Smart CO_2 refrigeration and heat pumping systems

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ABSTRACT

In February 2023 a proposal has been delivered for a restriction of per- and polyfluoroalkyl substances (PFASs) by Germany, the Netherlands, Norway, Sweden, and Denmark to the European Chemical Agency (ECHA) as the last process within REACH[1]. This restriction means that nearly all artificial refrigerants shall not be manufactured, used, or placed on the market after the restriction enters into force by law.

There are some exceptions with longer deadlines related to some application areas, however, the message is clear: Most of all new refrigeration and heat pumping systems are soon not at all allowed to apply any of these substances anymore. The transition towards the utilization of natural working fluids across all sectors must be taken seriously. Immediate action is needed especially of manufacturers and vendors still applying artificial refrigerants in their products for the market.

In this contribution examples are described and evaluated of future proof and energy efficient refrigeration and heat pumping systems applying carbon-dioxide/CO_2 as working fluid. There are many more working fluids/refrigerants to be considered namely: different types of hydrocarbons, ammonia/NH_3, water/H_2O and air/R729. All these alternative natural working fluids, with their individual properties, will contribute to support the entire refrigeration- and heat pumping sector in the required transition away from artificial refrigerants. End-users will appreciate these innovative, clean, and energy efficient systems having a long-term perspective without creating forced replacement requests by the authorities.

Keywords: Natural Refrigerants, Carbon Dioxide, Clean Heating & Cooling

1. INTRODUCTION

As stated by Lorentzen 1993 & 1995, Ciconkov 2018, and Kauffeld et. al 2021 there is no rational reason for humanity to continue destroying our environment due to the manufacturing, usage, and loss of artificial refrigerants. Since alternative refrigeration and heat pumping technology, based on natural substances, has either been continuously applied since the early start of mechanical refrigeration in the late 19th century, as it is the case for ammonia / NH3 / R717, or has been developed during the past decades applying the other natural working fluids. All these clean cooling- and heating system architectures and units are available and proven technology nowadays. These units are able fulfil all required heating and cooling demands of whatever application globally.

Beside the EU F-gas regulations, currently under revision, and the Amendment of the Montréal Protocol regulating the greenhouse gas related emissions of working fluids within our sector, finally, a new restriction (PFAS 2023) under the ECHA responsibility will sooner or later prohibit the production and usage of most currently common artificial refrigerants. The reason is the identified sever risks to the environment and human health when applying and releasing per- and polyfluoroalkyl substances, which are characterised by a very high persistence. If not restricted, as mineralization does not take place under natural conditions, the concentration of PFASs in the environment will increase. To inherit the removal of PFASs from soil, groundwater, surface water, sediment and biota to our next generation is immoral and reprehensible, as it is technically extremally difficult and very costly, if possible, at all.

This proposed restriction is good news for our sector and should be accepted as a well-intentioned guidance by the authorities. Following and not counteracting these proposals will avoid wasting investment-, research-,

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[1] REACH (EC 1907/2006) aims to improve the protection of human health and the environment through the better and earlier identification of the intrinsic properties of chemical substances.

and development resources when prolonging manufacturing of systems using artificial refrigerants. The entire sector can continue and must join forces to enable a fast implementation of natural working fluids. None of the experts and skilled workers in our field will become unemployed, many more candidates must be employed and made aware of the possibilities and future perspectives. The green transition with clean refrigeration and heat pumping technology requires educated and retrained personnel at all levels to enable a timely achievement of the climate-, environmental- and socioeconomic goals adopted of nations and the EU.

2. R717, R290++, R718, R729 IN A NUTSHELL

Ammonia - NH_3- R717

Ammonia has been the preferred refrigerant in industrial refrigeration for more than 140 years. Due to some accidents not related to refrigeration in 2013, the suppliers of these applications are forced by different stakeholders to reduce the refrigerant charges in the systems. This has led to new designs and innovations in the packaged Ammonia systems offered to the market.

Low charged R717 chillers are offered and installed in many different types of applications e.g., airports, hospitals office buildings but also for chilled- and cold-water production in industrial applications. Many global suppliers continuously develop R717 refrigeration and heat pump systems supporting vendors and end-users to implement energy efficient system solutions. Even high temperature heat pump applications are approaching the upper technology readiness levels (TRL). (Ahrens 2023)

Hydrocarbons – R600, R290, etc.

Nowadays propane (R290) is applied in heat pumps and in commercial refrigeration and freezer applications. Propane is also implemented in air-conditioning systems both in stationery and portable units. Several global suppliers manufacture a high number of R290 AC systems annually. As an example, for an early introduction, *Midea* made its first Eco-friendly air conditioner certified by Blue Angel in 2018, now also available across Europe. *Wabtec* develops and implements R290 based AC system for passenger trains of *Deutsche Bahn DB* as a long-term solution, including safety concepts to be implemented in the specification of DB. (Wabtec 2020)

In most domestic refrigerators iso-butane (R600a) it the standard refrigerant, more than 95% of all fridges in Europe are now based on this natural working fluid. Soon even American style fridges will not apply fluorinated hydrocarbons anymore.

Other working fluids within the hydrocarbon family are suitable for high temperature heat pumps able to supply heat at 250 °C. An analysis performed by, Pachai 2021, shows that the way up in temperature is possible by applying butane, pentane and for the very high temperatures heptane is identified as the most energy efficient alternative.

Water – R718 – H_2O

The market for some air-conditioning applications applying water as refrigerant is emerging. In addition to the AC market, high temperature heat pumps are another application area. Especially when producing steam for process plants by utilizing surplus heat in combination with a cascade heat pump. Water, in comparison to other refrigerants, has a relatively high boiling point at atmospheric pressure, 100 °C at sea-level. At typical AC operation temperatures, the pressures in the water cycle will be sub-atmospheric and the required swept volume in the compressor needs to be relatively large compared to similar systems e.g. based on ammonia. This drawback is reversed when the operation temperatures increase to levels above 100 °C or even 200 °C. For high temperature heat pumps water becomes a viable and energy efficient solution.

Air – R729

When applying sophisticated equipment, it is possible to reach supply and maintain storage temperatures as low as -160 °C with air as the working fluid. Atmospheric air can also be used in a circuit with compressors, intercoolers, and expanders to provide temperatures from -40 °C to about -130 °C. Such air cycle refrigeration systems are applied successfully since decades to store frozen tuna at about -60 °C in Japan. Air cycles are more energy efficient compared to traditional vapour compression units at temperatures below -50 to -60 °C.

3. SMART CO_2 / R744 SYSTEMS

Despite the initial scepsis of many experts in our sector, when Gustav Lorentzen and his team announced the revival of CO_2 as a working fluid (Lorentzen 1993), it has been proven to be an excellent alternative in many heat pumping and refrigeration applications in the last two decades.

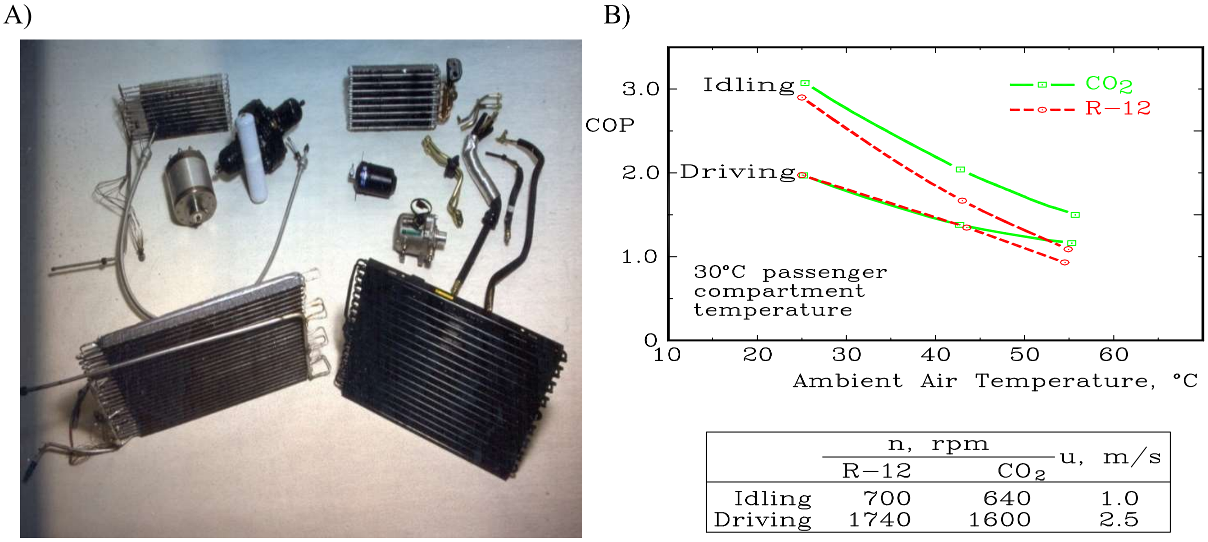
Three decades later, Shecco 2023 expects that more than 100.000 transcritical CO_2 refrigeration systems are in operation, globally.

The following chapter describes some of these applications and identifies the key advantages to encourage a widespread utilization of this clean cooling and heating technology.

Refrigeration: Mobile AC systems, Bus & Trian, Truck & Trailer, Container

By the time in the late 1980's when the Montréal Protocol was ratified to secure the protection of our ozone layer, the team of Gustave Lorentzen developed the first mobile AC system applying CO_2 as working fluid. The refrigerant leakage of mobile AC systems was comparable high by that time; therefore, a natural working fluid was proposed as a sustainable replacement instead of introducing HFCs.

As shown in Figure 1 A, the comparable in size components of a standard vehicle AC system, demonstrated already in 1990, during extensive experimental investigations, the performance potential of CO_2, as shown in Figure 1 B.



	n, rpm		u, m/s
	R–12	CO_2	
Idling	700	640	1.0
Driving	1740	1600	2.5

Figure 1A: CO2 prototype system (left) and BMW 520 R-12 system (right). 1B: Coefficient of Performance (COP) as a function of ambient air temperature for various operating conditions.

It took more than two decades before *Mercedes* introduced the first serial production car with an R744 mobile AC system in 2016. Nowadays, more and more vehicle manufactures can equip their cars with such clean cooling systems. The introduction of alternative power trains, mainly transferring to electric driven vehicles, as shown by VW, will support a wide introduction of R744 cooling and heat pumping solutions to secure a safe and energy efficient thermal management of the entire vehicle.

Several bus manufactures apply CO_2 as working fluid for the AC and nowadays heat pumping system. *Konvekta* was spearheading this technology and has supplied CO_2 AC systems since 2008. (Konvekta 2023).

For high-speed trains, Elbel (2022) demonstrated how to implement a CO_2 AC system within the same space configuration for the train HVAC unit. The team showed that the energy efficiency and cooling capacity were respectively 16 % and 14 % higher for the CO_2 unit, compared to the baseline R407C system. The fully functional prototype CO_2 unit was transferred to the project owner and sooner or later many similar systems will be implemented in new trains.

Ecooltec 2022, applies propene (R1270) and CO_2 (R744) in their *ECOOLTEC* unit and is thereby spearheading the clean cooling technology introduction for trucks and trailers. A roof-mounted refrigeration units has been developed. The air inside the cargo compartment is either heated or cooled by CO_2 while propene is applied inside the active outdoor refrigeration loop. The heat pipe principle is applied for the cargo air / CO_2 heat exchanger. CO_2 is utilized in an innovative and safe way as the working fluid between the cargo and the refrigeration unit, only by natural circulation without any pump or compressor unit.

Since 2013 container refrigeration systems applying CO_2 as working fluid are on the market, (Carrier 2013).

Commercial Refrigeration

In 2004, *Linde* commissioned the first all CO_2 transcritical refrigeration system in a supermarket located in Wettingen, Switzerland. After solving lubrication concerns and being able to apply a single lubricant, the following systems were built as booster systems. The evolution of CO_2 booster systems for supermarket applications can be summarised as indicated in Figure 1. The 1st generation, i.e. the booster system (left), is the most widely applied solution. The system fits best to cold climates, where the demand for AC is low or not present. In this system, the LT cabinets/evaporators are connected to a separate, booster compressor – hence the name booster system – which lifts the pressure to the medium temperature level. The cooled discharge gas from the booster is then merged with the gas coming from MT evaporators is compressed by the MT compressor to the heat rejection devices.

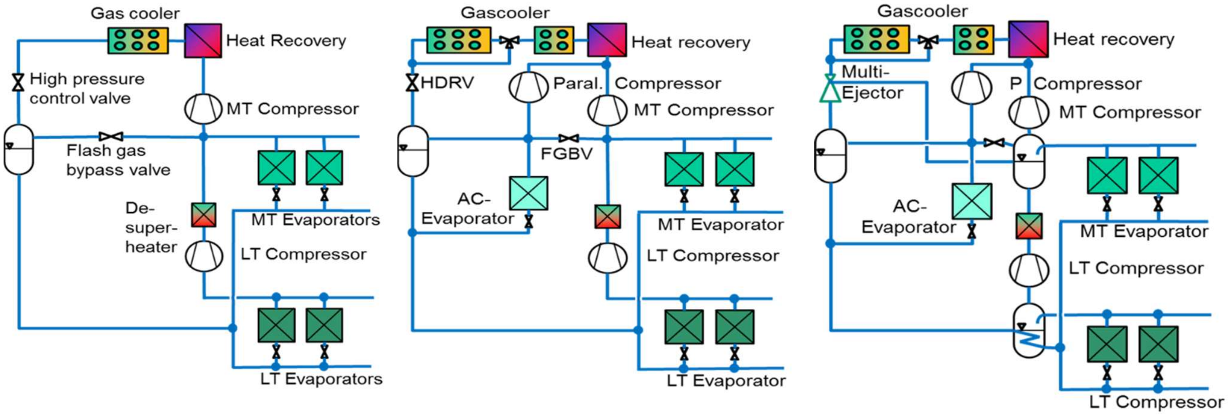


Figure 2: Evolution of CO2 Booster systems from simple booster (left), parallel compression (centre) and ejector supported parallel compression unit (right), (Hafner 2018)

The second generation are booster systems with parallel compression, as shown in the central part of Figure 2, first time introduced by *enex* in a Swiss supermarket in 2008. The amount of vapour downstream of the high-pressure control valve increases as the ambient temperature is rising. The reduced specific cooling capacity leads to an increment in the amount of refrigerant which has to be compressed from medium to high pressure, resulting in increased the power consumption of the MT compressors, especially during summertime. A solution to this challenge is to adopt an auxiliary or so-called parallel compressor with the purpose of compressing either a part or preferably the entire amount of vapour from the separator pressure level directly to the gas cooler pressure. Applying parallel compressors reduces the losses due to flashing and prevent MT compressors from liquid slugs. These parallel compressors are only operative if there is enough flash gas available. If the amount of flash gas is low, e.g. during winter-time, it is throttled via the FGBV as in a standard booster system and the parallel compressors are in standby.

To further increase the energy efficiency of transcritical booster systems, utilization of expansion work is a smart option. Therefore, in CO_2 commercial refrigeration technology for warm climate locations the high-pressure control valve is to replace with ejectors enabling for expansion work recovery, as illustrated in Figure 2 (right) and defined as the 3rd generation of booster systems. In 2014, *enex* and local vendors implemented the first ejector supported CO_2 supermarket refrigeration system in Switzerland. However, this ejector configuration can also be applied in cold climate locations, as even in the Nordic countries warm summer conditions are becoming more frequent. The ejector entrains partly the low-pressure fluid downstream of the MT evaporators by means of high-pressure fluid coming from the gas cooler, accelerated in the motive nozzle of the ejector. Kinetic energy is converted into static energy, i.e. the pressure level between the suction nozzle and ejector discharge is equal to the pressure difference between the MT evaporators and the separator. The amount of vapour pre-compressed by the ejectors and discharged into the separator is determined by the available expansion work. The ejectors extend the operation time of the parallel compressors by increasing the amount of vapour to be compressed. Ejectors hence shift a part of the MT compressor load to the parallel compressor, which has to overcome a significantly lower pressure lift, hence reducing the total power demand. A smart arrangement of suction port switching valves has been promoted by Hafner 2018, Pardiñas Á.Á. 2020, and Contiero L. 2021, to reduce the number of compressors in ejector supported systems. This can only be achieved if a smart controller is able to dedicate individual compressor capacity between the MT and the parallel compressors.

As such a controller is not available further simplifications are proposed to enable the utilization of work recovery when the refrigeration system is operating in transcritical mode. Hafner 2018 proposes an integrated system architecture with an ejector bypass valve when the system is operated in subcritical mode, as shown in Figure 3. The second heat exchanger downstream of the compressors is the main heat rejecting device, enabling a proper heat rejection of the entire heat to the ambient during summer via a drycooler. During the cold period, heat can be utilised from all heat exchangers downstream of the compressors. The main purpose of a third heat exchanger can be preheating of domestic hot water or providing heat to the outdoor floor heating system (snow smelter), replacing direct electrical heating which is applied in some countries to keep the entrance and delivery area free of ice.

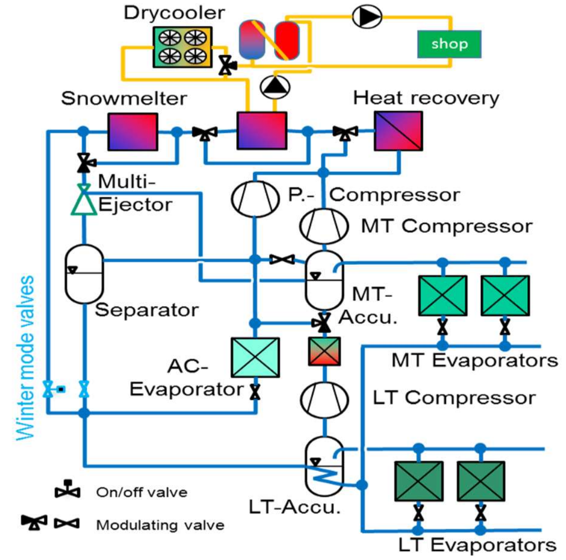


Figure 3: Integrated CO_2 based system for a supermarket in the Nordic regions. (Hafner 2018)

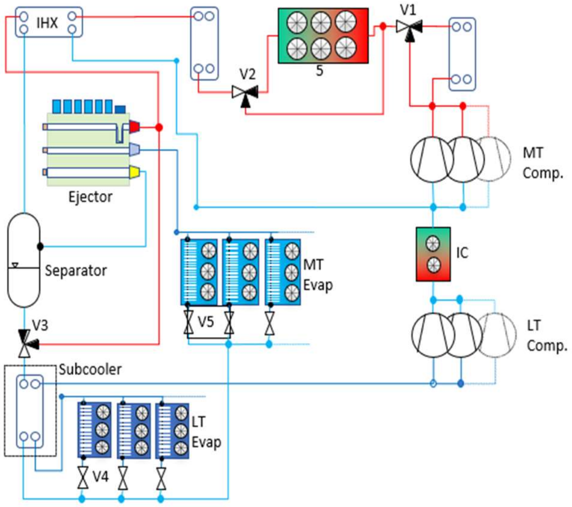


Figure 4: Energy efficient, simple ejector supported R744 commercial refrigeration unit.

Low ambient temperatures can be a challenge for traditional CO_2 booster systems, when the CO_2 temperature downstream of the heat rejecting devices becomes lower than 5 °C. Since this temperature represents the saturated temperature inside the separator at 40 bar. If the refrigerant temperature upstream of the separator drops below the saturation temperature, the pressure inside the separator is reduced due to partial condensation of the vapour inside the separator. Therefore, extra safety measures must be implemented to protect the separator pressure, which secures the liquid supply to all evaporators. However, this again reminds of the pressure maintenance actions required for HFC systems. To avoid the system to be dependent on the separator pressure a so-called winter mode upgrade for booster systems is proposed. When the ambient temperature is below a certain value, the ejector high pressure control and the separator are taken out of the main system circuit, i.e. the liquid refrigerant downstream of the heat rejection devices is directly supplied to the evaporator feeding valves, like in traditional subcritical systems. The main controller operates the total opening of all feeding valves to maintain a certain and safe high side pressure and a proper supply of liquid to all evaporators.

An innovative approach in continuing with the idea of partly bypassing the ejectors, is proposed by Pardiñas Á.Á. 2022, as shown in Figure 4. In this circuit the parallel compressors are not required, AC implementation is not shown for simplification. The ejector is active if there is sufficient expansion work available. In this active mode, the ejector acts as a booster device and pre-compresses the entire MT vapour flow rate towards the suction port of the MT compressor. At low ambient temperatures (below 15 °C to 20 °C), the temperature level of the CO_2 downstream of the gascooler and suction line heat exchanger is sufficiently low as well as the available expansion work due to low high side pressures, too. In this case all motive nozzles of the ejector are closed, the high-density CO_2 is directly supplied to the evaporators via the individual feeding valves. The MT compressor is maintaining and adapting the pressure level in the liquid receiver, in which the vapour from the evaporators returns via the passive ejector. The pressure drop via the passive ejector is below 0.1 bar (= 0.1 K) at maximum cooling capacity. The first system is built in 2023 and will be implemented in a supermarket on the Iberian Peninsula in 2023.

Cold Thermal Energy Storage (CTES): AC support, and -50 °C freezing

Thermal energy storage will become an important feature in the green transition of the entire energy sector. The cooling and freezing sector must contribute with smart solutions to enable thermal energy storage at various temperature levels, as historically done with ice-slurry systems and ice banks.

AC support with direct expansion inside the air handling unit evaporator

Selvnes 2023 describes the system architecture of a CTES unit developed for AC support of a supermarket building integrated into a standard booster system, as shown on Figure 5. The stationary CTES fluid is water and the phase change between the liquid and solid state is utilized to store cooling capacity, utilized by recondensing CO_2 which evaporates while cooling air inside the air handling unit (AHU).

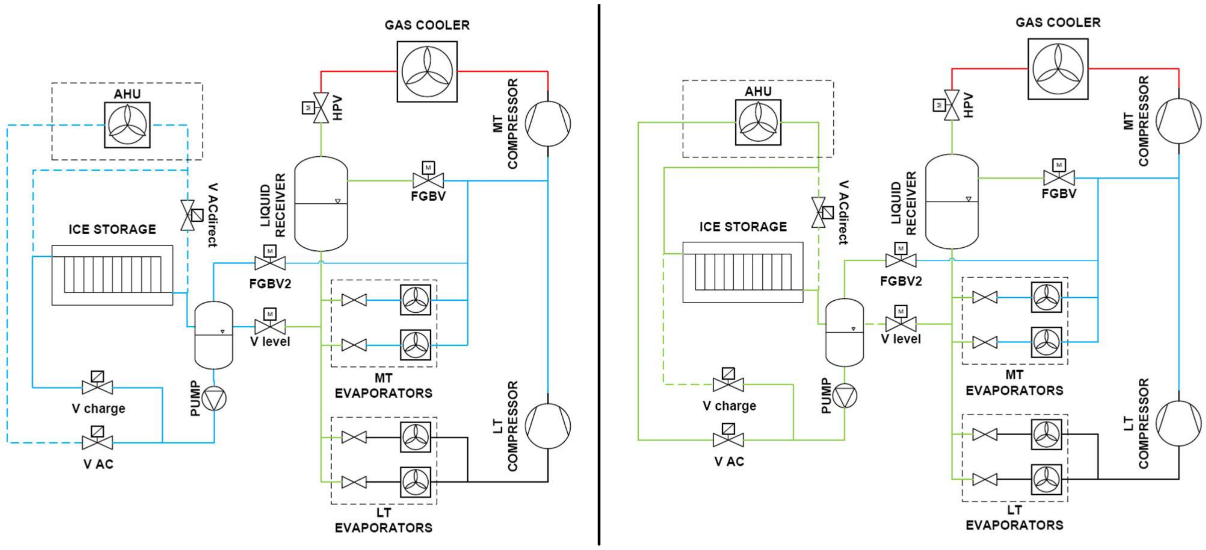


Figure 5: Simplified system circuit for supplying AC by CTES unit based on water/ice as the natural storage medium (PCM). The left-hand side shows the system in charging mode, the right-hand side shows the system in discharging mode. (Selvnes 2023)

This kind of CTES concept at temperature around the freezing point of water enables to charge the ICE storage during off peak power periods, and when the MT compressors are operated in part load. In the next development and demonstration step, dedicated display cabinets for food which requires elevated cooling temperature will be connected to the pumped loop, utilizing the storage during all seasons.

Storage of freezing energy at around -50 °C

Industrial freezing is an energy-intensive process which is a growing sector due to the increasing demand of frozen food products. This is exerting stress on electrical grids, especially at peak hours and has a significant cost impact for the owners and operators of the freezing plants. To tackle this issue, thermal energy storage has received attention; however, there is a gap in terms of suitable materials/fluids for thermal energy storage for the temperature range below -40 °C. Solid-liquid phase change of carbon dioxide has been conceptually considered by Mastani 2022 for cold thermal energy storage in a special type of heat exchangers known as pillow plate heat exchangers. Characteristically, these heat exchangers can withstand very high pressures which is a technical requirement for carbon dioxide thermal energy storage.

The concept of low-temperature thermal energy storage utilising the solid-liquid transition of CO_2 is to let CO_2 swing between the saturated solid and saturated liquid state and avoid going beyond the liquid region. The reason is that if the temperature is rather high, then CO_2 will cross the saturated liquid line and enter the liquid-vapour region. This vapour formation is undesirable for thermal energy storage applications as it needs a higher volume (due to its lower density compared to the liquid and solid phases). The thermal storage operates at around 10 bar, then temperatures above -40 °C should be avoided. Another natural refrigerant is applied to charge the thermal storage (i.e., for CO_2 solidification). Ethane (R170) is commonly used in the lower stage of cascade industrial refrigeration systems, due to favourable normal boiling point of -88.8 °C and can be applied for the charging of the storage by rejection the heat into the main refrigeration system.

Heat pump chillers for hotels and process plants

CO_2 has gained a lot of attention and has become the new norm for domestic hot water heat pumps in Japan[2].

CO_2 is an energy efficient option when simultaneous heating and cooling is required. As shown in Figure 6, hot water should be storage in multiple storage tanks connected in series, to enable a continues operation of the chiller. The bottom water connection must be equipped with a diffusor to avoid mixing inside the tank when a large amount of hot water is required. The heat pump can in addition provide both heating and comfort cooling to the building via the hot and cold-water lines. Each flat/room has a sub energy central containing on one side a heat exchanger for providing heat towards the hydronic heating loop. The supply temperature of the local hydronic loop for space heating is regulated by an electronic metering valve controlling the flow rate of hot water through the heat exchanger.

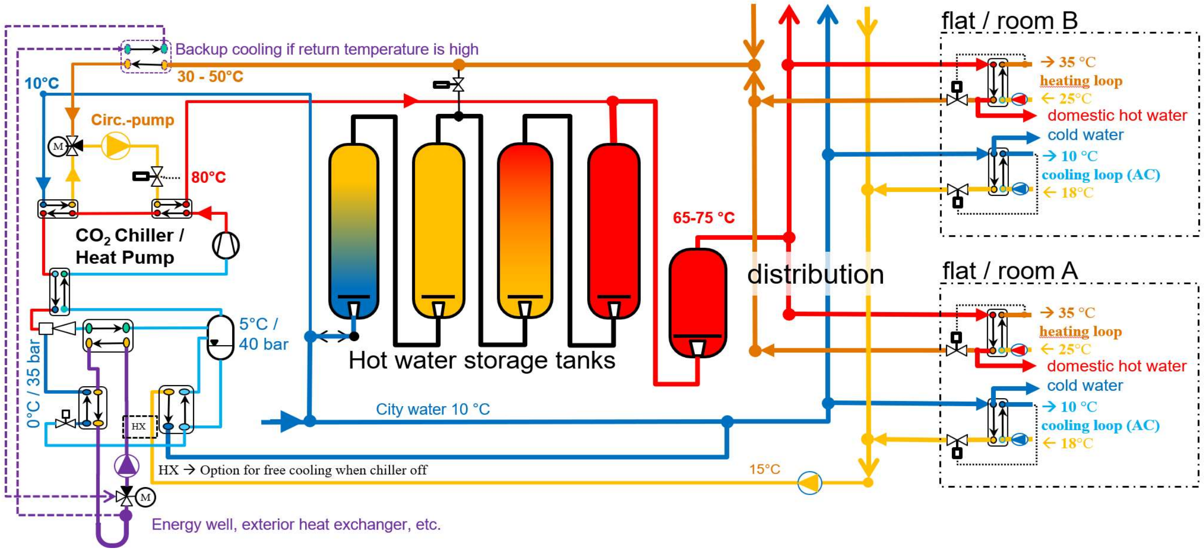


Figure 6: CO_2 heat pump chiller for a multifamily house or a hotel. Hot water tanks in the central part, four pipe distribution within the building to provide hot & real cold water, heating, and cooling (AC) on demand for each individual room or flat.

The secondary cooling loop of the room/flat, providing comfort cooling, is cooled by adjusting the amount of chilled cold water through heat exchanger. As event the chilled cold water is circulated throughout the entire building, a large amount of drinking water is saved, as the end uses do have access to cold drinking water immediately and does not need to release drinking water into the sink to get a glass of cold water.

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[2] More than 5 million *eco-cute* heat pumps with R744 are applied in Japan to produce hot water for apartments.

The heat uptake side of the heat pump chiller is characterised by a range of evaporators. Due to the ejector integration, there are two temperature levels, the upper temperature level is the saturation temperature corresponding to the pressure level of the receiver. At this temperature, indicated with 5 °C / 40 bar in Figure 6, cooling is provided to the circulated cold water by a water chiller with gravity-based circulation on the CO_2 side. The heat uptake from the external source, as example from an energy well or external air heat exchanger, could also be implemented with a gravity fed evaporator or as shown with an evaporator located downstream of the ejector exit. As the ejector is able to utilize some of the expansion work to boost the vapour out of the third evaporator, the pressure level can be several bars lower and thereby the secondary fluid is further cooled before leaving the heat pump. Thereby the exit temperature of the secondary fluid can be significantly lower than the saturation temperature inside the receiver, i.e. the suction pressure of the compressor and the energy efficiency of the system is significantly higher, due to the ejector support.

Such a two-stage cooling of a secondary fluid, enabled by the ejectors, are very attractive option for many process cooling plants. Designers and consultants should understand that in this case, the temperate difference of the secondary fluid can be significantly higher than the traditional 5 K (12 °C → 7 °C). This kind of technology is implemented in of the shelf CO_2 chillers from *enex,* as described and experimentally investigated by Girotto 2020.

CONCLUSIONS

A remarkable development of CO_2 refrigeration technology has taken place since the revival of the refrigerant in the late 1980s by Prof. Gustav Lorentzen. The development has led to many energy efficient CO_2 systems especially for hot water heat pumps and supermarkets. Commercial refrigeration has a remarkable number of successful market introductions globally with high growth rates. Heat pump chillers, as described in this work will follow this trend.

Utilisation and integration of solid-liquid phase change of carbon dioxide will enable Cold Thermal Energy Storage to support existing large scale freezing plants to become an active partner of the power grid operators. In this way, and with water/ice storage devices, the refrigeration systems can be an active thermal battery charging device.

The group of natural refrigerants can be the working fluids for all the applications which can be covered by fluorinated hydrocarbons and even more. None of the fluorinated hydrocarbons can go as high in temperature or as low as the natural refrigerants. The artificial fluids, harmful to the environment and human health, only cover the most profitable markets in the mid temperature range.

From 2023 on, reminded by the PFAS restriction proposal, there should be no doubt that our sector must leave the artificial refrigerant chapter behind us, the sooner the better. How dare you to continue jeopardizing the ground water sources, food, and health!

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