Next generation of refrigerants for residential heat pump systems

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Abstract

The increasing concentration of greenhouse gases (GHG) in the atmosphere arising from human activities is unquestionably taking its toll on the environment with severe consequences that cannot be ignored. It is therefore necessary to take measures to avoid or reduce GHG production and release. In this scope, the 2015 F-gas regulation aims at limiting the contribution of the refrigeration industry to the global warming effect by phasing-down refrigerants with high global warming potential (GWP).

This work contributes to this effort by analysing a number of refrigerants, i.e. R32, R152a, R290, R1270, R1234yf and R1234ze(E) that could substitute the current R410A in a 10 kW domestic heat pump typically used in a single family house in Sweden.

An EES model was thus created and the relevant outputs chosen to compare the refrigerants' options are the volumetric heating capacity, the coefficient of performance (COP), Seasonal coefficient of performance (SCOP) – obtained by the method found in the Standard BS EN 14825:2012, the discharge temperature, and the Total Equivalent Warming Impact (TEWI) factor.

The reductions observed for TEWI are remarkable. The overall lowest TEWI is obtained by refrigerants having the lowest GWPs, i.e. the HCs, of 54.2% and 54.6% for R1270 and R290 respectively. They are followed by R1234yf and R1234ze(E), with reductions of 52.5% and 53.7% respectively. R152a entails a reduction of 53.6%, due to its higher SCOP. R32 shows a reduction of 40.8%. Other parameters such as thermodynamic characteristics and safety issues are also considered during the analysis.

Keywords—CO_2, GHG, Heat pump, R410A, refrigerant, TEWI

Resumo

O aumento da concentração de gases de efeito de estufa (GHG) na atmosfera devido às atividades humanas é inquestionável, com consequências ambientais que não podem ser ignoradas (Andres, 2012). É por isso importante implementar medidas para reduzir e evitar a produção e libertação de GHG. Neste sentido, a regulamentação 2015 *F-gas* tem por objetivo limitar a contribuição da industria da refrigeração para o aquecimento global, retirando dos equipamentos os frigorigéneos com maior potencial de aquecimento global (GWP).

Esta tese pretendeu contribuir para este esforço, analisando-se vários fluidos - R32, R152a, R290, R1270, R1234yf and R1234ze(E) - que possam substituir o R410A numa bomba de calor para uso domestico de 10 kW, produzida na Suécia. Foi desenvolvido um modelo no programa EES de acordo com a norma BS EN 14825:2012 e os parâmetros escolhidos para comparar os fluidos foram a potência volumétrica, o COP nominal e sazonal (SCOP), a temperatura de descarga do compressor e, o mais importante, o impacto total equivalente para o aquecimento global (TEWI).

As reduções do TEWI foram assinaláveis, sendo as TEWI mais baixas observadas para os frigorigéneos com o menor GWP, os HCs, com -54,2% e -54,6% para o R1270 e o R290, respetivamente. Também os frigorigéneos R1234yf e R1234ze(E) mostram uma redução assinalável, respetivamente de -52,5% e -53,7%. O R152a apresenta uma redução de -53,6% devido ao seu elevado SCOP. O R32 apresenta uma redução de 40,8%. Na análise foram ainda considerados outros fatores importantes tais como as suas propriedades termodinâmicas e questões de segurança.

Palavras-chave—CO_2, GHG, bomba de calor, R410A, refrigerante, TEWI

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Nomenclature

COP_1	Coefficient of performance (heating mode)	[-]
COP_2	Coefficient of performance (cooling mode)	[-]
CFC	Chlorofluorocarbon	
c_p	Specific heat capacity	[kJ/kg-K]
E_{annual}	Annual energy consumption	[kWh/year]
elbu	Electric back-up	[kW]
F-gas	Fluorinated gas	
F-gas regulation	Regulation of the European Parliament and of the Council on fluorinated gases and repealing Regulation (EC) No 842/2006	
FC	Fluorocarbon	
GWP	Global warming potential	
h_1	Enthalpy at inlet of evaporator	[J/kg]
h_2	Enthalpy at outlet of evaporator/inlet compressor	[J/kg]
h_3	Enthalpy at outlet compressor/inlet condenser	[J/kg]
$h_{3,is}$	Enthalpy at outlet compressor (isenthalpic process)	[J/kg]
h_4	Enthalpy at outlet condenser/inlet expansion valve	[J/kg]
HC	Hydrocarbon	
HCFC	Hydrochlorofluorocarbon	
HFC	Hydrofluorocarbon	
HFO	Hydrofluoroolefin	
HP	Heat pump	
k	Thermal conductivity	[W/m-°C]
L_{annual}	Annual leakage rate	[kg_{ref}/year]
LMTD	Logarithmic mean temperature difference	[°C]
$\dot{m}/\dot{m}_{ref}$	Mass flow rate/mass flow rate of refrigerant	[kg/s]
m	Refrigerant charge	[kg]
N	Lifetime of system	[years]
ODP	Ozone depletion potential	
P	Pressure	[kPa]
P_{ratio}	Pressure ratio	[-]
q_1	Specific heating capacity	[J/kg]
$\dot{Q}_1$	Heating capacity	[kW]
SCOP	Season coefficient of performance	[-]
T	Temperature	[°C]
TEWI	Total equivalent warming impact	[kg CO_2]
$\dot{V}_{swept}$	Swept volume	[m^3/s]
VHC	Volumetric heating capacity	[kJ/m^3]
w	Compressor specific work	[J/kg]
w_{id}	Ideal required specific work	[J/kg]
$\dot{W}$	Compressor power	[kW]

Greek characters

$\alpha_{recovery}$	Recovery efficiency of refrigerant	[-]
β	CO_2 emission factor	[kg_{CO2}/kWh]
η_k	Efficiency of compressor	[-]
η_s	Volumetric efficiency	[-]
μ	Dynamic viscosity	[Pa/s]
ρ	Density	[kg/m^3]

Subscripts

1	Inlet evaporator/outlet expansion valve
2	Outlet evaporator/inlet compressor
3	Outlet compressor/inlet condenser
4	Outlet condenser/inlet expansion valve
j	Temperature bin

1. Introduction

Carbon dioxide (CO_2) emissions in the atmosphere arising from human doings, such as power production from combustion of fossil fuels, industrial activities and – in the matter in question – refrigeration, have become more of a concern as a result of their growing scale in the past decades. The increasing concentration of greenhouse gases (GHG) is taking its toll on the environment with severe consequences that cannot be ignored (Andres, 2012). It is therefore necessary to take measures to avoid or reduce GHG production and release.

In this instance, heat pumps (HP) come forward as an increasingly important player. In fact, they generally entail a lower electricity consumption when compared to equivalent electric radiator systems thus emitting less GHG; the magnitude of their benefit highly depends on the local energy mix used for electricity production (Forsén, 2005). Moreover, their impact is principally related to the refrigerant used, as it affects the CO_2 emissions of the system both directly and indirectly. As the number of installed heat pump systems increases in a high number of countries worldwide, the importance of operating with a low impacting refrigerant becomes crucial.

In Europe in 2013, the total HP capacity installed reached 24 GW, obtaining an estimated saving in CO_2 - equivalent of 2.12 Mt. The savings per country can be seen in Figure 1.1 (ehpa, 2014). On aggregated terms, since 1994 more than 6.7 million HPs were installed, which equals almost 224 GW of thermal capacity. If retrofitting of old radiator systems is considered, such is the case oftentimes in Sweden, this represents an impressive total CO_2 avoided emission (ehpa, 2014).

Sweden is one of the countries with the highest amount of HPs installed. They firstly became popular in the 1970s and the market for residential applications has been fluctuating since, depending on the prices of other sources of energy mainly, but is experiencing a steady growth since the 2000s. In 2012 already, a total of 958 000units were installed (Statens energimyndighet, 2012),

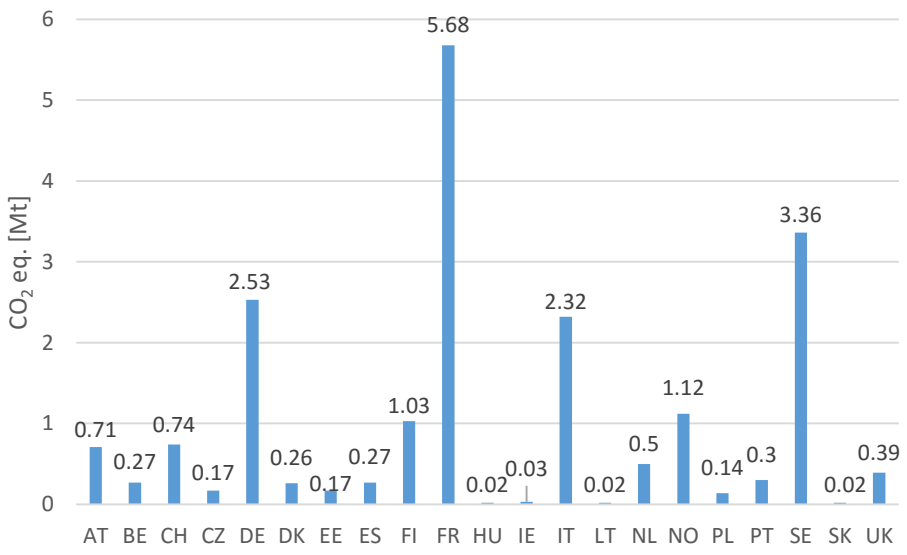

Figure 1.1. GHG emissions saved by 2013 heat pump stock, by country (in Mt) (ehpa, 2014)

Nevertheless, fluorinated gases – which represent the biggest share of refrigerants currently in use – still represent 2% of the GHG emissions in Europe (European Commission , 2014). New limitations have thus been imposed by the F-Gas regulation (European Union, 2014), in the form of a phase-down to be performed by 2030 and a number of other important measures in order to protect the environment by reducing emissions of fluorinated GHGs. The schedule of the reductions can be seen in Figure 1.2 and the summary of the envisaged bans is given in Table 1.1.

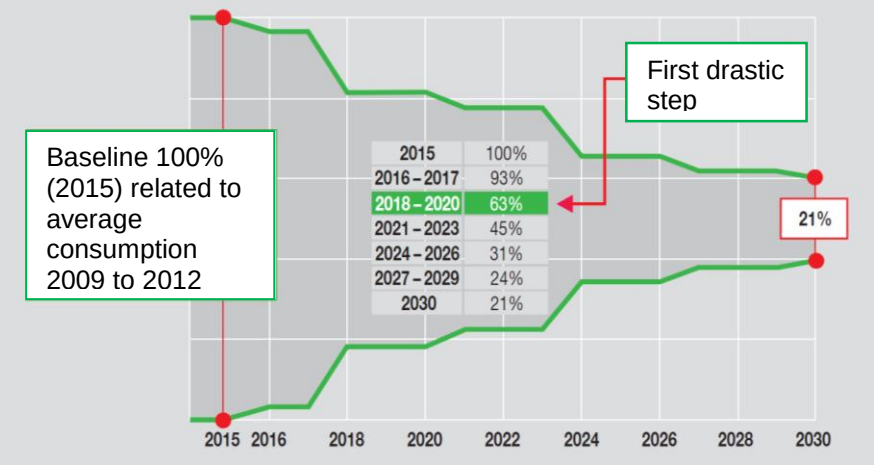

Figure 1.2. Phase-down of fluorinated gases' progress in time (Bitzer, 2014)

It is then evident that effort has to be put in finding an alternative to the current working fluids, that can maintain a good performance and at the same time entail lower CO_2 emissions, considering both the direct and the indirect effects through a Total Equivalent Warming Impact (TEWI) analysis.

The scope of this thesis is thus to identify one or more valid replacement options to the refrigerant currently in use (R410A) in a commercially available heat pump with domestic heating purposes. In doing that other criteria have to be met such as stability in the system, thermodynamic properties, flammability and toxicity, all of which will be developed further on.

Table 1.1. New products and equipment: F-gas ban summary table prepared by Gluckman consulting (2014) based on F-gas regulation (European Union, 2014)

Market sector	Product description	Scope of banned F-gases	Start date
Refrigeration	Non-confined direct evaporation systems	All HFCs and PFCs	2007
	Domestic refrigerators and freezers	HFCs with GWP > 150	2015
	Refrigerators and freezers for commercial use (hermetically sealed)	HFCs with GWP > 2500	2020
		HFCs with GWP > 150	2022
	All stationary refrigeration equipment	HFCs with GWP > 2500	2020
	Multipack central systems for commercial use with a cooling capacity above 40 kW	F-gases with GWP > 150	2022
Air-conditioning	Moveable, hermetically sealed air-conditioning	HFCs with GWP > 150	2020
	Single split systems containing 3 kg or less	F-gases with GWP > 750	2025
Insulating foam	One component foam aerosols	F-gases with GWP > 150	2008
	Extruded Polystyrene foam (XPS)	HFCs with GWP > 150	2020
	Other foams (including polyurethane)	HFCs with GWP > 150	2023
Fire protection	Systems using PFCS	All PFCs	2007
	Systems using HFC 23	HFC 23	2016
Aerosols	Novelty aerosols and signal horns	HFCs with GWP > 150	2009
	Techinical aerosols	HFCs with GWP > 150	2018
Other applications	Non-refillable containers for bulk product	All F-gases	2007
	Windows for domestic use	All F-gases	2007
	All other windows	All F-gases	2008
	Footwear	All F-gases	2006
	Tyres	All F-gases	2007

1.1. Objectives and methodology

The goal of this thesis is to identify one or more alternative refrigerants to R410A in a specific domestic heat pump, by evaluation of its overall environmental impact by the TEWI factor. This main task can be divided in different sub goals:

- Selection of alternative refrigerants
- Validation of the elaborated model
- Evaluation of performance of refrigerants in the model
- Elaboration of recommendations

In order to accomplish the above-mentioned objectives, the work has mainly consisted of two phases. First of all, a review of the state-of-the-art and of the latest research on the fourth generation refrigerants has been performed and used as a base for the selection of a shortlist of possible alternatives to R410A. The choice has been made following safety (no toxicity), environmental (no ODP and GWP lower than R410A), and thermodynamic (suitable pressure and temperature characteristics) criteria.
Secondly, a model has been created on EES reproducing the functioning of the studied HP, and validated against available experimental data and a second model created on IMST-ART.
The refrigerants have then been tested in such model, and results of environmental performance compared with the baseline R410A.

1.2. Limitations of the model

The main limitations of this work lie in the applicability of the model and consist of:

- Compressor efficiency correlations unavailable for R32 and R1234ze(E), hence assumed.
- Compressor efficiency correlations unavailable for R450A and R513A.
- UA correlations for the heat exchangers obtained from regression analysis, thus limited to the considered thermodynamic conditions and refrigerant
- Inlet brine temperature fixed at 0°C according to the Standard BS EN 14825:2012

The validity of the results can thus only be assured in the window of conditions considered in the creation of the model.

1.3. Thesis' structure

In chapter 2, an overview of the refrigerants' main characteristics is given. It is followed by a summary of the available literature on the most relevant possible alternatives to R410A. Finally, the selection of the short-list of fluids to be analysed in the model is performed and motivated.
In chapter 3 the model utilised for the analysis of the performance is described, along with the explanation of the calculations methods for the SCOP and TEWI factors.
Chapter 4 includes all the relevant results and the comparison between the contemplated options.
In chapter 5 the conclusion is given, and the necessary future work described.

2. Refrigerants

An overview of the different refrigerants' categories will be given hereby, along with an outline of their historical evolution. The main characteristics involved in the choice of alternatives will be developed, and a summary of relevant studies performed on the most relevant options for the scope of this work will be performed. Lastly, the shortlist of options to be further analysed will be illustrated.

2.1. Introductory concepts

The composition of a refrigerant, and thus some of its properties can be deduced by its name. The structure is Raxyz, where R simply stands for Refrigerant, and, according to the ASHRAE Standard 34 (ANSI/ASHRAE, 2013):

- x represents the number of Carbon atoms in the molecule, reduced by 1
  When the number is zero it is omitted from the name.
- y represents the number of hydrogen atoms, increased by 1
- z is the number of fluorine atoms
- a is the number of unsaturated carbon bonds. It is omitted when there are no double bonds.

It is to be noted that x=4 represents zeotropic mixtures (mixtures that experience a temperature glide during phase changes), x=5 azeotropic mixtures (mixtures that behave as a pure substance), x=6 organic compounds and x=7 inorganic compounds. The concept of zeotropic behaviour will be explained in section 2.2.1.

Although the vapour compression cycle was patented in the 19th century already (Balmer, 2011), the research of optimal refrigerants, thermodynamically, economically and environmentally performing is always ongoing. Throughout the history of the heat pump/refrigerating machine technology, different groups of refrigerants have been used according to the current requirements and needs, as can be seen in Figure 2.1.

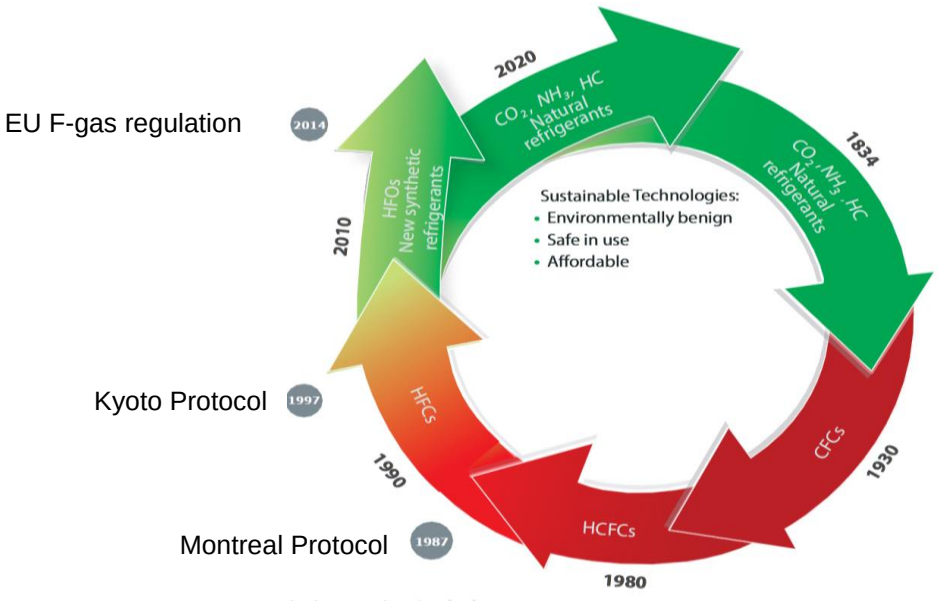

Figure 2.1. Evolution of refrigerants in time, adopted from Danfoss (2014)

Four refrigerant generations can be identified (Calm, 2008):

- First generation

The main actors in the first generation were natural refrigerants that could be easily found or produced, such as CO_2, NH_3, SO_2, ethers etc. The performance in the vapour compression cycle was satisfactory, but they presented issues with flammability and safety.

- Second generation: safety and durability

As the issues to safety rose from the first generation, the main focus was transferred to chlorofluorocarbons (CFCs) and hydrochlorofluorocarbons (HCFCs).

The main refrigerants created in this phase are R11, R12 and R115. Ammonia maintained a strong portion of the market. The refit of machines using this type of substances is not yet completed.

During the '50s HCFCs were introduced, including the most famous R22, as not completely halogenated carbon-based compounds.

- Third generation: ozone protection

In the '70s a link between the emission of CFCs and HCFCs and the depletion of the ozone layer was proven. This is due to the chlorine atom, which has the ability of decomposing the ozone molecule. Ozone Depleting Substances (ODSs) were banned with the Montreal Protocol, elaborated in the Vienna convention in 1987. In particular, CFCs were phased out (by 1996 or 2010 depending on the country) and HCFCs reduced, in a measure varying in different countries, and assumed the role of transition, undergoing a phase down such as 1996 (freeze at calculated cap), 2004 (65% of cap), 2010 (25%), 2015 (10%), and 2020 (0.5%) with full consumption phase out by 2030 in non-Article 5 countries (i.e. countries not operating under Article 5, paragraph 1 of the Montreal Protocol) and by 2015 for countries in the European Union (EIGA, 2014). Instead, Article 5 countries (mainly developing countries) (UNEP,

2011) began with a freeze in 2013, followed by declining limits starting in 2015 (90%), 2020 (65%), 2025 (32.5%), and 2030 (2.5%), phase out in 2040.
Hydrofluorocarbons (HFCs) were developed as a replacement, having an ODP=0. Specifically, R134a was created as a substitute of R12, entailing the possibility of keeping the same machine, provided proper cleaning and oil changing. The interest in natural refrigerants was also reborn, still in a limited measure.

- Fourth generation: global warming avoidance

As the concern for the global warming phenomenon increased, a great responsibility was proven to belong to the usage of fluorocarbons (FCs). New restrictions were established following the Kyoto protocol, and the "Regulation of the European Parliament and of the Council on fluorinated gases and repealing Regulation (EC) No 842/2006"or shortly, F-Gas regulation, was introduced. A first version appeared in 2006, followed by a newer and somewhat stricter one applied since January 2015. Its main aspects will be treated in section 2.2.5. Moreover, the "Directive 2006/40/ EC of the European Parliament and of the Council relating to emissions from air-conditioning systems in motor vehicles and amending Council Directive 70/156/EEC" (MAC regulation) regulates the use of fluorinated gases in mobile air-conditioning systems (MACs) and requires a refrigerant with GWP ≤ 150 in new models of cars after 2013.

It is important to understand that merely substituting an old refrigerant with a lower GWP may not be enough. In fact, if the low GWP substance does not yield an optimum performance in the system it can lead to an increase consumption of energy, and thus a greater indirect emission. A trade-off between GWP and performance has therefore to be considered.

2.2. Characterisation of refrigerants

When evaluating a refrigerant a number of aspects has to be kept into consideration. In fact, in order to be fit to operate in a heat pump, the fluid, pure or mixture, has to adhere to certain requirements that can be divided in different categories, namely thermodynamic properties, chemical properties, safety and environment issues. These groups will be treated in the following, and will be used as a starting point for the selection process developed further in the report.

2.2.1. Thermodynamic characteristics

The influence of the refrigerant is particularly important on the condensation and evaporation processes, as it defines the working pressures once that the temperatures are defined by the application. Consequently it influences the design of the compressor and the expansion valve, as well as heat exchange area in accordance to the required heat flux for the application.
In the case of a pure substance, to a certain saturated vapour pressure corresponds a particular temperature as seen in Figure 2.2.

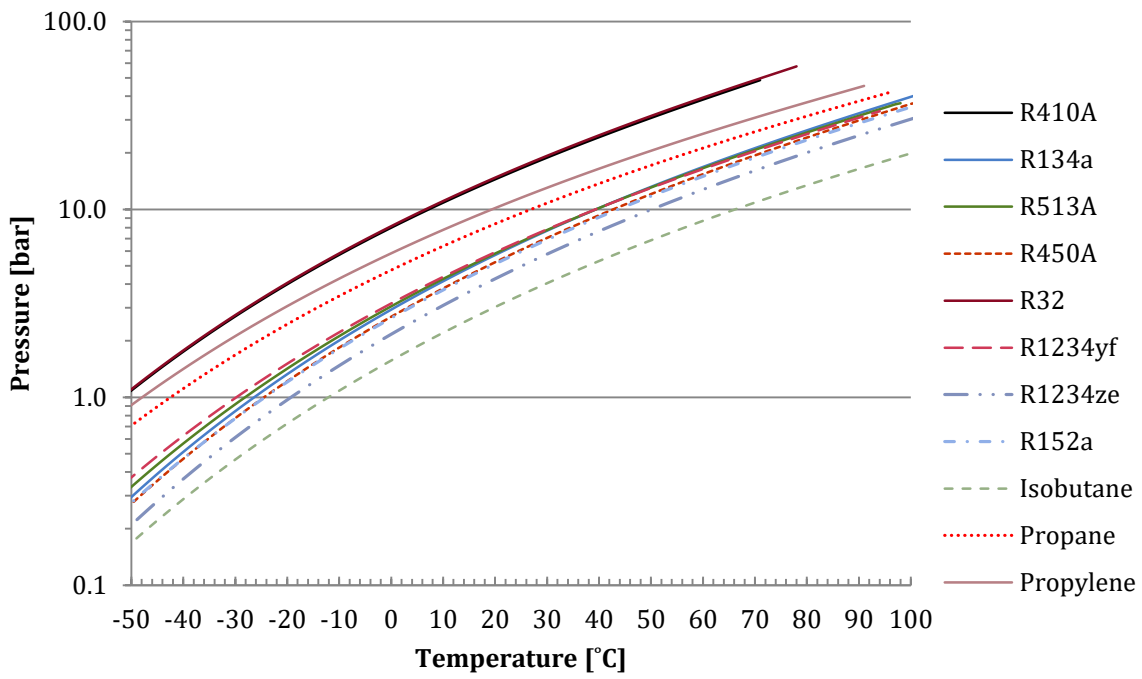

Figure 2.2. Saturated vapour pressure vs. temperature

Furthermore, the shape of the property diagram of a refrigerant influences the COP as it affects the values of enthalpy at the saturation points (Ekroth, 2011).

As far as thermal characteristics are concerned, low vapour heat capacity, low viscosity and high thermal conductivity should be maintained. The critical and boiling point temperatures must be chosen relatively to the application. Additionally, it would be preferable to work with a refrigerant having a small specific heat compared to the latent heat of vaporisation, in order to achieve smaller losses in the expansion valve (Rothlin, 2011).

Another aspect of great importance to treat when considering refrigerants is the mixtures. Their development and study is becoming increasingly important, as mixing different substances allows the creation of working mediums with more suitable properties and that can also result in the increase of the COP of the system.

According to their behaviour during evaporation and condensation, the mixtures can be classified as azeotropic, near azeotropic, or zeotropic, the differences residing in if – and in what measure – a temperature glide exists. In fact, when a pure refrigerant undergoes evaporation or condensation, it will maintain a constant temperature as long as the pressure is kept constant. In general, an increased pressure results in an increased saturated vapour pressure. Instead, in the case of a mixture of two or more components, the above mentioned processes will occur with temperature varying with the liquid-vapour composition.

- Azeotropic mixtures

In this case the glide effect is not present: the mixture acts as a single substance, thus maintains a constant boiling point, usually lower than either of the constituents. Most of these blends are binary and are most commonly used in low temperature refrigeration applications.

- Near azeotropic mixtures

It applies when the temperature glide is very small, of the order of 0.2 – 0.6 ºC. It is to be noted that the properties and composition of this kind of mixture can change if leakage occurs. They share most of the properties of the azeotropic mixtures, yet giving a broader range of possibilities (Mohanraj, 2011). R410A is an example of near-azeotropic mixture in residential HP application. The new mixtures R450A and R513A also belong to this category.

- Zeotropic mixtures

During the state changes the mixture will no longer behave as a single substance. The temperature glide needs to be considered in this case. Furthermore, the evaporation and condensation processes cannot be considered as isothermal anymore. In the first case the most volatile component – the one with the highest vapour pressure at a given temperature – will start the evaporation first; in the latter the opposite is true. Practically, this implies an increasing saturation temperature along the evaporator and a decreasing one along the condenser, as seen Figure 2.3. Moreover, the composition of the liquid will change throughout the vaporisation.

In this case a distinction must be made between “starting” and “stopping” evaporation temperature, and thus the bubble point temperature and the dew point temperature are defined.

This kind of mixture usually results from the addition of a third component, which can be needed to improve the characteristics of the substance. For example, such an addition could result in lower flammability, better oil miscibility etc. On the other hand, an enhanced leakage, due to the most volatile component is present (SWEP International AB, 2012).

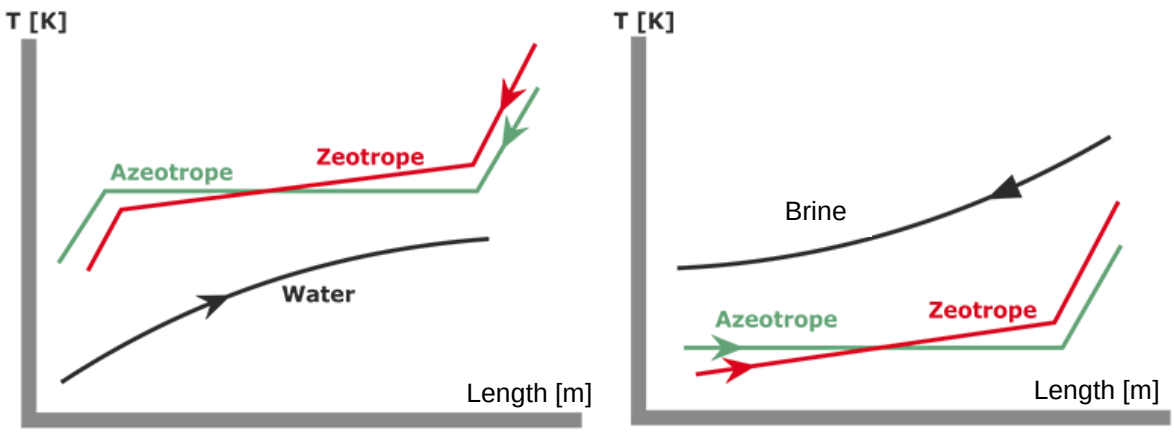

Figure 2.3. Condenser (right) and evaporator (left) temperature profiles (SWEP International AB, 2012)

When selecti ng a refrigerant a number of thermodynamic requirements exist, and can hardly be satisfied without any compromise. This phenomenon can be exemplified with a Pareto analysis, e.g. as in Figure 2.4. It represents the thermodynamic limit to the performance of a specific cycle, given the evaporation and condensation temperatures, and thus the application. It illustrates the trade-off between the volumetric capacity and the COP and states that it is not possible to achieve both a high COP and high capacity. The better the refrigerant, the closer it lies to the Pareto front (McLinden, 2014).

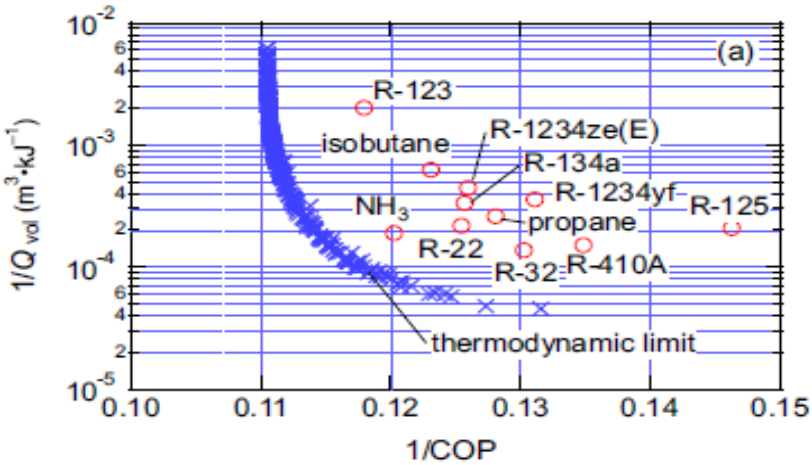

Figure 2.4. Pareto front (x) for the simple vapour compression cycle (air conditioned application) (McLinden, 2014)

2.2.2. Chemical characteristics

Chemically, the working medium has to be stable and inert, though stability has to be reasonable – the refrigerant has to decompose in the atmosphere in a not too long time. Moreover, absence of flammability and toxicity are ideal, as well as negligible effects on the environment (Rothlin, 2011).

In order to avoid corrosive compounds, the moisture level of the system should be kept low. Furthermore, in case it existed as free water and the temperature reached levels below the freezing point of water, ice would form on the expansion device and in the evaporator, resulting in malfunctioning of the system by impeding the refrigerant to flow properly. In general, the effect of the moisture is highly dependent on the fluid in use, as the absorption potential can vary greatly (Rothlin, 2011).

The refrigerant will encounter oil in the system, specifically in the compressor, and thus must be stable relatively to it (Rothlin, 2011).

2.2.3. Safety

Concerning safety parameters, ASHRAE Standard 34 classifies refrigerants based on their toxicity and flammability levels. Specifically, classes A and B categorize the toxicity – namely class A identifies refrigerants for which toxicity has not been found at concentrations less than or equal to 400 ppm; class B those with evidence of toxicity at concentrations below 400 ppm. Belong to class B notably NH_3.

Groups 1, 2 and 3 identify a growing flammability at given conditions of temperature (21°C), pressure (101 kPa) and heat of combustion. In addition, a class named “A2L” has been introduced in order to keep into account those refrigerants with mild flammability but high ignition power and low burning velocity (Institut International du Froid, 2011).

The traditional refrigerants such as R410A and R134a belong to group 1, whereas all the hydrocarbons, such as propane and propylene, belong to group 3. In group 2 R152a can be found, whereas R32 along with the majority of the new HFOs such as R1234yf and R1234ze(E) belong to group 2L.

2.2.4. Environmental issues

Nowadays, for a refrigerant to be considered benign to the environment, it has to entail no harm to the ozone, and low contribution to the greenhouse effect. Two indicators need thus consideration.

Firstly, the Ozone Depletion Potential (ODP) is used to evaluate the impact of the substance on the ozone layer. In fact, elements such as Chlorine and Bromine, when dispersed in the atmosphere, result in the breakdown of the ozone molecule O_3, in a sequence of loop reactions that lead to the destruction of many ozone molecules by a single Cl atom. The evaluation of the ODP is made by referring the effect of a substance to the one of R11, considered having ODP=1 (IPCC, 2005).

Secondly, the greenhouse effect contribution is assessed by the Global Warming Potential (GWP). The evaluation is made by comparing the ability of absorbing heat by the gas, per unit of weight, relatively to CO_2, which is considered to have GWP=1. The decay rate of the gas is also taken into account, i.e. the quantity removed from the atmosphere in a given number of years. It is easily understood that the shorter the lifetime in the atmosphere of the substance, the better (Global Greenhouse Warming, 2015).

For a complete evaluation of the environmental impact of the refrigerant, though, these two parameters are not sufficient. A more thorough analysis can be performed with a TEWI study. The TEWI indicator comprehends the total impact of the substance throughout the lifetime of refrigeration system, and considers not only the direct impact – due to leakages of the working fluid during the operation of the machine and during its dismissal – but also the indirect one, that is mainly due to the energy used for the functioning of the system, and is thus variable in accordance to the location and the energy sources used.

The calculation of this value, expressed in kg of CO_2 - equivalent emissions of GHG, can be performed as in equation (2.1).

$$TEWI = \underbrace{(GWP * L_{annual} * N) + GWP * m * \left(1 - \alpha_{recovery}\right)}_{\text{Direct: leakage}} + \underbrace{(N * E_{annual} * \beta)}_{\text{Indirect: operation}} \qquad (2.1)$$

where GWP is the global warming potential of refrigerant (kg_{CO2}/kg_{ref}), L_{annual} the leakage rate in the system (kg_{ref}/year), m is the refrigerant charge (kg_{ref}), N the lifetime of the system (years), $\alpha_{recovery}$ the recycling factor, E_{annual} the energy consumption per year (kWh/year), β the CO_2 emission factor (kg_{CO2}/kWh) (Mohanraj, 2011) (AIRAH, 2012).

2.2.5. Policies

In order to reduce the environmental impact of human activities, a number of protocols and regulations have been prepared along the years. Within the most famous are Kyoto protocol, Montreal protocol and lastly, aiming at protecting the environment by reducing emissions of fluorinated GHGs, and thus motivation behind this work, the F-gas regulation. A first version was adopted in 2006, followed by a second version to replace it, applied from the 1st January 2015.

The main goal is to reduce the contribution of the refrigeration industry to the global warming, by cutting the consumption of fluorinated gases (F-gases) by 79% by 2030, with start at 2009-2012 average level

(European Union, 2014). The expected outcome is a reduction of 1.5 Gt of CO_2-equivalent by 2030 and 5 Gt by 2050 from 2009-2012 average level. Currently, the F-gases represent 2% of the GHG emissions in Europe, and the growth has been of almost 60% since 1990. (European Commission , 2014).

Additionally, the regulation imposes the phase down of refrigerants with GWP over the allowed limits and the restriction on the marketing and use of some of these products; it aims also at improving the prevention of leaks that contribute to the direct impact of the refrigeration and air conditioning units.

The main points included in the new regulation are (Bitzer, 2014):

- Phase-down of the fluorinated gases currently in use. The percentage requirement is calculated on the CO_2 equivalent basis (Figure 1.2). It is to be noted that the phase down only applies to HFCs and not to other fluorinated gases such as FCs or sulphur hexafluoride (SF_6).

- Introduction of a quota system. For each producer or importer, quotas indicating maximum quantities for every year from 2015 will be specified. A baseline value is calculated on the 2009-2012 average volume placed on the market by each producer/importer, and the maximum quantity are calculated as percentages on this reference value (table in Figure 1.2). The quota received corresponds to 89% of the reference value multiplied by the percentage indicated for every year. The remaining 11% is allocated to new undertakings (AREA, 2014).

- The limitations will apply to products manufactured in countries that don't belong to the European Union as well, that will only be importable if subjected to the quota system.

- A maximum GWP is defined for some applications, thus limiting from 2015 already the usage of some refrigerants in particular segments, such as domestic refrigerators and freezers Table 1.1.

- Leakage prevention and treatment. A schedule of mandatory checks is prepared in accordance with the application and size of the technology used, for all cases where a refrigerant charge higher than 5 tons of CO_2 equivalent.

The application of such a quantitative limit implies the long-term usage of new refrigerants with GWP < 500 at the most, with repercussions on systems not currently directly affected by the bans, as the requirements for refrigeration are expected to increase (Bitzer, 2014).

Worldwide, other measures have been taken. In particular, in North America, the Significant New Alternatives Policy (SNAP) has been introduced as an EPA's (Environmental Protection Agency) program to evaluate and regulate substitutes for class I (ODP ≥ 0.2) and class II (ODP < 0.2) ozone depleting substances under the Clean Air Act indications and moved in 2014 towards the implementation of new rules, making certain high GWP refrigerants unacceptable in various end-uses (Environmental Protection Agency, 2015).

2.3. State of the art of the fourth generation of refrigerants

The new restrictions imposed by the F-gas regulation pushed the research of new refrigerants or blends that could be efficient replacements to high GWP refrigerants, with minimal modifications to current system technologies, at the lowest possible cost. Concerning the environmental aspect, it is fundamental to consider both the direct and indirect effect of the substances; e.g. by the means of the TEWI calculation. This way, wrong conclusions can be avoided; in fact, a refrigerant with low GWP could actually have a higher indirect impact because of the poorer performance in the system.

Generally, the literature available is rather limited, as some of the upcoming options are new substances and mixtures and still lack vast experimentation.
McLinden et al. (2014) conducted studies on over 56 000 molecules, with 15 or fewer atoms and comprising only the elements C, H, F, Cl, Br, O, N, and/or S that were successively screened by their ODP, GWP and various properties, reducing the number of candidates to 1200. When applying further criteria, such as having an appropriate critical temperature (between 300 and 400 K for almost all of the common refrigerating applications), 62 candidates were left. The most promising ones for residential heat pump systems, divided in categories, will be described in this section. A further elimination process will then be performed and motivated, leading to the shortlist of options presented in section 2.4.

2.3.1. HFCs

The most relevant for the considered application belonging to this category are R410A, R134a, R152a and R32. The GWP is still not optimal, and thus they should be regarded as medium term solutions.

- HFC/HC blends

The addition of a HC element to the HFC mixture improves the solubility with the lubricant, in extreme cases allowing the use of conventional oils, thus removing the need for retrofitting. Furthermore, the flammability of the HC blends can be reduced by the mixing of a HFC.

- R134a

Due to its high GWP (1300), it has been limited from MAC applications and banned in new vehicles' models from 2013 with the MAC regulation, and will be phased down in other applications. In fact, it will be allowed until 2022 in commercial hermetically sealed equipment (GWP<2500). In 2022 the limit to GWP will be set to 150, thus making R134a unacceptable.

- R152a

It has a critical temperature lower than 400 K, and presents a flammability level of A2. Usually used as a component in a mixture and can substitute, in a transitional manner, R134a. (McLinden, 2014).
The literature available regarding HP applications is limited, proving that the research on this refrigerant is still at an early stage. Ho-Saeng Leea et al. (2012) performed a study in a water source heat pump system on a R152a/R32 mixture, with varying percentual composition of R32. It was found that the tested system required a compressor power up to 13.7% lower when compared to an equivalent R22 system, along with an increased COP (up to 15.8%); the refrigerant charge diminishes of up to 27%. On the other hand, the compressor discharge temperature is increased up to 15.4 °C.

- R32

Its flammability is classified at A2L, and GWP is 675. Products using R32 are already in the market, such as the Daikin air-to-air heat pump (Daikin Global , 2014).

In an analysis by Barve et al. (2010), when compared to an R410A based equivalent HP and for an outdoor temperature varying between -8 to 46°C, the R32 system was found to have comparable cooling and heating capacities and similar COP. Though, an increase in the discharge pressure and temperature was measured which can be a concern to the compressor lifetime. An observable positive aspect is the decrease in the refrigerant charge that could lead to the usage of a smaller compressor.

Hakkaki-Fard et al. (2014) conducted a study with the goal of finding a refrigerant (pure or mixture) that could have a good performance in domestic applications (small/medium heat pumps), in comparison to an equivalent R410A, also involving the least number of modifications possible. Within a selection of 15 options, the mixture that emerged as best is R32/CO_2 (80/20). Combining the two elements has in fact the double advantage of reducing the flammability of R32 and mitigating the high pressure of CO_2. The obtained blend, furthermore, presents a higher heating capacity than R410A – that can be increased even more by augmenting the size of the heat exchangers – in spite of a slightly smaller COP. The GWP is reduced as approximately 25% of the baseline.

2.3.2. Natural Refrigerants

They present a low direct impact, with ODP=0 and low (or zero) GWP, accompanied with high efficiency that results in low indirect impact as well.

- Ammonia NH_3 (R717)

It is one of the oldest refrigerants known, and has zero GWP and ODP. It presents a low boiling point and is acknowledged as one of the most efficient refrigerants. The most common applications are industrial refrigeration, transport refrigeration, industrial/commercial air conditioning DX chillers and industrial/commercial centrifugal compressors. It is mainly being considered as a substitute for R22 and R134a (Linde, 2015). The main limits to its usage in other application rather than big industrial systems are its flammability and mild toxicity. By the means of a screw compressor, which results in a lower discharge temperature, and of plate type heat exchangers, that involve a smaller quantity of refrigerant, it is now possible to build relatively safe low charge ammonia systems. Though, its toxicity still prevents the diffusion in many locations, mainly where a warm climate is present (Bathkar, 2013). Evaluation of mixtures having ammonia as a component exists in the literature, and the general outcome is a lower discharge temperature, thus resulting in a longer life of the compressor (Mohanraj, 2011).

- CO_2 (R744)

As a natural refrigerant, as was the case for NH_3, CO_2 presents zero ODP and GWP=1. Moreover, it is a non-toxic and non-flammable substance. The most common applications are commercial, industrial and transport refrigeration, industrial/commercial air conditioning DX chillers, industrial/commercial centrifugal compressors and mobile air conditioning (Linde, 2015).

A drawback of its implementation is the necessity of significant modifications to the system, since CO_2 operates with much higher pressure than HFCs and with a lower critical temperature. On the other hand, it offers higher values of density, latent heat, specific heat, thermal conductivity and volumetric

cooling capacity. Because of the above-mentioned low critical temperature, R744 can be run in a trans-critical cycle. This means that the working medium would evaporate in the subcritical region and successively reject heat in a gas cooler instead of a condenser, at temperatures above the critical point (Bathkar, 2013).

2.3.3. HCs

An advantage with this type of refrigerants is their miscibility with synthetic lubricants and mineral oil. These fluids therefore do not have to be changed when switching from HCFC or HFC mixtures to HC ones. Besides, their short atmospheric life results in a very low GWP and they represent the best choice when considering their cost. On the other hand, they present problems because of their flammability. The two main HCs used as refrigerants are isobutane (refrigerators) and propane (small commercial appliances and residential heat pumps). Many examples of blends involving HCs, with different components and variable relative percentages in mass, exist in the literature. The general conclusion seems to be a lower energy consumption, compared to both equivalent R134a and R22 systems. In conclusion, HC mixtures are a good alternative in small applications such as domestic refrigeration, small capacity refrigeration and heat pump units and MAC systems (Mohanraj, 2011) (Bathkar, 2013).

- R290 (propane)

It has environmental and thermodynamic outstanding characteristics but, as HC, has high flammability and thus cannot be implemented in existing FC systems. Moreover, because of the safety issues it is only applicable in industrial/commercial refrigeration systems and air conditioning, as well as domestic air conditioning, provided proper refitting. Restrictions to the placement of the system and to the refrigerant charge are imposed by the Standard EN378 (EN 378, 2008). Despite the flammability concerns, research is active and products are being brought to the market from companies such as Ait-Deutschland (Maul, 2013).

In order to lessen the flammability, mixtures can be used. Ki-Jung Park et al. (2009) investigated for example a mixture of R170/R290 (with varying relative composition) in a heat pump as a substitute for R22, both in summer and winter conditions. The results showed an increase in the COP of up to 15.4%, despite a decrease in the capacity (up to -7.5%). Other observed improvements of the system are the decrease in the compressor discharge temperature and a reduction in the refrigerant charge.

Fan et al. (2013) investigated a R744/R290 mixture, finding an increased COP, along with an increased volumetric heating capacity when compared to an equivalent R22 system. Though, it is observed that the performance is efficient only when working with large heat-sink temperature rise.

- R1270 (propylene)

Literature is very limited, and major studies still need to be performed. The environmental characteristics are optimal, but propylene, as propane, implies an A3 flammability level and thus is not suitable for retrofitting existing systems. It is most adapt to low – medium temperature applications. (Linde , 2015). Propylene is an unsaturated molecule and therefore its stability is lower than that of propane. Therefore the latter is often given priority to the former when selecting an environmentally friendly refrigerant.

2.3.4. HFOs

HFOs have been on the rise since the 2010s, as they present a very low GWP, along with zero ODP. In fact, HFOs are derivatives of alkenes rather than alkanes and thus are unsaturated, i.e. they have a double bond in the molecule, which results in a short atmospheric life. The main disadvantage is the mild flammability of most HFOs, that can be a barrier to the implementation in small systems such as domestic and commercial refrigeration/heat pump units (Bathkar, 2013). Besides, they currently entail a much higher cost of manufacturing.

Between the possibilities offered by HFOs, the most promising solutions are represented by R1234yf, R1234ze(E) and R1234ze(Z) and their mixtures; they aim primarily at substituting R134a and R114 in domestic refrigeration and mobile air conditioning applications (R1234yf) and in commercial refrigeration, industrial air conditioning and heat pumps and heat transfer applications (R1234ze(E), R1234ze(Z)) (Linde, 2015).

The data found in the literature is limited and varies between different authors. The studies conducted by Zhang et al. (2014) had a positive outcome; the heat transfer coefficient of R1234yf was in fact estimated to be lower in the condenser and higher in the evaporator compared to an R134a equivalent system. Moreover, it belongs to the class A2L.
Concerning high temperature heat pumps, a number of mixtures were tested and good results were shown by the mixture M1A (R1234zf/HC-290, 60%/40% in the mass) such as higher COP and lower discharge temperature, compared to an equivalent R114 system (Zhang, 2014).

A series of 54 experiments on R1234yf and R1234ze(E) were carried by Mota-Babiloni et al. (2014) as drop-in replacements in R134a systems. In this case the average COP was reported to be lower that the baseline one, as well as the cooling capacity. The performance can be improved with the usage of an Internal Heat Exchanger (IHX), which affects in a bigger measure both HFOs' systems than the R134a one. It is to be noted that an R134a machine operates with a reciprocating compressor, whereas screw or centrifugal would be more appropriate for R1234ze(E). Furthermore, the difference in performance is reduced by increasing the condensation temperature (R1234yf) or increasing evaporation temperature (R1234ze(E)).

To overcome some of the limitations imposed by HFOs, mixtures can be used. Within the most interesting options are R450A and R513A.
Mota-Babiloni et al. (2014) investigated the performance of R450A (R1234ze(E)/R134a mixture, 58/42 in mass percentage) as a transitional replacement of R134a, having good performance, similar operation conditions but though a GWP still quite high (601). The resulting blend is also non-flammable, and near-azeotrope. The outcome is a higher COP, mainly due to a much lower compressor power consumption, and lower discharge temperature, in spite of a lower cooling capacity. In this case the IHX has a smaller influence in the way that it affects both systems in a similar way and thus doesn't have particular interest. R450A can be used satisfactorily in an R134a system, but a refit is advisable to optimise its performance.

Concerning R513A, a mixture of R134a/R1234yf (44/56 in mass percentage), the available literature is very limited. Similarly to R450A, it is non-flammable, and has a GWP of 631.
Schultz and Kujak (2013) performed drop-in tests of R513A in an R134a chiller, obtaining a comparable capacity, but an efficiency reduction of 3-4%.

2.4. Selected refrigerants for further analysis

When selecting the refrigerants to elaborate a shortlist of R410A replacement options within the described above, the criteria kept into consideration can be summarised as follows:

- Low GWP, no ODP
- Non-toxic
- Chemical and thermal stability, inert
- Suitable physical and thermodynamic properties:
  - Critical point and boiling point temperatures appropriate for the application
  - Low vapour heat capacity
  - Low viscosity
  - High thermal conductivity
- Compatibility with materials, miscibility with lubricants
- Other:
  - High dielectric strength of vapour
  - Low freezing point
  - Easy leak detection
  - Low cost

It is evident that a compromise must be sought, as no refrigerant currently available can satisfy all of the characteristics ideally requested.
A low GWP is considered for a preliminary round of elimination, as the alternative refrigerant has to have a GWP at least inferior to R410A (2088). This eliminates R134a.
As far as safety is concerned, toxic refrigerants (classified B by the ASHRAE 34) will not be considered as options, whereas flammability will not be a deterring in this phase of the research. Hence, ammonia will not be analysed further.
The main thermodynamic aspects to be kept into account can be summarised in Figure 2.5, applied to the saturated vapour pressure curves, seen in Figure 2.2. The operational envelope identified in the figure by the red square is built by combining pressure and temperature boundaries to the refrigerants.

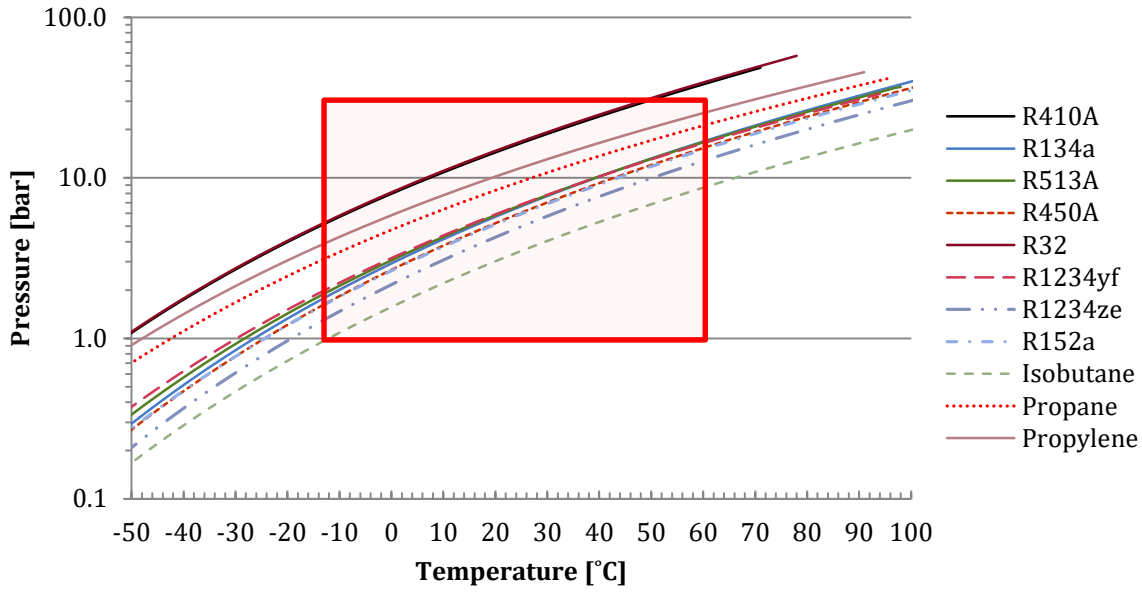

Figure 2.5. Pressure and operation criteria

Regarding the temperatures, the lower and upper limits coincide with the working interval of the heat pump, here taken as -10°C to 60 °C. Considering the pressures, the lower limit is set to the atmospheric pressure, as operation under such limit would imply contamination of system with air form the surroundings and thus possible damage to the system. The upper limit, is set in relation to equipment limitations such as pipes' thickness etc. It is to be noted that R410A already operates at the highest pressure considered, and thus the equipment available can already support all of the alternatives' options, except CO_2. Hence, it will not be regarded as a valid alternative.

Moreover, it can be seen on the graph that the isobutene would entail an operation pressure very close to the lower limit, and therefore will not be considered for further analysis.

When observing R32, it is evident that its operational conditions are very similar to R410A. In fact, R32 represent an almost perfect drop-in replacement; restrictions due to its flammability though exist, and

retrofitting is thus necessary. With the considerations above, a shortlist of eight refrigerants is elaborated and is illustrated in Figure 2.6. Their main characteristics can be seen in Table 2.1.

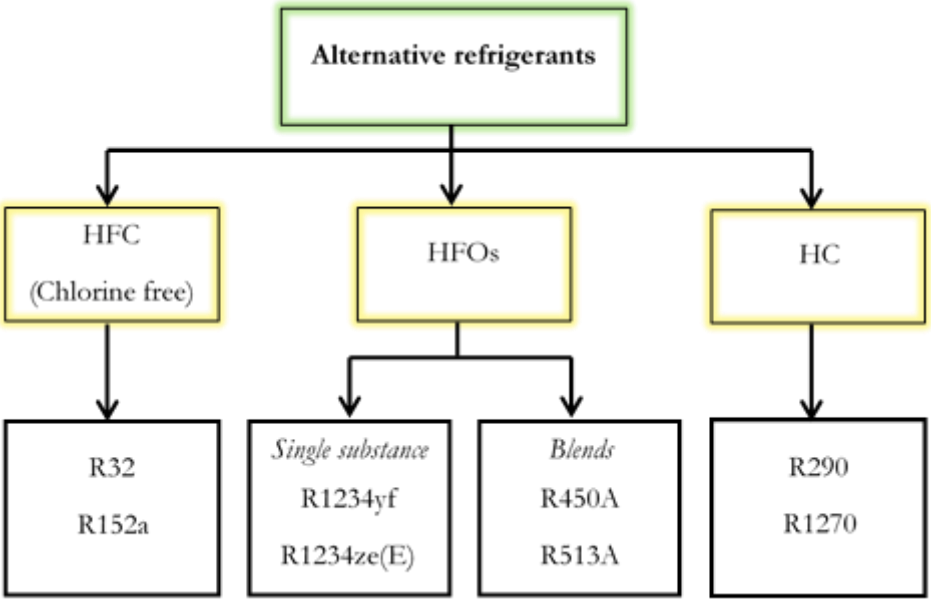

Figure 2.6. Selected alternatives to R410A

Table 2.1. Characteristics of the alternative refrigerants to R410A

Refrigerant	GWP*	Flammability	T critical [°C]	P critical [bar]	Nat. boiling point [°C]
R410A	2088	A1	72.8	48.6	-48.5
R513A	631	A1	101.1	36.8	-29
R450A	601	A1	105.7	40.8	-24
R1234yf	4	A2L	94.7	33.8	−29.5
R1234ze(E)	7	A2L	109.4	36.3	-19
R32	675	A2L	78.1	57.8	- 52
R152a	124	A2	113.3	45.2	-25
R290	3	A3	96.7	42.5	- 42.2
R1270	2	A3	91.1	45.6	-47.6

3. Analysis of the developed model

The product considered in the scope of the testing is a commercial model available in the market as the representative of domestic heat pump installed in a Swedish single family house, with 10 kW heating capacity. The modelling of the said heat pump has been conducted in the EES software, an equation solver tool able to solve systems of thousands of non-linear equations. Its major feature and main reason for its choice is the fact that it contains all the thermodynamic properties of the major refrigerants and comprises an extensive library of correlations.

In order to evaluate the indirect effect that has to be kept into account while calculating the TEWI, the SCOP is obtained from the model.

3.1. Heat pump model

The components of the system are illustrated in Figure 3.1; the pumps for the secondary fluids are not considered.

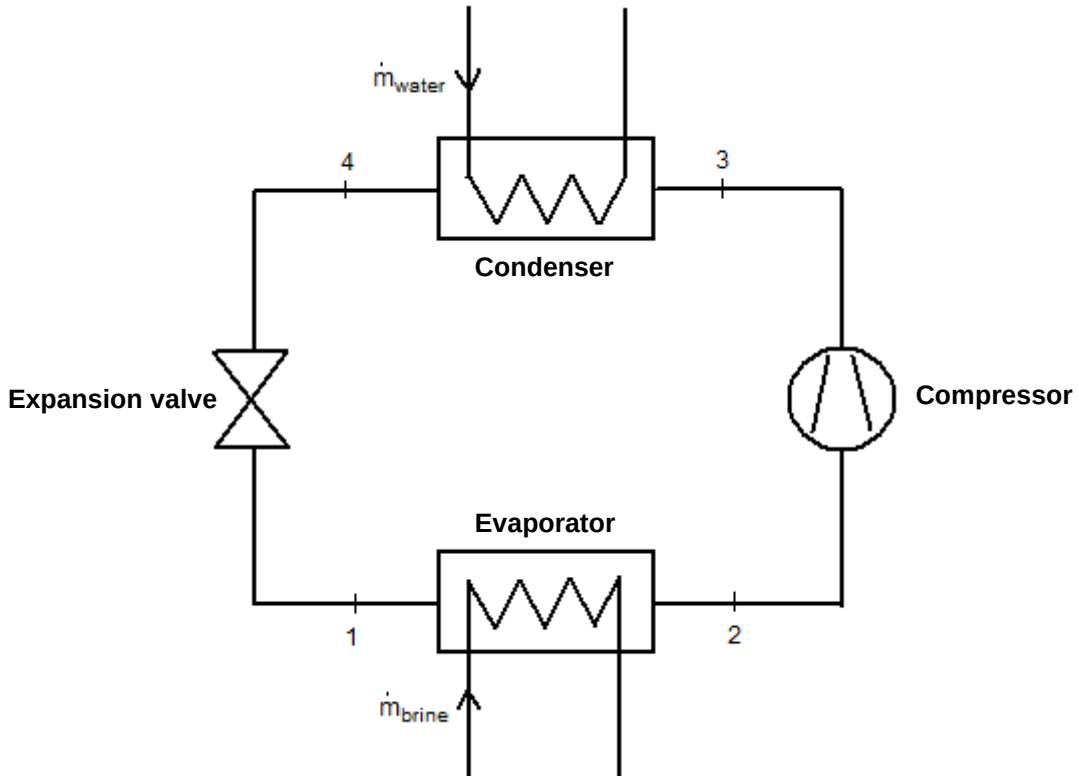

Figure 3.1. Heat pump system

The evaporator and the condenser are plate heat exchangers, the compressor is hermetic scroll type and the expansion valve is thermostatic. The secondary fluids are brine in the evaporator (mixture of water and ethyl alcohol at fixed concentration of 29%) and water in the condenser.

In order to understand how some of the parameters that will be used in the comparative analysis between the alternative refrigerants are defined, an overview of their expression will be given hereby.

In Figure 3.2 the basic vapour compression cycle – followed by the HP considered – is represented in the pressure-enthalpy (left) and temperature-entropy (right) diagrams. From 1 to 2 the evaporation of

the refrigerant occurs, with superheating, by the means of the heat absorbed from the secondary fluid. Point 1', at the intersection of the isobaric process line at evaporation pressure and the saturated vapour line, represents the start of the superheating phase. 2 to 3 is the compression phase, where the full line is the ideal, isentropic one, and the dashed line the real. From 3 to 4 the refrigerant undergoes the condensation process, consisting of desuperheating (3 to 3', crossing of isobaric at condensation pressure and saturated vapour line), condensation (3' to 3'', crossing of the isobaric at condensation pressure and saturated liquid line) and subcooling (3'' to 4), releasing heat to the secondary fluid. The process from 4 to 1 is the expansion.

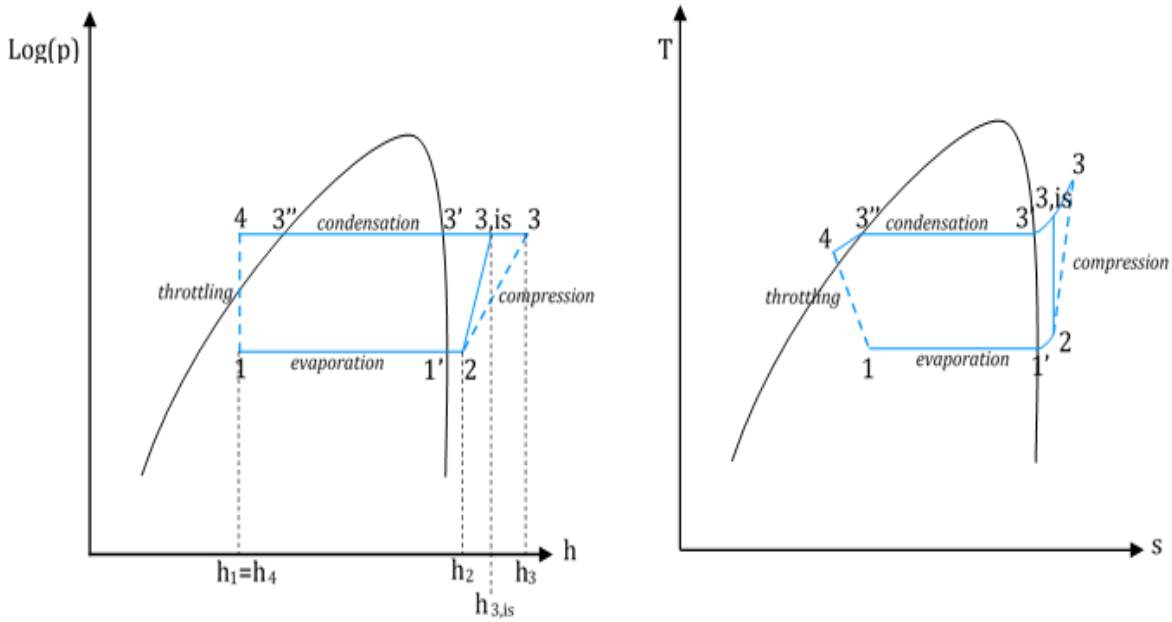

Figure 3.2. Vapour compression cycle in log(p)-h diagram (left) and T-s diagram (right)

In the case of the heat pump application of the cycle, the sought product is the rejected heat during the condensation process and can be expressed as in equations (3.1) and (3.2).

$$q_1 = h_3 - h_4 \tag{3.1}$$

$$\dot{Q}_1 = \dot{m}(h_3 - h_4) \tag{3.2}$$

where q_1 and $\dot{Q}_1$ expressed in J/kg and W respectively are the heat rejected, or condenser load, h_3 the enthalpy and the inlet of the condenser, h_4 the enthalpy at its outlet, in J/kg and $\dot{m}$ the refrigerant mass flow, in kg/s.

The heat absorbed by the refrigerant during the evaporation process is given by equations (3.3) and (3.4).

$$q_2 = h_2 - h_1 \tag{3.3}$$

$$\dot{Q}_2 = \dot{m}(h_2 - h_1) \tag{3.4}$$

where q_2 and $\dot{Q}_2$ expressed in J/kg and W respectively are the heat absorbed, or evaporator load, h_1 and h_2 the enthalpies and the inlet and outlet of the evaporator respectively, in J/kg and $\dot{m}$ the refrigerant mass flow, in kg/s.

The required work, ideal and real, are given by equations (3.5) and (3.6).

$$w_{id} = h_{3,is} - h_2 \tag{3.5}$$

$$w = h_3 - h_2 \tag{3.6}$$

where w_{id} and w are expressed in J/kg.

In a real vapour compression system, the enthalpy at the exit of the compressor differs from the isentropic one, as the losses in this component cannot be neglected.
The isentropic efficiency of the compressor can thus be defined according to (3.7).

$$\eta_{is} = \frac{h_{3,is} - h_2}{h_3 - h_2} \tag{3.7}$$

The performance of a refrigerating cycle is evaluated through the coefficient of performance (COP).
To represent the difference in the purpose of the heat pump and the refrigerating machine, two different COP can be expressed. In the case of a heat pump, the desired product is the rejected heat and thus the COP is given by (3.8); in the case of a refrigerating machine, the sought effect is the absorbed heat and therefore the COP is given by (3.9).

$$COP_1 = \dot{Q}_1/\dot{W} \tag{3.8}$$

$$COP_2 = \dot{Q}_2/\dot{W} \tag{3.9}$$

where $\dot{Q}_1$ is the rejected heat during the condensation process, $\dot{Q}_2$ the absorbed heat during evaporation and W is the required net work input, in kW.

The COP_1 of the heat pump can also be thought of as a multiplier, representing the number of times the used work is gained as heat at the higher temperature level.
The relationship between the two COPs, in the same machine – operating at the same conditions – can be expressed as seen in (3.10).

$$COP_1 = COP_2 + 1 \tag{3.10}$$

3.1.1. Basic assumptions

A set of experimental data obtained from runs of the real heat pump were available and were used as starting points for the creation of the model. Specifically, the runs were classified by inlet temperature of brine in the evaporator (0, 5, -5 °C) and outlet temperature of water in the condenser (35, 45, 55 ºC), creating a combination of nine runs. Superheat is set at 4.8 °C and subcooling at 4 °C.
Overall, the input data chosen are as seen in Table 3.1:

Table 3.1. Input data

	Amount of superheat	[ºC]
	Amount of subcooling	[ºC]
	Inlet temperature of brine	[ºC]
	Outlet temperature of water	[ºC]
Brine/water	Mass flow	[kg/s]
	Specific heat	[kJ/kg-°C]

3.1.2. Evaporator

A typical temperature profile observed in an evaporator can be seen in Figure 3.3.

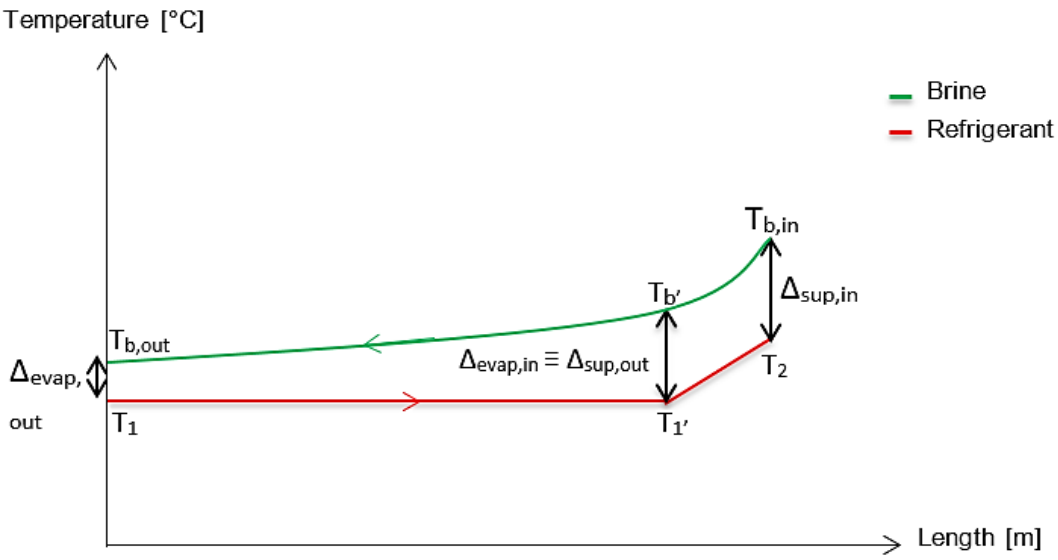

Figure 3.3. Temperature profiles of brine and refrigerant in the evaporator

On the brine side, the water-ethanol mixture enters at $T_{b,in}$ and leaves at $T_{b,out}$. $T_{b'}$ occurs when the evaporation line crosses the saturated vapour line (x=1), and thus separates the evaporation phase from the superheating phase.

On the refrigerant side, in the evaporation phase the temperature is constant at $T_1 = T_{1'} = T_{evap}$ and is increased to T_2 (compressor inlet temperature) in the superheating phase.

In order to define the performance of the evaporator, two major parameters need to be calculated: the LMTD and the UA value. In order to obtain results closer to the real case, both these indicators have been identified for the evaporation and for the superheating phases separately. Equations (3.11) and (3.12) have been used, all the temperature differences mentioned are stated graphically in Figure 3.3.

$$\mathrm{LMTD}_{\mathrm{evap}} = \frac{\Delta_{\mathrm{evap,in}} - \Delta_{\mathrm{evap,out}}}{\ln\left(\Delta_{\mathrm{evap,in}} / \Delta_{\mathrm{evap,out}}\right)} \tag{3.11}$$

for the evaporation phase and

$$\mathrm{LMTD_{SH}} = \frac{\Delta_{\mathrm{SH,in}} - \Delta_{\mathrm{SH,out}}}{\ln\left(\Delta_{\mathrm{SH,in}} / \Delta_{\mathrm{SH,out}}\right)} \tag{3.12}$$

for the superheating.

As a first approach for the modelling, the UAs have been inserted as inputs. The inserted values could be obtained from a second, separate model, after defining all the thermodynamic properties of the major points of the cycle. As the values for temperature and pressure were available as experimental outputs, the enthalpies could be determined. Data for mass flows and specific heat were also present, thus allowing the calculation of the UAs for evaporation and superheat. The calculated values were used as input in the main model of the heat pump. The energy balance was solved in EES and is illustrated by equations (3.13), (3.14), (3.15), here stated in a general way and in the software applied to both evaporation and superheating phases.

$$\dot{Q} = \dot{m}_{ref} * \Delta h_{ref} \tag{3.13}$$

$$\dot{Q} = \dot{m}_{brine} * cp_{brine} * \Delta T_{brine} \tag{3.14}$$

$$\dot{Q} = LMTD * UA \tag{3.15}$$

Where $\dot{Q}$ is the heat in kW, $\dot{m}_{ref}$ the mass flow of refrigerant in kg/s, Δh_{ref} the enthalpy difference the refrigerant undergoes in the considered process in kJ/kg, $\dot{m}_{brine}$ the mass flow of brine in kg/s, cp_{brine} the specific heat of the brine in kJ/kg-°C, ΔT_{brine} the temperature difference experienced by the brine in the considered process, LMTD as defined previously.

In a second approach, two correlations for the UAs have been obtained through a regression analysis, applied to the UA values obtained. It is important to point out that due to the scarcity of available experimental data (only 9 set of points), this procedure essentially consists of an interpolation, rather than a statistical study (hence the neglect of presentation of statistical characteristics such as standard deviation, R^2 etc.).

The values used in (3.15) are thus now obtained by equations (3.16) and (3.17).

$$UA_{SH} = 22.2465 - 253.989 * k_{1'} - 298.449 * k_2 - 1511947 * \mu_{1'} - 284923 * \mu_2 - 2.2384 * \rho_{1'} - 0.4587 * \rho_2 + 0.10934 * P_{evap} \tag{3.16}$$

$$UA_{evap} = 323.01 + 19158.8042 * k_{1'} - 49773038.92 * \mu_{1'} + 88.612 * \dot{m}_{ref} + 0.4796 * T_{evap} \tag{3.17}$$

Where $k_{1'}$ and k_2 are the thermal conductivity of the refrigerant in points 1' and 2 in W/m-°C, $\mu_{1'}$ and μ_2 are the dynamic viscosity of the refrigerant in points 1' and 2 in Pa/s, $\rho_{1'}$ and ρ_2 are the density of the refrigerant in points 1' and 2 in kg/m^3, P_{evap} and T_{evap} are the evaporation pressure in kPa and temperature in °C.

3.1.3. Compressor

The correlation for the isentropic efficiency has been found by fitting of data obtained from the compressor manufacturer (Emerson climate technologies, 2015). A large number of values were available for several combinations of evaporation and condensation temperatures. For the same combinations the pressure ratio was defined and a diagram of the efficiency vs. the pressure ratio was thus obtained Figure 3.4. The fitting polynomial (3.18) was then extracted. The values obtained with (3.18) were compared with the experimental data available, and a relative difference between the two set of values calculated

$$\eta_{is} = 0.0024 * {P_{ratio}}^3 - 0.0363 * {P_{ratio}}^2 + 0.1377 * P_{ratio} + 0.5531 \tag{3.18}$$

The calculated difference above mentioned allowed to obtain values closer to the real case, from the manufacturer's data. It is assumed to be applicable to the alternative refrigerants as well. Hence, the provided correlations for R1234yf, R290, R1270 and R152a – obtained for other operating conditions – could be adjusted to be applied to the studied heat pump case. The resulting correlations for the available refrigerants, function of the pressure ratio, can be seen in Figure 3.4.

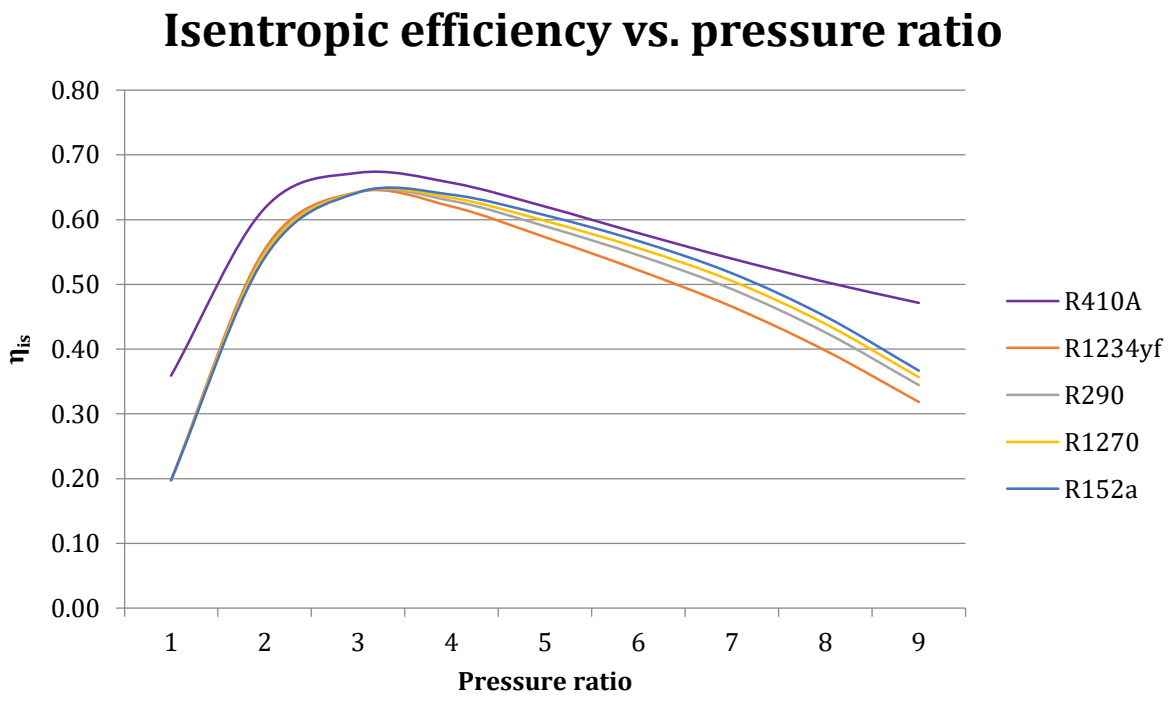

Figure 3.4. Isentropic efficiency of compressor for different refrigerants

For the refrigerants for which the correlation was not available to start with, assumptions were made. Specifically, it was assumed that R32 could operate with the same compressor efficiencies as R410A, due to its similarities in temperature and pressure levels. Concerning R1234ze(E), it was assumed to operate with the same correlation as R1234yf.

No assumptions regarding the compressor could be made for R450A and R513A, because of the limited access to data. For this reason, the analysis of these two refrigerants is left for the future steps of the work.

Concerning the volumetric efficiency of the compressor (η_s), another correlation was elaborated. The value for the swept volume ($\dot{V}_{swept}$) was available for the specific compressor at the given operating conditions (50 Hz or 3000 rpm) on the Emerson online software (Emerson climate technologies, 2015) and equals to 6.93 m^3/h (0.001925 m^3/s).

The relation between the mass flow of the refrigerant and the volumetric efficiency is given by equation (3.19) (Ekroth, 2011):

$$\dot{m}_{ref} = \rho_2 * \dot{V}_{swept} * \eta_s \tag{3.19}$$

Where $\dot{m}_{ref}$ is the mass flow of refrigerant in kg/s, ρ_2 the density of the refrigerant in point 2 of the cycle in kg/m^3, $\dot{V}_{swept}$ the swept volume in m^3/s and η_s the volumetric efficiency of the compressor.

With the other data ($\dot{m}_{ref}$ and ρ_2) issued from the model, η_s could be calculated for each point, and related to the corresponding pressure ratio, thus obtaining the correlation seen in (3.20).

$$\eta_s = 0.0015 * {P_{ratio}}^2 - 0.0356 * P_{ratio} + 1.0583 \tag{3.20}$$

3.1.4. Condenser

The condenser used is the H62L-CX, micro-plate heat exchanger. The typical temperature profile in a condenser is observed in Figure 3.5.

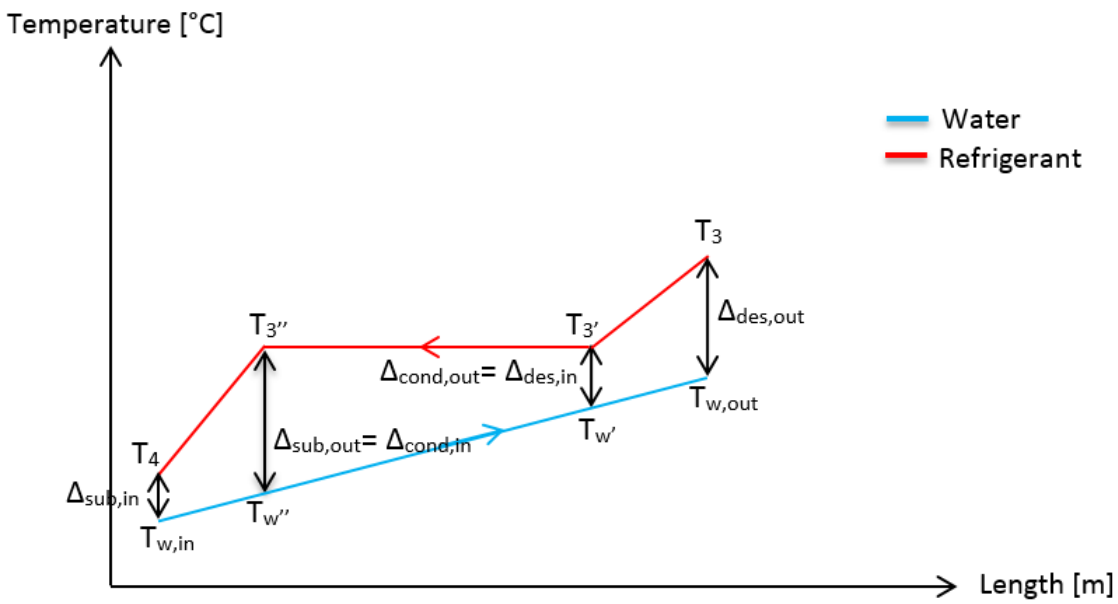

Figure 3.5. Temperature profiles of water and refrigerant in the condenser

On the water side the water comes in at $T_{W,in}$ and leaves at $T_{W,out}$. Two other main temperatures are identified, $T_{W''}$ corresponding to the crossing of saturated vapour line on the refrigerant side at the

condensation pressure, and $T_{W'}$ corresponding to its crossing of the saturated liquid line. These temperatures on the refrigerant side are identified, respectively, by $T_{3''}$ and $T_{3'}$. The latter thus divide, respectively, the subcooling from the condensation and the condensation from the desuperheating stages.

Similarly to the evaporator case, the LMTD calculation has been fragmented in the three different stages of the process. In the order of occurrence on the refrigerant side (3.21), (3.22), and (3.23). All the temperature differences used are defined graphically in Figure 3.5.

$$\mathrm{LMTD_{des}} = \frac{\Delta_{\mathrm{des,in}} - \Delta_{\mathrm{des,out}}}{\ln\left(\Delta_{\mathrm{des,in}} / \Delta_{\mathrm{des,out}}\right)} \tag{3.21}$$

$$\mathrm{LMTD_{cond}} = \frac{\Delta_{\mathrm{cond,in}} - \Delta_{\mathrm{cond,out}}}{\ln\left(\Delta_{\mathrm{cond,in}} / \Delta_{\mathrm{cond,out}}\right)} \tag{3.22}$$

$$\mathrm{LMTD_{sub}} = \frac{\Delta_{\mathrm{sub,in}} - \Delta_{\mathrm{sub,out}}}{\ln\left(\Delta_{\mathrm{sub,in}} / \Delta_{\mathrm{sub,out}}\right)} \tag{3.23}$$

In the case of the condenser, as done in the evaporator case, the UAs have been calculated with two successive approaches. Firstly, they were calculated from experimental data in a separate model and then used as input in the main model. The systems of equations used are the same ones stated in the evaporator section ((3.13), (3.14), (3.15)), and applied to the three stages occurring in the condenser. Secondly, these UA values were used in a regression analysis which issued the following correlations (3.24), (3.25), (3.26).

As stated in the evaporator section as well, this procedure is relatable to an interpolation, as the starting data were not sufficient to perform a more thorough statistical analysis.

$$UA_{des} = -2.6208 + 2.4611 * \dot{m}_{ref} + 287997 * \mu_{3'} - 0.0372 * T_{cond} \tag{3.24}$$

$$UA_{cond} = 124.1569 - 1092.0017 * k_{3''} - 69.6615 * \dot{m}_{ref} - 0.7917 * T_{cond} \tag{3.25}$$

$$UA_{sub} = -450.716 + 2941.455 * k_{3''} - 1005.03 * k_4 + 0.027 * P_{cond} + 0.1058 * \rho_{3''} - 30.3314 * \dot{m}_{ref} + 1.5201 * T_{cond} \tag{3.26}$$

Where $k_{3''}$ and k_4 are the thermal conductivity of the refrigerant in points 3'' and 4 in W/m-°C, $\mu_{3'}$ is the dynamic viscosity of the refrigerant in point 3' in Pa/s, $\rho_{3''}$ is the density of the refrigerant in points 3'' in kg/m^3, P_{cond} [kPa] and T_{cond} [°C] are the condensation pressure and temperature.

3.1.5. Expansion valve

The expansion valve is a thermostatic type and the throttling process is considered to be isenthalpic, and thus h_1=h_4. This conclusion is drawn from the first principle of thermodynamics, expressed by (3.27).

$$\Delta h + \Delta e_k + \Delta e_p = q - w \tag{3.27}$$

where Δh is the enthalpy variation, Δe_k the kinetic energy variation, Δe_p the potential energy variation, q the specific heat exchanged and w the specific work required in the expansion valve, all in J/kg.

The process is assumed to occur without a variation of potential or kinetic energy and the work required is null. Considering an adiabatic expansion valve, the throttling process can then be treated as isenthalpic.

With the procedures and assumptions presented in the previous sections 3.1.1. to 3.1.5., the most relevant outputs, such as heating capacity and COP, obtained values within the margin of error of ±10% when compared to the experimental data, as is represented in Figure 3.6 in the case of the COP. This interval is considered acceptable. The main difference between the model's output and the experimental data resides in a lower evaporation pressure, thus lower evaporation temperature in the case of the model.

The variation in the discharge temperature reaches +11.2%, mainly due to the necessary approximation of the compressor's correlation.

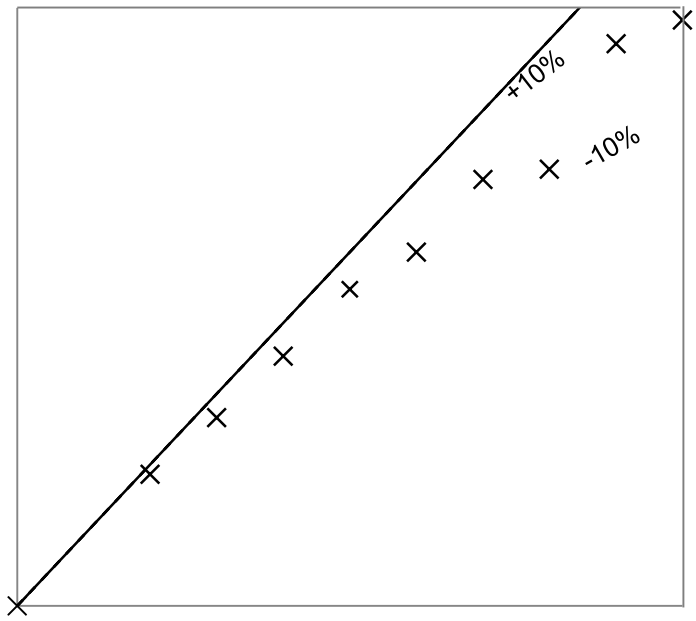

Figure 3.6. Relative differences of results with experimental data

3.2. SCOP calculation

The calculation of the SCOP has been performed following the Standard BS EN 14825:2012 (BSI, 2012). This document provides data to characterize the heating season, and specifically for the colder climate area (identified with Helsinki), the temperature bins – i.e. the number of hours for which every temperature occurs are as seen in the following Figure 3.7.

The heating demand curve is also obtained, in this case not considering an auxiliary heating system. Thus, the heating demand at the lowest possible outdoor temperature, -22 °C, corresponds to the maximum capacity of the heat pump considered, 10 kW.

The heating demand, or partial load curve seen in Figure 3.7, is obtained for colder as in equation (3.28) (BSI, 2012):

$$\text{Partial load} = \frac{\mathrm{T_j} - 16}{-22 - 16} * P_{designh} \tag{3.28}$$

where Pdesignh is 10 kW (the capacity of the considered HP), and T_j every integer temperature value occurring during the heating season, i.e. from -22 °C to 16 °C.

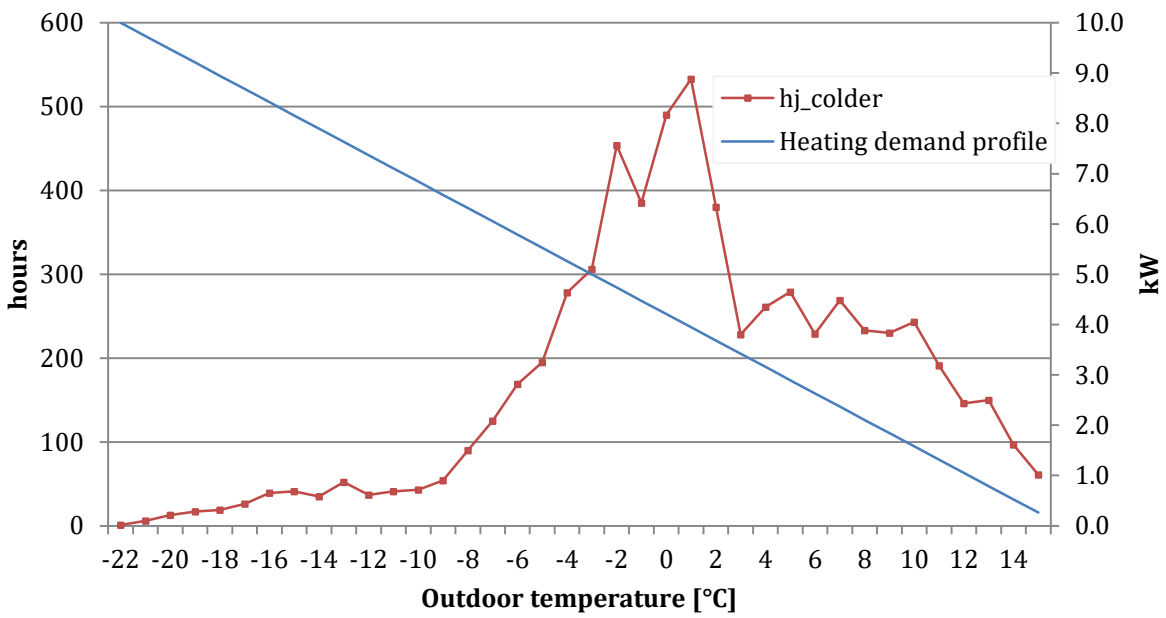

Figure 3.7. Temperature and heating demand profiles in colder climate scenario (BSI, 2012)

The Standard also provides information on the requirements for secondary fluids' temperatures. For ground source heat pump in colder climate, the data is as seen in Table 3.2.

Table 3.2. Requirement for secondary fluid temperatures (BSI, 2012)

		T_water_out [°C]	
Outdoor T [°C]	**T_brine_in [°C]**	**Floor heating [°C]**	**Radiators [°C]**
-22	0	35	55
-7	0	30	44
2	0	27	37
7	0	25	32
12	0	24	28

Once the heating season was characterised along with the secondary fluid temperatures' values, the SCOP can be calculated by equation (3.29) (BSI, 2012).

$$SCOP_{ON} = \frac{\sum_{j=1}^{n} h_j * Ph(T_j)}{\sum_{j=1}^{n} h_j * (\frac{Ph(T_j) - elbu(T_j)}{COP_{partial}(T_j)} + elbu(T_j))} \quad (3.29)$$

Where h_j is the number of hours for which the outdoor temperature T_j [°C] occurs, $Ph(T_j)$ is the heating demand corresponding to the outdoor temperature T_j [kW], $elbu(T_j)$ is the eventual power obtained from an electric back-up unit [kW], and $COP_{partial}$ (T_j) is the COP calculated at the specific outdoor temperature T_j.

In the case of this study, it is assumed that no back-up unit is present.

For the baseline, R410A, the SCOP is calculated as 4.14.

3.3. TEWI calculation

The TEWI factor is calculated according to equation (2.1). A certain number of inputs, besides the GWP and the SCOP, are required in order to describe the system performance and their first assumed values are presented in Table 3.3.

Table 3.3. TEWI input parameters

Annual leakage rate	2%/year
Lifetime [years]	15
β [kg CO_2/kWh$_e$]	0.023
α recovery	0.7
Charge [kg]	2.3*
Annual heating demand [kWh]	27547.35

* Example of charge value for R410A. The value adjusted for other refrigerants in accordance to the values presented below.

The input parameters consist of:

- Annual leakage rate, in % of the charge of the system.

For a self-contained refrigerating system, the value is assumed at 2% (AIRAH, 2012).

- Lifetime of the system, in years

- β or CO_2 emission factor, in kg CO_2/kWh$_e$

The value is based on the average emission of the electricity sector of a country or area, thus is dependent on the energy mix of the considered location. In Sweden this factor is equal to 0.023 kg CO_2/kWh$_e$ (Convenant of Mayors, 2012).

- α or recovery efficiency, from 0 to 1

It indicates the proportion of refrigerant charge that is recovered from a system when decommissioned. Chosen by default at 0.7.

- The charge, in L or m^3

The quantity of charge in kg is known from the experimental data, and equals 2.3 kg of R410A. Through its specific volume at the temperature range operated by the machine, the charge in volume was obtained. When considering the other alternative refrigerants, a constant volumetric charge was assumed, in order to obtain different mass values by the means of the specific volumes (Table 3.4).

Table 3.4. Charge values by refrigerant

Refrigerant	sp. volume [L/kg]	Charge [kg]
R410A	1.05	2.300
R32	1.07	2.257
R152a	1.15	2.100
R290	2.10	1.150
R1270	0.56	4.275
R1234yf	0.91	2.657
R1234ze(E)	0.90	2.683

- The annual heating demand, in kWh

The value is calculated from the guidelines given by the Standard BS EN 14825:2012 (BSI, 2012) and is used in order to obtain the energy consumption per year E_{annual}, in kWh/year, through equation (3.30).

$$E_{annual} = {Total\ heating\ demand}/{SCOP} \tag{3.30}$$

4. Results and discussion

The performance and environmental characteristics of the chosen alternative refrigerants were evaluated through a series of parameters: discharge temperature, COP, volumetric heating capacity (VHC), SCOP and TEWI. As the Standard (BSI, 2012) identifies two different types of applications (radiator and floor type of heating), both scenarios are evaluated. The obtained results will be presented and discussed hereby.

4.1. Discharge temperature

The discharge temperature is the temperature measured at the exit of the compressor and mainly affects the lifetime and performance of the latter. In fact, an increase in the temperature above the safety limit placed at 110 °C can entail heavy consequences on the machine, such as acid formation and oil breakdown. If coking or carbonising of the oil occurs on the valve plate, leaking can be induced thus worsening the capacity of the machine (Danfoss, 2011).

The results for the discharge temperature in case of radiator heating can be seen in Figure 4.1. They are presented versus the outdoor temperature, as every working condition of the heat pump is defined according to this parameter. Concerning the floor heating case, the pattern shown is similar, implying generally lower temperatures; the graph is omitted from the report as it does not present any temperature above the safety limit and therefore does not add weight to the choice of a refrigerant over another.

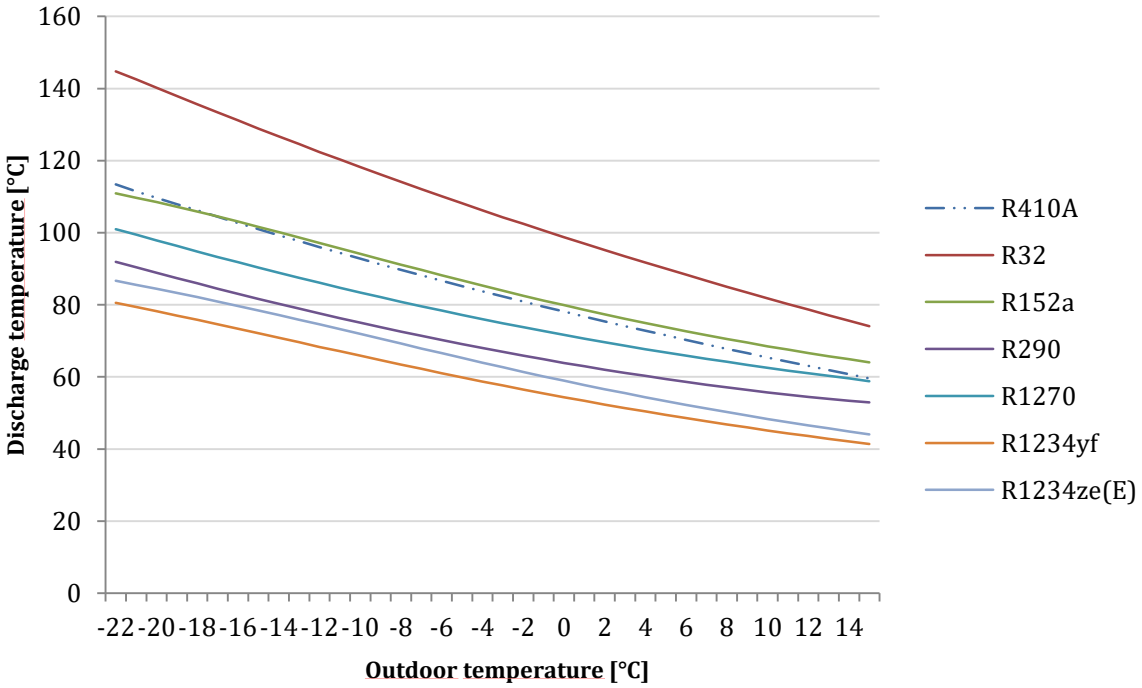

Figure 4.1. Discharge temperature vs. outdoor temperature (radiator heating)

It is evident that every tested refrigerant has the same trend, i.e. decreasing discharge temperature with increasing outdoor temperature, corresponding to a decreasing condensation pressure.

It can be observed that the HCs and the HFOs present lower discharge temperatures than R410A, whereas R152a and R32 entail a higher one, fact that confirms the observations of Ho-Saeng Leea (2012). R152a surpasses the baseline values from an outdoor temperature of -12 °C, and an increase up to 7.4% at the highest temperatures is detected.

Concerning R32, it entails the highest discharge temperatures between the alternatives, with a maximum increase of 27.8% at the lowest temperatures of the evaluated range. It has to be noted that below -6 °C, R32 operates at temperature above the safety limit for the compressor, as also observed by Barve et al. (2010) As a consequence, careful consideration of materials and other substances must be taken.

It can be pointed out that in this case the correlation for the compressor efficiency is not optimal for R32, as it was assumed to be the same obtained with R410A. The results could thus be improved with the better knowledge of the compressor's performance with the specific refrigerant.

4.2. Volumetric heating capacity

The results obtained for the volumetric heating capacity (VHC) can be seen in Figure 4.2 in the case of radiator heating, and in Figure 4.3 for the case of floor heating. The values of VHC are here obtained for an evaporation temperature of -8 °C, with a subcooling amount of 4 °C and superheat of 4.8 °C.

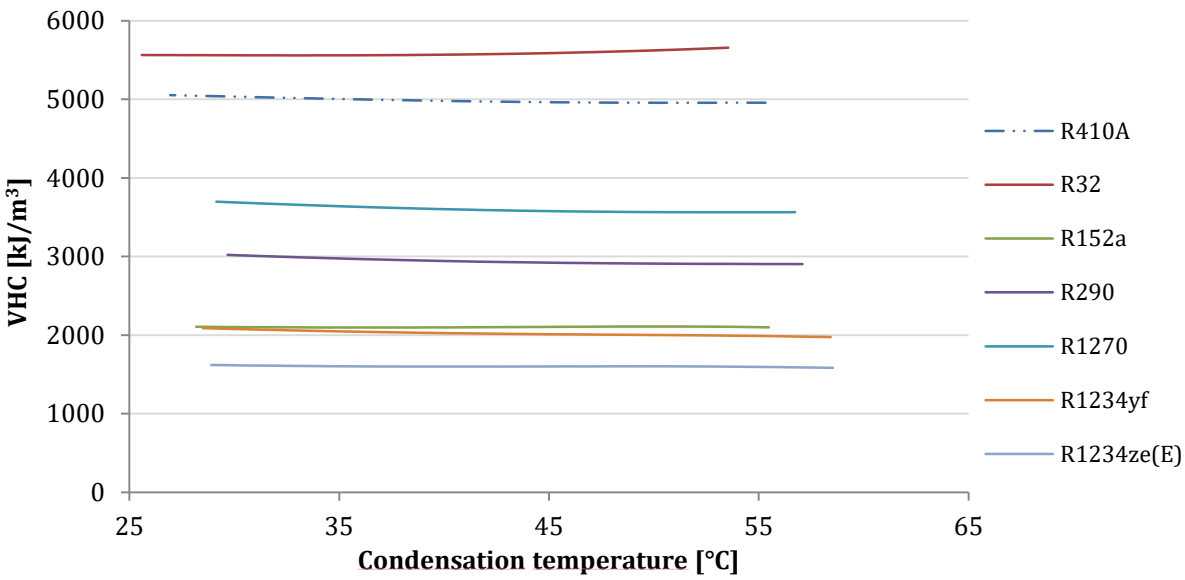

Figure 4.2. Volumetric heating capacity vs. condensation temperature (radiator heating)

It can be noticed from the graph Figure 4.2 that all refrigerants imply a lower VHC when compared to R410A, except for R32.

In average, R32 entails an increase in the VHC of 12.4%. As mentioned, the other options all involve lower VHCs. The HFOs own the biggest reduction, of averagely 59.9% and 68% for R1234yf and R1234ze(E) respectively.

It can be noticed that propylene, presents a higher VHC than propane; propylene could thus in this case represent a better option between the two hydrocarbons. Concerning the HFOs, it can be observed that

R1234ze(E) entails a lower VHC than R1234yf, while its COP was higher. Their performance can thus be balanced out at this point.

It is evident that the higher the VHC, the smaller compressor can be used to provide similar heating effect. Within the options considered, R32 is the only one resulting in such a possibility

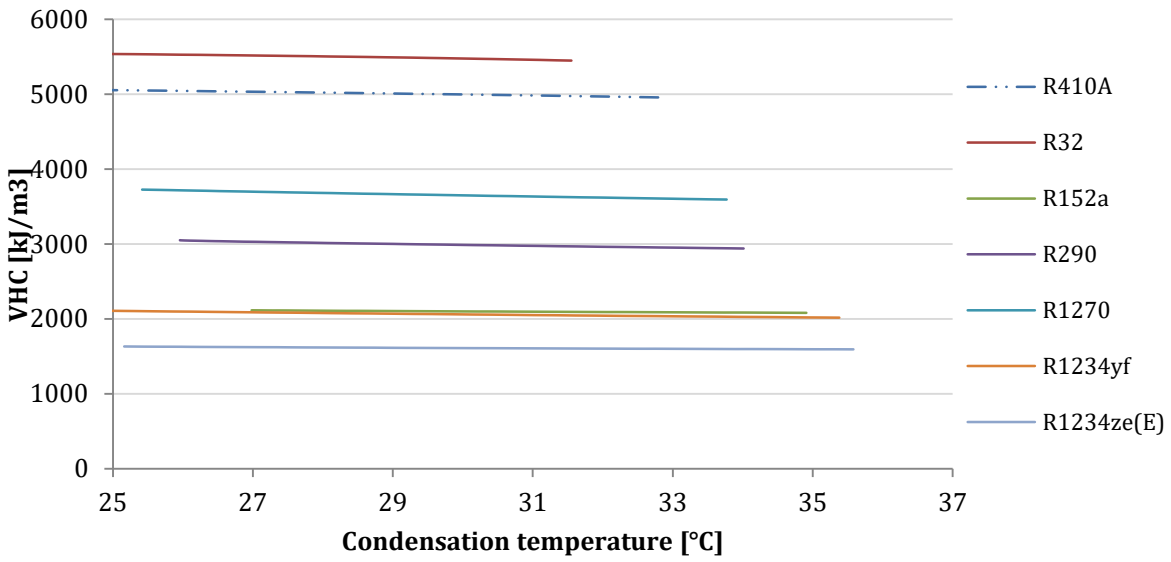

Figure 4.3. Volumetric heating capacity vs. condensation temperature (floor heating)

The trend and relationships between the different refrigerants observed in the radiator heating case, can be found in the floor heating case as well, represented in Figure 4.3.

4.3. Coefficient of performance (COP)

In this section the coefficient of performance for the heat pump application will be considered (COP_1 as calculated in equation (3.8)), similarly to the previous case, in relation to the outdoor temperature. The results can be observed in Figure 4.4, in case of radiator heating and in Figure 4.5 in case of floor heating.

The general trend of the COP is common to every refrigerant, and consists of its increase with increasing outdoor temperature, thus increased heating capacity. The rates of growth though, are different within the options thus making the identification of their relationships not straightforward.

Generally, it can be remarked that R32 outperforms every other substance from outdoor temperature of -17 °C. It reaches the maximum increase compared to R410 at the lowest and highest temperatures of the range, respectively of 8.2% and 7.7%. The divergence is reduced in the central values of the range.

It can be observed that below -17 °C, the best performance is offered by R152a.

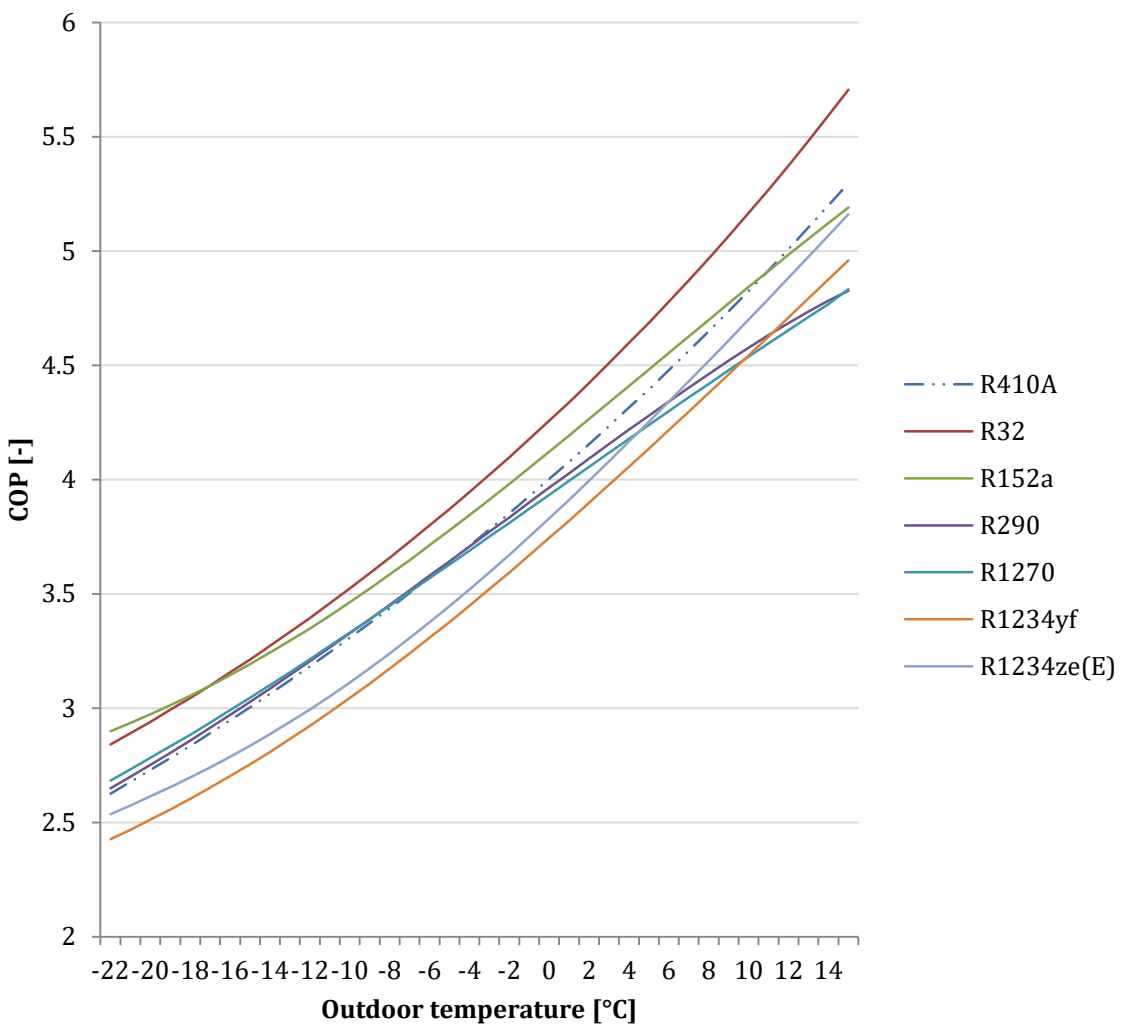

Figure 4.4. COP vs. outdoor temperature (radiator heating)

When focusing on the lowest temperatures of the range, it can be observed that up to -7 °C the baseline R410A is also outperformed by both the hydrocarbons, R290 (up to -5 °C) and R1270. In the case of propane, the relative difference below -7°C is smaller than 1%. R1270 presents a slightly higher COP along all the range, and reaches an increase up to 2.2% compared to R410A at the lowest temperature evaluated. Along the range they maintain a very close growth trend. Concerning the HFOs, R1234yf and R1234ze(E), it appears that they present the lowest COPs overall. The latter maintains along the range a higher COP, with a relative difference with R1234yf almost constant.

At higher temperatures, the overall best COP is shown by R32. The excess to R410A increases with increasing temperature. Propane and propylene experience a slowdown in their growth rate, thus being outperformed by every other refrigerant along the range. Specifically, R1234ze(E) outperforms R1270 and R290 respectively at 5 °C and 6°C, and R1234yf and 11 °C and 12 °C. They register the highest decrease compared to R410A at the highest temperature of the interval, equal to -8.9% for R290 and -8.8% for R1270.

At 12 °C, R410A outperforms R152a, thus offering the best performance at the highest temperatures, excluding R32.

The observations can only partly be confirmed what was found in the literature, as no equivalent studies can be found. In particular, the lower COP for the HFOs agrees with the findings of Mota et al. (2014) – though the comparison was made with an equivalent R134a system. Concerning R32, Barve et al. (2010) found a similar COP when compared to R410A equivalent system, instead of a higher one as in this work.

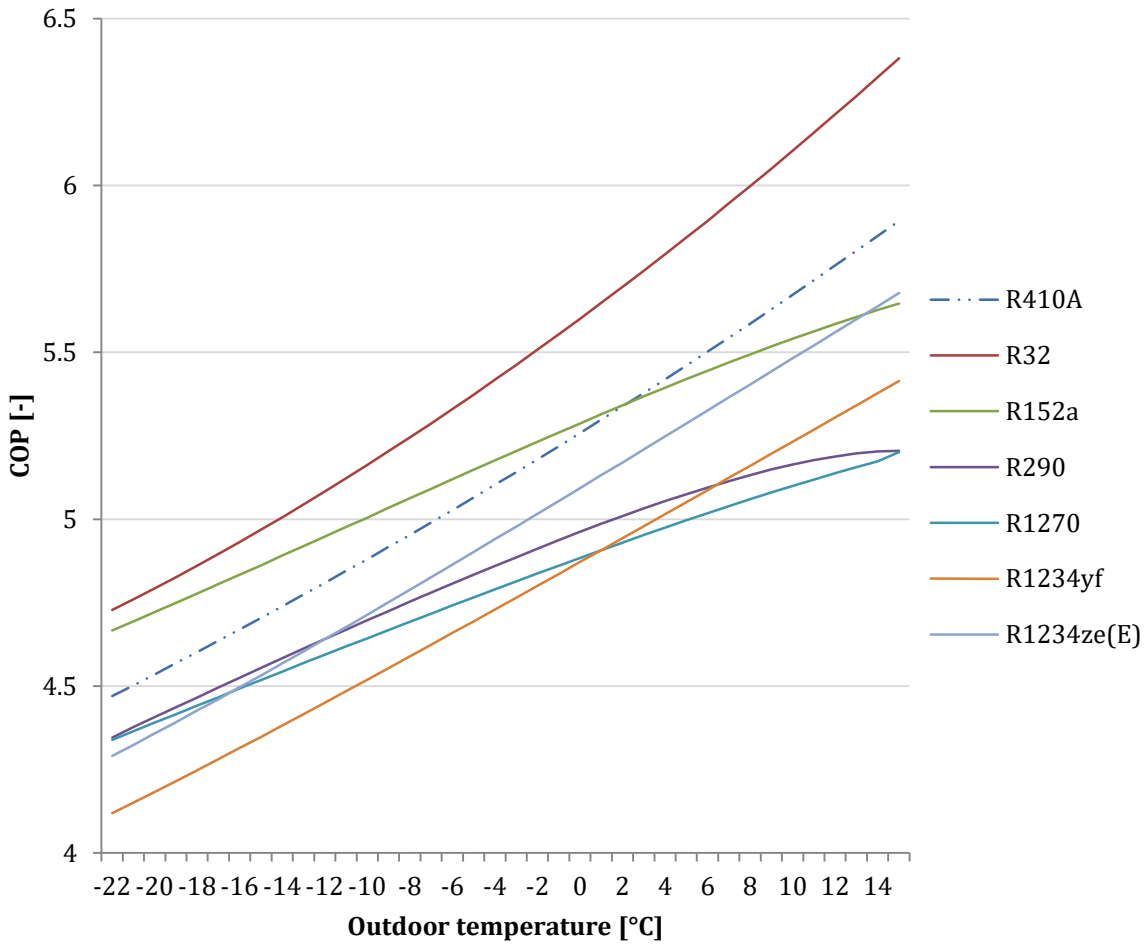

Figure 4.5. COP vs. outdoor temperature (floor heating)

Concerning the floor heating, it can be observed that the COP is generally higher than in the radiator heating case. This is due to the generally lower temperature lift between heat source and sink. R32 now presents the best performance along the whole temperature range; the relative difference with R410A increases with the outdoor temperature and ranges from 5.8% to 8.3%. Up to 2 °C, R410A is also outperformed by R152a with a maximum divergence observed at -22 °C of 4.4%.

It can be seen than in this case, R1234ze(E) outperforms the HCs much earlier than in the radiator case, specifically R1270 at -17 °C and R290 at -13 °C . Moreover, it also shows a higher COP than R152a from 13 °C up. Similarly, R1234yf now outperforms R1270 at 1 °C and R290 at 5 °C – both lower temperatures than in the radiator heating case.

4.4. Seasonal coefficient of performance (SCOP)

When evaluating the COPs of the refrigerants, it was evident that an overall ranking of performance was difficult to elaborate, as their relationships varied with varying conditions. The SCOP is then a powerful indicator that allows assessing of the performance along the whole heating season.

In Figure 4.6 the results, obtained from the method presented in section 3.2, are shown for both the cases of radiator and floor heating.

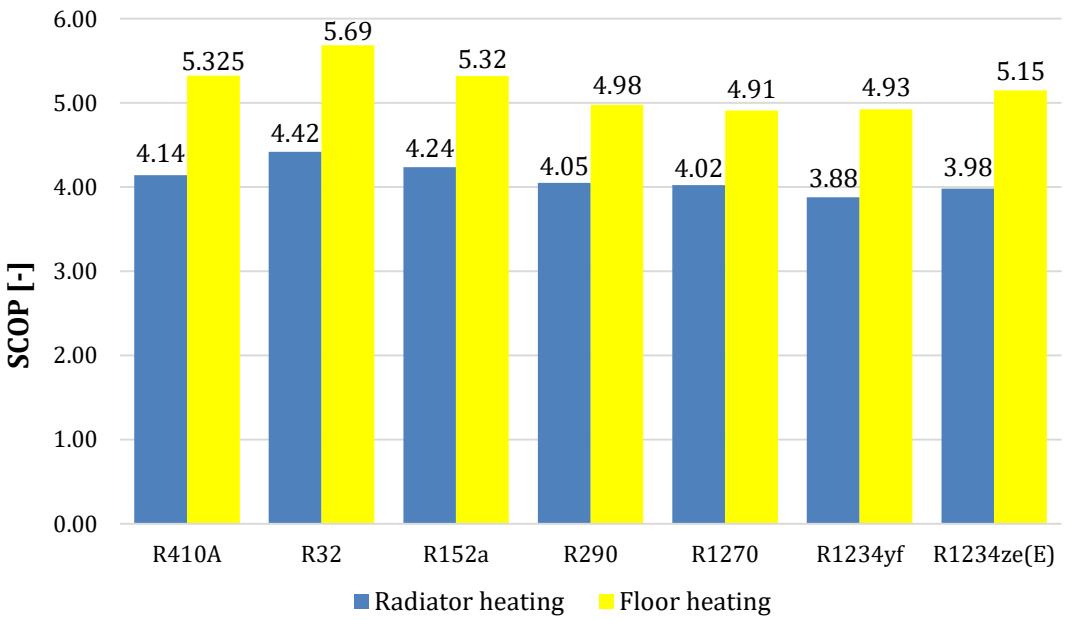

Figure 4.6. SCOP by refrigerant over the heating season for colder climate scenario (radiator and floor heating)

As expected, R32 presents the highest seasonal performance (+6.5% compared to R410A for radiator heating, +6.8% for floor heating), as it maintains the highest COP in almost all the range of temperatures comprising the heating season. It is followed by R152a (+2.3% radiator, +0.1% floor), both outperforming R410A. The relative differences are shown in Figure 4.7 and Figure 4.8.

In the radiator heating case, the lowest SCOP is obtained by R1234yf, with a total reduction compared to R410A of -6.4%, followed by R1234ze(E) with -3.9%. The hydrocarbons entail a smaller reduction, with -2.9% for propylene and -2.2% for propane.

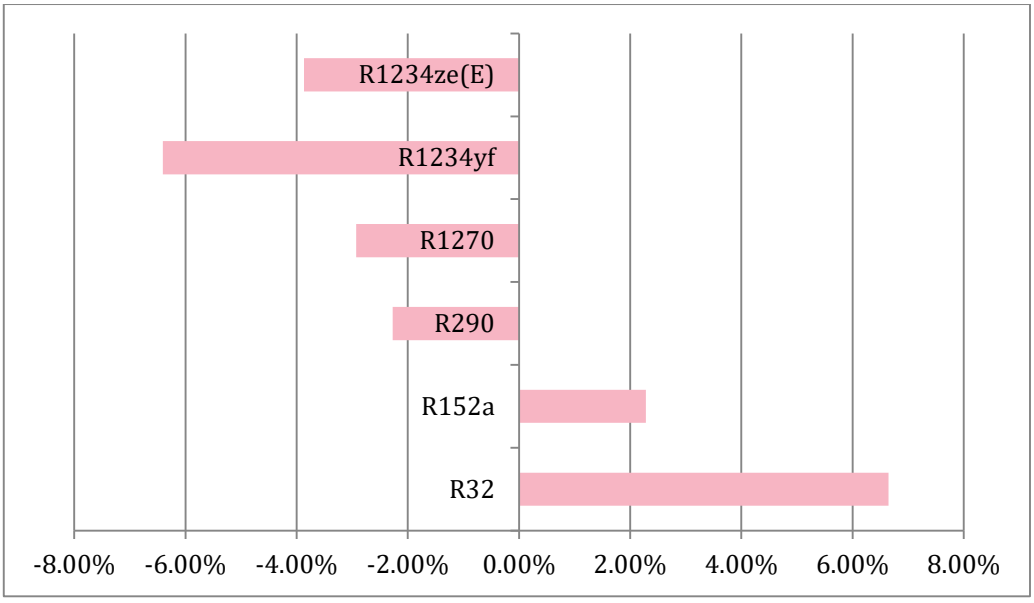

Figure 4.7. Relative differences (%) of SCOP compared to R410A (radiator heating)

At lower condensing temperatures – involved in the floor type of heating – R410A registers a better performance. Therefore, over the heating season, the alternative refrigerants entail a bigger decrease in the overall SCOP. The larger reduction is now given by R1270, -7.75% compared to R410A. R290 also shows a drastic decrease, now equals to -6.46%.

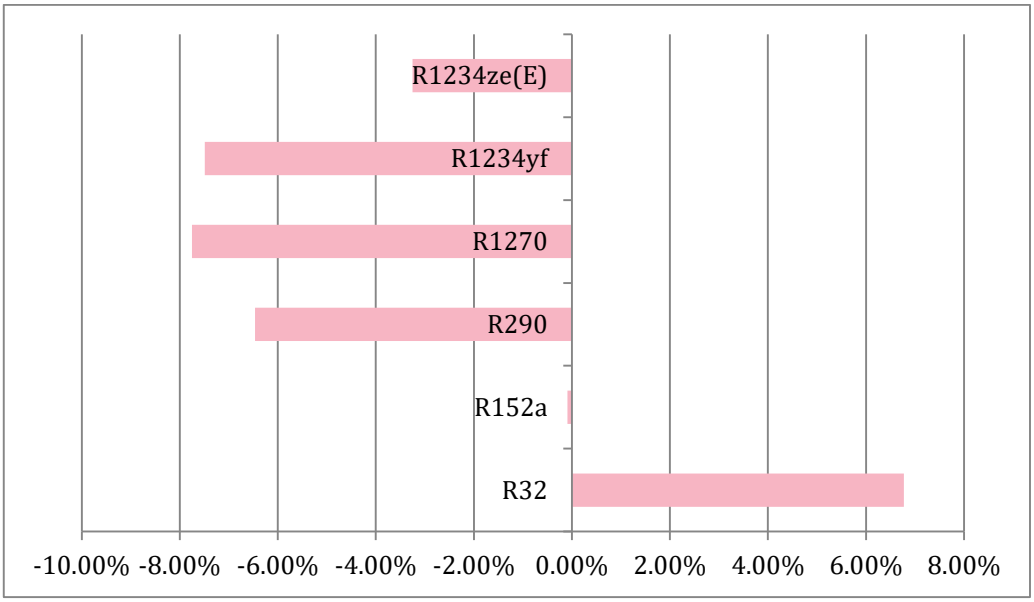

Figure 4.8. Relative differences (%) of SCOP compared to R410A (floor heating)

It is important to point out that the seasonal COP is highly dependent on the climate group region (colder, average, warmer). The results presented are only valid when applied to a colder region, such as Sweden.

4.5. Total equivalent warming impact (TEWI)

In order to evaluate the overall environmental performance of a refrigerant, considering both the direct effect (linked to GWP – effect of the refrigerant itself on the environment), and the indirect one (linked to SCOP – emissions linked to the power consumption of the heat pump), the TEWI parameter was calculated.

The results will be presented for both radiator and floor heating conditions according to the input data presented in section 3.3. Furthermore, a sensitivity analysis is conducted in order to investigate the influence of the main parameters characterising the system. In addition, results are shown for a CO_2 emission factor calculated as an average for the whole European grid.

4.5.1. Results

In **Error! Reference source not found.** the values calculated for Sweden in the case of radiator heating are shown. For the baseline R410A, the values are 5174.63 kg $_{CO2\text{-equivalent}}$ for radiator heating, and 4666.26 kg $_{CO2\text{-equivalent}}$ for floor heating.

It is evident that the Hydrocarbons, R290 and R1270, along with R1234yf and R1234ze(E) present an almost inexistent direct effect, due to the low GWP. The indirect effect, instead, doesn't show a major variation between the options.

In general, the reduction of TEWI compared to R410A is astounding. This is justified by the fact that Sweden has a very clean energy mix for energy production, and thus does not entail a large indirect effect. The lowest reduction is obtained by R32, with a reduction of 40.8%.

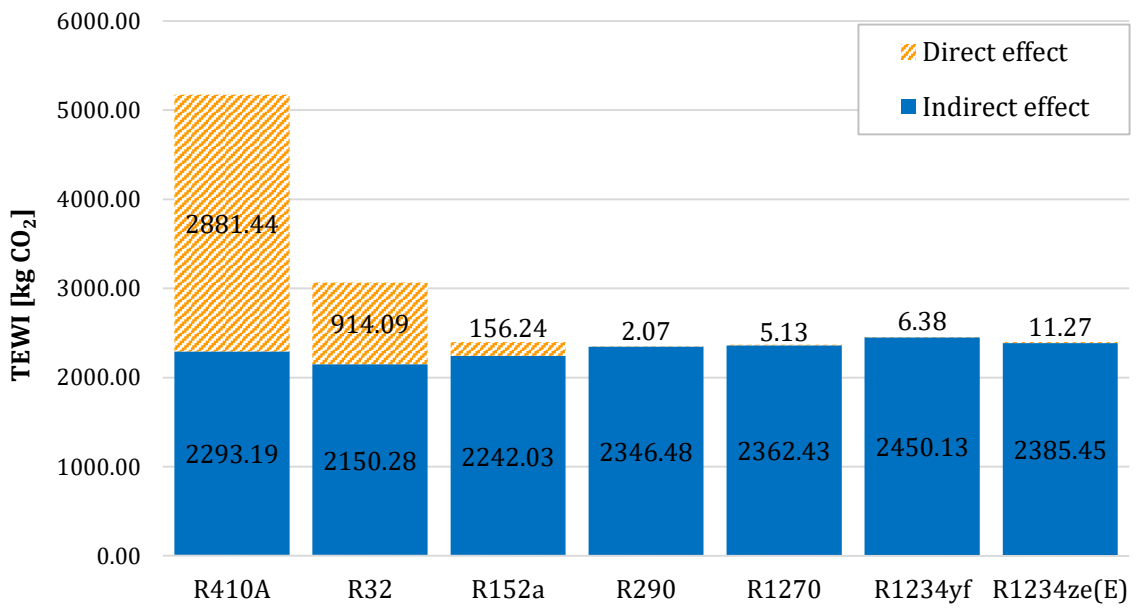

Figure 4.9. Figure 4.9. TEWI - Direct and indirect effect (radiator heating)

The HCs offer overall the lowest TEWI, thus the best environmental performance with reductions of 54.2% and 54.6% for R1270 and R290 respectively. They are closely followed by R1234yf and R1234ze(E) that register respectively -52.5% and -53.7%. Due to the good SCOP and the low GWP,

R152a also entails a good reduction, equal to 53.6%. The above mentioned values can be observed in Figure 4.10.

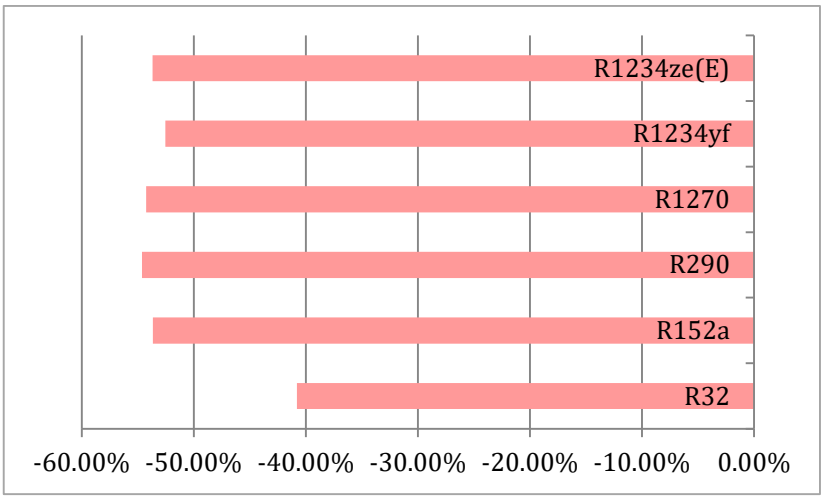

Figure 4.10. Relative difference (%) of TEWI compared to R410A (radiator heating)

In the case of floor heating the results can be seen in Figure 4.11. The pattern already observed in the radiator heating case is respected in this case already. Due to the overall higher SCOP values, the TEWI is generally lower thanks to a lower indirect effect. The direct effect is of course unchanged. Every refrigerant obtains a TEWI round 5-6% lower. The outcome can be seen in Figure 4.12.

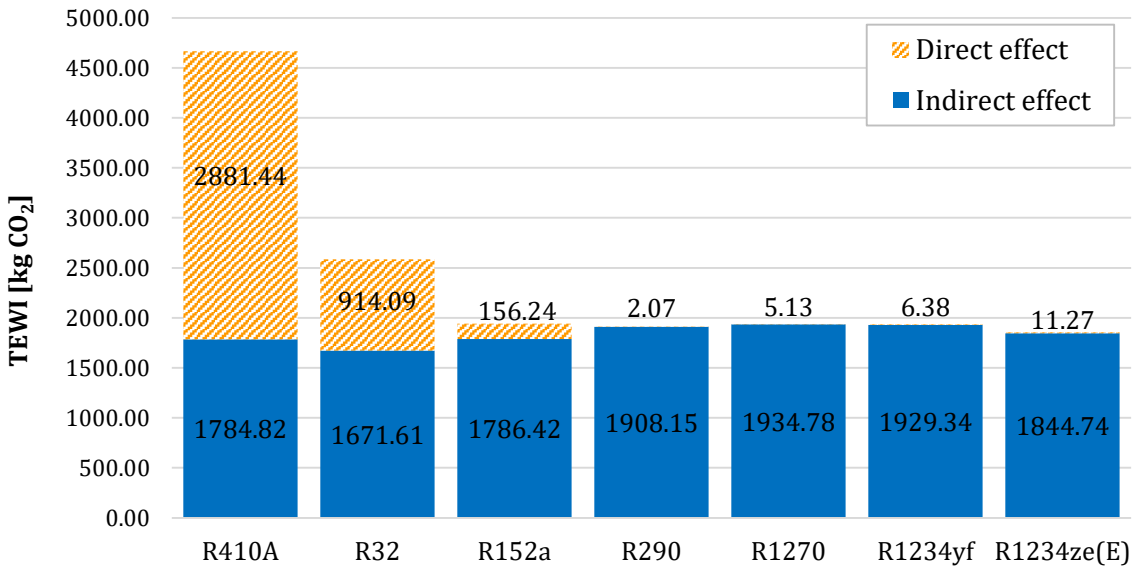

Figure 4.11. TEWI - Direct and indirect effect (floor heating)

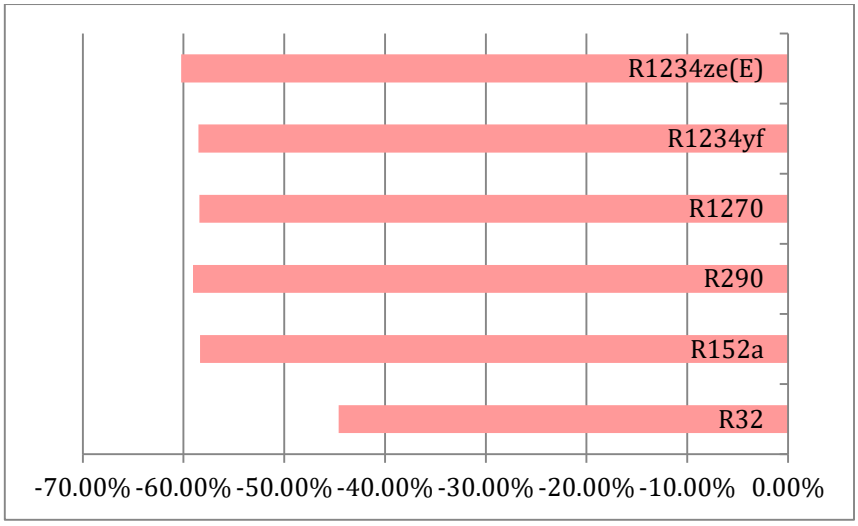

Figure 4.12. Relative differences (%) of TEWI compared to R410A (floor heating)

4.5.2. Sensitivity analysis

In order to evaluate the influence of the characteristics of the system on the TEWI, a sensitivity analysis was performed on three of the parameters: leakage rate, lifetime, and recovery factor.

Moreover, at the end of the section, the results will be shown while considering a different region of operation, and thus another CO_2 emission factor.

The outcome is here presented in the case of radiator heating. In fact, the behaviour of the floor heating results when modifying the parameters of the TEWI calculation is the same, and therefore does not provide any additional information.

- **Leakage rate**

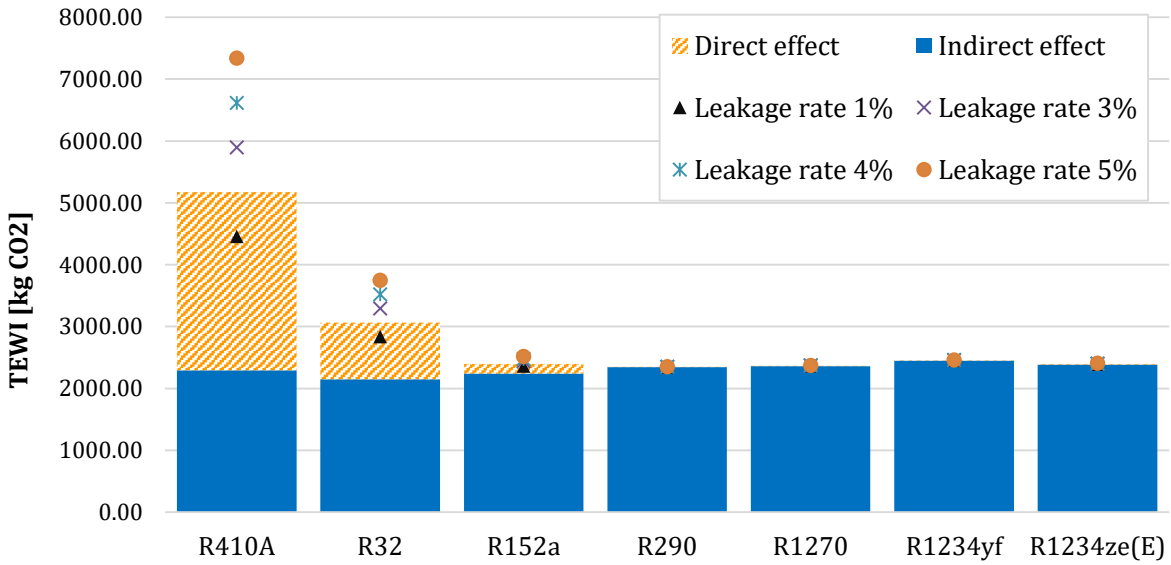

Figure 4.13. Leakage rate sensitivity analysis results on TEWI

The leakage rate, originally assumed at 2%, was varied between 1% to 5%, thus from a better to worse situation, and the results are shown in Figure 4.13. This parameter only affects the direct effect (2.1),

as it implies a dispersal of substance in the environment. Thus, only the refrigerants with significant GWP are influenced by its variation. The higher the GWP, the more pronounced are the consequences of a leakage increase. In the case of R410A, in fact, the TEWI can increase up to 41.8% for a leakage increase of 3 percentage points.

When considering the HCs and the HFOs, instead, an imperceptible variation is observed, being maximum 0.066%, 0.16%, 0.19% and 0.35% respectively for R290, R1270, R1234yf and R1234ze(E). This could represent a further advantage in the usage of such refrigerants, as the number of leakage checks could be reduced and thus the maintenance cost.

- **Lifetime**

The lifetime of the system was assumed to 15 years, and results are now presented for the range 10 – 20 years. It is evident that the longer the lifetime of the system, the higher the overall CO_2 emission. This factor, as seen in (2.1), is present in the calculation of both direct and indirect effect, but entails the major impact in the indirect one. Therefore, the range of values keeps approximately the same width for every refrigerant.

The HCs and HFOs, presenting a very close TEWI, involve a very close variation range, equal to averagely ±33%. R410A, R32 and R152a, as they have a slightly lower indirect effect (higher SCOP), show a lower range; ±24%, ±28% and ±32% respectively.

The outcome of the sensitivity analysis is found in Figure 4.14.

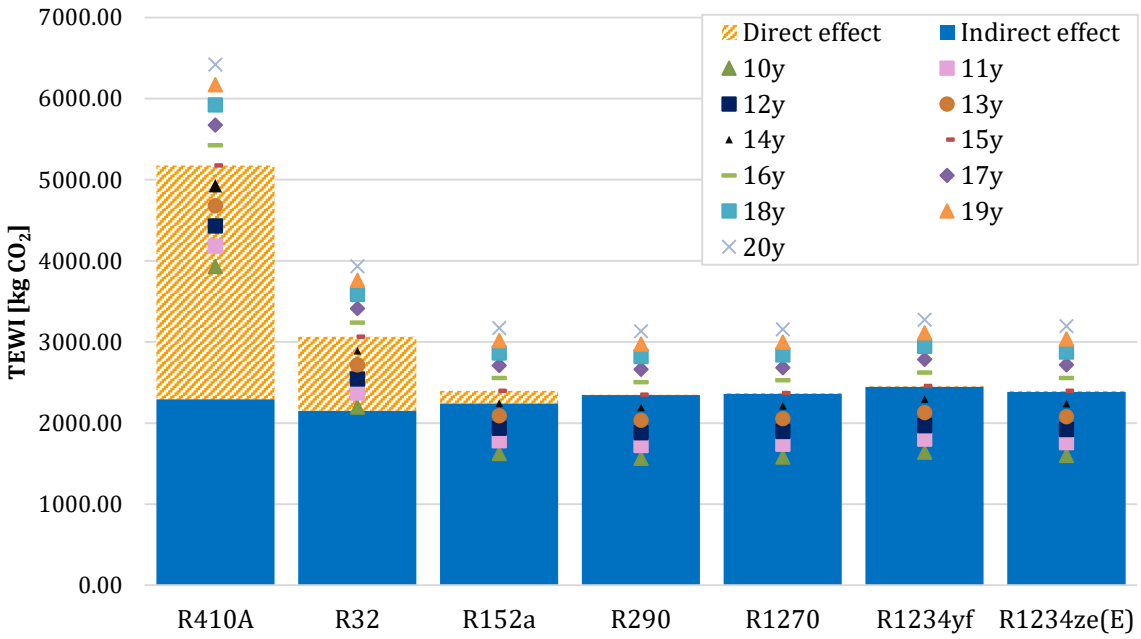

Figure 4.14. Lifetime sensitivity analysis on TEWI

- **Recovery efficiency**

The recovery factor is varied from 0.5 to 1, around the original value of 0.7, and the results are shown in Figure 4.15. It is evident that the higher the recovery efficiency, the lower the TEWI, as less refrigerant is lost in the environment at the decommissioning of the heat pump.

The considered parameter only influences the direct effect, thus a variation in the final TEWI value in only observable for the refrigerants with a significant GWP, increasing with increasing GWP. The maximum variation range is shown by R410A, evidently, and equals -27% to +18%. In the case of HCs and HFOs the range is below ±1%.

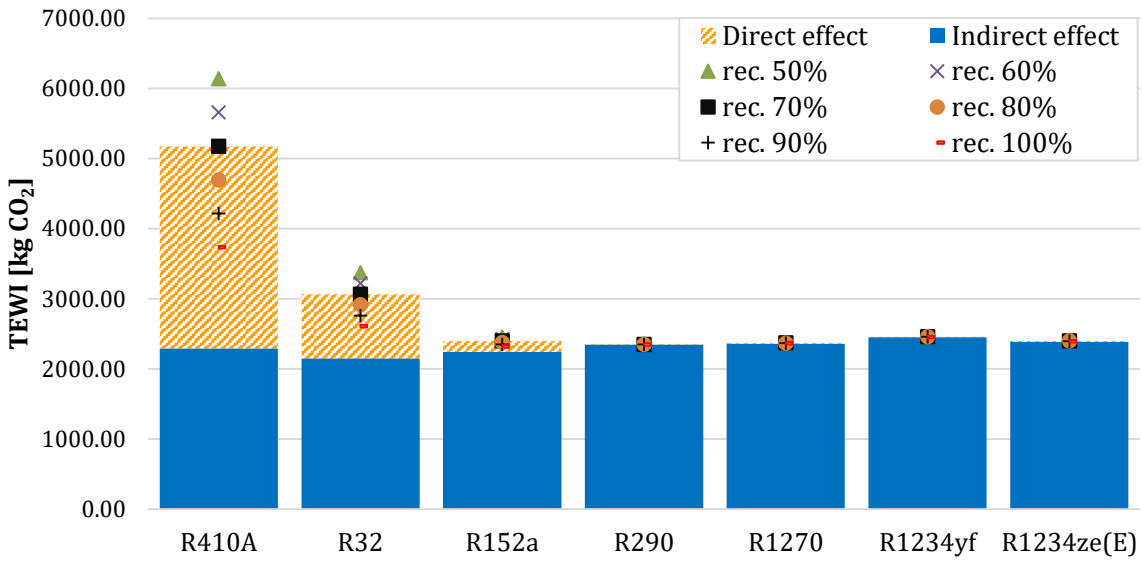

Figure 4.15. Recovery efficiency sensitivity analysis on TEWI

- **Emission factor**

All the results presented above are valid when considering a heat pump operating in Sweden, and thus exploiting electricity supplied from the Sweden energy mix. The CO_2 emission factor in that case was β=0.023 kg CO_2/kWh$_e$.

When evaluating TEWI with the emission factor for the European average, i.e. β=0.4261 (Itten, 2012), the outcome is as seen in Figure 4.16. It has to be noted that this value is bound to decrease in the future, and reach values more similar to the Swedish case; in fact the renewable energies' share keeps on increasing, hence implying an electricity production involving less GHG emissions. (Eurostat, 2015)

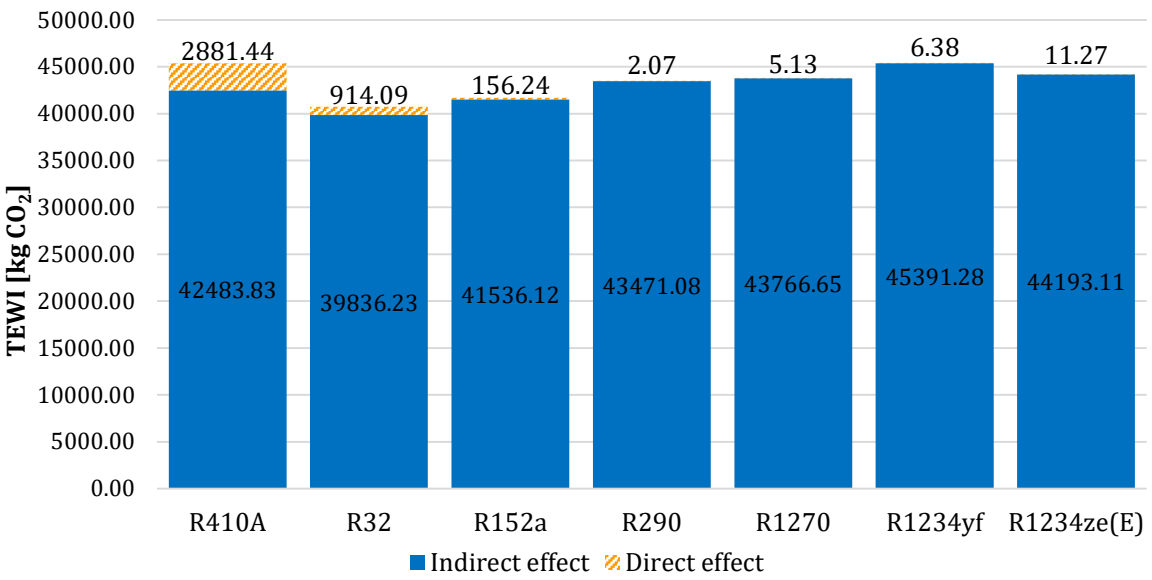

Figure 4.16. TEWI calculated with ENTSO-E grid average

The used β is calculated by the European Network of Transmission System Operator for Electricity (ENTSO-E), as an average value at the interconnection of all the major European grids.

While not affecting the direct effect of the refrigerants, the increase of the emission factor entails a dramatic increase in their indirect effect and thus in the overall TEWI. This provokes a levelling of the lifetime emission of the heat pump within the refrigerants. The major increases are experienced by the "most consuming" refrigerants, thus the ones with lower SCOP. Specifically, the HCs measure an increase of 1751% and 1748% for propane and propylene respectively. They are closely followed by the HFOs that augment of 1748% and 1744% for R1234yf and R1234ze(E) respectively.

4.6. Summary of results for each refrigerant

It is clear that there is no straightforward choice of one single refrigerant. Not only they cannot fulfil all the mentioned requirements at once, but the evaluation of performance also changes for the same refrigerant within the temperature range. This fact can be exemplified in Figure 4.17, where the whole range of operating conditions is represented in terms of relative difference of the VHC obtainable by a refrigerant versus the relative difference of COP, when compared to R410A that is thus placed at the intersection of the axes. This way, every point in the graph represents the VHC and COP at outdoor temperatures ranging from -22 °C to 16 °C.

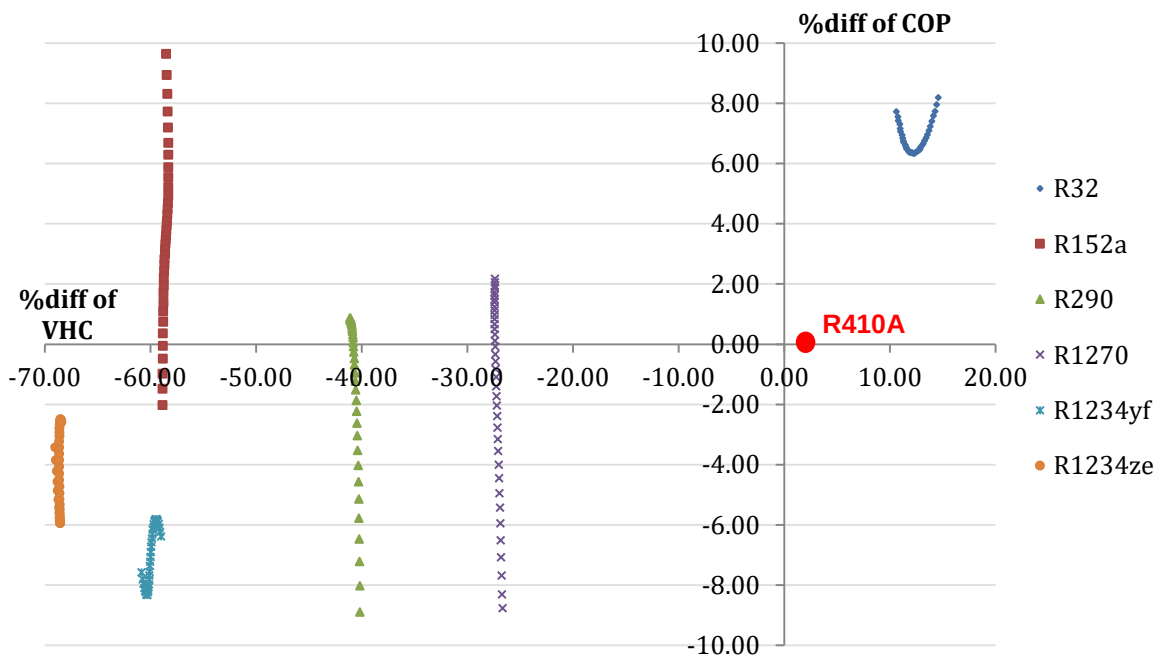

Figure 4.17. Relative difference (%) of COP vs. relative difference (%) of VHC compared to R410A at operating conditions corresponding to outdoor T ranging from -22 °C to 16 °C.

It can be observed that not all of the options maintain the same placement in the whole range of operation. Specifically, R32 is always in the up-right corner, thus always entailing a better COP and a better heat production than R410A. R1234yf and R1234ze(E) always belong to the bottom-left one instead, thus implying a lower COP and a lower VHC at every outdoor temperature evaluated.
Regarding the three other alternatives, R152a, R290 and R1270 though, the performance changes with varying operating condition, thus offering a better COP at the lowest temperatures but a worse one at the highest.
It is then evident that the optimal choice may vary greatly according to the climate area or the temperature range that is being considered.

Furthermore, as mentioned, no refrigerant fulfils all the ideal requirements at once. It is then fundamental to ponder both pros and cons of each alternative. In this concern, a summary of the main parameters that need to be considered is made in the following section. It comprises the discharge temperature, the COP and the VHC calculated at 0 °C (temperature with the highest occurrence), SCOP and TEWI factors on the overall heating season. The comparisons made are valid in a colder climate region, with a the Swedish emissions' factor of the energy mix and for a type of heating using radiators. Moreover, other relevant considerations regarding flammability and costs are made.

4.6.1. R32

Overall, at the evaluated conditions R32 offers a better performance than R410A in terms of COP, at every outdoor temperature. Moreover, the VHC is higher, thus entailing a possible smaller size of compressor.

On the other hand, the TEWI factor is subjected to the lowest reduction (when assuming a constant volumetric charge). Furthermore, at certain conditions the discharge temperature can reach level above the safety threshold set for the protection of the compressor. These outcome can be observed in Figure 4.18.

Flammability issues must also be kept into account, as R32 belongs to the A2L category. The system could then be required to comply with restrictions in terms of amount of charge and location of the heat pump. It has to be noticed that for the particular characteristics of this category, the limitations could be reduced in the future – differently than the 2 class

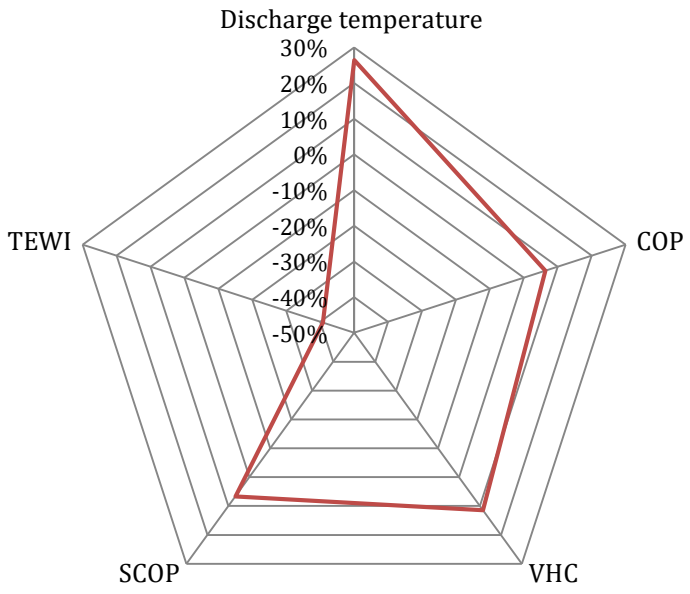

Figure 4.18. Summary of evaluated parameters for R32

4.6.2. R152a

The use of R152a results in an increase of the SCOP, when considering radiator heating applications, and a decrease in the TEWI bigger than in the case of R32. At the very low temperatures the discharge temperature is reduced compared to R410A, and the COP is increased, as seen in Figure 4.19. At the highest temperatures, instead, the refrigerant at the exit of the compressor reaches higher temperatures than R410A, though remaining below the safety limit. The COP worsen. Furthermore, the VHC is lower, thus implying the necessity of using more charge to obtain the same heating effect.

R152a is also flammable, thus requiring restrictions as in the previous case.

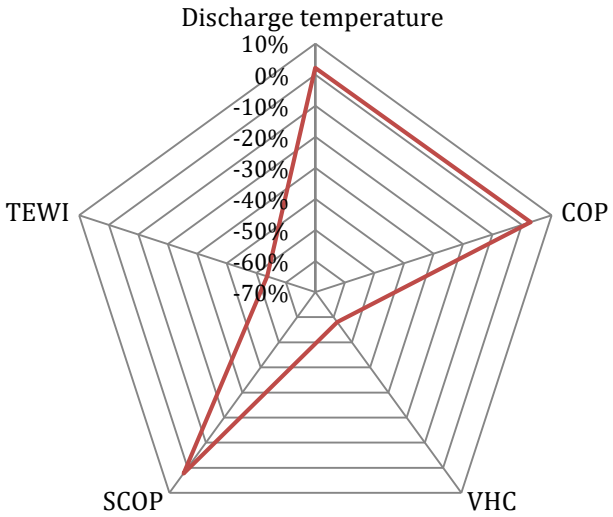

Figure 4.19. Summary of evaluated parameters for R152a

4.6.3. R290

The results for R290 are summarised in

Figure 4.20. Propane offers the overall lowest TEWI between the alternatives. This is mainly due to its much lower GWP, as the SCOP is subjected to a reduction thus implying a slightly higher indirect effect. The discharge temperatures are significantly lower than with R410A, which could benefit the compressor's lifetime.The considerably lower VHC would cause the use of higher charge if the heating capacity wants to be preserved.

At the lowest temperatures this hydrocarbon has a higher COP than R410A, but undergoes a decline along the temperature range; at the highest temperatures, it obtains the lowest COP.

Though, R290 is highly flammable and thus subjected to strict regulations in terms of charge quantity and location of the heat pump. This refrigerant can then be considered as optimal for smaller systems.

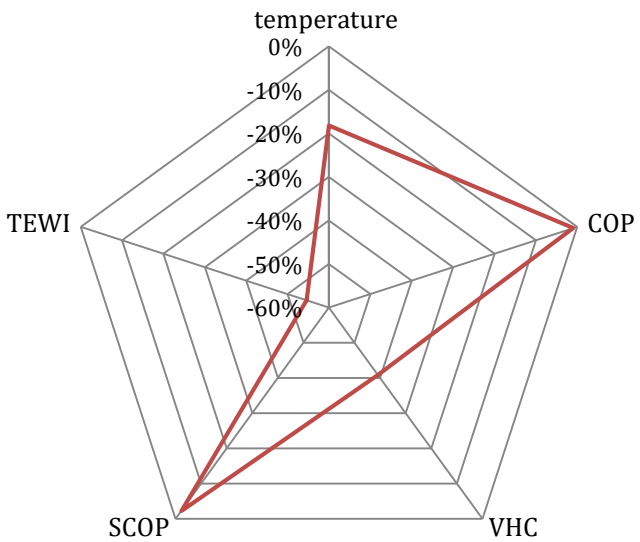

Figure 4.20. Summary of evaluated parameters for R290

4.6.4. R1270

The considerations on propylene are very similar to the ones made for propane, as it is evident when comparing

Figure 4.21 to the previous

Figure 4.20. The reduction in COP is comparable. Though, the heating capacity reduction from R410A is lower, as the volumetric heating capacity is higher. Between the two options therefore, R1270 can be seen as a better choice in terms of producible heat, or, if constant heating capacity, in terms of smaller charge needed. The discharge temperatures reached are generally slightly higher than with R290, but still well below the limit and R410A values.

This refrigerant is also highly flammable, and concerns can be raised on its chemical stability at high temperatures. It could then be seen as a better solution for restricted low temperature applications.

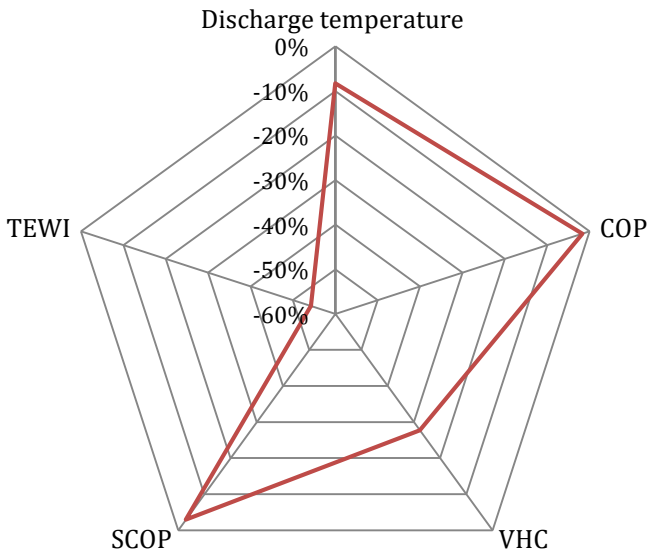

Figure 4.21. Summary of evaluated parameters for R1270

4.6.5. R1234yf

As can be observed in Figure 4.22, the use of R1234yf entails a reduction of all the parameters involved. The reduction in TEWI is remarkable, though as its SCOP is the lowest between the evaluated alternatives, its indirect effect is the highest one. The discharge temperature is also decreased when compared to R410A, bringing benefits to the compressor's lifetime.

The volumetric heating capacity is very low, so the same charge considerations seen previously can be applied in this case as well.

In addition, R1234yf belongs to the flammability category A2L, that in many countries' regulations is still considered equal to A2, thus requiring restrictions more severe than necessary.

Being a relatively new substance, moreover, its cost is still quite high.

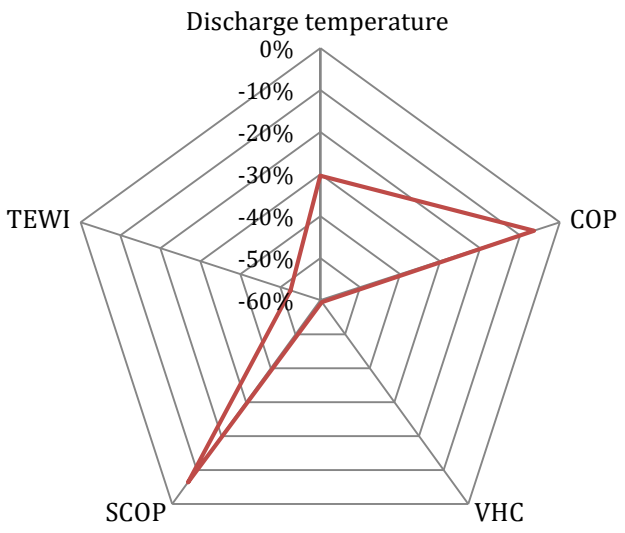

Figure 4.22. Summary of evaluated parameters for R1234yf

4.6.6. R1234ze(E)

R1234ze(E) has very similar performance as the previous R1234yf, as seen from Figure 4.23.

It can be noticed that its volumetric heating capacity is even lower, thus putting more strain on the size of the system. Its COP is generally higher than the other HFO, and therefore the final TEWI is comparable to the HCs' result. Regarding the flammability, the same comment as for R1234yf can be made.

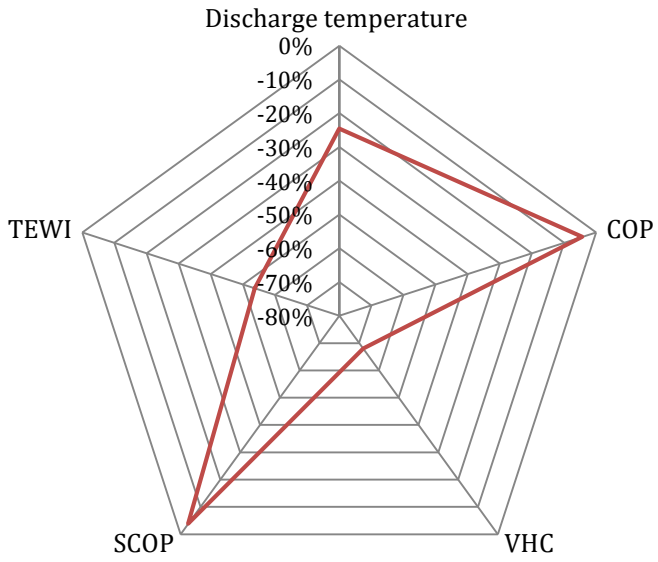

Figure 4.23. Summary of evaluated parameters for R1234ze(E)

5. Conclusions and further work

As a result of the F-gas regulation implemented in 2015, the refrigeration industry has to move towards the reduction of its contribution to the emissions of fluorinated gases, as they have a non neglectable role in the global warming. To contribute to this effort, this work investigates possibile alternatives to R410A, currently in usage in commerically avaliable heat pump, typically used in a single house in Sweden. Eight options were identified, six of which were analysed in the model created, namely R32, R152a, R290, R1270, R1234yf and R1234ze(E). The study of the remaining two, i.e. R450A and R513A, is postponed to a second phase, as the data available was no sufficient to perform a valid comparison.

The most relevant results considered in the scope of this study were obtained for both radiator and floor types of heating systems and consist of:

- the VHC, in the temperature range -22 °C to 16 °C
- the COP of the heat pump, in the temperature range -22 °C to 16 °C
- the discharge temperature, in the temperature range -22 °C to 16 °C
- the SCOP, for the overall heating season
- the TEWI factor

It is important to understand that the results obtained are highly dependent on the area for which they have been calculated, namely Sweden – colder climate scenario, and low CO_2 emission factor of the national energy mix. Therefore, the conclusion drawn from this study are only valid in the mentioned specific climatic characteristics.

The performance of the heat pump with the alternative refrigerants, as seen through the COP, was variable. At the lowest temperatures, R410A presents a lower COP than R32, R152a and both the HCs (up to -7 °C). With the increasing outdoor temperature, the baseline performance improves but remains poorer than R32 along the whole temperature range (8.19% and 7.72% relative difference respectively at -22 °C and 16 °C). The worst COPs were shown by the HFOs.

The overall highest SCOP was thus given by R32 (+6.46% for radiator, +6.77% for floor heating), outperforming R410A in both radiator and floor heating cases. R152a also presented positive outcome, having a higher SCOP than R410A in radiator heating case (+2.28%), and an almost identical one in the floor heating case (-0.089%). The other options entailed lower seasonal performances, with the worst result obtained by the HFOs (and in particular R1234yf with -6.4%).

When evaluating the overall environmental impact of the refrigerants, through TEWI a general reduction of CO_2 equivalent emissions is calculated. Whereas the indirect effect is similar for every option considered – slightly increasing with decreasing SCOP – the direct effect is drastically reduced with the decrease of the GWP. In fact, both the HCs and the HFOs obtain a remarkable reduction of the TEWI factor (in order for R290, R1270, R1234ze(E) and R1234yf: -54.6%, -54.2%, -53.7%, -52.5%), in accordance to their extremely low GWP. The lowest emissions' reduction is obtained by R32 (-40.8%), which, in spite of an improved performance in the machine, still has a considerable GWP.

Moreover, the reaching by R32 of discharge temperatures above the safety limit cannot be neglected, as it could endanger the compressor's functioning. On the other hand, this drawback could be mitigated by the use of a smaller refrigerant charge. In fact, R32 presents a higher VHC when compared to R410A (+12.4%). The other evaluated options all present a lower one, with the biggest reduction owned by the HFOs.

The interpretation of these results and the selection of a most favourable option is then closely related with the direction that the manufacturer wants to take. If the preference is to keep a certain heating capacity, R32 offers the possibility of using smaller charge and thus smaller systems. This way, the final result in the TEWI evaluation would be a further reduction, due to a smaller direct effect. Furthermore, if the aim is to reduce the CO_2 as much as possible, the HFOs and the HCs represent a better option in a country with a high share of renewable, clean energies and thus a small CO_2 emission factor.
It is also paramount to keep into consideration the different flammability levels of the refrigerants. None of the options evaluated in this study are non-flammable, and thus they all require some restrictions in their use, e.g. charge limitations, location of the installation restrictions. HCs are the most subject to limitations, as they belong to the A3 – high flammability – category. R32, R1234yf and R1234ze(E) belong to the A2L category. As of today, regulations do not differentiate between A2L and A2 levels. This situation could be modified in the near future, representing an advantage for these three refrigerants, as it would mean less strict limitations in use.
In this concern, the two remaining options that could not be evaluated at this stage – R450A and R513A – present the advantage over the other refrigerants as they are not flammable.

In order to further this Thesis' work, future steps will aim at integrating the two refrigerants that were left out in this first phase, i.e. R450A and R513A, and at improving the existing model.
Specifically, the first task can easily be performed once valid compressor's models exist for the the two refrigerants; in order for the results to be included in the presented report and compared with the other alternatives, the correlation for the compressor needs to be obtained in the same way as for all studied fluids. This information was not available at this time.
Secondly, a few aspects can be treated in order to enhance the model created. In particular, the UAs model can be improved by elaborating correlations from a wider range of experimental data. Moreover, some of the compressor's isentropic efficiency correlations (R32 and R1234ze(E)) were not available, and thus had to be assumed by similarity with other refrigerants. With more precise information, more accurate efficiencies in these two cases can be integrated.
Lastly, detailed recommendations can be elaborated with deeper knowledge of the preferences of the manufacturing company. Combining them with the restrictions imposed by the Standard EN378, an accurate set of operating conditions to be respected, and consequently an improved calculation of the CO_2 emissions' reduction, can be provided.

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Appendix

- EES code -

It has to be noted that in the code in EES the nomenclature is a bit different that in the theory section. Specifically:

- **1' is 1.5**
- **3' is 3.35**
- **3'' is 3.7**

```
"Input data" {-----------------------------------------------------------------------------------------------------------------}
{m_dot_water}          {input in parametric table, from experimental data Thermia}
{m_dot_brine}          {input in parametric table, from experimental data Thermia}
{rho_water}            {input in parametric table, from experimental data Thermia}
{cp_water}             {input in parametric table, from experimental data Thermia}
{rho_brine}            {input in parametric table, from experimental data Thermia}
{cp_brine}             {input in parametric table, from experimental data Thermia}
{delta_T_sub}          {input in parametric table, from experimental data Thermia}
{delta_T_sup}          {input in parametric table, from experimental data Thermia}
{T_brine_in=0}         {input in parametric table, from Standard}

V_dot_water=m_dot_water/rho_water                    {m^3/s}
V_dot_water_per_hour=V_dot_water*3600
V_dot_brine=m_dot_brine/rho_brine                    {m^3/s}
V_dot_brine_per_hour=V_dot_brine*3600

T_water_out=0.0036*T_amb^2-0.8342*T_amb+38.391                {Radiator heating}
{T_water_out=0.0007*T_amb^2-0.3233*T_amb+27.579}              {Floor Heating}

Rho_1=Density(R410A,h=h_1,P=P_evap)
Rho_1.5=Density(R410A,x=1,P=P_evap)
Rho_2=Density(R410A,h=h_2,P=P_evap)
Rho_m=(Rho_1+Rho_2)/2
Rho_3=Density(R410A,h=h_3,P=P_cond)
Rho_3.35=Density(R410A,x=1,P=P_cond)
Rho_3.7=Density(R410A,x=0,P=P_cond)
Rho_4=Density(R410A,h=h_4,P=P_cond)

{Cp_1=Cp(R410A,h=h_1,P=P_evap)}
Cp_1.5=Cp(R410A,x=1,P=P_evap)
Cp_2=Cp(R410A,h=h_2,P=P_evap)
Cp_3=Cp(R410A,h=h_3,P=P_cond)
```

```
Cp_3.35=Cp(R410A,x=1,P=P_cond)
Cp_3.7=Cp(R410A,x=0,P=P_cond)
Cp_4=Cp(R410A,h=h_4,P=P_cond)

mu_1.5=Viscosity(R410A,x=1,P=P_evap)
mu_2=Viscosity(R410A,h=h_2,P=P_evap)
mu_3=Viscosity(R410A,h=h_3,P=P_cond)
mu_3.35=Viscosity(R410A,x=1,P=P_cond)
mu_3.7=Viscosity(R410A,x=0,P=P_cond)
mu_4=Viscosity(R410A,h=h_4,P=P_cond)

k_1.5=Conductivity(R410A,x=1,P=P_evap)
k_2=Conductivity(R410A,h=h_2,P=P_evap)
k_3=Conductivity(R410A,h=h_3,P=P_cond)
k_3.35=Conductivity(R410A,x=1,P=P_cond)
k_3.7=Conductivity(R410A,x=0,P=P_cond)
k_4=Conductivity(R410A,h=h_4,P=P_cond)

VHC=Rho_2*(h_3-h_4)                                    {Volumetric heating capacity}

"Thermodynamic cycle" {-----------------------------------------------------------------------------------------------------}

T_3.35=Temperature(R410A,P=P_cond,x=1)                 {temp of refrigerant on the saturated vapour
line on the condensation pressure line}
T_3.7=Temperature(R410A,P=P_cond,x=0)                  {temp of refrigerant on the saturated liquid
line on the condensation pressure line}
T_1=Temperature(R410A,P=P_evap,h=h_1)                  {inlet of evaporator, outlet of expansion
valve}
T_2=T_evap+delta_T_sup                                 {inlet of compressor, outlet of evaporator
(after superhating)}
T_3=Temperature(R410A,P=P_cond,h=h_3)                  {outlet of compressor, inlet of condenser}
T_4=T_cond-delta_T_sub      {outlet of condenser, inlet of expansion valve}

h_1=h_4                                                {isenthalpic expansion}
h_1.5=Enthalpy(R410A,P=P_evap,x=1)
h_2=Enthalpy(R410A,T=T_2,P=P_evap)
{h_3=Enthalpy(R410A,T=T_3,P=P_cond)}                   {calculated with isentropic efficiency of
compressor}
h_3.35=Enthalpy(R410A,P=P_cond,x=1)
```

h_3.7=Enthalpy(R410A,P=P_cond,x=0)

h_4=Enthalpy(R410A,T=T_4,P=P_cond)

s_2=Entropy(R410A,T=T_2,h=h_2)

h_3_is=Enthalpy(R410A,s=s_2,P=P_cond)

eta_is=(h_3_is-h_2)/(h_3-h_2)

"Temperature differences for the calculation of LMTDs for the UAs of the evaporator and condenser in single and two phase condition"

delta_T_brine_evap= T_brine_0.5-T_brine_out {T brine 0.5 is the temperature of the brine on the saturated vapour line, dividing evaporation and superheating of the refrigerant corresponding to T1.5, Tbrine out is the outlet temp of brine corresponding to T1}

delta_T_brine=T_brine_in-T_brine_out {Total Temperature difference over the evaporater on the brine side}

delta_T_water_des=T_water_out-T_water_0.35 {T water 0.35 is the temperature of the water on the saturated vapour line, corresponding to T3.35, T water out is the outlet temperature of the water, corresponding to T3}

delta_T_water_cond=T_water_0.35-T_water_0.7 {T water 0.7 is the temperature of the water on the saturated liquid line, corresponding to T3.7}

{delta_T_water_sub=T_water_0.7-T_water_in} {T water in is the inlet temperature of the water, corresponding to T4}

delta_T_water=T_water_out-T_water_in {Total Temperature difference over the condenser on the water side}

P_cond=Pressure(R410A,T=T_cond,x=1) {pressure on the high pressure side of the cycle}

P_evap=Pressure(R410A,T=T_evap,x=0) {pressure on the low pressure side of the cycle}

P_ratio=P_cond/P_evap {pressure ratio}

omega_comp = (3000/60) {speed of the compressor is fixed}

V_dot_swept= 0.001925 {m^3/s , as calculated from compressor data sheet from Copeland select online, 6.93 m^3/h, 50 Hz which is 3000 rpm}

"Cycle components:" {----------}

"Evaporator"

UA_sup=22.24649-253.989*k_1.5-298.449*k_2-1511947*mu_1.5-284923*mu_2-2.23844*Rho_1.5-0.45872*Rho_2+0.109339*P_evap

UA_evap=323.0086+19158.80422*k_1.5-49773038.92*mu_1.5+88.612*m_dot_ref+0.479561316*T_evap

"Two phase evaporation stage, between T1 and T1.5" {----------}

delta_evap_in= T_brine_0.5-T_evap

delta_evap_out=T_brine_out-T_evap

(delta_evap_in/delta_evap_out)=exp((delta_evap_in-delta_evap_out)/LMTD_evap)

Q_dot_evap=m_dot_ref*(h_1.5-h_1)

Q_dot_evap=m_dot_brine*cp_brine*delta_T_brine_evap

Q_dot_evap=UA_evap*LMTD_evap

"Single phase superheating stage, from T1.5 to T2" {----------}

delta_sup_in= T_brine_in-T_2

(delta_sup_in/delta_evap_in)=exp((delta_sup_in-delta_evap_in)/LMTD_sup)

Q_dot_sup=m_dot_ref*(h_2-h_1.5)

Q_dot_sup=m_dot_brine*cp_brine*delta_T_brine_sup

Q_dot_sup=UA_sup*LMTD_sup

Q_dot_2=Q_dot_evap+Q_dot_sup {Cooling capacity}

COP_2= Q_dot_2/E_dot_comp

"Condenser" {----------}

UA_des=-2.6208+2.4611*m_dot_ref+287997*mu_3.35-0.0372*T_cond

UA_cond=124.1568724-1092.001679*k_3.7-0.791741052*T_cond-69.6615*m_dot_ref

UA_sub=-450.716+2941.455*k_3.7-1005.03*k_4+0.026945*P_cond+ 705593.4*mu_4+

0.105813*Rho_3.7+1.520151*T_cond-30.3314*m_dot_ref

"Single phase desuperheating stage, from T3 to T3.35" {----------}

delta_des_in=T_cond-T_water_0.35

delta_des_out= T_3-T_water_out

(delta_des_in/delta_des_out)=exp((delta_des_in-delta_des_out)/LMTD_des)

Q_dot_des=m_dot_water*cp_water*delta_T_water_des

Q_dot_des=UA_des*LMTD_des

{Two phase condensation stage from T3.35 to T3.7} {----------}

delta_cond_in=T_cond-T_water_0.7

(delta_cond_in/delta_des_in)=exp((delta_cond_in-delta_des_in)/LMTD_cond)

```
Q_dot_cond=m_dot_ref*(h_3.35-h_3.7)
Q_dot_cond=m_dot_water*cp_water*delta_T_water_cond
Q_dot_cond=UA_cond*LMTD_cond

{Single phase subcooling stage from T3.7 to T4} {-----------------------------------------------------------------}
delta_sub_in=T_4-T_water_in
(delta_sub_in/delta_cond_in)=exp((delta_sub_in-delta_cond_in)/LMTD_sub)

Q_dot_sub=m_dot_ref*(h_3.7-h_4)
Q_dot_sub=m_dot_water*cp_water*delta_T_water_sub
Q_dot_sub=UA_sub*LMTD_sub

Q_dot_1=Q_dot_des+Q_dot_cond+Q_dot_sub                    {heating capacity}
COP_1=Q_dot_1/E_dot_comp

"Compressor" {-------------------------------------------------------------------------------------------------------}
eta_is=0.0024*P_ratio^3-0.0363*P_ratio^2+0.1377*P_ratio+0.5531
eta_s=0.0015*P_ratio^2-0.0356*P_ratio+1.0583
rho_ref_2=Density(R410A,h=h_2,P=P_evap)          {density of refrigerant at inlet of compressor}
m_dot_ref=rho_ref_2*V_dot_swept*eta_s
E_dot_comp=m_dot_ref*(h_3-h_2)                   {Total power input to the compressor}

delta_P=((m_dot_ref/0.00018727)^2)/(2*Rho_1)*((1-1.4829^2+(0.42*(1-1.4289^2)^2))+
4*1.2028*(Rho_1/Rho_m)+2*(Rho_1/Rho_2-1)-((1-0.51074^2-(1-0.51074)^2)*(Rho_1/Rho_2)))

"SCOP calculation"  {-------------------------------------------------------------------------------------------------}
heating_season_tot= 6446
COP_partial=COP_1*hj/heating_season_tot
SCOP=SumParametric('SCOP_Rad','COP_partial')
SCOP=SumParametric('SCOP_Floor','COP_partial')
```