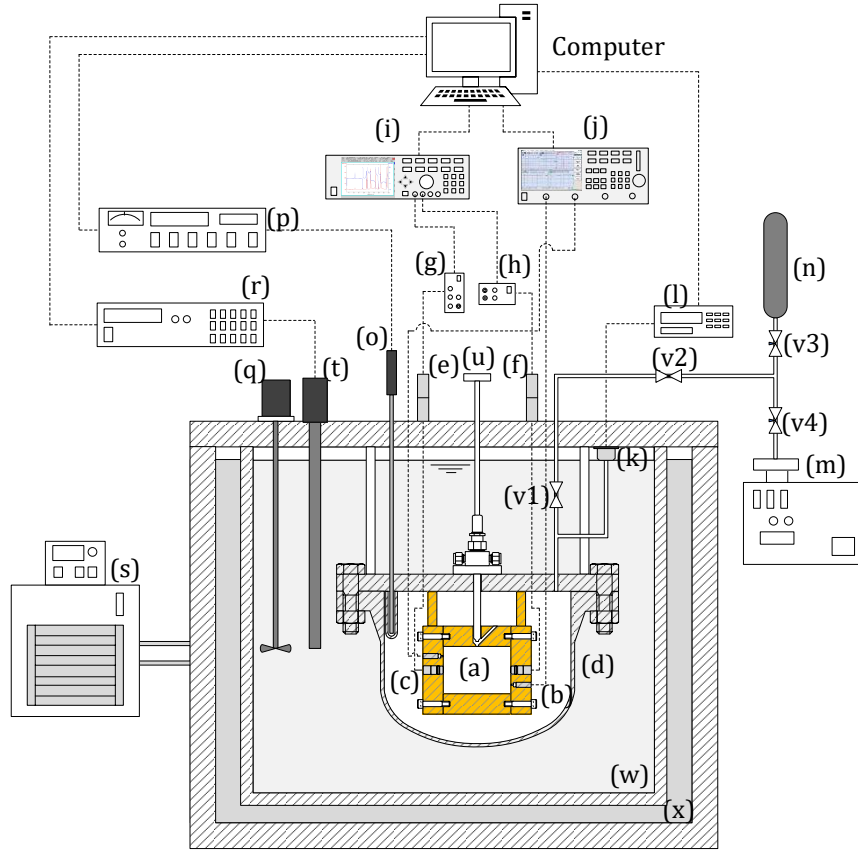
$$w^2 = \frac{RT\gamma^0}{M} \left\{ 1 + B_a \left(\frac{p}{RT} \right) + (C_a - B_\rho B_a) \left(\frac{p}{RT} \right)^2 + \dots \right\} \quad (3.1-2)$$

Here, R denotes the gas constant, T denotes the fluid temperature, γ^0 denotes the ideal-gas heat-capacity ratio, M denotes the molar mass, B_a denotes the second acoustic-virial coefficient, C_a denotes the third acoustic-virial coefficient, and B_ρ denotes the second density-virial coefficient. By extrapolating Equation (3.1-2) to the ideal-gas state at zero pressure, the ideal-gas isobaric heat capacity c_p^0 can be derived from gas-phase speed-of-sound measurements, as follows:

$$\lim_{p \rightarrow 0} w^2 = \frac{RT\gamma^0}{M} = \frac{RTc_p^0}{M(c_p^0 - R)} \quad (3.1-3)$$

where c_p^0 is a fundamental thermophysical property required for evaluating the ideal-gas term in the equations of state and is, therefore, essential for developing highly accurate equations of state.

Meanwhile, gas-phase density can be derived from the dielectric permittivity of the sample gas by measuring the microwave resonance frequency in the cylindrical resonator shown in Figure 3.1-1. Microwave resonance is measured using two antennas mounted at both ends of the cylindrical cavity. The antennas are fabricated by flat-cutting the end faces of copper semi-rigid coaxial cables and are mounted such that the end faces are flush with the inner surface of the cavity. The antennas are connected to copper semi-rigid coaxial cables and then connected through hermetic feedthroughs to equipment located outside the pressure vessel under room-temperature conditions. Microwave resonance is measured using a vector network analyzer (VNA), and resonance frequency characteristics can be obtained by measuring the microwave transmission characteristics (S-parameters) inside the cylindrical resonator.



(a) acoustic-microwave resonator, (b) microwave antennas, (c) acoustic transducer, (d) pressure vessel, (e) acoustic emitter preamplifier, (f) acoustic receiver preamplifier, (g) acoustic emitter amplifier, (h) acoustic receiver amplifier, (i) acoustic resonance frequency analyzer, (j) microwave resonance frequency analyzer, (k) pressure sensor, (l) pressure monitor, (m) evacuating device, (n) sample cylinder, (o) standard platinum resistance thermometer, (p) AC resistance bridge, (q) centrifugal type stirrer, (r) DC power supply, (s) external refrigerated circulator, (t) sheath heater, (u) sample admission valve, (v1-4) valves, (w) main thermostatic bath, (x) outer thermostatic layer

Figure 3.1-2 Schematic of the experimental setup for measuring the speed-of-sound and density in the gas phase using the cylindrical acoustic-microwave resonator (Kano, 2023b)

The microwave resonance frequency f_{em} of the transverse magnetic (TM) mode in the cylindrical resonator and the relative dielectric permittivity ϵ_r of the sample gas are related as follows (Kano, 2020).

$$f_{em} = \frac{c}{2\pi\sqrt{\epsilon_r}} \sqrt{\left(\frac{\varphi_{pq}}{r}\right)^2 + \left(\frac{\pi s}{L}\right)^2} - \Delta f_{em} \quad (3.1-4)$$

Here, c denotes the speed of light in a vacuum, φ_{pq} denotes the eigenvalue of the microwave resonance mode, s denotes the microwave resonance mode order, and Δf_{em} denotes the perturbation-theory correction term for the microwave resonance frequency. From Equation (3.1-4), the dielectric permittivity of the sample gas can be obtained using Equation (3.1-5) by obtaining the ratio of the microwave resonance frequencies under vacuum and sample-gas conditions.

$$\varepsilon_r = \left[\frac{(1 + \chi p)(f_{\text{em}}^{\text{vac}} + \Delta f_{\text{em}}^{\text{vac}})}{(1 + 2\chi p)(f_{\text{em}}^{\text{gas}} + \Delta f_{\text{em}}^{\text{gas}})} \right]^2 \quad (3.1-5)$$

Here, the superscripts “vac” and “gas” denote values measured under vacuum and sample-gas conditions, respectively. The expanded uncertainty of the gas-phase dielectric permittivity measurements using the present apparatus is approximately 0.02 %, and the validity of the measurement method has been confirmed using argon, whose gas-phase dielectric permittivity is well established.

In addition, the cylindrical cavity length L_0 in Equation (3.1-1), which is required for speed-of-sound measurements, can be determined using Equation (3.1-6) by measuring the resonance frequencies of two different microwave resonance modes under a vacuum.

$$L_0 = \frac{c}{2} \sqrt{\frac{s_2^2 - s_1^2}{(f_{\text{em}_s2}^{\text{vac}} + \Delta f_{\text{em}_s2}^{\text{vac}})^2 - (f_{\text{em}_s1}^{\text{vac}} + \Delta f_{\text{em}_s1}^{\text{vac}})^2}} \quad (3.1-6)$$

Here, s_1 and s_2 denote different resonance mode orders satisfying $s_1 < s_2$. Thus, by measuring the microwave resonance frequency under a vacuum, the dimensions of the cylindrical cavity at the measurement temperature can be determined based on the speed of light in a vacuum ($299,792,485 \text{ m s}^{-1}$).

Generally, the dielectric permittivity in the low-density gas phase can be expressed by the Clausius–Mossotti equation:

$$\frac{\varepsilon_r - 1}{\varepsilon_r + 2} \frac{M}{\rho} = \frac{N_A \alpha}{3\varepsilon_0} \quad (3.1-7)$$

Here, M denotes the molar mass, N_A denotes Avogadro’s constant, α denotes the polarizability, and ε_0 denotes the permittivity of a vacuum. The gas-phase dielectric permittivity can be expressed by the dielectric-virial equation (Kano, 2023a)

$$\frac{\varepsilon_r - 1}{\varepsilon_r + 2} \frac{RT}{p} = A_\varepsilon^0 + (B_\varepsilon - B_\rho A_\varepsilon^0) \left(\frac{p}{RT} \right) + (C_\varepsilon - A_\varepsilon^0 C_\rho + 2A_\varepsilon^0 B_\rho^2 - 2B_\varepsilon B_\rho) \left(\frac{p}{RT} \right)^2 + \dots \quad (3.1-8)$$

Here, A_ε^0 denotes the molar polarization in the ideal-gas state, B_ε denotes the second dielectric-virial coefficient, C_ε denotes the third dielectric-virial coefficient, and C_ρ denotes the third density-virial coefficient. By extrapolating Equation (3.1-8) to the ideal-gas state at zero pressure, the dipole moment μ and molecular polarizability α_m can be derived from gas-phase dielectric permittivity measurements using the Debye equation:

$$\lim_{p \rightarrow 0} \left(\frac{\varepsilon_r - 1}{\varepsilon_r + 2} \frac{RT}{p} \right) = A_\varepsilon^0 = \frac{N_A}{3\varepsilon_0} \left(\alpha_m + \frac{\mu^2}{3k_B T} \right) \quad (3.1-9)$$

Here, k_B denotes the Boltzmann constant.

In addition, using the values of A_ε^0 , B_ε , C_ε ..., obtained by fitting the measured gas-phase dielectric permittivity data to Equation (3.1-8), the gas-phase density can be derived as follows (Kano, 2021).

$$\rho = \frac{(\varepsilon_r - 1)}{A_\varepsilon^0(\varepsilon_r + 2)} - \frac{B_\varepsilon}{A_\varepsilon^0} \left[\frac{(\varepsilon_r - 1)}{A_\varepsilon^0(\varepsilon_r + 2)} \right]^2 + \frac{2B_\varepsilon^2 - A_\varepsilon^0 C_\varepsilon}{A_\varepsilon^{0^2}} \left[\frac{(\varepsilon_r - 1)}{A_\varepsilon^0(\varepsilon_r + 2)} \right]^3 + \dots \quad (3.1-10)$$

The expanded uncertainty of gas-phase density measurements using this apparatus is approximately 1%. The validity of the measurement method has also been confirmed using argon (Kano and Kuramoto, 2021), whose gas-phase density is well established.

3.2 Measurement Method for Speed-of-Sound and Density in the Liquid Phase

Figure 3.2-1 shows a schematic of the apparatus for measuring the speed-of-sound and density in the liquid phase developed by the Research Institute for Engineering Measurement at the National Institute of Advanced Industrial Science and Technology (Nishihashi et al., 2024). For speed-of-sound measurements in the liquid phase, the ultrasonic-pulse propagation speed-of-sound sensor shown in Figure 3.2-2 (L-Sonic 6100, Anton Paar) was used. Ultrasonic pulses at approximately 4 MHz are transmitted and received between piezoelectric elements located in the sample liquid, and the speed-of-sound is obtained from Equation (3.2-1) by measuring the time t required for the pulse to propagate between the elements.

$$w = \frac{D_0(1 + \alpha T)(1 + \beta p)}{t - C_0(1 + C_1 T + C_2 T^2)} \quad (3.2-1)$$

The numerator term in Equation (3.2-1) corresponds to the propagation distance of the ultrasonic-pulse, where D_0 denotes the distance between the elements at the representative temperature, α denotes the temperature compensation coefficient, and β denotes the pressure compensation coefficient. The denominator term in Equation (3.2-1) corresponds to the propagation time of the ultrasonic-pulse, and C_0 to C_2 denote the delay-time compensation coefficients associated with temperature. In this apparatus, pure water (Wagner and Pruss, 2002) and R1336mzz(Z) (McLinden and Akasaka, 2020), whose speed-of-sound values in the liquid phase are known with high accuracy, were measured as reference fluids to calibrate the speed-of-sound sensor. The speed-of-sound of the reference fluids was measured over a temperature range from -10 to 70 °C and at pressures up to 7 MPa. Each parameter in Equation (3.2-1) was determined using the least-squares method based on the reference values for the speed-of-sound. The speed-of-sound calibration equation in Equation (3.2-1), using the determined parameters, reproduces the speed-of-sound of the reference fluids with an average absolute deviation of 0.015% .

The speed-of-sound sensor is precisely temperature-controlled within ± 5 mK in a liquid thermostatic bath. The platinum resistance thermometer and temperature-measuring instrument were calibrated in advance by comparison with a standard platinum resistance thermometer calibrated according to ITS-90. The sample pressure was adjusted by varying the volume within the apparatus system using a piston-type hand pump, and the pressure was measured using a quartz oscillation type pressure sensor installed outside the thermostatic bath. The standard uncertainties of the temperature and pressure measurements are estimated to be 10 mK and 0.6 kPa, respectively. The expanded uncertainty of the speed-of-sound measurements in the liquid phase using the present apparatus is approximately 0.17% , and the validity of the measurements has also been confirmed from measurement results for R1234yf (Nishihashi et al., 2024), whose speed-of-sound values in the liquid phase are well known.

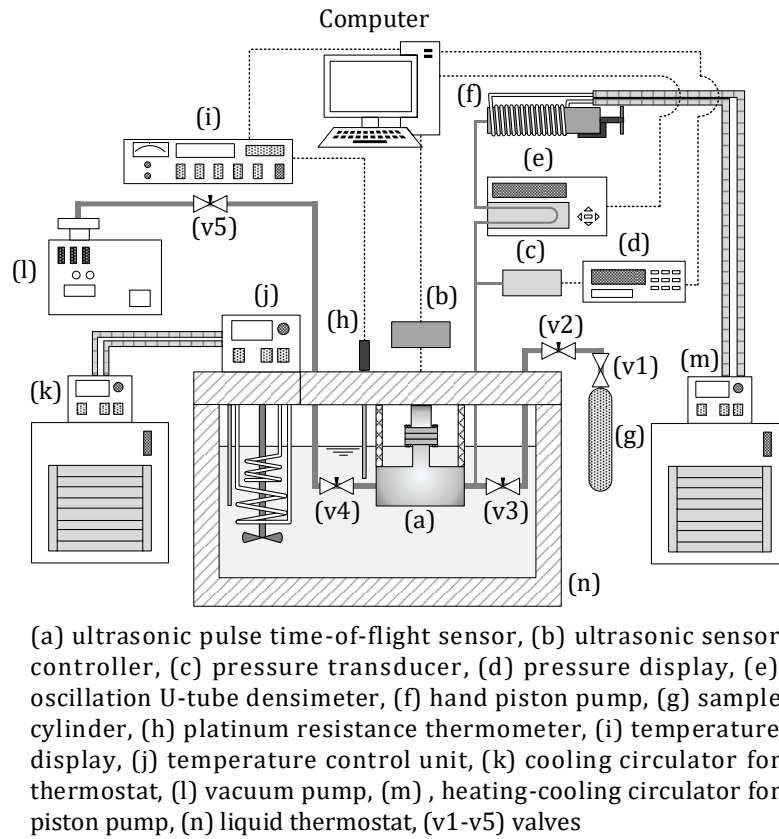


Figure 3.2-1 Schematic of the experimental setup for measuring the speed-of-sound and density in the liquid phase using ultrasonic-pulse and oscillating U-tube sensors (Nishihashi et al., 2024)

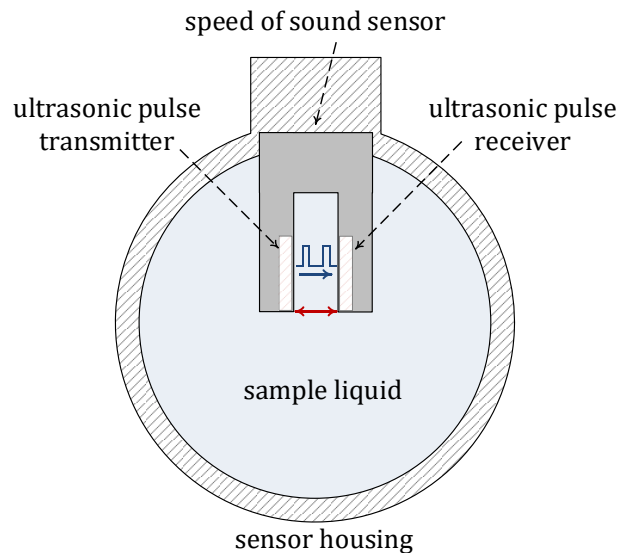


Figure 3.2-2 Cross-sectional view of the ultrasonic-pulse sensor for measuring the speed-of-sound in liquids (Nishihashi et al., 2024)

For density measurements in the liquid phase, a pressure-resistant oscillation U-tube densimeter (DMA HP, Anton Paar) is used. As shown in Figure 3.2-1, the oscillation U-tube densimeter installed outside the thermostatic bath is connected to the piping system of the speed-of-sound sensor located inside the thermostatic bath, thereby enabling simultaneous measurements of the speed-of-sound and density of the liquid sample. The oscillation U-tube densimeter is equipped with a temperature-control mechanism based on a Peltier system, enabling precise temperature control at the same temperature as that of the speed-of-sound sensor. For temperature measurement, a capillary-type standard platinum resistance thermometer calibrated in advance according to ITS-90 is inserted into the well of the oscillating densimeter. From the measurement of the oscillation period τ when the sample liquid is enclosed in the U-tube, the density of the sample liquid is obtained using

$$\rho = (E_0 + E_1T + E_2T^2)(F_0 + F_1p)(\tau^2 - \tau_0^2) \quad (3.2-2)$$

Here, E_0 to E_2 and F_0 to F_1 denote the apparatus constants for temperature and pressure, respectively, which represent the relationship between the oscillation period and density, and τ_0 denotes the oscillation period when the inside of the U-tube is under a vacuum. The apparatus constants were determined by calibrating the densimeter through measurements using pure water and R1336mzz(Z), whose density values in the liquid phase are known with high accuracy. The density of the reference fluids was measured over the temperature range from -10 to 70 °C and at pressures up to 7 MPa. Each parameter in Equation (3.2-2) was determined using the least-squares method based on the reference density values. The density calibration equation in Equation (3.2-2), using the determined parameters, reproduces the density of the reference fluids with an average absolute deviation of 0.029% , and the expanded uncertainty of density measurements in the liquid phase is estimated to be approximately 0.08% .

Thus, the speed-of-sound and density of refrigerant samples in the liquid phase can be measured simultaneously under identical temperature and pressure conditions. Because the isentropic compressibility κ_s can be determined from the obtained speed-of-sound and density data based on the thermodynamic relation in Equation (3.2-3), useful information for evaluating the thermophysical properties of next-generation refrigerants can be obtained.

$$w^2 = \left(\frac{\partial p}{\partial \rho} \right)_s = \frac{1}{\rho \kappa_s} \quad (3.2-3)$$

3.3 Measurement Results for Speed-of-Sound and Density of Low-GWP Refrigerant Mixtures

Using the apparatus for measuring speed-of-sound and density in the gas phase described in Section 3.1, as well as the apparatus for measuring speed-of-sound and density in the liquid phase described in Section 3.2, we conducted measurements for binary or ternary refrigerant mixtures primarily composed of HFO1123 and R1132(E). Table 3.3-1 summarizes the list of refrigerants measured to date. The measurement results for the speed-of-sound and density of each refrigerant are summarized in Figures 3.3-1 to 3.3-10.

Table 3.3-1 List of the measured refrigerants

Refrigerants	Number of data	Temperature range	Pressure range
R1132(E)	42 (speed-of-sound in gas)	253–343 K	100–1030 kPa
	42 (density in gas)	253–343 K	100–1030 kPa
	72 (speed-of-sound in liquid)	263–343 K	1000–7000 kPa
	64 (density in liquid)	265–315 K	1000–7000 kPa
R1132(E)/R1234yf (22.7/77.3 mass%)	17 (speed-of-sound in gas)	273–313 K	130–850 kPa
	17 (density in gas)	273–313 K	130–850 kPa

R1132(E)/R1234yf (31.8/68.2 mass%)	17 (speed-of-sound in gas) 17 (density in gas)	273–313 K 273–313 K	130–960 kPa 130–960 kPa
R1132(E)/R1234yf (23.5/76.5 mass%)	91 (speed-of-sound in liquid) 35 (density in liquid)	268–343 K 268–343 K	1000–7000 kPa 1000–7000 kPa
R1132(E)/R1234yf (29.0/71.0 mass%)	51 (speed-of-sound in liquid) 49 (density in liquid)	273–353 K 273–353 K	1000–7000 kPa 1000–7000 kPa
HFO1123/R1234yf (50.0/50.0 mass%)	19 (speed-of-sound in gas) 19 (density in gas)	273–313 K 273–313 K	110–980 kPa 110–980 kPa
HFO1123/R1234yf (75.0/25.0 mass%)	20 (speed-of-sound in gas) 20 (density in gas)	273–313 K 273–313 K	130–1070 kPa 130–1070 kPa
R1132(E)/R1234yf/R32 (21.6/27.1/51.3 mass%)	29 (speed-of-sound in liquid) 29 (density in liquid)	293–343 K 293–343 K	1000–7000 kPa 1000–7000 kPa
HFO1123/R1234yf/R32 (19.0/26.0/55.0 mass%)	18 (speed-of-sound in gas) 18 (density in gas)	273–313 K 273–313 K	170–1450 kPa 170–1450 kPa

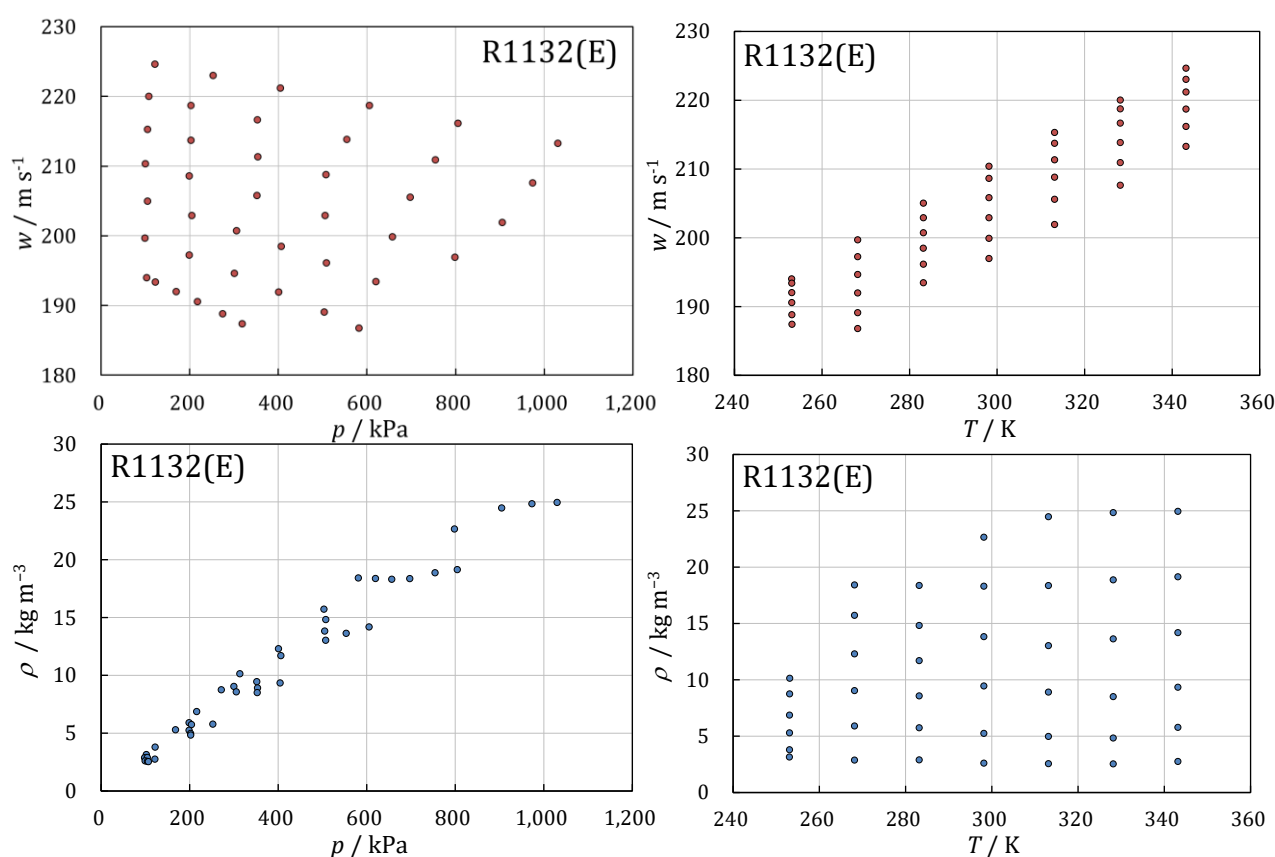


Figure 3.3-1 Measurement results for the speed-of-sound (upper diagrams) and density (lower diagrams) of R1132(E) in the gas phase

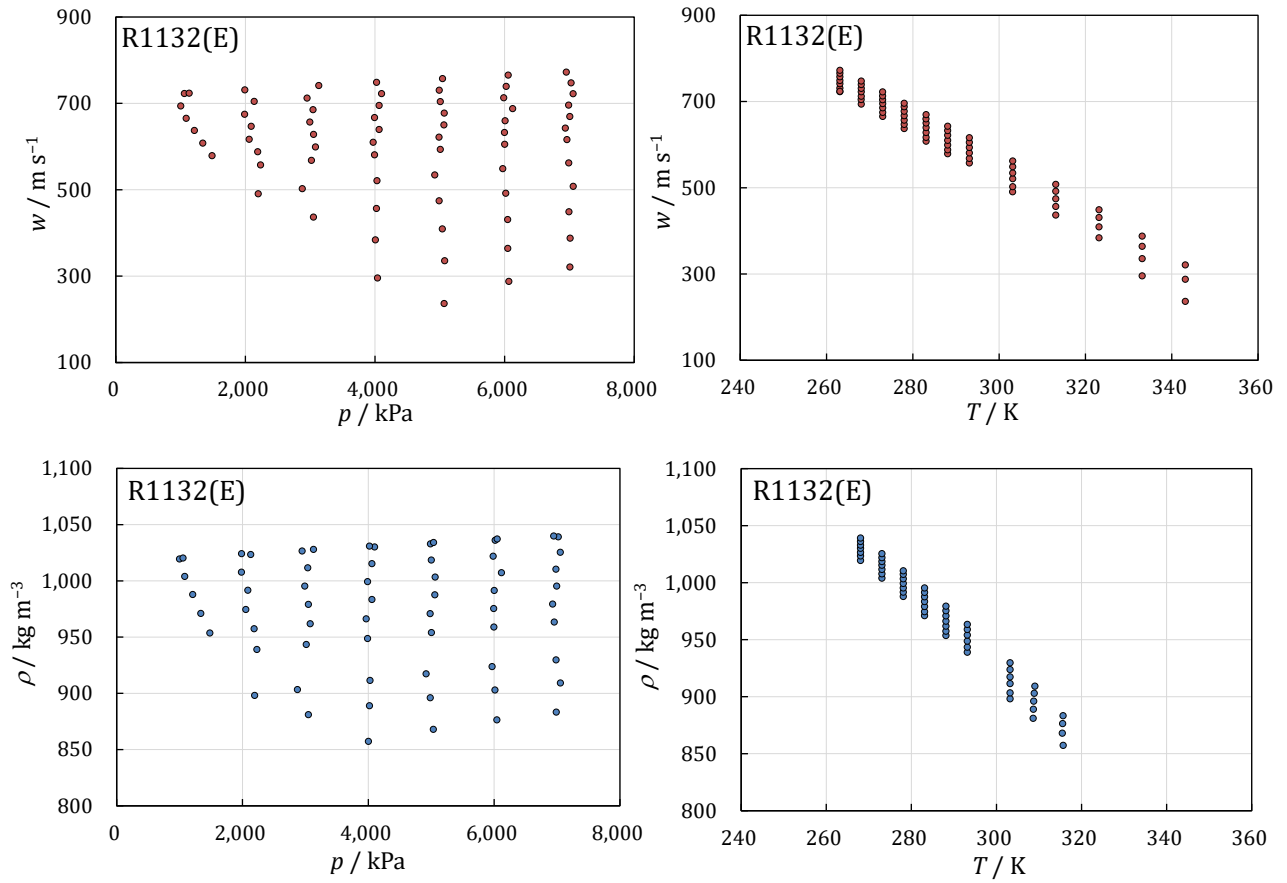


Figure 3.3-2 Measurement results for the speed-of-sound (upper diagrams) and density (lower diagrams) of R1132(E) in the liquid phase

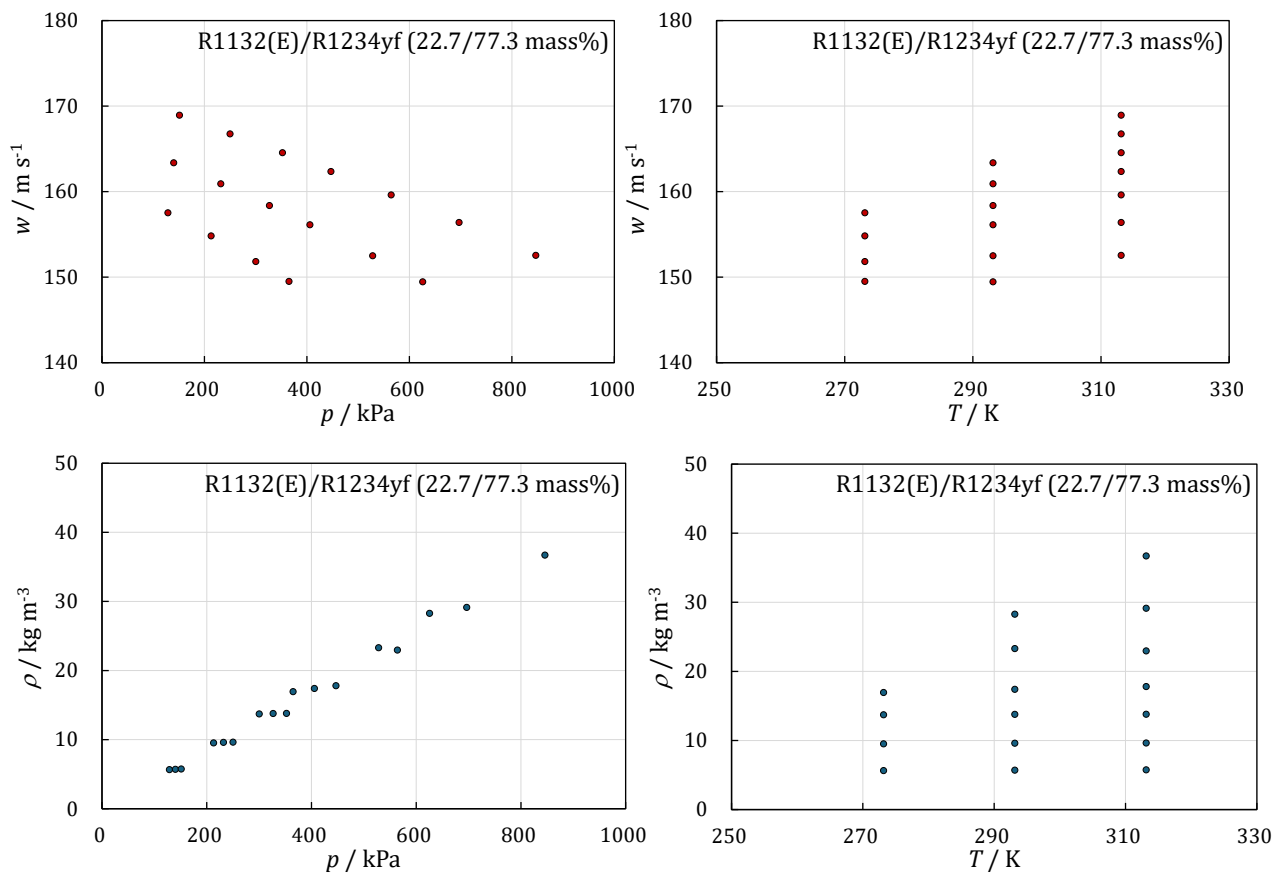


Figure 3.3-3 Measurement results for the speed-of-sound (upper diagrams) and density (lower diagrams) of R1132(E)/R1234yf with a mass ratio of 0.227/0.773 in the gas phase

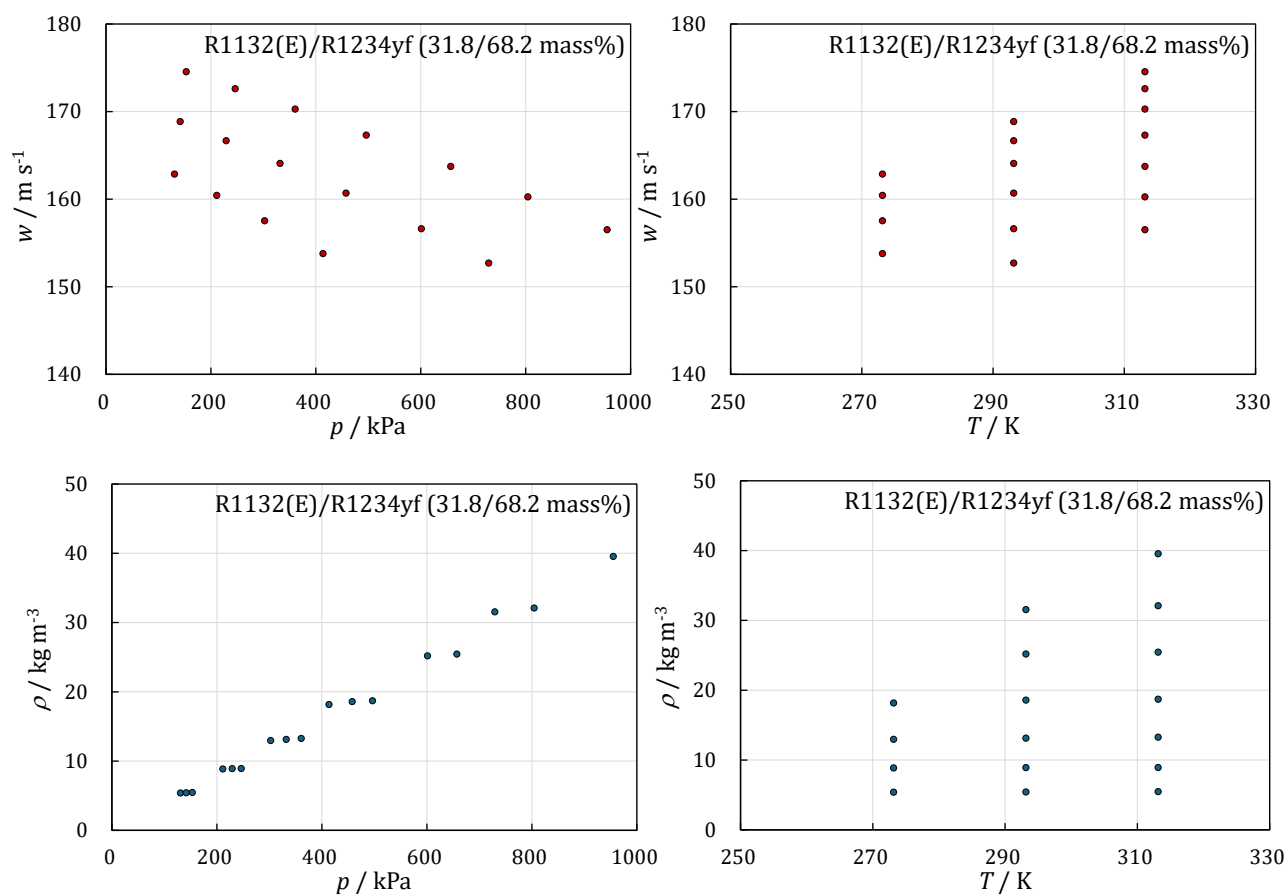


Figure 3.3-4 Measurement results for the speed-of-sound (upper diagrams) and density (lower diagrams) of R1132(E)/R1234yf with a mass ratio of 0.318/0.682 in the gas phase

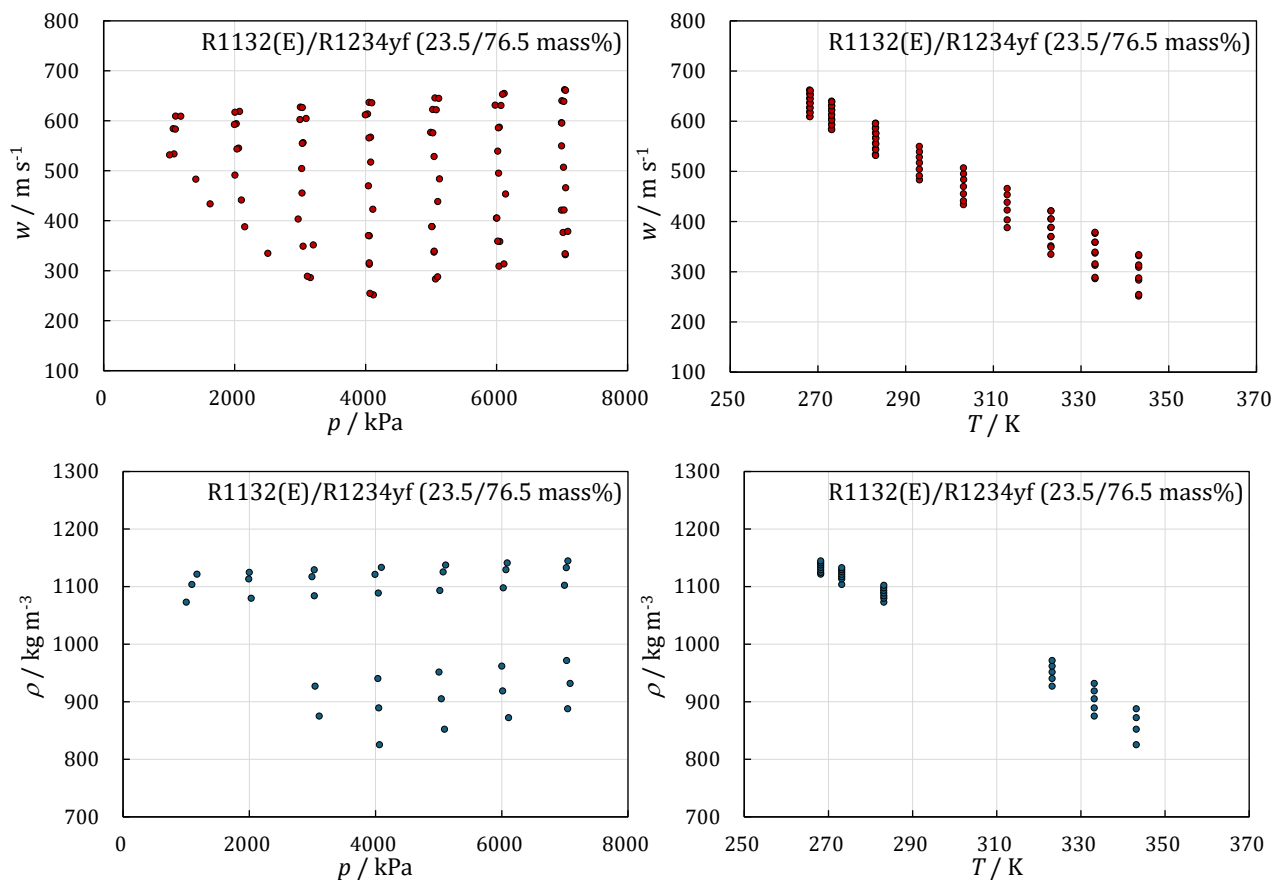


Figure 3.3-5 Measurement results for the speed-of-sound (upper diagrams) and density (lower diagrams) of R1132(E)/R1234yf with a mass ratio of 0.235/0.765 in the liquid phase

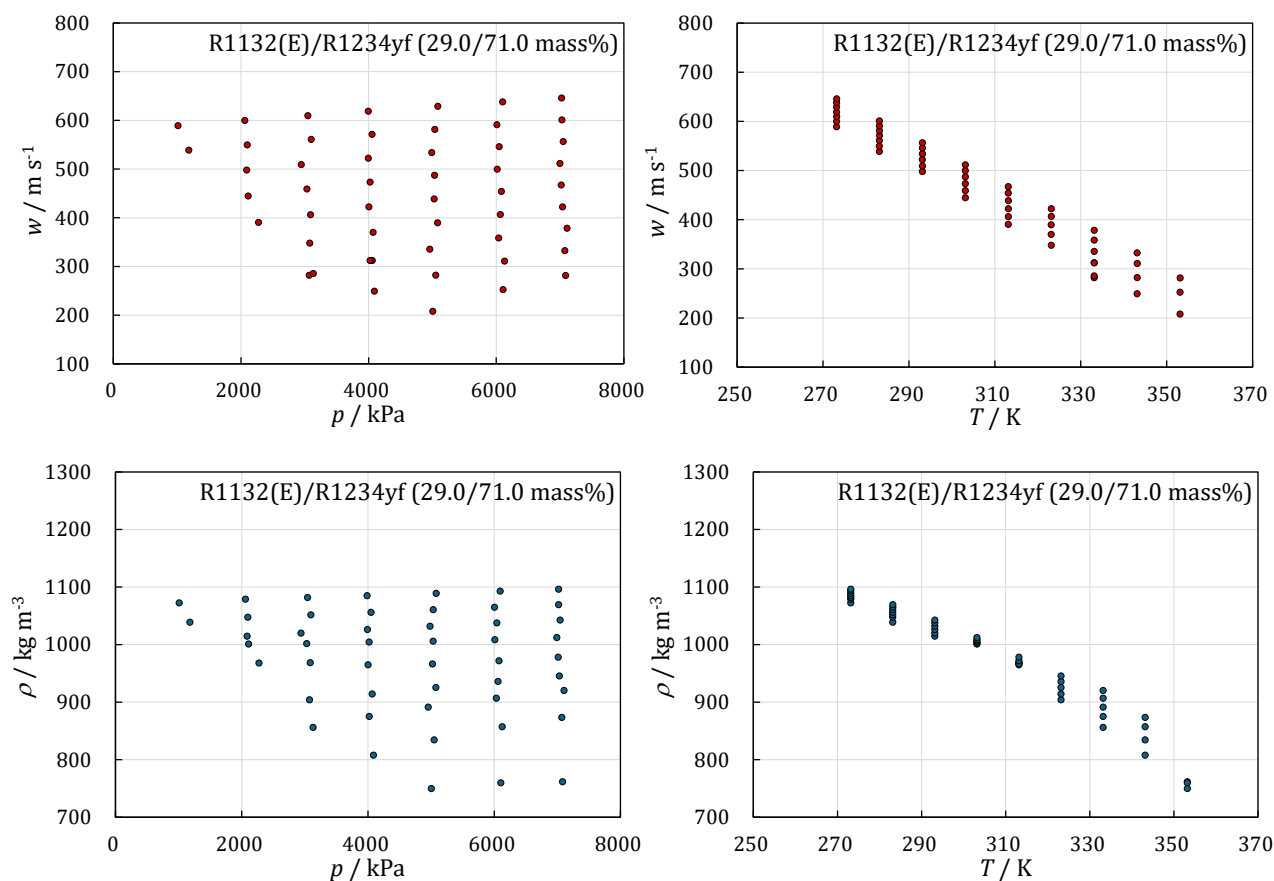


Figure 3.3-6 Measurement results for the speed-of-sound (upper diagrams) and density (lower diagrams) of R1132(E)/R1234yf with a mass ratio of 0.290/0.710 in the liquid phase

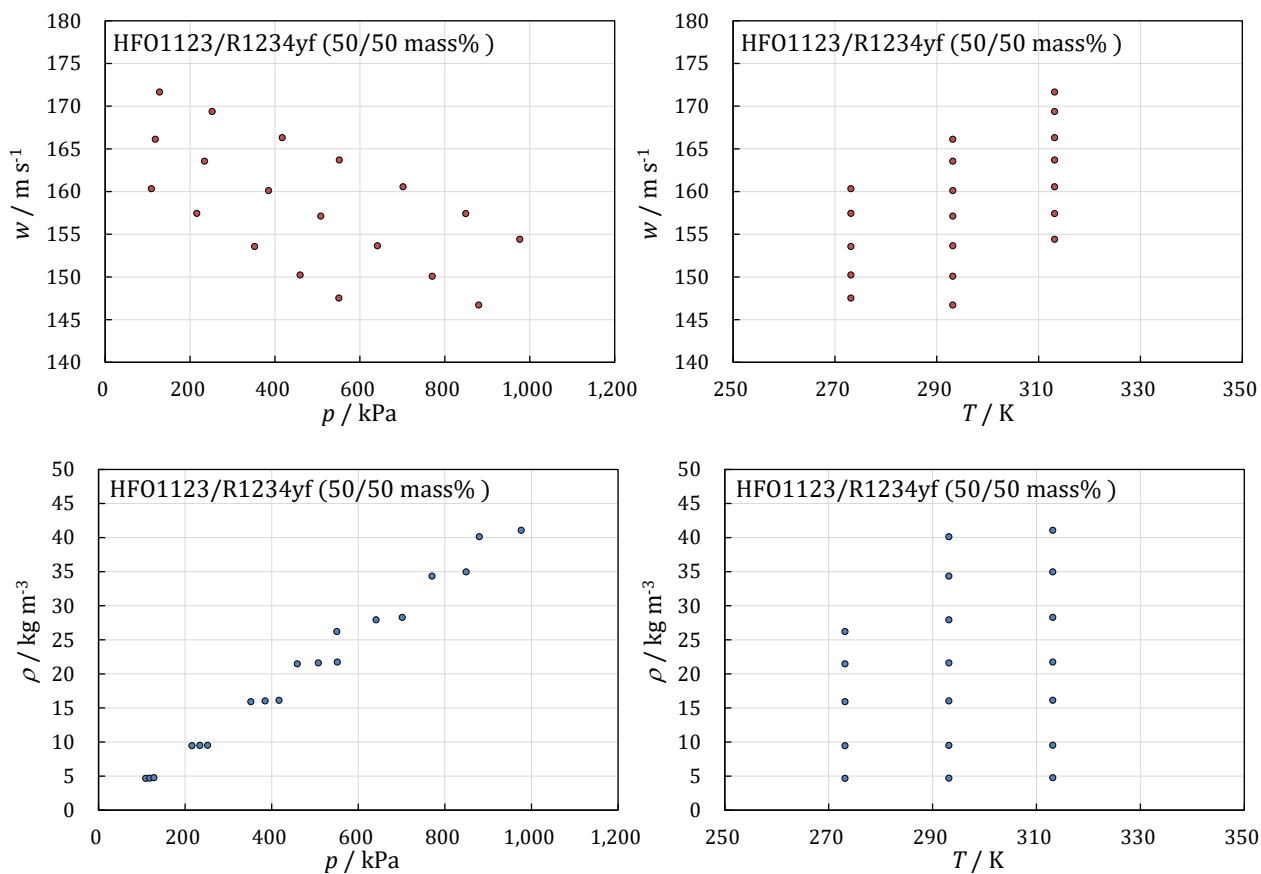


Figure 3.3-7 Measurement results for the speed-of-sound (upper diagrams) and density (lower diagrams) of HFO1123/R1234yf with a mass ratio of 0.500/0.500 in the gas phase

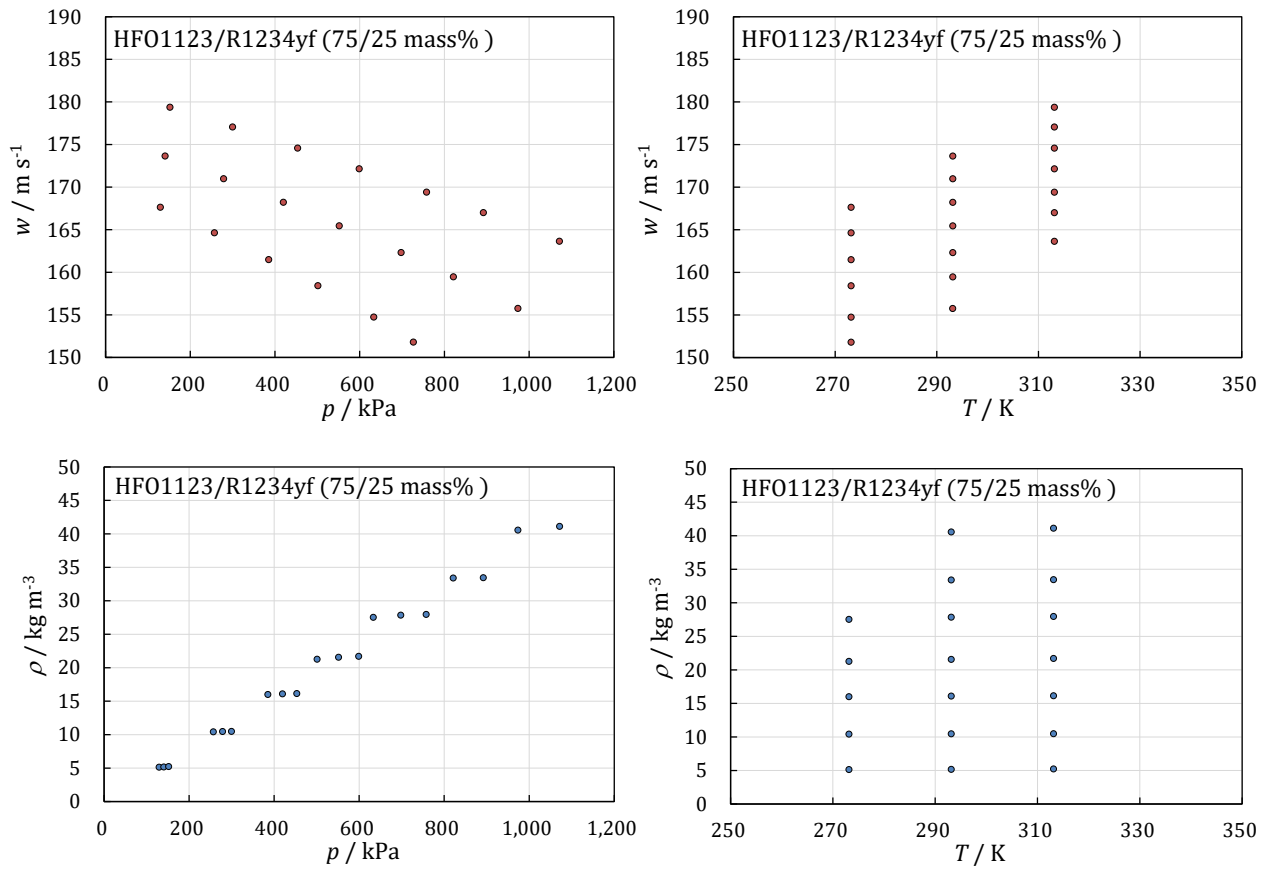


Figure 3.3-8 Measurement results for the speed-of-sound (upper diagrams) and density (lower diagrams) of HFO1123/R1234yf with a mass ratio of 0.750/0.250 in the gas phase

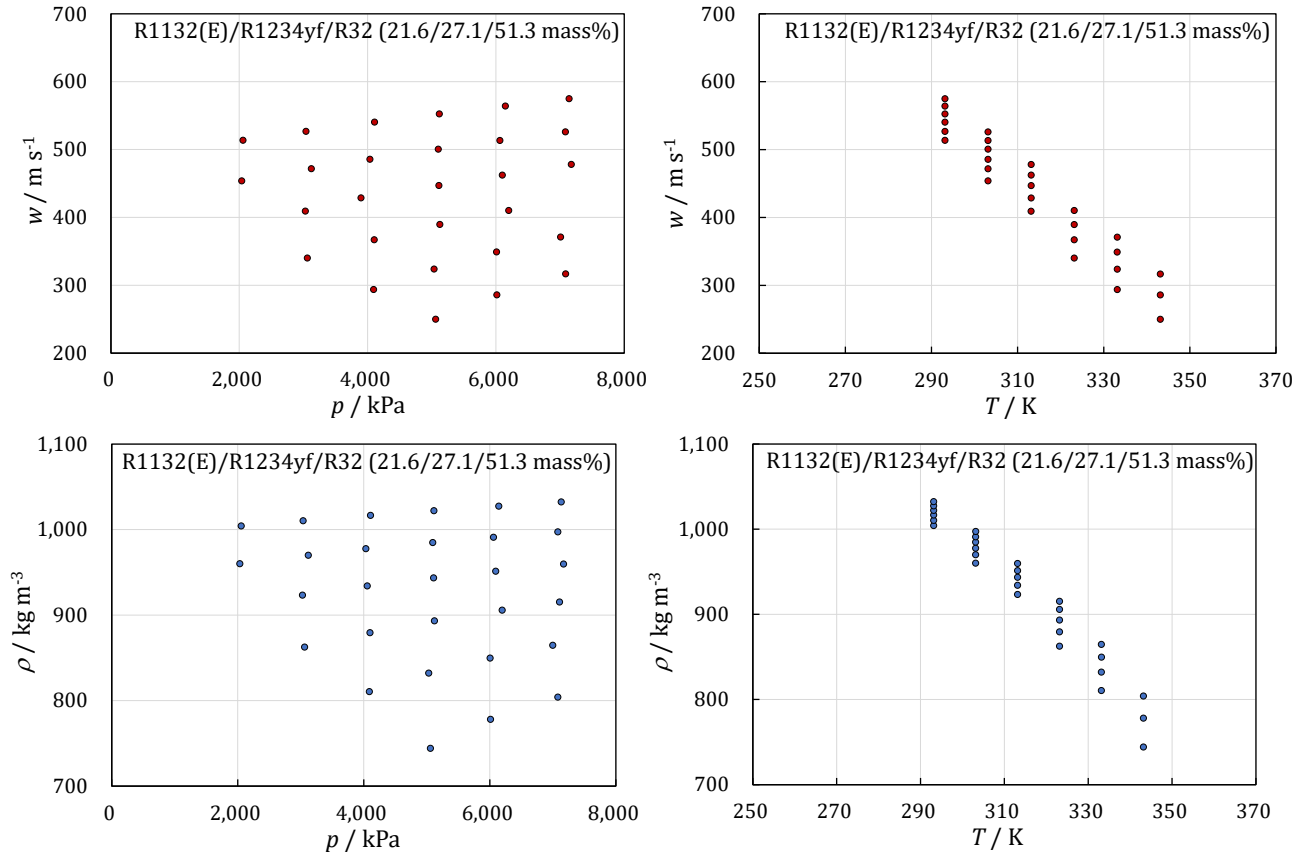


Figure 3.3-9 Measurement results for the speed-of-sound (upper diagrams) and density (lower diagrams) of R1132(E)/R1234yf/R32 with a mass ratio of 0.216/0.271/0.513 in the liquid phase

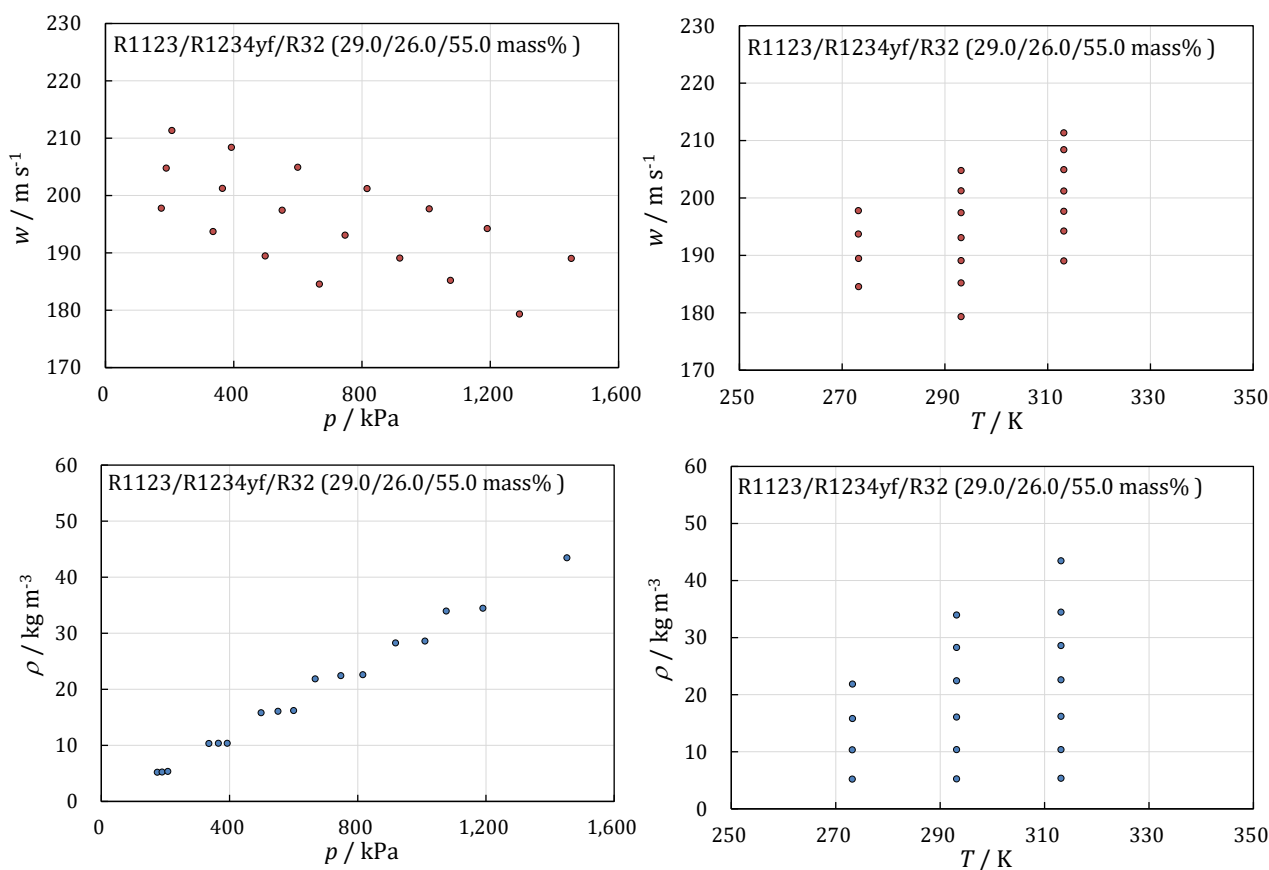


Figure 3.3-10 Measurement results for the speed-of-sound (upper diagrams) and density (lower diagrams) of R1123/R1234yf/R32 with a mass ratio of 0.290/0.260/0.550 in the gas phase

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4. Development of Equations of State and Mixing Models for Low-GWP Refrigerant Mixtures (Kyushu Sangyo University)

4.1 Helmholtz-Type Equations of State for Pure Low-GWP Refrigerants

4.1.1 Overview

In the system evaluation of vapor power cycles and refrigeration cycles, as well as in the design of components such as heat exchangers, compressors, and piping, the thermodynamic properties of the working fluid, namely saturation properties, PVT (p, ρ, T) relationships, enthalpy, specific heat, speed of sound, and related quantities, must be calculated systematically for various combinations of independent variables. For highly optimized systems to be constructed, an equation of state is required that can calculate the thermodynamic properties of the working fluid with uncertainties comparable to those of experimental measurements. Furthermore, the state surface for both vapor and liquid phases should be represented by a single function to ensure thermodynamic consistency and continuity of derivatives.

The Helmholtz-type equation of state, hereafter referred to as the Helmholtz equation, is one form of equation of state that satisfies these requirements, and its theoretical basis lies in the principle of corresponding states. In fields such as steam engineering and refrigeration and air-conditioning engineering, where accurate values of saturated vapor pressure, density, specific heat, and related properties are required, it has been widely accepted as a standard equation of state and has been adopted in international standards such as ISO 17584 for refrigerant properties (ISO, 2022) and in thermophysical property databases such as REFPROP (Lemmon et al., 2018).

The final objective of this research task is to develop a mixing model for low-GWP refrigerant mixtures containing R-1132(E). However, because the optimization of mixing parameters strongly depends on the reproducibility of the equations of state for the pure components, an equation of state for pure R-1132(E) that can accurately reproduce existing experimental data was first developed. The fundamental constants of R-1132(E) used in this research task are shown in Table 4.1-1.

Table 4.1-1 Fundamental constants and other characteristic properties of R-1132(E)

Property	Value	Reference
CAS number	1630-78-0	
Chemical formula	$C_2H_2F_2$	
Molar mass	$64.035 \text{ g} \cdot \text{mol}^{-1}$	
Critical temperature	348.82 K	Sakoda et al. (2022)
Critical pressure	5.1737 MPa	This work
Critical density	$6.793 \text{ mol} \cdot \text{dm}^{-3}$	This work
Triple-point temperature	184.9 K	Tomassetti et al. (2022)
Normal boiling point temperature	220.51 K	This work
Acentric factor	0.245	This work

4.1.2 Functional Form of the Equation of State

Generally, the Helmholtz equation is expressed with temperature T and specific volume v , or density ρ , as independent variables and the Helmholtz free energy a as the dependent variable, as shown in the following equation.

$$a = a(T, v) \quad (4.1-1)$$

This functional form is one of the four fundamental thermodynamic equations, from which all single-phase thermodynamic properties can be derived solely by differentiation. This is the principal advantage of the Helmholtz equation. For example, the pressure p and isochoric heat capacity c_v are expressed as follows:

$$p = -\left(\frac{\partial a}{\partial v}\right)_T \quad (4.1-2)$$

$$c_v = -\left(\frac{\partial^2 a}{\partial T^2}\right)_v \quad (4.1-3)$$

However, such general relations merely indicate the existence of functional relationships among the individual state properties, and numerical values of the state properties cannot be obtained unless a specific functional form is provided. An equation of state is developed to assign an appropriate functional form to the fundamental equation that lies at the apex of the general thermodynamic relations.

Even when the Helmholtz equation is used, the determination of saturation states requires iterative calculations to satisfy the so-called Maxwell criteria, namely equality of temperature, pressure, and Gibbs free energy in the vapor and liquid phases; therefore, saturation properties can only be obtained numerically.

Although Equation (4.1-1) represents the general form of the Helmholtz equation, the development of an actual equation of state uses a nondimensionalized functional form, as shown below. Density tends to be preferred over specific volume as an independent variable.

$$\frac{a(T, \rho)}{RT} = \alpha(\tau, \delta) = \alpha^\circ(\tau, \delta) + \alpha^r(\tau, \delta) \quad (4.1-4)$$

Here, τ and δ denote the dimensionless temperature and dimensionless density, respectively, and α° and α^r denote the ideal-gas and residual parts, respectively, of the dimensionless Helmholtz free energy α . The residual part corresponds to the difference between the real fluid and ideal gas. Generally, the critical temperature and critical density are used as the nondimensionalization parameters for temperature and density. Because the values of the critical temperature and critical density strongly affect the reproducibility of saturated vapor pressure and density, the selection of these values is highly important in developing an equation of state. In particular, because the critical density is difficult to measure accurately, reported values may scatter, and careful consideration is required when selecting the optimal value.

The ideal-gas part α° represents the Helmholtz free energy resulting from the translational, rotational, and vibrational motions of individual molecules. It can be derived from the ideal-gas isobaric heat capacity $c_p^\circ(T)$ using the following equation.

$$\alpha^\circ(\tau, \delta) = \frac{h_{\text{ref}}^\circ \tau}{RT_c} - \frac{s_{\text{ref}}^\circ}{R} - 1 + \ln \frac{\delta \tau_0}{\delta_0 \tau} - \frac{\tau}{R} \int_{\tau_0}^{\tau} \frac{c_p^\circ}{\tau^2} d\tau + \frac{1}{R} \int_{\tau_0}^{\tau} \frac{c_p^\circ}{\tau} d\tau \quad (4.1-5)$$

The ideal-gas isobaric heat capacity $c_p^\circ(T)$ may be obtained analytically from quantum-chemical calculations or from extrapolated values of experimentally determined gas-phase speed of sound. Simple estimation methods, such as the Joback method (Joback and Reid, 1987), may also be used. Because these methods involve relatively large uncertainties, the resulting values are treated as provisional and are finally adjusted so that measured values of the speed of sound and heat capacity of the real fluid are accurately reproduced. In Equation (4.1-5), h_{ref}° and s_{ref}° denote the specific enthalpy and specific entropy, respectively, at an arbitrary reference state. The reference state is selected according to the intended application. For refrigerants, for example, h_{ref}° and s_{ref}° are determined such that the specific enthalpy and specific

entropy of the saturated liquid at 273.15 K are 200 kJ·kg⁻¹ and 1.0 kJ·kg⁻¹·K⁻¹, respectively. Thus, information at the reference state can also be incorporated into the Helmholtz equation.

In this research task, the following equation for c_p° of R-1132(E) was obtained using quantum-chemical calculation results from Gaussian 09 D.01 and the c_p° measurements obtained in Refrigeration A-2.

$$\frac{c_p^\circ}{R} = n_0^\circ + \sum_{i=1}^2 n_i^\circ \left(\frac{m_i^\circ}{T}\right)^2 \frac{\exp(m_i^\circ/T)}{[\exp(m_i^\circ/T) - 1]^2} \quad (4.1-6)$$

This functional form is known as the Planck–Einstein form and appropriately represents the qualitative behavior of c_p° over a wide temperature range. In optimizing Equation (4.1-6), the coefficients and exponents were determined by considering the reproducibility of both c_p° and the gas-phase speed of sound. The coefficients in Equation (4.1-6) are given in Akasaka and Lemmon (2024).

Figure 4.1-1 compares the values calculated using Equation (4.1-6) with the experimentally obtained c_p° values from Refrigeration A-2. The average deviation between the calculated and experimental values is approximately 1%, which is nearly equal to the expanded uncertainty of the experimental values.

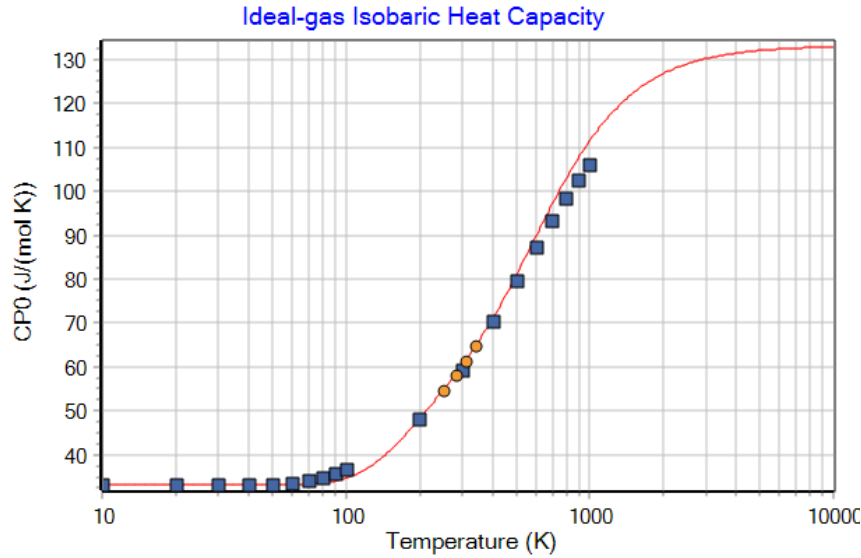


Figure 4.1-1 Ideal-gas isobaric heat capacity of R1132(E):

● Measured values in A-2, ■ Gaussian 09 D.01, — Equation (4.1-6)

By applying Equation (4.1-6) to Equation (4.1-5), the following equation is obtained.

$$\alpha^\circ(\tau, \delta) = \ln(\delta) + n_3^\circ + n_4^\circ \tau + (n_0^\circ - 1) \ln \tau + \sum_{i=1}^2 n_i^\circ \left[1 - \exp\left(-\frac{m_i^\circ \tau}{T_c}\right) \right] \quad (4.1-7)$$

The values of n_3° and n_4° are also given by Akasaka and Lemmon (2024). These values are reported with many significant digits for the specific enthalpy and specific entropy at the reference state described above to be reproduced exactly.

The residual part α^r is a term that comprehensively represents the Helmholtz free energy resulting from intermolecular forces and governs liquid-phase density, vapor pressure, behavior near the critical point, and related properties. Currently, no method has been established to accurately represent the residual part based on theoretical grounds. It is determined by optimizing, or fitting, an empirically selected functional form to measured values. In other words, the

functional form is optimized based on macroscopic state properties externally observed as a result of complex intermolecular forces. This approach is fundamentally different from microscopic methods, such as molecular dynamics (MD) calculations, in which interactions are directly obtained from intermolecular potentials.

In recent developments of Helmholtz equations, a functional form such as the following equation has been used to represent the residual part.

$$\alpha^r(\tau, \delta) = \sum n_i \tau^{t_i} \delta^{d_i} + \sum n_i \tau^{t_i} \delta^{d_i} \exp(-g_i \delta^{e_i}) + \sum n_i \tau^{t_i} \delta^{d_i} \exp[-\eta_i (\delta - \epsilon_i)^2 - \beta_i (\tau - \gamma_i)^2] \quad (4.1-8)$$

On the right-hand side, the first $\sum$ is referred to as the polynomial terms and represents the state properties of gases and high-pressure liquids. The second $\sum$ is referred to as the exponential term and represents the state properties of high-pressure gases and liquids in general. Furthermore, the third $\sum$ is referred to as the Gaussian bell-shaped term and represents steep variations in state properties near the critical point. Such a functional form is entirely empirical, and minimal theoretical basis exists for the contribution of each term to the behavior of the state properties.

In optimizing the functional form of the residual part, a multi-property fitting approach is adopted, in which the equation is fitted to experimental values of various state properties, including saturation properties, (p, ρ, T) relationships, specific heat, speed of sound, and virial coefficients. However, because the uncertainties of the experimental values differ substantially depending on the type of state property, appropriate weights must be assigned to the input values used for fitting.

The exponents and coefficients in Equation (4.1-8) are not completely arbitrary. For example, the exponent d_i of δ must be a positive integer. This requirement follows from the thermodynamic constraint that all virial coefficients, including the second, third, fourth, and higher-order virial coefficients, must approach zero as the density approaches an infinitesimal value, that is, as the state approaches the ideal-gas limit. Although real numbers are allowed for the exponent t_i of τ , negative exponents tend to be avoided in recent equations because they may cause unstable behavior of the equation of state in the low-temperature region.

In this research task, because the experimental data available for R-1132(E) are limited, a reliable Helmholtz equation for a similar refrigerant was used as the initial functional form. Additionally, the allowable ranges for changes in the exponents and coefficients were restricted to avoid correlations among the terms, namely, strong dependence among parameters. Specifically, the residual part of the Helmholtz equation for R-1234yf (Lemmon and Akasaka, 2022) was adopted as the initial form, and optimization was performed by fixing the number of terms and the density exponents while limiting the ranges over which the coefficients, temperature exponents, and parameters of the Gaussian terms could vary. This type of optimization avoids destabilization of the equation of state and prevents the breakdown of the extrapolated behavior even when the input data are limited.

Because the functional form of Equation (4.1-8) is empirical, optimization based only on experimental values may lead to inappropriate curvature or extrapolation behavior of the state surface. Therefore, in optimizing Helmholtz equations, constrained optimization is performed by imposing numerous conditions to ensure thermodynamic soundness, namely, thermodynamically correct behavior is reproduced at least qualitatively. The constraints are evaluated using the so-called “greater-than and less-than concepts.” In other words, if the equation of state violates a condition, a penalty corresponding to the degree of violation is assigned; if the condition is satisfied, the penalty is zero. This penalty is added to the residual sum of squares in the objective function in the same manner as the deviations between experimental and calculated values. Here, the weights are set such that penalties for the constraints are several orders of magnitude larger than the deviations of experimental values. This procedure emphasizes thermodynamic soundness, enables experimental values that do not satisfy soundness criteria to be excluded, and avoids overfitting to physically inconsistent data points. Examples of the constraints considered in this research task are shown below.

- The shape of isotherms on the $p - \rho$ diagram must increase monotonically on the high-density side and must not exhibit extreme divergence or discontinuities.
- The second, third, and fourth virial coefficients must exhibit the theoretically predicted temperature dependence, namely divergence to negative infinity at low temperatures and asymptotic approach to zero at high temperatures.
- Derived state properties involving higher-order derivatives of the Helmholtz free energy, such as isochoric heat capacity and speed of sound, must not exhibit unnatural behavior near the critical point or in extrapolated regions.
- The isobars and isotherms of the phase identification parameter (PIP) must be smooth, and their values, slopes, and curvatures must be reasonable in both vapor and liquid phases.

These constraints are intended to ensure reliability in regions that have not been verified experimentally. As described later, the Helmholtz equation for R-1132(E) developed in this research task exhibits reasonable behavior over wide ranges of temperature and pressure.

The coefficients and exponents of Equation (4.1-8) obtained as a result of the optimization described above are reported in Akasaka and Lemmon (2024).

4.1.3 Comparison with Experimental Values

The available experimental values for R-1132(E) are shown in Table 4.1-2. These values were previously obtained in Refrigerations A-1 and A-2. The table also lists the average absolute relative deviation (AAD) from the Helmholtz equation for each group of experimental values. The AAD for a given experimental data group X is defined by the following equation.

$$AAD_X = \frac{100}{N_{\text{exp}}} \sum_{i=1}^{N_{\text{exp}}} \left| \frac{X_{i,\text{exp}} - X_{i,\text{calc}}}{X_{i,\text{exp}}} \right| \quad (4.1-9)$$

Here, N_{exp} is the number of data points included in the experimental data group, and $X_{i,\text{exp}}$ and $X_{i,\text{calc}}$ are the i-th experimental and corresponding calculated values, respectively. For the (p, ρ, T) relationship, the deviation in density is shown. Although R-1132(E) has been reported to undergo a disproportionation reaction depending on the conditions, the report by Goto et al. (2024) indicates that the experimental values listed in Table 4.1-2 are not substantially affected by this reaction.

Table 4.1-2 Available experimental data of R-1132(E)

Author	N	T/K	p/MPa	AAD (%)
<i>Vapor pressure</i>				
Perera et al. (2022)	24	240-348		0.08
<i>Saturated liquid density</i>				
Sakoda et al. (2022)	6	317-348		0.83
<i>Saturated vapor density</i>				
Sakoda et al. (2022)	6	304-348		1.57
<i>(p, ρ, T) data</i>				
Sakoda et al. (2022) (liquid)	27	318-351	2.92-6.50	0.03
Sakoda et al. (2022) (vapor)	28	310-400	1.97-6.40	0.17
<i>Sound speed</i>				
Kano (2022)	24	253-343	0.10-1.03	0.04
<i>Ideal-gas isobaric heat capacity</i>				
Kano (2022)	4	253-343		1.03

Figure 4.1-2 shows the relative deviations between the experimental vapor-pressure values and the values calculated from the Helmholtz equation. The experimental vapor-pressure data from 240 K to near the critical temperature were reproduced with an average deviation of 0.08%. In particular, above 275 K, the relative deviations were within 0.05%, and the absolute deviations were also comparable to the experimental uncertainty, approximately 1.0 kPa. Although the relative deviations increase at low temperatures because the vapor pressure itself is small, the absolute deviations remain within a practically acceptable range.

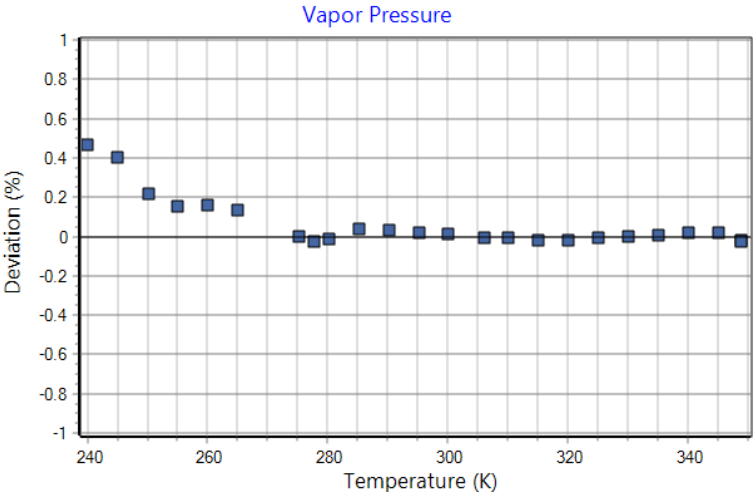


Figure 4.1-2 Relative deviations in experimental vapor pressures from values calculated from the equation of state:

■ Perera et al. (2022)

Figure 4.1-3 shows the saturation boundary calculated from the Helmholtz equation plotted on a $T - \rho$ diagram as well as the experimental values of saturated liquid density and saturated vapor density. The shape of the saturation boundary calculated from the Helmholtz equation is highly reasonable, and the rectilinear diameter, that is, the average of the saturated liquid and saturated vapor densities, remains nearly linear from the low-temperature region to the critical point. This confirms that thermodynamic soundness is ensured. The densities of the saturated liquid and vapor are reproduced by the equation of state with average relative deviations of 0.83% and 1.57%, respectively.

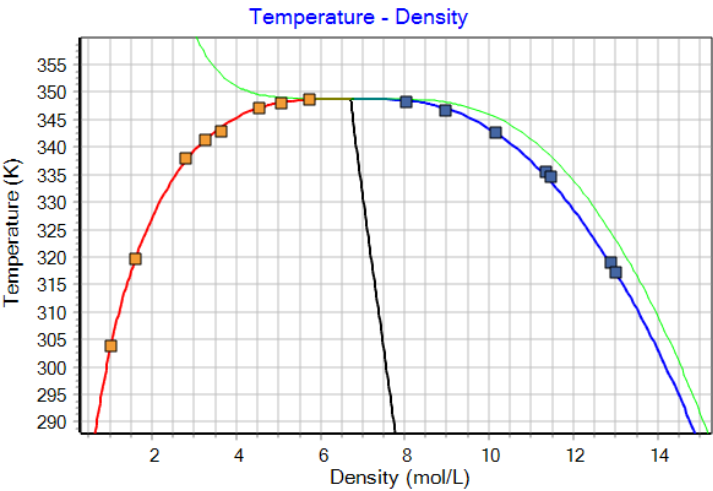


Figure 4.1-3 Saturation boundary obtained from the equation of state and experimental data for the saturated liquid and vapor densities: ■ ■ Sakoda et al. (2022)

Figure 4.1-4 shows a comparison of density for the (p, ρ, T) relationship. The isochoric lines in the liquid phase exhibit excellent agreement, with an average deviation of 0.03%, and all data points are reproduced within the experimental uncertainty. The isochoric lines in the vapor phase are also reproduced reasonably well, with an average deviation of 0.17%, which is comparable to the measurement uncertainty of approximately 0.15%. In contrast, relatively large deviations are observed for the isochoric lines near the critical density, with a deviation of approximately 2.9% at the data point closest to the critical point. This is considered to be due to the increased uncertainty in density determination near the critical point, where maintaining an equilibrium state is difficult, and because the Helmholtz equation developed in this research task does not fully reproduce the divergent behavior at the critical point, such as the divergence of specific heat. For such behavior to be quantitatively reproduced correctly, precise density and heat-capacity data near the critical point are required.

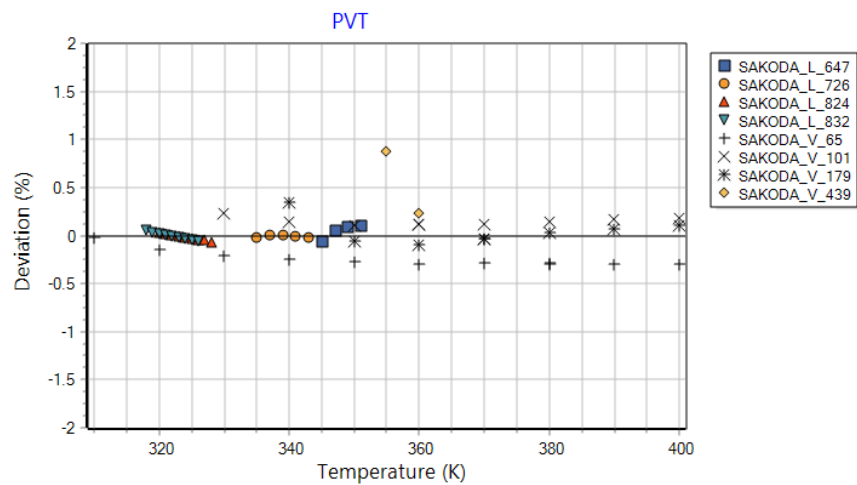


Figure 4.1-4 Relative deviations in experimental densities (Sakoda et al., 2022) from values with the equation of state

A comparison of the vapor-phase speed of sound is shown in Figure 4.1-5. The experimental values of the vapor-phase speed of sound are reproduced by the Helmholtz equation with an average deviation of 0.04%, and all data points fall within 0.08%. In the analysis of refrigeration cycles, accurate reproduction of the vapor-phase speed of sound is important because changes in specific heat and entropy during the compression process affect performance prediction.

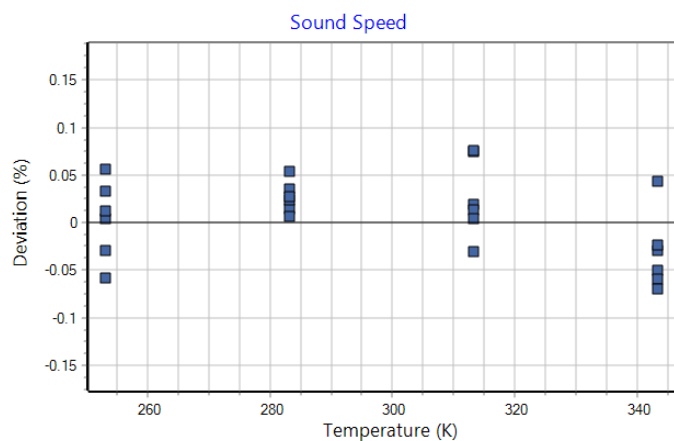


Figure 4.1-5 Relative deviations in experimental vapor-phase sound speeds (Kano et al., 2022) from values with the equation of state

4.1.4 Verification of Thermodynamic Soundness

For an equation of state constructed from limited data using an empirical functional form, the behavior in extrapolated regions, such as unnatural extrema, negative heat capacities, or anomalous sound speeds, may break down. As described earlier, in this research task, constraints for ensuring the thermodynamic soundness of the equation of state were considered during optimization. Figure 4.1-6 shows the behavior of the fourth virial coefficient, isochoric heat capacity, speed of sound, and PIP. As shown in these figures, each state property exhibits physically reasonable behavior over wide ranges of temperature and pressure, and no unnatural undulations or divergences are observed. These results confirm that the Helmholtz equation developed in this research exhibits good extrapolation performance even in regions where no experimental values are available.

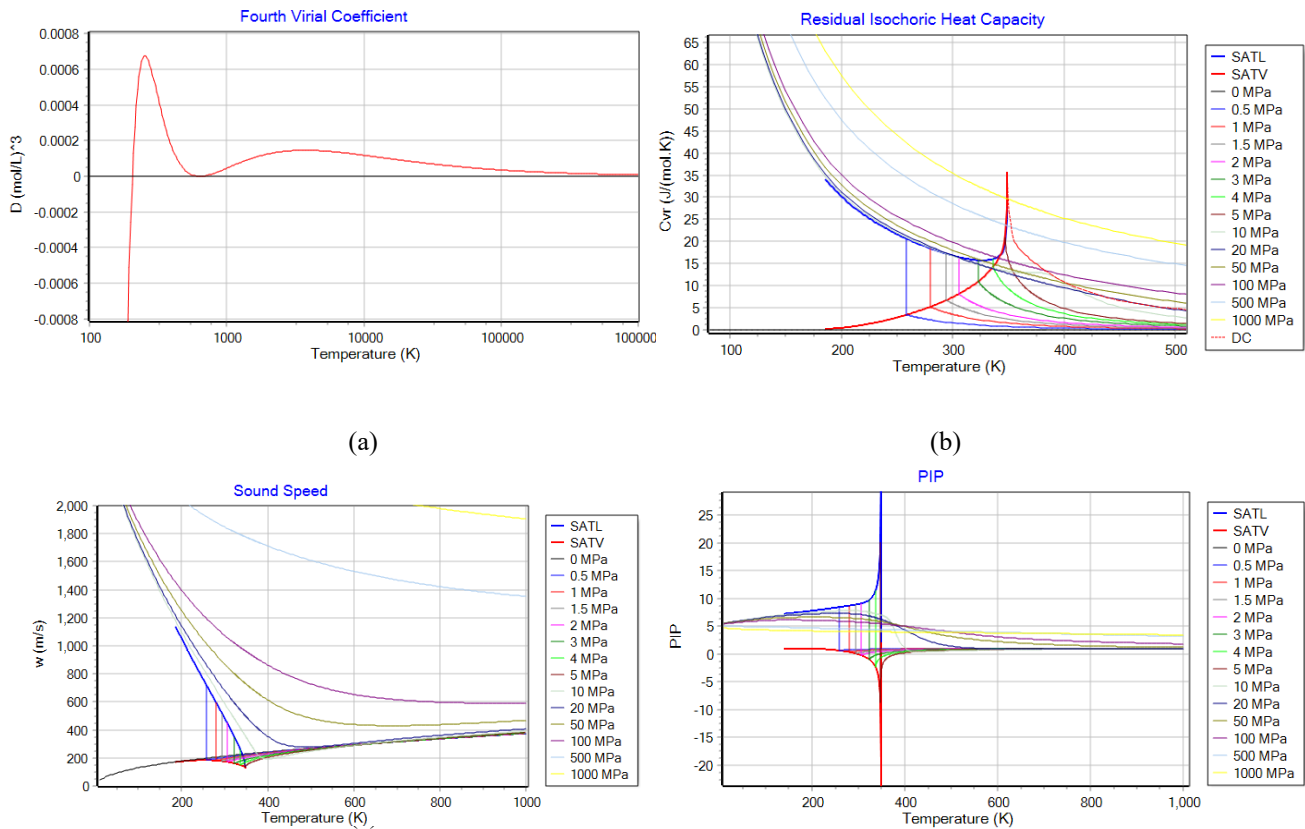


Figure 4.1-6 Verifications of the extrapolated behavior of the equation of state: (a) Fourth virial coefficients, (b) Residual isochoric heat capacity, (c) Sound speed, (d) Phase identification parameter (PIP).

4.2 Mixing Models for Low-GWP Refrigerant Mixtures

4.2.1 Overview

The thermodynamic model developed in this research task is based on the multi-fluid approximation founded on the Kunz–Wagner (KW) model (Kunz et al., 2007; Kunz and Wagner, 2012). Over the past 20 years, the KW model has been applied to many industrial fluids, including refrigerant mixtures, liquified natural gas, and hydrogen-containing mixtures. It is currently considered one of the most practical approaches for modeling the thermophysical properties of mixtures and is also implemented in REFPROP (Lemmon et al., 2018).

The concept of the multi-fluid approximation for binary systems is shown in Figure 4.2-1. In the multi-fluid approximation, the dimensionless Helmholtz energy α of a mixture is expressed as the sum of the ideal-mixture contribution α^{idmix} and the excess term, or departure term, α^{E} , as follows:

$$\frac{a}{RT} = \alpha = \alpha^{\text{idmix}} + \alpha^E \quad (4.2-1)$$

The ideal-mixture contribution α^{idmix} is given by taking the mole-fraction-weighted average of the ideal-gas and residual parts of the Helmholtz-type equation of state for each component i and by adding a term corresponding to the increase in mixing entropy.

$$\alpha^{\text{idmix}}(T, \rho, \mathbf{x}) = \sum_{i=1}^n x_i [\alpha_i^{\circ}(T, \rho) + \alpha_i^r(\tau, \delta) + \ln x_i] \quad (4.2-2)$$

Here, $\mathbf{x} = (x_1, x_2, \dots, x_n)$. In mixing the residual part, the reducing temperature $T_{\text{red}}(\mathbf{x})$ and reducing density $\rho_{\text{red}}(\mathbf{x})$ are defined as functions of the mole composition $\mathbf{x}$ from the mixture temperature T and density ρ . Subsequently, the independent variables of the mixture model and those of the equations of state for pure substances are treated consistently using the dimensionless temperature $\tau = T_{\text{red}}/T$ and dimensionless density $\delta = \rho/\rho_{\text{red}}$. In this research task, the equation of state described in the previous section was used for pure R-1132(E), whereas the Tillner-Roth–Yokozeki equation (Tillner-Roth and Yokozeki, 1997) and Lemmon–Akasaka equation (Lemmon and Akasaka, 2022) were used for R-32 and R-1234yf, respectively.

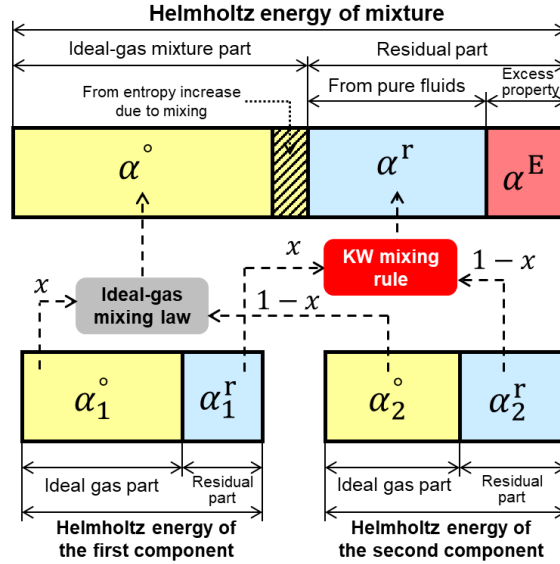


Figure 4.2-1 Basic concept of the multi-fluid mixture model for binary mixtures

In the KW model, the reducing temperature $T_{\text{red}}(\mathbf{x})$ and reducing density $\rho_{\text{red}}(\mathbf{x})$ are given by the following equations, respectively.

$$T_{\text{red}}(\mathbf{x}) = \sum_{i=1}^n x_i^2 T_{c,i} + \sum_{i=1}^{n-1} \sum_{j=i+1}^n 2x_i x_j \beta_{T,ij} \gamma_{T,ij} \frac{x_i + x_j}{\beta_{T,ij}^2 x_i + x_j} \times \sqrt{T_{c,i} T_{c,j}} \quad (4.2-3)$$

$$\frac{1}{\rho_{\text{red}}(\mathbf{x})} = \sum_{i=1}^n \frac{x_i^2}{\rho_{c,i}} + \sum_{i=1}^{n-1} \sum_{j=i+1}^n 2x_i x_j \beta_{v,ij} \gamma_{v,ij} \frac{x_i + x_j}{\beta_{v,ij}^2 x_i + x_j} \times \frac{1}{8} \left(\frac{1}{\rho_{c,i}^{\frac{1}{3}}} + \frac{1}{\rho_{c,j}^{\frac{1}{3}}} \right)^3 \quad (4.2-4)$$

Here, $\beta_{T,ij}$, $\gamma_{T,ij}$, $\beta_{v,ij}$, and $\gamma_{v,ij}$ are mixing parameters defined for each component pair (i, j) in the mixture and are determined from experimental values for that component pair. Generally, $\beta_{T,ij}$ and $\gamma_{T,ij}$, which correspond to the reducing temperature, strongly affect the reproducibility of vapor–liquid equilibrium. In contrast, $\beta_{v,ij}$ and $\gamma_{v,ij}$, which

correspond to the reducing density, have a relatively small influence on vapor–liquid equilibrium but affect the reproducibility of the (p, ρ, T) relationship, particularly density. For binary systems, Equations (4.2-5) and (4.2-6) can be simplified as follows:

$$T_{\text{red}}(x) = x^2 T_{c,1} + (1-x)^2 T_{c,2} + 2\beta_T \gamma_T \left[\frac{x(1-x)}{(\beta_T^2 - 1)x + 1} \right] \times \sqrt{T_{c,1} T_{c,2}} \quad (4.2-5)$$

$$\frac{1}{\rho_{\text{red}}(x)} = \frac{x^2}{\rho_{c,1}} + \frac{(1-x)^2}{\rho_{c,2}} + 2\beta_v \gamma_v \left[\frac{x(1-x)}{(\beta_v^2 - 1)x + 1} \right] \times \frac{1}{8} \left(\frac{1}{\rho_{c,1}^{\frac{1}{3}}} + \frac{1}{\rho_{c,2}^{\frac{1}{3}}} \right)^3 \quad (4.2-6)$$

Here, $x = x_1$ and $1-x = x_2$, and the subscript ij has been omitted.

Furthermore, in the KW model, the excess term, that is, the excess Helmholtz free energy α^E , is expressed as follows.

$$\alpha^E(\tau, \delta, x) = \sum_{i=1}^{n-1} \sum_{j=i+1}^n x_i x_j F_{ij} \alpha_{ij}^E(\tau, \delta) \quad (4.2-7)$$

Here, α_{ij}^E is a departure function defined or generalized for a specific component pair (i, j) , and F_{ij} is a parameter that adjusts its contribution. The contribution of α^E becomes significant in the high-pressure region, where it affects both vapor–liquid equilibrium and the (p, ρ, T) relationship. However, for refrigerant mixtures, the relative influence of α^E is small; when experimental values in the high-pressure region are limited, α^E may be neglected, or $F_{ij} = 0$ may be imposed. In this research task, parameter optimization was performed using the departure function generalized for hydrocarbon mixtures, referred to as KW0 in REFPROP, while considering a model with $F_{ij} = 0$, referred to as XR0 in REFPROP, depending on its effect on the reproducibility of experimental values.

As shown earlier, when Equation (4.2-7) is written for a binary system, it becomes

$$\alpha^E(\tau, \delta, x) = x(1-x) F_{12} \alpha_{12}^E(\tau, \delta) \quad (4.2-8)$$

4.2.2 Optimization of Mixing Parameters

In this research task, the mixing parameters of the KW model for the R-32/1132(E) and R-1132(E)/1234yf systems, namely β_T , γ_T , β_v , γ_v , and F_{12} , were determined through nonlinear least-squares fitting to experimental values obtained in Refrigeration A-1. The experimental values used for optimization primarily consisted of single-phase (p, ρ, T) relationships and vapor–liquid equilibrium data, including saturated liquid density, saturated vapor density, and bubble-point pressure. The departure function generalized for hydrocarbon mixtures was used. The objective function S used in the optimization is given by the following equation.

$$S = \sum W_\rho X_\rho^2 + \sum W_{\rho_{\text{sat}}} X_{\rho_{\text{sat}}}^2 + \sum W_{p_{\text{bub}}} X_{p_{\text{bub}}}^2 \quad (4.2-9)$$

Here, X_ρ , $X_{\rho_{\text{sat}}}$, and $X_{p_{\text{bub}}}$ denote the relative deviations of density, saturated density, and bubble-point pressure, respectively, and W_ρ , $W_{\rho_{\text{sat}}}$, and $W_{p_{\text{bub}}}$ represent the corresponding weights assigned to each set of experimental data. The weights are determined according to the type of experimental data and phase, with typical values of 1 for vapor-phase density, saturated liquid density, and bubble-point pressure, 0.1 for saturated vapor density, and 10 for liquid-phase density. In other words, greater emphasis is placed on liquid-phase density because of its significant contribution to cycle calculations and mixture-model accuracy, as well as its relatively high measurement precision. In contrast, the influence of saturated vapor density, which has larger uncertainty, is intentionally reduced in the optimization.

The initial values for the optimization were set to 1 for β_T , γ_T , β_v , and γ_v , and to 0 for F_{12} . The parameters were then adjusted not through simultaneous optimization but by cyclically updating one parameter at a time in the order $\gamma_T \rightarrow$

$\beta_T \rightarrow \gamma_v \rightarrow \beta_v \rightarrow F_{12}$. This procedure was adopted because the mixing parameters of the KW model strongly affect numerical calculations such as vapor–liquid equilibrium calculations. Additionally, the simultaneous variation of multiple parameters tends to cause iterative solutions for density and bubble-point pressure to diverge.

During parameter updating, quadratic interpolation was used to search for the minimum of the objective function, and the parameters were successively modified in directions that reduced the objective function. When the contribution of F_{12} to the objective function was considered negligible, F_{12} was excluded from the optimization and fixed at 0.

Furthermore, in addition to minimizing the objective function, the behavior of vapor–liquid equilibrium curves, specific heat, speed of sound, and related properties was monitored in the critical region and extrapolated regions during the optimization process. This was done to avoid physical inconsistency and numerical instability caused by overfitting. In the optimization of mixture models, excessive fitting to experimental values tends to destabilize vapor–liquid equilibrium calculations, causing iterations not to converge or to converge to physically unreasonable points. When unnatural inflections or extrema were observed in the monitored thermophysical properties, the selection of experimental values included in the objective function and their weights were reviewed. The final parameters were determined after adjusting the mixture model such that it behaved smoothly even in the critical and extrapolated regions. Establishing this procedure for determining mixing parameters while balancing reproducibility of experimental values with extrapolation validity and numerical stability is one of the major outcomes of this research task.

4.2.3 Comparison with Experimental Values

Figure 4.2-2 shows the experimental and calculated values of isobaric vapor–liquid equilibrium for the R-32/1132(E) and R-1132(E)/1234yf systems. The experimental values were obtained in Refrigeration A-1, and two sets of calculated values are shown: one using the estimated parameters in REFPROP (Lemmon et al., 2018) and the other using the parameters optimized in this research task.

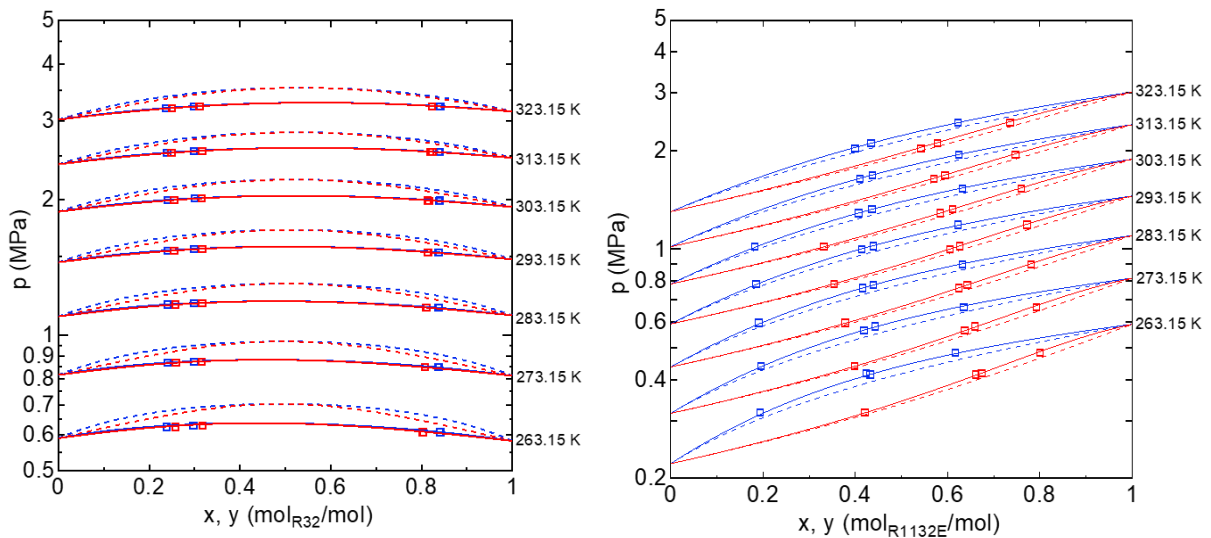


Figure 4.2-2 Isobaric vapor–liquid equilibrium of R-32/1132(E) (left panel) and R-1132(E)/1234yf (right panel) mixtures. $\square$: Experimental value (A-1); dashed line: REFPROP; solid line: This work

When the estimated parameters from REFPROP were used, particularly large deviations were observed for the R-32/1132(E) system. In contrast, when the mixing parameters optimized in this research task were used, the relative deviations from the experimental bubble-point pressures were within 1% for both systems, indicating sufficient reproducibility for practical applications.

Figure 4.2-3 compares the calculated saturation boundaries with the experimental saturated liquid and vapor densities for the R-32/1132(E) and R-1132(E)/1234yf systems. Two sets of calculated values are shown: those obtained using the

estimated parameters in REFPROP and those obtained using the parameters optimized in this research task. The optimized parameters improved the reproducibility of saturated densities in both systems. For the R-32/1132(E) system, the relative deviations of the saturated liquid and vapor densities were approximately 1%. For the R-1132(E)/1234yf system, the saturated liquid density was reproduced with deviations of approximately 2%, whereas the saturated vapor density exhibited somewhat larger deviations of approximately 3% to 5%. This relatively poor reproducibility of the saturated vapor density is considered to result from the use of the KW0 departure function, which was generalized for hydrocarbon mixtures. A departure function specific to this system is required to quantitatively reproduce the maximum condensation temperature and maximum condensation pressure when the temperature on the saturated-vapor side exceeds the critical point.

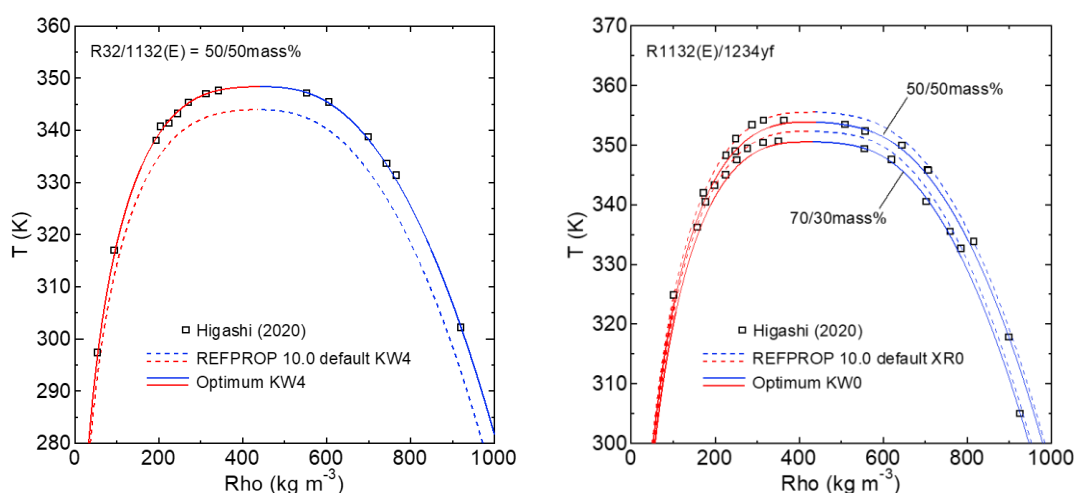


Figure 4.2-3 Saturation boundary of R-32/1132(E) (left panel) and R-1132(E)/1234yf (right panel) mixtures and experimental data for the saturated liquid and vapor densities. $\square$: Experimental value (A-1); dashed line: REFPROP; solid line: This work

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5. Evaluation of Safety Characteristics Contributing to the Screening of Low-GWP Refrigerant Mixtures

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5.1 Introduction

In the development of next-generation refrigerants, in addition to refrigerant performance in intended applications, environmental characteristics, such as GWP, and safety characteristics, including toxicity and flammability, should be considered. With respect to flammability, refrigerants with lower flammability impose fewer restrictions on operating conditions and require fewer safety measures when used in refrigeration and air-conditioning equipment. Because the practically acceptable degree of flammability depends on the refrigerant charge amount, application, safety technologies, and other factors, this study aimed to support both the development of new refrigerants and appropriate refrigerant selection by users through an accurate evaluation of the weak flammability of various refrigerants. In this research and development project, the objective was to quantitatively evaluate the flammability characteristics of candidate refrigerants and obtain data that support the screening of refrigerant mixtures, thereby advancing the development of next-generation refrigerants with low GWP and high safety.

Candidate refrigerants considered in this study were primarily ternary mixtures containing low-GWP fluoroethylene-based refrigerants. The dependence of various flammability characteristics on mixture composition and refrigerant concentration was evaluated, and the composition ranges satisfying refrigerant safety criteria under consideration in Japan and overseas were clarified. These include, for example, composition ranges that provide safety equal to or higher than that of gases classified as “lower flammability class (Class 2L)” under the international standard ISO 817 (“Refrigerants — Designation and safety classification”) and designated as “specified inert gases” under Japan’s High Pressure Gas Safety Act and related regulations. In ISO 817, refrigerant flammability is classified into the four classes shown in Table 5.1-1. Among these, refrigerants in the lower flammability class have attracted interest as low-GWP candidates and have been registered most frequently over the past decade. Although lower-flammability refrigerants are flammable, the conditions required for flame propagation, including the flammable concentration range and ignition energy, are stringent, and their burning velocities are small (approximately one-quarter or less of those of hydrocarbons). Therefore, flame propagation is unlikely to occur under practical conditions. R32 and R1234yf, which have recently been adopted worldwide for room and automotive air conditioners, are also lower-flammability refrigerants. No severe accidents caused by these refrigerants have been publicly reported to date, indicating accumulated safety experience. Accordingly, this study focused particularly on flammability limits and burning velocity, which are essential for evaluating lower flammability and defining its classification.

To date, the flammability characteristics of the CO₂/HFO1123/R290 and R1132(E)/R32/R1234yf systems have been evaluated. The flammability characteristics of binary mixture systems and pure components required for evaluating ternary mixture systems were also assessed as necessary. During these evaluations, for refrigerants with extremely low flammability that were found to be difficult to assess under normal gravity, microgravity experimental equipment and a lightweight quenching-distance measurement apparatus were used to enable accurate measurement of quenching distance and burning velocity. Furthermore, for the two candidates identified by the Group for Refrigerant Property Evaluation, evaluations were conducted using the flammability-limit measurement method adopted in ASHRAE Standard 34. This provided data that can serve as supporting evidence for international and domestic registration under ASHRAE 34, ISO

817, and Japan's High Pressure Gas Safety Act and related regulations.

Table 5.1-1 Refrigerant flammability class according to ISO 817

Flammability class	Definition
Class 3	$H_c \geq 19 \text{ MJ kg}^{-1}$ or $\text{LFL} \leq 3.5 \text{ vol\%}$
Class 2	$H_c < 19 \text{ MJ kg}^{-1}$ and $\text{LFL} > 3.5 \text{ vol\%}$
Class 2L	In Class 2, $S_{u0,\text{max}} \leq 10 \text{ cm s}^{-1}$
Class 1	No flame propagation

H_c : heat of combustion, LFL: lower flammability limit, $S_{u0,\text{max}}$: maximum burning velocity.

5.2 Evaluation Methods for Flammability Characteristics

As a common procedure for the flammability evaluation, refrigerant gas and air at prescribed pressures were charged using the partial-pressure method into a cylindrical or spherical sealed combustion vessel equipped with observation windows, and a premixed gas of the prescribed concentration was prepared by stirring with an impeller. The concentration adjustment error using the partial-pressure method, expressed as absolute error, was on average $+0.021/-0.003 \text{ vol\%}$ with respect to the mixed-refrigerant concentration (vol%) and $0.005 \text{ vol\%}$ with respect to the component-refrigerant concentration (vol%) in the evaluation of flammability, or explosion, limits. For the ignition of the premixed gas, the flammability-limit measurements used an AC spark generated by a neon transformer with a secondary voltage of 15 kV, current of 30 mA, and discharge duration of 0.2 s. For burning velocity and quenching distance, a DC high-voltage power supply was used. The gas ignition method was based on charging a capacitor at a voltage low enough not to cause discharge, referred to as the main discharge, and superimposing a short high-voltage pulse, or trigger, to initiate dielectric breakdown between opposing electrodes and thereby start the main discharge.

5.2.1 Evaluation Method for Flammability Limits

The flammability limits were measured using the explosion-limit measurement method for fluorocarbons, hereafter referred to as the HPGSA method. It was adopted in Japan's High Pressure Gas Safety Act and related regulations in April 2021, as described in the JSRAE standard. A test apparatus conforming to the EN1839B method was used. As the judgment criterion, a mixture concentration at which the maximum pressure rise during the combustion test reached 30% or more of the initial pressure was considered flammable. Subsequently, the lower flammability limit (LFL), upper flammability limit (UFL), and flammability inhibition concentration (FIP) were determined. The LFL values of refrigerants shown for comparison are also based on evaluation results obtained according to the JSRAE standard. Measurements were conducted at a total premixed-gas pressure of 760 Torr (1 Torr = 133.32 Pa) for each concentration and at a temperature of $23 \text{ or } 35 \pm 1 \text{ }^\circ\text{C}$. The difference between the flammability limits at 35 and 23 $^\circ\text{C}$ is very small and is considered to be within the measurement uncertainty.

5.2.2 Evaluation Method for Burning Velocity

Burning velocity was evaluated under normal gravity and microgravity using two measurement and analysis methods: the spherical-vessel central-ignition (SV) and schlieren visualization (SP) methods. Details of each measurement method are given by Takizawa et al. (2012, 2013).

The premixed gas was ignited between opposing tungsten needle electrodes placed at the center of the vessel, with an electrode diameter of 0.3 mm and an electrode gap of approximately 4–5 mm. Typical discharge conditions were a discharge energy of 100 mJ and a discharge duration of 0.3 ms.

For the SV method, a spherical SUS vessel with an inner diameter of 18 cm was used. For each concentration,

measurements were conducted three to six times at total premixed-gas pressures of 650, 760, and 850 Torr. The temporal change in pressure associated with combustion was measured using a strain-gauge pressure transducer. In the SV method, S_u is obtained as a function of the unburned-gas temperature and pressure, and the relationship is expressed as follows:

$$S_u = S_{u0} \cdot (T/298.15)^\alpha \cdot P^\beta \quad (5.2-1)$$

The relationship can be expressed in this form. The three sets of data for the dependence of S_u on T and P obtained at the three initial pressures were fitted using Equation (5.2-1), and S_{u0} , α , and β were determined.

For the SP method, a cylindrical SUS vessel with acrylic or glass windows and an inner diameter and length of 20 cm was used. The flame ball after ignition at the center of the vessel was visualized using the SP method, and the spatial propagation of the flame was recorded using a high-speed video camera at 1000 fps. For each concentration, one measurement was conducted at a total premixed-gas pressure of 760 Torr and temperature of 25 ± 1 °C to identify the trend in the concentration dependence of burning velocity for each mixture composition. In the SP method, the burning velocity S_u was obtained from the temporal change in the measured flame radius r_f using the following equation:

$$S_u = (dr_f/dt) \cdot (\rho_b/\rho_u) \quad (5.2-2)$$

Here, r_f was evaluated over the range of 1.5–4.5 cm, where the influence of the ignition discharge becomes small and the pressure rise is sufficiently small to be neglected.

A typical example is shown in the direct photographs in Figure 5.2-1. With a low flame propagation (or burning) velocity, for CO₂/R290 (90/10 wt%) at the stoichiometric concentration, the flame ball propagated upward under normal gravity (1G) because of buoyancy, with a recessed lower portion and extinction at the upper portion. Thus, accurate evaluation was difficult. Therefore, by using a microgravity (mg) environment, an ideal spherically propagating flame unaffected by buoyancy, not in contact with the vessel wall, and free from cooling effects was obtained. The experiments were conducted using an indoor drop facility constructed at the AIST Hokkaido Center, with a free-fall distance of approximately 10 m. In this facility, experimental preparation and release of the drop capsule are performed on the fourth-floor level of the building. The drop capsule is decelerated and stopped without contact by a linear-motor brake at the first-floor level and then recovered to the fourth-floor level. The microgravity duration is approximately 1.3 s, the microgravity level is 10^{-3} G, and the impact during braking is at most 6 G, which is exceptionally small for a drop-tower system. This enables repeated experiments without damaging optical equipment or readjusting the optical system. The combustion apparatus basically used the same equipment as that used under 1 G and was controlled by wiring in the same manner as the experiments under 1 G; therefore, 25 m power and communication cables were connected.

A cylindrical SUS combustion vessel with an inner diameter and length of 15.5 cm was used. Because ignition of extremely weakly flammable gases requires a high-capacity discharge device, the power supply for the main discharge had to be placed outside the drop capsule. However, generating a trigger between the electrodes through a 25 m cable from outside the drop capsule is technically difficult. Therefore, only the trigger-generation mechanism was separately installed near the combustion vessel so that the trigger pulse would not be attenuated. During the microgravity period, the refrigerant–air mixture in the combustion vessel was ignited, pressure and combustion behavior were measured, and the burning velocity was obtained using the SV method.

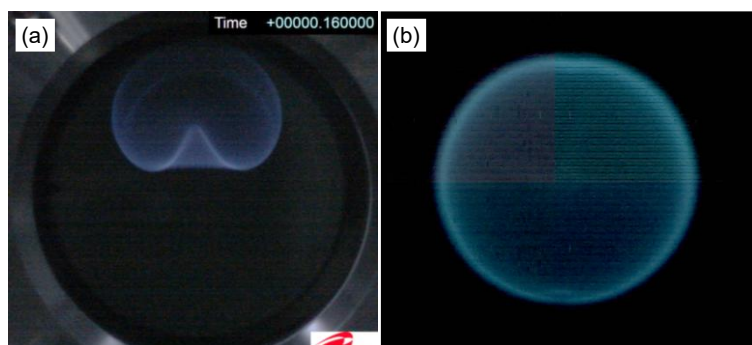


Figure 5.2-1 Example of flame propagation for low-burning-velocity CO₂/R290 (90/10 wt%) mixture: Under (a) normal gravity (1 G) and (b) microgravity (mg). $\phi = 1$.

5.2.3 Evaluation Method for Quenching Distance

Immediately after spark energy is supplied, an initial flame smaller than the minimum flame-ball diameter is extinguished if it experiences large heat loss. Flame propagation continues, although decelerated, even if heat loss occurs after the flame has grown larger than the minimum flame-ball diameter. The quenching distance is considered to correspond to the diameter of the minimum flame ball capable of self-sustained propagation. Compounds with low burning velocities have low heat-release rates and, therefore, large quenching distances. By placing solid parallel plates at an electrode spacing corresponding to the minimum flame-ball diameter, the quenching distance can be determined more clearly than for propagation in the gas phase. As described by Takizawa et al. (2015), the measurements were performed using an apparatus based on the ASTM E582 apparatus modified for the evaluation of weakly flammable gases. For weakly flammable flames, when parallel plates with a diameter of 25 mm are placed vertically, as in the ASTM E582 method, the flame rising owing to buoyancy escapes from the upper side between the plates, resulting in underestimation of the quenching distance. Therefore, larger parallel plates with a diameter of 100 mm were placed horizontally to prevent the flame from escaping from between the plates owing to buoyancy. The quenching distance d_q was defined as the average of the maximum plate spacing at which sustained propagation did not occur, or quenching occurred, and the minimum plate spacing at which sustained propagation occurred. First, the refrigerant concentration was varied over a wide range, and the obtained values of d_q at each concentration were fitted with a quadratic or cubic function to determine the minimum value of d_q and the concentration at which it occurred. Next, additional ignition tests were conducted at that concentration, and the final quenching distance, $d_{q,min}$, was defined as the average of the maximum plate spacing at which no sustained propagation occurred in 10 trials and the minimum plate spacing at which sustained propagation occurred at least once. The measurement error was defined as the sum of half the difference between these two spacings and the parallelism error of the plates, which was at most 0.05 mm. Measurements were conducted at a total premixed-gas pressure of 760 Torr and temperature of 25 ± 1 °C for each concentration.

5.3 Evaluation of Flammability Characteristics of Candidate Refrigerant Mixtures

5.3.1 Evaluation of the R1132(E)/R32/R1234yf Mixture System

HFO-1132(E) is a low-boiling-point compound with a GWP of less than 1 and has attracted interest in the Group for Refrigerant Property Evaluation as a next-generation refrigerant candidate from the perspectives of both GWP and availability. To date, R1132(E)-based refrigerants developed by refrigerant manufacturers and registered in international standards include the R474 series (R1132(E)/R1234yf) and R479 series (R1132(E)/R32/R1234yf).

First, the dependence of the flammability characteristics of the R1132(E)/R1234yf mixture system on mixture

composition is depicted in Figures 5.3-1 to 5.3-4. For comparison, Figure 5.3-2 also shows the evaluated values for the worst-case formulation (WCF) compositions of R474A and R474B, i.e., the WCF compositions from the perspective of flammability considering tolerances during production of the refrigerant mixtures. Only the LFL of R474B(WCF) appears to deviate downward from the overall trend of the present evaluation results; however, this is because the concentration interval in the LFL measurements for these two refrigerants was 1 percentage point, and the deviation from the present evaluation is within 1 percentage point, which can be considered within the error range. Consequently, the R1132(E)/R1234yf system was found to fall into Class 2 or 2L at all mixture ratios and to be mildly flammable when the R1132(E) fraction is 61 wt% or less. In addition, although neat R1132(E) has a quenching distance as small as that of R290, the quenching distance became $d_{q,min} > 5$ mm, comparable to those of existing mildly flammable refrigerants, when the R1132(E) fraction was approximately 50 wt% or less.

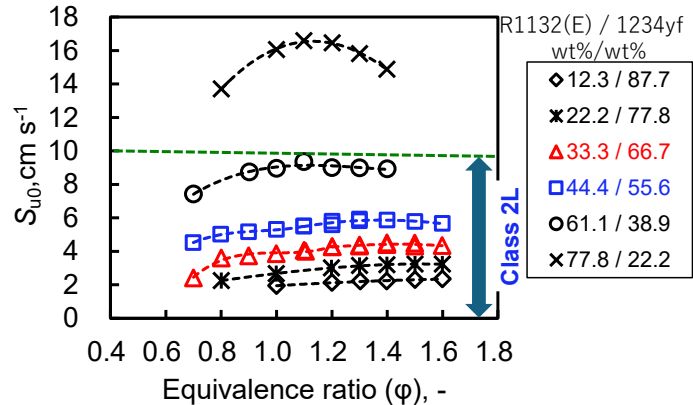


Figure 5.3-1 Concentration dependence of S_{u0} for R1132(E)/R1234yf mixtures

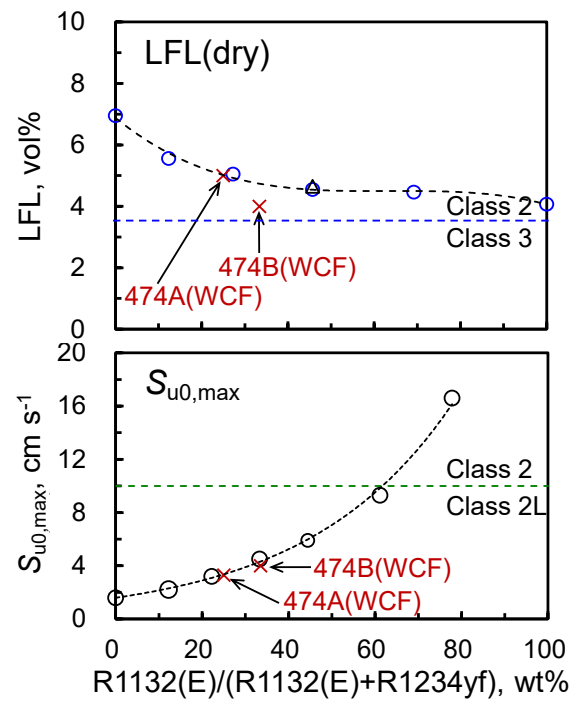


Figure 5.3-2 Flammability characteristics and flammability class of R1132(E)/R1234yf mixtures as a function of mixture composition

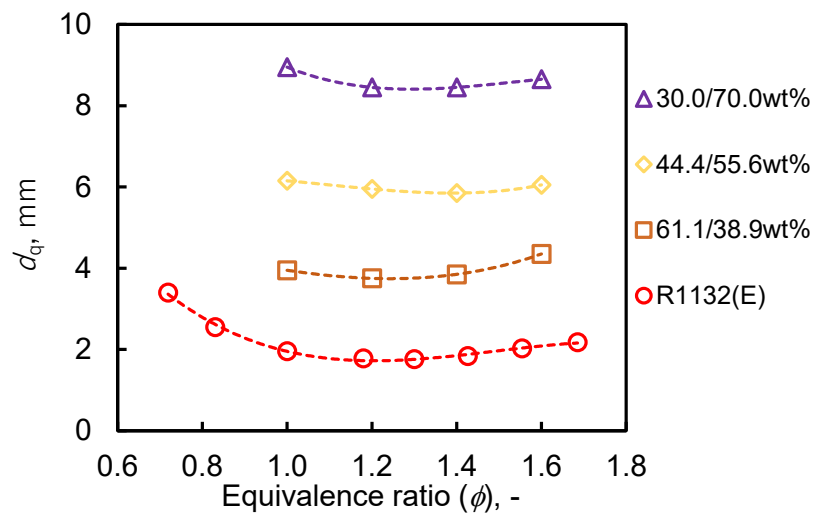


Figure 5.3-3 Concentration dependence of d_q for R1132(E)/R1234yf mixtures in the standard test condition

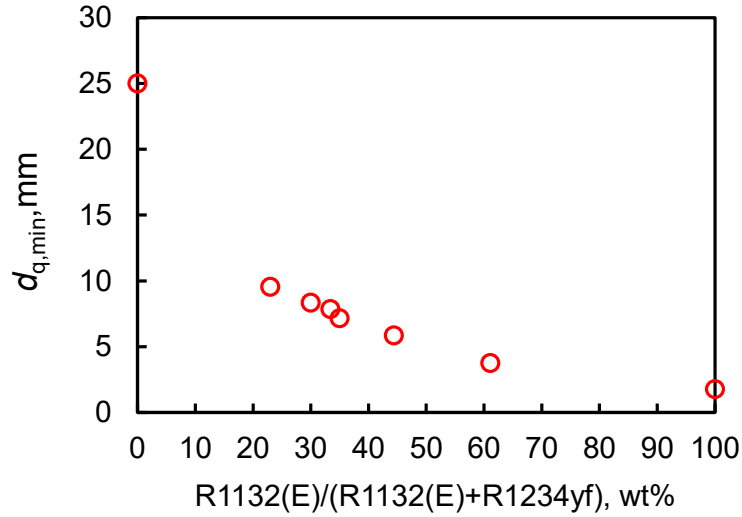


Figure 5.3-4 $d_{q,min}$ of R1132(E)/R1234yf mixtures as a function of mixture composition

Next, the addition of R32 to R1132(E)/R1234yf is considered to improve refrigerant performance. However, because this also increases the GWP, the Group for Refrigerant Property Evaluation evaluated the R1132(E)/R32(10 wt%)/R1234yf system by fixing the R32 addition at 10 wt% (GWP <70) as a refrigerant candidate.

The dependence of the flammability characteristics of the R1132(E)/R32(10 wt%)/R1234yf mixture system on mixture composition, with the R1132(E) fraction varied from 0 to 90 wt%, is depicted in Figures 5.3-5 to 5.3-8. The R1132(E)/R32(10 wt%)/R1234yf system was found to fall into Class 2 or 2L at all mixture ratios and to be mildly flammable when the R1132(E) fraction was 57 wt% or less. Regarding the quenching distance, as shown in Figure 5.3-7, the concentration dependence of the quenching distance for R1132(E)/R32/R1234yf (30/10/60 wt%) was measured, yielding $d_{q,min} = 7.45 \pm 0.10$ mm. This value was comparable to that of neat R32. Furthermore, as summarized in Figure 5.3-8, based on the relationship between the minimum quenching distance and the maximum burning velocity obtained to date for the R1132(E)/R32/R1234yf system, the following correlation between the quenching distance and burning velocity was obtained for mixture compositions excluding neat R1234yf. Essentially, the quenching distance was found to be inversely proportional to the burning, or mass burning, velocity. This indicates that the quenching distance of this mixture system can be estimated with reasonable accuracy for arbitrary mixture compositions.

$$d_{q,min} = 41.65 \cdot (\rho_u \cdot S_{u0,max})^{-0.935} \quad (5.3-1)$$

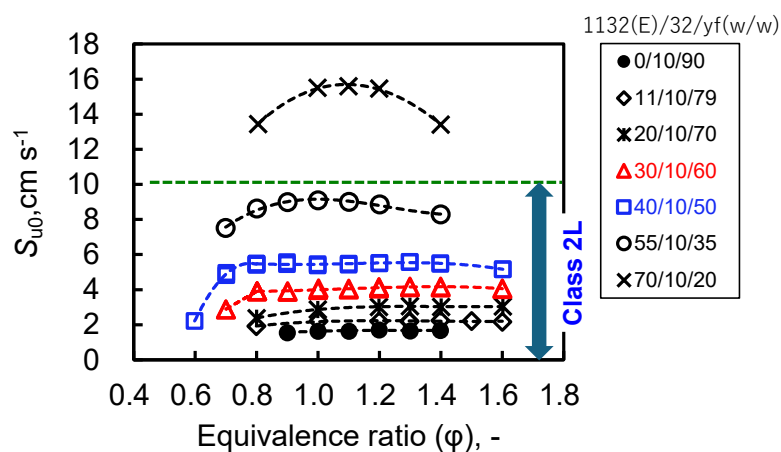


Figure 5.3-5 Concentration dependence of S_{u0} for R1132(E)/R32 (10 wt%)/R1234yf mixtures

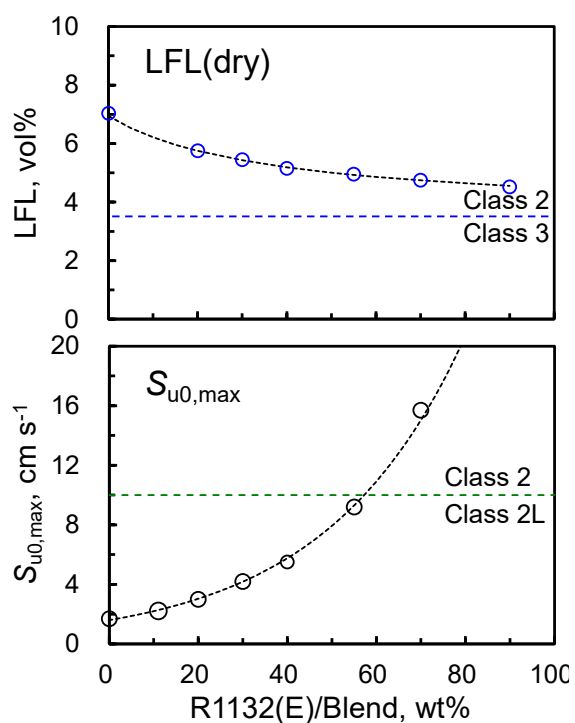


Figure 5.3-6 Flammability characteristics and flammability class of R1132(E)/R32(10 wt%)/R1234yf mixtures as a function of mixture composition

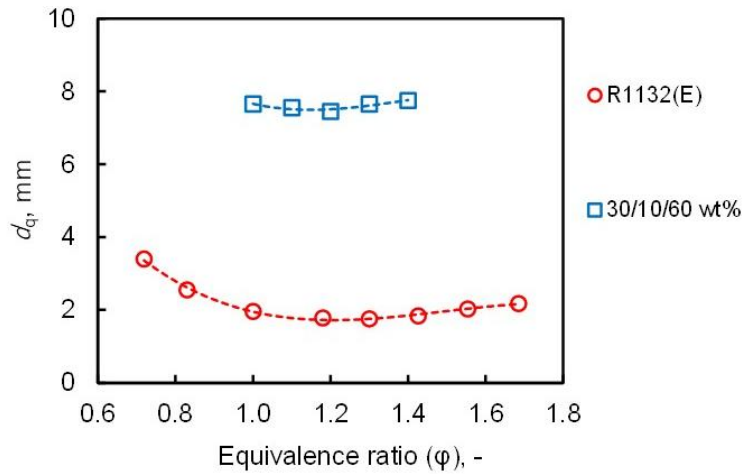


Figure 5.3-7 Concentration dependence of d_q for R1132(E)/R32/R1234yf (30/10/60 wt%) mixture in the standard test condition

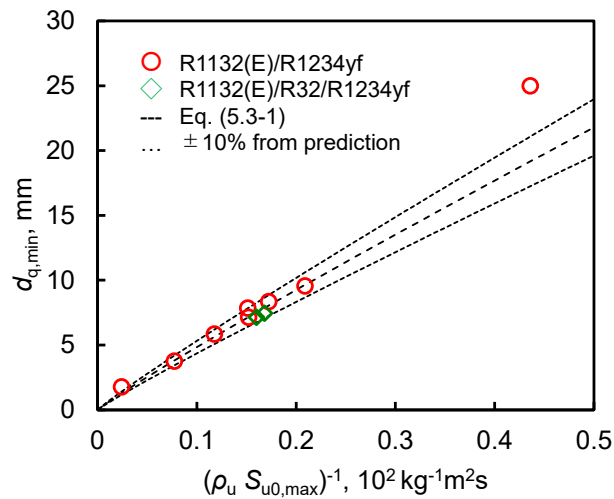


Figure 5.3-8 Relationship between $d_{q,min}$ and $S_{u0,max}$ for R1132(E)/R32/R1234yf mixtures

Among these, two compositions further narrowed down by considering the self-decomposition explosibility, or disproportionation, of R1132(E) under high-temperature and high-pressure conditions, namely 30/10/60 wt% and 40/10/50 wt%, are shown in Table 5.3-1 together with R479A and R479B. For these two candidates, flammability-limit measurements were also conducted using the ASHRAE method, and the corresponding values are shown. Both candidates have low GWP and are mildly flammable, and their flammabilities are considered to be only slightly higher than that of neat R1234yf.

Table 5.3-1 Summary of the flammability characteristics of two candidates narrowed down in the group for refrigerant evaluation

R1132(E)/32/1234yf, wt%	LFL, vol%		LFL by ASHRAE method, vol%		$S_{u0,max}$, cm s ⁻¹	Flammability class
	0%RH	50%RH	23 °C, 50% RH	60 °C, 50% RH@23 °C		
① 30/10/60	5.45	5.25	5.5	5.2	4.2	2L
② 40/10/50	5.15	5.15	5.2	5.1	5.5	2L
R479A(WCF) 30/19.5/50.5	5.0	5.0	6.1 ^a		4.4	2L
R479B(WCF) 25/42/33	7.0	7.0	7.9 ^a		6.6	2L

^a Data from ASHRAE Standard 34.

5.3.2 Evaluation of the CO₂/HFO-1123/R290 Mixture System

Among the components of this ternary mixture system, CO₂ and propane (R290) are representative low-GWP natural refrigerants and are also used as components in a wide variety of refrigerant mixtures. Therefore, the flammability characteristics of CO₂/R290 mixtures, with a CO₂ fraction of 0–100 wt%, were first quantified and formulated. Details are described by Takizawa et al. (2024), and the results are summarized in Figures 5.3-9 and 5.3-10. The burning velocity under low-flammability conditions with a CO₂ fraction of 90 wt% was evaluated under microgravity, thereby enabling quantification of burning velocity in a mildly flammable region that had previously been difficult to assess. Consequently, the flammability characteristics from high flammability to near nonflammability could be formulated with good accuracy based on the thermal dilution effect of CO₂. Consequently, the CO₂ mass fractions required to reduce the mixture to specified flammability classes, denoted as y_n , where n represents the flammability class, were obtained as $y_2 = 0.59$, $y_{2L} = 0.85$, and $y_1 = 0.915$. These results indicate that most of the mixture must consist of CO₂ to reduce the flammability of CO₂/R290.

Next, regarding the estimation of the quenching distance for the CO₂/R290 mixture system, an estimation method for the quenching distance of mixtures of R50 with N₂ and CO₂ had previously been examined, and the following equation was derived from the heat-loss theory of flame balls (Takizawa et al., 2020).

$$d_{q,min} = a \cdot [0.0258 \cdot (T_m/298)^{0.7} / (\rho_u \cdot S_{u0,max})] \quad (5.3-2)$$

Here, a is a parameter representing the similarity of the minimum flame-ball structure, independent of the compound. $a = 9.95$ was obtained from experimental results for 17 chemical species. The same equation was adopted without modification in this study. This function is shown by the solid line in Figure 5.3-10. The measured results for neat R290 ($d_{q,min} = 1.745$ mm) and CO₂/R290 (85/15 wt%) are also shown in the figure. Even when Equation (5.3-2) was applied directly without adjustment, the results agreed within an error of approximately 10%. For further improved accuracy, a can be recalculated using 18 chemical species by adding the CO₂/R290 (85/15 wt%) result obtained in this study to the original dataset. In any case, $d_{q,min}$ can be estimated with reasonable accuracy for arbitrary mixture ratios.

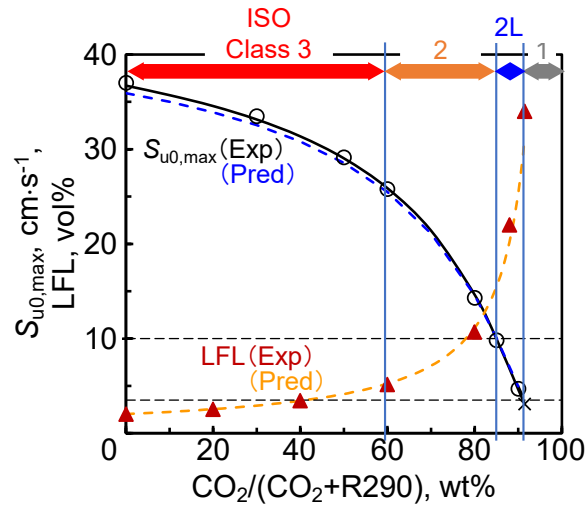


Figure 5.3-9 Flammability characteristics and flammability class of CO₂/R290 mixtures as a function of mixture composition

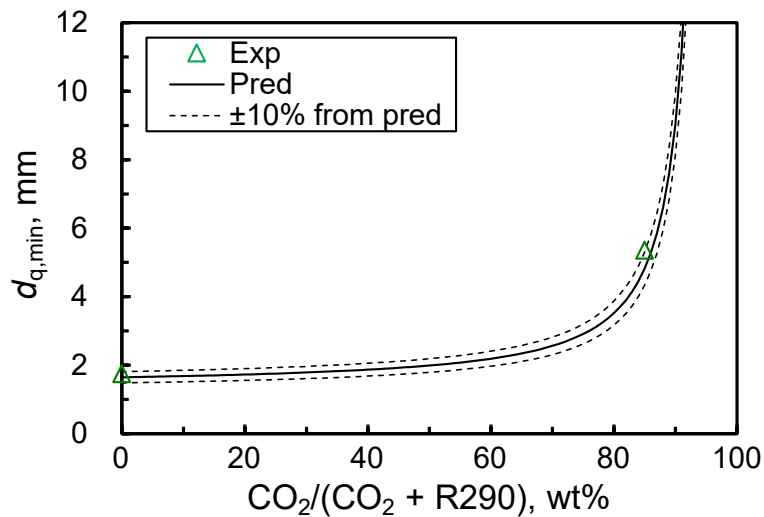


Figure 5.3-10 $d_{q,min}$ of CO₂/R290 mixtures as a function of mixture composition

As described earlier, because the flammability characteristics of the CO₂/R290 system could be formulated, we expect that the flammability characteristics of mixture systems containing an additional third component can also be quantified with good accuracy. As an example, the results for the flammability limit (LFL) of the CO₂/HFO-1123(50 wt%)/R290 system and the CO₂ fraction required to reduce the flammability of the CO₂/HFO-1123/R290 mixture system are shown in Figures 5.3-11 and 5.3-12. Neat HFO-1123 corresponds to a mildly flammable refrigerant, and 31 wt% CO₂ is required to render it nonflammable, that is, $y_1 = 0.31$. However, when R290 is added to HFO-1123, the required amount of CO₂ increases substantially. For HFO-1123/R290 = 88/12 wt%, $y_{2L} = 0.52$, and for 75/25 wt%, $y_{2L} = 0.66$. Thus, a large amount of CO₂, comparable to that required for the CO₂/R290 system, was found to be necessary to reduce the mixture to the mildly flammable class.

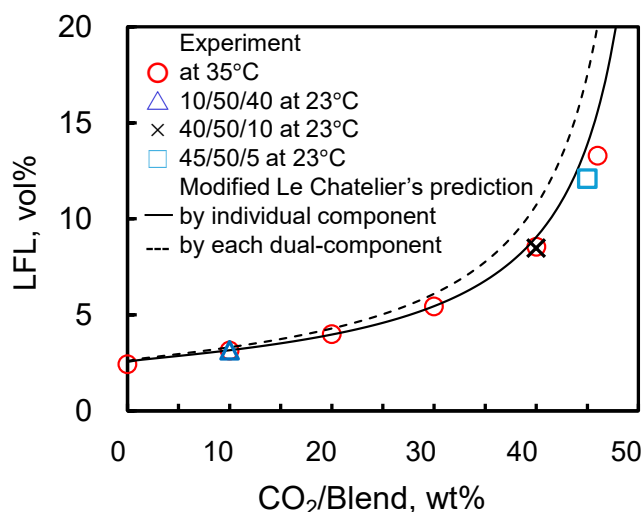


Figure 5.3-11 LFL of CO₂/HFO-1123(50 wt%)/R290 mixtures in the dry condition.

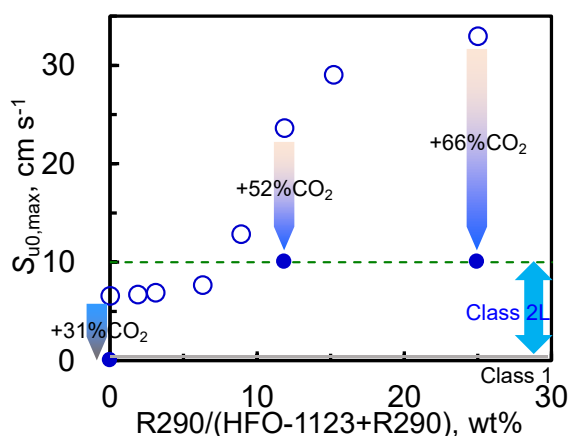


Figure 5.3-12 $S_{u0,max}$ and CO₂ composition ratio (by mass) necessary for lower flammability classes for CO₂/HFO-1123/R290 mixtures

5.4 Summary

To contribute to the screening of refrigerant candidates examined by the Group for Refrigerant Property Evaluation from the perspective of flammability evaluation, we evaluated the dependence of various flammability characteristics on mixture composition for the R1132(E)/R32/R1234yf and CO₂/HFO-1123/R290 systems. These flammability characteristics are the flammability limits, burning velocity, and quenching distance. In particular, for mildly flammable conditions corresponding to specified inert gases, where the maximum burning velocity is 10 cm s⁻¹ or less, reliability was confirmed through microgravity experiments, comparison of evaluation results obtained by the HPGSA and ASHRAE methods, and cross-validation between burning velocity and quenching distance. The following outcomes were obtained.

The flammability characteristics of the R1132(E)/R32(10 wt% fixed)/R1234yf mixture system, which was selected as a refrigerant candidate by the Group for Refrigerant Property Evaluation, were evaluated. First, various flammability characteristics of neat R1132(E), for which flammability characteristics had not been clarified, were evaluated under a range of conditions. Next, the binary mixture system R1132(E)/R1234yf was evaluated under standard conditions, and the resulting data were formulated as equations. Based on these results, the dependence of the flammability characteristics

of the ternary mixture system on mixture composition was clarified, and the mixture conditions under which the system is classified as mildly flammable were identified. Furthermore, for the two candidates narrowed down by the Group for Refrigerant Property Evaluation, namely 30/10/60 and 40/10/50 wt%, LFL measurements were conducted using the ASHRAE method specified in the international standard ISO 817. Thus, data suitable for applications for domestic and international standard registration were obtained.

The flammability characteristics of the ternary CO₂/HFO1123/R290 mixture system were also evaluated. First, for the required binary CO₂/R290 mixture system, flammability characteristics such as flammability limits, burning velocity, heat of combustion, and quenching distance were evaluated under standard conditions and formulated as equations. Thus, flammability-characteristic data for arbitrary mixture compositions ranging from nonflammable to highly flammable were obtained. Subsequently, the ternary mixture system was evaluated, and the mixture conditions corresponding to the mildly flammable class were clarified.

In addition, consistency between measured values, such as burning velocity and quenching distance, and theoretical models was examined to improve reliability, while efforts are also being made to establish methods for estimating flammability. Based on these outcomes, comprehensive refrigerant evaluation with a view toward practical use in actual equipment will be advanced through collaboration with the Group for Refrigerant Property Evaluation and other research groups.

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6. Cycle Characteristics of Low-GWP Refrigerant Mixtures and Performance

Evaluation Using a Refrigeration Cycle Model Test Apparatus

(Kyushu Sangyo University)

This section summarizes the results of comparing the cycle characteristics of the conventional refrigerant R32 and the low-GWP refrigerant mixture R474B using a refrigeration cycle model test apparatus intended for residential air-conditioning applications. The discussion focuses on three points: (1) the performance differences that appear between the two refrigerants under the same test apparatus and evaluation indices; (2) the dominant factors causing these performance differences; (3) the positioning of R474B in future applications based on the comparison results.

In particular, this study used six main indicators: the coefficient of performance (COP) of the entire system, the COP of the cycle alone, the temperature distribution in the heat exchangers, the pressure ratio, irreversible losses, and compressor efficiencies. Rather than simply comparing capacity, the objective was to clarify where losses are concentrated within the cycle. This approach enables discussion not only of the current performance of R474B but also of the extent of its potential if equipment design is optimized in the future.

6.1 Experimental Apparatus and Evaluation Method

A schematic of the apparatus is shown in Figure 6.1-1. The test apparatus used in this study consisted of a refrigerant loop composed of a compressor, a cross-fin tube condenser, an electronic expansion valve, a cross-fin tube evaporator, and two heat-source water loops on the condenser and evaporator sides. This basic configuration simulates the vapor-compression heat-pump cycle of a residential air-conditioning system. Temperature and pressure measurement points were installed at the main locations in the refrigerant loop, and refrigerant mass flow rate, heat-source water flow rate, compressor input power, and heat exchange rate were measured.

Cross-fin tube heat exchangers were used for both heat exchangers in the test section. On the heat-source side, water was used to simulate the boundary conditions of an air heat source, and the flow rates on both the condenser and evaporator sides were controlled such that the inlet–outlet temperature differences of the heat-source water remained within prescribed ranges. Simulating the heat source with water in this manner improved experimental reproducibility and facilitated comparison of differences in refrigerant-side temperature distribution and pressure loss.

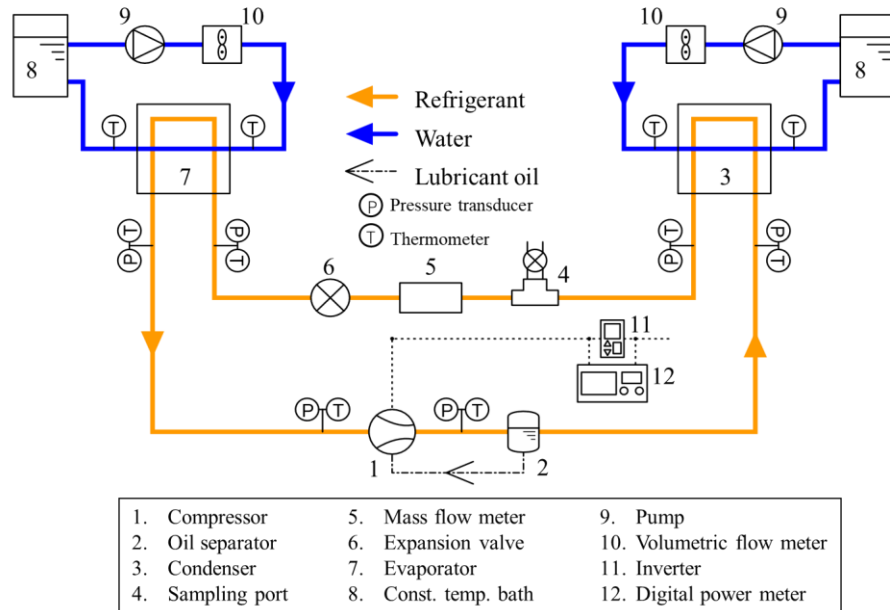


Figure 6.1-1 Schematic view of the cycle experimental loop

Among the refrigerants compared in this section, R32 is a conventional refrigerant widely used in current residential air conditioners and is positioned as the reference refrigerant. In contrast, R474B is a refrigerant mixture aimed at reducing GWP and is considered promising from the perspective of reducing environmental impact while being characterized by low-pressure operation and temperature glide. Therefore, the comparison between the two refrigerants must consider not only the magnitude of GWP but also the temperature distribution in the heat exchangers, pressure loss, and compressor compatibility.

In the experiments, the heat-source water temperatures were fixed for heating and cooling conditions, and the compressor frequency was adjusted for the heat exchange rate to reach the prescribed value. Refrigerant charge amounts of 1.45 kg for R32 and 1.92 kg for R474B were adopted. These conditions enable stable cycle operation for each refrigerant and representative performance comparisons. For R32, based on the results of examining the optimum charge amount, a condition was used that avoided an increase in condensing pressure due to excessive subcooling.

The evaluation indices used were the COP of the entire system, including the inverter (COP_{system}), COP of the cycle alone, excluding the inverter (COP_{cycle}), temperature distribution in the heat exchangers, pressure ratio, total irreversible loss and its breakdown, overall compressor efficiency, inverter efficiency, compressor efficiency, isentropic compression efficiency, and volumetric efficiency. These indices enable us to separate the performance difference of the overall system from the internal factors that generate it. The COP_{system} and COP_{cycle} are respectively expressed as follows:

$$COP_{system} = m_r \Delta h / E_{inv} \quad (6.1-1)$$

$$COP_{cycle} = m_r \Delta h / E_{compr} \quad (6.1-2)$$

In data reduction, state properties at each point were calculated from the measured temperature and pressure values, and the heat exchange rates of the heat exchangers, compressor efficiencies, irreversible losses, and COP were evaluated. In particular, irreversible losses were separately organized into contributions from the condenser, evaporator, expansion valve, compressor, and pressure losses, thereby clarifying in which component the difference became larger. When evaluating low-GWP refrigerant mixtures, comparison based only on the overall COP makes identifying the dominant factors difficult; therefore, such component-wise organization is effective.

The heat exchange rate was calculated from the temperature difference and flow rate of the heat-source water, and the compressor efficiencies were evaluated from the compressor inlet and outlet state properties and the input power.

Table 6.1-1 shows the experimental conditions. These conditions were set to represent heating and cooling operation.

The heat-source inlet temperatures were determined based on the JIS standard, and the temperature changes of the indoor and outdoor units were set to 7 and 5 °C, respectively.

Table 6.1-1 Experimental conditions

			Experimental condition	
			Heating	Cooling
Water temperature (in→out)	Condenser	[°C]	20→27	35→40
	Evaporator		10→5	27→20
Heat exchange amount		[kW]	2.0~2.8	2.0~2.6

6.2 Cycle Performance Based on the Existing Refrigerant as a Reference

In evaluating a new refrigerant, first, the cycle characteristics exhibited by the reference refrigerant R32 should be organized on the same test apparatus. R32 has an established record of use as a refrigerant for current residential air conditioners and exhibits behavior close to the design assumptions of this test apparatus in terms of operating pressure, compressor compatibility, and temperature distribution in the heat exchangers. Therefore, the results for R32 serve as the reference axis for evaluating the performance of R474B.

From the perspective of refrigerant charge amount, the cycle using R32 became stable at approximately 1.45 kg, and the condition that provided the best balance between increasing subcooling and rising condensing pressure was obtained. When the charge amount was increased, the subcooling at the condenser outlet increased. However, the increase in compressor work owing to the increase in condensing pressure became relatively large, and the COP of the overall system instead decreased. Thus, the optimum charge amount can be understood as the balance point between securing capacity and limiting compressor load.

Figure 6.2-1 shows the cycle COP of R32 under heating and cooling conditions. An overview of the cycle characteristics of R32 under both conditions indicates that the cycle COP gradually decreases as the heat exchange rate increases. This is because the compressor frequency and input power increase to accommodate the increased heat exchange rate, while the pressure ratio and pressure losses also increase. However, the decreasing trend is relatively moderate, and the temperature distribution in the heat exchangers does not exhibit any extreme discontinuity. Hence, R32 is a suitable reference refrigerant.

Figure 6.2-2 shows the temperature distribution in the heat exchanger for R32 under the heating condition. For the temperature distribution in the heat exchanger, R32 exhibits a relatively straightforward change in the temperature difference between the refrigerant and the heat-source water in both the condenser and evaporator, and the cycle changes in a reasonable manner in response to changes in the heat exchange rate. In particular, the temperature change in the two-phase region reflects the characteristics of a pure refrigerant, and no additional temperature difference caused by temperature glide, as observed in zeotropic refrigerant mixtures, occurs. Therefore, the interpretation of irreversible losses is also relatively clear, providing the basis for explaining the differences from R474B.

Figure 6.2-3 shows the pressure ratio of R32 under heating and cooling conditions. The pressure ratio of R32 also increases with an increasing heat exchange rate, but the rate of increase is limited. This is because the pressure on the evaporator side is maintained to a certain extent, and the decrease in compressor inlet pressure is limited. Avoiding an excessively large pressure ratio suppresses decreases in compressor efficiency and isentropic compression efficiency, thereby mitigating the decrease in the overall cycle COP.

Figure 6.2-4 shows the total irreversible loss of R32 under heating and cooling conditions. Although not all irreversible

losses in the individual components are shown, from the perspective of irreversible losses, the losses in the condenser, evaporator, compressor, and expansion valve increase with the increasing heat exchange rate for R32. However, the contributions of the individual components are relatively well balanced, and no single component deteriorates dominantly. In particular, although irreversible loss in the condenser tends to be large, this is an inherent contribution of heat exchange accompanied by a temperature difference and remains within an acceptable range in this test apparatus.

Figure 6.2-5 shows the overall compressor efficiency of R32 under heating and cooling conditions. Although not all individual compressor efficiencies are shown, R32 exhibits high compatibility with the compressor and lubricating oil used in this test apparatus, and no major inconsistency is observed in the overall compressor efficiency or volumetric efficiency. The inverter efficiency is also stable and does not decrease significantly with increasing input power. Therefore, the results for R32 can be understood as those of a refrigerant that is well matched to the current system and are appropriate as reference performance for comparison with new refrigerants. The compressor efficiency of refrigerant mixtures is discussed based on these results.

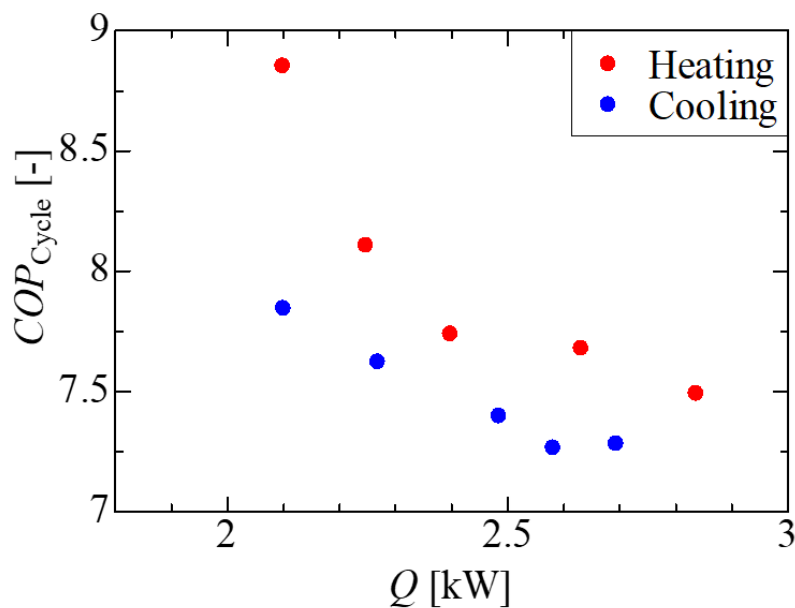


Figure 6.2-1 Cycle COP of R32

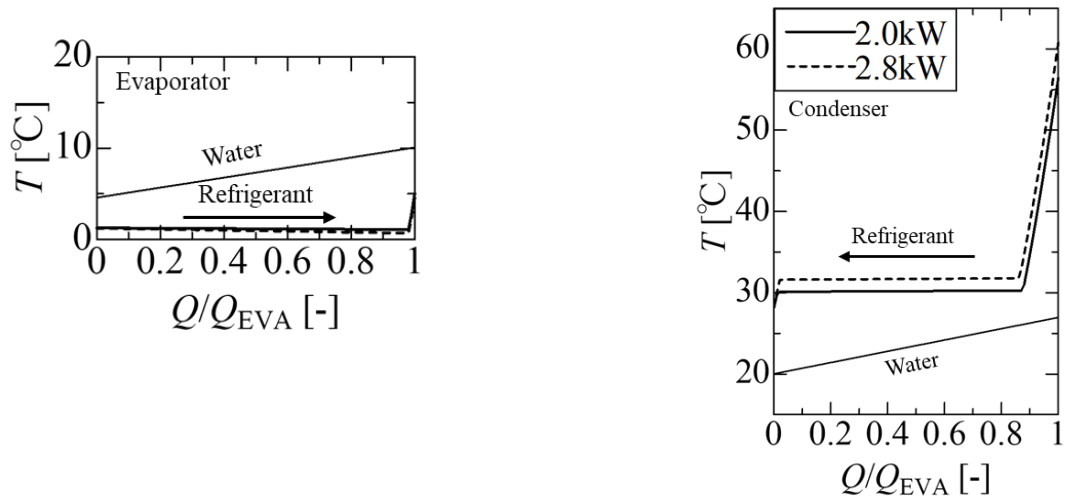


Figure 6.2-2 Temperature distribution of the heat exchanger in the heating condition of R32

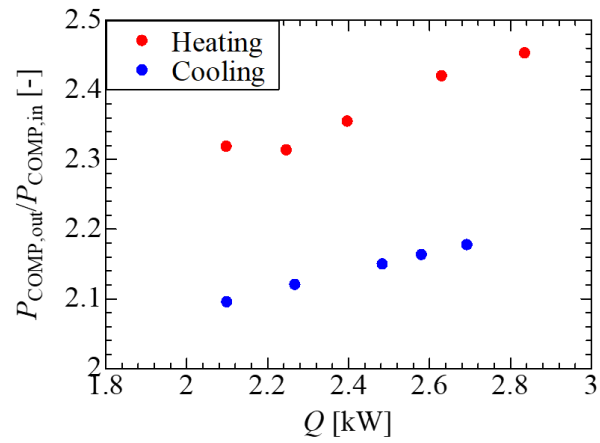


Figure 6.2-3 Pressure ratio of the compressor in the cooling condition

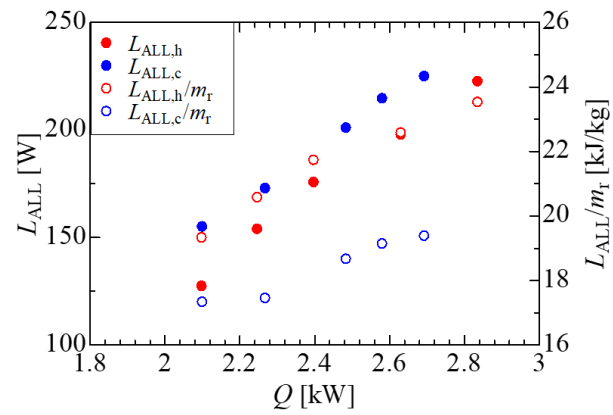


Figure 6.2-4 Irreversible loss in the heating and cooling method of R32

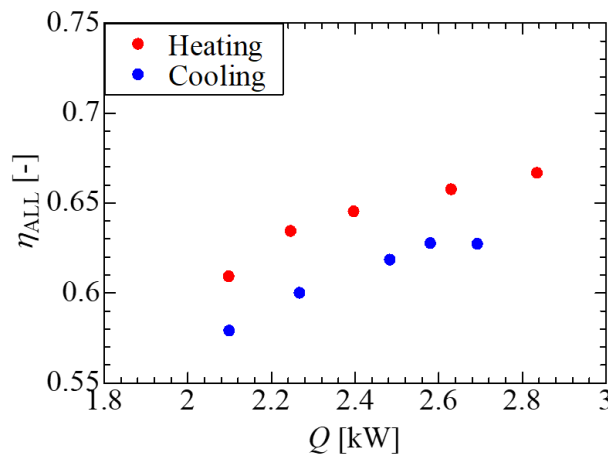


Figure 6.2-5 Total efficiency of the compressor of R32

6.3 Performance Comparison between the New and Existing Refrigerants

6.3.1 Comparison under Heating Conditions

Figures 6.3-1 and 6.3-2 show the system COP and cycle COP of R32 and R474B under heating conditions. Under heating conditions, both the overall system COP and the cycle COP of R474B were lower than those of R32. Although both refrigerants exhibited the same basic tendency for the COP to decrease as the heat exchange rate increased, the decrease was larger for R474B, and the difference tended to widen as the heat exchange rate increased. Therefore, when discussing the heating performance of R474B, in addition to comparing rated points, the point at which the difference is amplified as the load increases should be identified.

One of the most important factors is the difference in operating pressure. Figure 6.3-3 shows the pressure ratio across the compressor under heating conditions. Because R474B operates at a lower pressure than R32, the vapor density decreases when the same heat exchange rate is to be obtained, resulting in a higher refrigerant flow velocity. An increase in flow velocity leads to greater pressure losses in the piping and heat exchangers and causes a decrease in compressor inlet pressure. When the compressor inlet pressure decreases, the pressure ratio and compressor work increase, thereby reducing COP.

Another major factor is the temperature glide resulting from the zeotropic nature of R474B. Figure 6.3-4 shows the temperature distributions in the heat exchangers at a heating capacity of 2.4 kW. The left and right panels represent the temperature distributions in the evaporator and condenser, respectively. In R32, the temperature in the two-phase region remains nearly constant, whereas in R474B, the temperature changes continuously during condensation and evaporation. Consequently, local temperature differences in the heat exchangers tend to increase, enhancing heat-transfer irreversibility. In particular, on the condenser side, the larger difference between the refrigerant temperature and the heat-source water temperature directly leads to an increase in condenser irreversibility and, thus, to a degradation in heating performance.

The comparison of the temperature distributions in the heat exchangers also clearly shows the disadvantage of R474B. For R474B, the condenser inlet temperature and evaporator inlet temperature tend to be lower than those for R32, and the influence of temperature glide in the two-phase region increases the overall temperature difference between the refrigerant and the heat-source water. On the condenser side, this increase in temperature difference is directly reflected in increased irreversible loss, whereas on the evaporator side, it worsens the compressor inlet condition in combination with increased pressure loss.

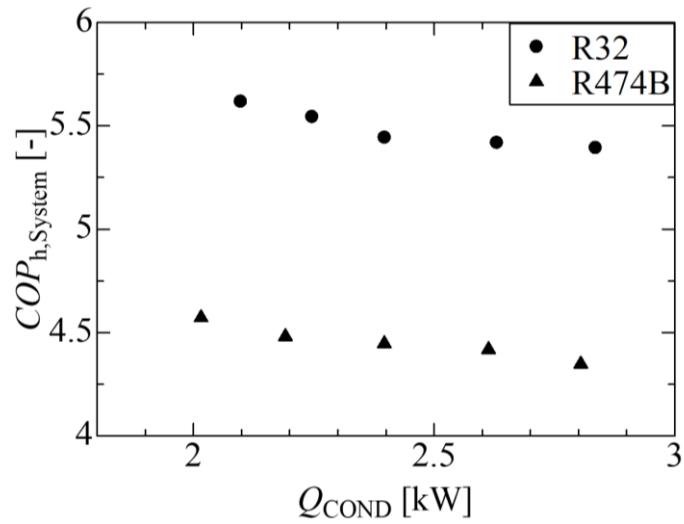


Figure 6.3-1 System COP in the heating condition

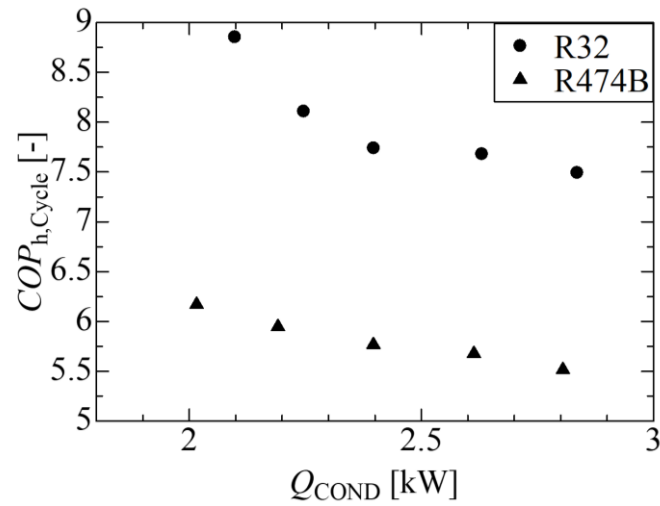


Figure 6.3-2 Cycle COP in the heating condition

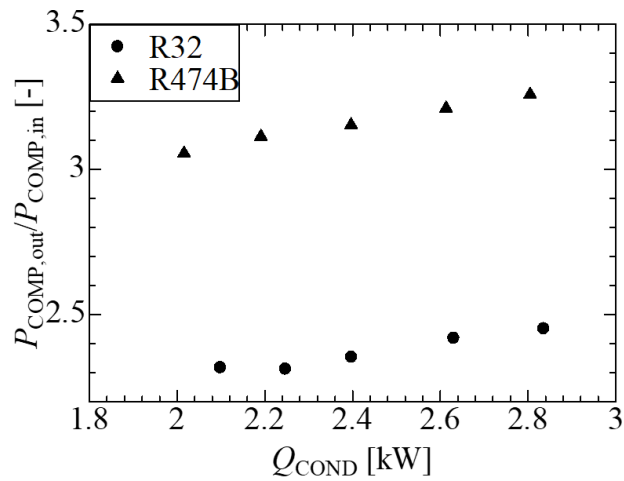


Figure 6.3-3 Pressure ratio of the compressor in the heating condition

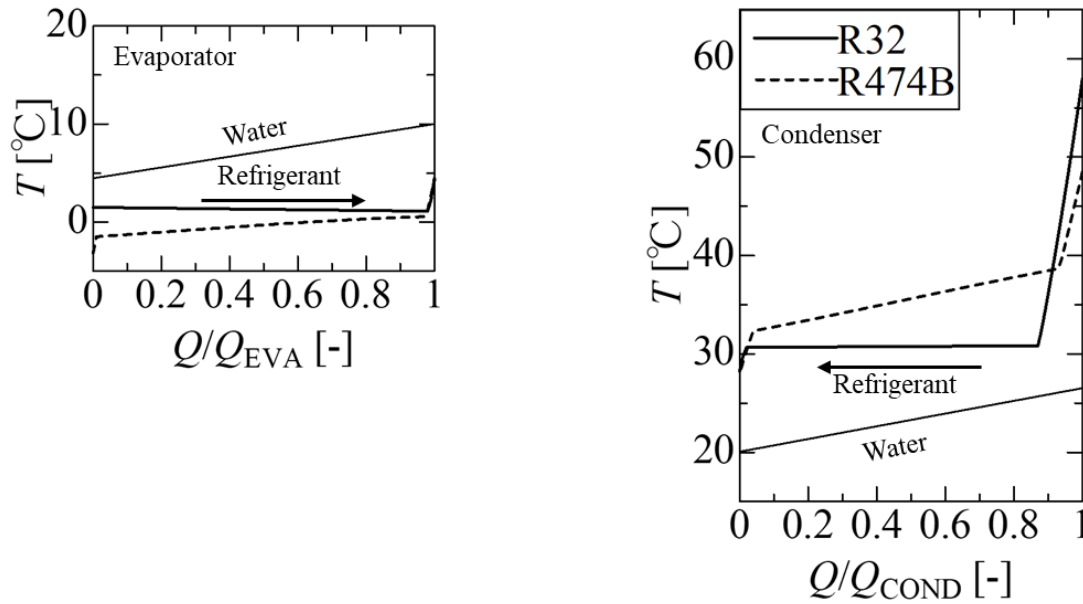


Figure 6.3-4 Temperature distribution of the heat exchanger in the heating condition at 2.4 kW

Figure 6.3-5 shows the total irreversible loss under heating conditions. The breakdown of irreversible losses indicates that the total irreversible loss for R474B exceeds that for R32. In particular, three contributions are dominant: losses caused by temperature differences in the condenser, losses caused by the pressure ratio in the compressor, and pressure losses. In contrast, when considering irreversible loss per unit mass flow rate alone, R474B is not necessarily disadvantageous for all components. This is because the refrigerant mass flow rate itself is larger for R474B, thereby amplifying the total amount of loss.

In summary, for heating conditions, the performance degradation of R474B is not attributable to a single factor but to the combined effects of low-pressure operation, temperature glide, increased pressure loss, and increased pressure ratio. In equipment designed for the current R32 system, these disadvantages act in a superimposed manner, indicating that simple replacement is difficult from the perspective of heating performance.

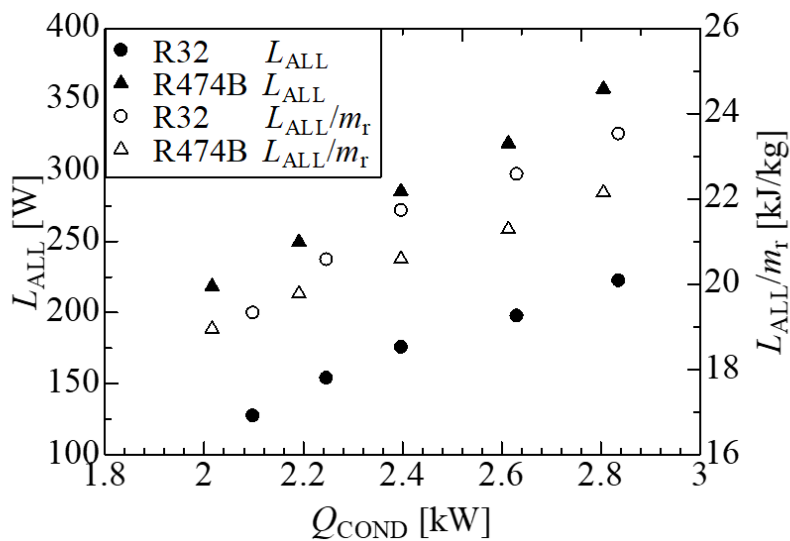


Figure 6.3-5 Irreversible loss in heating condition

6.3.2 Comparison under Cooling Conditions

Figures 6.3-6 and 6.3-7 show the system and cycle COPs of R32 and R474B under cooling conditions. Under the cooling conditions as well, the COP of R474B was lower than that of R32; however, the difference was smaller than under heating conditions. This is because, under cooling conditions, the evaporation temperature and compressor inlet pressure are relatively easier to maintain, and the increase in pressure ratio is not as pronounced as under heating conditions. In other words, although the unfavorable thermophysical properties of R474B also affect cooling operation, the manner in which their influence appears differs considerably depending on the operating conditions.

Figure 6.3-8 shows the temperature distributions in the heat exchangers at a cooling capacity of 2.4 kW. The left and right panels represent the temperature distributions in the evaporator and condenser, respectively. A comparison of the temperature distributions in the heat exchangers indicates that, even under cooling conditions, the temperature difference between the refrigerant and the heat-source water is larger for R474B than for R32, confirming the continuing influence of temperature glide as a zeotropic refrigerant mixture. However, because the pressure drop on the evaporator side is not as severe as under heating conditions, the deterioration of the compressor inlet condition is limited. This contributes to the relatively better performance of R474B under cooling conditions.

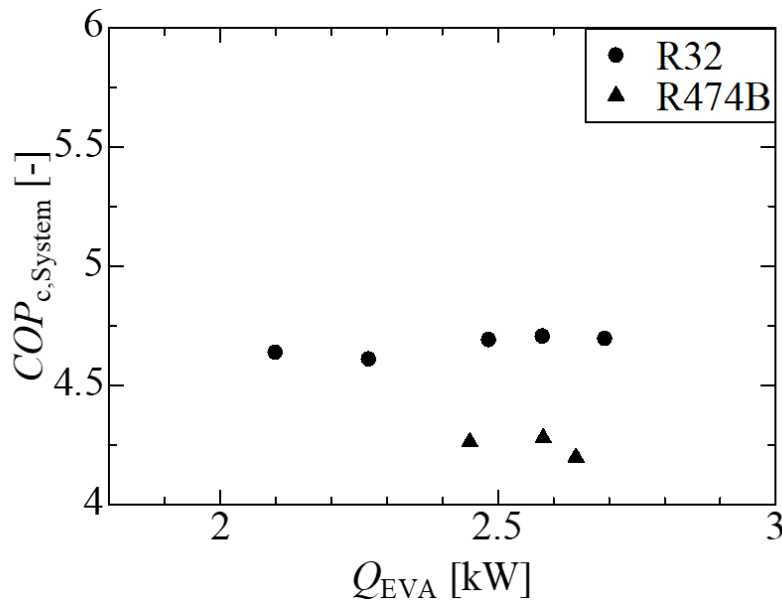


Figure 6.3-6 System COP in the cooling condition

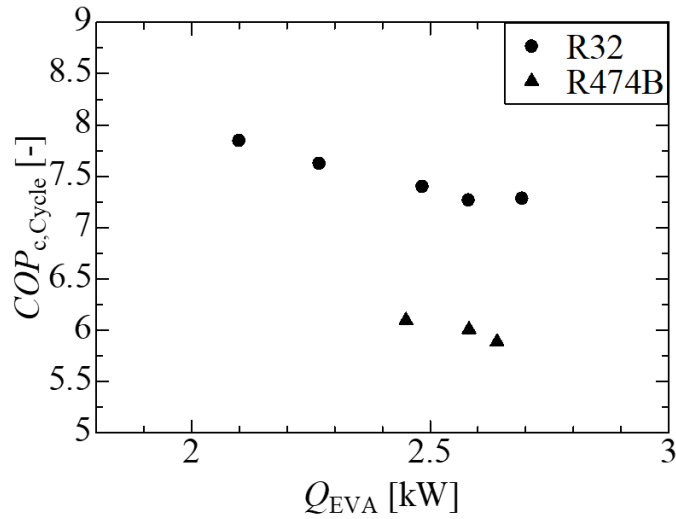


Figure 6.3-7 Cycle COP in the cooling condition

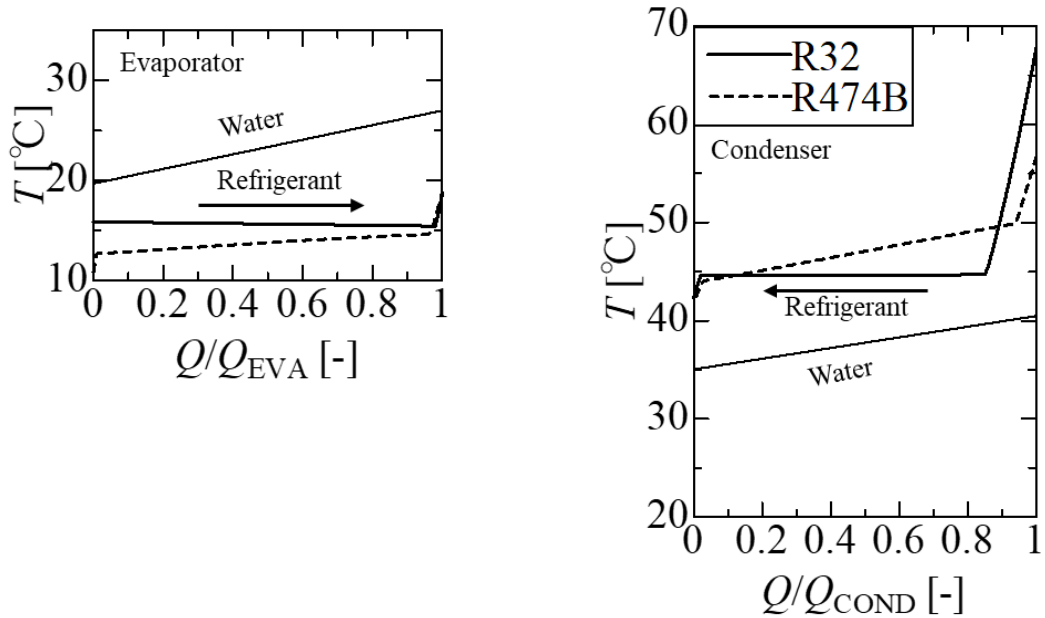


Figure 6.3-8 Temperature distribution of the heat exchanger in the cooling condition at 2.4 kW

Figure 6.3-9 shows the pressure ratio across the compressor under cooling conditions. In terms of pressure ratio, R474B still exhibits higher values than R32 under cooling conditions, but the values are not as high as under heating conditions. The results in the original paper indicate that, under cooling conditions, the pressure ratio remains nearly constant as the heat exchange rate increases, and the rapid deterioration observed under heating conditions is not confirmed. Consequently, compressor irreversibility becomes smaller than under heating conditions, and the disadvantage of R474B is relatively mitigated.

Figure 6.3-10 shows the total irreversible loss under cooling conditions. The breakdown of irreversible losses shows that, even under cooling conditions, the total irreversible loss for R474B exceeds that for R32. However, compared with heating conditions, the dominant factors causing the difference change somewhat, with the contributions of temperature differences in the heat exchangers and increased flow rate becoming relatively more prominent than compressor losses. In other words, under cooling conditions, the more essential problem is not a substantial deterioration in pressure ratio but rather the heat-exchange mismatch resulting from handling a refrigerant mixture with temperature glide in existing

heat exchangers.

These results indicate that the evaluation of R474B should not be determined solely based on heating performance. Although simple replacement is difficult under heating conditions, cooling conditions leave room for design optimization, and practical applicability may be expected by limiting the target applications and operating range.

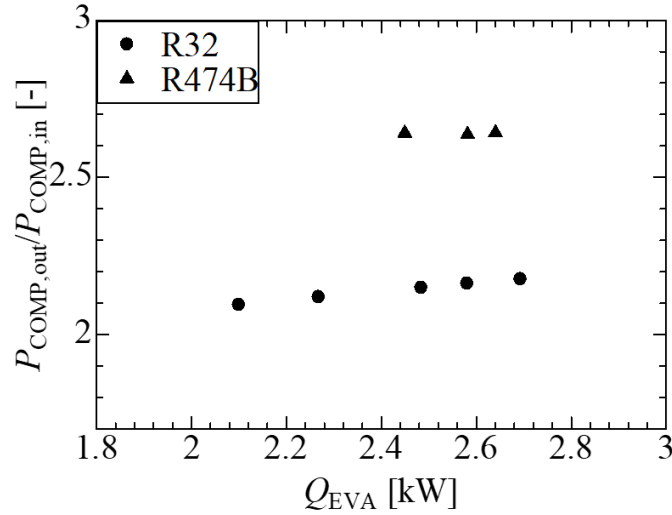


Figure 6.3-9 Pressure ratio of compressor in the cooling condition

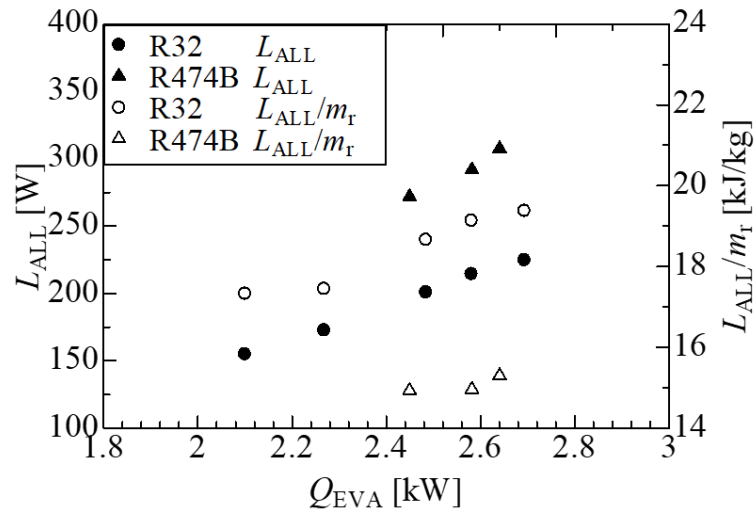


Figure 6.3-10 Irreversible loss in the cooling condition

6.3.3 Comparison of Compressor Efficiencies

Figure 6.3-11 shows the results for the overall compressor efficiency. The overall compressor efficiency was calculated as the product of inverter, compressor mechanical, and isentropic compression efficiencies. In the comparison of overall compressor efficiency, R474B had values lower than those predicted based on R32 under both heating and cooling conditions. Therefore, the performance difference of R474B is related not only to problems on the heat-exchanger side but also to compatibility with the compressor system. When the individual components that constitute the overall efficiency are examined separately, the inverter efficiency itself does not exhibit a substantial difference, whereas differences tend to appear in compressor efficiency and volumetric efficiency.

Figure 6.3-12 shows the results for inverter efficiency. With respect to inverter efficiency, when input power was used

as the basis, that of R474B was comparable to that of R32, and it was slightly higher in some scenarios. This indicates that the inverter of the present test apparatus is not severely incompatible with R474B. Therefore, the performance degradation of R474B cannot be attributed solely to the inverter. Greater emphasis should be placed on the internal behavior of the compressor and its interaction with the lubricating oil, both of which originate from the thermophysical properties of the refrigerant.

Figure 6.3-13 shows the product of compressor mechanical and isentropic compression efficiencies as the compression efficiency. The compression efficiency was lower for R474B. This suggests that the difference in refrigerant thermophysical properties and compatibility with compressor oil are major factors. In other words, even when the same mechanical components are used, changing the refrigerant may alter internal leakage losses, friction losses, and cooling conditions within the compressor. Consequently, the fraction of effective compression work is reduced. Therefore, an appropriate compressor oil should be examined.

Figure 6.3-14 shows the results for volumetric efficiency in the compressor. The volumetric efficiency of R474B was slightly lower than that of R32 under heating conditions, whereas it was not necessarily disadvantageous under cooling conditions. This is because, under heating conditions, the decrease in evaporation temperature and increase in pressure ratio tend to reduce the suction volume, whereas under cooling conditions, the heat-source water temperature on the evaporator side is relatively high and the suction condition is maintained. Therefore, the compressor compatibility of R474B should not be understood as universally poor, but rather as strongly dependent on operating conditions.

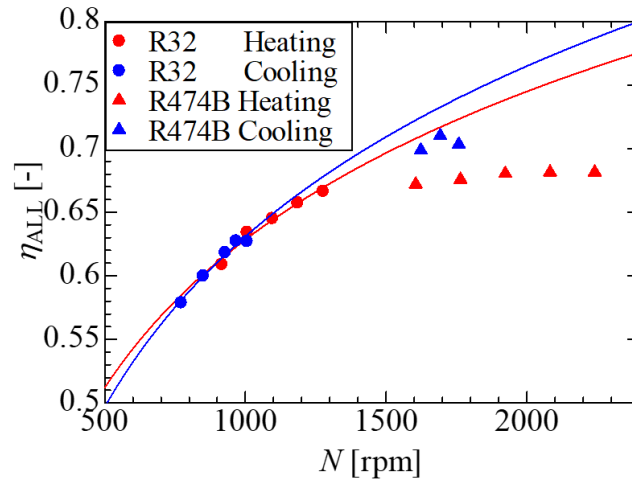


Figure 6.3-11 Total efficiency of the compressor

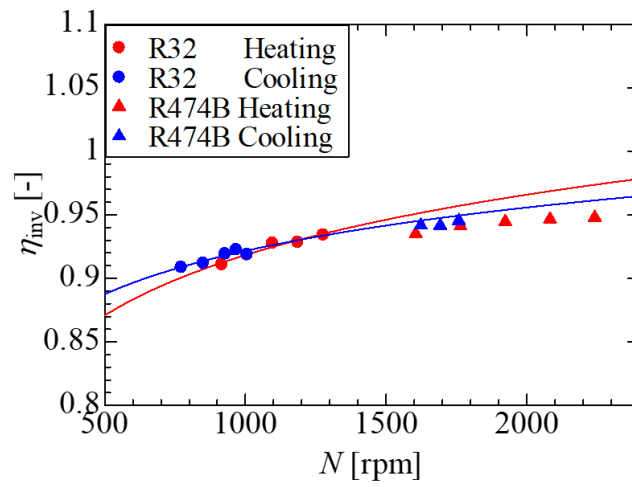


Figure 6.3-12 Inverter efficiency

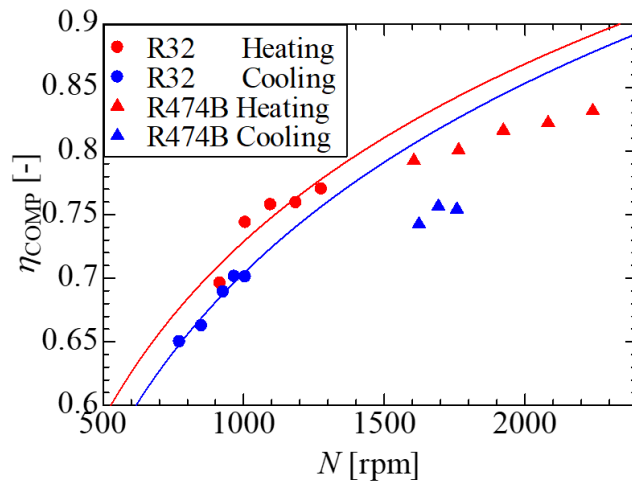


Figure 6.3-13 Compression efficiency of the compressor

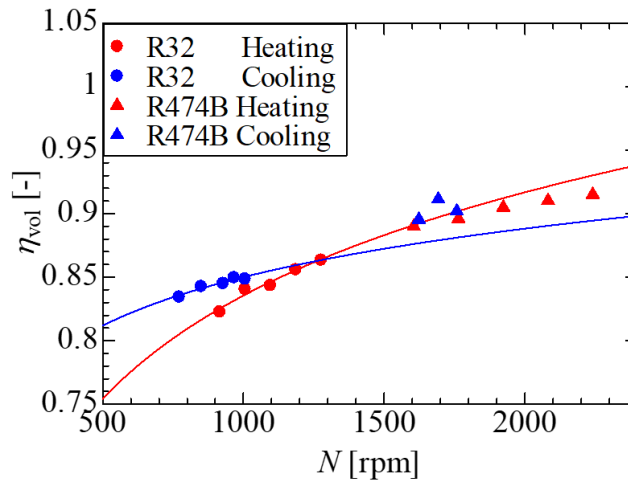


Figure 6.3-14 Volumetric efficiency of the compressor

6.4 Applicability of the New Refrigerant

Based on the comparison results described above, R474B generally exhibited lower performance than R32 in the present test apparatus. However, this evaluation cannot be summarized by a simple binary judgment of whether direct replacement is possible or not. The important point is to identify under which conditions the disadvantages become apparent and to what extent they can be mitigated through changes in equipment design and compressor selection.

The first clear challenge is the large refrigerant flow velocity and pressure loss resulting from low-pressure operation. In flow passages, piping, and heat exchangers designed for R32, the circulation rate required for R474B cannot be sufficiently accommodated, and the increase in pressure loss directly leads to a decrease in the COP. Therefore, when R474B is applied, a low-pressure-loss design of the entire cycle, including the flow cross-sectional area of the heat exchanger, pressure losses in the piping system, and distribution among internal circuits, is essential.

Second, the treatment of temperature glide is important. The temperature glide of a refrigerant mixture tends to appear as an increase in irreversible losses in existing heat exchangers. However, if the temperature profile is appropriately matched with that of the heat source, the temperature difference may instead be reduced. In other words, the temperature glide of R474B is not always disadvantageous but should be evaluated in combination with heat-exchanger design. In the present test apparatus, heat exchangers designed for R32 were used without modification, and this caused the disadvantages to become apparent; however, improvement may be achieved through dedicated design.

Furthermore, compatibility with the compressor and lubricating oil is a factor that determines the potential of a new refrigerant. In the present results, no major problem was observed for inverter efficiency, whereas differences were found in compressor efficiency and volumetric efficiency. This suggests that refrigerant properties and miscibility with the lubricating oil, leakage losses, cooling conditions, required torque, and related factors may be involved. Therefore, improving the performance of R474B requires not only reconsideration of the heat exchangers but also investigation of a compressor and oil combination suitable for the refrigerant.

Additionally, R474B has clear advantages. Its greatest one is the reduction of the GWP; having a lower warming impact than existing refrigerants has significant value as requirements for reducing environmental impact become increasingly stringent. In addition, under cooling conditions, the difference from R32 was smaller than under heating conditions, suggesting realistic applicability if the target applications and operating range are limited. In particular, in systems primarily used for cooling operation, with heat exchangers and compressors optimized for R474B, sufficient competitiveness may be achieved.

Therefore, the applicability of R474B should not be evaluated as direct replacement in current R32 systems, but rather as a refrigerant for next-generation systems redesigned on the premise of low-pressure operation and temperature glide.

This evaluation enabled us to quantitatively indicate that position.

6.5 Summary

The existing refrigerant R32 and the low-GWP refrigerant mixture R474B were comparatively evaluated using a refrigeration cycle model test apparatus, and the factors responsible for differences in cycle performance and the potential of the new refrigerant were organized.

R474B exhibited a lower COP than R32 under both heating and cooling conditions, but the difference was larger under heating conditions. The main factors were increased pressure loss due to the low-pressure operation of R474B, increased temperature differences in the heat exchangers caused by the temperature glide characteristic of refrigerant mixtures, and the accompanying increase in irreversible losses and pressure ratio.

Moreover, the disadvantages under cooling conditions were less pronounced than those under heating conditions, and volumetric efficiency did not necessarily deteriorate consistently. This indicates that the applicability of R474B strongly depends on operating conditions and equipment matching.

Accordingly, although R474B still presents challenges as a simple drop-in replacement for current R32 systems, it is promising as a refrigerant for next-generation systems premised on low-pressure-loss heat exchangers, compatible compressors and lubricating oils, and heat-exchanger design that accounts for temperature glide. Future studies should proceed from the perspective of system redesign, including heat-exchanger configuration, compressor selection, and optimization of circulation rate.

6.6 Detailed Discussion of the Comparative Results

6.6.1 Loss Structure by Component

The differences in the COP, compression ratio, and compressor efficiency reported in the preceding sections are examined here in terms of the loss structure of each cycle component. In evaluating the performance of low-GWP mixed refrigerants, reliance on a single representative index may obscure the dominant loss mechanisms. Therefore, the condenser, evaporator, expansion valve, compressor, and piping pressure losses should be assessed separately.

In the condenser, the irreversible loss for R474B is greater than that for R32. This is attributable to the temperature glide of the mixed refrigerant, which causes the temperature in the two-phase region to vary continuously and increases the temperature difference from the heat-source water over the condenser length. Under heating conditions in particular, the condenser is the primary heat-rejection component. Therefore, this mismatch is reflected prominently in the overall system performance. Thus, improving the heating performance of R474B requires, as a priority, better matching of the condenser temperature profile.

In the evaporator, R474B also exhibits increased irreversible loss, although this contribution is less dominant than that in the condenser. In addition to the larger temperature difference caused by temperature glide, an increase in pressure loss changes the inlet pressure and affects the evaporation temperature and suction state. Under heating conditions, the evaporator operates on the low-temperature side; therefore, even a small increase in pressure loss can substantially affect the compressor inlet conditions.

Irreversible loss in the expansion valve depends on the refrigerant enthalpy difference and pressure conditions. Therefore, it is sensitive to refrigerant replacement. However, the present results indicate that the performance difference of R474B is governed not by the expansion valve alone, but by its interaction with the downstream evaporator and compressor after expansion. More specifically, the key issue is the influence of the low-pressure two-phase state after expansion on the evaporator pressure loss and volumetric efficiency.

A particularly large difference in compressor irreversible loss was observed under heating conditions. As the

compression ratio increases, both the work required for adiabatic compression and the relative contribution of internal leakage and friction losses tend to increase. In R474B, compressor loss and pressure-loss effects act simultaneously, leading to a pronounced decrease in COP under heating conditions. Therefore, compressor compatibility is a critical factor in determining the feasibility of applying a new refrigerant.

6.6.2 Reasons for the Differences Between Heating and Cooling Conditions

The differences between R474B and R32 are more pronounced under heating conditions than under cooling conditions. One reason is that, under heating operation, the evaporator is exposed to more severe low-temperature conditions, making a decrease in compressor inlet pressure more likely. Because R474B intrinsically operates at lower pressure, evaporator-side pressure loss has a relatively large influence, and the resulting decrease in inlet pressure directly increases the compression ratio.

A second factor is that the heating operation requires greater heat rejection in the condenser, making the effect of temperature glide more apparent throughout the condenser. Consequently, the temperature difference between the heat-source water and refrigerant increases, thereby increasing the condenser's irreversible loss. While R32, as a pure refrigerant, exhibits relatively uniform temperature variation, R474B tends to accumulate thermodynamic mismatch along the heat exchanger.

A third factor is the compressor operating point. Under heating conditions, the required compressor work increases, and internal losses tend to become more apparent as rotational speed rises. For R474B, decreases in volumetric and compressor efficiencies are more pronounced under heating operation and are reflected in the overall system COP. In contrast, under cooling conditions, the evaporation temperature is relatively high and the suction state is more readily maintained, mitigating part of the disadvantage.

6.6.3 Perspectives on New Refrigerant Selection Based on the Comparative Results

The selection of a new refrigerant requires simultaneous consideration of environmental performance, safety, thermodynamic performance, and equipment compatibility. The comparative results indicate that R474B has an advantage in environmental performance but encounters challenges in thermodynamic performance and compatibility with the current R32 system. Therefore, new refrigerants should be evaluated in two stages: first, the extent to which performance can approach that of the current system, and second, the degree of improvement achievable through dedicated equipment design.

Compared with pure refrigerants, mixed refrigerants such as R474B exhibit temperature glide. This makes performance disadvantages likely when heat exchangers designed for existing pure refrigerants are used without modification. This should be interpreted not as an inherent limitation of the mixed refrigerant itself, but as a mismatch with the underlying design assumptions. The performance gap may be reduced by adopting heat exchangers designed to match the heat-source temperature profile, reducing piping pressure losses, and reconsidering compressor selection.

These results further suggest that prioritizing compatibility with current equipment alone may lead to an underestimation of promising low-GWP refrigerant candidates. Although direct application of R474B to current R32 equipment is associated with substantial disadvantages, its environmental benefits may still be exploited if the design flexibility of next-generation equipment is utilized.

7. Analysis of In-Cycle Component Losses for Low-GWP Mixed Refrigerants (Nagasaki University)

Drop-in experiments and numerical simulations were performed to identify component-level losses and evaluate the performance of an air-conditioning vapor-compression refrigeration cycle using low-GWP refrigerant mixtures. Compressor efficiencies were measured using a 2 kW-class experimental apparatus, and a cycle simulation model was developed based on the measured characteristics. The simulation was validated against the experimental results, and the COP, volumetric capacity, and irreversible loss were analyzed for the ternary mixtures R32/HFO-1123/R1234yf and R32/R1132(E)/R1234yf. The relationship between temperature glide and COP degradation was then examined.

7.1 Experiment

7.1.1 Experimental Apparatus

Figure 7.1-1 presents an overview of the 2 kW-class experimental apparatus. The apparatus consists primarily of a refrigerant loop and two heat-source water loops. The refrigerant loop comprises a compressor, two cross-finned tube heat exchangers, and an electric expansion valve. Table 7.1-1 lists the specifications of the cross-finned tube heat exchanger and compressor used in the experiments. The heat exchanger was installed in a water tank for heat to be exchanged with the heat-source water flowing in a cross-flow configuration. The finned section was placed inside the water tank downstream of three perforated baffle plates. Thermal insulation was used to block flow paths around the bend sections and other non-finned regions. Figure 7.1-1(c) shows a velocity-vector distribution of the heat-source water at the mid-height of the water tank. Ansys Fluent (ANSYS, 2020) was used as the computational solver. The simulation confirmed that the heat-source water entering from the center of the tank passed through the three baffle plates and approached the heat exchanger uniformly at a very low velocity. Thus, heat exchange was performed under conditions approximating an air heat source, and the heat-source water flow rate was adjusted to maintain a temperature difference between the water-tank inlet and outlet of approximately 3–6 K.

The symbols P and T in Figure 7.1-1(a) indicate the pressure and temperature measurement locations, respectively. Table 7.1-2 lists the measuring instruments and their accuracies. All thermocouples (JIS class 1) were calibrated from –10 to +80 °C using traceable platinum resistance thermometers calibrated in accordance with ITS-90. The calibration yielded a measurement uncertainty of ± 0.19 °C at a coverage factor of 2. Pressure was measured using pressure transducers selected according to the high-pressure side, low-pressure side, and refrigerant type. Pressure taps were installed at each measurement location, extended with 1/8-inch piping, and switched using valves to measure the pressure at each point.

The refrigerant composition was analyzed by instantaneously sampling approximately 1 cc of circulating refrigerant from the liquid line upstream of the expansion valve and completely vaporizing the sample in a vessel. A GC-2014 gas chromatograph equipped with Porapak Q and N packed columns (50/80 mesh, SUS3 ϕ $\times$ 3 m) was used for the analysis. Calibration curves were prepared using samples of known composition, and the refrigerant composition was determined from these curves.

The experimental conditions are summarized in Table 7.1-3. Experiments were completed for pure R32, pure R1234yf, and their mixtures. Owing to differences in refrigerant properties, the same apparatus was operated primarily at capacities of 2.6 kW for R32 and 1.2 kW for R1234yf. The refrigerant charge was adjusted for the condenser subcooling to approach 4 K. Because the highest COP was often observed near this degree of subcooling, refrigerant-charge adjustment tests were conducted at Kyushu Sangyo University.

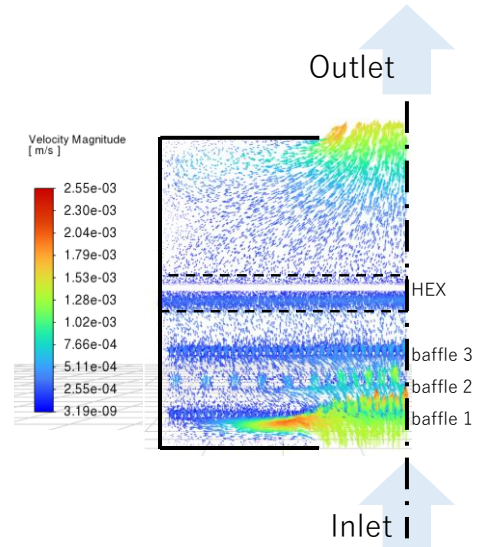
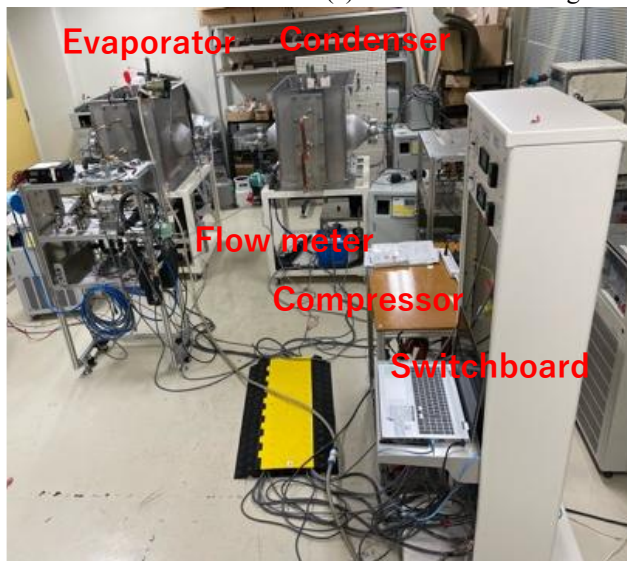
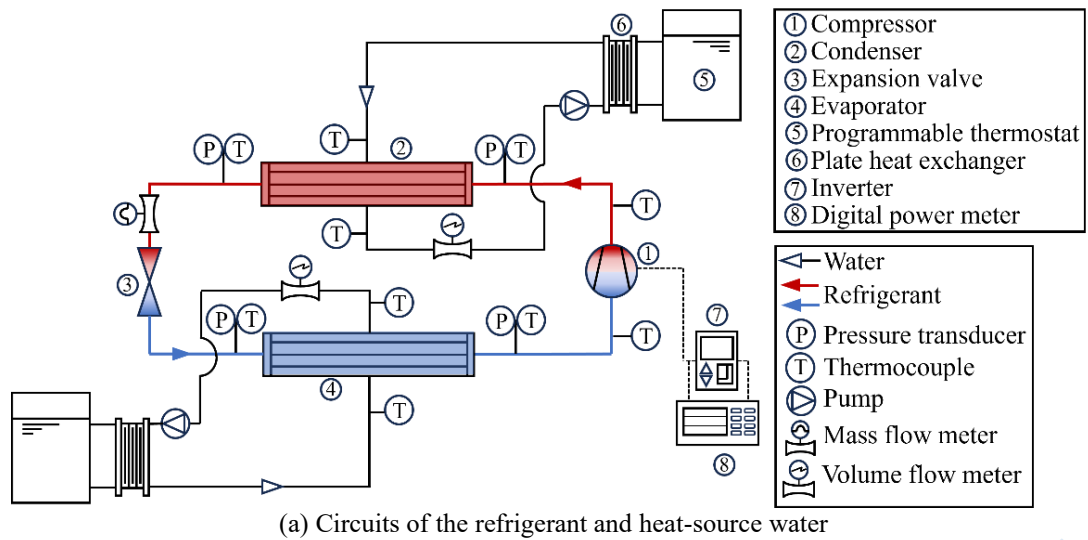


Figure 7.1-1 Experimental setup

Table 7.1-1 Dimensions of the cross-finned tube heat exchanger and specification of the compressor.

Heat exchanger		
Outer diameter D_o	[mm]	9.53
Inner diameter D_i	[mm]	7.53
Fin pitch P_f	[mm]	4.00
Longitudinal tube pitch P_L	[mm]	18.7
Traversing tube pitch P_T	[mm]	26.9
Effective tube length	[mm]	650
Total number of tubes	[-]	36
Thermal conductivity of tubes	$[W \cdot m^{-1} \cdot K^{-1}]$	370
Number of circuits	[-]	2
Number of rows	[-]	2
Compressor		
Type	Twin rotary	
Lubricant oil	ROTEX RP2201-E68B (POE VG68)	
motor	4-pole DC	
Displacement volume	$[cm^3]$	24

Table 7.1-2 Measurement instruments and uncertainty ($k = 2$).

Measured parameter	Instrument type	Accuracy
Temperature	K type thermocouple of $\Phi 1.0$ mm (Yamari Thermic, Type K(S), JIS 1 class)	± 0.19 °C
Flow rate of water	Gear type volume flow meter, (Oval, LGV45A30-G130)	$\pm 0.5\%$ of reading
Flow rate of refrigerant	Coriolis type mass flow meter, (Oval, CN03-2833)	$\pm 0.25\%$ of reading at 5 kg/h $\pm 0.12\%$ of reading at 50 kg/h
Pressure of refrigerant (Max. 5 MPa)	Absolute pressure transducer, (Kyowa, PAV-50KR)	$\pm 0.1\%$ of reading
Pressure of refrigerant (Max. 1 MPa)	Absolute pressure transducer, (Kyowa, PAV-10KR)	$\pm 0.02\%$ of reading
Input power	Digital power meter, (Yokogawa, WT332E)	$\pm 0.15\%$ of reading

Table 7.1-3 Experimental conditions.

Refrigerant		R32	R1234yf
Charge amount	[kg]	0.87	1.33
Water	Condenser inlet $T_{\text{water,cond}}$	29.5 (25.1~35.6)	35.2 (25.4~45.0)
temp.	Evaporator inlet $T_{\text{water,eva}}$	23.2 (21.9~26.2)	24.3 (19.4~27.1)
Pinch temp.	Condenser $\Delta T_{\text{pinch,cond}}$	2.6 (2.3~2.8)	2.4 (1.7~4.8)
	Evaporator $\Delta T_{\text{pinch,eva}}$	3.8 (3.0~5.5)	4.7 (1.1~7.9)
	Condenser subcooling ΔT_{SC}	2.1 (1.7~3.6)	4.1 (3.8~4.3)
	Evaporator superheat ΔT_{SH}	7.9 (2.5~14.0)	11.3 (3.1~15.3)
Heat transfer rate	[kW]	2.6 (2.3~3.2)	1.2 (0.9~1.5)

7.1.2 Data Reduction Method

The refrigerant state quantities at each measurement point were calculated from the measured pressure, temperature, and circulating composition using REFPROP 10.0 (Lemmon et al., 2018). For FLD files other than those for R32 and for the mixture parameters used in this study, files developed primarily at Kyushu Sangyo University based on measurement data from Kyushu University and other sources were employed. Various compressor efficiencies were then calculated from the obtained state quantities using the following equations: the isentropic efficiency η_{is} ; the mechanical efficiency η_{m} , representing the difference between compressor input power and refrigerant compression power; the volumetric efficiency η_{v} , representing the difference between the theoretical displacement and the actual refrigerant circulation rate; and the inverter efficiency η_{inv} , representing electrical losses in the inverter.

$$\eta_{\text{is}} = \frac{h_2^{\text{ideal}} - h_1}{h_2 - h_1} \quad (7.1-1)$$

$$\eta_{\text{m}} = \frac{m_r (h_2 - h_1)}{E_{\text{comp}}} \quad (7.1-2)$$

$$\eta_{\text{v}} = \frac{m_r}{0.5 \rho_1 f V_{\text{comp}}} \quad (7.1-3)$$

$$\eta_{\text{inv}} = \frac{E_{\text{comp}}}{E_{\text{inv}}} \quad (7.1-4)$$

where h_1 and h_2 are the specific enthalpies at the compressor inlet and outlet, respectively, and h_2^{ideal} is the compressor outlet specific enthalpy under isentropic compression. m_r and ρ_1 are the refrigerant mass circulation rate and compressor inlet density, respectively, and V is the theoretical compressor displacement volume. f is the compressor frequency, and E_{inv} and E_{comp} are the electric power values before and after the inverter, respectively. COP was calculated from the electric power after the inverter while accounting for mechanical efficiency, as shown in the following equation.

$$\text{COP}_{\text{system}} = \begin{cases} Q_{\text{cool}}/E_{\text{comp}} = m_r (h_1 - h_4)/[m_r (h_2 - h_1)/\eta_m] \\ Q_{\text{heat}}/E_{\text{comp}} = m_r (h_2 - h_3)/[m_r (h_2 - h_1)/\eta_m] \end{cases} \quad (7.1-5)$$

7.1.3 Compressor Efficiency Measurement Results

Table 7.1-2 presents the measurement results for the compressor efficiencies described above. The horizontal axis represents the pressure ratio or compressor frequency, and the vertical axis represents each efficiency. The isentropic compression efficiency remained unchanged across R32, R1234yf, and R32/R1234yf and agreed well with the empirical correlation proposed by Seki et al. (1990). In contrast, the mechanical and volumetric efficiencies depended on the refrigerant. The miscibility of polyolester (POE) oil with refrigerant differs substantially between HFC R32 and HFO R1234yf. Because R1234yf dissolves more readily in the oil, the oil viscosity is considered to decrease, thereby increasing leakage loss. Increased leakage loss induces unnecessary rotation and associated sliding loss, reducing mechanical efficiency. In addition, compression of high-density vapor requires higher torque, and greater leakage loss requires higher frequency; thus, compressor characteristics are strongly influenced by refrigerant properties. R32, with its higher vapor density and smaller leakage loss, consequently exhibits higher inverter efficiency.

Therefore, the cycle simulation was performed using these compressor characteristics. The dashed curves in the figure were implemented in the simulation program. Results other than the compressor efficiencies, including COP, were compared with the simulation results.

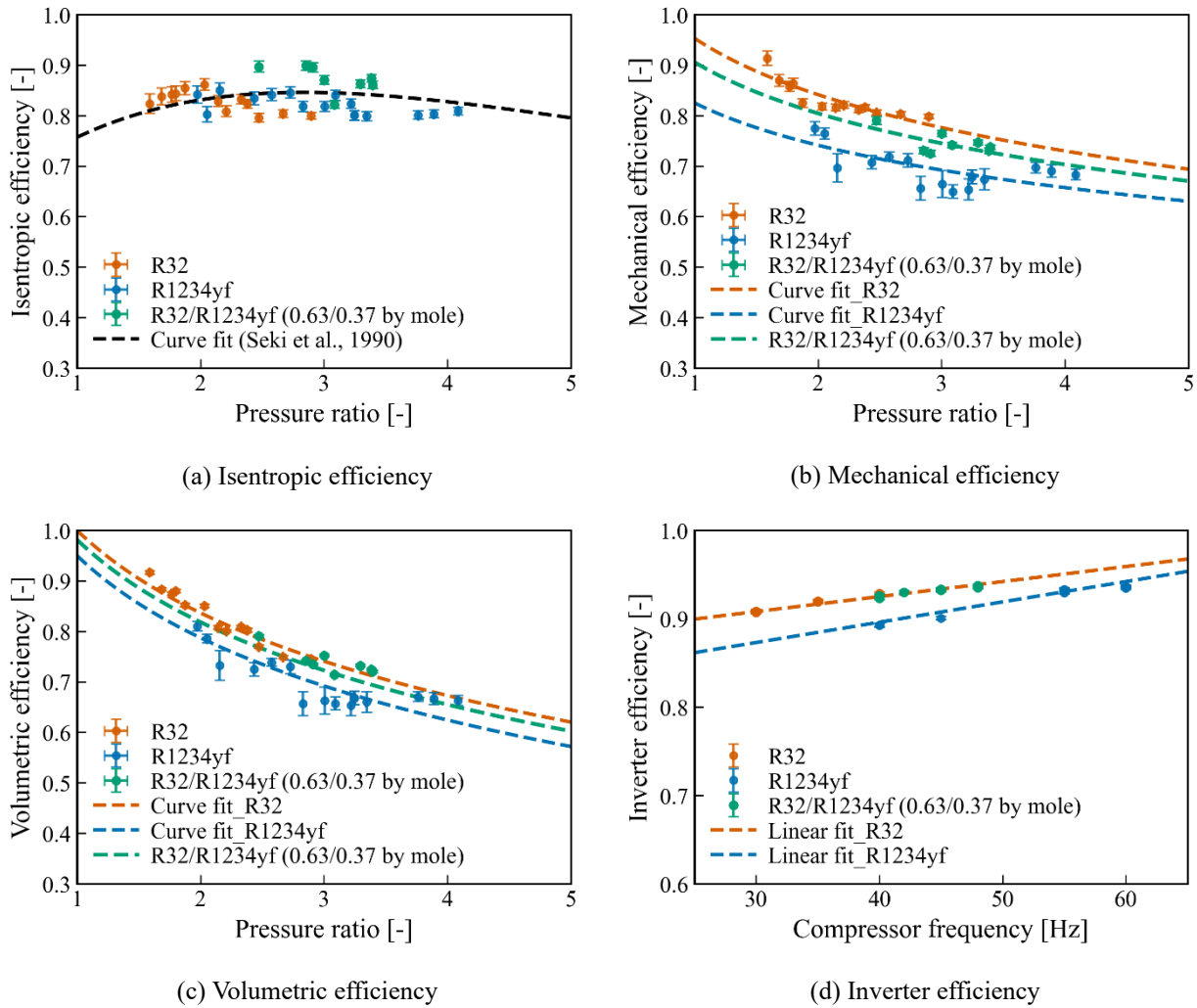


Figure 7.1-2 Measured compressor efficiencies.

7.2 Simulation

7.2.1 Simulation Method

Figure 7.2-1 shows a T - s diagram and heat-exchanger schematic illustrating the simulation method. The degree of subcooling, degree of superheating, and inlet conditions of the heat source, namely air or water, are summarized in Table 7.2-1. The heat exchanger size was optimized to satisfy these conditions. Two cycles were calculated: one shown by the bold line, which accounts for pressure loss, and one shown by the dashed line, which neglects pressure loss. The area between these two lines corresponds to the irreversible loss $L_{\Delta P}$ caused by pressure loss. The compressor loss L_{comp} and expansion valve loss L_{valve} were also calculated as areas, as shown in the figure.

The cross-finned tube heat exchanger was assumed to have two rows and two passes. The superheated and subcooled regions were divided into 5–15 and 3–10 segments, respectively, and the vapor–liquid two-phase region was divided into 100 segments. Refrigerant state quantities and heat transfer coefficients were calculated for each segment. After the total heat-exchanger tube length was calculated, the flow was assumed to return to the second row at half the total length. Dry air was assumed as the heat-source fluid, and the average air temperature at the outlet of the first row was uniformly assigned as the inlet air temperature of the second row. The frontal air velocity was set to 1.2 m s^{-1} for the indoor unit and 1.4 m s^{-1} for the outdoor unit. Under these conditions, the temperature effectiveness for R32 was confirmed to be approximately 87% on the indoor-unit side and 66% on the outdoor-unit side. The following equations define the heat transfer rate ΔQ_n and overall heat transfer coefficient K_n for segment n .

$$\Delta Q_n = \Delta h_n m_r = K_n (T_{r,n} - T_{\text{air}}) (\pi D_i A l_n) \quad (7.2-1)$$

$$\frac{1}{K_n} = \frac{1}{\alpha_{r,n}} + \frac{1}{\alpha_{\text{air}} (A_{\text{air}}/A_r)} + \frac{(D_o - D_i)/2}{\lambda_{\text{tube}}} \quad (7.2-2)$$

where Δh_n and Δl_n denote the enthalpy change and length of segment n , respectively. α_{air} and $\alpha_{r,n}$ are the air-side and refrigerant-side heat transfer coefficients, respectively. The air-side heat transfer coefficient was assumed to be uniform at $50 \text{ W m}^{-2} \text{ K}^{-1}$, and the correlations used to calculate the refrigerant-side heat transfer coefficient are listed in Table 7.2-2. In addition, λ_{tube} denotes the thermal conductivity of the heat transfer tube; the value for pure copper, $370 \text{ W m}^{-1} \text{ K}^{-1}$, was used. The required heat-exchanger size was calculated using this procedure.

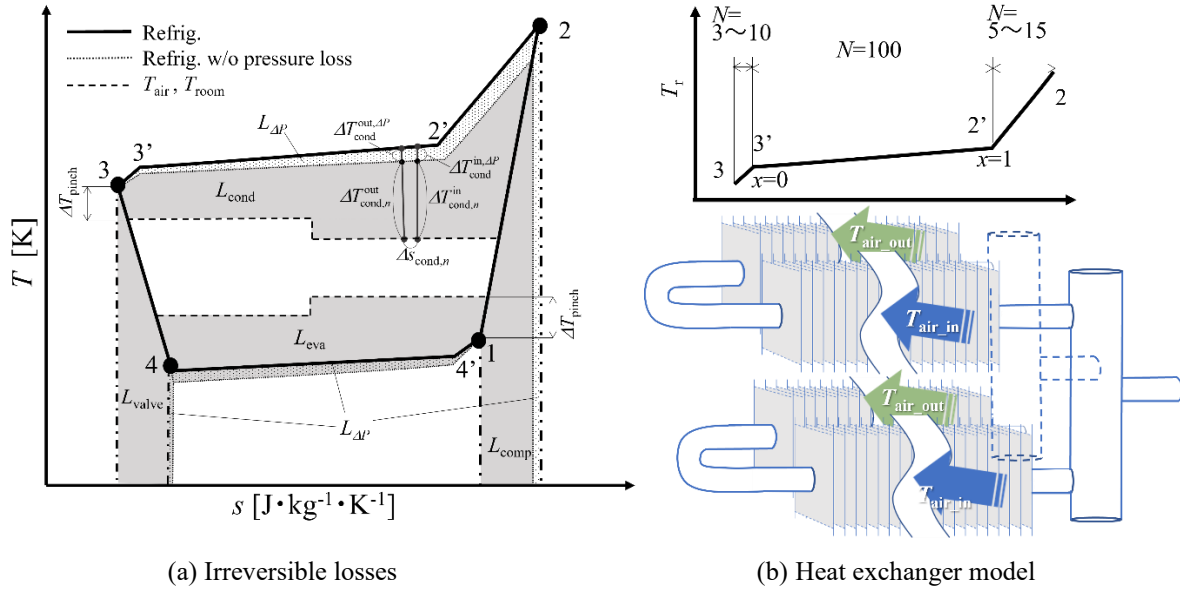


Figure 7.2-1 Simulation method.

Table 7.2-1 Simulation conditions for performance assessment.

Cooling capacity	Q_{cooling}	[kW]	2.0
Heating capacity	Q_{heating}	[kW]	2.2
Heat sink inlet temp. in condenser	$T_{\text{water,cond}}$	[°C]	37
Heat source inlet temp. in evaporator	$T_{\text{water,eva}}$	[°C]	25
Pinch temp. in condenser	$\Delta T_{\text{pinch,cond}}$	[°C]	2.5
Pinch temperature in evaporator	$\Delta T_{\text{pinch,eva}}$	[°C]	4.0
Degree of subcooling	ΔT_{SC}	[°C]	4.0
Degree of superheating	ΔT_{SH}	[°C]	8.0

Table 7.2-2 Correlations for the refrigerant-side HTC and pressure drop.

Two-phase condensation process	
HTC	Deng et al., 2019
Pressure drop	Koyama, 2006
Two-phase evaporation process	
HTC	Kondou et al., 2013
Pressure drop	Kondou, 2008
Single-phase heat transfer process	
HTC	Goto et al., 2005
Pressure drop	Carnavos, 1980

7.2.2 Comparison of Simulation and Experimental Results

Figure 7.2-2 compares the experimental results, shown by symbols, with the simulation results, shown by red lines, on the P - h diagram. The cooling capacity was set to the value obtained under the experimental conditions. However, in the R32 experiment, the refrigerant charge was insufficient, and the degrees of subcooling and superheating did not reach the calculation conditions of 4.0 and 8.0 K, respectively. Therefore, the measured degree of subcooling was used as an input to the simulation. As shown in the figure, the experimental and simulation results agreed well, confirming the validity of the simulation model.

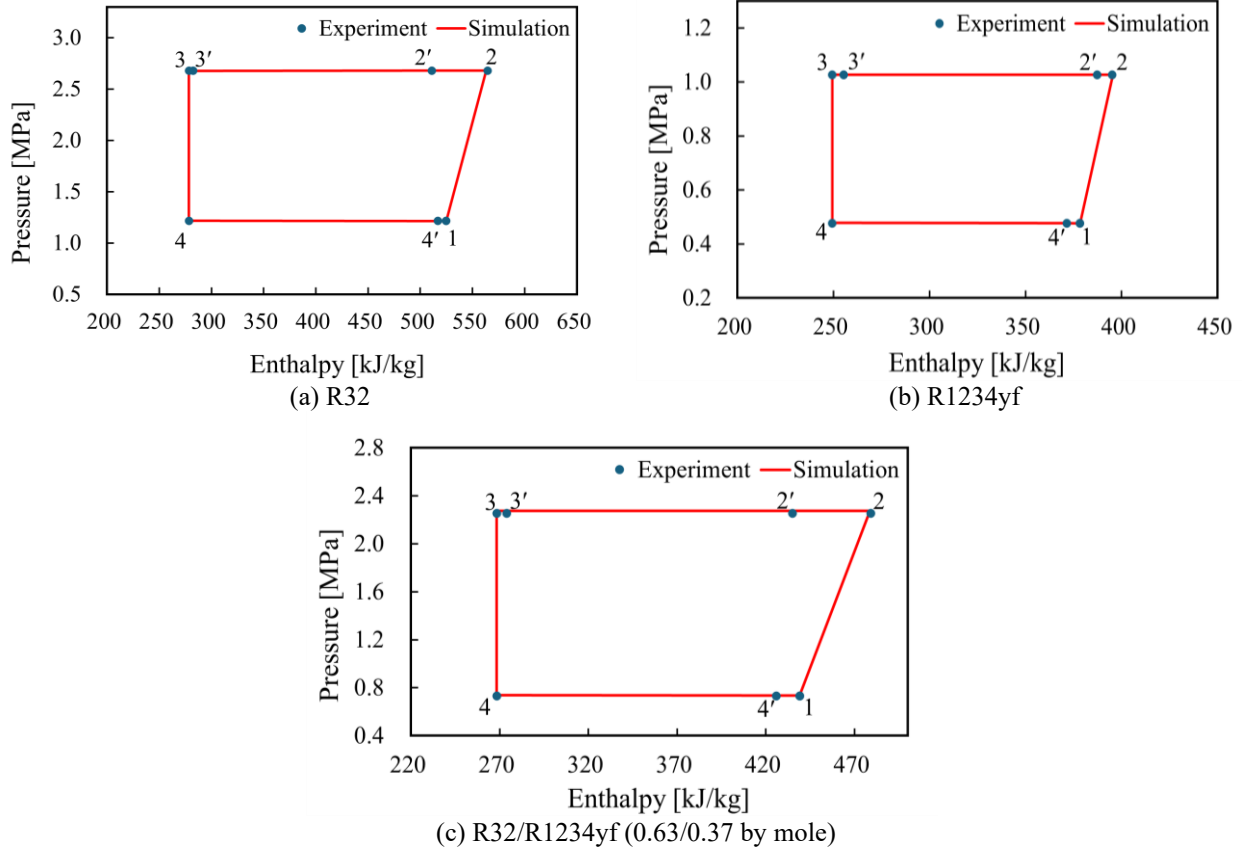


Figure 7.2-2 P - h diagram for the validation cases.

7.2.3 Simulation Results

Figures 7.2-3 and 7.2-4 present the simulation results for R32/HFO-1123/R1234yf and R32/R1132(E)/R1234yf, respectively, at a cooling capacity of 2.0 kW. The mass composition is indicated along each side of the ternary diagram, and the COP, evaporator temperature glide, volumetric capacity, and evaporator heat transfer area are shown as contours. The heat transfer area represents the refrigerant-side area inside the tube and does not include the area enlargement factor associated with helical grooves. The shaded region on the R32 side corresponds to compositions with a GWP of 150 or higher, whereas the shaded regions on the HFO-1123 and R1132(E) sides indicate compositions with a risk of disproportionation reaction. The disproportionation-risk region was defined as an HFO-1123 mass fraction of 0.6 or higher (Otsuka et al., 2018) and an R1132(E) mass fraction of 0.4 or higher (Usui et al., 2025). These thresholds are currently being refined through more accurate measurements in this project and may be updated. The simulation results were compared after excluding these composition regions.

The maximum COP was 3.4 for R32/HFO-1123/R1234yf and 4.1 for R32/R1132(E)/R1234yf. A larger temperature glide resulted in a lower COP and a greater required heat transfer area. Because the maximum COP is strongly influenced by the regions excluded based on GWP and disproportionation-reaction risk, accurate evaluation of disproportionation risk is essential for predicting COP and determining the optimal composition. The maximum volumetric capacity was 7500 kJ m^{-3} for R32/HFO-1123/R1234yf and 6500 kJ m^{-3} for R32/R1132(E)/R1234yf, reversing the relative trend observed for maximum COP. The maximum volumetric capacity occurred at compositions with lower R1234yf fractions and, similarly to COP, was strongly affected by the excluded regions associated with GWP and disproportionation-reaction risk.

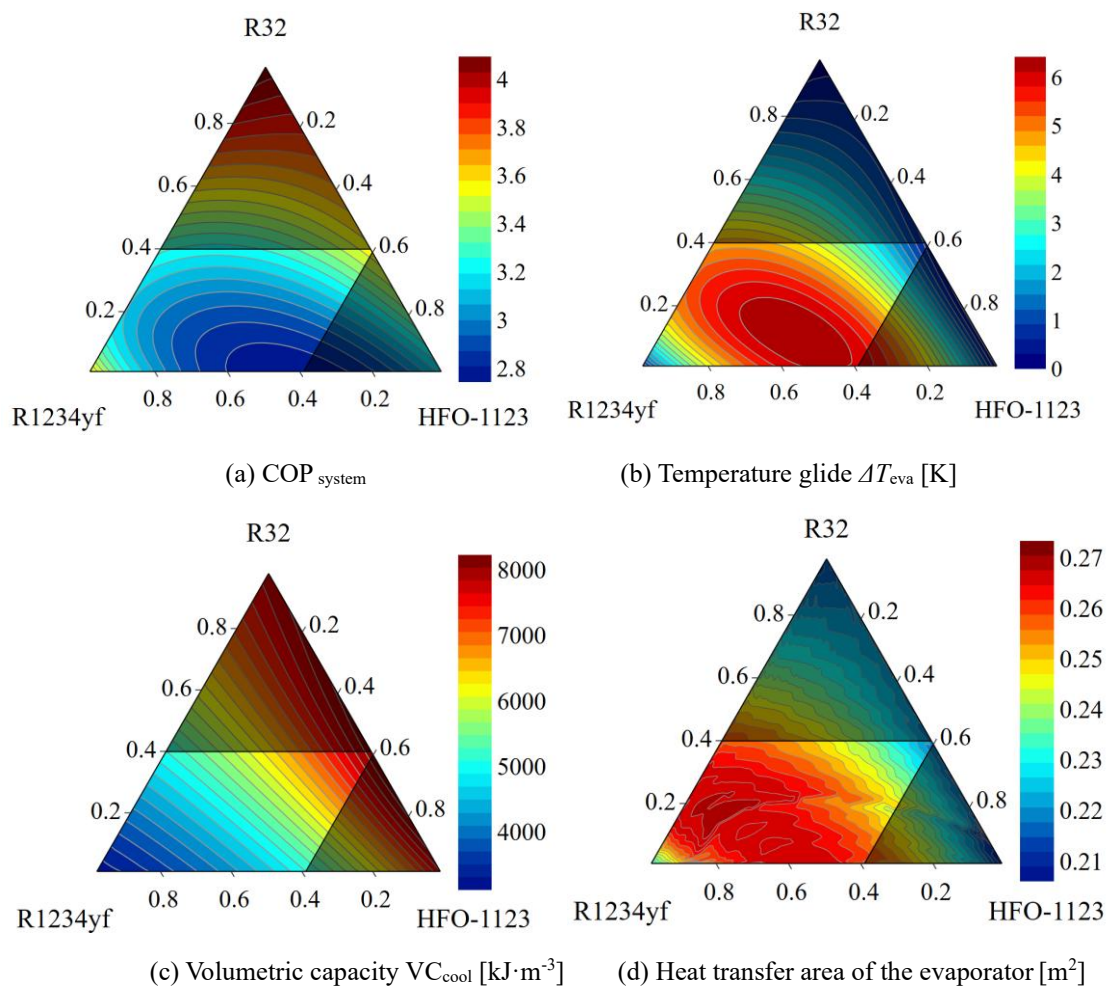
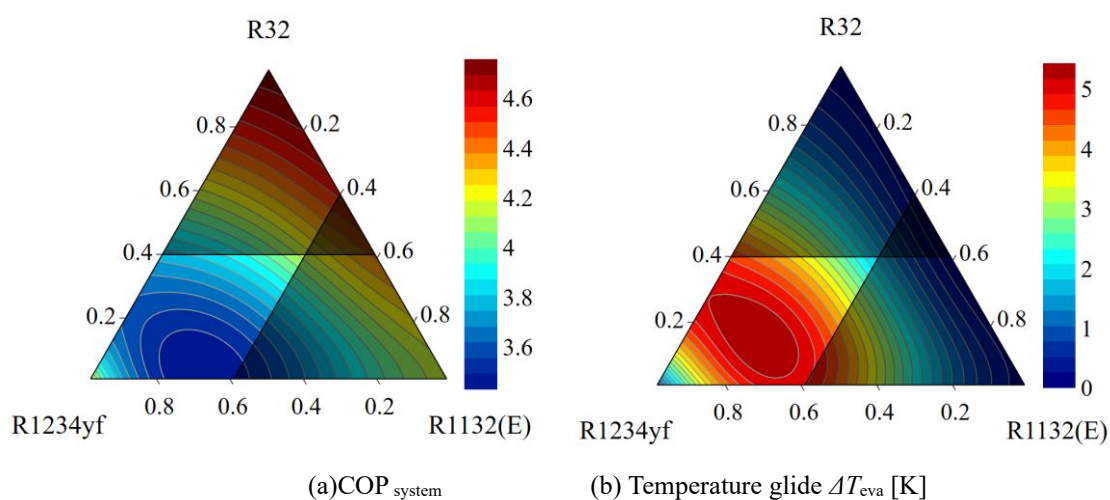
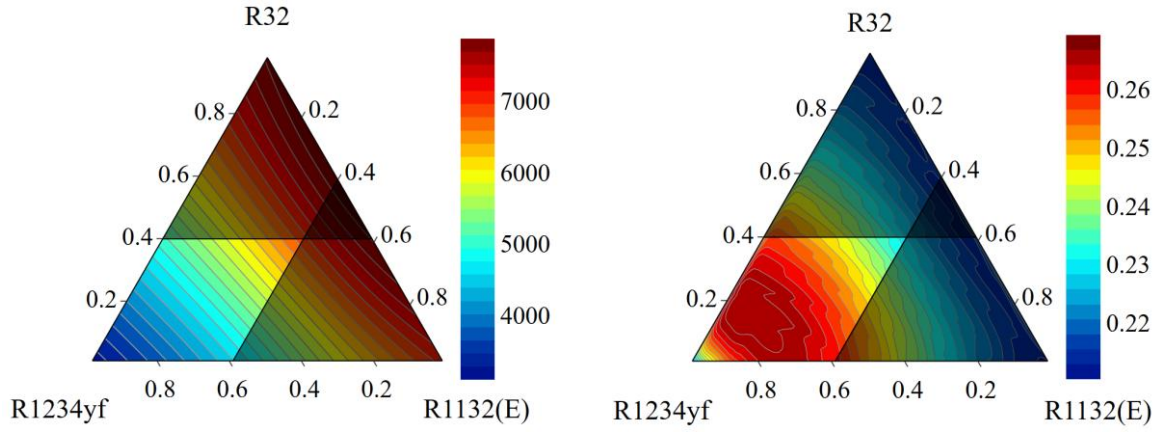


Figure 7.2-3 Simulated heat pump performance simulated for R32/HFO-1123/R1234yf in cooling mode at 2.0 kW.





(c) Volumetric capacity VC_{cool} [$\text{kJ}\cdot\text{m}^{-3}$] (d) Heat transfer area of the evaporator [m^2]

Figure 7.2-4 Simulated heat pump performance simulated for R32/R1132(E)/R1234yf in cooling mode at 2.0 kW.

Figure 7.2-5 shows the breakdown of irreversible losses obtained from the simulation results. The bar chart classifies the irreversible losses in the condenser (Cond), evaporator (Eva), pressure drop (DP), expansion valve (Exp), and compressor (Comp) for the mass composition 0.4/0.4/0.2, which yielded the highest COP in the R32/R1132(E)/R1234yf mixture system. Under the present calculation conditions, which assumed a helically grooved tube and high volumetric capacity, the irreversible loss due to pressure drop was negligible. The condenser and evaporator each accounted for approximately 30% of the total irreversible loss, whereas the expansion valve and compressor each accounted for slightly less than 20%.

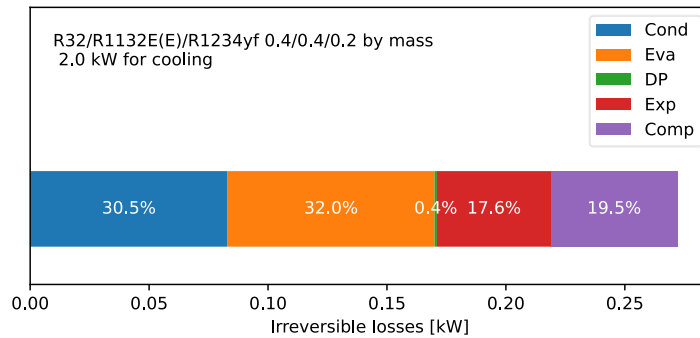


Figure 7.2-5 Breakdown of irreversible losses for R32/R1132(E)/R1234yf (0.4/0.4/0.2 by mass) cooling mode.

7.2.4 Correlation Between the COP Reduction Rate and Temperature Glide

Using the simulation results, a simplified correlation was formulated relating COP to temperature glide for system design. Figures 7.2-6 and 7.2-7 show the results for R32/HFO-1123/R1234yf and R32/R1132(E)/R1234yf, respectively. In these figures, COP_{ideal} denotes the value obtained by combining the COP values of the individual refrigerants without temperature glide according to their mole fractions. ΔT_{eva} denotes the evaporator temperature glide, defined as $T'_{eva} - T_{eva,in}$. For visualization, only data with a mass fraction of 0.5 or higher are plotted. The COP reduction ratio, expressed as COP/COP_{ideal} , exhibited an approximately linear correlation with temperature glide. The slopes were -0.0345 for R32/HFO-1123/R1234yf and -0.0375 for R32/R1132(E)/R1234yf, corresponding to an average value of approximately -0.036 . The mean absolute percentage errors (MAPEs) for these linear correlations are 1.03% and 0.65%, respectively, indicating that COP can be predicted using this simplified method with an error of approximately 2%.

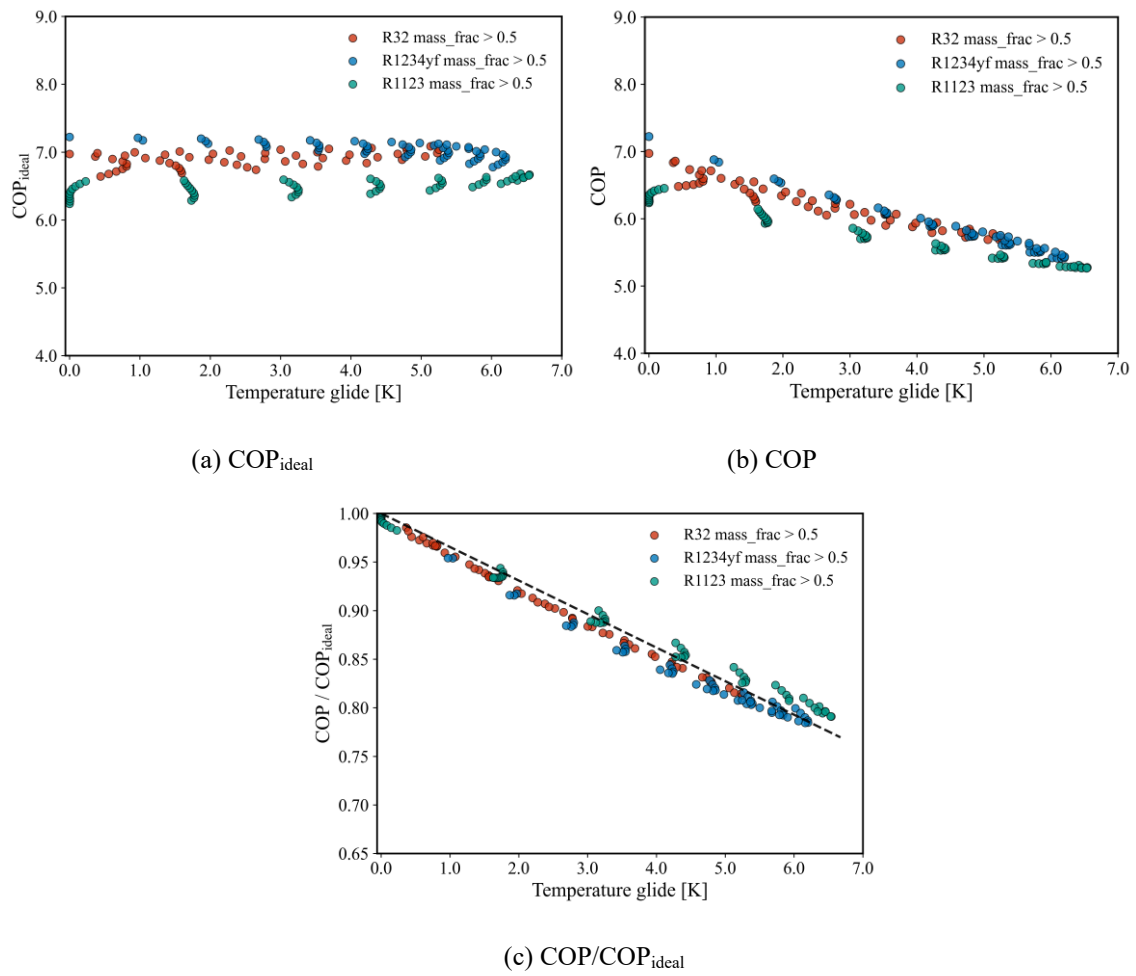


Figure 7.2-6 COP decrement associated with temperature glide simulated for R32/HFO-1123/R1234yf. Linear fit:

$$COP/COP_{ideal} = 1 - 0.0345 \Delta T_{eva}, \quad MAPE = 1.03\%.$$

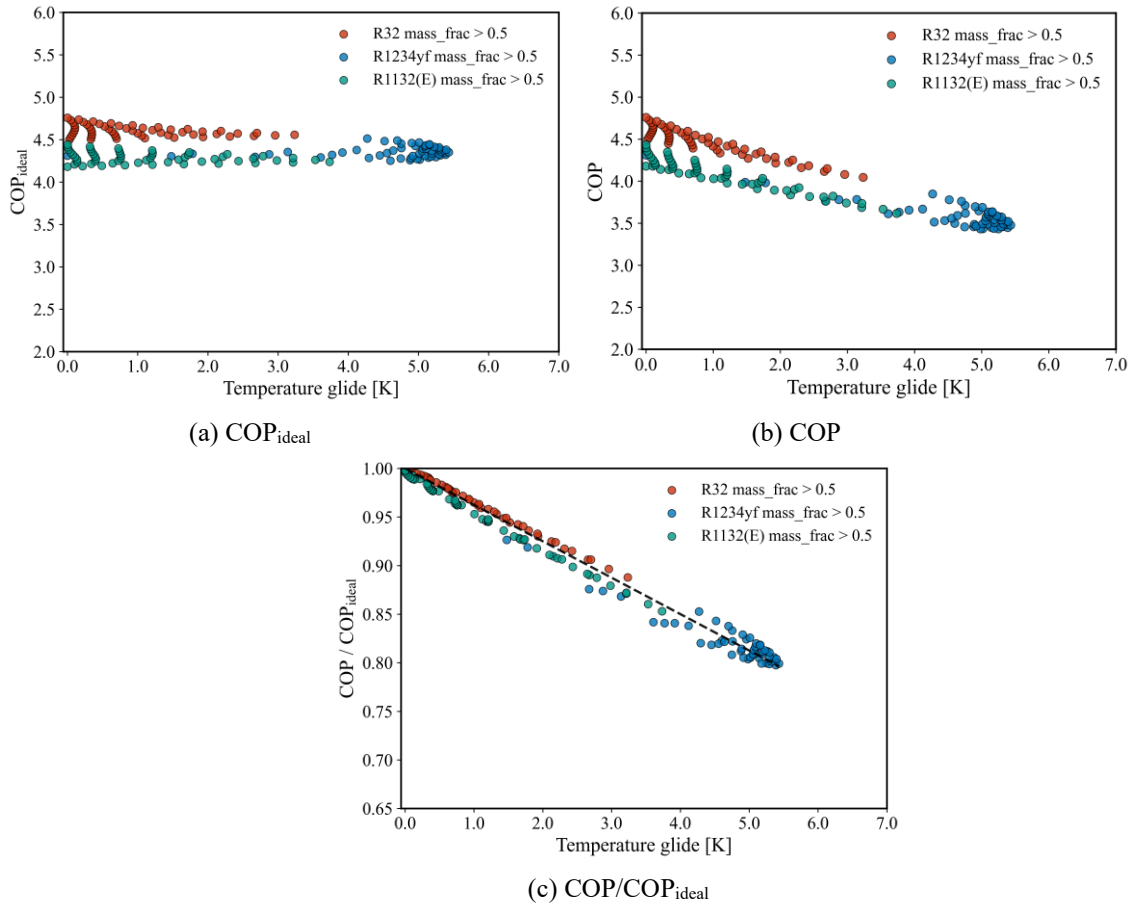


Figure 7.2-7 COP decrements associated with temperature glide simulated for R32/R1132(E)/R1234yf. Linear fit: $COP/COP_{ideal} = 1 - 0.0375 \Delta T_{eva}$, MAPE = 0.65%.

7.3 Summary

This study evaluated the performance of an air-conditioning vapor-compression refrigeration cycle using low-GWP refrigerants by combining compressor-efficiency measurements with a 2 kW-class experimental apparatus and cycle simulations based on the measured characteristics. The apparatus consisted of a compressor, two cross-finned tube heat exchangers, and an electric expansion valve. Refrigerant state quantities were calculated from the measured temperature, pressure, and composition using REFPROP, and the isentropic, mechanical, volumetric, and inverter efficiencies were evaluated. The target refrigerants were R32, R1234yf, and their mixtures.

The measurements showed that the isentropic efficiency exhibited only limited refrigerant dependence and agreed well with existing correlations, whereas the mechanical and volumetric efficiencies exhibited clear refrigerant dependence. For R1234yf in particular, its high miscibility with POE oil is considered to reduce oil viscosity and increase leakage loss, thereby decreasing mechanical efficiency. Because R32 has a high vapor density and small leakage loss, it tends to exhibit higher inverter efficiency. Based on these findings, a cycle simulation incorporating the compressor model and segmented heat-exchanger calculations was developed, and good agreement with the experimental results was confirmed on the P - h diagram.

Performance predictions were further conducted for the ternary mixtures R32/HFO-1123/R1234yf and R32/R1132(E)/R1234yf. The maximum COP values were 3.4 and 4.1, respectively, confirming that increased temperature glide reduces COP and increases the required heat transfer area. In contrast, the maximum volumetric capacities were 7500 and 6500 kJ m^{-3} , respectively, and occurred at compositions different from those yielding the maximum COP. The maximum COP and volumetric capacity were also shown to be strongly affected by GWP constraints and

disproportionation-reaction risk. Finally, an approximately linear relationship was identified between evaporator temperature glide and the COP reduction ratio, demonstrating that COP can be predicted within a mean absolute error of approximately 2% using a correlation with an average slope of -0.036 .

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8. Development of an LCCP Evaluation Method and AI Analysis for Air-Conditioning Equipment Compatible with Low-GWP Mixed Refrigerants

(Aizoth)

8.1 Overview of Research and Development

Figure 8.1-1 provides an overview of this research and development item. This work integrates LCAs and demand estimation for air-conditioning equipment compatible with low-GWP mixed refrigerants and evaluates the future environmental impacts associated with the diffusion of such equipment throughout Japan. The results are fed back to the participating research institutes and companies to support the formulation of research and business strategies. Safety assessments are also conducted and integrated with life cycle climate performance (LCCP)/LCA evaluation methods to establish an evaluation framework that accounts for social acceptability. In addition, artificial intelligence (AI)-based analytical tools are developed and utilized to support the efficient implementation of related research and development activities.

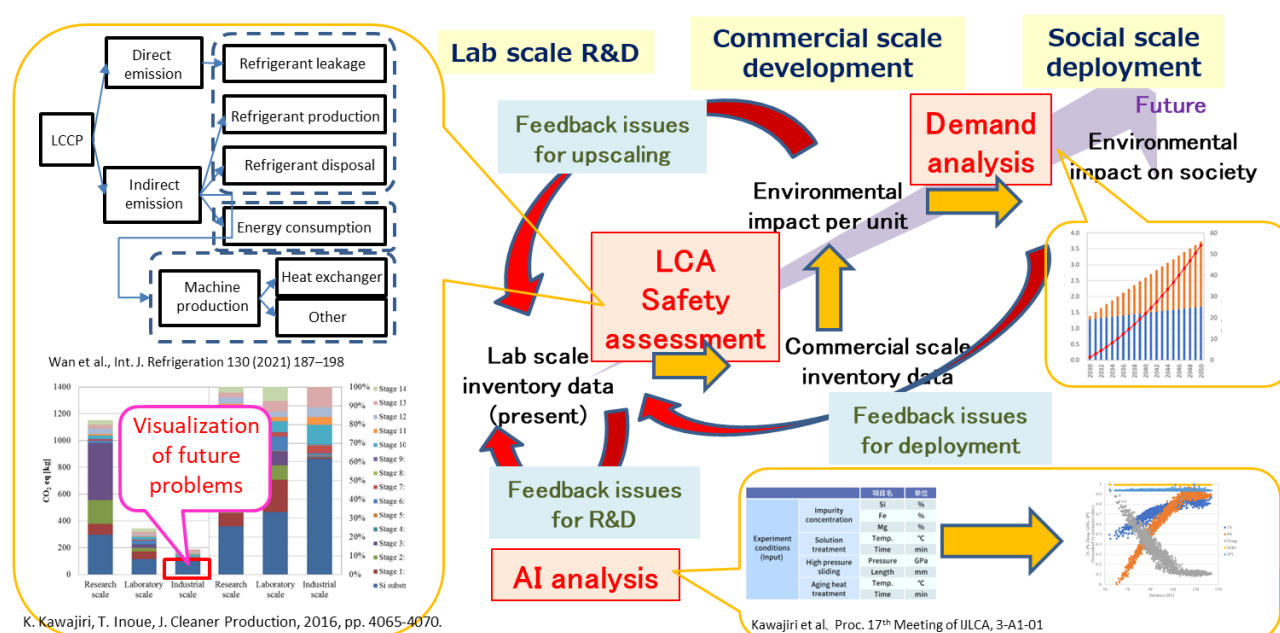


Figure 8.1-1 Research overview

8.2 LCA Evaluation

LCA is a method for quantitatively evaluating the environmental impacts that occur throughout the life cycle of a product, from raw material extraction to manufacturing, distribution, use, disposal, and recycling. Its methodological framework has been standardized in ISO 14040/14044, and it has been widely applied to evaluate the environmental impacts of diverse products, technologies, and services.

LCCP is an environmental impact assessment method derived from LCA and is used particularly for refrigeration and air-conditioning equipment; relevant guidelines have been issued by the International Institute of Refrigeration (IIR). Figure 8.2-1 shows the system boundary for the LCCP evaluation in this research and development item. In the LCCP

evaluation, global warming is selected as the impact category, and the life-cycle environmental impact of refrigeration and air-conditioning equipment is assessed by considering both direct impacts from refrigerant leakage and indirect impacts associated with refrigerant and equipment manufacturing, electricity consumption during operation, disposal, and recycling. From a practical perspective, LCCP evaluation is characterized by the use of standard coefficients and estimation equations to analyze the environmental impact at each stage without collecting all inventory data within the system boundary.

Because this study focused on residential air conditioners, the evaluation was conducted using the LCCP framework. Standard coefficients for Japan were used to assess environmental impacts, whereas foreground data for refrigerant and equipment manufacturing were collected based on patent information, as described in the following. LCA was then performed for these stages, and the global-warming coefficient was calculated from the results. Energy consumption was estimated using the cycle simulator developed by the Kondo Laboratory at Nagasaki University.

8.2.1 Purpose of Evaluation and Functional Unit

In this research and development item, the functional unit is defined as one air conditioner using a low-GWP mixed refrigerant, with rated capacities of 2000 W for cooling and 2200 W for heating. The objective is to evaluate the environmental impact per unit and identify the optimal mixed-refrigerant composition. The evaluation adopts the LCCP framework, selects global warming as the impact category, and applies LCA and cycle simulation to selected life-cycle stages. In addition to the environmental impact per unit, the environmental impact associated with the projected future stock of air conditioners in Japan is evaluated. The service life of the air conditioner is assumed to be 12 years.

8.2.2 Survey Method

<Inventory analysis>

- Foreground data: The inventory data for refrigerant manufacturing are collected from patents held by each company. Electricity consumption of air conditioners is estimated using the cycle simulation developed by the Kondo Laboratory at Nagasaki University.

- Background data: Inventory data for air-conditioner manufacturing and for the production of R290 and R744 are calculated using AIST-IDEA v3.5. The environmental impact of air-conditioner manufacturing is evaluated by considering the air-conditioner size for each refrigerant, using the pipe length obtained from the cycle simulation.

<Impact assessment>

- Impact assessment: Greenhouse gas (GHG) emission factors from AIST-IDEA v3.5 and the coefficients used in LCCP are applied. The GWP values of the refrigerants are obtained from the IPCC Fifth Assessment Report (Myhre et al., 2013), and the GWP of each mixed refrigerant is calculated as the mass-fraction-weighted average of the GWP values of the constituent refrigerants.

- Impact category: Global warming

System boundary:

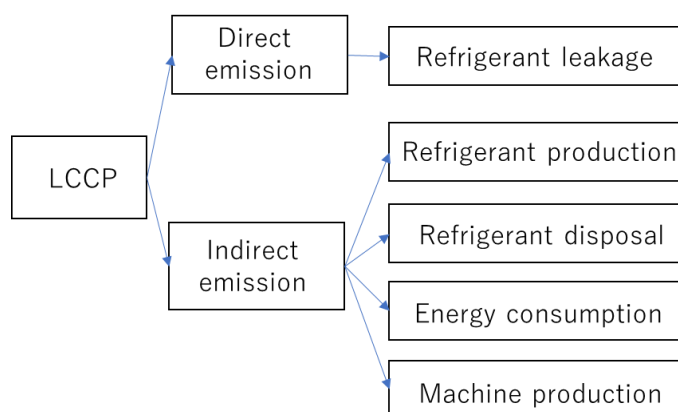
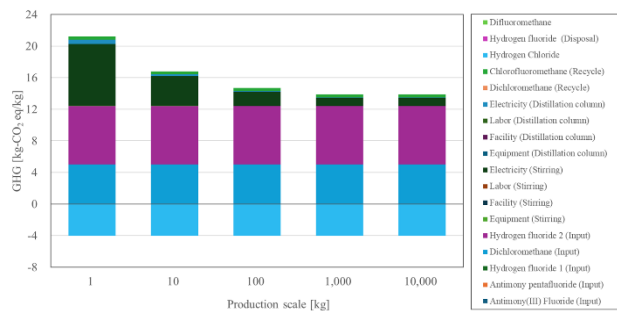


Figure 8.2-1 System boundary of LCCP

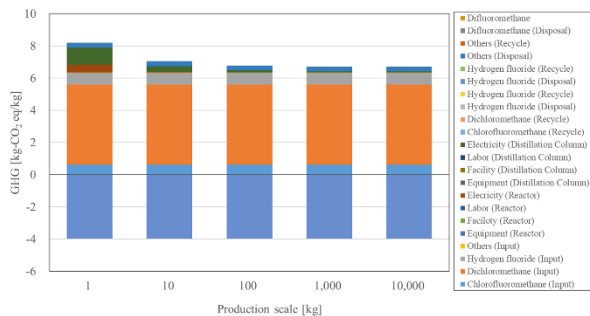
Figure 8.2-2 shows the GHG emissions per kilogram of refrigerant for various refrigerants. The investigated refrigerants were R32, R1234yf, R1132, HFO1123, R1123, R1234ze, R1132E, R290, and R744, which are potential mixed-refrigerant candidates in this project. When multiple patents were available for the same compound, the evaluation results are presented separately by company.

For the inventory analysis, the scale-up analysis method proposed by Kawajiri and Inoue (2016) was used to evaluate environmental impacts at each manufacturing scale. When organic compounds were generated as by-products, credits associated with their recovery and utilization were considered. For R290 and R744, the values for propane and carbon dioxide included in AIST-IDEA v3.5 were adopted, namely, 1.81 and 0.7 kg-CO₂ eq/kg, respectively.

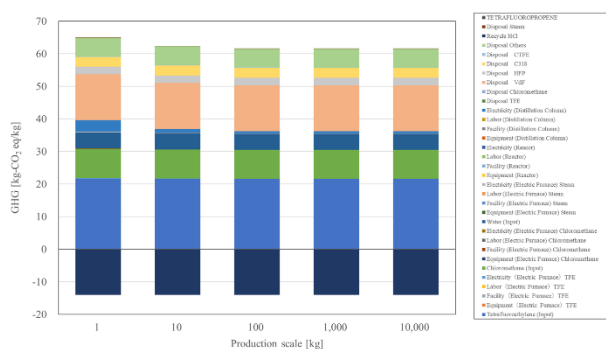
The results indicate that the environmental impact of refrigerants is generally governed by the environmental impact of the organic compounds used as raw materials and by the process yield. The effect of yield is particularly significant; depending on the refrigerant type and manufacturing route, extremely low yields may lead to large environmental impacts. R1234yf, R1132, and R1123 exhibit large environmental burdens regardless of the manufacturing route. In contrast, R1234ze and R1132E exhibit smaller environmental impacts, whereas the environmental impact of R32 varies substantially depending on the manufacturing route. Natural refrigerants such as propane and carbon dioxide have smaller manufacturing-stage environmental impacts than synthesized refrigerants.



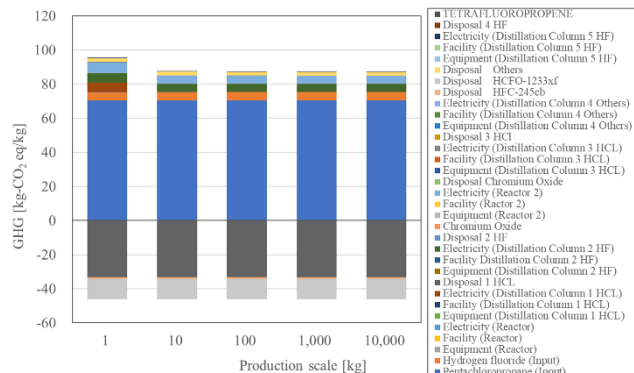
R32 (Company A)



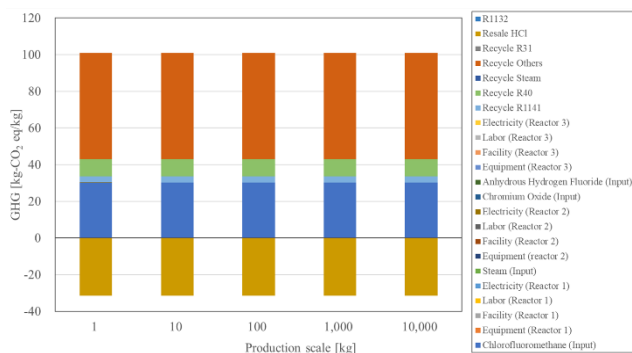
R32 (Company B)



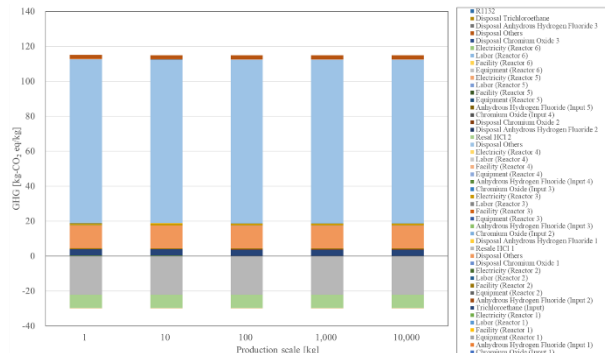
R1234yf (Company C)



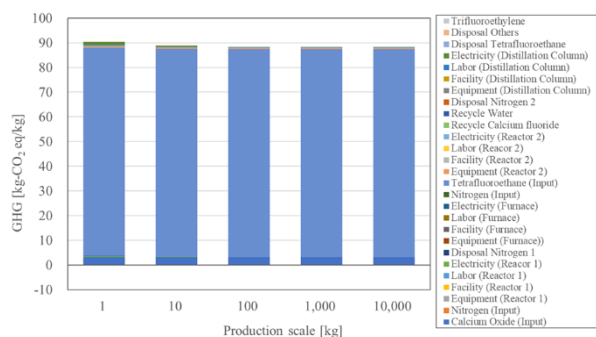
R1234yf (Company A)



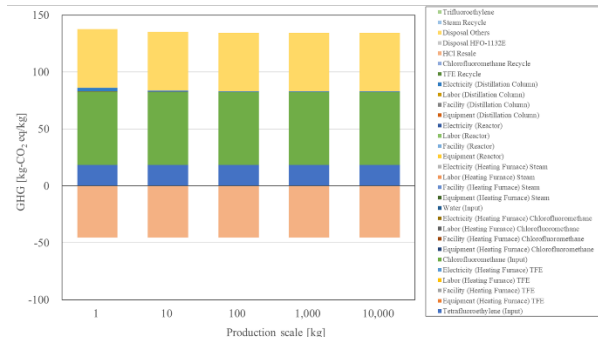
R1132 (Company C)



R1132 (Company A)



HFO1123 (Company C)



R1123 (Company C)

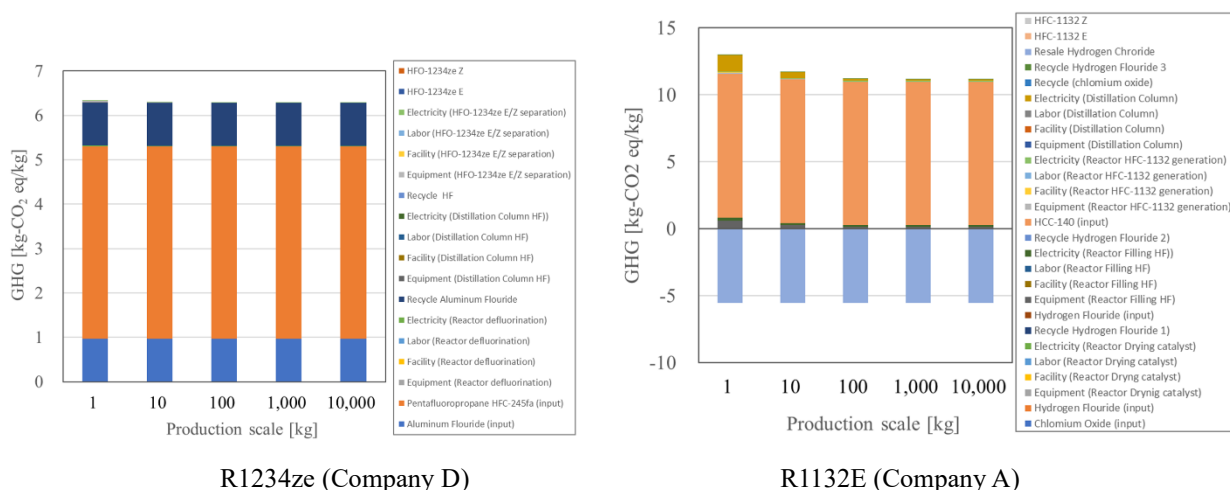


Figure 8.2-2 GHG emissions per 1 kg refrigerant

Figure 8.2-3 shows the estimated annual electricity consumption of air conditioners using various single-component and mixed refrigerants. In this estimation, cycle simulations were performed under the Tokyo standard temperature conditions specified in JIS C 9612, COP was estimated, and annual electricity consumption was calculated using the operating-rate data reported by Hihara (2010).

The results show that electricity consumption was lowest for single-component R1132(E), followed by single-component R32, R1234yf, propane, and R1234ze(E). In contrast, mixed refrigerants tended to have higher electricity consumption than single-component refrigerants, with the CO₂/R1234yf mixture at a composition of 5/95 exhibiting the highest value. Thus, among the seven refrigerant substances considered in this research and development item, single-component refrigerants generally resulted in lower electricity consumption than mixed refrigerants.

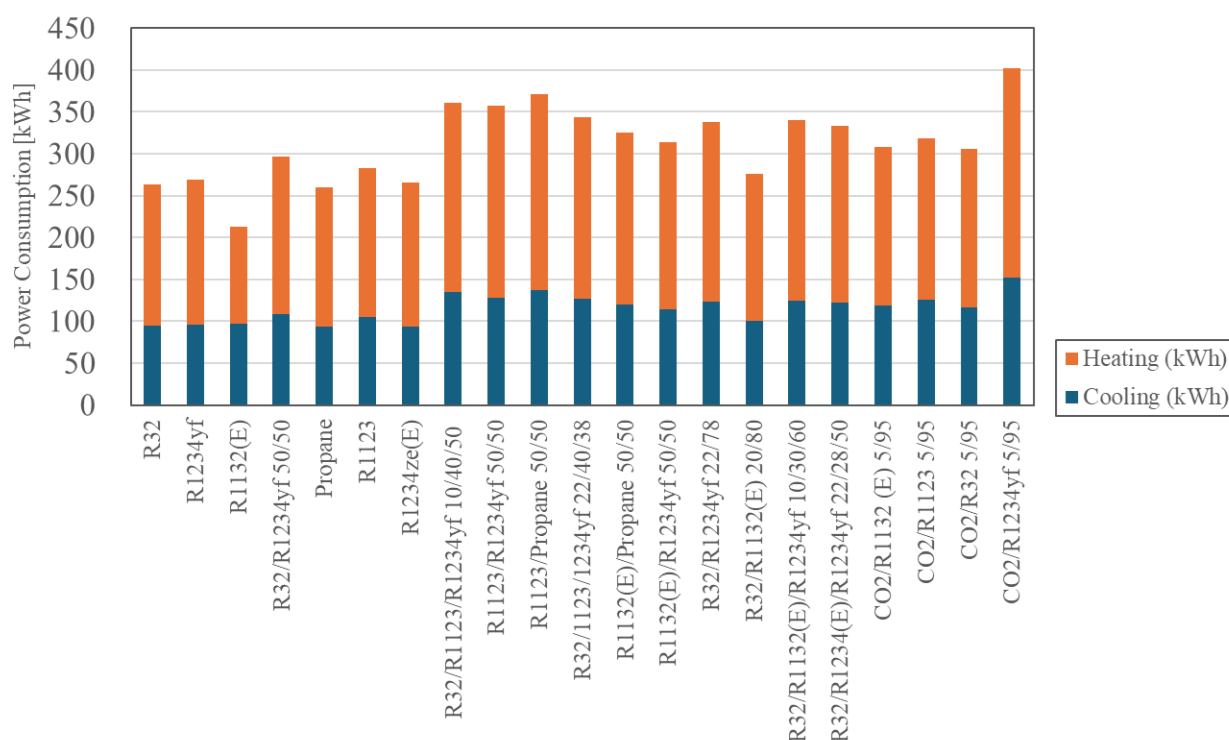


Figure 8.2-3 Comparison of annual energy consumption by refrigerants (5/95 represents % of refrigerants)

Figure 8.2-4 presents the LCCP evaluation results per residential air conditioner for R32 and R1123/CO₂ (95/5). Electricity consumption reflects the results for R32 and R1123/CO₂ (95/5) shown in Figure 8.2-3 and constitutes the largest contribution to total LCCP. GHG emissions from air-conditioner manufacturing are larger for R1123/CO₂ (95/5), because this refrigerant requires a longer pipe length and a larger air-conditioner size than R32. In addition, GHG emissions from refrigerant manufacturing for R1123/CO₂ (95/5) are more than ten times larger than those for R32, thereby increasing the LCCP. In contrast, direct emissions (DE) associated with refrigerant leakage during operation are larger for R32, because the GWP of R32 is 677 kg-CO₂ eq/kg, whereas that of R1123/CO₂ (95/5) is 4.8 kg-CO₂ eq/kg.

These results show that electricity consumption accounts for the majority of air-conditioner LCCP. Therefore, even when the refrigerant itself has a low GWP, a decrease in air-conditioner energy efficiency can increase LCCP and may offset the intended environmental benefit. Therefore, refrigerant selection from an environmental perspective must consider not only refrigerant GWP but also life-cycle impacts as a whole.

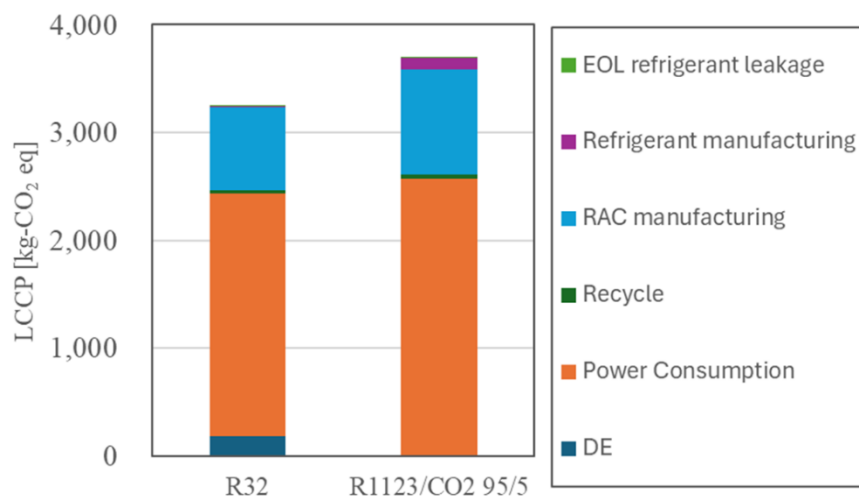


Figure 8.2-4 Comparison of LCCPs of R32 and R1123/CO₂ (95/5)

Figure 8.2-5 shows the relationship between air-conditioner LCCP and refrigerant GWP for the investigated refrigerants. R32, with a high GWP of 677 kg-CO₂ eq/kg, is plotted on the right side of the figure. Refrigerants plotted near the GWP = 0 line include R1234yf, R1123, R1132(E), R1234ze(E), and their mixtures with CO₂. Refrigerants in the intermediate region are mixtures of R32 with R1234yf, R1123, R1132(E), or R1234ze(E). Although no clear relationship was observed between the refrigerant type and LCCP, favorable results in terms of both low GWP and low LCCP were obtained for single-component R1132(E), R1234ze(E), and R290, as well as for mixed refrigerants such as R1123/propane (50/50) and R1132(E)/R1234yf (50/50).

However, R290 is highly flammable and cannot be handled in the same manner as R32, which is currently the mainstream refrigerant for air conditioners. Measures to address flammability are required not only for the air conditioner itself but also during manufacturing, transportation, and maintenance. Therefore, future refrigerant selection must consider safety in addition to the global-warming perspective described above.

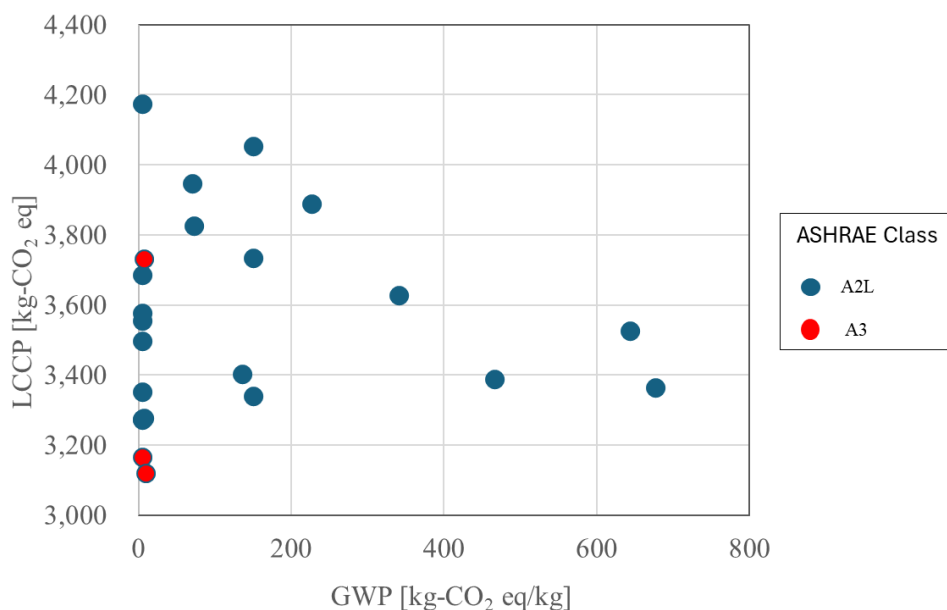


Figure 8.2-5 GWPs and LCCPs of refrigerants

8.3 Social Impact Assessment

Figure 8.3-1 shows the projected number of operating air conditioners in Japan by capacity through 2050, estimated using statistical data from sources including the Cabinet Office (2021) and the National Institute of Population and Social Security Research (2024). The operating stock of air conditioners is expected to decline gradually with population decrease, from 116 million units in 2020 to 103.11 million units in 2050. By capacity class, 2.2 kW units account for the largest share at 40%, followed by 2.8 kW units at 22% and 2.5 kW units at 16%; together, these small-capacity units account for 78% of the total. In contrast, units of 2.2 kW or less account for only 1%, and 3.2 kW units account for only 0.1%, indicating substantial variation by capacity class. Large-capacity units of 4 kW or higher account for only 7%. In future research, these stock estimates will be combined with the environmental impact per air conditioner presented in Section 8.2.1 to estimate the environmental impact associated with the diffusion of air-conditioning equipment compatible with low-GWP mixed refrigerants.

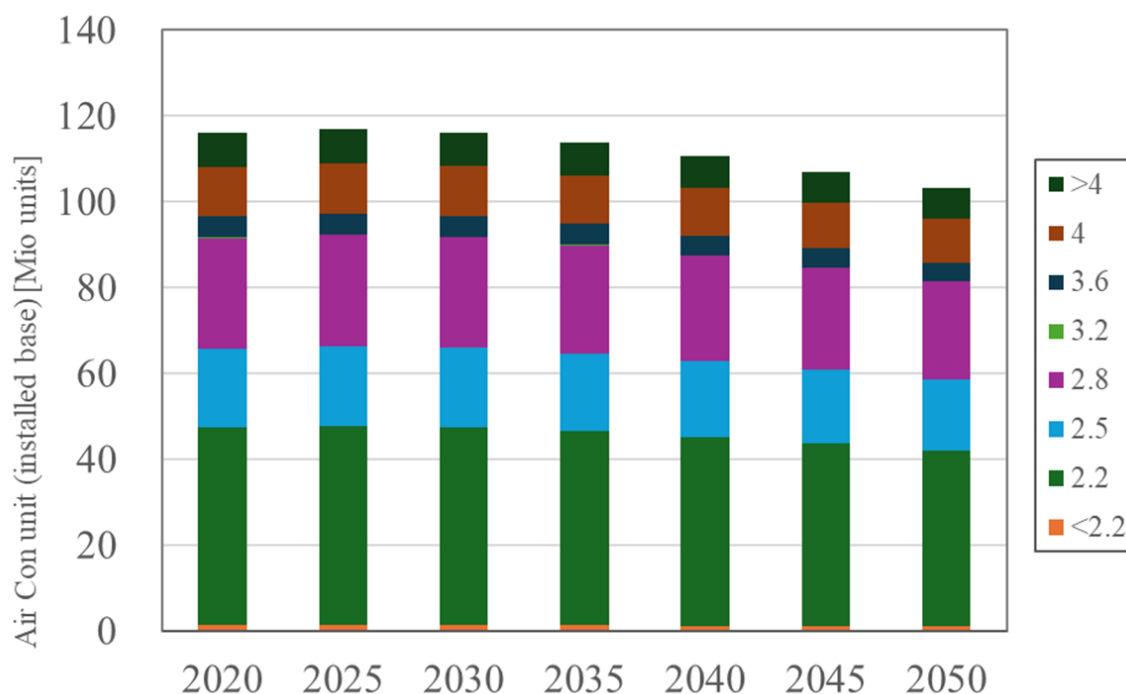


Figure 8.3-1 Number of installed air conditioners with different capacities kW in Japan from 2020 to 2050

8.4 AI Analysis

In this research and development item, AI is used primarily to predict refrigerant physical properties and to optimize air-conditioner specifications based on the predicted properties. This section reports the machine-learning-based prediction of refrigerant physical properties, focusing particularly on the prediction of refrigerant GWP.

The ultimate objective of this research and development item is to optimize refrigerant combinations and air-conditioner specifications to minimize the LCCP. Optimization algorithms require a model capable of estimating GWP for arbitrary refrigerant combinations. Accordingly, this study developed an analytical framework for predicting the 100-year GWP (GWP100) of single-component refrigerants using molecular descriptors and dimensionality reduction (Figure 8.4-1). Principal component analysis and quantile transformation were combined with descriptor sets obtained from RDKit, Mordred, and alvaDesc, and an ensemble neural network was trained. The RDKit-based model exhibited the

highest performance, achieving a root mean square error (RMSE) of 481.9 and coefficient of determination (R^2) of 0.918 for the test data (Figure 8.4-2). Factor analysis indicated that molecular weight, lipophilicity, and functional groups such as nitrile groups and allyl oxides contributed substantially to GWP. For improved usability, a web tool was also developed to return GWP predictions using descriptors calculated by RDKit as inputs. This analytical framework enables efficient screening of refrigerant candidates. For mixed refrigerants, because GWP can be estimated as a composition-weighted average of the component refrigerants, the tool can also be used to estimate the GWP of mixed refrigerants. These analyses have been published as academic papers (Rajapriya and Kawajiri, 2024; Rajapriya and Kawajiri, 2025).

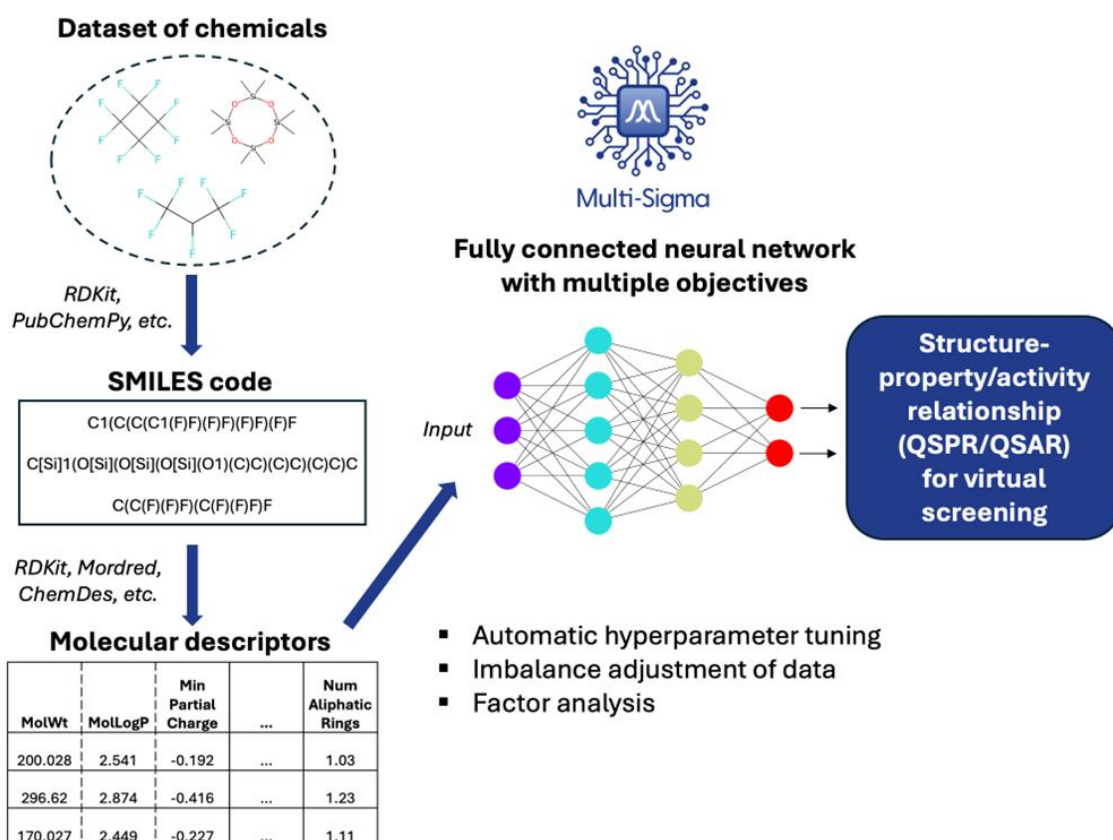


Figure 8.4-1 Framework to estimate the GWP of chemicals

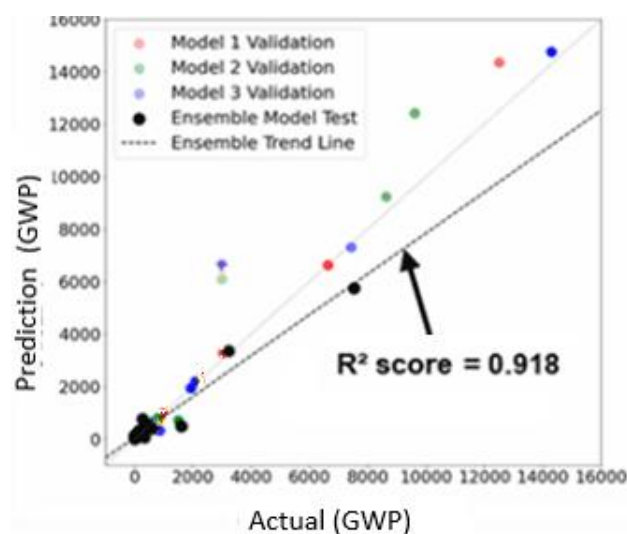


Figure 8.4-2 Accuracy of the GWP prediction model

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