Selection of next-generation low global-warming-potential refrigerants by using a risk trade-off framework

— Risk trade-off assessment for R-1234yf —

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Because the refrigerants currently used in air-conditioners have high global-warming-potential (GWP), substances with lower GWP, such as R-1234yf, are being sought as candidate next-generation refrigerants. However, low-GWP substances often have comparatively high chemical reactivity and may carry increased risks of combustibility, toxicity, generation of degraded products, and CO_2 emission increase caused by poor energy-saving performance. It is therefore possible that there is a risk trade-off between currently used refrigerants and low-GWP ones. In this research, I proposed a framework for evaluating this risk trade-off in the following five categories: (1) environmental characteristics; (2) combustion characteristics; (3) toxicity; (4) volume of greenhouse gas emissions; and (5) applicability to air-conditioning equipment. I then selected substances well suited as next-generation refrigerants in accordance with a specific screening process. I showed the importance of clearly specifying the combination of a number of end points and assessment criteria in the process of decision-making based on risk trade-off. This yields a rapid understanding of the necessary data, as well as flexible decision-making that is relevant to the social conditions.

Keywords **:** Refrigerant, global warming, energy saving, flammability, toxicity

1 Development of refrigerant materials and next-generation refrigerants

The materials used to date as refrigerants for air-conditioners can be roughly categorized into four generations.[1]

In the first generation (from 1830 to the 1930s), the most important consideration was the development of functioning refrigeration systems. For this reason, even materials with toxicity, flammability, and corrosive properties were used as refrigerants owing to their superior properties as refrigerants. In the second generation (from 1931 to the 1990s), safety and chemical stability were pursued and materials such as chlorofluorocarbons (CFCs) and hydrochlorofluorocarbons (HCFCs) were introduced. In the third generation (from the 1990s to the 2010s), hydrofluorocarbons (HFCs), which do not contain chlorine, were introduced to prevent depletion of the ozone layer. In the fourth generation (from 2010 onwards), a search for refrigerants that have lower global-warming-potential (GWP)[Term 1] than materials such as HFCs and unlike CFCs do not contribute to depletion of the ozone layer has begun. We are currently in a period of transition from the third to the fourth generation of refrigerants. For the purpose of this paper, refrigerants that belong to the fourth generation will be called “next-generation refrigerants.”

2 Risk trade-off relationship among requirements for the next-generation refrigerants

A risk trade-off occurs when a reduction in a certain type of risk leads to an increase in a different type of risk. Next-generation refrigerants are required to have lower GWPs than today’s refrigerants, but in most cases such refrigerant materials have comparatively high chemical reactivity. In other words, to reduce GWP either a low infrared absorption coefficient or a short atmospheric lifetime is needed, but the latter implies high atmospheric reactivity. It is therefore possible that there is a risk trade-off between materials that have low GWPs and those that do not, because the former choice may lead to higher risks in terms of flammability, toxicity, generation of degradation products, and energy-saving performance (i.e. more energy may be needed to operate the air-conditioning equipment).

Presently, the requirements for next-generation refrigerants can be summarized into the following five categories:

1. Do not contribute to ozone layer depletion (ozone depletion potential = 0) and have sufficiently low GWPs. [Environmental characteristics]
2. Have low flammability that falls within the range of risk management, or are nonflammable. [Combustion characteristics]
3. Are intrinsically of low toxicity. [Toxicity]
4. Have good heat-cycle performance (energy-saving performance) as refrigerants. [Energy-saving performance]
5. Cause no problems when they are being charged into, and used in, air-conditioning equipment. [Applicability to air

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conditioning equipment]

In light of all of these requirements, my aim here was to use a risk-trade-off framework to assess refrigerant materials in the above five categories, which are highly important to the introduction of low-GWP next-generation refrigerants that can replace HFCs.

3 Status of development of next-generation refrigerants

Examination of the impacts of refrigeration and air-conditioning equipment on global warming has given a total estimated refrigerant emission (values for FY 2010, carbon dioxide (CO_2) converted volume) of 17.1 million t CO_2. The breakdown was 11.3 million t CO_2 from business-use refrigerators and air-conditioning equipment (66 %), 2.9 million t CO_2 from home-use air-conditioning equipment (17 %), 2.5 million t CO_2 from automotive air-conditioning equipment (15 %), and 400,000 t CO_2 from home-use refrigerators (2 %).[2]

The analysis of low-GWP refrigerants is more advanced in the case of automotive air-conditioning than for other types of air-conditioning. 2,3,3,3-Tetrafluoropropene (CH_2=$CFCF_3$), an olefin compound with the number R-1234yf, has a GWP of 4 and is one of the most promising next-generation refrigerant candidates.[3] (For more on refrigerant numbers see Note 2 at the end of this paper.)

Although R-1234yf is likely a highly viable replacement candidate for R-134a (the current refrigerant used for automotive air-conditioning), particularly high refrigerant performance is expected of the next-generation refrigerants used in stationary air-conditioning. This is because refrigerants such as R-410A used in stationary equipment have greater refrigerant performance than R-134a (i.e. their energy consumption rates while the air-conditioning equipment is in use are low). What this means is that an increase in energy consumption during the operation of air-conditioning equipment can become a greater problem in the replacement of refrigerants for stationary air-conditioners than for automobile air-conditioners.

In addition, because home-use stationary equipment has a shorter life than its business-use counterpart, greenhouse gas (GHG) emission reductions due to replacement with low-GWP refrigerants are expected to appear fairly quickly. Therefore, the results achieved by studying home-use equipment should benefit changes in business-use equipment. From this perspective, I chose to use a risk trade-off framework in my evaluation and selection of next-generation refrigerants for home-use air-conditioning, and I paid particular attention to changes in energy consumption during equipment operation.

4 Selection of next-generation refrigerants by using a risk trade-off framework

In choosing an ideal refrigerant material when there are multiple risk assessment categories, such as combustibility, toxicity, and global warming potential, the risks in each category should first be quantified by using a uniform risk measure. The material with the smallest total risk should then be selected. However, a uniform quantification technique applicable to different types of risks is not yet available for practical use.

For this reason, I aligned all risk categories sequentially and chose candidate materials by following a step-by-step screening method. The order of the categories began from the category connected to the property of the candidate material itself and progressed through to the category connected to the property of the candidate material when it was used as a refrigerant.

The assessment framework used in this study and the results of the assessment are shown in Table 1. Appropriate environmental characteristics (does not deplete the ozone layer and has low GWP) were placed at Stage 1 of the assessment. These environmental characteristics have only recently (i.e. since the advent of the third-generation refrigerants) started to be seen as important. Combustibility was placed at Stage 2. This was because choosing materials with high atmospheric chemical reactivity as a way of reducing GWP will directly result in increased combustibility. Toxicity was placed at Stage 3. Although it is possible that toxicity can also increase because of increased chemical reactivity in the atmosphere, it was placed at the third stage of the assessment on the assumption that its change was likely to be smaller than the change in combustibility. Thus assessment categories related to the properties of the candidate material itself were placed at Stages 1 to 3. Placed at Stage 4 was life cycle assessment (LCA), which requires the incorporation of information regarding the use of equipment. At Stage 5 was the assessment of applicability to air-conditioning equipment, which requires the incorporation of information on equipment design. The assessment categories from Stage 4 onward were deeply dependent on the environment in which the refrigerants were to be used. The stages were thus ordered so that increasingly more detailed information was required with each stage.

Tests on burning velocity and flammability limit were especially important in the combustion characteristics assessment, as was toxicity testing in the toxicity assessment.

In Stage 1 of the assessment, likely candidates for next-generation refrigerants were screened against the GWP value of the current refrigerant R-410A. A number of materials,

Table 1. Framework of the risk trade-off assessment and the results of screening of candidate materials for next-generation low-GWP refrigerants

Assessment stage	Description of assessment category	Step-by-step selection of candidate materials
Stage 1	Assessment of environmental characteristics (selection of materials that do not deplete the ozone layer and have low GWP)	R-1234yf, R-32, R-152a, R-290, R-600a, R-717, R-744
	In assessing GWP, the GWP value of 1730 for R-410A, the refrigerant currently used for home-use stationary air-conditioning equipment, was used as a reference value.	
Stage 2	Assessment of combustion characteristics	R-1234yf, R-32, R-717, R-744
	Materials classified by ISO 817 or ASHRAE 34 as Class 3 (higher flammability) or Class 2 (lower flammability) were excluded; only those classified as Class 2L (lower flammability with a maximum burning velocity of ≤ 10 cm/s) or Class 1 (no flame propagation) were left.	
Stage 3	Assessment of toxicity	R-1234yf, R-32, R-744
	An atmospheric exposure assessment was performed on the decomposition products of those refrigerants with short atmospheric lifetimes.	
Stage 4	LCA	See subchapter 5.4.
	The sum of direct (air emissions from refrigerants) and indirect (GHG emissions due to energy use) GHG emissions from air-conditioning equipment using each candidate refrigerant was quantified.	
Stage 5	Assessment of applicability to air-conditioning equipment	See in chapter 6.
	Assessment of the applicability of refrigerants to actual refrigeration and air-conditioning equipment. This included assessment of safety measures for leakage from equipment.	

including R-1234yf, R-32, R-152a, R-290, R-600a, R-717, and R-744, were considered to be candidates. During this process, R-1234ze(E), an isomer of R-1234yf, was not included in the list of materials to be assessed because of its poor data availability. Nevertheless, because R-1234ze(E) is similar to R-1234yf in terms of chemical structure and physical properties (combustion characteristics and GWP), its assessment result would likely be comparable to that of R-1234yf.

In Stage 2 (combustion characteristics), to exclude materials that were clearly flammable, materials classified by ISO 817 and ASHRAE 34 as Class 3 (higher flammability) and Class 2 (lower flammability) were excluded and only those classified as Class 2L (lower flammability with a maximum burning velocity of ≤ 10 cm/s) or Class 1 (no flame propagation) were left. Hydrocarbon refrigerants R-290, R-600a, and R-152a were thus excluded from the list of candidates. R-1234yf and R-32 are classified as Class 2L. The combustion characteristics of these two types of refrigerants will be described in detail in subchapter 5.1.

In Stage 3 (toxicity), R-717 was excluded because of its strong toxicity. Details of the toxicity assessment and the decomposition products of R-1234yf will be given in subchapters 5.3 and 5.4, respectively; in brief, this compound was considered to carry no notable risk in terms of toxicity and decomposition products.

Besides R-1234yf, this leaves R-32 (a conventional refrigerant with slightly increased GWP) and the natural refrigerant R-744 as candidate refrigerants.

In Stage 4 (LCA), reduction of GHG emissions by the candidate materials remaining after the above-described screening had been performed was quantified. Further details on this point are given in subchapter 5.4.

Although evaluation of the applicability to air-conditioning equipment (Stage 5 of the assessment) could not be performed in this study because of a lack of data, it will be considered qualitatively in chapter 6.

5 Detailed assessment of viable candidate materials in each risk category

5.1 Assessment of combustion characteristics

After the screening for environmental characteristics, combustion characteristics, and toxicity, R-1234yf, R-32, and R-744 remained as candidate materials (see Table 1). Because R-744 is nonflammable, it does not require an assessment of combustion characteristics. Both R-1234yf and R-32 are classified as Class 2L by ISO 817 and ASHRAE 34, the international standards for the combustion characteristics of refrigerants. However, according to the relevant Japanese laws and regulations (the High Pressure Gas Safety Act and Refrigeration Safety Regulations), R-1234yf is classified as a combustible gas, whereas R-32 is not. Therefore, whether or not mixed refrigerants comprising these two refrigerants are deemed flammable or nonflammable depends on their mixing ratio.

Therefore, a combustion experiment was performed to see whether or not the measured flammability limits for the mixed refrigerant R-1234yf – R-32 coincided with the values predicted by Le Chatelier’s Principle on the basis of their

Table 2. Flammability limits of mixed refrigerants comprising R-1234yf and R-32

R-1234yf : R-32 (volume ratio)	Lower flammability limit (vol%)		Upper flammability limit (vol%)	
	Measured value	Predicted value	Measured value	Predicted value
100 : 0	5.53 (0.10)	5.53	13.3 (0.5)	13.30
80 : 20	6.22 (0.05)	6.27	14.5 (0.5)	14.80
60 : 40	7.2 (0.1)	7.24	17.0 (0.6)	16.69
50 : 50	7.78 (0.05)	7.85	18.5 (0.5)	17.82
40 : 60	8.53 (0.08)	8.56	19.9 (0.7)	19.12
20 : 80	10.45 (0.05)	10.48	23.6 (0.7)	22.39
0 : 100	13.5 (0.1)	13.50	27.0 (0.5)	27.00

mixing ratios. Measurements were conducted in air at a humidity of 50 % and a temperature of 296.15 K. The results are shown in Table 2. For example, Table 2 shows that a mixed gas with a volume ratio of 50:50 burns when it exists in air at a range of 7.78 % to 18.5 %. The value of the lower flammability limit (LFL) coincided well with the predicted value, and the value of the upper flammability limit (UFL) coincided fairly well with the predicted value.

Next, the dependence of maximum burning velocity ($S_{u0, max}$) on mixture ratio for the mixed refrigerant R-1234yf – R-32 was measured (Fig. 1). The results of measurement of the LFL and GWP values for the mixed refrigerant are also shown for reference. On the one hand, an increase in the ratio of R-32

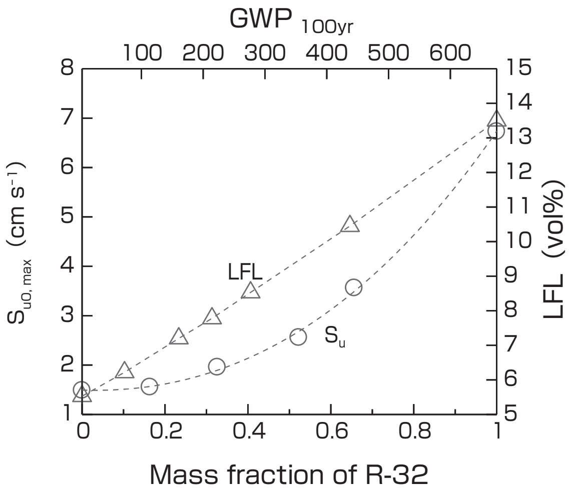

Fig. 1 Dependence of maximum burning velocity on mass fraction of R-32 in the mixed refrigerant R-1234yf – R-32
$S_{u0, max}$: maximum burning velocity; LFL: lower flammability limit

increased the LFL value and made the mixture nonflammable, but on the other hand it also increased the maximum burning velocity and the burning velocity once it started to burn. In addition, the increase in burning velocity increased with the increase in the ratio of R-32.

The related laws and regulations in Japan define a flammable refrigerant gas as follows: either the LFL value is 10 % or less, or the difference between the UFL value and the LFL value is 20 % or more. What this means is that to realize non-flammability in compliance with this definition, the percentage of R-1234yf by volume in the mixture needs to be 36.2 % or less, or 55.4 % or less in terms of weight ratio.[Note] The GWP of the mixed refrigerant based on this mixing ratio (44.6 % R-32 by weight) was estimated to be about 300. In addition (see Figure 1), the burning velocity at this mixing ratio was not dramatically greater than that of pure R-1234yf. Therefore, this mixing ratio was used as one of the many conditions for the LCA (see subchapter 5.4).

5.2 Toxicity assessment

Because R-32 and R-744, but not R-1234yf, are presently used as refrigerants and can be considered to have low toxicity, only R-1234yf was assessed for toxicity. R-32 is a component of R-410A, and R-744 is used as a refrigerant in heat-pump-type water heaters.[Term 2] The results of toxicity testing of R-1234yf are shown in Table 3. An acute toxicity test, repeated exposure test, cardiac sensitization test, and two-generation reproduction study conducted with extremely high concentrations (tens of thousands of ppm) did not result in any particular toxicity. In addition, from the results of the genotoxicity test it was inferred that R-1234yf was not genotoxic in vivo. Among those tests that did reveal adverse effects, the one in which R-1234yf had adverse effects at the lowest concentration was the developmental toxicity test in rabbits. However, the concentration at which death of a pregnant rabbit was observed was high (at 5500 ppm or more). In contrast, in rats, not only were there no recorded deaths of mother rats in the developmental toxicity test and the two-generation reproduction study, but also there were no adverse effects even in repeated exposure testing at a high concentration (50,000 ppm). These findings suggest that rabbits have greater sensitivity than rats to R-1234yf. After a comprehensive examination of the results shown in Table 3, it was judged that R-1234yf was of low toxicity.

Minor[5] states that the toxicity level of R-1234yf is similar to that of the present-day refrigerant R-134a. Rinne,[6] Schuster *et al.*[7] and the Japan Society of Refrigerating and Air Conditioning Engineers[8] also state that the toxicity of R-1234yf is low. However, because there are currently no publicly available data on the details of toxicity testing, published toxicity test reports are awaited in future so that we can ensure objective and transparent toxicity assessment.

Table 3. Summary of toxicity information on R-1234yf

Endpoint	Test content	Test results	References
Acute toxicity	Rats, inhalation, 4 h	No deaths observed until 400,000 ppm	[5],[6],[9]
Repeated inhalation toxicity	Rats, inhalation, 2 weeks	NOEL=50,000 ppm	[9]
	Same as above, 4 weeks	NOAEL=50,000 ppm	[9]
	Same as above, 13 weeks	NOAEL=50,000 ppm	[5],[6],[9]
Cardiac sensitization potential	Dogs, inhalation	No adverse effect until 12 % (120,189 ppm)	[5],[6],[9]
Genomics	13 weeks	No activation until 50,000 ppm	[5],[6]
Developmental toxicity	Rats, inhalation (nasal cavity)	NOAEL=50,000 ppm	[5],[6]
	Rabbits, inhalation (whole body)	NOAEL/LOAEL=4,000/5,500 ppm	[5],[6],[9],[10]
Two-generation toxicity	Rats, inhalation, 6 h/day	NOAEL=5,000 ppm	[5],[6]
Genotoxicity (Ames test)	*S.typhimurium* (TA1535, TA98, TA100)and *E.coli* (WP2uvrA)	Positive at 20 % or more for both TA 100 and WP2uvrA; the remaining results were negative	[9]
Genotoxicity (human cells)	Human lymphocytes, 4 h	Negative at 760,000 ppm	[9]
Genotoxicity (in vivo micronucleus test)	Mice, inhalation, 4 h	Negative (maximum 200,000 ppm)	[9]
	Rats, inhalation, 4 h	Negative (maximum 50,000 ppm)	[9]
Unscheduled DNA synthesis inhibition test	Rats, inhalation, 4 weeks	Negative (maximum 50,000 ppm)	[9]

NOEL: No observed effect level,
NOAEL: No observed adverse effect level,
LOAEL: Lowest observed adverse effect level

5.3 Atmospheric exposure assessment

Because R-1234yf has higher atmospheric reactivity than conventional refrigerants, relatively high concentrations of decomposition products could be generated. For this reason, the volume of R-1234yf emitted into the atmosphere was estimated for the case in which the refrigerants used in all types of air-conditioning equipment (home use, business use, and automotive use) were replaced by pure R-1234yf refrigerant. Studies of the use of R-1234yf as a refrigerant for automotive use are far more advanced than those of its use for home or business use; nevertheless, to calculate maximum rates of emission it was assumed that the use of R-1234yf in all types of air-conditioning equipment. Additionally, although there is a strong possibility that R-1234yf will be used in mixtures because it can be mixed in different ratios, it is assumed that R-1234yf was used as a pure refrigerant so as to determine the maximum emission rates. The atmospheric concentration of R-1234yf after its atmospheric emission and the atmospheric concentrations of the atmospheric decomposition products of ozone, formaldehyde, and trifluoroacetic acid (TFA) were also estimated to study their impact on human health and ecology (aquatic organisms).

Table 4. Atmospheric concentrations of R-1234yf and its decomposition products with the use of R-1234yf as a refrigerant (annual average, Kanto region)

	R-1234yf [ppb]	Ozone [ppb]		Formaldehyde [ppb]	
		–	Increase*1	–	Increase*1
Max. value	0.28	44	+0.13	2.9	+0.012
Min. value	0.0068	11	−0.03	1.1	−0.005
Average	0.050	34	+0.03	2.0	+0.002

*1 : Increase compared with the control case (no replacement of refrigerants)

To estimate emissions from the refrigerants, the refrigerants used in all newly produced air-conditioning equipment, beginning in 2011, were assumed to be switched to R-1234yf, and emissions from the refrigerants after 40 years of use were estimated for each type of equipment and for each stage of its lifecycle. The estimated parameters, including the number of items of equipment manufactured, the emission factors, and the recycling rates at the time of disposal, were assumed to be the same as those for current-day equipment. The purpose of this assumption was not to forecast the future, but to estimate emissions under the hypothetical scenario in which all refrigerants used in today's air-conditioning equipment were completely replaced by R-1234yf. The estimated total annual emission rate was 15,172 t. Breakdown of the emissions by type of equipment revealed that the majority was from home use (6,366 t/year) and business use (6,734 t/year); in terms of equipment lifecycle stage, the largest source of emissions was the disposal stage (8,744 t/year).

The atmospheric model used for this purpose was ADMER-PRO,[11]-[13] in which are embedded the reaction processes of nitrogen oxides (NOx), volatile organic compounds (VOCs), and ozone and the dry deposition process. The reaction process beginning with the reaction of R-1234yf and OH radicals and proceeding to the generation of the intermediate product trifluoroacetyl fluoride [$CF_3C(O)F$] and of the final product, TFA, as well as the process of wet deposition of TFA, was added to ADMER-PRO for the purpose of computation. The overall reaction rate constant for the process, in which TFA was generated as a result of hydrolysis of the intermediate product $CF_3C(O)F$ in cloud water, was measured by using an experimental method (two-phase flow method).

The concentrations of R-1234yf, ozone, and formaldehyde computed by the atmospheric model are shown in Table 4.

The maximum concentration of R-1234yf was estimated to be 0.28 ppb; because this was 10 million times lower than the lowest NOAEL (4,000 ppm in rabbit developmental toxicity testing; see Table 3) in the toxicity assessment, the chronic impact on humans of inhalation exposure to R-1234yf in the ambient air is likely to be negligible. Moreover, the increase in the average concentration of ozone or formaldehyde compared with the control cases (i.e. no replacement of refrigerants) was only about 0.1 %. Because these values are sufficiently small, the impact of R-1234yf on the generation of oxidants can be presumed to be extremely small.

In addition, the annual maximum average concentration of TFA in rainwater was estimated at 3.4 μg/L. The NOEC (no observed effect concentration) of TFA in aquatic organisms was 100 μg/L[14] for *Selenastrum capricornutum*, which was the most sensitive alga among various aquatic organisms (fish, crustaceans, and algae). Because the estimated maximum concentration was well below this NOEC, the possibility of TFA in rainwater having any impact on aquatic organisms is extremely small.

5.4 LCA

5.4.1 Scope of the assessment

GHG emissions throughout product life cycles were estimated by using the LCA method on the basis of the assumption that each candidate material was used as a refrigerant for home-use air-conditioning. GHG emissions were roughly divided into two categories: emissions from energy and emissions from refrigerants. Emissions from energy are estimates of the CO_2 generated from electricity consumption while air-conditioning equipment was in use, as well as from the energy consumed to manufacture air-conditioning equipment. Emissions from refrigerants are estimates of the greenhouse effect of leakage of refrigerant. If refrigerants were replaced by low-GWP materials, refrigerant-related GHG emissions would be reduced because of the reduction in GWP, but GHG emissions from energy would be increased if the performance of the refrigerant were to be lower. To verify whether or not the net GHG emissions were reduced, it is needed to check the reduction in total GHG emissions from energy and refrigerants.

After the screening described in chapter 4, three materials—R-1234yf, R-32, and R-744—remained as candidates. However, because the data required to conduct an LCA on R-744 as a refrigerant for home-use stationary air-conditioning equipment could not be found, it is deemed impossible to sufficiently examine the possibility of using R-744 as a next-generation refrigerant. Therefore R-744 is excluded from the assessment. However, if data showing an increase in CO_2 emissions due to poorer energy-saving performance when R-744 is used as a refrigerant in home-use stationary air-conditioning equipment become available in future, it is likely that R-744 will achieve an LCA result similar to that for R-1234yf; moreover, its suitability as a refrigerant is likely to be judged similar to those of others described later in this section.

In addition to the two pure refrigerants R-1234yf and R-32, a mixture of the two is assessed. The mixing ratio was R-1234yf : R-32 = 55.4 : 44.6 (by weight); this mixture would be deemed a nonflammable gas according to the relevant Japanese laws and regulations in Japan. (See subchapter 5.1 on the assessment of combustion characteristics.)

The scope of the assessment covered the entire product life cycle, and GHG emissions due to energy and refrigerants were estimated separately for each stage of manufacture of a refrigerant, manufacture of equipment, use of equipment, and disposal of equipment. The place of manufacture, use, and disposal of air-conditioning equipment was assumed to be Japan. CO_2, nitrous oxide (N_2O), and methane (CH_4) were included as GHGs in the estimate in addition to the refrigerant materials and were converted to CO_2 equivalents on the basis of GWP.

5.4.2 Questionnaire survey on status of use of air-conditioning equipment

The amount of GHGs generated in the use stage of air-conditioning equipment is equivalent to the consumption of electrical power, but power consumption depends greatly on the actual status of use of the air-conditioning equipment. To compute a power consumption rate that closely reflects the actual status of use of the air-conditioning equipment, a nationwide survey consisting of detailed items (household attributes, housing attributes, specifications of air-conditioning equipment, use of the equipment, hours of equipment use, etc.) was conducted. The questionnaire survey was conducted on the internet twice—the first time in February 2010 and the second in December 2010. In the first survey, 4,000 households nationwide (10 regions with 400 households in each region) were surveyed. In the second survey, in addition to the follow-up survey of the households subjected to the first survey, another 4,000 households nationwide (10 regions with 400 households in each region) were included. Valid responses were collected from 7,090 households. On the basis of the data collected in the survey, the average annual hours of use of each air-conditioner are calculated. The average annual hours of use for each region are shown in Fig. 2. According to the survey results, the reason why regions with low outdoor temperatures, such as Hokkaido and northern Tohoku, had comparatively fewer hours of use of heating was because more than half of the households in these regions mainly used equipment other than air-conditioners for heating.

In addition, on the basis of the survey results, the schedule of use of air-conditioning equipment was computed over each 24 h for 365 days; by taking the outdoor temperature and the hours of continuous operation into consideration, the average annual power consumption was calculated per item of equipment for each region.

5.4.3 Results of assessment of candidate refrigerant materials

An LCA was performed on a total of four types of refrigerant: the present-day refrigerant R-410A, the pure refrigerants R-1234yf and R-32, and the mixed refrigerant R-1234yf – R-32. The characteristics of the refrigerants subjected to the LCA are shown in Table 5. The numbers ①, ②, and ③ below the columns indicate different types of power consumption assumptions made to estimate GHG emissions from energy. Because the performance of the refrigerant R-1234yf is poorer than that of R-410A,[15] a positive value was assumed for increases in power consumption with pure R-1234yf and its mixed refrigerant; a zero or a negative value was assumed in the case of R-32, because its performance as a refrigerant is superior to that of R-410A.

The GHG emissions from each next-generation refrigerant per home-use air-conditioner are shown in Fig. 3. When viewed in terms of their contributions to GHG emissions in each life cycle stage, for every refrigerant the contributions from the refrigerant in the manufacture stage (manufacture and equipment) and from energy in the disposal stage were very small. For refrigerants with large GWPs the contributions from refrigerant in the disposal stage were large, and for those with small GWPs the contributions from energy in the manufacture and use stages were large. As a general trend, it was evident that a decrease in GWP of a refrigerant correspondingly reduced GHG emissions. However, when R-32 was used, the GHG emission was approximately 1,100 kg CO_2 for all energy-saving performances; this is about 50 % of 2,300 kg CO_2, the estimated emission with R-410A. In comparison, the GHG emission with mixed refrigerant was approximately 920 kg CO_2—not much different from that with a pure R-32. For this reason, the advantage of using mixed refrigerant compared with R-32 in terms of reduction in GHG emission was not large. In contrast, with pure R-1234yf the emission came to between about 670 and 740 kg CO_2, thus reducing GHG emission to about 40 % of that with conventional refrigerant.

Table 5. Characteristics of refrigerants subjected to LCA

Refrigerant	GWP	Refrigerant used per item of equipment [kg]	Increase in power consumption due to use of equipment [%]*2
R-410A	1730	1.2	
R-32	650	1.0	①-2.5 %, ②0 %
R-1234yf/ R-32*1	300	1.1	①+2.5 %, ②+5 %
R-1234yf	4	1.1	①+5 %, ②+10 %, ③+20 %

*1) R-1234yf : R-32=55.4 : 44.6 (weight ratio)
*2) R-410A values were used as a baseline.
The numbers ①, ②, and ③ indicate different types of assumption made regarding increases in power consumption. For R-1234yf and its mixed refrigerant, the data of Endo *et al.*[15] were used for the adjustment.

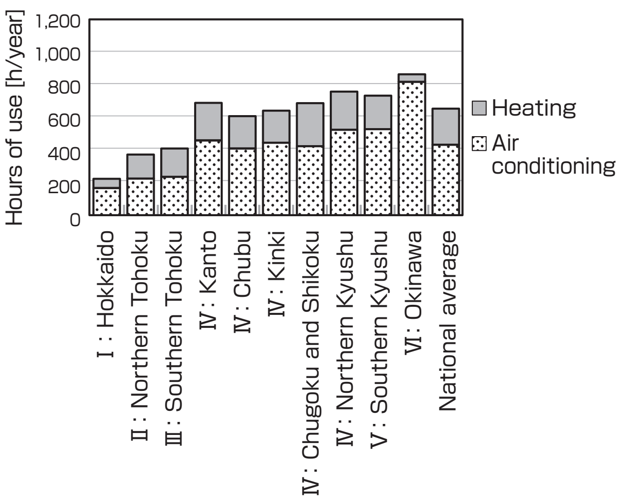

Fig. 2 Average annual hours of use per air-conditioner in each region (I through VI indicate the category of each region, in accordance with the Act on the Rational Use of Energy.)

6 Discussion and conclusions: selection of next-generation refrigerants

In this chapter, I discuss the results of the assessment and

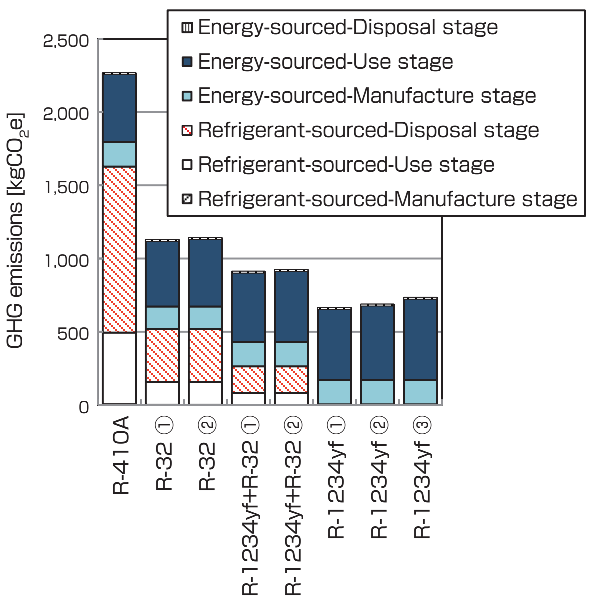

Fig. 3 Results of estimation of GHG emissions throughout the life cycles of home-use air-conditioning equipment when the refrigerants used were replaced (for information on each type of refrigerant on the horizontal axis, see Table 5)

the challenges faced by this study. Qualitative references to Stage 5 of the assessment, namely the applicability of refrigerants to air-conditioning equipment, are made.

The reduction in GHG emissions that could be achieved by introducing pure R-1234yf refrigerant was so huge that an even larger reduction can be expected in comparison with the emissions with the two other refrigerants (pure R-32 and mixed refrigerant) compared here. However, the price of R-1234yf is high, and the challenge for the future is to reduce this price. In addition, if R-1234yf is to be introduced, the technical problems regarding its use in stationary air-conditioning equipment must be solved: for example, the size of the compressor is likely to increase because of changes in the design of bent pipes.

If pure R-32 were to be introduced, although it would result in a smaller reduction in GHG emissions than that produced by using R-1234yf, the reduction would not be negligible. Because R-32 is a component of present-day refrigerants, there would be few problems in relation to its use in air-conditioning equipment. This refrigerant is also cheap and thus can be considered a candidate next-generation refrigerant. However, even though R-32 is classified as a Class 2L (lower flammability with a maximum burning velocity of $\leq$ 10 cm/s) refrigerant, it has a greater burning velocity than that of R-1234yf (in dry ambient air); therefore, measures to ensure its safe use are necessary.

The mixture of R-1234yf and R-32 can qualify as a candidate next-generation refrigerant, because its reduction of GHG emissions, its price, and its flammability all fall into a range mid-way between the values for the two pure refrigerants. Its only likely flaw is the difficulty in handling the refrigerant when charging it into the equipment; this is characteristic of non-azeotropic refrigerant mixtures.

For these reasons, it is important that Stage 5 of the assessment—applicability to air conditioning equipment—is conducted quantitatively on the three refrigerants examined here after measures are taken to correct the defects and problems described above. Also, because the results in Stage 5 depend strongly on the design of the equipment and are affected by the price of the refrigerant, the assessment needs to be conducted in close cooperation with equipment manufacturers, researchers, and government.

In addition, as was pointed out in the details on Stage 3 (toxicity assessment), the details of toxicity tests have not yet been made publicly available. Therefore, to ensure an objective and transparent assessment, we await the future publication of toxicity test reports by the manufacturers of refrigerants. In Stage 4 of the assessment, LCA could not be performed on R-744 because there were insufficient data. It is therefore clear that publication of data by the manufacturers of home-use air-conditioning equipment on CO_2 emission increases due to reduced energy-saving performance of equipment using R-744, as well as assessments based on such data, remain as problems for the future.

The results of my assessment must be viewed with caution, as in their current state they cannot necessarily be applied to air-conditioning equipment other than that used at home. This is because, among the five stages of assessment shown in Table 1, Stage 4 (LCA) and 5 (applicability assessment) are strongly affected by such factors as the form of equipment used and the relationship with present refrigerants.

Although here I used the risk trade-off framework to propose a decision-making method for choosing next-generation refrigerants, the method is likely applicable not only to the selection of next-generation refrigerants but also to decision-making processes in general that use risk trade-off frameworks, for the following reasons. The method clearly defines multiple assessment categories and indicates clear assessment standards. The method combines a step-by-step screening process and a detailed assessment, making it possible to point out the types of data that are required or are insufficient at each step. These characteristics of the method should enable easy reassessment that is reasonably consistent with previous assessments, even when new assessment categories are added or changes in assessment standards are required. Moreover, because the connection between the necessary data and decision-making can be easily grasped, use of the method should help to promote the establishment of cooperative relationships that encourage the exchange of data with other research organizations.

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Note) The flammability limit values[4] of the following pure substances, measured in accordance with the ASTM International’s Standard Test Method (ASTM E681-01), were used to calculate the flammability limit value of the mixed substance: R-1234yf, LFL = 6.2 and UFL = 12.3; R-32, LFL = 14.4 and UFL = 29.3 (all units are in vol%).

Terminologies

Term 1. Global-warming-potential (GWP). The GWP expresses the strength of the greenhouse effect of a particular gas in the atmosphere relative to the same concentration of CO_2. If not otherwise stated, all GWP values are taken from the *IPCC Second Assessment Report: Climate Change 1995*.

Term 2. Refrigerant numbers and chemical formulas

Refrigerant number	Chemical formula	GWP
R-1234yf	CH_2=$CFCF_3$	4
R-1234ze(E)	CHF=$CHCF_3$	6
R-134a	CH_2FCF_3	1300
R-410A	1:1 (weight ratio) mixture of CH_2F_2(R-32) and CHF_2CF_3(R-125)	1730
R-32	CH_2F_2	650
R-152a	CH_3CHF_2	140
R-290	$CH_3CH_2CH_3$	6[a)]
R-600a	$CH_3CH(CH_3)_2$	7[a)]
R-717	NH_3	1300
R-744	CO_2	1

a) Indirect GWP values are from IPCC/TEAP *Safeguarding the Ozone Layer and the Global Climate System: Issues Related to Hydrofluorocarbons and Perfluorocarbons* (2005). However, the value for R-600a (isobutane) is the value for an isomer of butane.

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paper, focused on assessment scenario selection and airborne exposure assessment.

Discussions with Reviewers

1 Selection of refrigerants for the assessment

Comment (Hiroshi Tateishi: AIST Tsukuba)

Though I am not sure since the terms used are inconsistent, judging from the content, the argument of this paper seems to be focused on refrigerants for home-use air-conditioning equipment. However, the world is no doubt filled with business-use air-conditioning equipment, mobile air-conditioning equipment for automobiles, etc., and with much other equipment such as home-use and business-use refrigerators, freezers, etc. that use similar refrigerants. Therefore, a comprehensive discussion that considers all these factors should be needed from the perspective of preventing global warming. Considering the purpose of this paper, a comprehensive survey is not necessary, but I think that at least some remarks should be made on the following points:

・The position of home-use air-conditioning equipment relative to other uses as seen from the amount of refrigerants used.

・Relationship between home-use and business-use air-conditioning equipment.

・Whether or not the limiting of the discussion to home-use air-conditioning equipment has an impact on the risk trade-off assessment framework.

Response (Hideo Kajihara)

From the perspective of preventing global warming, I think it is important to indicate the share of home-use air-conditioning equipment in the total refrigeration and air-conditioning equipment. In chapter 3, the amount of refrigerant emission was used to explain the ratio of refrigerants used in business-use, home-use, and automotive-use equipment in the total refrigeration and air-conditioning equipment. As for the relationship between home-use and business-use air-conditioning equipment, I stated that “because home-use stationary equipment has a shorter life than its business-use counterpart, greenhouse gas (GHG) emission reductions due to replacement with low-GWP refrigerants are expected to appear fairly quickly. Therefore, the results achieved by studying home-use equipment should benefit changes in business-use equipment.”

As for the question on whether or not the limiting of use to home-use air-conditioning equipment has an impact on the risk trade-off assessment framework, I believe that limiting to home-use air-conditioning equipment should not have much impact on the assessment results of environmental characteristics (ozone layer depletion and the GWP values), combustion characteristics, toxicity, and generation of degraded products. However, the result of the LCA is thought to be greatly influenced by the energy-saving performance and the GWP of the present refrigerants, the length of time equipment is in use, operating conditions, etc. and this point was added to chapter 6.

2 Concept of the assessment scheme

Question (Hiroshi Tateishi)

The framework of the risk trade-off assessment as shown in Table 1 is at the very basis of the entire paper and it must be the reason why this paper deserves to be a paper for *Synthesiology*, but it is used a priori without any clear explanation on how this framework was formed and therefore gives a sense of incongruity. Only obvious assessment categories are listed here, so where is the ingenuity of the author and why was the content of each of these assessment categories defined as such and placed in this order? Moreover, explanations on the techniques needed to assess these categories were also missing here, though they were later given in a different place. For example, why were refrigerants with “lower flammability with a maximum burning velocity of ≤ 10 cm/s” not excluded in Stage 1 of the assessment?

Answer (Hideo Kajihara)

I added an explanation at the beginning of chapter 4 in response to the remark pointing out that the reasoning behind the framework of the risk trade-off assessment shown in Table 1 was missing. The gist of the added explanation is as follows: “ideally, a uniform indicator should be used for comparison purposes, but since such an assessment technique is yet to be established, I aligned all risk categories sequentially and chose candidate materials by following a step-by-step screening method.” The explanations on the techniques needed to assess each category were also added.

As for the handling of refrigerants with “lower flammability with a maximum burning velocity of ≤ 10 cm/s” in the combustion characteristics, the explanation was revised to stress that materials classified into Classes 2 and 3 were excluded because the combustibility classification by ISO 817 and ASHRAE 34 goes as Class 1 (no flame propagation), Class 2L (lower flammability with a maximum burning velocity of ≤ 10 cm/s), Class 2 (lower flammability), and Class 3 (higher flammability) and the objective of the step-by-step screening method was to exclude materials with clear combustibility.

Question (Hiroaki Tao: Research Institute for Environmental Management Technology, AIST)

This paper proposes a method for selecting next-generation refrigerants by using a risk trade-off framework. However, I think it is highly important for the paper to include information on various assessment methods proposed to this day and the novelty and the ingenuity of this proposed assessment method in comparison to existing methods. To make this point clear, I think it necessary to include information on assessments done in the past, problems identified, and the ideas introduced into this method so as to overcome such problems. Since this paper states that “R-1234yf is likely a highly viable replacement candidate for … the current refrigerant used for automotive air-conditioning,” and thus can be assumed that some assessments have already been done until now, could you not include information on the things that have been improved compared with these past assessments?

Answer (Hideo Kajihara)

The existing methods that assessed R-1234yf as a refrigerant for automotive air-conditioning equipment checked whether or not the candidate material subjected to the assessment posed a problem or not by itself or in contrast to the current refrigerant materials for each of the assessment categories of toxicity, combustibility, refrigerant property, etc. (for example, see reference [4]). However, as explained in chapter 1, the materials used as refrigerants have historically gone through many changes. Since this can be said to be the result of shifts and additions made to the assessment categories in each era, there is always the possibility of further evolution of refrigerant materials in the future. Under such circumstances, the most important thing to do seems to be to clearly state the assessment criteria used in decision-making in each era. In this research, after showing each assessment category and the assessment criterion in the form of a list (Table 1 Framework of the risk trade-off assessment), the candidate materials were gradually selected from the many possible materials following a step-by-step screening method. By doing it this way, I think it offers the advantage of placing the decision-making of this time in the history of refrigerant selection. I added such a view to the end of chapter 6 and the Abstract.

The differences between past assessments on refrigerants for automotive air-conditioning equipment and the assessment on refrigerants for home-use air-conditioning equipment, which was the subject of this research, were added to chapter 3. The main difference between the two assessments is the difference in the performance level expected of the refrigerants, because current refrigerants used for each equipment are different.

3 Appropriateness of excluding certain materials from the assessment

Question (Hiroshi Tateishi)

In section 5.4.1, you (the author) said that “because the data required to conduct an LCA on R-744 … could not be found … I therefore excluded R-744 from the assessment.” But would it be permissible to allow such an exclusion that can be deemed arbitrary in this way? You should at least identify the type of data that was unavailable and the reason why the lack of such data can make the assessment meaningless, as well as remark on the possibility of R-744 being reconsidered as a candidate material depending on future examination.

Answer (Hideo Kajihara)

Since the description stating that R-744 was excluded from the assessment due to insufficient data could be interpreted as an arbitrary decision, I added the following explanation to section 5.4.1 so as to show that R-744 still remains a candidate material: “However, if data showing an increase in CO_2 emissions due to poorer energy-saving performance when R-744 is used as a refrigerant in home-use stationary air-conditioning equipment become available in future, it is likely that R-744 will achieve an LCA result similar to that for R-1234yf; moreover, its suitability as a refrigerant is likely to be judged similar to those of others described later in this section.” In addition, the following description was also added to Chapter 6 so as to clarify the problems left for the future: “In Stage 4 of the assessment, LCA could not be performed on R-744 because there were insufficient data. It is therefore clear that publication of data by the manufacturers of home-use air-conditioning equipment on CO_2 emission increases due to reduced energy-saving performance of equipment using R-744, as well as assessments based on such data, remain as problems for the future.”

Comment (Hiroaki Tao)

If a certain material is to be excluded from being a candidate material because of insufficient data for the assessment, it may raise questions on the reliability of such an assessment. If it is a viable candidate material, missing data should be collected and used for the assessment. Instead of simply stating that the assessment was not done because of insufficient data, if there are other facts that support the rationality of the decision, then it is advisable to state these facts in the paper. If not, then maybe the collection and assessment of such data should be stated as issues for the future. As said in the comment 2 above, making others aware of the existence of currently unavailable data and of the importance of conducting experiments for acquiring such data are also an important role of the assessment.

Response (Hideo Kajihara)

Since identification of insufficient data and clarification of additionally required studies and experiments within the overall assessment framework are highly important, I revised the description in the paper accordingly. To be more precise, I added the following to section 5.4.1: “However, if data showing an increase in CO_2 emissions due to poorer energy-saving performance when R-744 is used as a refrigerant in home-use stationary air-conditioning equipment become available in future, it is likely that R-744 will achieve an LCA result similar to that for R-1234yf; moreover, its suitability as a refrigerant is likely to be judged similar to those of others described later in this section.” In addition, I also added in chapter 6 that the collection and assessment of such data were problems for the future.

4 Generalization of the assessment scheme

Comment (Hiroaki Tao)

I believe the method proposed in this paper can be generalized so as to deal not only with individual problems such as the selection of next-generation refrigerants, but also with cases where decisions are needed to be made using a risk trade-off framework. I believe the techniques needed would be a combination of a screening method and a detailed examination, the means needed to collect assessment data would be data mining for existing data and experiments and/or questionnaires for non-existent data. In the case of this paper, the author himself seemed to have collected data by conducting experiments and questionnaires, but another effective way to do this might be to publicize the type of data that is needed so as to encourage universities, research institutes, corporations, etc. to voluntarily provide such data. By generalizing the application of the method from the selection of a refrigerant to a more general decision-making using a risk trade-off framework, I believe this paper would be able to propose a new assessment method for the future.

Response (Hideo Kajihara)

I believe it can be said that the significance of this paper is that it illustrates, through an actual example, the importance of the provision of a step-by-step decision-making process, various assessment categories, and assessment criteria for each assessment category in decision-making using a risk trade-off framework. It also shows that it is important to identify the type of data that is needed for the assessment and the type of assessments that can be done using such data. This significance of this paper was also added to chapter 6 and the Abstract.

5 Intention of the assessment experiment

Question (Hiroaki Tao)

It says in the footnote that the literature data [4] for the following flammability limit value, measured in accordance with the ASTM International’s Standard Test Method (ASTM E681-01), were used in the calculation. Does this mean that the value of 55.4 % was not obtained from the experiment result (Figure 1), but can be computed from the literature data? If so, for what purpose was this experiment conducted? Was the LFL experiment done to confirm the accuracy of the literature value? Could it be that the meaning of this experiment was in finding out the maximum burning velocity not included in the document? It may be because of my lack of understanding, but I would think it better to clearly state the purpose of the experiment.

Answer (Hideo Kajihara)

The description of the purpose of the experiment, which was done to assess combustion characteristics, was not clearly written. The main purpose of the experiment was to confirm that the experimental values for the mixed substance between R-1234yf and R-32 agreed with the LFL and UFL values for the mixed substance as estimated from the LFL and UFL values of the pure substances. The paper and the footnote were revised to clarify this point. In the second paragraph in subchapter 5.1, I added, “I therefore performed a combustion experiment to see whether or not the measured flammability limits for the mixed refrigerant R-1234yf – R-32 coincided with the values predicted by Le Chatelier’s Principle on the basis of their mixing ratios.” In the footnote, the word “pure substances” was added.

6 Toxicity assessment

Question (Hiroaki Tao)

Was a toxicity assessment conducted on R-32 and R-744? I think a toxicity assessment should especially be conducted on R-32. If it was not, I think it advisable to include the reason (may be because it was already done somewhere else?) in the paper. Since R-1234yf and R-32 were examined in subchapters 5.1, 5.3, and 5.4 of chapter 5, I think it would be better to include some description in subchapter 5.2 as well.

Answer (Hideo Kajihara)

A toxicity assessment was not conducted on either R-32 or R-744 because both are presently used as refrigerants. The following description was added to the beginning of subchapter 5.2: "Because R-32 and R-744, but not R-1234yf, are presently used as refrigerants and can be considered to have low toxicity, only R-1234yf was assessed for toxicity. R-32 is a component of R-410A, and R-744 is used as a refrigerant in heat-pump-type water heaters (see Term 2)." In the column for R-410A in the table in Term 2, I added the refrigerant number (R-32, etc.) to the chemical formula of the components of R-410A. Also, there was a typing error in the table in Term 2 where R-744 was mistakenly typed as R-747, so the error was corrected.