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Refrigerants with low global warming potential

Köldmedier med låg växthuseffekter

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Energimyndigheten

Förord

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Sammanfattning

Projektet har syftat till att ta fram underlag och förutsättningar för alternativa köldmedier med låg GWP vid utfasning av R134a, R410A och R404A köldmedier för befintliga och nya värmepumpar/kylanläggningar. Fokus har varit på nya köldmediers egenskaper, krav som ställs på säkerhetsutrustning, komponenter och anläggningens energiprestanda.

Målet med projektet har varit kompetensförsörjning till kyl- och värmepumpbranschen och kompetensuppbyggnad vid Institutionen för Energiteknik rörande nya köldmedier. Detta innebär att kunskapssammanställningar och informationsspridning har varit centrala delmål i det här projektet. Arbetet har fokuserat på såväl ersättningsmedier för befintliga anläggningar med HFC köldmedier som på val av köldmedium och komponenter till nya anläggningar. Syftet med projektet har varit vidareuppbyggnad av kunskap om nya syntetiska köldmedier/köldmedieblandningar och deras termodynamiska egenskaper. Kontinuerlig informationsspridning om utvecklingen på köldmediefronten, inkluderande HFC köldmedier, naturliga medier, blandningar och nya syntetiska köldmedier har varit i fokus. Projektet har tittat på köldmediers olika alternativs kända inverkan på närmiljö och global miljö, hälsoaspekter, kompatibilitet med polymerer, metaller, stabilitet i och utanför systemet samt kombination med oljor, kompatibilitet med polymerer, metaller, brandfarlighet, toxicitet för personal och för omgivande och global miljö.

Ett huvudsyfte har varit också att sprida dessa kunskaper till den svenska kyl- och värmepumpbranschen på ett korrekt, lättförståeligt och neutralt sätt. Dessa kunskaper är av väsentlig betydelse för branschen för val av köldmedium och utformning av nya anläggningar, samt för bedömning av möjligheter till, och konsekvenser av, konvertering av befintliga anläggningar till nya medier.

Ersättning av R134a, R410A och R404A köldmedier med rena medier är ofta problematiskt på grund av t ex förändringar i volymetrisk köldalstring, massflöde, kompressorns hetgastemperaturökning, samt ökad brännbarhet.

Tillgängliga köldmedier och köldmedieblandningar med reducerad GWP som kan ersätta R134a, R410A och R404A har identifierats under projektets gång. Baserat på resultaten av litteraturstudier och numerisk modellering, har ett begränsat antal köldmedier valts ut för experimentell utvärdering.

Resultaten av projektet visar att det finns ett antal låg GWP alternativ till R134a, R404A och R410A. Alternativen kan ses som ”drop-in” ersättare (dvs. alternativ som kan användas i befintliga system, med mindre eventuella ändringar inom systemet) när

ändringarna som orsakas av konvertering är acceptabla för ett givet system. Därför har det varit svårt att dra generella slutsatser.

Projektet har genomförts som ett doktorandprojekt under ledning av flera seniora forskare på Kungliga Tekniska Högsollan (KTH) på institutionen energiteknik.

Summary

The project aims to provide data, information, and support for the utilization of alternative refrigerants with low global warming potential (GWP) for existing and new heating/cooling systems at the phasing out of hydrofluorocarbon (HFC) refrigerants. The focus has been set on the thermal properties of new refrigerants, requirements for the safety of components, and energy efficiency.

The aim of the project is to provide skills and knowledge to the refrigeration and heat pump industry and the Department of Energy Technology regarding new refrigerants. This means that knowledge compilation and information dissemination are the central goals of this project. The study is focused on the replacement of high GWP refrigerants in existing plants as well as on the choice of refrigerants and components for new plants. The purpose of the project includes the further development of knowledge about new synthetic refrigerants/refrigerant mixtures and their thermodynamic properties. The focus is set on the continuous dissemination of information pertaining to the development of refrigerants, including HFCs, natural media, mixtures, and new synthetic refrigerants. This report presents the known effects of refrigerants on the following aspects: health, internal and external stability, compatibility with oils, polymers and metals, flammability, human toxicity, and the local and global environment.

Moreover, the purpose is to spread this knowledge to the Swedish refrigeration and heat pump industry in a correct, easy-to-understand, and neutral manner. These knowledge are essential to the industry in choosing the appropriate refrigerant and design of new facilities, as well as for assessing the potential for, and consequences of, the conversion of existing facilities suitable for the utilization of new refrigerants.

The replacement of refrigerants R134a, R410A, and R404A to pure alternatives is typically problematic because of the changes in volumetric refrigeration capacity, refrigerant mass flow, compressor discharge temperature rise, and increased flammability of such fluids. Because of the fact that no ideal pure fluid is available, refrigerant mixtures are proposed.

Available pure refrigerants and mixtures with reduced GWP that can replace R134a, R410A, and R404A are investigated in this study. Based on the results of studies reported in literature and numerical modelling, a limited number of refrigerants are selected for experimental evaluation.

The results of this study show that there are a number of low GWP alternatives to R134a, R404A, and R410A. The options can only be regarded as drop-in replacements (i.e., options that can be used in existing systems with minor changes to the system),

when the changes caused by replacement are acceptable for a given system. Therefore, it has been difficult to draw general conclusions.

The work has been conducted as a PhD student project led by several senior researchers at the Royal Institute of Technology (KTH) at the Department of Energy Technology.

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Nomenclature

c_p	isobaric specific heat, kJ kg^{-1} K^{-1}
k	coefficient of thermal conductivity, mW m^{-1} K^{-1}
P	pressure, MPa, bar
q	refrigerating effect, kJ kg^{-1}
q_v	volumetric cooling capacity, kJ m^{-3}
T	temperature, °C
$\rho_{sat,v}$	saturated vapour density, kg m^{-3}

Subscripts

cond	condensing
crit	critical
evap	evaporation

Abbreviations

AR4 IPCC Fourth Assessment Report: Climate Change 2007

AR5 IPCC Fourth Assessment Report: Climate Change 2013

ASHRAE 34 American Society of Heating, Refrigerating and Air-Conditioning Engineers ANSI/ASHRAE Standard 34 2016 Designation and Safety Classification of Refrigerants

CO_2-eq. carbon dioxide equivalent

COP coefficient of performance

EU the European Union

F-gas Regulation Regulation (EU) No 517/2014 of the European Parliament and of the Council of 16 April 2014 on fluorinated greenhouse gases and repealing Regulation (EC) No 842/2006

GHG greenhouse gas

GWP global warming potential for 100 years (AR4 values, if not otherwise stated)

HFC hydrofluorocarbon

HFO hydrofluoroolefin

HTC heat transfer coefficient

LCCP life cycle climate performance

MAC Directive Directive 2006/40/EC of the European Parliament and of the Council of 17 May 2006 relating to emissions from air conditioning systems in motor vehicles

MAC mobile air conditioning

NBP Normal boiling point

RAC refrigeration and air conditioning

TEWI total equivalent warming impact

TFA trifluoroacetic acid

UNEP United Nations Environment Programme

Background

There is a long-term trend of global mean temperature increase since the beginning of the industrial revolution. As shown in Figure 1, in the 136-year recorded history, 17 of the 18 warmest years have occurred in the current century, largely as a result of the increased carbon dioxide and other man-made greenhouse gas emissions (GISTEMP Team, 2018). The International Institute of Refrigeration estimates that 7.8% of the global greenhouse gas emissions are accounted to the refrigeration sector, heat pumps, and cryogenics. More than a third of these are direct emissions of fluorinated refrigerants, whereas the rest is related to the production of energy required to drive refrigeration systems (IIR/IIF, 2017). In order to limit the global climate change to a temperature increase of 2 °C, fluorinated substances are being controlled by a number of environmental protection regulations, and their consumption has to be significantly reduced in the future, both in the European Union (European Parliament and the Council of the European Union, 2014) and worldwide (Ozone Secretariat, 2018).

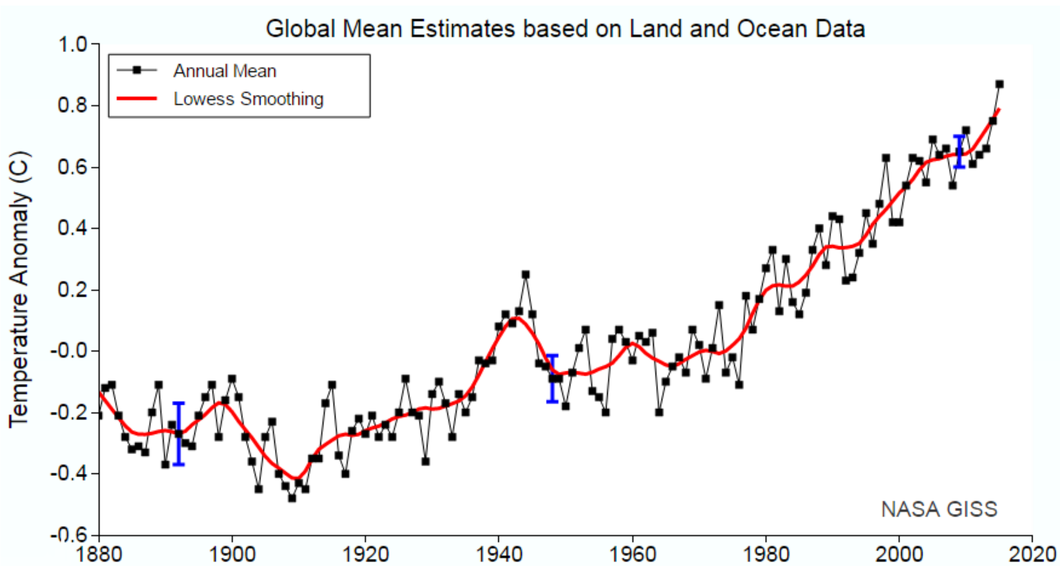

Figure 1. Global mean temperature estimates (Ozone Secretariat, 2018)

In the European Union, a regulatory action has been implemented to control hydrofluorocarbons (HFCs) and other fluorinated gases through the European Union Regulation No 517/2014, also known as F-gas Regulation (European Parliament and the Council of the European Union, 2014). The target is to reduce the volume (in tonnes of CO_2-eq.) of HFCs placed on the market by 79% in comparison with the 2009–2012 annual average levels. Moreover, this regulation has been supported by additional national legislations on the use of HFCs with high global warming potential (GWP), taxes (Denmark, France, Poland, Slovenia, Spain), or promotion of low GWP and natural fluids (Belgium).

The Directive 2006/40/EC (The European Parliament and the Council of the European Union, 2006), also known as MAC Directive, placed the first HFC prohibition, which imposed a 150-GWP limit on mobile air conditioners of personal vehicles.

Outside the European Union, some developed countries (e.g., Japan, New Zealand, Switzerland, and the USA) have exerted efforts for the promotion of low GWP refrigerants. In the case of the USA, which has the highest HFC emission level among all developed countries (United Nations, 2018), the US Environmental Protection Agency has included fluids with reduced GWP in their list of acceptable substances (US EPA, 2017).

In February 2017, the European Commission has adopted a proposal to ratify the Kigali's amendment to the Montreal Protocol to gradually limit the HFC production and use. A drastic reduction in the consumption of these chemicals would potentially aid in limiting the global temperature rise well below 2 °C by 2100 (European Commission, 2017). The 197 Montreal Protocol parties reached a compromise, under which developed countries will start to phase down HFCs by 2019. Then, the developing countries will follow with a freeze of HFC consumption levels in 2024, with some countries freezing consumption in 2028. By the late 2040s, all countries are expected to consume no more than 15–20% of their respective baselines, as shown in Figure 2 (UNEP, 2016a).

At the European Union level, the phase down of HFC has already started. The recent statistics reported by the European Commission shows that the level of HFC placed in the EU market in 2015 was within the limits set by the F-gas Regulation (European Environmental Agency, 2017). However, there is a noticeable spike in HFCs placed in the European market in 2014 (measured in megatonnes of CO_2 equivalent, Mt CO_2-eq.), which was the last year before the F-gas Regulation limited this amount. According to the requirements of the regulation, by the beginning of 2018, the maximum quantity of hydrofluorocarbons to be placed in the market has to be reduced to 63% of the 2009–2012 baseline (by 32% from the currently allowed level). Thus, the conventional HFC replacement with low GWP refrigerants will help in achieving further reduction.

Natural fluids are low/no GWP refrigerants and have always been considered for refrigeration and air conditioning systems. However, because of different reasons (safety, cost of equipment, etc.) their implementation has been limited to selected applications. Nowadays, the implicit GWP restrictions provide another opportunity for the use of natural refrigerants. Several authors have reviewed the particularities of the most relevant natural refrigerants used in vapour compression systems in the last few years. For instance, Bansal (2012) focused on the CO_2 low-evaporation temperature operation, whereas Ma et al. (2013) focused on the CO_2 transcritical cycle operation. Pearson (2008) and Palm (2008) discussed the opportunities of ammonia and hydrocarbons, as working fluids, respectively.

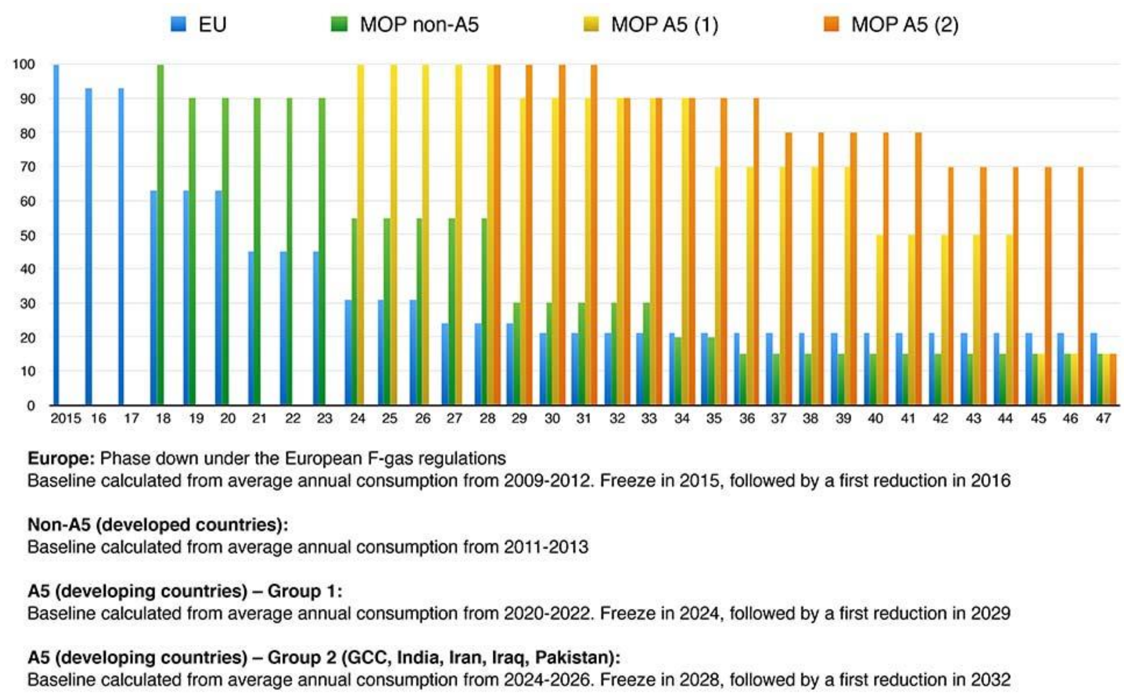

Figure 2. Global HFC phase down will work under the Montreal Protocol (UNEP, 2016a).

Apart from the possibility of using available natural refrigerants, researchers and manufacturers are considering low-GWP synthetic refrigerant alternatives. It was shown, however, that taking into account the stability and toxicity characteristics, as well as suitable thermodynamic properties, the limits of chemistry only result in 62 low GWP fluids that are usable in refrigeration and air conditioning equipment (McLinden et al., 2014); most of these fluids are flammable. From among these fluids, none is ideal in all respects; trade-offs should be performed. The refrigerant mixtures could address these trade-offs because they can provide altered properties to these fluids, especially reduced flammability and GWP.

Some recently developed low GWP refrigerants and their mixtures have been investigated in a number of studies. However, the knowledge pertaining to the consequences of the utilization of pure and mixed HFOs in vapour compression systems is still at an early stage. Given the demand for new low GWP refrigerants from the Swedish refrigeration industry, this project has been undertaken to provide unbiased information about new fluids/mixtures as well as their implementation. Thereafter, such information has been disseminated at various levels.

Project participants

The project is performed at the Department of Energy Technology, KTH Royal Institute of Technology and financed by the Swedish Energy Agency (Energimyndigheten) through Effsys Expand program and the following project partners:

- Bosch Thermoteknik AB;
- Danfoss Värmepumpar AB;
- Kylbranschens Samarbetsstiftelse;
- Nibe AB, Nowab;
- Svensk Energi & Kylanalys AB;
- Svenska Kyltekniska Föreningen.

The project partners have partly financed the undertaking and contributed to it by sharing their expertise and resources.

Aim

The aim of this project is to provide data, information, and support for the use of alternative refrigerants with low GWP for existing and new heating/cooling systems at the phasing out of HFC refrigerants. The focus is set on the thermal properties of new refrigerants, requirements for the safety of components, and energy efficiency.

- Identification of conditions for the phasing out of R134A, R410A, and R404A refrigerants and assessment of new refrigerants in terms of energy efficiency
- Investigation of the thermal properties and safety of new low GWP refrigerants and the consequence analysis of the phasing out of HFC refrigerants and the introduction of new refrigerants on system performance
- Experimental determination of heat transfer and pressure drop for evaporation and condensation with new low GWP refrigerants
- Experimental study of compatibility with polymers, metals, and stability inside and outside the system, and the performance of compressors, heat exchangers, and expansion valves with different oils.

Implementation

The project objectives were achieved by means of a literature study that was continuously performed during the entire duration of the project, as well as a few case studies that centred on the detailed investigation of alternatives to refrigerants R134a, R410A, and R404A. The results of the literature review have been published in 28 articles in the industrial magazine, Kyla&Värme (former name, Kyla+ Värmepumpar).

Based on the results of the literature study and the insights provided by the project partners, a few case studies have been designed to provide unbiased information regarding low-GWP refrigerant replacements. The studies have been prioritised based on the demand from the Swedish refrigeration industry and availability of commercial low GWP replacements.

The refrigerant R404A is one that has been used in the majority of the Swedish supermarket systems. Low GWP refrigerants, such as carbon dioxide and propane can be used to satisfy refrigeration and freezing requirements in such systems. The implementation of such refrigerants requires systems to be adapted to their use. This has also been identified by other entities. Furthermore, a few projects within EffsysExpand have been dealing with this refrigerant application, e.g., Effsys Expand 'The energy efficient supermarket of tomorrow' (P04) and 'Technology carrier—Best technology for a ground source heat pump' (P24) (EffsysExpand, 2018).

Because of the requirements of the F-Gas Regulation, several supermarket systems are required to replace R404A without significant modifications to their existing systems. This project approached this problem by identifying potential R404A replacements (Makhnatch et al., 2017a) and performing a case study of four refrigeration systems (representing typical Swedish supermarket refrigeration systems) in two different locations (Figure 3 and Figure 4 illustrate a machine room of the analysed system and a schematic of one of the analysed systems, respectively). The results of the case study have been communicated through a report (Rogstam et al., 2016), conference publications (Makhnatch and Khodabandeh, 2015) (Makhnatch and Khodabandeh, 2016) (Makhnatch et al., 2018e) (Makhnatch et al., 2018f), and a publication in a scientific journal after its further analysis (Makhnatch et al., 2017e).

Figure 3. Photograph of the machine room of the analysed supermarket system (Rogstam et al., 2016)

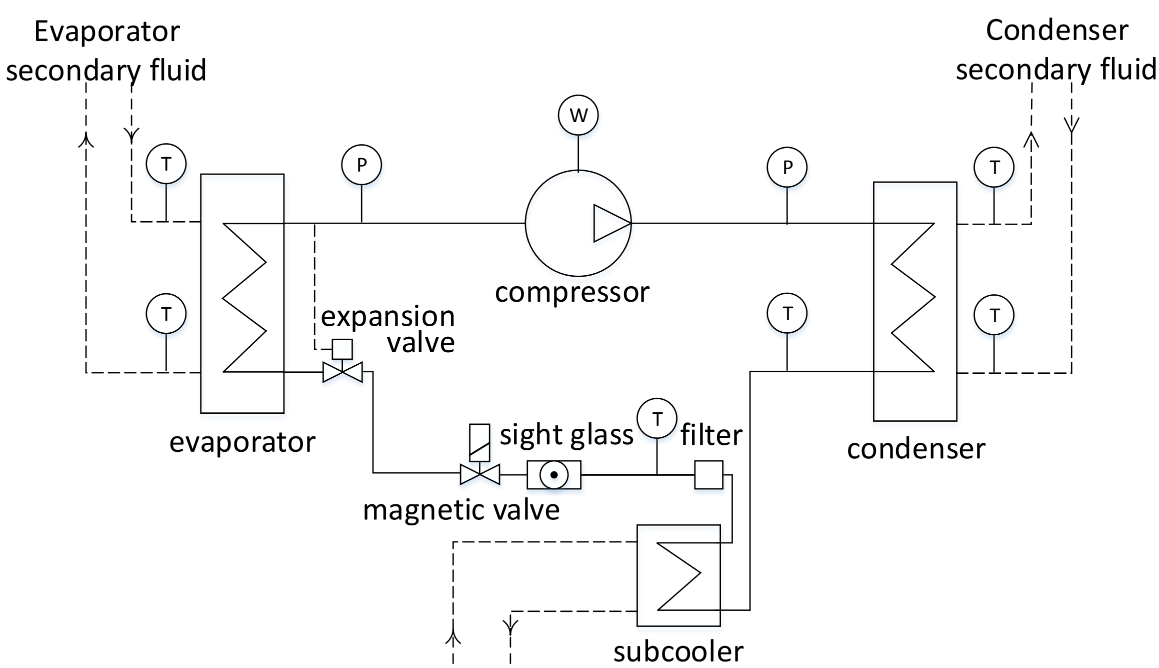

Figure 4. Schematic of one of the analysed R404A vapour compression systems

Refrigerant R134a was introduced to replace R12 in mobile air conditioning systems, and stationary refrigeration systems and chillers with medium evaporation temperature; it has gradually become the most abundant HFC in the atmosphere (World Meteorological Organization, 2014). Identifying suitable low GWP alternatives to R134a for mobile air conditioning systems (MACs) of personal vehicles has been a subject of early research. At this stage, hydrofluoroolefins (HFOs), specifically R1234yf and R1234ze, have been identified as low-GWP alternatives with operating pressures similar to that of the baseline R134a; R1234yf has become the preferred refrigerant for MACs. A literature survey has determined that both R1234yf and R1234ze were already well-studied refrigerants when the project was initiated. However, there is a dearth of information regarding HFO/HFC mixtures, whose commercialisation has already begun. Refrigerants R513A and R450A are examples of HFO/HFC mixtures that are proposed as alternatives to R134a that have lower GWP. An experimental setup has been prepared for the energy performance evaluation of these mixtures as illustrated in Figure 5 (the corresponding schematic is presented in Figure 6).

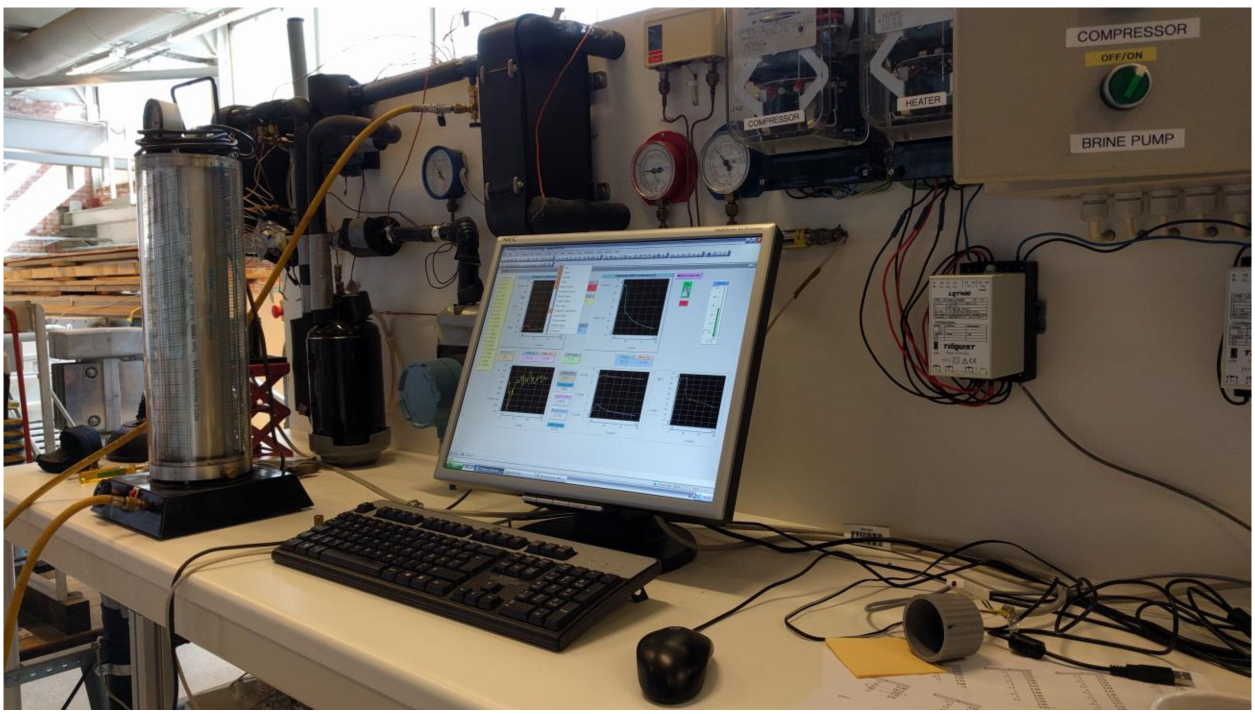

Figure 5. Photograph of the experimental test rig used to evaluate R134a alternatives

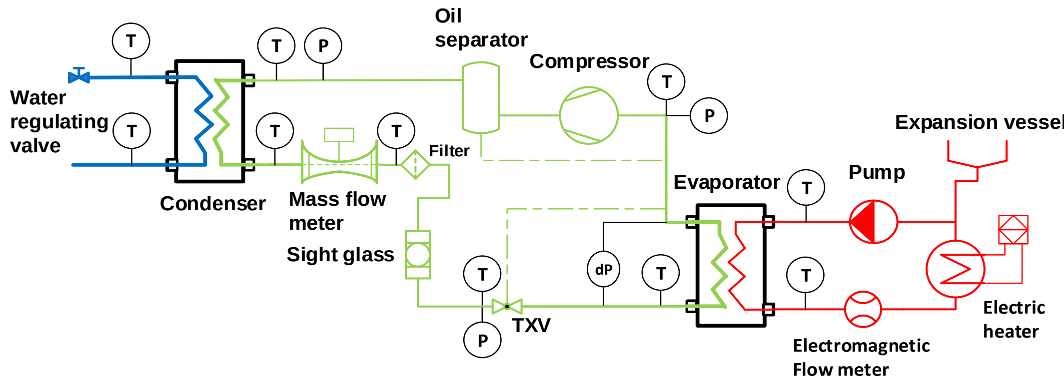

Figure 6. Schematic of the experimental test bench

The results of the evaluations of R134a alternatives have been published covering the use of R152a (Makhnatch et al., 2016a) (Makhnatch et al., 2016b), R1234ze(E) (Adrián Mota-Babiloni et al., 2017a), R450A (Adrián Mota-Babiloni et al., 2017a) (Makhnatch et al., 2017d), and R513A (Adrián Mota-Babiloni et al., 2017b). The evaluations of R450A and R513A at high ambient temperatures have been studied both theoretically and experimentally (Makhnatch et al., 2018g) (Makhnatch et al., 2018c).

A number of flammable pure low-GWP refrigerants, as well as flammable refrigerant mixtures, have been identified as R410A alternatives. These alternatives are designed to match R410A performance or its cooling/heating capacity. However, the apprehension regarding flammability does not allow any of these refrigerants to be considered as drop-in alternatives to R410A. Alternatives to R410A have been discussed in several popular science publications (Makhnatch et al., 2018a) (Makhnatch et al., 2017b). Natural refrigerants, such as propane, can be used in applications where R410A is currently used. The usage of propane, as discussed in such publications, is a subject of a few other Effsys Expand projects (EffsysExpand, 2018). Another alternative, R32, can provide greater energy efficiency and higher cooling capacity than R410A. The implications of using R32 have been reviewed in a scientific paper (Adrián Mota-Babiloni et al., 2017c).During the project implementation, several topics have been identified as important for the adoption of low GWP alternatives to R134a, R404A, and R410A. These have been subjects of specific investigations that resulted in its publications in Kyla&Värme and/or as a conference article. The complete list of publications made during the project implementation consists of 28 publications in Kyla&Värme, 11 conference publications, 1 field study report, and 7 publications in scientific journals.

Results

The replacement of high GWP refrigerants with low GWP refrigerants is necessary in order to comply with the requirements of existing legislations, e.g., the MAC Directive, F-Gas Regulation, and the Kigali Amendment to the Montreal Protocol. As a result of the project reported herein, the general conclusion is that there are no low GWP alternatives to R134a, R404A, and R410A that can be considered as ‘drop-in’ (or ‘design compatible’) alternatives. Any alternative to the conventional high GWP refrigerant implies a variation in one or several characteristics of new refrigerants that must be considered when using any alternative in an existing refrigeration system, or designing a new system for a low GWP refrigerant. In other words, there is a trade-off among the characteristics of low GWP refrigerants when using them as alternatives to R134a, R404A, or R410A; this trade-off differs depending on the intended application. Accordingly, low GWP alternatives that are available for each of the application, as presented in the MAC directive and F-Gas Regulation, are discussed in this paper.

Defining low GWP

As of the moment, there is no widely accepted definition of ‘low GWP’ refrigerant. The first attempt to define GWP range for ‘low GWP’ fluids was made by the United Nations Environment Programme (UNEP) in their report in 2010 (UNEP, 2010). The report discussed that the terms are of comparative nature, and therefore has to be related to some mean GWP value; the estimated moderate value was 1000, as presented in Figure 7. However, to date, this value has not been officially established as a standard. In fact, even the UNEP only uses terms such as ‘low/lower’ GWP and ‘high/higher’ GWP in its recent report (UNEP, 2016b).

This report does not attempt to define ‘low GWP’; instead, the focus is on identifying new refrigerants and refrigerant mixtures that can be proposed to replace R134a, R404A, and R410A in existing and new applications. These replacements must have lower GWP values (compared to the GWP of the refrigerant to be replaced) so that their implementation as substitutes can facilitate the gradual reduction in the use of fluorinated refrigerants, as required by the F-gas Regulation and the Kigali amendment to the Montreal Protocol.

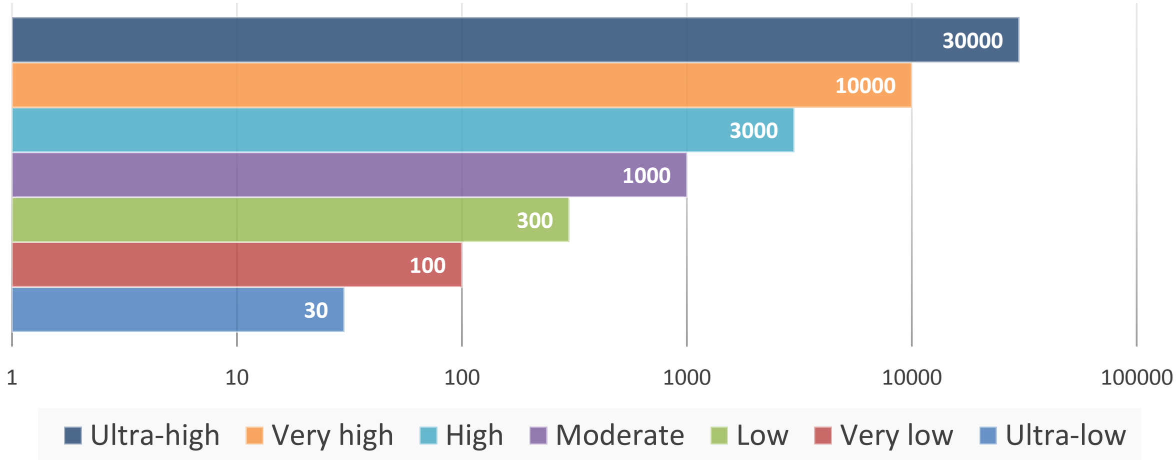

Figure 7. Proposed GWP classification of greenhouse gases (UNEP, 2010)

The GWP is the metric that integrates the radiative forcing of a substance over a chosen time horizon relative to that of CO_2. These values are updated regularly; thus, a single refrigerant may have different values when stated by various sources. Unless clearly stated otherwise, this report implements the GWP values of fluorinated gases as stated in Regulation (EU) No. 517/2014 of the European Parliament and of the Council of 16 April 2014 on fluorinated greenhouse (European Parliament and the Council of the European Union, 2014).

Low GWP refrigerants

The amount of single-component fluids that is suitable for the use as refrigerant in vapour compression cycle is limited. Several years ago, Thomas Midgley noticed that only a limited amount of components are capable of forming sufficiently volatile compounds that can suitably become refrigerants; therefore, only a certain number of elements has to be considered, as shown in Figure 8 (Midgley, 1937). Back then, he identified a number of fluids that have satisfied refrigeration requirements for years.

Currently, the demand for a remarkable refrigerant is great. A few years ago, Domanski and McLinden have initiated the project to search for the potential new low- GWP refrigerants. They performed a procedure similar to what Midgley implemented several years earlier, but they considered significantly larger amounts of compounds. They began by screening more than 60 million chemical structures that are listed in the PubChem database and gradually applied different refrigerant selection criteria, thus reducing the number of potential new refrigerants to 138. After deliberations, the number was further reduced.

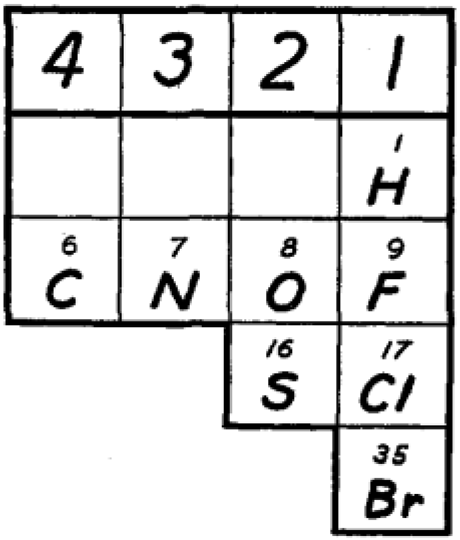

Figure 8. Elements that have been identified to form volatile compounds suitable for refrigeration application (Midgley, 1937)

After considering a typical unitary air conditioning application, their screening identified 27 potential refrigerants (McLinden et al., 2017), of which 24 have a GWP below 150. This list includes a few novel mixtures, as well as known refrigerants, such as R32 and CO_2. The complete list of fluids is summarised in Table 1. The GWP values of the fluids presented in Table 1, unless otherwise noted, are values from AR4 and F-gas Regulation. For the limited number of newly identified fluids the GWP values are those listed in AR5 or estimated by McLinden et al. (2017).

Table 1. Chemical names and GWP of the fluids identified by McLinden et al. (2017)

Fluid name	**ASHRAE designation**	**GWP**
Hydrocarbons and dimethylether		
Ethane	R-170	6
Propene (propylene)	R-1270	2
Propane	R-290	3
Methoxymethane (dimethylether)	R-E170	1
Cyclopropane	R-C270	86*
Fluorinated alkanes (HFCs)		
Fluoromethane	R41	92
Difluoromethane	R32	675
Fluoroethane	R161	12
1,1-Difluoroethane	R152a	124
1,1,2,2-Tetrafluoroethane	R134	1100

Fluid name	**ASHRAE designation**	**GWP**
Fluorinated alkenes (HFOs) and alkynes		
Fluoroethene	R-1141	<1^
1,1,2-Trifluoroethene	R-1123	3*
3,3,3-Trifluoroprop-1-yne	NA	1.4*
2,3,3,3-Tetrafluoroprop-1-ene	R-1234yf	4
(E)-1,2-difluoroethene	R-1132(E)	1*
3,3,3-Trifluoroprop-1-ene	R-1243zf	<1^
1,2-Difluoroprop-1-eney	R-1252ye	2*
(E)-1,3,3,3-tetrafluoroprop-1-ene	R-1234ze(E)	7
(Z)-1,2,3,3,3-pentafluoro-prop-1-ene	R-1225ye(Z)	<1^
1-Fluoroprop-1-ene	R-1261ze	1*
Fluorinated oxygenates		
Trifluoro(methoxy)methane	R-E143a	756
2,2,4,5-Tetrafluoro-1,3-dioxole	NA	1*
Fluorinated nitrogen and sulfur compounds		
N,N,1,1-tetrafluormethaneamine	NA	20*
Difluoromethanethiol	NA	1*
Trifluoromethanethiol	NA	1*
Inorganic compounds		
Carbon dioxide	R744	1
Ammonia	R717	0
Current HFCs		
Pentafluoroethane	R125	3500
R-32/125 (50.0/50.0)	R410A	2088
1,1,1,2-Tetrafluoroethane	R134a	1430

* GWP values as estimated by McLinden et al. (2017)

^ GWP values as listed in AR5

In the list, only two refrigerants, CO_2 and R1225ye(Z), are non-flammable. Although CO_2 is a known refrigerant, it cannot be considered as a drop-in alternative to R404A, R134a, and R410A because of its low critical temperature (hence, its use in trans-critical cycle under typical conditions). It should be noted that CO_2 is seen as a major alternative to R404A in the commercial refrigeration sector when the R404A system is to be replaced with a new one.

Refrigerant R1225ye(Z) has a theoretically estimated cooling capacity of approximately a quarter of that of R410A and is toxic to some extent. The majority of alternatives are therefore flammable. If low flammability is desired, some refrigerants can be used as components in mixtures with non-flammable refrigerants with higher GWP. Such mixtures are currently being developed, and several that are commercialised are analysed in this report (e.g., R448A, R449A, R450A, and R513A).

In conclusion, there is a limited number of potential future refrigerants. Some of the refrigerants are already previously known, and their characteristics are known to introduce trade-offs in existing refrigeration systems (e.g., flammability and toxicity). A number of alternatives can further be excluded by additional analysis, for instance, because of stability and material compatibility problems.

R134a

Refrigerant R134a is identified as a dominant contributor to global warming among all the hydrofluorocarbons (Intergovernmental Panel on Climate Change, 2014). It presents a GWP of 1430 and is a fluorinated refrigerant used in air conditioning and refrigeration systems. Although R134a has a high GWP, its use continues to increase in developing countries as an R12 retrofitting replacement (Hu et al., 2010). According to the UNEP estimates, the global production of HFCs is dominated by the production of R134a (223 kt), of which 123 kt are produced in developing countries (UNEP Technology and Economic Assessment Panel, 2015). Therefore, reducing the use of R134a is necessary in order to achieve the global environmental goals.

Among the different viable candidates to replace R134a (isobutane, CO_2, and synthetic refrigerants and mixtures), most are flammable or, in case of CO_2, operate at excessive pressures. Meanwhile, non-flammable HFC/HFO mixtures are technically considered as possible substitutions (Mota-Babiloni et al., 2015a). Table 2 lists 'low GWP' synthetic refrigerants and refrigerant mixtures that are proposed as alternatives to R134a.

Table 2. 'Low GWP' synthetic alternatives for R134a

ASHRAE 34* designation	Composition	GWP	Safety group
R450A	R1234ze(E)/134a	605	A1
R513A	R1234yf/134a	631	A1
R513B	R1234yf/134a	596	A1
R515A	R1234ze(E)/227ea	393	A1
R516A	R1234yf/152a/134a	142	A2L
R456A	R32/134a/1234ze(E)	687	A1
R1234yf	pure	4	A2L
R1234ze(E)	pure	7	A2L
R152a	Pure	124	A2
R444A	R32/152a/1234ze(E)	93	A2L

* ASHRAE 34 standard on designation and classification of refrigerants (2016)

Refrigerant R134a is also dominant in MAC applications in the European Union (EU). It is estimated that approximately 80% of the total direct MAC CO_2-eq. emissions are caused by R134a leakages from the service process because of the high service rate and non-recycling of refrigerants (Su et al., 2015). Consequently, operational emissions represent 17% of the total, followed by the end-of-life emissions, and then initial emissions. Therefore, it has a strong greenhouse gas (GHG) emission reduction potential in MACs.

To mitigate greenhouse gas emissions from MACs, the EU has introduced the European Directive 2006/40/EC pertaining to emissions from air conditioning systems in motor vehicles (also known as the ‘MAC Directive’). The MAC Directive, introduced in 2006, has imposed several limitations to automotive manufacturers, among which the most significant is the complete ban of MACs designed to use fluorinated greenhouse gases with a GWP higher than 150 (currently in place for all newly produced personal vehicles). Carbon dioxide, hydrocarbons, R152a, R1234yf, and several refrigerant mixtures have been considered as potential substitutes to R134a.

The properties of R1234yf and its applicability as an R134a replacement have been investigated by a number of studies. For instance, Zilio et al. (2011) published a pioneering paper pertaining to the usage of R1234yf as R134a drop-in alternative in MAC systems. The lower system performance that they observed in using R1234yf led them to propose an enhancement of the condenser and evaporator area by 20 and 10%, respectively, and an overridden compressor to match the coefficient of performance (COP). The early technical notes of Lee and Jung (2012) quantified the loss in COP using R1234yf between 0.8 and 2.7%, whereas the loss in the cooling capacity was as high as 4.0%. The other previous studies pertaining to R1234yf performance in air conditioning systems can be found in Wang (2014).

According to the previous studies, R1234yf appears to be the most important alternative to R134a in MAC because the transition to R1234yf does not require substantial MAC system modifications. However, the observed R1234yf cooling capacity and energy performance drop compared with that of R134a hinder the extended use of the HFO in MACs. Accordingly, more papers that focused on MAC modelling and the influence of its components have been published to provide a better insight on the effects of refrigerant replacement on system performance. Other synthetic refrigerants usable in mobile air conditioners are R152a, R444A, and R445A (GWP of 124, 93, and 135, respectively). For a complete review of available publications, the reader is referred to Mota-Babiloni et al. (2017).

According to a recent survey study (Öko-Recherche, 2017), a majority of the newly installed commercial refrigeration systems in Europe today still use HFCs as well as a number of natural refrigerants, as shown in Figure 9. The most frequently used synthetic refrigerants indicated by the survey are R134a, R404A, R407 series, R410A, and R507A; the most used natural refrigerants are CO_2, ammonia, and propane.

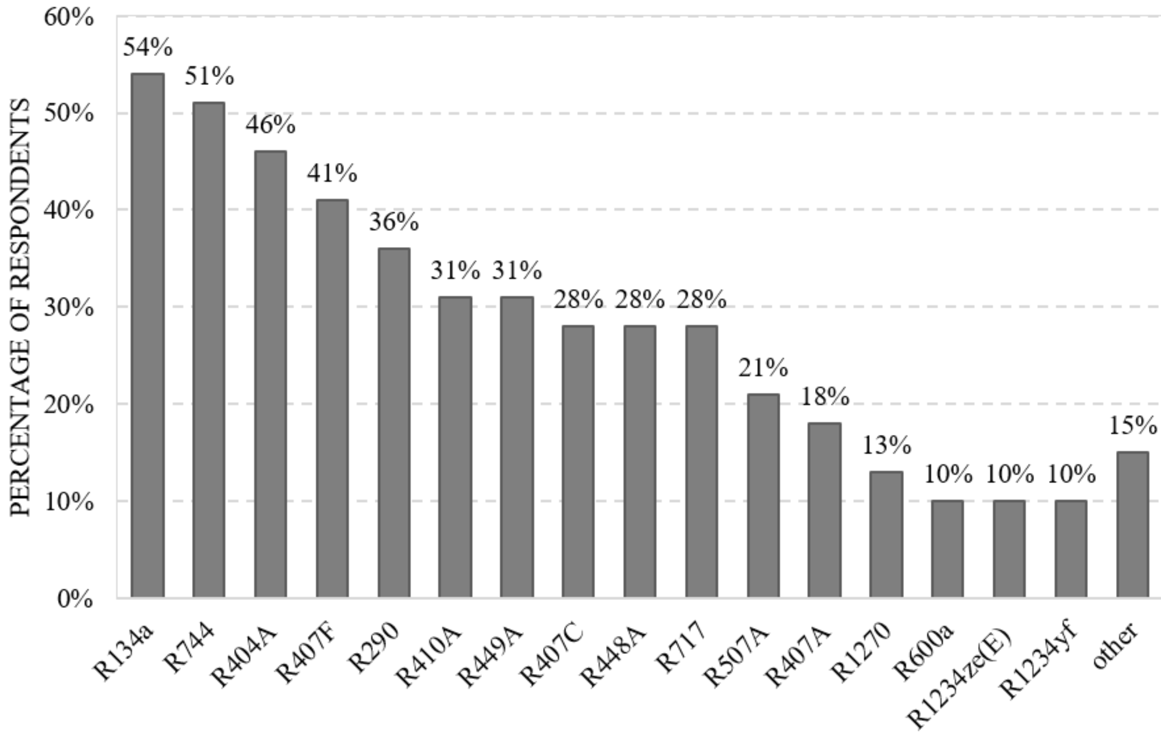

Figure 9. Percentage of questionnaire respondents indicating a particular refrigerant they currently use for commercial refrigeration (Öko-Recherche, 2017)

The data presented in Figure 9 confirms that R134a is the widely used refrigerant in commercial refrigeration systems. Jarall (2012) compared R1234yf with R134a in refrigeration systems, and concluded that R1234yf yields a lower refrigerating capacity, COP, and compressor efficiency in a small refrigeration unit. Refrigerant R1234ze(E) was also considered in these systems (Mota-Babiloni et al., 2016b). A detailed review of available publications is provided by Mota-Babiloni et al. (2017).

Refrigerant R152a (1,1-Difluoroethane) has a considerably low GWP value of 124. Its applicability has been actively studied since the beginning of the 1990s because it was considered to be a potential replacement to R12 in medium-temperature air conditioning systems. However, eventually, R134a superseded R152a and became one of the mostly used refrigerants. Today, R152a is considered as the replacement for the R134a refrigerant.

The normal boiling point of R152a is slightly higher than that of other alternatives, including R134a (Table 3). However, the minor difference between R152a and R134a allows R152a to be used in most applications where R134a is used. The critical temperature is also higher, thus affording the potential use of R152a in heat pump cycles with higher condensing temperatures.

Table 3. Main properties of R152a and analogous refrigerants

Refrigerant	R134a	R1234yf	R152a	R290
Chemical formula	$C_2H_2F_4$	$C_3H_2F_4$	$C_2H_4F_2$	C_3H_8
P_{crit} (MPa)	4,06	3,38	4,52	4,25
T_{crit} (°C)	101,1	94,7	113,3	96,7
NBP (°C)	−26,1	−29,5	−24,0	−42,1
ASHRAE Safety group	A1	A2L	A2	A3
GWP	1430	4	124	3*

* Indirect GWP as stated in AR4

Refrigerant R152a is further analysed in a simple refrigeration cycle where the evaporating temperature is −10 °C, the condensing temperature is 35 °C, and the isentropic efficiency is 70%. It is assumed that there is no subcooling and superheating.

This refrigerant is characterised by a higher latent heat of vapourisation than that of R134a; therefore, it has a higher cooling effect (Figure 10 and Table 4). However, its vapour mass density is significantly lower. Overall, R152a has a slightly lower volumetric cooling capacity; therefore, it will require a slightly larger compressor to satisfy a similar cooling demand. The difference between the mass densities of the two indicates a significant reduction in the mass flow of R152a compared to that of R134a. Furthermore, this reduced mass flow leads to pressure drop reduction in the evaporator, as confirmed by a limited number of experimental studies (Bryson et al., 2011).

Table 4. Basic refrigeration cycle properties at Tevap = −10 ˚C, Tcond = 35 °C, no SH and SC, compressor isentropic efficiency is 0.7

Refrigerant	R134a	R1234yf	R152a	R290
P_{evap}, bar	2.01	2.22	1.82	3.45
P_{cond}, bar	8.87	8.95	7.94	12.18
PR, -	4.42	4,04	4.37	3.53
$\rho_{sat,v}$, kg m^3	10.0	12.6	5.9	7.6
q, kJ kg^{-1}	143.7	109.1	238.1	270.8
q_v, kJ m^{-3}	1442.5	1369.9	1393.5	2066.9
COP	3.25	3.07	3.39	3.21
COP, % to R134a	-	−5.5%	4.3%	−1.4%

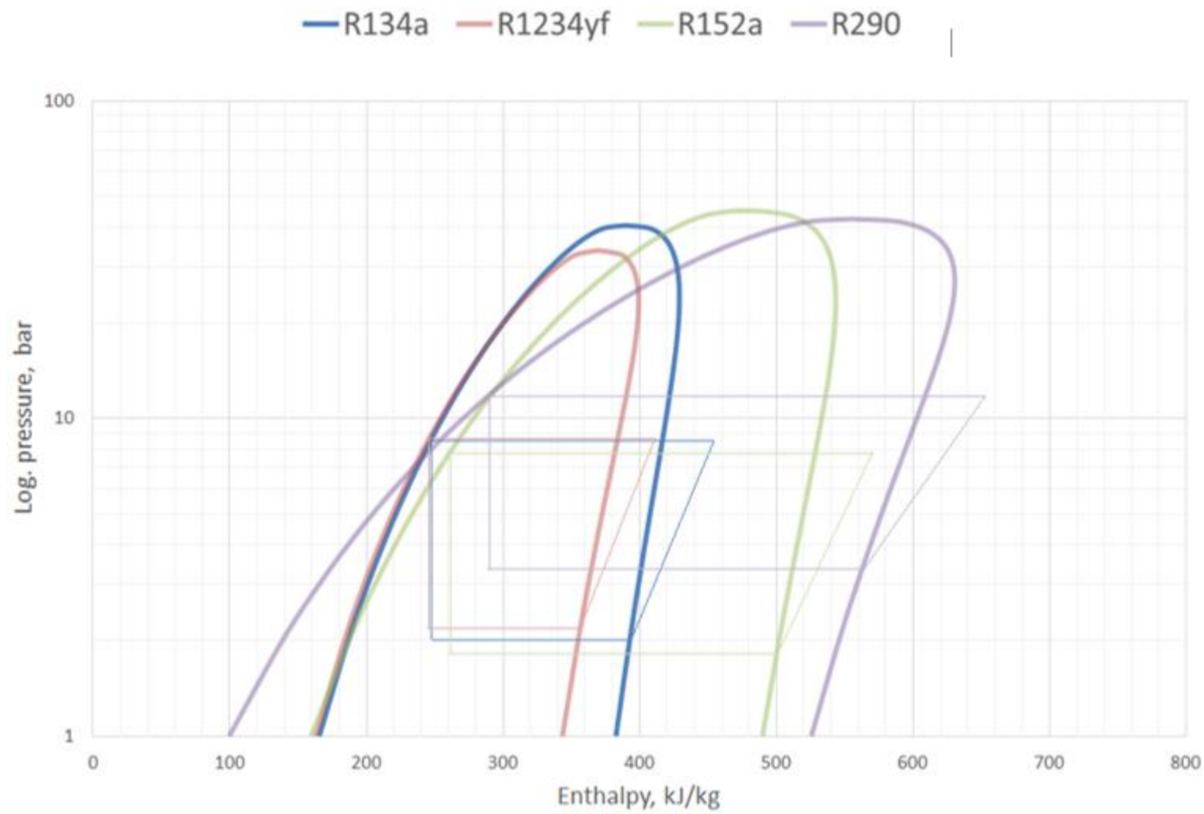

Figure 10. Basic refrigeration cycle examples at Tevap = −10 ˚C, Tcond = 35 °C, no SH and SC, compressor isentropic efficiency is 0.7

In the presented cycle, the COP of R152a is the highest and is theoretically 4.3% higher for any given cycle. Furthermore, this increase in COP, compared with that of R134a, is supported by a few experimental studies. The results of a recent experimental study of the vapour refrigeration system of R134a that has been retrofitted as an R152a system, show that COP improvement is as high as 13.2% (11.7% without an internal heat exchanger) despite the reduction in the cooling capacity of approximately 10%. Other observations include the decrement in the refrigerant mass flow, which is 41.5% lower in R152a than that in R134a. Moreover, the slight increase in the compressor discharge temperature (approximately by 5 K) results in higher compressor thermal losses. The study leads to the conclusion that R152a can be successfully used as a drop-in replacement for R134a (Cabello et al., 2015) given that the difference in the refrigerant properties is taken into account. Another experimental study of R152a as a replacement for R134a in a domestic refrigerator confirms the energy consumption benefits of R152a as shown by a COP value, which is 4.7% higher than that of R134a on average (Bolaji, 2010). It should be noted that the number of experimental studies on R152a is limited.

From a thermodynamic perspective, R152a is a suitable replacement for R134a and provides greater energy efficiency. Nevertheless, its major drawback is its flammability.

It is classified as A2 in the flammability class and is therefore considered as more flammable than, for instance, R1234yf. Its superior thermodynamic properties and low GWP are occasionally exploited in refrigerant mixtures, such as in R444B (developed to replace R22), which is the mixture of R152a, R32, and R1234ze(E).

Mixtures composed of HFOs and HFCs have also been proposed to replace R134a in stationary refrigeration systems as a trade-off solution. Refrigerant R450A and R513A are non-flammable substances that are considered to replace R134a with minor system modifications. Both are blends of R134a with an HFO; R1234ze(E) in the case of R450A, and R1234yf in that of R513A. Because of the difference between their components and compositions, the thermodynamic properties of both fluids are relatively different. Table 5 summarises the main properties of both mixtures and R134a.

Table 5. Main characteristics of R134a and its alternatives (Lemmon et al., 2013)

	R134a	**R513A**	**R450A**
Composition	pure R134a	R134a/1234yf 44/56 wt%	R134a/R1234ze(E) 42/58 wt%
ANSI/ASHRAE Standard safety classification	A1	A1	A1
GWP	1430	631	605
Average molar mass, kg mol^{-1}	102.03	108.43	108.69
Critical temperature, °C	101.06	94.9	104.47
Critical pressure, MPa	4.06	3.65	3.82
Boiling point at 0.1 MPa, °C	−26.36	−29.82	−23.35
Glide at 0.1 MPa, °C	0.00	0.10	0.61
Latent heat of vapourisation [a], kJ kg^{-1}	198.6	175.9	188.8
Liquid density [a], kg m^{-3}	1294.8	1221.9	1259.6
Vapour density [a], kg m^{-3}	14.43	17.23	13.18
Liquid c_p [a], kJ kg^{-1} K^{-1}	1.34	1.31	1.33
Vapour c_p [a], kJ kg^{-1} K^{-1}	0.90	0.92	0.89
Liquid thermal conductivity [a], mW m^{-1} K^{-1}	92.01	79.21	86.23
Vapour thermal conductivity [a], mW m^{-1} K^{-1}	11.51	11.74	11.70
Liquid viscosity [a], μPa s	266.53	227.10	264.23
Vapour viscosity [a], μPa s	10.73	10.51	11.16

[a] At saturation, 0 °C

In a small unit, R513A (GWP of 631) (Mota-Babiloni et al., 2016a) presented better energy values than R134a at low evaporating and condensing temperatures. In a larger unit, R450A (GWP of 605) (Mota-Babiloni et al., 2015b) and R134a have comparable

COPs; however, the former has a lower cooling capacity than the latter. In both studies, the similar or higher COP and lower GWP can lead to a reduction in CO_2-eq. emissions with minor system modifications.

Both R450A and R513A have been compared to R134a in terms of their energy performance in a small-capacity refrigeration unit. Tests have been performed at three different condensing temperatures (40, 50, and 60 °C) and at various evaporating temperatures. The measured superheating temperature average was 11.4 °C for R513A and 11.5 °C for other alternatives; the measured subcooling temperature average was 10.0 °C for R450A, and 9.8 °C for R513A and R134a.

In this drop-in replacement, the volumetric and cooling capacities of R513A are on average 1.5 and 2.5% higher than those of R134a, respectively; 7.0 and 14.3% lower than those of R450A, respectively. As a result, the average COP of R513A is 1.8% greater than that of R134a; however, the average value of R450A is reduced by 5.3% compared with that of HFC, as shown in Figure 11. For the rest of the experimental data and its analysis, the reader is referred to the scientific publications of the project.

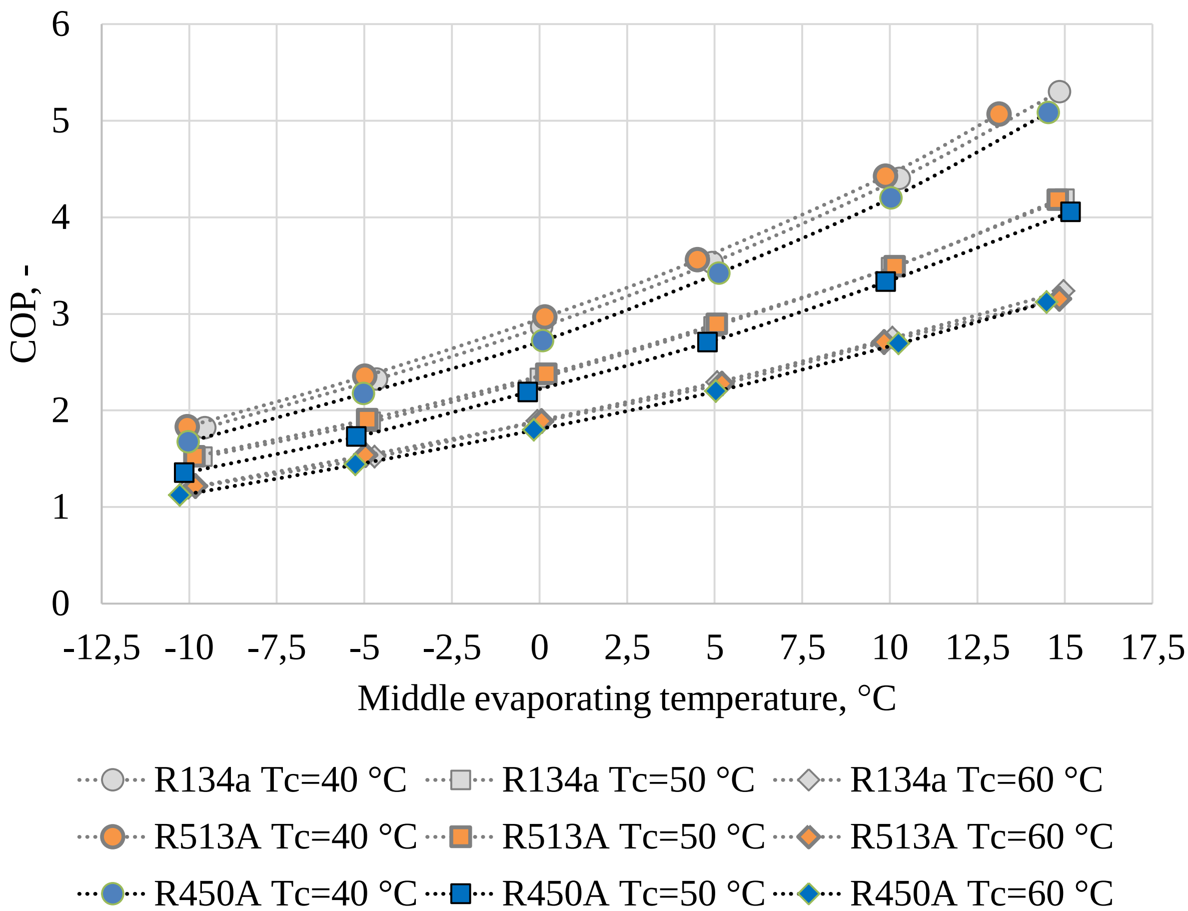

Figure 11. COP of R450A and R513A compared with R134a under the testing conditions

Overall, R134a has several alternatives with reduced GWP values to choose from. However, the flammability of some low GWP refrigerants limits their potential use. Meanwhile, non-flammable refrigerants with GWP within the range 393–687 also exist; however, the GWP values of these refrigerants remain extremely high to be considered as long-term solutions.

R404A

Refrigerant R404A is a widely used refrigerant in commercial refrigeration devices (Figure 9). Nevertheless, by 2020, it will be prohibited to install stationary refrigeration equipment that contains refrigerants with GWP≥2500 (with the exception of equipment designed to cool products to temperatures below −50 °C). In addition, it will be prohibited to use these refrigerants to service or maintain refrigeration equipment with a charge size of 40 t of CO_2-eq. or more (also called ‘service ban’). Only recycled refrigerants will be allowed for this purpose until 2030. Thus, the usage of R404A in such systems will be significantly affected. Its alternatives can be selected from among the non-flammable refrigerant mixtures with GWP under 2500. Two synthetic options are identified: the HFC and HFC/HFO mixtures.

Another potential low-GWP alternative to R404A is the complete replacement of the system by using CO_2 as the refrigerant in the new optimised system; small stand along propane solutions are also possible. Regarding synthetic alternatives to R404A, the available pure HFOs have significant thermodynamic differences from R404A (GWP of 3922) and cannot be considered as retrofitting alternatives to this refrigerant. The substitution of R404A refrigerants with pure HFOs is problematic because of the resulting large volumetric capacity drop and the flammability of such fluids (Pigani et al., 2016).

A number of non-flammable refrigerant mixtures have been developed by major manufacturers to replace R404A. Table 6 summarises refrigerants that are listed in ASHRAE 34 Standard and considered as replacements for R404A in existing systems.

As can be observed in the list, all manufacturers have replaced the high GWP components of R143a in their mixtures to reduce the GWP of alternatives. The presence of R32 in the composition not only contributes to good energy properties of the mixture, but also leads to the increase in compressor discharge temperature. Moreover, the presence of flammable R32 requires greater amounts of non-flammable components, such as R125 and R134a.

Refrigerants R449A and R448A have been known for a considerable time. For instance, R449A has been evaluated as a drop-in replacement to R404A in a number of Swedish supermarkets, and experimental results for R448A are available as well. The results of these studies can be consulted in other publications (Rogstam et al., 2016) (Makhnatch et al., 2017e) (Mota-Babiloni et al., 2015c). Generally, refrigerants cannot be considered as mere ‘drop-in’ replacements because the attention should focus on the increase in compressor discharge temperature, slight decrease in cooling capacity, consequences of significantly lower refrigerant mass flow, and high temperature glide.

Table 6. Composition of R404A and its non-flammable alternatives

Refrigerant	GWP	R143a	R32	R125	R1234yf	R134a	R1234ze(E)
		Normal boiling point, °C					
		−47.2	−51.7	−48.1	−29.5	−26.1	−19.0
		Mass in composition, %					
R404A	3922	52	-	44	-	4	-
R407A	2107		20	40	-	40	-
R407F	1825		30	30	-	40	-
R407H	1495		32.5	15.0	-	52.5	-
R448A	1387		26.0	26.0	20.0	21.0	7.0
R449A	1397		24.3	24.7	25.7	25.3	-
R449B	1412		25.2	24.3	23.2	27.3	-
R449C	1251		20.0	20.0	31.0	29.0	
R460B	1352		28.0	25.0	-	20.0	27.0
R452A	2140		11.0	59.0	30.0	-	-
R460A	2103		12.0	52.0	-	14.0	22.0

Refrigerant R449B is considerably recent in the list and its behaviour has not been studied experimentally. However, given its composition and that allowed by the standard composition tolerance levels of ASHRAE 34, R449B is practically identical to R449A. Thus, considerably similar behaviours are expected between these refrigerants.

Another alternative refrigerant is R449C, which was developed by Chemours along with the widely available R449A. Compared with R449A, the concentration of high GWP components, R125 and R32, in R449C is low; instead high concentrations of R1234yf and R134a are present. As a result, R449C has the lowest GWP among all the refrigerants listed in Table 1. Because of the considerably significant alterations in composition of R449C, its behaviour is anticipated to be different from those of R448A and R449A. However, considering the already substantial marketing efforts that Chemours has expended to promote R449A, it is improbable that the commercialisation of R449C is forthcoming.

Refrigerant R460B is a refrigerant promoted by Mexichem. It is observed that its composition resembles that of R448A. The composition levels of components R32, R125, and R134a are extremely close between both alternatives (especially when composition tolerance levels are considered). The amount of R1234ze(E) in R460B composition is similar to the sum of R1234yf and R1234ze(E) contained in R448A. To a certain extent, the group of refrigerants R448A, R449A, R449B, R449C, and R460B represents similar refrigerants with comparable characteristics. With the exception of R449C, the combined concentration of components R134a, R1234yf, and R1234ze(E) in the rest of the mixtures is considerably similar and is within 47–51% of the entire refrigerant composition. Moreover, this is similar to another refrigerant, R407H, which contains 52.5% R134a.

Another new refrigerant in the list, developed by Daikin, is R407H. It is promoted as an alternative to R404A, with an emphasis on the absence of expensive HFOs (R1234yf or R1234ze(E)) in its composition. Given the series of recent price increases in conventional HFCs (European Commision, 2018), this argument gradually loses its significance. Moreover, other previously mentioned alternatives, such as R407H, cannot be considered as a ‘drop-in’ for every system, primarily because of the implications of high discharge temperature (DAIKIN Chemical Europe GmbH, 2018). Further information about this refrigerant can be found in a recent experimental study (Llopis et al., 2017).

Refrigerants R407A and R407F are composed of the same fluids as R407H, but with different compositions. Although they have been proposed for the same application as R404A, they have not become popular because of the lack of incentives. Considering their high GWP values and drawbacks (in the form of temperature glide and high discharge temperature) similar with those of other alternatives, their use is not advantageous.

Two other refrigerants on the list are R452A and R460A. Compared with the other previously mentioned alternatives, they have lower amounts of R32 in their composition. Whereas R460A has been recently introduced, R452A has been known for some time.

Refrigerant R452A was proposed to replace R404A in transport refrigeration systems, where the compressor discharge temperature is limited because of its potentially high condensing temperatures that can occur in such application. However, compared with other alternatives, such as R448A and R449A, R452A, with its lower cooling capacity, it is approximately 5% less energy-efficient.

As has been observed in practice, it should be noted that the high theoretical COP values of R404A alternatives are reduced by the lower heat transfer performance of these fluids. Thus, when the total system performance of R452A system is analysed, refrigerant R452A is expected to have lower COP than baseline R404A, whereas R449A is shown to have comparable energy efficiency, when heat transfer performance is considered (Rogstam et al., 2016).

All of the non-flammable R404A alternatives discussed above are refrigerants with GWP in the range 1250–2140; R404A with a GWP below that range is a mixture of flammable HFC/HFO. The new mixtures, specifically R454C, R455A, R457A, and R459B, have been recently identified as low GWP candidates to replace R404A (Bitzer, 2016).

Different from A1 (non-flammable) HFC and A1 HFC/HFO mixture alternatives to R404A, A2L HFC/HFO mixtures have not been widely studied until now. Consequently, available reports are few, and published results are limited.

As reported by Makhnatch et al. (2018f) in a recent conference publication, two low-GWP mixture refrigerants, namely R454C and R455A, have been analysed as R404A replacements. The primary information on these fluids, summarised in Table 7, is used to compare some of their characteristics with those of other refrigerants and to predict their possible behaviour in refrigeration systems.

Table 7. Properties of A2L HFO/HFC mixtures and R404A

Refrigerant	R404A	R454C	R455A
Composition	R125: 44% R143a: 52% R134a: 4%	R32: 21.5% R1234yf: 78.5%	R744: 3.0% R32: 21.5% R1234yf: 75.5%
Developer	Various	Chemours	Honeywell
Safety classification (ASHRAE)	A1	A2L	A2L
Critical temperature, °C	72.04	88.47	87.53
Critical pressure, MPa	3728.8	4553.4	4821.8
Normal boiling point, °C	−46.22	−45.56	−52.02
Temperature glide (at 100 kPa), K	0.75	7.80	12.85
Molecular weight, g mol^{-1}	97.6	87.5	90.8
Latent heat of vapourisation (at 100 kPa), kJ kg^{-1}	201.1	227.5	239.6
Liquid/Vapour density [a], kg m^{-3}	1150.0/30.32	1136.3/20.43	1128.8/20.98
Liquid/Vapour c_p [a], kJ kg^{-1} K^{-1}	1.388/1.001	1.410/0.975	1.433/0.975
Liquid/Vapour k [a], mW m^{-1} K^{-1}	73.11/12.86	86.16/11.90	87.99/12.05
Liquid/Vapour viscosity [a], µPa s	179.3/11.01	174.4/10.92	170.60/11.07
GWP	3922	148	148

[a] at 0 °C

Both R404A replacements, i.e., R454C and R455A, show considerably similar compositions. Being the base compositions of HFO R1234yf (A2L and a GWP of 4), refrigerants R454C and R455A, in the proportions of 75.5 and 78.5%, respectively, are used to maintain the GWP below 150. New mixtures use 21.5% of HFC R32 (A2L and GWP of 675). In the case of R455A, the mixture is completed using a small percentage of natural refrigerant R744 (A1 and GWP of 1). For a complete review of analysed alternatives, readers are referred to the publication (Makhnatch et al., 2018f).

R410A

Over 60 million chemical structures have been previously analysed in search of new low GWP refrigerants (McLinden et al., 2017). By applying a set of filters, substances that contain the required molecule to be considered as refrigerants are identified and added to the list of potential refrigerants (or components in refrigerant mixtures). For a typical refrigeration and air conditioning (RAC) application, this list was gradually narrowed down to 28 substances (Domanski et al., 2017).

Out of the 28 low GWP substances identified by Domanski et al. (2017), CO_2 is the only non-flammable and non-toxic fluid that has been identified. As a refrigerant, CO_2 has been popularly used in heat pumps designed for domestic water heating, which has been developed by a number of Japanese manufacturers. However, because of its low critical temperature of 31 °C, it can only be used in transcritical cycles operating at considerably higher pressures compared with conventional subcritical cycles. Although it is suitable for niche application, it cannot be considered as a direct replacement for R410A.

The substances ethane (R170), fluoromethane (R41), and 1-1-difluoroethene (R1132a) are also fluids with relatively low critical temperatures (32, 44, and 51 °C, respectively); therefore they cannot be operated in the traditional subcritical cycle, provided that their condensing temperatures are above the aforementioned critical temperature levels. Moreover, they are flammable and potentially toxic, such as the case of R1132a.

Another non-flammable identified substance is 1,2,3,3,3-pentafluoropropene-R1225ye(Z). The substance has been primarily developed as a foam-blowing agent; however, after it was observed that its toxicity resulted in several adverse effects in test animals (Schuster, 2009), its use has been discontinued. Because of the lack of non-flammable low-GWP refrigerants, the interest in developing refrigerant mixtures that use R1234ye(Z) was generated. Compared with R410A, the toxicity of R1225ye(Z), coupled with its very low cooling capacity and lower COP, makes it improbable to be commercialised as an alternative to R410A in the foreseeable future.

The rest of the discovered refrigerants are flammable. The complete list of analysed fluids includes a small number of novel molecules, but a majority are well known, including ammonia (R-717), propane (R-290), and a number of HFOs. The HFOs constitute the largest group in the list with nine fluids.

The identified fluid performances have been simulated in a basic vapour compression cycle (e.g., a basic cycle composed of an evaporator, a condenser, compressor, and an expansion valve) (Domanski et al., 2017). The simulation uses a vapour compression cycle model called CYCLE_D-HX, which considers thermodynamic and transport characteristics of the refrigerant (Brown et al., 2017). Moreover, the model considers differences among the transport properties of different refrigerants. In such a case, there is a trade-off between pressure drop and heat transfer coefficient at different mass flux values that can be maintained at the heat exchanger. It therefore provides a more realistic representation of a heat pump system that is optimised for a particular refrigerant.

The comparison between simulated results and R410A baseline is presented in Figure 12. Several high GWP refrigerants are also modelled for reference purposes. The reference conditions correspond to an evaporating temperature of −10 °C and a condensation temperature of 30 °C. The isentropic efficiency of the compressor is assumed to be a function of the pressure ratio at an average of approximately 70% (Domanski et al., 2017) (Brown et al., 2017). Several other modelling parameters are not described; however, this study can still be used for further comparisons of refrigerants.

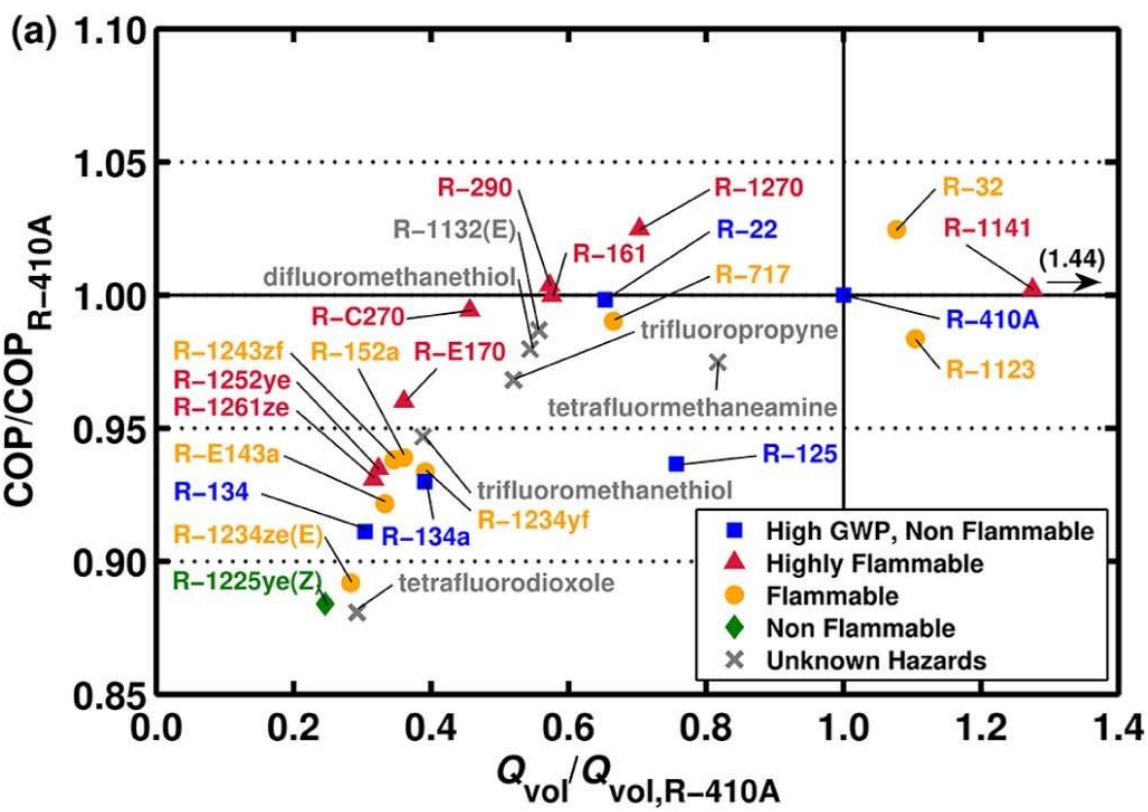

Figure 12. Modelled COP and volumetric capacity of a heat pump operating with R410A and its alternatives (Domanski et al., 2017)

Six novel molecules have been identified in the screening: tetrafluorodioxole, trifluoromethanethiol, trifluoropropyne, difluoromethanethiol, (E)-1,2-difluoroethene (R-1132(E)), and tetrafluoromethaneamine. Their COP and volumetric capacity are not superior to that of well-known refrigerants (e.g., R32, ammonia, and propane/propene); they are flammable and can present unknown hazards.

Under simulated conditions, only a few refrigerants are superior to R410A in terms of COP and/or cooling capacity. In terms of COP and volumetric capacity, propane (R290) is similar to fluoroethane (R161), but lower than propene (R1270); all of them are highly flammable. Ammonia provides a slightly lower COP at a higher volumetric cooling capacity than propane. However, ammonia is toxic in moderate concentrations and not compatible with all materials (for example, copper). In terms of COP, R1141 is comparable to R410A, but provides better volumetric cooling capacity (which often corresponds to higher vapour pressure at the same temperature). The critical temperature of R1141 is considerably low (54 °C); thus, its use in heat pumps is limited.

Only one refrigerant, R32, is superior to R410A in terms of COP and cooling capacity. With a GWP of 675, R32 is being considered as an alternative to R410A (GWP of 2088) for air conditioning appliances in Europe and the USA. The current state of refrigerant R32 has been presented in a scientific publication prepared with this project as well (Adrián Mota-Babiloni et al., 2017c).

The thermodynamic properties of R32 are well-defined, and current studies have focused on defining the most accurate mixture properties achievable. Furthermore, it is less flammable than hydrocarbons, and the amount of refrigerant allowed is sufficient for refrigerating and air conditioning systems (RACs). Its toxicity is below other synthetic fluids, and precautions taken with such refrigerants can also be applied to R32. The new mixtures of HFC/HFC have a greater content of R32 than conventional HFC mixtures (e.g., R410A). They are classified as A2L according to ASHRAE 34, but have allowable compressor discharge temperatures.

The heat transfer coefficient (HTC) of R32 inside condensation tubes is higher than those of R22 and R410A. For the pressure drop, the highest level was observed in R32 because of its thermophysical properties. In evaporation studies, the HTC of R32 is significantly higher than those observed in R32 mixtures because of temperature glide effects. Pure and blended R32 HTCs have also been compared with R1234yf, which are notably larger than the HFO.

In terms of the cooling and heating modes of RACs, R32 presents a similar or slightly higher performance than R410A. However, all studies reviewed in Mota-Babiloni et al. (2017c) recommend modifications in the system to reduce the increased compressor discharge temperatures, particularly under extreme operating conditions.

A number of HFC/HFO blends (e.g., R447B, R452B, R454B, and R459A) have recently been introduced as alternatives to R410A. These mixtures are combustible and cannot be considered as drop-in replacements for R410A in heat pump systems. Such mixtures can reduce the compressor discharge temperature, but in some cases, their performances are slightly below that of pure R32 and therefore cannot be beneficial in terms of the final CO_2-eq. emissions. Additionally, a non-flammable refrigerant mixture with a GWP below 750 has been announced by a major refrigerant manufacturer (Cooling post, 2018). It received a preliminary designation of R466A and is seen as the only non-flammable alternative to R410A. Because of the significant difference between the composition of R466A and R410A, their properties are expected to differ. However, any detailed study of this refrigerant has not yet been published; hence, no conclusions can be made regarding its applicability as an R410A alternative.

As a result, there remains no direct replacement for R410A from among the low GWP substances. Most of the available alternatives, including a few HFC/HFO mixtures, are flammable. The only non-flammable and non-toxic alternative is CO_2; however, its low critical temperature limits the design of the CO_2 heat pump systems. Propane is a flammable alternative that is being adopted by a number of manufacturers, but it has a flammability class of A3 and cannot be used as a direct R410A replacement.

Other relevant considerations

In the evaluation of low GWP refrigerants as alternatives to R134a, R404A, and R410A, a number of problems have been identified as common among several replacement refrigerants. For instance, several low GWP alternatives are flammable. Therefore, a clear understanding of flammability and its implications are vital in the implementation of low GWP refrigerants as replacements. During the project period, a research on flammability has been conducted, and the Swedish refrigeration industry has been updated with relevant information by means of several publications. One such publication discusses a recent investigation on the safe use of flammable refrigerants (Makhnatch et al., 2018b), and another discusses different types of standards and roles relevant to the refrigeration industry (Makhnatch et al., 2017c).

The risk involved in implementing low GWP refrigerants is not limited to flammability. Potential negative impacts of decomposition products of synthetic refrigerants that can form trifluoroacetic acid (TFA) also exist. We have discussed the potential danger of TFA in a publication in Kyla+ Värmepumpar (Makhnatch et al., 2015).

The GHG emissions from a refrigeration system not only occur as a result of a refrigerant leakage directly from the system (and proportional to the mass of the leaked refrigerant and its GWP), but also as a result of the energy used by an operating refrigeration system. Refrigeration systems with low contributions to global warming should not only utilise low GWP refrigerants, but also have excellent energy efficiency in order to indirectly minimise GHGs emissions that result from the use of energy.

The total equivalent warming impact (TEWI) and life cycle climate performance (LCCP) are the methodologies used to evaluate the total global warming impact of a refrigeration system during its operation (TEWI) or entire lifetime (LCCP). The calculation of global warming impact using these methodologies relies on the use of a number of uncertain input parameters. An evaluation of the different methods of dealing with the uncertainty of input data to TEWI and the LCCP calculations is performed in a student thesis project (Boström and Ljungberg, 2018). The work presents different uncertainties that are associated with the global warming impact assessment of refrigeration systems using TEWI and the LCCP methodologies.

For the complete list of the project's publications, as well as the scope of the topics covered, the readers are referred to such list at the end of this report.

Goal completion

The aim of this project has been completely fulfilled in terms of providing data, support, and information relating to alternative refrigerants with low GWP at the phasing out of HFC refrigerants for existing and new heating/cooling systems. The foregoing has been provided at different levels of communication and includes 28 publications in national Swedish journals, 7 peer-reviewed scientific journal publications, 11 conference publications, 1 report, and several presentations to relevant audiences. The content of these publications and presentations reflects the findings of the project.

Suggestions for future work

Although the current project has identified several low GWP refrigerants that are proposed as alternatives to R134a, R404A, and R410A (further referred as ‘baseline refrigerants’) in existing and new systems, only a few refrigerants have been examined in experimental studies. Given the limited number of experimental studies published, future research can extend the number of refrigerants investigated through experimentation.

The project found that several replacements for baseline refrigerants are refrigerant mixtures composed of a few substances mixed in specific proportions. Such mixtures often exhibit temperature glide. The implications of a temperature glide on the performance of refrigeration systems have been analysed in Makhnatch et al. (2018d). This research suggested that investigations should be extended to include more refrigerant mixtures and various systems. The difference in transport properties between a baseline refrigerant and its alternative indicates that the energy performance of a retrofitted system can be lower than one that is theoretically predicted because of the impact of higher temperature differences among heat exchangers of a refrigeration system. In future research, the heat transfer characteristics of new fluids should be investigated in more detail.

The results of a literature study suggest that the long-term environmental impact of new synthetic refrigerants has not been well-scrutinised to date. For instance, given the current rate of introduction and adoption of HFOs, the environmental impact of trifluoroacetic acid formation should be evaluated in future research. The holistic global warming impact has to be assessed as well through a wider implementation of TEWI or the LCCP analysis.

Although a number of refrigerants have been evaluated in this project, there is a continuing necessity for refrigerant analysis because of the continuous development of new refrigerants (10 new refrigerants and refrigerant mixtures have been introduced in 2017).

Given the ongoing transition to low GWP refrigerants, there is a continuous demand for future research in this area in order to facilitate such a transition and avoid negative environmental and safety impacts.

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