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LOW GWP REFRIGERANT FOR STATIONARY APPLICATIONS

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ABSTRACT

Refrigerants play an important role in the environmental sustainability of refrigeration, air-conditioning and heating, both in terms of direct refrigerant emissions and of energy efficiency of the equipment operation. The revised EU F-Gas regulation reduces the further use of hydrofluorocarbons (HFCs) and refrigerant mixtures containing HFCs with high Global Warming Potentials (GWPs). At the same time, the use of some natural refrigerants with lower GWPs, which are not subject to F-gas regulation, reaches safety limits towards high pressure or flammability. This is the case in several applications, where the safety guidelines of hydrocarbons (HCs) and the building codes, as well as the surrounding conditions set limits R-474A is classified as an A2L refrigerant according to ISO817. Compared to A3 classified HCs, R-474A can be installed in larger quantities in accordance with safety standards such as EN378 or ISO5149.

The presentation will briefly address the current legal situation in Europe. Potential areas of application are identified based on existing safety standards. The main part presents results from studies of oil compatibility, compressor and system performance and the usability of R-474A in stationary air condition (AC) and heat pump (HP) under the use of current series appliances as drop-in to evaluate a possible adoption. An outlook on the further development program concludes the lecture.

Keywords: HFC replacement, RACHP, stationary refrigeration and air conditioning technology, safety standards, filling quantity restrictions, oil compatibility, compressor tests, next-generation refrigerant

1. INTRODUCTION

Regulations and standards have a significant influence on the development, applicability and availability of refrigerants. The continuous substitution of fluorine with hydrogen in refrigerant molecules reduces the global warming potential of refrigerants. At the same time, however, the flammability is increased, which is highest with pure carbon-hydrogen compounds. Flammability is a significant risk in the operation of refrigeration systems. Standards set limits on the use of flammable refrigerants for safety reasons. These depend on the design of the refrigeration system and the individual degree of flammability. Hydrofluoroolefins (HFOs) have a reduced global warming potential, comparable to pure hydrocarbons, but with reduced flammability. With R-1132(E) as a mixture component, the application range of low GWP HFO mixtures is extended into the pressure range of R-404A and R-410A, which previously could only be covered by propane from a GWP point of view.

2. MAIN SECTION

Under the current EU commission (EC), the EC has defined the EU Green Deal as a climate policy framework. These include climate neutrality by 2050, reducing pollution, supporting companies in clean products and technologies and a just and inclusive transition to the defined targets. The initiative for the new EU F-Gas Regulation and the current Per- and polyfluoroalkyl substances (PFAS) Restriction Initiative can be derived directly from the Green Deal.

2.1. EU F-Gas Regulation (EU) 2024/573

The new EU F-Gas Regulation has been in force since 11 March 2024. New features of the F-Gas Regulation include adjustments to the Kigali Amendment and the extension of containment measures for HFOs. However, the main innovation is the tightening of the phase-down (see Figure 1) up to a phase-out for fluorinated greenhouse gases in 2050.

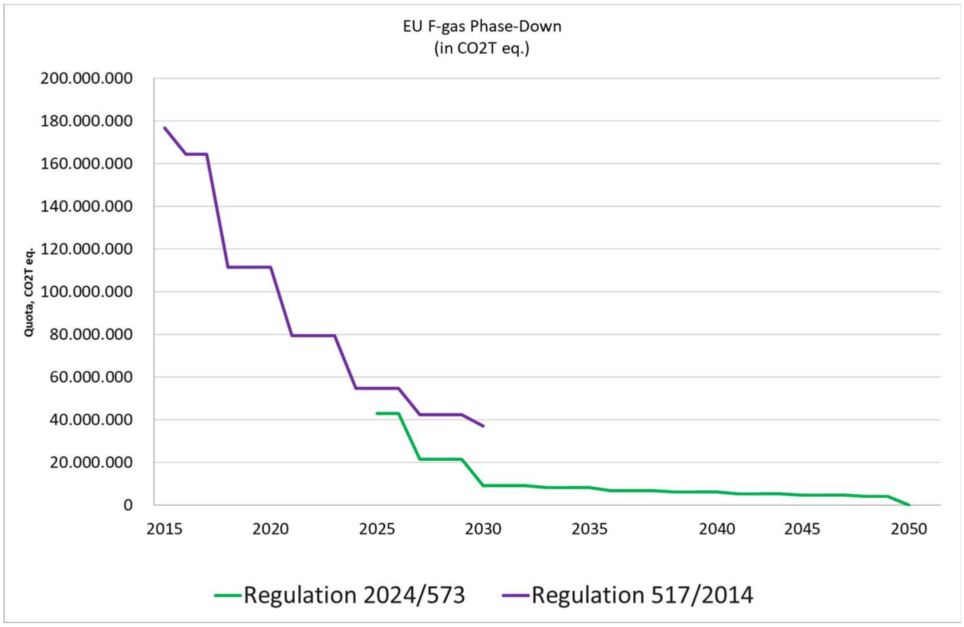

Figure 1: Phase-Down new F-Gas Regulation (EU)2024/573

Due to the drastic reduction steps of the new EU F-Gas Regulation, only 5.2 % of the initial value of 176.7 MtCO_2eq. will be available in 2030. If the amount of refrigerant used remains constant in a saturated market, the share of the refrigeration, air conditioning and heat pump (RACHP) sector would have to be reduced from 155.3 MtCO_2eq. to 8.1 MtCO_2eq. or the average GWP of refrigerants would have to be reduced from 2098 CO_2eq. in 2015 to 109 CO_2eq. in 2030 (EEA Report 2023). Even if the demand for refrigerants is partially replaced by recycled refrigerants, the average GWP value of the refrigerants must be reduced as much as possible. Existing systems that use A2L refrigerants are relatively new. For them, there is a clear need for an alternative that has the same safety classification as the lowest possible GWP.

2.2. Safety standards and charge limits

Safety standards define the maximum permissible refrigerant charge depending on the flammability of the refrigerant and the design of the refrigeration system. The most important standards relating to refrigerant charge quantities are shown in table 1. The maximum permissible refrigerant charges differ in some standards, depending on whether they are product-specific or generic. In general, the maximum permissible refrigerant charge of A2L refrigerants is significantly higher than that of A2 or A3 refrigerants.

Table1: Overview of safety standards in the RACHP sector

Field		International	US	Europe
Classification		ISO817	ASHRAE 34 UL 2182	-NA- (based on ISO)
Application standards Practical limits & other safety requirements	Generic	ISO5149	ASHRAE 15	EN378
	Specific products	IEC60335-2-40 IEC60335-2-75 IEC60335-2-89 IEC60335-2-24	UL 207 UL 250 UL 471 UL 474 UL 484 UL 984 UL 1995 UL 60335-2-40	EN60335-2-40 EN60335-2-75 EN60335-2-89 EN60335-2-24

As an example, figure 2 (Vonsild, 2022) shows the relationship between room size and the amount of refrigerant that can be used, using AC systems as an example. While sufficient capacity can be realised with A2L and A3 refrigerants for small room sizes, this is no longer the case for A3 refrigerants above a certain room size. To enable A3 refrigerants, an individual risk assessment and additional cost-causing measures are necessary. Further restrictions may result from outdoor installation of system parts containing flammable refrigerants. This may be the case in dense residential building areas.

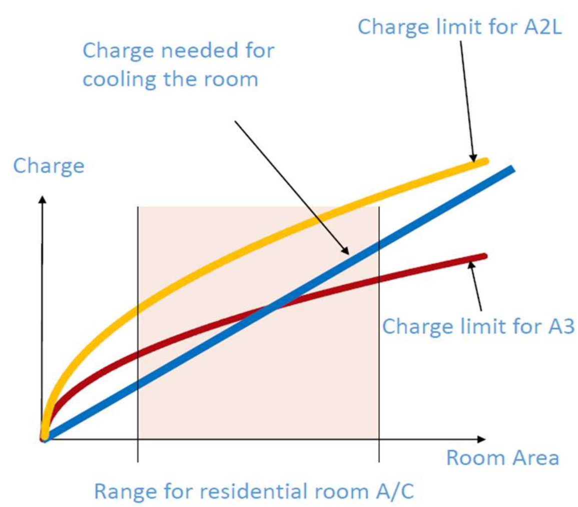

Figure 2: Relation charge limits, room space and refrigerant safety classes

Both in generic standards such as EN378-1 and in product standards such as IEC60335-2-40, the M1 value is the highest charge of flammable refrigerant that can be installed without further safety measures. The M1 value is calculated as following depending on the safety class in equation 1 and 2.

A3 refrigerant:

$$M1 = 4 \times LFL$$ Eq. (1)https://szchkt.org/a/conf/submissions/623/upload_paper?locale=en_GB

A2L refrigerant:

$$M1 = 4 \times LFL \times 1.5$$ Eq. (2)

Where LFL is the lower flammability limit in kg/m³.

Table2: System capacities and refrigerant charges based on LFL considerations

	R-290	R-474A
MM, mol/g	44.1	96.7
LFL v.%	2.1	5.4
LFL, kg/m³	0.04	0.21
M1, kg	0.15	1.28
ρ', 0°C, kg/m³	529	1129
ρ', 40°C, kg/m³	467	979
ration M1 vs. R-290	1	8.46
Ratio ρ' (0°C) vs. R-290	1	2.14
Ratio ρ' (40°C) vs. R-290	1	2.09
Factor additional capacity	1	4.04

Based on the LFL values, the density can theoretically be used to calculate the additional refrigerant mass that could be installed in a system or the factor by which the system could be enlarged. Assuming the M1 case, the system could be increased by factor 4.04 for R-474A (see Table 2).

2.3. Potential areas of application are identified based on existing safety standards

A closer look at the restrictions that exists for flammable class 2 + 3 refrigerants in the safety standards reveals the following areas of applications for low GWP <10 and A2l refrigerants:
Low and medium temperature commercial and industrial refrigeration systems formerly designed for high GWP HFC and HCFC refrigerants such as R-22, R-404A, R-507, and R-407 series but adopted to A2L refrigerants
Supermarkets - Distributed system - Walk in cooler/freezer, prep rooms, etc.
Condensing units (e.g. in food service)
Cold Storage Refrigeration
Residential and commercial heat pumps (air to water, brine to water, etc.)

2.4. Material- and thermo-physical properties of R-1132(E) and R-474A

R-474A is a binary mixture of R-1132(E) (23 wt %) and R-1234yf (77 wt %). R-1234yf has been known as a refrigerant for several years. R-1132(E) is relatively new and has been named and classified as a refrigerant under ISO817 since May 2022. The thermophysical properties of R-1132(E) and R-474A are listed in the Table 3 below.

Various mixed refrigerants using R-1132(E) are currently being developed for various applications. Table 3 shows the basic properties of R-474A which is already registered as a refrigerant. R-474A is a mixture of R-1132(E) and R-1234yf that was developed as an ultra-low GWP refrigerant, with a GWP of less than 10. R-474A has a low boiling point of -40 °C or lower. Furthermore, compared to R-454C or R-455A (GWP<150), which is expected by the authors to be the next-generation refrigerant for refrigeration and residential air conditioning applications, R-474A can achieve a GWP<1 while having equivalent physical properties. R-474A has already been registered as an A2L refrigerant in ISO 817 in 2022. Overall, R-474A has the same safety classification, similar thermophysical properties and a significantly lower GWP than other HFO blends e.g. R-454C or R-455A. This makes R-474A an interesting alternative to these HFO blends like R-454C or R-455A, taking into account future reductions in CO_2 quotas under the new EU F-Gas Regulation and the Kigali Amendment to the Montreal Protocol.

Table 3. Basic properties of R-1132(E) and R-474A

Refrigerant	R-1132(E)	R-474A
Formular / Composition	CHF=CHF(E)	R-1132(E)/R-1234yf (23.0/77.0 ma%)
Boiling point [°C]	-52.5	-43.4
Critical Temperature [°C]	75.7	87.8
Critical Pressure [MPa]	5.17	4.05
Vapor Pressure at 25 °C [MPa]	1.67	1.59
LFL for WCF [vol%]	4.4	5.4
Safety Class acc. ISO817	B2	A2L
GWP100	<1	<1

Additionally, Table 4 shows the results of theoretical cycle calculations of different refrigerants based on calculations conducted under the following conditions: evaporation temperature of 5°C, condensation temperature of 45 °C, superheat of 5 °K, supercooling of 5 °K, and compression efficiency of 70 %.

Table 4. Calculated cycle parameters of different refrigerants

Refrigerant	R-474A	R-454C	R-1234yf	R-290	R-404A	R-410A	R-32
GWP_{100}	1	148	1	1	3920	2088	675
COP $_{R\text{-}410A = 100}$	105	104	104	106	98	100	103
Cap. $_{R\text{-}410A=100}$	60	66	42	59	70	100	110
Glide eva./con.	4.7 / 5.8	5.9 / 7.2	-	-	0.4 / 0.3	0.1 / 0.1	-
Disch.temp.[°C]	63	68	54	63	61	77	95
Disch.pres. [MPa]	1.6	1.8	1.2	1.5	2.1	2.7	2.8

2.5. Material Compatibility of R-474A

R-474A consists largely of R-1234yf and a smaller proportion of R-1132(E). Therefore, a high compatibility and similar behavior to the R-1234yf standard oils and materials can be expected. This has been confirmed by tests described below. Gobo (2021) conducted a series of accelerated tests with lubricant and refrigerant coexisting in a sealed glass tube. The tested oil types were Polyolester Oil (POE) and Poly Vinyl Ether oil. The total acid number was then measured in order to evaluate the degradation of the lubricant collected after the test. The results are presented in Table 5. The test conditions were as follows: temperature 175 °C, 336 hours, and the refrigerant charge and the amount of coexisting metal were the same as above. There was no change in appearance or precipitation observed in either the R-1132(E) or mixed refrigerant with R-1234yf test samples. Furthermore, no increase in the total acid number of the lubricants was observed. This outcome indicates that the refrigerant, when mixed with HFO-1132(E) or a mixed refrigerant with R-1234yf, remains stable within the refrigeration cycle system. Consequently, the performance of the refrigerant is not expected to be altered.

Table 5. Oil compatibility tests

Condition					Result	
Refrigerant	Lubricant	Metals	Temp. [deg C]	Time [hour]	Appearance	TAN [mgKOH/g]
R-1234yf	PVE	Cu, Fe, Al	175	336	No change	< 0.01
	POE				No change	< 0.01
R-1132(E)	PVE				No change	< 0.01
	POE				No change	< 0.01
R-474A	PVE				No change	< 0.01
	POE				No change	< 0.01

2.6. Performance evaluation of R-474A

The vapour pressure curve of R-1132(E) is similar to that of R-32 over a wide range. When mixed with R-1234yf, R-1132(E) increases the pressure level and the volumetric cooling capacity. Refrigerants with a higher pressure level reduce the heat transfer resistance in the heat exchanger and therefore have better heat transfer behavior compared to refrigerants with a lower pressure level. In addition, an improved heat transfer can be expected, which is not taken into account in the subsequent compressor tests and theoretical cycle simulations.

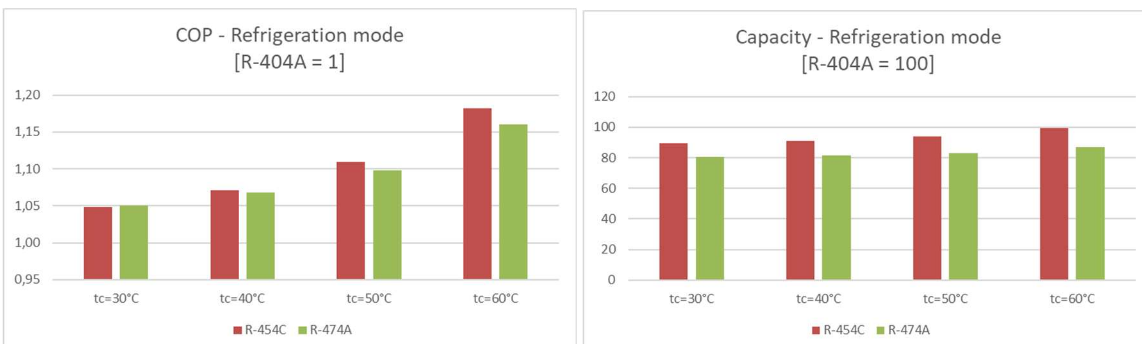

Figure 3: Performance of R-454C and R-474A compared to R-404A in refrigeration mode

Figure 3 shows the performance of R-454C and R-474A compared to R-404A at a constant evaporation temperature of -30 °C and various condensation temperatures. The simulation parameters are to = const at -30 °C, tc variable between 30 °C and 60 °C, T_{suph} = 5 K, $T_{subcooled}$ = 5 K, compressor efficiency f(po/pc). Slightly improved values are achieved for the COPs. When it comes to cooling capacity, both R-454C and R-474A fall to the same extent as R-404A.

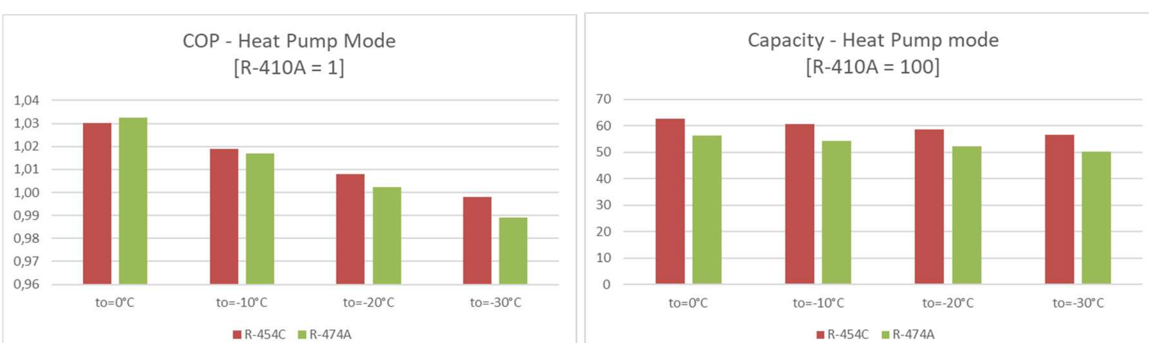

Figure 4: Performance of R-454C and R-474A compared to R-410A in heat pump mode

Figure 4 shows the performance of R-454C and R-474A compared to R-410A under typical heat pump operation conditions. The simulation parameters are tc = constant at 60 °C, to variable between 0 °C and -30 °C, T_{suph} = 5 K, $T_{subcooled}$ = 5 K, compressor efficiency f(po/pc). The efficiency of both refrigerants is comparable to R-410A and differs between +3 % and -2 %. The capacity is significantly lower of both refrigerants when compared to R-410A.
In direct comparison to R-454C, R-474A has slightly lower COPs and minor power losses. However, these are likely to play a smaller role. In principle, operation with R-474A in systems designed for R-454C should therefore be possible.

2.7. Outlook

The next steps in application development will be compressor and system tests across a wide range of stationary applications. Further tests of non-metal materials like elastomers and plastic materials will be done in parallel.

While R-474A is affected by the ongoing PFAS discussions due to the required availability of R-1234yf, R-1132(E) itself does not fall under the definition of PFAS as currently being discussed in the EU. R-1132(E) has limitations as pure refrigerant from its thermal stability and needs to be mixed with other components (Goto et al, 2024). In general, R-1132(E) can be used as a refrigerant in mixtures with many non-PFAS components, e.g. as a booster component with R-152a. However each of these possible blends requires separate testing.

3. CONCLUSIONS

R-474A has shown potential as an A2L refrigerant in refrigeration and air conditioning applications with a GWP<1. The pressure / temperature behaviour is in the same range of already commercialised and used refrigerants in RACHP applications. R-474A is a suitable solution fulfilling the stringent quota reduction requirements in future set by the EU while keeping the safety risk of using a flammable refrigerant as little as possible.

NOMENCLATURE

MM	molecular weight (g/mol)	LFL	Lower Flamability Limit (kg/m³)
M1	Cap value acc. EN378-1	ρ’	saturated liquid density (kg/m³)
T	Temperature	RACHP	Refrigeration Air Conditioning Heat Pumps
COP	Coefficien of Performance	po	Pressure evaporation
pc	Pressure condensation		

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