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Application of natural refrigerants in the industrial refrigeration and heat pumps in the future

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ABSTRACT

For more than 150 years natural refrigerants have been used in various industrial applications reaching temperatures from -273°C to more than 300°C and the level of the high temperature limit is difficult to estimate at the time of writing this paper.

Ammonia, NH_3, R-717 has been the preferred refrigerant for normal everyday industrial refrigeration in strong competition with hydrochlorofluorocarbon (HCFC) R-22.[i]

In other applications carbon dioxide, CO_2, R-744 used to be one of the preferred working fluids in the early days of refrigeration. In the 1980's it became apparent that chlorine, Cl, was destroying the ozone layer that protects all life on earth from the dangerous ultraviolet (UV) rays emitted by the sun. The discussion leading up to the Montreal Protocol elaborated on what would be the right way to choose if chlorinated and fluorinated hydrocarbons were not the way to go. Many alternative fluids were suggested, and Gustav Lorentzen suggested to reconsider carbon dioxide, which he saw in operation in his young days when sailing as marine engineer.

Others suggested hydrocarbons, which are a large family of various types of natural occurring gasses with many different properties. Hydrocarbons have been used in the chemical process plants in various applications and temperature levels for more than 130 years.

Keywords: Natural refrigerants, Carbon Dioxide, Ammonia, ORC, heat recovery

1. INTRODUCTION

In the high temperature range, heat pumps can be applied to further upgrade surplus heat and to provide heat at a required temperature level. Many industrial and district heating heat pumps are using NH_3 up to about 93°C - 95°C. However, there are also heat pumps providing up to 130°C towards customers in cities where circumstances demand higher temperatures. Heating accounts for about 51% of the global energy consumption. Heat pumps in industrial applications can contribute to the decarbonisation of the heat production with temperatures up to 250°C and in the future even higher. From this level there is a stretch to the next large consumption at 800°C and up, which is too high for heat pumps to make sense – at least with the technologies we have at hand today.

Heat recovery is a special topic, however, when focusing on the (Organic) Rankine Cycle ((O)RC), there are working fluids operating at very high temperatures and expanding trough an expander which is directly connected to a generator. In this way it is possible to generate electrical power from waste heat, e.g. flue gas from cement production or heat from steel production. The applied working fluids must be stable at even very high temperatures and not generate to high pressures – but still enough to drive the expander. The fluids used in the past are e.g. R-245fa and similar synthetic fluids, however, also natural fluids like CO_2 and different hydrocarbons have been investigated and applied in demonstrators.

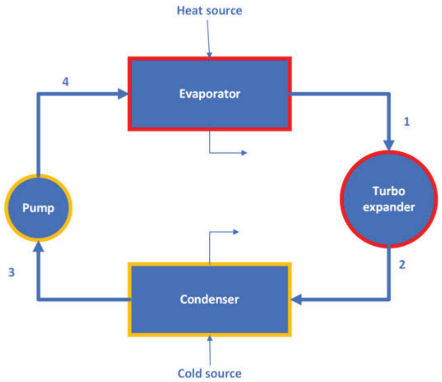


Figure 1 The Rankine Cycle (power cycle) is basically moving in the oposite direction compared to a Carnot cycle

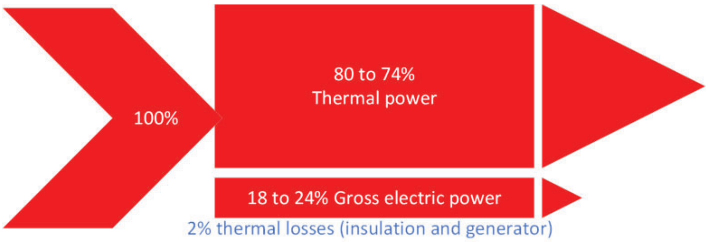


Figure 2 The (O)RC unit can recover the heat otherwise lost with the flue gas

From Figure 1 point 1 the hot vapor enters the expander which is connected to the generator. The expanders can be of different types, e.g. screw or turbo expanders and scroll types have been suggested, however even more sophisticated expanders are available. It is important that for a safe operation that no liquid is formed inside the expander. The gas downstream of the expander enters the condenser. The liquid formed (point 3) can be pumped to the evaporator. Compared to a standard refrigeration unit, the pump is providing the pressure lift comparable to the compressor and the generator corresponds to the expansion device.

If the heat generated by burning a fuel for producing district heating water, about 74 to 80% of the energy is transferred to the water. 18 to 24% of the energy can be recovered to produce electric power resulting in a total efficiency of about 96 to 98%.

The ORC can also be used when recovering the heat from motors e.g. ship engines or similar and many other applications where hot fluids (air, etc.) are released at high temperatures.

When the surplus temperature levels are lower the heat can be recovered by a heat pump working with a normal Carnot cycle. This has become a very profitable business in especially remote DH systems where all the heat can be used for district heating. Here NH_3 has been used successfully in many cases. The system serves different purposes as the hot exhaust is going through a scrubber system where carbon dioxide and other impurities are washed out of the flue gas. A large amount of the heat is also absorbed and can be used as source for the heat pump.

Figure 3 An ORC unit

In the future we will see other fluids such as CO_2, pentane, tuloene, water vapor and some hydrocarbons. Some long chain hydrocarbons do have very high boiling points and do not introduce extreme high pressures even at about 400°C, and by superheating the working fluid the pressure does not increase dramatically.

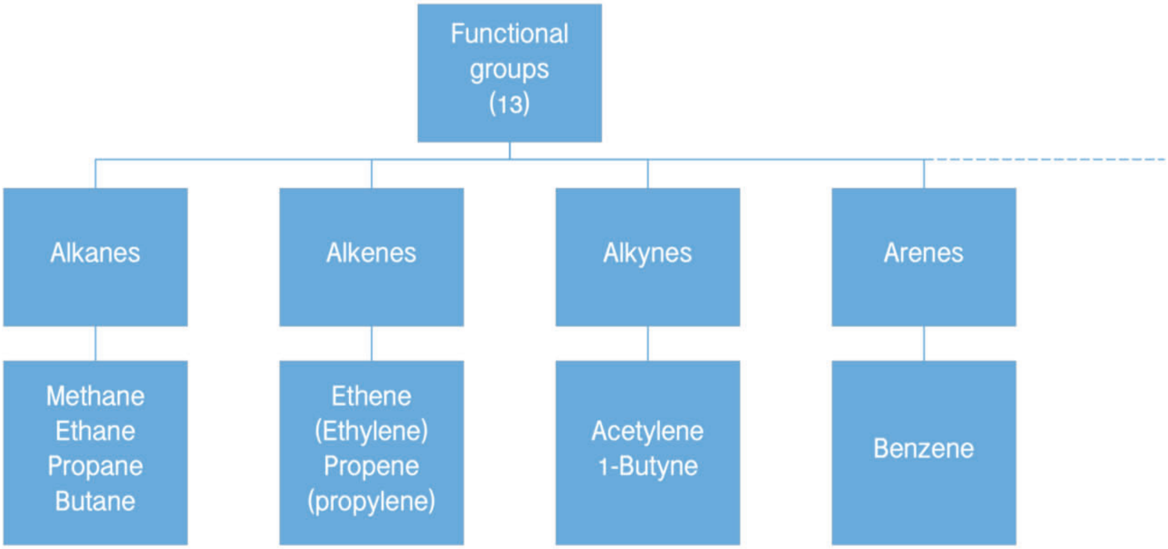
The future will also be about hydrocarbon refrigerants. Traditional hydrocarbon refrigerants have been R-600a (iso-butane), R-290 (propane) and for low temperatures R-170 (ethane); all alkanes. Also, two alkenes, sometimes sold as olefins, R-1270 (propene) and R-1150 (ethene) has been applied especially for low temperatures below -100°C.

When extreme low temperatures are required, i.e. in cryogenic applications, the naturally occurring noble gases can be applied. In cascade systems helium, He, is utilized to maintain and reach temperature levels above and close to absolute zero at -273,15°C. This cycle rejects the heat towards another circuit using hydrogen, H, and thereafter methane, CH_4, and then ethene, C_2H_4, to ethane, C_2H_6 ending the cascade system with NH_3 on the high/ambient temperature stage[ii].

Power production and the consumption of fossil fuels resulting in emissions of thousands of different substances into the environment every year is the path to "The sixth mass Extinction" according to Thomas Resl, 2021[iii]. One thing is the extinction of habitat and other living species than humans, however, it is observed that annually 4.2 million humans are dying from breathing ambient/outdoor air according to WHO[iv] and it says "91% of the world's population live in places where air pollution levels exceed WHO guideline limits[v]". This can only be changed if humanity collectively does something about it. History tells us that we can do something about a problem if we decide to do it, e.g. The Montreal Protocol. This threat to the humanity and the future of new generations requires quick and decisive action and not just "Blah, Blah, Blah[vi]" as correctly stated by Greta Thunberg.
The refrigeration sector must contribute to this effort to avoid unnecessary environmental impacts, and the most simple and effective path is to eliminate the usage of non-natural working fluids in all new applications. No job will be lost within the sector, nevertheless, the end-users are welcoming system solutions which do not turn out to be an environmental-, safety and health problem for the owner.

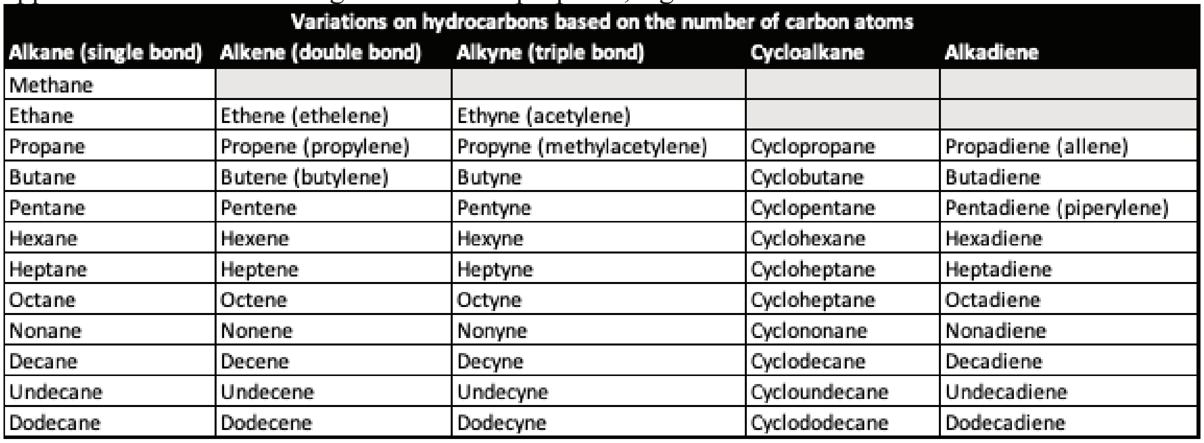
2. THE HYDROCARBONS

According to International Union of Pure and Applied Chemistry (IUPAC) acyclic and cyclic hydrocarbons having one or more carbon–carbon double bonds, apart from the formal ones in aromatic compounds. The class olefins subsume alkenes and cycloalkenes and the corresponding polyenes.



The fluorinated alkanes where the first generations of synthetic refrigerants the industry saw on the market after their invention in 1939. With the first problems occurring related to the ozone depletion, quantified by the ozone depletion potential (ODP) of a substance, on the horizon, the chemical companies where able to quickly turn around and offer a new series of refrigerants, marketed under the HFC label. However, the day after the signing of the Montreal Protocol it was already obvious that the next problem would become the Global Warming Potential (GWP) of these synthetic fluids. The desire to find solutions that could then solve the GWP problem was to look for the alkene series, which were known since the 1950's, however, were left unutilized because of problems with stability and reactivity, which is the feature of the alkenes that are used in the chemical industry[vii].

The most used alkenes in refrigeration is propene and ethene but in the future the industry might appreciate others in the ranges for various purposes, e.g. ORC.



Variations on hydrocarbons based on the number of carbon atoms				
Alkane (single bond)	**Alkene (double bond)**	**Alkyne (triple bond)**	**Cycloalkane**	**Alkadiene**
Methane				
Ethane	Ethene (ethelene)	Ethyne (acetylene)		
Propane	Propene (propylene)	Propyne (methylacetylene)	Cyclopropane	Propadiene (allene)
Butane	Butene (butylene)	Butyne	Cyclobutane	Butadiene
Pentane	Pentene	Pentyne	Cyclopentane	Pentadiene (piperylene)
Hexane	Hexene	Hexyne	Cyclohexane	Hexadiene
Heptane	Heptene	Heptyne	Cycloheptane	Heptadiene
Octane	Octene	Octyne	Cycloheptane	Octadiene
Nonane	Nonene	Nonyne	Cyclononane	Nonadiene
Decane	Decene	Decyne	Cyclodecane	Decadiene
Undecane	Undecene	Undecyne	Cycloundecane	Undecadiene
Dodecane	Dodecene	Dodecyne	Cyclododecane	Dodecadiene

Gas name	Refrigerant, ISO 817	ODP	GWP$_{100}$, AR6	Atmospheric lifetime, years	Critical pressure, bar(A)	Critical temperature, °C	Molecular mass, g mol^{-1}	Normal boiling point °C
Propane	R-290	0	0,02	0,041	38	63,74	44	-42,2
n-Butane	R-600	0		6,8 days	38	152	58,12	-0,5
iso-Butane	R-600a	0	0,006	12±3	36,4	134,7	58,1	-11,6
Pentane	R-601	0		12±3	33,58	196,6	72,1	36,1
iso-Pentane	R-601a	0		12±3	33,78	187,8	72,1	27,7
Propene	R-1270	0		0,001	46,7	91,061	42,1	-47,7
Ethane	R-170	0		0,167	48,7	32,2	30,1	-88,6
Etene	R-1150	0		12±3	50,4	9,19	28,05	-103,7
1-Butene	-	0			40,05	146,14	56,1063	-6,35
2-Butene	-	0			42,1	162,45	56,106	0,8 to 3,7
1,3-Butadiene	-	0			43,2	151,85	54,09	-4,55
1-Pentene	-	0			35,99	192,59	70,13	29,89
Benzene	-				49,073	288,87	78,112	80,07
Cyclo-hexane		0			40,805	280,45	84,159	80,72

The different fluids have advantages for different purposes. With a high boiling point the fluids can be a good substitute in ORC systems low boiling points make the fluid good for refrigeration purposes. Some of the hydrocarbons have over time been halogenated with one or more of the halogens chlorine, fluorine, bromine or iodine. It is the halogens that give the hydrocarbon the higher global warming potential (GWP) or their ozone depleting potential (ODP). It is also the halogens that give the hydrocarbon base molecule its toxic properties, e.g. COF_2 (carbonyl fluoride) or HF (hydrogen fluoride). The hydrocarbons cannot produce these acids as they do not contain the halogens, that is a man-made invention initiated by Thomas Midgley Jr. (1889-1944) in the second part of the 1930's, and who died due to another invention of himself.

The halogenated alkenes as a molecule have a short atmospheric life. One rule in organic chemistry is that when a molecule breaks down it breaks into something more stable or acids. These acids reacts with organic compounds found in most densely populated cities around the world, making the air acid and unhealthier. Olefin comes from French Gaz Olefiant and means oil forming. Some alkenes are known to react when in contact with air. This requires that the person charging the refrigerant vessels is carefully evacuating it before filling the fluid into the vessel. The procedure should be required from the refrigeration technicians and fitter to avoid polyamides forming.

It is often claimed that TFA is found naturally in nature. It has never been proven and a recent paper questions these claims[viii]. Some TFA is seemingly produced near under water volcano vent pipes resulting in slighter higher TFA concentration a research paper from 2005 shows[ix]. The concentrations found are relatively high in the North-Atlantic and less on the other. At great depths no TFA was found in the less saline waters. The papers also say that no TFA is found in the old Danish ground water. Therefore, claiming that TFA is natural to unsalted water is not true.

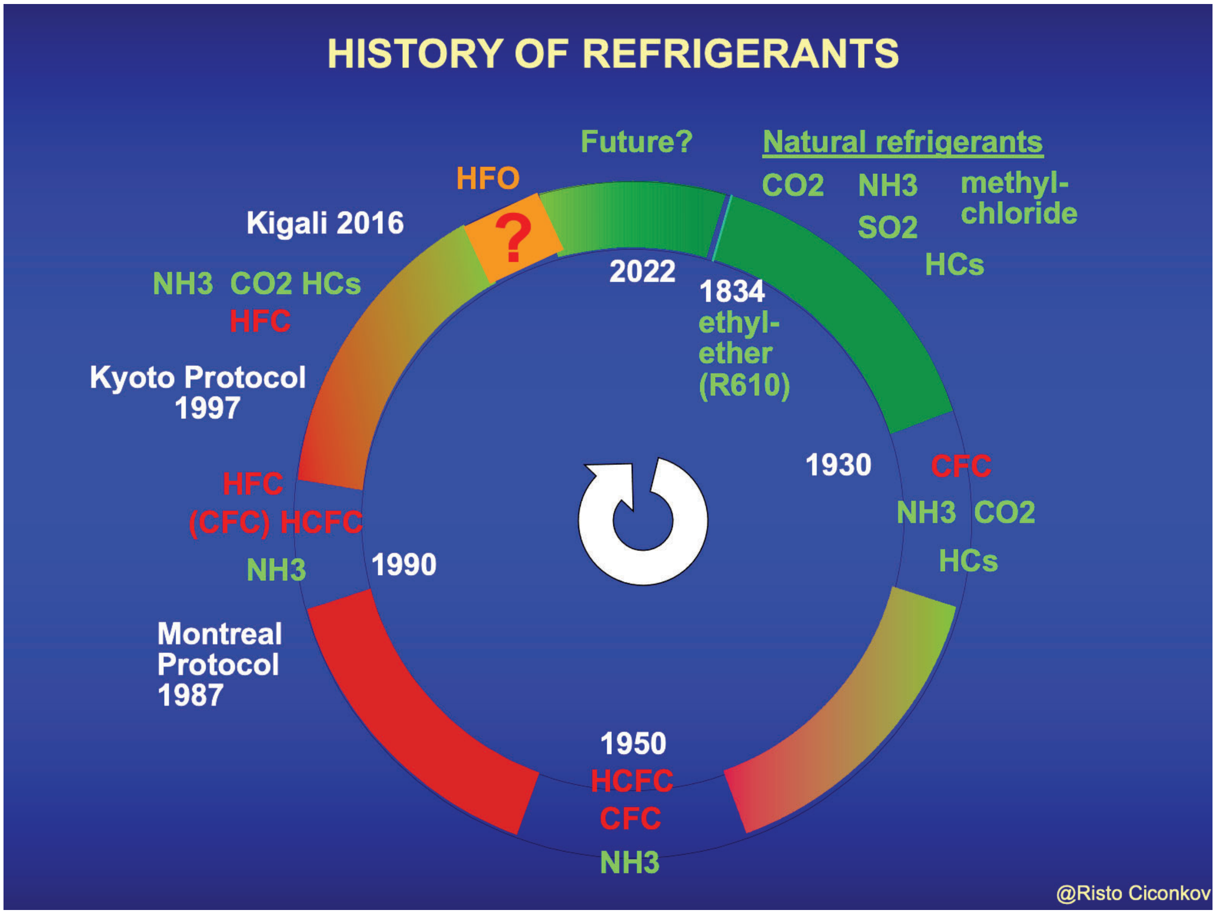


Figure 4 The history or evolution of refrigerants.

Different alkanes and alkenes have been used since the early days of refrigeration, especially in petrochemical installations. This will continue as long as the petrochemical industry will exist because it is natural to them. They have them as part of their production at a reasonable price, they know how to handle them safely, and they know how to handle them in case of leakage or need to incinerate them. Availability of these fluids applied as refrigerant is not an issue in the petrochemical plant producing different types of hydrocarbon gases.

Over 90% of domestic fridges and freezers are today based on a hydrocarbon, mainly R-600a, iso-butane, and commercial systems are often based on R-290, propane. For vaccine freezers R-170, ethane, is used in cascade systems on the low temperature side. There have been some attempts to introduce, with some success, auto cascade systems where you use a blend of refrigerants to reach low temperatures as well. Auto cascade systems only have one compressor, and the refrigerant is condensed in stages where the liquid phase of one fluid is evaporated to condense another fluid. The price for such a simplified system layout is the efficiency, which is lower than the cascade system with R-170/R-290 as the working fluids. The first cost is the driver for the auto cascade systems.

In some areas there is also a market for auto cascade systems based on a blend of hydrocarbons and noble gases. These units can reach -160°C to -180°C. Both land-based systems and sea going gas tankers are using this technology. Onboard ships it is also about space and weight which are both precious to the ship owners.

3. OTHER NATURALLY OCCURRING WORKING FLUIDS

The megatrend in most markets, in early 2022, is the wider use of CO_2 especially in the commercial refrigeration market (Supermarkets), larger commercial installations and small industrial systems[x]. One of the drivers is the energy efficiency, another is the pressure from the regulation and phase down of the halogenated hydrocarbons. The fact that some customers have seen first the phase out of ODS and then GWP substances is enough. The new lower and low GWP substances are expensive and already now show problems with environmental acceptability. Especially retailers and customer interaction companies have their eyes and ears open and any negative information is quickly transformed into action in order not to have a pushback from customers.

In the last several years, the R&D on CO_2 systems contributed to significant improvement of their energy efficiency. The transcritical operation can be improved with the following modifications (Hafner et al., 2015; Ciconkov, 2016):

- to install a parallel compressor(s);
- to build an internal heat exchanger;
- to install an external subcooler;
- to install ejectors as an expansion device;

The subcritical operation of CO_2 systems is very efficient and it can be achieved using an evaporative condenser. The subcritical operation can also be achieved at an air-cooled condenser combined with a water spray or / and with a wet pad (using evaporative effect).

Integrated approach of CO_2 systems can simultaneously provide refrigeration as low as -50°C, air conditioning, space heating and sanitary hot water (Hafner, 2017). Such concept outperforms all other HFC systems regarding the energy efficiency.

The market has also witnessed that one of the largest container lines in the world, Maersk Line, are now considering how they can decarbonise their fuel consumption and their choice on refrigerants are also revised. Up to this day the traditional solution has been halogenated hydrocarbons but the considerations are very much in favour of natural refrigerants. Onboard ships from other international shipping lines using methanol or hydrogen is also being considered. With more than 700 ships, just one company!, it is a major task and it will take time before all fleet is converted. Maersk has ordered the first 8 ships[xi].

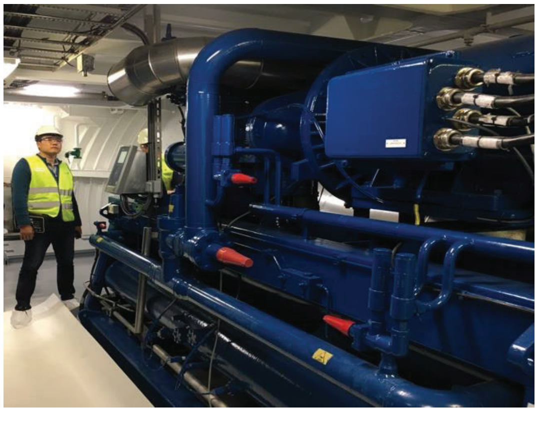


Figure 5 An ammonia system onboard a fishing vessel

NH_3 is already being used onboard fishing vessels[xii], with sufficient motor power to have a production and freezing plant onboard, and where the crew are all aware of the working fluids and are trained in safety. In these applications there are no concerns about the refrigerants. In the fish factory ships NH_3 is a natural part of the process because it provides fast defrosting of the freezers. The newer NH_3/CO_2 cascade systems are even more popular in Europe, however, even in North America more and more units are implemented.

The use of H_2, hydrogen, in the machine room have also opened the doors for alternative refrigerants such as NH_3, ammonia. What a lot of people forget is that H_2 is a tricky little atom that can get through almost anything. Also, the flame propagation is faster than any hydrocarbon. Most hydrocarbons have a flame propagation around 40cm/s and hydrogen is around 300cm/s. In this context the flammability of NH_3, less than 10cm/s, is very slow and almost safe. Another feature of NH_3 is the smell that will away even small leaks so something can be done about it before it becomes a serious problem.

NH_3, ammonia, has been installed now in a variety of buildings and applications, e.g. chillers and heat pumps in airports, hospitals, hotels, conference facilities and office buildings, but it is also the preferred refrigerant in large industrial factories with capacities of 100MW or more, where energy efficiency is the most important driver. Also cascade systems with NH_3 and CO_2 as working fluids are used in very large systems.

As the safety reason is the main barrier, new concepts of ammonia systems are developed where the refrigerant charge is reduced. It can be achieved mostly using new types of heat exchangers and new scheme avoiding receivers and pump system. The following solutions can be used:
- dry expansion (DX) evaporators,
- plate heat exchangers and "shell-and-plate" heat exchangers,
- microchannel heat exchangers,
- ammonia semi-hermetic compressors (non-compatability of copper windings is avoided),
- a new concept - all components incorporated in a container.

4. CONCLUSION

Naturally occurring working fluids – often called natural refrigerants – and noble gases can be utilised for all temperature needs from the extreme low temperatures to high temperatures of about 250°C to 350°C. This will cover more than 90% of the needs. Above these temperatures there is a gap up to drying cement at about 1000°C and melting steel/iron about 1250°C which will probably never become an object for heat pumps – but never say never – one cannot know about the future.

Figure 6 Aircooled hydrocarbon chiller (R-290)

Hydrocarbons are a large family of fluids with many possibilities and options. If we have the fossil fuels these gases will be part of the options and so will the fluorinated variants – unless they are regulated due to environmental concerns.

NH_3 – the old workhorse – will remain as a refrigerant also after there is no more gas, because it will be a by-product of the hydrogen production derived from water. It is a very safe and efficient refrigerant which has been used by industry since the early days of refrigeration.

Figure 7 NH_3/CO_2 cascade system

Figure 8 CO_2 transcritical heat pump

CO_2 is a veteran that has been around as long as NH_3, although almost disappeared between 1960 – 1990's before its revival due to Gustav Lorentzen and others.

H_2O is the most used of all refrigerants – mostly as a secondary working fluid, sometimes blended with glycol or salts to reduce the freezing point, but also as a primary refrigerant. It has been researched since the 1980's and is reaching market matureness within a few years. Demo sites are in operation here and there with different grades of success.

Air is used as a working fluid especially for extreme low temperatures, around -90°C to -140°C. Air is a cheap refrigerant and one of the most used secondary working fluids. Air is also used for tuna freezing / storage at temperatures below -60°C in Japan and in the Pacific.

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