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TRI-HP – Heat Pump Systems for Heating and Cooling with Photovoltaic and Natural Refrigerants ¹

Abstract

TRI-HP is a research and development project within the European research and innovation action "Horizon 2020", aiming at the development and demonstration of flexible energy-efficient and affordable trigeneration systems. Based on natural refrigerant heat pumps with advanced controls, the systems allow for three heat sources: solar, ground, and ambient air. They are coupled with renewable electricity generators (PV), using cold (ice slurry), heat and electricity storages to provide heating, cooling, and electricity to residential buildings.

Different heat pumps with propane and carbon dioxide have been developed and manufactured. These heat pumps have been already tested at component level and very soon will be tested within a complete system. Results of the ice-slurry-heat pumps built and tested are presented in this paper.

Zusammenfassung

TRI-HP ist ein Forschungs- und Entwicklungsprojekt innerhalb des EU-Förderprogramms für Forschung und Innovation "Horizont 2020" mit dem Ziel, flexible, energieeffiziente und erschwingliche Kraft-Wärme-Kälte-Kopplungssysteme zu entwickeln. Basierend auf Wärme-pumpen mit natürlichem Kältemittel und fortschrittlicher Steuerung ermöglichen sie drei Wärmequellen: Solar, Erdreich und Umgebungsluft. Sie sind mit erneuerbarer Stromerzeugung (PV) gekoppelt und nutzen Kälte (Eisbrei), Wärme und Stromspeicher, um Wohngebäude mit Wärme, Kälte und Strom zu versorgen.

Verschiedene Wärmepumpen mit Propan und CO₂ wurden entwickelt und hergestellt. Diese Wärmepumpen sind als Komponenten ausgemessen worden und werden demnächst innerhalb eines gesamten Systems geprüft. Dieser Bericht zeigt Ergebnisse der bereits gebauten und getesteten Eisbrei-Wärmepumpen.

¹ Wärmepumpensysteme zum Heizen und Kühlen mit Photovoltaik und natürlichen Kältemitteln

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Introduction

Heat pumps are known to offer an efficient way to reduce greenhouse gas emissions caused by heating and cooling. According to the IEA, the stock of installed heat pumps must rise from 180 million units today to 600 million in 2030 worldwide to be in line with the scenario of net zero emissions by 2050 [1]. With 1.6 million units sold in Europe alone, the current heat pump stock amounts to nearly 15 million units while sales grew by 7.4 % in 2020 [2], confirming current and future potential towards sustainability.

Direct greenhouse gas emissions need to be tackled by using natural refrigerant with very low global warming potential such as R290 and R744. Synthetic refrigerants such as HFC (hydrofluorocarbons) or HFO (hydrofluorolefine) should be replaced by natural options due to their high global warming potential and problematic decomposition products such as TFA (trifluoroacetic acid), which is very stable and remains in water bodies as an anthropogenic component, contrary to the TFA that exist naturally [3].

Heat pumps are supported by declining cost of PV systems increasing the renewable and onsite share use. In many residential applications, the natural refrigerants, e.g. CO₂ and propane, offer equal or slightly better energy efficiency compared to currently used synthetic refrigerants. Heat pumps capable of supplying hot water at 65 °C or more, as mostly seen with natural refrigerants, can cover market segments of space heating and domestic hot water supply due to their physical properties for both, new and renovated buildings. Also, solar ice-slurry systems can offer a renewable alternative where ground, water reservoirs or air cannot serve as heat source because of noise, special restrictions or ground regulations. In those systems, solar energy is used to regenerate the ice-slurry storage that serves as heat source for the heat pump.

Three different heat pumps with natural refrigerants have been developed and built for residential applications. Some results of the developed and tested heat pump prototypes are presented hereafter together with a brief overview of some elements of the TRI-HP project as part of the research and innovation action Horizon 2020.

TRI-HP in a nutshell

The overall goal of the TRI-HP project is the development and demonstration of flexible energy-efficient and affordable trigeneration systems ("tri" standing for heating, cooling and electricity). The systems are based on electrically driven natural refrigerant heat pumps coupled with renewable electricity generators (photovoltaics), using cold (ice slurry), heat and electricity storages to provide heating, cooling and electricity to multi-family residential buildings with an on-site renewable share of 80 %. The systems developed include advanced controls, managing electricity, heat and cold in a way that optimizes the performance of the system and increases its reliability via failure self-detection.

The innovations proposed aim at reducing the system cost by at least 10 - 15 % compared to current heat pump technologies with equivalent energetic performances. Flexibility is achieved by allowing for three heat sources: solar (with ice/water as storage medium), ground and ambient air.

Two natural refrigerants with very low global warming potential, propane, and carbon dioxide, are used as working fluids for adapted system architectures that specifically target the different heating and cooling demands across Europe. The newly developed trigeneration systems will find application in both new and refurbished multi-family buildings, allowing to cover a major part of Europe's building stock and reduce GHG emissions by 75 % compared to gas boilers and air-cooled chillers. The TRI-HP project provides the most appropriate knowledge and technical solutions to cope with stakeholder's needs (e.g., end-users, installers, investors, architects, engineering offices), building demand characteristics, local regulations (e.g., relating to ground/water protection or GHG refrigerant emissions), and social barriers (e.g., aesthetics, noise, confidence). Two system concepts are developed for two different combinations of heat sources:

- a) dual ground/air source and
- b) solar with ice-slurry as intermediate storage

Three complete systems are being developed and tested in the laboratory using a hardware-inthe-loop system test:

- dual-source with propane heat pump (tested at IREC in Spain)
- solar ice-slurry with CO₂ heat pump (tested at SPF in Switzerland)
- solar ice-slurry with propane heat pump (tested at SPF in Switzerland)

Figure 1 shows the dual system where ground and air serve as heat source and heat sink with a reversible heat pump. This system is targeting South European climates with needs of active heating and cooling.

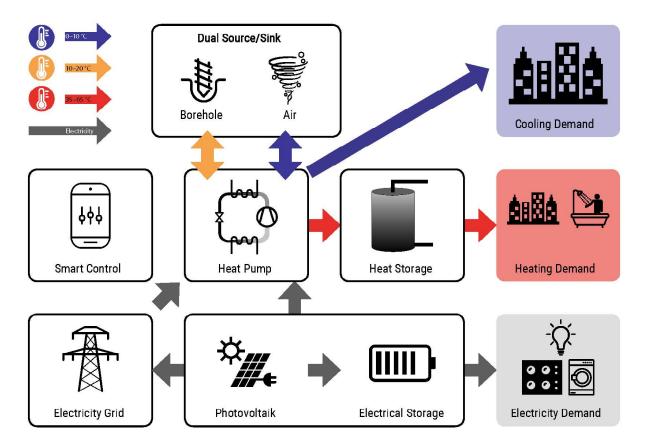


Figure 1: dual-source system developed with ground and air as renewable heat source

Figure 2 illustrates a solar ice-slurry system combined with solar thermal collectors. This system is targeting Central European climates with large heating demands with free-cooling as add-on feature.

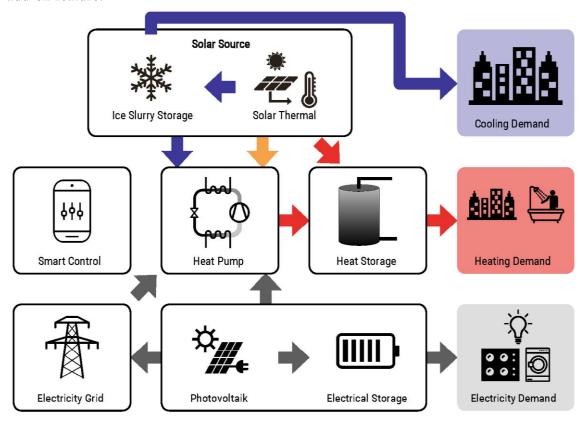


Figure 2: slurry-ice system developed with solar as renewable heat source

TRI-HP systems target many areas of international objectives to reduce energy use and green-house gas emissions in general. Amongst others, they also cover the demand for building retrofitting solutions, monitoring tools and highly performant renewable technologies, cost reduction, new materials and cross-cutting heating and cooling technologies for buildings. Key innovative results from TRI-HP are presented in following. The technical readiness level (TRL) of most of the systems and components are increased from level 3/4 to level 5/6.

- Heat exchanger developments (all finished):
 - A tri-partite gas cooler for CO2 that allows to produce SH and DHW simultaneously with an increase of efficiency of X % respect to current gas coolers.
 - Double source/sink heat exchangers for a propane heat pump with direct exchange between heat transfer fluids (air and glycol/water)
 - Evaporators able to supercool water up to 3 4 K in a controlled steady state environment thanks to icephobic coatings
- Heat pump developments (all finished):
 - A propane heat pump with supercoolers able to supercool water by at least 2 K in real working conditions
 - A CO₂ heat pump with supercoolers and a tri-partite gas cooler able to supercool water by at least 2 K in real conditions and produce simultaneous SH and DHW with a COP of X
 - A dual source/sink propane heat pump able to use simultaneous air and ground heat sources

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- Control strategies:
 - Self-detecting algorithms for heat pump faults
 - An advance energy management system (AEMS) using model predictive control that reduces the energetic cost by 15 - 20 % using variable electricity prices and optimizing operation of energy flows
- Complete tri-generation systems (hardware-in-the-loop system test ongoing):
 - A solar ice-slurry system using solar thermal collectors, a propane heat pump
 - A solar ice-slurry system using solar thermal collectors, a CO2 heat pump and PV to achieve 80 % on on-site renewable share. Use of the AEMS and comparison with rulebase-control
 - A dual source/sink propane heat pump system for borehole/air heat sources targeting a borehole length reduction of 50 %
 - All systems make use of PV and electrical batteries and target to achieve 80 % on onsite renewable share
- Recommendations on user needs and stakeholder's acceptance

The TRI-HP project is led by SPF (OST) in Rapperswil and involves 12 partners from 7 different European countries (Switzerland, Spain, Sweden, Germany, Norway, Denmark and Belgium). Among the partners there are research institutes and universities summing up to a total of seven R&D partners (SPF-OST, TECNALIA, IREC, ISOE, NTNU, DTI, IKKU), two SMEs (HEIM, ILAG), a large industry partner (ALFA LAVAL), and a NGO (REHVA). TRI-HP brings a multidisciplinary consortium together and covers the whole value chain with strong scientific, technological and manufacturing skills, strengthened by societal expertise. The research institutes and universities are some of the most well recognized institutes in the fields.

Application of ice-slurry systems

TRI-HP provides a system solution for heating, cooling and electricity generation with an on-site renewable share of 80 %. For building owners, this poses a new option to replace carbon-intensive heating and cooling systems by newer ones to adapt their buildings to changing political and regulatory framework conditions.

The solar ice-slurry concept is a particular case of solar-ice system which is based on using solar thermal collectors as the only source for the heat pump. If the sun shines or the ambient temperature is not too low, solar collectors act as a direct source for the heat pump. During cold nights or days with low irradiation, when the low-grade energy from the solar collectors is insufficient to run the heat pump directly, the ice storage is used as a temporary heat source. The ice storage can store low-grade heat from solar collectors with a high volumetric storage capacity, increasing the solar energy yield by a factor of two compared to a solar system without an ice storage.

Among the renewable technologies, solar energy systems and ground source heat pumps appear as the most preferred and reliable options. Among them, ice-slurry systems offer an attractive option to replace oil- or gas fired heating systems in general. Specifically, they are particularly appealing for the use in multi-family-buildings for several reasons: medium sized and big buildings are more likely to be in densely populated areas where the application of an air-to-water heat pump is problematic because of noise. Likewise, space is often limited for installing an outdoor unit. Both challenges are avoided with an ice-slurry system as the ice storage will only

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occupy a little footprint while being flexible in shape. The surface required for the solar collectors generally is available.

Energetic simulations and cost estimations have shown that a solar ice-slurry system with 1.5 m^2 of collector area and 1 m^3 of ice storage volume per MWh of heat demand can reach system performance factors and heat generation costs comparable to ground source heat pump systems.

Heat pumps with natural refrigerants

After studying the state-of-the-art of heat pumps with natural refrigerants, refrigeration and hydraulic layouts were defined. Three different heat pumps with a nominal heating capacity of 10 kW have then been designed and manufactured as summarized in Table 1.

	heat pump 1	heat pump 2	heat pump 3
refrigerant	Propane (R-290)	Propane (R-290)	CO ₂ (R-744)
modes	heating and cooling	heating	heating
heat source	ground/air ¹	ice-slurry	ice-slurry
source heat exchanger	dual-source1	brazed plate	brazed plate
¹ heating mode		-	•

Table 1: heat pump types designed and produced

The design included careful consideration of different aspects like efficiency, safety, refrigerant charge, cost, and availability of components.

The first experimental campaign of all three heat pumps delivered results on performance and function, which allowed to modify the heat pumps and rebuilt each of them for a second experimental campaign. The two ice-slurry heat pumps were tested at the premises of the Institut für Solartechnik (SPF) and compared in three different modes of operation, providing medium temperatures for space heating (30 - 45 °C) and high temperatures for domestic hot water $(50-70 \,^{\circ}\text{C})$. The heat pump performance was measured at different operating points with reference to the design conditions following the relevant standard [4] and additional points to address the main operation range of interest.

In extract, experiences with the two ice-slurry heat pumps (type 2 and 3) are presented hereafter. Results of the heat pump with propane refer to the second prototype while the ones for the heat pump with CO₂ refer to first prototype as the results for modified version are not yet available.

Ice-Slurry Propane (R-290)

Two variable speed propane heat pump prototypes with a nominal heating capacity of 10 kW were developed with the goal of showing good performance in refurbished building with high share of space heating demand compared to the total demand, including domestic hot water.

Figure 3 shows the layout of the second heat pump prototype produced and its specialties compared to a state-of-the-art heat pump: the prototype contains an evaporator coated with an ice-phobic surface for supercooling water directly in the evaporator (supercooler). The ice slurries are generated outside the heat pump in a crystallizer. Within the project TRI-HP different ice-phobic coatings were developed and tested before applying the most promising to a plate heat

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exchanger that was implemented in the heat pump. The latent heat content of the supercooled water is then released by targeted crystallization creating an ice slurry that is then pumped into the ice storage tank. The desuperheater serves to extract heat for domestic hot water in addition to the condenser liquifying the refrigerant.

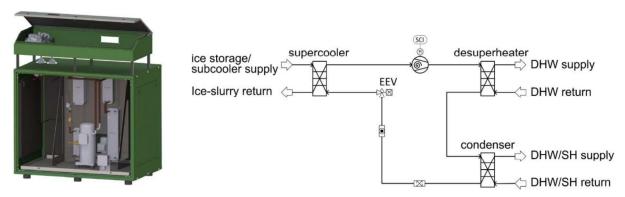


Figure 3: Ice-Slurry heat pump with propane refrigerant build-up (left) and simplified refriger-ation circuit diagram (right)

The refrigeration circuit mainly consists of a variable speed scroll compressor together with the corresponding drive, an electronic expansion valve, a filter dryer and plate heat exchangers. An air fan together with an alarm system inside the frame is used to safely vent the enclosure should a leakage of the flammable refrigerant inside be detected inside the frame. A refrigerant charge of 650 g was achieved, leading to a specific charge of 35 g kW of maximum heating capacity. Thermal and electronic controls were specifically developed for the heat pumps. Besides standard functions like evaporator superheat control or safety functions, the controller additional functions for defrosting the supercooler, adjusting external valves and regulating external pumps were implemented. Compressor speed is controlled following the internal or external set point while covering compressor application limits such as operation envelope or absorbed current.

Compared to the first prototype tested in the project, the second prototype achieved 5 - 10% better performance [5]. This was mostly achieved by using a more efficient compressor and evaporator while reducing the heat loss cause by the safety system.

In the experimental campaign of the second prototype, a COP between 4.3 and 4.7 for 0/30-35 °C (evaporator inlet /condenser inlet-outlet temperatures) and a COP between 2.2 and 2.3 for 0/57-65 °C were achieved. Figure 4 shows the measured COP and heating capacity at a compressor speed of 54 % of its maximum speed. Those results refer to operating the heat pump only for space heating and thus only running the condenser, representing only one of the possible operation modes.

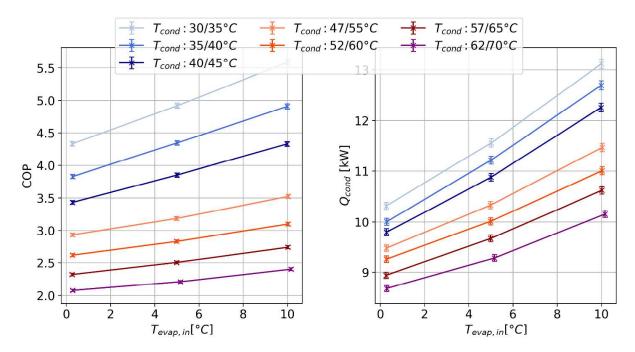


Figure 4: COP (left) and hating capacity (right) at compressor speed of 54%

Ice-Slurry CO₂ (R-744)

A variable speed CO₂ heat pump prototype with a nominal heating capacity of 10 kW was developed with the goal of showing good performance in refurbished building with high share of domestic hot water demand compared to the total demand, including space heating.

Figure 6 shows the layout of the first heat pump prototype produced. A CO₂ heat pump generally needs a high temperature difference at the sink side to reach good efficiency. Therefore, a combination of three gas coolers as proposed by on of the project partners [6] was first assessed in the lab and then built into the heat pump. The refrigerant at high pressure and high temperature reaches the tri-partite gas cooler, and the gliding temperature of CO₂ at transcritical conditions is used to produce domestic hot water in gas cooler 1 (pre-heater) and 3 (re-heater), and/or space heating in gas cooler 2. Very compact, brazed plate heat exchangers for high pressures were used. A suitable ejector was selected among the available off-the shelf technologies as a throttling device, allowing to run an overfeed evaporation.

The CO₂ heat pump was designed and tested in three different operating modes:

- 1. domestic hot water (gas cooler 1 and 3)
- 2. space heating mode (gas cooler 2)
- 3. parallel mode (gas cooler 1, 2 and 3)

Because parallel mode best matches the properties of transcritical heat rejection, heat demand should be leading to parallel mode as much as possible. In the experimental campaign, a COP between 3.4 and 3.7 for 0/30-35 °C (evaporator inlet /gas cooler inlet - outlet) and a COP between 2.9 and 3.2 for 0/20-65 °C in domestic hot water mode were achieved. In this mode a COP of up to 3.6 was measured for temperatures of 0/10-65 °C.

Representing one example of performance, Figure 5 shows the measured COP and heating capacity in parallel mode at a compressor speed of 55 % of its maximum speed. The heat provided

from the heat pump is shown as sum of gas cooler 2 (space heating) and gas cooler 1 and 3 (domestic hot water). Additionally, the share between gas cooler 2 and gas cooler 1 and 3 is shown. A ratio of 0.2 means that 20 % of the heating power is provided for space heating at low temperature level while 80 % is provided for domestic hot water at a high temperature level. At temperatures of 10-70 °C (inlet-outlet) for gas cooler 1 and 3, around 50 % of the heating power is provided for domestic hot water while for temperatures of 10-55 °C the share reaches about 75 %. In parallel mode, a COP of 4 was measured at a source temperature of 0 °C for domestic hot water produced at 10-60 °C and space heating at 30-35 °C, confirming the well-suited use of temperature glide in transcritical CO₂ gas cooling.

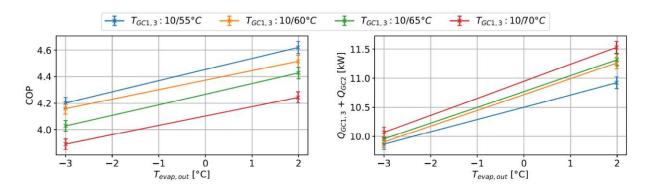


Figure 5: CO_2 heat pump performance example in parallel mode at a source inlet temperature of 0 °C and compressor speed of 55 %

The high heat losses of around 15 % of the total heat produced observed in the first design needs to be examined and reduced in the second prototype which is expected to lead to even better performance.

The refrigeration circuit mainly consists of a variable speed rotary compressor together with a corresponding drive, an ejector, a liquid separator, a filter dryer and plate heat exchangers. The heat source was a glycol-water mixture for the first prototype described while a second prototype equipped with a supercooler as described above is currently being manufactured.

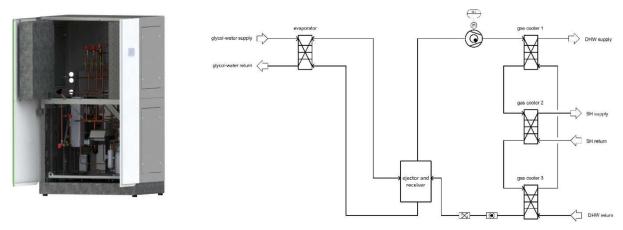


Figure 6: Ice-Slurry heat pump with CO₂ refrigerant build-up (left) and simplified refrigeration circuit diagram (right)

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Supercooling

A major innovation within TRI-HP is the development of an evaporator in the ice-slurry heat pumps allowing for supercooling water below its freezing point in a meta-stable liquid form. Different icephobic coatings have been compared, developed, and applied to commercially available corrugated flat plate heat exchangers made of stainless steel. Testing the different coatings was done in the laboratory of SPF with a glycol-water mixture on the cold side of the heat exchanger. Results are summarized in Figure 7 [7].

The black lines indicate the range of results from the seven cycles performed in each test. Colors on the coatings are used to differentiate among chemical families.

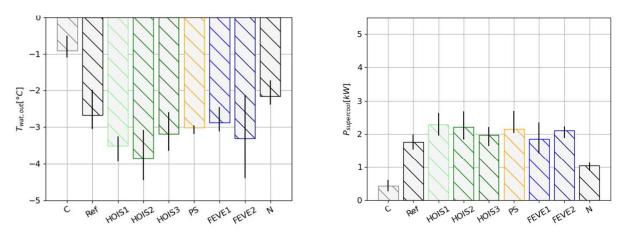


Figure 7: Supercooling temperature (left) and supercooling power (right) at 1'000 kg/h of water flow in a plate heat exchanger with different coatings

For the supercooling experiments the water side of the plate heat exchanger were coated with six different coatings of two material classes: three Hybrid Organic-Inorganic Silane sol-gel (HOIS), one room temperature curing PolySiloxane (PS) and two FluoroEthylene Vinyl Ether (FEVE). Moreover, a commercially available ceramic anti-fouling coating was tested as well (C). As a reference, a heat exchanger without any coating was used (Ref).

The most promising coating was then applied to the heat exchanger built into the second ice-slurry propane prototype described above. It is worth noting that the coatings improve supercooling by up to 40% compared to the untreated supercooler (Ref). Some coatings achieve a supercooling of up to 4 K, which is a very promising result. Supercooling systems with technology are likely to play an important role in thermal energy storage while being economically competitive.

Self-diagnosis efficiency system

Even though heat pumps are very efficient, faults in operation often remain undetected and can lead to severe increase in energy consumption. Within TRI-HP, a fault detection and diagnosis (FDD) system was developed and validated. The FDD method contains a self-learning functionality that enables its adaptation to any variable speed heat pump system to monitor efficiency drift and identify the cause of fault operation.

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To validate the method, some of the most common faults on the variable-speed propane heat pump were emulated and summarized [8]. The heat pump covered the demand generated by nearly all the faults at the expense of increasing the power consumption. The features of each fault have been summarized in a chart, which could be used as table for diagnosing faults. The faults tested were evaporator fouling (EF), compressor valve leakage (CVL), liquid line restriction (LL) and refrigerant overcharge (OC). Evaporator fouling was the fault with least COP degradation and compressor valve leakage with the most (7 % and 56 % COP reduction, respectively). Figure 8 summarizes the impact of faults in the heat pump operation while FI as an absolute value represents the ratio between difference in flow rate (EF, CVL), pressure drop (LL) or mass (OC) and their nominal value. For the study, two steady-state conditions were tested: one with a heating load of around 10 kW and the other with a load of around 12 kW represented with the index in the graph.

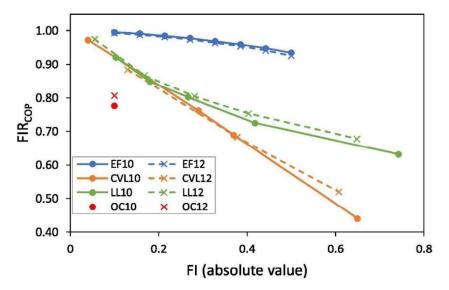


Figure 8: Fault impact ratio on the COP (FIR_{COP}) for each fault intensity (FI) at steady state conditions for heating loads of 10 kW and 12 kW respectively

Experiences in using natural refrigerants in heat pumps

Due to the EU F-Gas regulation and the Kigali agreement, working fluids with a global warming potential (GWP) value below 50 can be applied on a global base. This will become the common target for all vapor compression systems in the future, due to the quota system on refrigerants. In this case, besides CO₂, the only available alternative working fluids are flammable refrigerants. The chosen direction of focusing on natural working fluids for the TRI-HP units secures a long-term perspective and maximizes the exploitation of the technology, since these natural substances will not be affected by legal restrictions in the future, nor do they harm the environment when produced or released into the atmosphere.

The prototypes developed within TRI-HP have allowed the researchers to gain valuable insight into the application of natural refrigerants for heat pumps. Besides the high environmental safety of propane, the main advantages compared to synthetic refrigerants lies in a wide application range of the compressor together with high efficiency and high sink temperatures that could be confirmed in the tests. Experiences with flammable refrigerants showed the importance of minimal and correct refrigerant charge.

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In terms of CO₂, the simplicity in applying the non-flammable and non-toxic refrigerant was appreciated. Also, high system pressures faced with CO₂ did not represent great challenges as often claimed, especially because the refrigerant circuit is small and thus components are widely available. Experiences with commissioning the CO₂ heat pumps showed the importance of well prepared controls. The compressor used was very compact and efficient but came with the drawback of a limiting application envelope to some extent. Ongoing developments are hoped to cover this gap in the future.

Acknowledgment

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Nomenclature

СОР	coefficient of performance (-)	HOIS	hybrid organic-inorganic silane sol- gel
CVL	compressor valve leakage	IEA	Internation Energy Agency
EEV	electronic expansion valve	LL	liquid line restriction
EEVD	electronic expansion valve for defrosting	OC	refrigerant overcharge
EF	evaporator fouling	PS	PolySiloxane
FDD	fault detection and diagnosis	PV	Photovoltaik
FEVE	FluoroEthylene Vinyl Ether	P _{supercool}	supercooling power
FI	fault intensity	Tcond	water temperature at condenser (°C)
FIR	Fault impact ratio	TFA	trifluoroacetic acid
GC	gas cooler	TRI-HP	Tri-Generation-Heat-Pump System
GHG	green house gas	TRL	Technology Readiness Level
GWP	global warming potential	t _{wat.out}	water outlet temperature at super- cooler (°C)
HFC	hydrofluorocarbons	T _{evap,in}	water inlet temperature evaporator (°C)
HFO	hydrofluorolefine		

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References

- [1] T. Abergel, "IEA Reports, Heat Pumps," November 2021. [Online]. Available: https://www.iea.org/reports/heat-pumps
- [2] "Market Report 2021," European Heat Pump Association, 2021. [Online]. Available: https://www.ehpa.org/market-data/market-report-2021/
- [3] S. Joudan, "Insufficient evidence for the existence of natural trifluoroacetic acid," *Environmental Science: Processes & Impacts*, pp. 1641-1649, 04 10 2021
- [4] SN EN 378, Swiss Association for Standardization (SNV), 2021
- [5] R. Gerber, M. Schubert, K. Erb and D. Carbonell, "Residential heat pump for indoor installation operating with R-290 and ice-slurry heat-source," in *IIR Gustav Lorentzen Conference on Natural Refrigerants*, Trondheim, 2022
- [6] J. Stene, "Residential CO2 heat pump system for combined space heating and hot water heating," *International Journal of Refrigeration*, pp. 1259-1265, 2005
- [7] M. Schubert and O. Schmid, "Experimental results of supercoolers, deliverable number D4.6," 2021
- [8] I. Bellanco, F. Belío, M. Vàlles, R. Gerber and J. Salom, "FDD method for a variable-speed heat pump with natural refrigerants," *International Journal of Refrigeration*, pp. 259-266, 2022
- [9] S. Holberg et al., "Natures contrarian strategies to cope with ice formation and their technical application," in *Nano S+T congress*, 2011