Development of R-1132(E)-based refrigerant blends

○**Tomoyuki GOTO*, Yasufu YAMADA*, Takashi USUI*, Taichi OZAKI*, Kaito SANTA*, Tomohito INOUE*, Masahiro ABE*, Sakura SUGA***

Chemicals Division, Daikin Industries, Ltd., 1-1, Nishi-Hitotsuya, Settsu, Osaka 566-8585, Japan

ABSTRACT

In response to the Kigali Amendment to the Montreal Protocol, various refrigerant blends containing R-1132(E) have been developed as new medium- and high-pressure refrigerants. We have considered a broad range of GWP values and performance levels to address each country's regulations and application needs. This paper discusses the development concept of these R-1132(E) blends and the flammability data that contributed to determining the refrigerant composition.

Keywords: R-1132(E), R-474A, R-474B, R-479A, R-479B, ultra low GWP

1. INTRODUCTION

With the 2016 Kigali Amendment, emission reductions based on the CO_2 equivalent of HFCs have become mandatory, and refrigerants are being shifted to those with lower global warming potential (GWP) for various applications [1]. In developed countries, including Japan, the target is to reduce emissions by 80% by 2034 and 85% by 2036. Furthermore, among developed countries, each country and region has established its own regulations, requiring the practical application of low-GWP refrigerants and the expansion of refrigerant recovery and recycling. In selecting refrigerants for refrigeration and air conditioning equipment, four points - safety, environmental impact, energy efficiency, and economic viability - are comprehensively evaluated for each application, and refrigerants are selected based on their suitability for the specific application. For instance, air conditioners are being converted R-32 (GWP 675, Lower Flammability) to replace R-410A (GWP 2090, No Flame Propagation). And for refrigeration, R-407H (GWP 1495, No Flame Propagation) and R-448A (GWP 1387, No Flame Propagation) are being used as replacements of R-404A (GWP 3920, No Flame Propagation). So, refrigerants have been provided based on their applications. To achieve the reduction targets of the future Kigali Amendment and carbon neutrality, the development of new refrigerants with even lower GWP, improved safety, and enhanced energy efficiency is essential. We have conducted research and development on new refrigerants and identified a new refrigerant component, R-1132(E). This paper reports on the development of R-1132(E)-based refrigerant blends and their characteristics.

2. DEVELOPMENT OF R-1132(E)-BASED REFRIGERANTS BLENDS

2-1. BASIC PROPERTIES OF R-1132(E)

The new refrigerant component, R-1132(E) (trans-1,2-difluoroethylene), is an ethylene-based hydrofluoroethylene (HFO) compound with a GWP of less than 1 and a very low impact on global warming [2]. Its saturated vapor pressure has a value close to that of R-32, which is currently a broadly used refrigerant (Fig. 1) [3, 4]. R-1132(E) is highly valuable as a component of mixed refrigerants, as there has been no refrigerant substance with a GWP below 1 in this pressure range so far. International standard ISO 817 and US standard ASHRAE 34, which specify the safety of refrigerants, classify toxicity into two categories (Lower chronic toxicity: A, higher chronic toxicity: B) and flammability into four categories (No Flame Propagation: Class 1, Lower Flammability: Class 2L, Flammable: Class 2, Higher Flammability: Class 3). In July 2022, R-1132(E) was registered with a safety classification of B2. However, in November 2024, the toxicity criteria in the international standard were revised, and R-1132(E) became A2 class (lower chronic toxicity, low flammability). Table 1 shows the basic characteristics of R-1132(E).

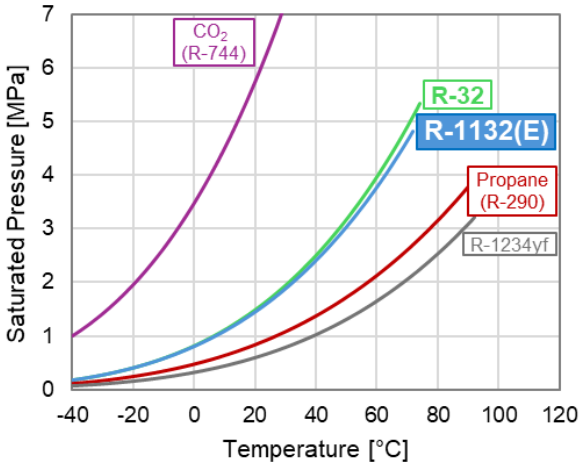

Fig.1 Saturated vapor pressure curves for each refrigerant.

Table 1 Fundamental properties of R-1132(E).

Refrigerant	**R-1132(E)**	**R-32**
Formula	trans-CHF=CHF	CH_2F_2
Molecular Weight [g・mol^{-1}]	64.0	52.0
Critical Temperature [°C]	75.7	78.1
Critical Pressure [MPa]	5.17	5.78
Boiling Point [°C]	-52.6	-51.7
Vapor Pressure at 25 °C [MPa]	1.67	1.69
Vapor Density at 25 °C [kg・m^{-3}]	55.9	47.3
Liquid Density at 25 °C [kg・m^{-3}]	916.5	961.0
Latent Heat at 25 °C [kJ・kg^{-1}]	213.7	270.9
Lower Flammability Limit [vol%]	4.4	14.4
Burning Velocity [cm・s^{-1}]	30.5	6.7
GWP	0.0056 [2]	675 (AR4)

2-2. R-1132(E)-BASED REFRIGERANT BLENDS

Since R-1132(E) brings concerns regarding self-decomposition reactions if applied to refrigeration and air-conditioning equipment as a single component [5], it is being developed for various applications as a mixed refrigerant. Internationally, the use of flammable refrigerants in refrigeration and air conditioning equipment is limited. Therefore, we have designated the development of lower flammability refrigerants similar to R-32 and R-1234yf, which are standard in air conditioning equipment worldwide, as our development target. Figure 2 summarizes the lower flammability limit (LFL) and burning velocity (BV) of conventional refrigerants, other next-generation refrigerants under consideration, and the new R-1132(E) blends. Many refrigerants present no flame propagation or lower flammability and considering their application to existing systems, lower flammability refrigerants are preferable.

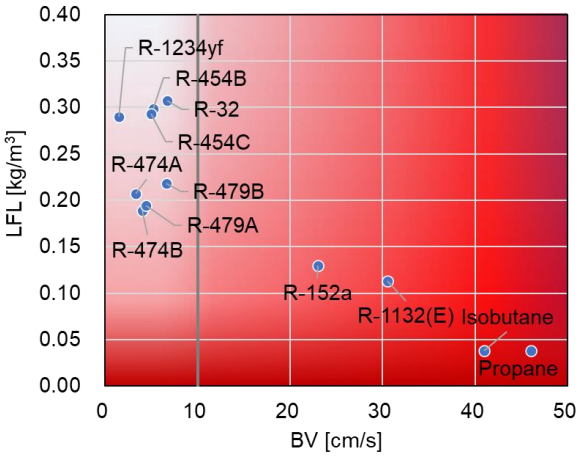

Fig.2 Flammability properties of each refrigerant.

R-1132(E) is flammable as a single refrigerant but can be easily controlled to be lower flammability (BV ≤ 10 cm/s) by mixing it with other lower flammability refrigerants. Four new lower flammability refrigerants - R-474A, R-474B, R-479A, and R-479B - and one new flammable refrigerant, R-491A, were developed. Regarding the development of lower flammability refrigerant blends, the R-1132(E) composition was adjusted for R-474B, R-479A, and R-479B to achieve a maximum burning velocity limit of 10 cm/s or less. The fundamental properties of these five mixed refrigerants, which are already registered under ASHRAE 34, are shown in Table 2. Below, the development concepts and characteristics of each refrigerant are introduced in detail.

Table 2 Refrigerant cycle performance of R-1132(E) blends.

Refrigerant		**R-474A**	**R-474B**	**R-479A**	**R-479B**	**R-491A**
Composition	R-1132(E) [mass%]	23.0	31.5	28.0	23.0	35.0
	R-1234yf [mass%]	77.0	68.5	50.5	33.0	-
	R-32 [mass%]	-	-	21.5	44.0	-
	R-152a [mass%]	-	-	-	-	65.0
Physical Property	Boiling Point [°C]	-43.4	-45.8	-50.5	-51.9	-39.5
	Critical Temp. [°C]	87.8	85.2	80.5	78.1	101.8
	Critical Pres. [MPa]	4.05	4.22	4.81	5.23	4.98
	Pres. at 25 °C [MPa]	1.07	1.18	1.46	1.61	0.972
Flammability	LFL for WCL [kg・m^{-3}]	0.207	0.189	0.194	0.218	0.123
	BV for WCL [cm・s^{-1}]	3.3	4.0	4.4	6.6	n.d.
Toxicity	ATEL [vol ppm]	58000	50500	63600	81100	56800
	OEL [vol ppm]	440	420	510	610	600
Safety Class		A2L	A2L	A2L	A2L	A2

LFL: Lower Flammability Limit, BV: Burning Velocity, OEL: Occupational Exposure Limit
WCF: Worst Case of Formulation for flammability, ATEL: Acute-Toxicity Exposure Limit

R-474 series

To develop an ultra-low GWP refrigerant with a GWP of 10 or less and lower flammability, a two-component blend refrigerant concept composed of R-1132(E) and R-1234yf was developed. R-474A (R-1132(E)/1234yf = 23.0/77.0) was designed to suppress flammability while improving refrigeration capacity compared to R-1234yf. Table 3 shows the results of theoretical cycle performance calculations for EV applications [Evaporation temperature: 5 °C, Condensation temperature: 60 °C, Superheat: 5 K, Subcooling: 5 K, Compression efficiency: 70%]. The calculations were performed using REFPROP ver10.0 [6] incorporating R-1132(E) and the mixing rules for each refrigerant. This refrigerant is expected to be used as an alternative to R-1234yf in electric vehicles (EVs). EVs have traditionally used electric heaters for heating because they cannot utilize engine waste heat. However, as EVs become more energy-efficient, heat pump systems are increasingly being adopted. The boiling points of the currently prevalent refrigerants R-134a and R-1234yf are relatively high at -26.1 °C and -29.5 °C, respectively. This results in low gas density during periods of low outside air temperature, making rapid heating using heat pumps difficult. Consequently, electric heaters become necessary, leading to significant battery drain. In contrast, R-474A has a low boiling point of -43.4 °C, enabling stable operation even in cold ambient temperatures. For EV air conditioning applications, it delivers higher performance than R-1234yf under low-temperature conditions.

Table 3 Refrigerant cycle performance of R-474A.

Refrigerant	**R-474A**	**R-1234yf**
GWP (AR4)	3*	4
COP (R-1234yf = 100)	99	100
Capacity (R-1234yf = 100)	140	100
Glide Eva. /Cond. [K]	3.6/5.0	-
Discharge Temp. [°C]	80.7	70.0
Cond. Pres. [MPa]	2.3	1.6

* The GWP for R-1132(E) is calculated as 0.0056.

R-474B (R-1132(E)/1234yf = 31.5/68.5) has a boiling point of -45.8 °C and is designed to maintain positive pressure even at -40 °C, making it suitable for refrigeration and freezing applications. Table 4 shows the results of theoretical cycle performance calculations for refrigeration applications [Evaporation temperature: -40°C, Condensation temperature: 40 °C, Superheat: 20 K, Subcooling: 5 K, Compression efficiency: 70%]. Refrigeration equipment such as showcases is transitioning from high-GWP refrigerants like R-448A to non-fluorinated alternatives with GWP < 10, with natural refrigerants like R-290 and R-744 increasingly being adopted. However, challenges remain, including restrictions on refrigerant charge due to its higher flammability, the need for ultra-high pressure compatibility, equipment size requirements, and energy efficiency. R-474B has a GWP equivalent to natural refrigerants and is defined as a non-fluorocarbon refrigerant in Japan. R-474B is a refrigerant that combines safety and energy efficiency, making it a promising alternative alongside natural refrigerants.

Table 4 Refrigerant cycle performance of R-474B.

Refrigerant	**R-474B**	**R-448A**
GWP (AR4)	3*	1386
COP (R-448A = 100)	99	100
Capacity (R-448A = 100)	87	100
Glide Eva. /Cond. [K]	3.8/6.1	4.1/5.0
Discharge Temp. [°C]	100	119
Cond. Pres. [MPa]	1.6	1.8

* The GWP for R-1132(E) is calculated as 0.0056.

Both R-474A and R-474B possess physical properties similar to R-454C (GWP < 150), which is expected to be the next-generation refrigerant for refrigeration and air conditioning applications. This similarity also makes it possible to achieve ultra-low GWP through drop-in equivalent development from R-454C.

R-479 series

To improve the performance of R-474 series refrigerants with GWP < 10, we developed R-479A (R-1132(E)/1234yf/32 = 28.0/50.5/21.5), a three-component blend refrigerant composed of R-32, and R-479B (R-1132 (E)/1234yf/32 = 23.0/33.0/44.0) were developed. Table 5 shows the results of theoretical cycle performance calculations for air conditioning applications [Evaporation temperature: 5 °C, Condensation temperature: 45 °C, Superheat: 5 K, Subcooling: 5 K, Compression efficiency: 70%]. R-479A has a GWP < 150 and 1.4 times the refrigeration capacity of R-474A. Its temperature glide is approximately 5 K, equivalent to R-407C. This refrigerant is a viable option for meeting GWP < 150 regulations in many countries and regions, regardless of application, including air conditioning, refrigeration, and EVs. R-479B was developed by further increasing the R-32 composition ratio, achieving a GWP < 300. Its refrigeration capacity is equivalent to R-410A, widely used globally in air conditioning, and R-454B, gaining traction in North American air conditioning applications. Its temperature glide is 2.5 K, potentially avoiding significant equipment redesigns. For countries and regions using R-410A (GWP 2088) as their baseline refrigerant, it is considered a viable option for meeting the Kigali Amendment's 2036 target of an 85% reduction.

R-491 series

Finally, to significantly improve COP and as an alternative to R-290, we developed the flammable refrigerant R-491A (R-1132(E)/152a = 35/65) blended with R-152a. To address the safety concerns of the higher flammability refrigerant R-290, we achieved a flammability 2 classification at equivalent pressures. Table 6 shows the results of theoretical cycle performance calculations for EV applications [Evaporation temperature: 5 °C, Condensation

temperature: 60 °C, Superheat: 5 K, Subcooling: 5 K, Compression efficiency: 70%]. We consider this a viable option for applications where R-290 adoption is progressing but where safety concerns prevent its installation.

Table 5 Refrigerant cycle performance of R-479A and R-479B.

Refrigerant	**R-479A**	**R-479B**	**R-410A**	**R-454B**	**R-32**	**R-454C**
GWP (AR4)	147*	299*	2088	466	675	147
COP (R410A = 100)	102	102	100	102	102	104
Capacity (Theoretical)	82	95	100	98	110	65
Glide Eva. /Cond. [K]	5.0/5.2	2.5/2.5	0.1/0.1	1.3/1.4	-	5.9/7.2
Discharge Temp. [°C]	73.0	78.9	76.9	83.2	95.0	68
Cond. Pres. [MPa]	2.2	2.6	2.7	2.5	2.8	1.8

* The GWP for R-1132(E) is calculated as 0.0056.

Table 6 Refrigerant cycle performance of R-491A.

Refrigerant	**R-491A**	**R-290**
GWP (AR4)	81*	4
COP (R-290 = 100)	104	100
Capacity (R-290 = 100)	103	100
Glide Eva. /Cond. [K]	4.8/5.6	-
Discharge Temp. [°C]	100.8	81.0
Cond. Pres. [MPa]	2.1	2.1

* The GWP for R-1132(E) is calculated as 0.0056.

Figure 3 compares the boiling points and GWPs of the five new R-1132(E)-based refrigerant blends described above with various conventional refrigerants. The numbers in parentheses indicate the temperature glide when performing theoretical cycle calculations for air conditioning applications. The four new lower flammability refrigerant blends, excluding R-491A, are the refrigerants with the lowest GWP in the -40 °C to -50 °C range and are candidates to replace conventional high-GWP refrigerants. Furthermore, even in applications where low-GWP refrigerants are already widely used, these new refrigerants offer the potential for higher capacity, enabling smaller equipment and improved energy efficiency. However, a closer look into temperature glide reveals a tendency for it to increase as GWP decreases. Temperature glide is the characteristic change in temperature at a constant pressure when a non-azeotropic mixed refrigerant evaporates or condenses. Generally, a larger temperature glide necessitates improvements to heat exchangers and the system. The larger the boiling point difference between the refrigerants being mixed, the larger the temperature glide. There are no low-GWP refrigerants with boiling points comparable to widely used R-410A, R-32, or R-404A other than R-1132(E). Furthermore, since R-1132(E) cannot be used alone, designing ultra-low-GWP blends requires mixing it with refrigerants like R-1234yf that have relatively distant boiling points. To reduce the temperature glide, blending with R-32 is essential, but this increases the GWP, creating a trade-off between GWP and the extent of equipment modifications required. Refrigerant selection must be tailored to the application. Ultra-low GWP refrigerants are expected to be applied in applications where equipment can accommodate temperature glide. Conversely, when addressing temperature glide would significantly increase the overall environmental impact, refrigerants with a GWP between 150 and 300, blended with R-32, are considered preferable.

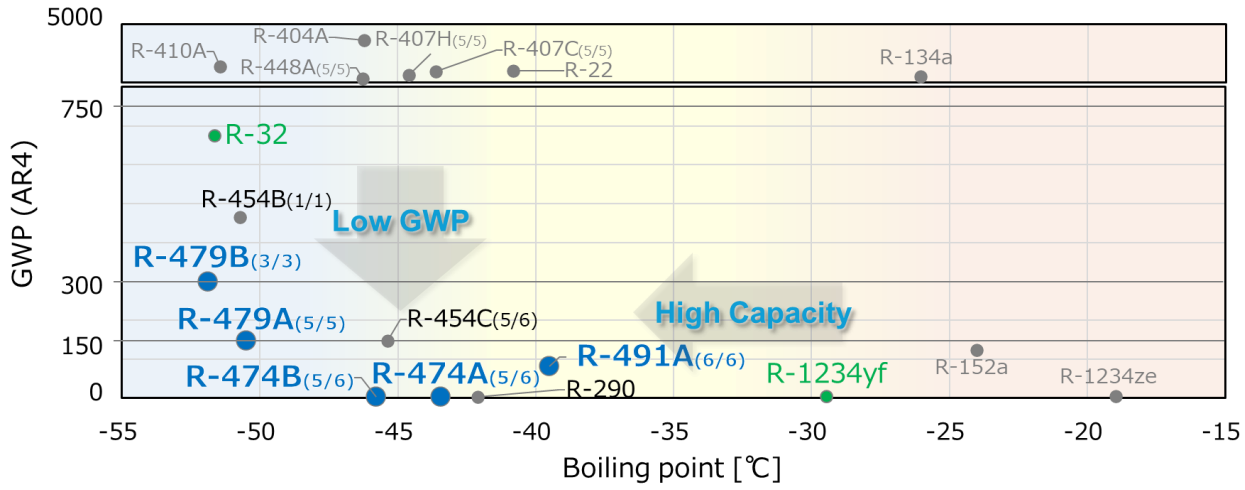

Fig.3 GWP and boiling point of each refrigerant.

CONCLUSIONS

Various R-1132(E)-based refrigerant blends have been developed. R-474A and R-474B, which are lower flammability 2L and have a GWP < 10, are recognized as ultra-low GWP refrigerants for EV, refrigeration, and air conditioning applications. Furthermore, based on refrigerant physical properties, drop-in replacement from R-454C is also anticipated. R-479A (GWP < 150) and R-479B (GWP < 300) enhance capacity while successfully reducing temperature glide, enabling the provision of high-performance refrigeration and air-conditioning equipment while maintaining low to moderate GWP values. We will contribute to global environmental issues by proposing R-1132(E)-based refrigerants tailored to specific regions, applications, and regulations, and by promoting their adoption.

NOMENCLATURE

AR4 : IPCC Fourth Assessment Report
COP : Coefficient of performance

REFERENCES

[1] UNEP Ozone Secretariat: ”Report of the Twenty-Eighth Meeting of the Parties to the Montreal Protocol on Substances that Deplete the Ozone Layer” Kigali, Rwanda (2016).
[2] K. Tokuhashi, T. Uchimaru, K. Takizawa, S. Kondo: J. Phys. Chem. A., 123, 4834 (2019).
[3] U. A Perera, N. Sakoda, T. Miyazaki, K. Thu, Y. Higashi: Int. J. Refrig., 135, 148 (2022).
[4] N. Sakoda, U. A Perera, K, Thu, Y. Higashi: Int. J. Refrig., 140, 166 (2022).
[5] T. Goto, T. Usui, T. Yoshimura, Y. Yamada: Int. J. Refrig., 163, 71 (2024)
[6] E. W. Lemmon, I. H. Bell, M. L. Huber, and M. O. McLinden: NIST Reference Fluid Thermodynamic and Transport Properties Database (REFPROP) Version 10.0 (2018).

ACKNOWLEDGMENTS

This paper is based on results obtained from a project, JPNP18005, subsidized by the New Energy and Industrial Technology Development Organization (NEDO).

R-1132(E)混合冷媒の開発
Development of R-1132(E)-based refrigerant blends

後藤 智行・山田 康夫・臼井 隆・尾崎 太一・三田 海人
井上 智仁・阿部 晟大・菅 咲来　　ダイキン工業（株）

Tomoyuki GOTO*, Yasufu YAMADA*, Takashi USUI*, Taichi OZAKI*, Kaito SANTA*, Tomohito INOUE*, Masahiro ABE*, Sakura SUGA*
* Daikin Industries, Ltd., 1-1, Nishi-Hitotsuya, Settsu, Osaka 566-8585, Japan

In response to the Kigali Amendment to the Montreal Protocol, various refrigerant blends containing R-1132(E) have been developed as new medium- and high-pressure refrigerants. Since it is necessary to select refrigerants appropriate for each country's regulations and applications, we have not only considered next-generation refrigerants with a GWP < 10 but also low-GWP refrigerants that prioritize refrigerant performance to address energy issues. This paper discusses the development concept of these R-1132(E) blends and the flammability data that contributed to determining the refrigerant composition.

Key Word: R-1132(E), trans-1,2-difluoroethylene, R-474A, R-474B, R-479A, R-479B, ultra low GWP

１．はじめに

2016 年のキガリ改正に伴い、HFC の CO_2 換算量を基にした削減が義務付けられ[1)]、冷媒は様々な用途で地球温暖化係数（GWP）の低い冷媒へと転換されている。我が国を含む先進国では 2034 年に 80%削減、2036 年に 85%削減の目標が掲げられ、さらに先進国の中でも国や地域によって独自の規制が設けられており、低 GWP 冷媒の実用化や冷媒の回収再生の拡大が求められている。

冷凍空調機器の冷媒選択については、用途ごとに安全性、環境性、エネルギー効率、経済性の四つの観点から総合的に評価され、適材適所で冷媒が選ばれてきた。例えば、空調機用の冷媒としては、R-410A（GWP2090、不燃性）の代替として、R-32（GWP675、微燃性）へ転換が進んでいる。また冷凍冷蔵用としては、R-404A（GWP3920、不燃性）の代替として、R-407H（GWP1495、不燃性）や R-448A（GWP1387、不燃性）へと転換されており、このように用途に応じた冷媒がこれまで提供されてきた。

将来のキガリ改正の削減目標およびカーボンニュートラルを達成するためには、これまで以上の低 GWP 化が求められ、さらに安全性と省エネ性に優れた新冷媒の開発が必須となる。我々は新冷媒の探索および開発を行い、新たな冷媒成分である R-1132(E)を見出した。本稿では R-1132(E)を主とした混合冷媒の開発およびその特徴について報告する。

２．R-1132(E)混合冷媒の開発

２－１．R-1132(E)の基本物性

新しい冷媒成分である R-1132(E)（トランス-1,2-ジフルオロエチレン）はエチレン系の HFO 化合物であり、GWP が 1 以下で地球温暖化への影響が極めて小さい物質である[2)]。その飽和蒸気圧は、現在主に使用されている R-32 に近い値を有する[3, 4)]（図 1）。この圧力領域で GWP1 以下の冷媒物質は他に無く、R-1132(E)は混合冷媒成分として利用価値が高い。冷媒の安全性を規定する国際規格 ISO 817 や米国規格 ASHRAE 34 では、毒性を 2 つの区分（低毒性：A、高毒性：B）、燃焼性を 4 つの区分（不燃性：Class1、微燃性：Class2L、弱燃性：Class2、強燃性：Class3）に分類している。2022 年 7 月、R-1132(E)は安全性区分が B2 で登録されたが、2024 年 11 月に国際規格における毒性基準の見直しが行われ、R-1132(E)は A2（低毒性、

弱燃性）となる。R-1132(E)の基本特性を表 1 に示す。

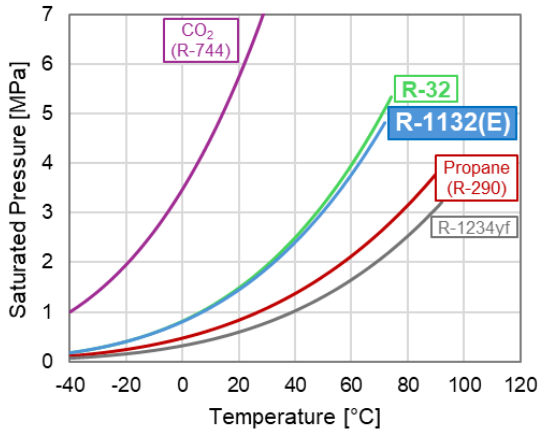

Fig.1 Saturated vapor pressure curves for each refrigerant.

Table 1 Fundamental properties of R-1132(E).

Refrigerant	**R-1132(E)**	**R-32**
Formula	trans-CHF=CHF	CH_2F_2
Molecular Weight [g･mol^{-1}]	64.0	52.0
Critical Temperature [°C]	75.7	78.1
Critical Pressure [MPa]	5.17	5.78
Boiling Point [°C]	-52.6	-51.7
Vapor Pressure at 25 °C [MPa]	1.67	1.69
Vapor Density at 25 °C [kg･m^{-3}]	55.9	47.3
Liquid Density at 25 °C [kg･m^{-3}]	916.5	961.0
Latent Heat at 25 °C [kJ･kg^{-1}]	213.7	270.9
Lower Flammability Limit [vol%]	4.4	14.4
Burning Velocity [cm･s^{-1}]	30.5	6.7
GWP	0.0056 [2]	675 (AR4)

2－2．R-1132(E)混合冷媒

R-1132 (E) 単体での冷凍空調機器への適用は自己分解反応の懸念を有することから [5]、混合冷媒として様々な用途に対して展開を図っている。国際的に弱燃性冷媒の冷凍空調機器への適用は限定的である。そのため、世界の空調機器でスタンダードになっている R-32 や R-1234yf と同様の微燃性冷媒を開発ターゲットとした。図 2 に従来冷媒とこれまで検討されている主な次期冷媒、および新たな R-1132(E)混合冷媒の燃焼下限界（LFL）と燃焼速度（BV）をまとめた。多くの冷媒は不燃性もしくは微燃性であり、既存システムへの適用を考慮すると微燃性冷媒であることが好ましい。

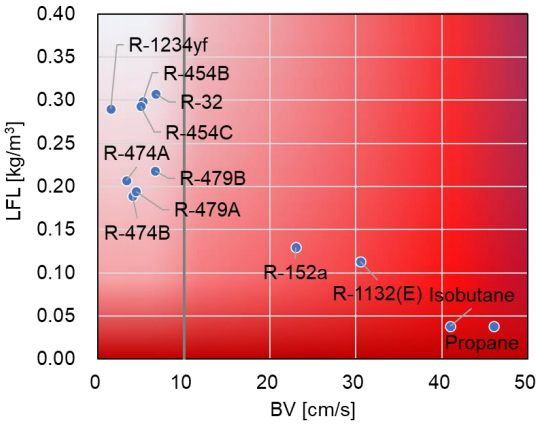

Fig.2 Flammability properties of each refrigerant.

R-1132(E)は単一冷媒では弱燃性であるが、他の微燃性冷媒と混合することで、容易に微燃性（BV≤10cm/s）に制御することができる。新たな微燃性冷媒として R-474A、R-474B、R-479A、R-479B の 4 冷媒と、弱燃性冷媒として R-491A を新規に開発した。微燃性混合冷媒を開発するにあたっては、R-474B、R-479A、R-479B は燃焼速度が 10cm/s 以下の最大限界となるよう R-1132(E)組成量を調整した。これらの既に冷媒登録済である 5 種の混合冷媒について、その基本特性を表 2 に示す。以下、各冷媒の開発コンセプトや特徴について詳細に紹介する。

R-474 series

GWP が 10 以下の微燃性超低 GWP 冷媒を開発する為、R-1132(E)と R-1234yf を混合した 2 成分混合冷媒を開発した。R-474A（R-1132(E)/1234yf = 23.0/77.0）は燃焼性を抑えながら冷凍能力を R-1234yf よりも向上させることを目指し設計した。表 3 に EV 用途における理論サイクル性能計算の結果を示す［蒸発温度：5℃、凝縮温度：60℃、過

熱：5K、過冷却：5K、圧縮効率：70%］。計算は REFPROP ver10.0 [6]に R-1132(E)と各冷媒の混合則を組み込んで行った。この冷媒は電気自動車用（EV）の R-1234yf 代替としての利用が期待される。EV はエンジン廃熱の利用ができないために暖房には電気ヒーターが使用されてきたが、EV の省エネルギー化に伴いヒートポンプシステムが採用されつつある。現在普及している R-134a や R-1234yf の沸点はそれぞれ-26.1℃、-29.5℃と比較的高く、低外気時のガス密度が低くなるため、ヒートポンプを活用しての急速暖房が困難であり、電気ヒーターが必要になることで電池の消耗が激しくなる。一方、R-474A は沸点が-43.4℃と低いため、寒冷な外気温下でも安定した運転が可能で、EV 用空調用途において R-1234yf よりも低温条件下で高い性能を発揮することができる。

Table 2 Refrigerant cycle performance of R-1132(E) blends.

Refrigerant		R-474A	R-474B	R-479A	R-479B	R-491A
Composition	R-1132(E) [mass%]	23.0	31.5	28.0	23.0	35.0
	R-1234yf [mass%]	77.0	68.5	50.5	33.0	-
	R-32 [mass%]	-	-	21.5	44.0	-
	R-152a [mass%]	-	-	-	-	65.0
Physical Property	Boiling Point [°C]	-43.4	-45.8	-50.5	-51.9	-39.5
	Critical Temp. [°C]	87.8	85.2	80.5	78.1	101.8
	Critical Pres. [MPa]	4.05	4.22	4.81	5.23	4.98
	Pres. at 25 °C [MPa]	1.07	1.18	1.46	1.61	0.972
Flammability	LFL for WCL [kg・m^{-3}]	0.207	0.189	0.194	0.218	0.123
	BV for WCL [cm・s^{-1}]	3.3	4.0	4.4	6.6	n.d.
Toxicity	ATEL [vol ppm]	58000	50500	63600	81100	56800
	OEL [vol ppm]	440	420	510	610	600
Safety Class		A2L	A2L	A2L	A2L	A2

LFL: Lower Flammability Limit, BV: Burning Velocity, OEL: Occupational Exposure Limit
WCF: Worst Case of Formulation for flammability, ATEL: Acute-Toxicity Exposure Limit

Table 3 Refrigerant cycle performance of R-474A.

Refrigerant	R-474A	R-1234yf
GWP (AR4)	3*	4
COP (R-1234yf = 100)	99	100
Capacity (R-1234yf = 100)	140	100
Glide Eva. /Cond. [K]	3.6/5.0	-
Discharge Temp. [°C]	80.7	70.0
Cond. Pres. [MPa]	2.3	1.6

* The GWP for R-1132(E) is calculated as 0.0056.

R-474B（R-1132(E)/1234yf = 31.5/68.5）は沸点が-45.8℃であり、-40℃でも陽圧を維持できるよう設計しており、冷凍冷蔵用途での適用が見込まれる。表 4 に冷凍用途での理論サイクル性能計算の結果を示す［蒸発温度：-40℃、凝縮温度：40℃、過熱：20K、過冷却：5K、圧縮効率：70%］。ショーケース等の冷凍冷蔵機器は GWP の高い R-448A 等から GWP<10 のノンフロン化が進展しており、自然冷媒である R-290 や R-744 が採用されつつある。しかし強燃性による冷媒充填量の制約や、超高圧対応に伴う機器の大型化、省エネ性が課題となっている。R-474B は GWP が自然冷媒と同等であり、国内ではノンフロン冷媒として定義されている。安全性と省エネ性を兼備する冷媒であり、自然冷媒に並ぶ選択肢として期待できる。

Table 4 Refrigerant cycle performance of R-474B.

Refrigerant	R-474B	R-448A
GWP (AR4)	3*	1386
COP (R-448A = 100)	99	100
Capacity (R-448A = 100)	87	100
Glide Eva. /Cond. [K]	3.8/6.1	4.1/5.0
Discharge Temp. [°C]	100	119
Cond. Pres. [MPa]	1.6	1.8

* The GWP for R-1132(E) is calculated as 0.0056.

また R-474A も R-474B も、冷凍冷蔵用途や空調用途等において次世代冷媒として期待される R-

454C (GWP<150) と類似した物性であり、R-454C からドロップイン相当の開発での超低 GWP 化も期待できる。

R-479 series

GWP<10 の R-474 series の性能を向上させるため R-32 を混合した 3 成分混合冷媒である R-479A (R-1132(E)/1234yf/32 = 28.0/50.5/21.5) と、R-479B (R-1132(E) /1234yf/32 = 23.0/33.0/44.0) を開発した。表 5 に空調用途での理論サイクル性能計算の結果を示す［蒸発温度：5℃、凝縮温度：45℃、過熱：5K、過冷却：5K、圧縮効率：70%］。R-479A は GWP<150 で、R-474A に対し 1.4 倍の冷凍能力を有する。また温度グライドは約 5K であり、R-407C 同等である。この冷媒は空調や冷凍冷蔵、EV 等、用途を問わず多くの国や地域における GWP<150 規制に対して有効な選択肢と言える。

R-479B はさらに R-32 の組成比率を高め、GWP<300 の冷媒として開発した。冷凍能力はグローバルの空調用途で広く普及している R-410A や、北米空調用途で普及が進む R-454B と同等の特性を有する。温度グライドは 2.5K であり、機器の大幅な仕様変更を避けられる可能性がある。キガリ改正における 2036 年 85%削減の目標に対して、基準年に R-410A (GWP2088) を使用されている国や地域においては、選択肢の一つになると考えられる。

Table 5 Refrigerant cycle performance of R-479A and R-479B.

Refrigerant	**R-479A**	**R-479B**	**R-410A**	**R-454B**	**R-32**	**R-454C**
GWP (AR4)	147*	299*	2088	466	675	147
COP (R410A = 100)	102	102	100	102	102	104
Capacity (Theoretical)	82	95	100	98	110	65
Glide Eva. /Cond. [K]	5.0/5.2	2.5/2.5	0.1/0.1	1.3/1.4	-	5.9/7.2
Discharge Temp. [°C]	73.0	78.9	76.9	83.2	95.0	68
Cond. Pres. [MPa]	2.2	2.6	2.7	2.5	2.8	1.8

* The GWP for R-1132(E) is calculated as 0.0056.

R-491 series

最後に、COP の大幅向上および R-290 の代替として、R-152a と混合した弱燃性冷媒 R-491A (R-1132(E)/152a = 35/65) を開発した。強燃性冷媒 R-290 の課題である安全性の改良として、同等の圧力で燃焼性区分を弱燃性とした。表 6 に EV 用途での理論サイクル性能計算の結果を示す［蒸発温度：5℃、凝縮温度：60℃、過熱：5K、過冷却：5K、圧縮効率：70%］。R-290 の採用が進む用途で安全上設置できない等の課題を持つ用途に対し、可能性があると考える。

Table 6 Refrigerant cycle performance of R-491A.

Refrigerant	**R-491A**	**R-290**
GWP (AR4)	81*	4
COP (R-290 = 100)	104	100
Capacity (R-290 = 100)	103	100
Glide Eva. /Cond. [K]	4.8/5.6	-
Discharge Temp. [°C]	100.8	81.0
Cond. Pres. [MPa]	2.1	2.1

* The GWP for R-1132(E) is calculated as 0.0056.

これまで述べた新たな 5 種の R-1132(E)混合冷媒について、種々の従来冷媒の沸点と GWP を図 3 で比較した。() 内の数字は空調用途における理論サイクル計算を行った場合の温度グライドである。R-491A を除く 4 種の新たな微燃性混合冷媒は、-40℃から-50℃の沸点領域において最も GWP の低い微燃性冷媒であり従来の高 GWP 冷媒の代替候補となる。また、すでに低 GWP 化が進んでいる

用途においても、高能力化が期待でき、機器の小型化や省エネ性向上が見込まれる。一方で温度グライドに着目すると、GWP が低くなるほど温度グライドが大きくなる傾向が見られる。温度グライドは非共沸の混合冷媒が蒸発や凝縮する際に、一定の圧力下で温度が変化する特性であり、一般に、温度グライドが大きいほど熱交換器やシステムの改良が必要となる。温度グライドは混合する冷媒の沸点差が大きくなるほど増大する。現在広く使用されている R-410A、R-32 や R-404A 相当の沸点領域の低 GWP 冷媒種は R-1132(E)以外に存在せず、また R-1132(E)単体では使用できないため、超低 GWP 混合冷媒の設計には R-1234yf のような比較的沸点が離れた冷媒を混合しなければならない。温度グライドを小さくするためには、R-32 との混合が不可欠であるが、GWP が上がることとなり、GWP と機器改良の程度がトレードオフとなる。冷媒は用途に応じた選定が求められ、機器側で温度グライドの対応が可能な用途においては超低 GWP 冷媒の適用が見込まれる。一方で温度グライドの対応によって総合的な環境への影響が大きくなる場合には、R-32 を混合した 150 から 300 の冷媒の適用が好ましいと考えられる。

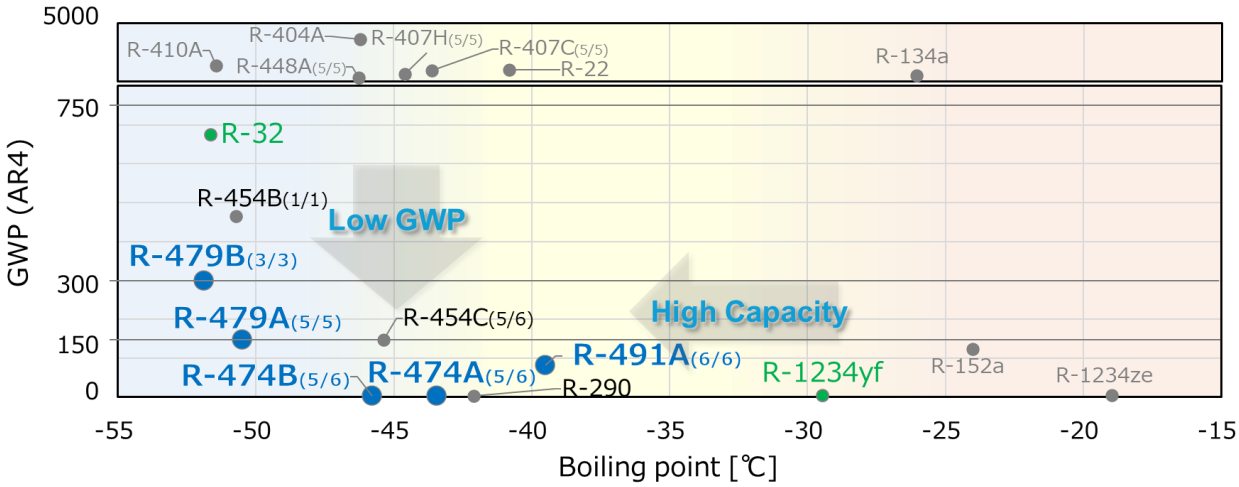

Fig.3 GWP and boiling point of each refrigerant.

4．まとめ

R-1132(E)を主とした種々の混合冷媒を開発した。微燃性かつ GWP<10 の R-474A、R-474B は EV 用、冷凍冷蔵用、空調用で超低 GWP 冷媒として評価されている。また冷媒物性から R-454C からのドロップインも期待できる。GWP<150 の R-479A、GWP<300 の R-479B は能力を向上させるとともに、温度グライドの低減に成功し、高性能な冷凍空調機器の提供が可能になる。我々は R-1132(E)を軸に地域・用途・規制に合わせた適材適所な冷媒を提案し、普及を図ることで地球環境問題に貢献していく。

参考文献

1）UNEP Ozone Secretariat：“Report of the Twenty-Eighth Meeting of the Parties to the Montreal Protocol on Substances that Deplete the Ozone Layer” Kigali, Rwanda (2016).

2）K. Tokuhashi, T. Uchimaru, K. Takizawa, S. Kondo：J. Phys. Chem. A., 123, 4834 (2019).

3）U. A Perera, N. Sakoda, T. Miyazaki, K. Thu, Y. Higashi：Int. J. Refrig., 135, 148 (2022).

4）N. Sakoda, U. A Perera, K, Thu, Y. Higashi:Int. J. Refrig., 140, 166 (2022).

５）T. Goto, T. Usui, T. Yoshimura, Y. Yamada：Int. J. Refrig., 163, 71 (2024)
６）E. W. Lemmon, I. H. Bell, M. L. Huber, and M. O. McLinden ： NIST Reference Fluid Thermodynamic and Transport Properties Database (REFPROP) Version 10.0 (2018).

謝辞

この成果は、国立研究開発法人新エネルギー・産業技術総合開発機構（NEDO）の助成事業（JPNP18005）の結果得られたものです。