Manuscript ID: 1030
DOI: 10.18462/iir.icr.2019.1030

The advantages of natural working fluids

Armin HAFNER[1]

[1] Norwegian University of Science and Technology, NORWAY, Armin.Hafner@ntnu.no

ABSTRACT

The manufacturers of refrigeration equipment are facing challenges related to the legislative requirements forcing them to implement less conventional refrigerants with lower Global Warming Potential (GWP) in their new products.

Natural working fluids like Ammonia, Carbon Dioxide and Propane have demonstrated to be energy efficient and environmentally benign alternatives. Ammonia refrigeration systems have been successfully in the market for more than 140 years. Especially at high ambient temperature conditions, these units can outperform conventional HFC systems. The cost, availability and detection of the fluid are no issue on a global base. Hydrocarbon based AC split units, applying propane, are in focus and large-scale production lines are under preparation. The fluid- and thermosphysical properties of CO_2 are quite different from most other working fluids. Therefore, the refrigeration system design has to be carefully adapted to the properties of CO_2, thereby maximising the energy efficiency and minimising the total cost of ownership.

The article describes the challenges related to conventional refrigerants and examples of the latest system developments applying natural working fluids in industrial-, commercial and marine refrigeration will be described in the work.

Keywords: Natural Working fluids, Ammonia, CO_2 refrigeration systems

1. INTRODUCTION AND CURRENT STATUS

In his very last publication, Lorentzen (1995) outlined in a detailed way why it does not seem very logical to replace synthetic refrigerants having a significant environmental impact with another family of related halocarbons equally foreign to nature. By that time, it was the initial phase of the Montreal Protocol, i.e. the replacement of CFCs with HFCs, starting to protect the ozone layer of planet earth, but ignoring the possible impact to global warming. Lorentzen describes sustainable solution for the refrigeration sector focusing on systems applying natural working fluids. He concludes that three proposed refrigerants are sufficient for long-term solutions; these are ammonia, propane and carbon dioxide. Even if the forced change of refrigerants was seen as a costly problem, the perspective for the refrigeration industry applying natural working fluids were foreseen good. Especially with respect to the immense opportunities for engineers solving the technical issues and developing innovative system concepts, which end-users are able to implement and achieve cost savings. As summarised by Ciconkov (2018), there is still a long way to go and lots of time has been used discussing endless phase down scenarios instead of focusing on a new approach: The phase in of natural refrigerants. On the other hand, despite the limited support, tremendous development steps within refrigeration systems applying natural working fluids happened during the past decades. As an example, the entire supermarket sector nowadays takes responsibility and introduces refrigeration equipment with natural working fluids globally, whenever local contractors are able to support them. Reputation and safety of customers is very important in this sectors as well as energy savings, leading to significant operational cost reductions. Within the heat pump market, hot water heat pumps, applying CO_2 as working fluid, are state of the art, too.

Due to the EU F-gas regulation and the Kigali amendment to the Montreal Protocol business as usual for decades within the refrigeration and heat pump sector is finally not possible any more.

Currently there are three main groups of refrigerant in the market place, the **saturated hydrofluorocarbons**, representing proposed substitutes from the chemical companies for CFC's and HCFC's under the umbrella of the Montreal Protocol. Their initial advantage was to protect the ozone layer, which was realised at a great success due to the Montreal Protocol. As the recovery of the Ozone layer has rapidly stopped during the past years as recently discovered by Montzka et al. (2018), there are still issues for some countries to follow up international agreements and educating their industries avoiding such huge and unnecessary emission.

However, due the high Global Warming Potential of the widely introduced HFCs, the churning of manmade refrigerants enters nowadays into a new era. The **unsaturated hydrofluorocarbons** are now the preferred solution provided by the chemical companies for all kind of applications. On the other hand, due to the intense effort from researchers and scientists, nowadays, **natural working fluids** became real alternatives for many application areas within the HVAC & refrigeration sector.

1.1. Saturated hydrofluorocarbons

Saturated single component hydrofluorocarbons do have a relative long atmospheric lifetime and a corresponding high global warming potential. The mostly applied fluids were and are:
R-134a (CF_3CH_2F): This saturated HFC refrigerant is property wise comparable to R-22 and is widely used in medium temperature refrigeration systems. It has a $GWP_{100years}$ of 1430 $kg_{CO2}/kg_{R\text{-}134a}$ and it is possible to use it for some time under the EU F-gas directive if the GWP quota system certificates are in place for the supplier and end-user. It is non-flammable and classified in safety group A1.
R-152A (CHF_2CH_3): Property wise very similar to R-134a. It is mainly applied for blends, however, it is being used more now mostly due to the low GWP100years of 124 $kg_{CO2}/kg_{R\text{-}152A}$. It is flammable and classified in safety group A2.
R-32 (CH_2F_2): Property wise very similar to R134a. It is mainly applied for blends. Especially split AC units apply nowadays R-32, mostly due to the reduce $GWP_{100years}$ of 675 $kg_{CO2}/kg_{R\text{-}32}$. It is flammable and classified in the ASHRAE safety group: A2L.
Common hydrofluorocarbons blends, which are widely used:

- **R-404A** (CF_3CH_3 / CF_3CHF_2 / CF_3CH_2F; $GWP_{100years}$ = 3922 $kg_{CO2}/kg_{R\text{-}404A}$)
- **R-507** (CF_3CH_3 / CF_3CHF_2; $GWP_{100years}$ = 3985 $kg_{CO2}/kg_{R\text{-}507}$)
- **R-407C** (CH_2F_2 / CF_3CHF_2 / CF_3CH_2F; $GWP_{100years}$ = 2107 $kg_{CO2}/kg_{R\text{-}407C}$)
- **R-410A** (CH_2F_2 / CF_3CHF_2; $GWP_{100years}$ = 2088 $kg_{CO2}/kg_{R\text{-}410A}$)

When converting traditional HCFC plants these HFC blends are substitutes to eliminate ozone depletion. However, all of them do have high GWP values, which limits their usage significantly in the future. This is already the case in Europe where they are taken from the market, as no emission quotas are reserved for such high GWP fluids anymore. The refrigerant suppliers forces the manufactures and contractors to apply unsaturated hydrofluorocarbons or their blends with lower GWP values.

1.2. Unsaturated hydrofluorocarbons

Unsaturated hydrofluorocarbons represent another kind of HFCs, which are potential replacements for HCFCs and saturated HFCs. In general, unsaturated hydrofluorocarbons react more rapidly with OH radicals and their atmospheric lifetimes is much shorter, as described by Hurley et al. (2008). Due to their short lifetime, they do have lower global warming potentials than saturated hydrofluorocarbons. Mostly applied are:
R-1234yf ($CF_3CF{=}CH_2$; $GWP_{100years}$ = 4 $kg_{CO2}/kg_{R\text{-}1234yf}$): This unsaturated HFC refrigerant does have a chemical double bound and is a so-called hydro fluoro olefin (HFO). Its GWP value on a 100-year perspective is low since atmospheric lifetime is very short (~11 days) and the double bound is reacting with OH radicals present in the ambient. R-1234yf is defined as mildly flammable and classified in the newly developed safety group A2L. The auto-ignition temperature is 405 °C. $CF_3C(O)F$ is the major atmospheric oxidation product of R-1234yf. The atmospheric fate of $CF_3C(O)F$ is hydrolysis, which occurs on a time scale of approximately 10 days, ending up as $CF_3C(O)OH$ (trifluoroacetic acid = TFA) and HF (hydrogen fluoride)

- The acidity of TFA is approximately 34,000 times stronger than that of acetic acid. TFA is harmful when inhaled, causes severe skin burns and is toxic for water organisms even at low concentrations. TLV (Threshold Limit Value) = 5 ppm; IDLH (Immediately dangerous to life or health) = 30ppm.
- Upon contact with moisture, including tissue, HF immediately converts to hydrofluoric acid, which is highly corrosive and toxic, and requires immediate medical attention upon exposure. Breathing in hydrogen fluoride at high levels or in combination with skin contact can cause death from an irregular heartbeat or from fluid build-up in the lungs. TLV = 3 ppm; IDLH = 30ppm.

The TLV, i.a. the maximum allowed concentration at a work place in Germany for R1234yf is 200 ppm.

R-1234ze(E) ($CF_3CH{=}CHF$; $GWP_{100years}$ = 7 $kg_{CO2}/kg_{R\text{-}1234ze}$) This unsaturated HFC refrigerant has also a chemical double bound. Exhibits flame limits at temperatures in excess of 28 °C. The auto-ignition temperature is 368 °C. When $CF_3CH=CHF$ is reacting with OH radicals present in the ambient, due to partly oxidation, both HC(O)F and CF_3CHO are formed

- HC(O)F (Formyl fluoride): decomposes autocatalytically near room temperature to carbon monoxide (CO) and hydrogen fluoride (HF)
- 2,2,2 –Trifluoroethanal: CF_3CHO → photolysis → CF_3 + HCO; $CF_3 + O_2$ → CF_3O_2 → COF_2

COF_2 -Carbonyl fluoride (Fluorophosgene) is extremely poisonous with a threshold limit value of 2 ppm for short-term exposure.

Example of blends:
R-513A ($CF_3CF=CH_2$/ CF_3CH_2F; $GWP_{100years}$ = 631 kg_{CO2}/kg_{R-513A}) & R-450A ($CF_3CH=CHF$/ CF_3CH_2F; $GWP_{100years}$ = 605 kg_{CO2}/kg_{R-450A}) are blends of the R-1234yf and R-1234ze(E) with R-134a. The refrigerants still exhibit non-flammable characteristics like R-134a and are classified in the safety group A1 as long as it is inside the system. However, decomposition of the fluids takes place as described for the single fluid when released into the ambient.

Decomposition takes also place when exposing these substances to hot surfaces, as experimentally investigated (JSRAE, 2017). The researchers show that independent of the absolute humidity the entire refrigerant concentration of 2.5 vol. % is decomposed on a hot surface of 600 °C and reaches HF concentration of 1.5 vol. % HF (1.5 vol % =15 000 ppm) for R-1234yf and around 1 vol. % HF (10 000 ppm) for R-32.

1.3. Natural working fluids

Natural working fluids do have favourable thermodynamic and fluid properties enabling energy efficient refrigeration system configurations. In addition, their environmental impact is well known and safety standards are established.

R-717 (ammonia, NH_3; $GWP_{100years}$ = 0): Ammonia has been used as a refrigerant during the last 140 years and is still widely used, especially for large industrial plants for food processing. It has neither a global warming potential and is not depleting the Ozone layer. R-717 will not be restricted under the F gas directive. Ammonia has very high latent heat and the refrigeration capacity per unit mass flow is the highest of all refrigerants used in traditional vapour compression systems. Because ammonia has low molar mass it can have much higher particle velocities than all other refrigerants and therefore allows for small pipe sizes. It is important to avoid copper components, because ammonia and water will corrode copper, zinc and their alloys. For example, ammonia and water will destroy the copper windings of the electrical motor in a hermetic compressor. It is flammable and toxic; therefore, it classifies for the safety group B2L and does require extra safety measures, similar to the HFCs with a short lifetime described above. TLV (Threshold Limit Value) = 50 ppm. IDLH (Immediately dangerous to life or health) = 300 ppm. It is necessary that the ammonia refrigeration system is located in a separate room, that personnel is well trained and has appropriate safety equipment available as for other flammable working fluids.

R-744 (carbon dioxide CO_2; $GWP_{100years}$ = 1 kg_{CO2}/kg_{R-744}): Carbon dioxide is a working fluid in refrigeration systems since the late 19th century. It disappeared from marine applications in the 1950's mainly due to technical difficulties and the introduction of synthetic working fluids, operating at lower working pressures. Engineers and researchers solved these technical difficulties nowadays and there is a wide range of applications where CO_2 is the preferred working fluid (freezing applications, commercial refrigeration, hot water heat pumps, mobile AC and heat pumping units, etc.) as described by Lorentzen (xxx), Nekså et al. (xxx), Pettersen et al.(xxxx).
R-744 is the only long-term non-flammable working fluid neither affecting the ozone layer nor contributing to global warming. During production, no environmentally unfriendly emissions occur, which is the reason for having the lowest direct environmental impact of all refrigerants. R-744 is the only non-flammable, low-GWP single working fluid classified as A1. It is non-toxic and will not be restricted under the F-gas directive. Independent on the concentration of oxygen in the air, the human lung needs to reject CO_2 into the atmosphere; therefor the TLV is 5.000 ppm. The IDLH threshold for CO_2 is 40.000 ppm.

R-290 (propane, C_3H_8; $GWP_{100years}$ = 3 kg_{CO2}/kg_{R-290}): Propane is an example of another group of natural working fluids, the hydrocarbons. It has a very low GWP. Systems with R-290 are in operation globally since many years and is an energy efficient alternative to all HFCs. Currently it is widely used within compact systems with low charges such as light commercial refrigeration equipment. There are no charge limitations if these kinds of units applying hydrocarbons are located outdoors in restricted areas, sufficient refrigerant charge to achieve the required capacities is possible even if the equipment is located indoors when following existing standards and regulations. The major disadvantage is the high flammability; therefore, hydrocarbons are all classified in the safety group A3.

2. FAVOURABEL SYSTEM CONFIGURATIONS FOR NATURAL WORKING FLUIDS

This chapter highlights some examples of successful applications applying natural working fluids. Some of them have gained a significant market share while others have a significant growth.

Ammonia units:
Traditionally ammonia refrigeration units are characterised by high capacity and high refrigerant charges. The development focus in this sector is currently to enable low charge systems for a wide range of applications, to increase the market shares in chillers, cooling & freezing units, Lamb (2017). These so-called packaged systems reduce installation time, and enable smaller air-cooled units, located close to the point of cooling.

Cold store applications are favourable for ammonia refrigeration, enabling significant annual energy saving as described by Jensen et al. (2018)

In the northern part of Europe, marine installations, like refrigerated sea water coolers, are often utilised with ammonia refrigeration systems. Cascade units with CO_2 in the low stage, i.e. the freezing part, are nowadays state of the art. This configuration is also successfully applied in low temperature cold stores Hattori et al. (2019), it combines and strengthens the beneficial properties of these two natural working fluids by eliminating the challenge of low evaporation temperatures for ammonia and the high rejection temperatures for CO_2 units.

Hydrocarbon units:
After the fall of the Berlin wall Greenpeace (1992) encouraged a company in the Easter part of Germany to develop the first series of fridges, GreenFreez refrigerators, applying isobutene as working fluid. Decades later this has become a global standard. Beside the introduced household refrigeration devices like fridges and freezers, end-users of light commercial cabinets are also requesting more and more units equipped with propane as working fluid. When following the standards, there are no technical restrictions related to the required refrigerant charge for these units located in sales areas. This is ongoing and more and more companies are following this trend, as demonstrated by ‘Refrigerants, Naturally!’ the global, non-profit initiative of companies in the food and drink, food service and consumer goods sectors, with the non-profit

In 2018, the ‘All Easy Series R-290’ residential single-split air conditioner from Midea were certified by the German ecolabel "Blue Angel" for its ultra-low global warming potential (GWP), high energy efficiency, low noise, and stringent material safety control. These units and other similar units, e.g. developed by Godrej, will have a significant growth in the next years. End users will be aware of the local risk and environmental impact. As nowadays flammable synthetic refrigerants are dominating this market segment, there will be no restrictions to apply natural working fluids in the residential AC and heat pumping market. The households are familiar with gas fired cooking equipment and do have in many cases several natural gas cylinders in their storage places. Therefore, a RAC unit with a relative low charge of propane, compared to the equipment in the kitchen, will not represent an additional risk compared to flammable HFCs. When end user are aware of the additional risk of being exposed to decomposition products and the unknown total environmental impact of the newly introduce refrigerants, there will be a demand for alternative systems as developed by Midea, Godrej and others.

Carbon Dioxide units:
As mentioned above, CO_2 refrigeration applications are outperforming any other fluid in the temperature range below -35 °C and above -55 °C with respect to energy efficiency, compactness and safety. Therefore, a tremendous increase in industrial refrigeration units are utilised within the food- and processing industry. Even if the total amount of these kind of systems are low compared to mass-produced units, their impact on food safety and quality is significant.

Commercial refrigeration systems with integrated AC are becoming a trend due to reduced maintenance cost and the trust of end-users to apply natural working fluids all over the supermarket building (Hafner 2014 & 2016; Girotto, 2016). Figure 1 shows the development of such an integrated MultiPACK unit, able to provide all the required cooling for the products inside the supermarket. The unit is equipped with a Multi Ejector and parallel compressors. In addition, the MultiPACK unit supplies heating and cooling to several indoor air handling units (IAHU). In case of heating demand inside the building, hot gas is supplied directly towards the IAHU's. The individually flow rates are controlled locally by feeding valves, located upstream of each IAHU. The cooled refrigerant enters the high side pressure part of the Multi Ejectors. If the building requests cooling, liquid CO_2 is supplied towards the IAHU's. The entire vapour of all IAHU's is sucked by the AC-Ejectors, discharging it towards the separator. The parallel / AC compressors maintain the pressure level of the separator, i.e. providing the cooling capacity for the building.

In many cases, when existing building infrastructure has to be taken into consideration during a refurbishment of a supermarket, AC needs to be integrated through a chilled water loop. Figure 2 shows the development of such an integrated MultiPACK unit with a standard Multi Ejector and parallel compressors. Besides providing all the required cooling capacities for cabinets for chilled and frozen products inside the supermarket, the unit is equipped with the innovative chiller. The liquid receiver supplies liquid refrigerant towards the evaporators of the chiller producing cold process water. Two evaporators absorb the heat from the process water at different evaporation pressure levels, which reduces the exergy destruction of the process.

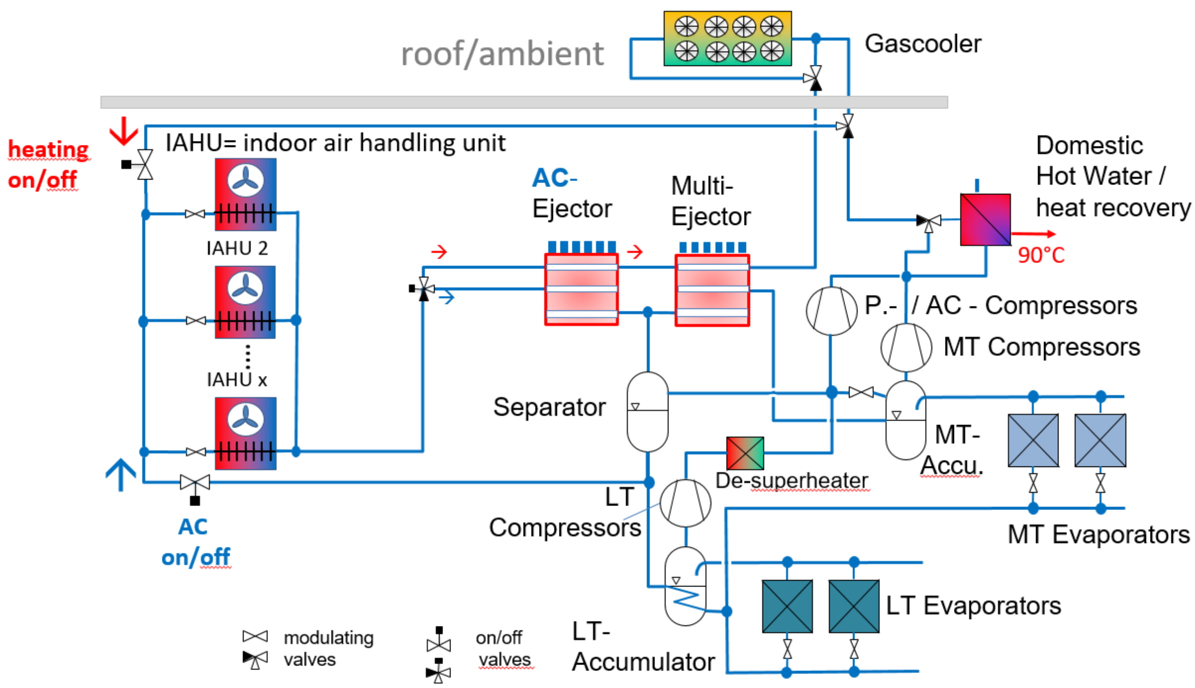

Figure 1: MultiPACK unit design with several individual indoor air handling units.

The CO_2 chiller part shown in Figure 2 represents an innovative approach to adapt water chillers to the properties of CO_2. This concept can also be applied in an AC chiller / heat pump application. The evaporators of the chiller part in combination with the Multi Ejectors allow an elevated suction pressure of the (parallel) compressors. The first chiller sections is connected to the liquid receiver tank at 42 bar ($t_o \approx +7$ °C). The liquid refrigerant is supplied by gravity and allows the pre-cooling of the process water at 12 °C. The second evaporator provides more cooling capacity, since it is able to further reduce the temperature of the process water to 7 °C. The suction pressure inside the second chiller evaporated is at 38 bar ($t_o \approx +3$ °C), due to the usage of the Multi Ejectors, which are able to suck all the vapour out of the second evaporator and supply it back to the liquid receiver where the (parallel) compressors maintain the pressure level. The pressure level inside the separator can be adjusted to adapt the cooling capacity provided towards the building by the chilled water loop. In case of additional heating demand during the cold season, an outdoor heat exchanger is able to supply external heat via the second ejector, in this case acting as the Heat Pump (HP) ejector.

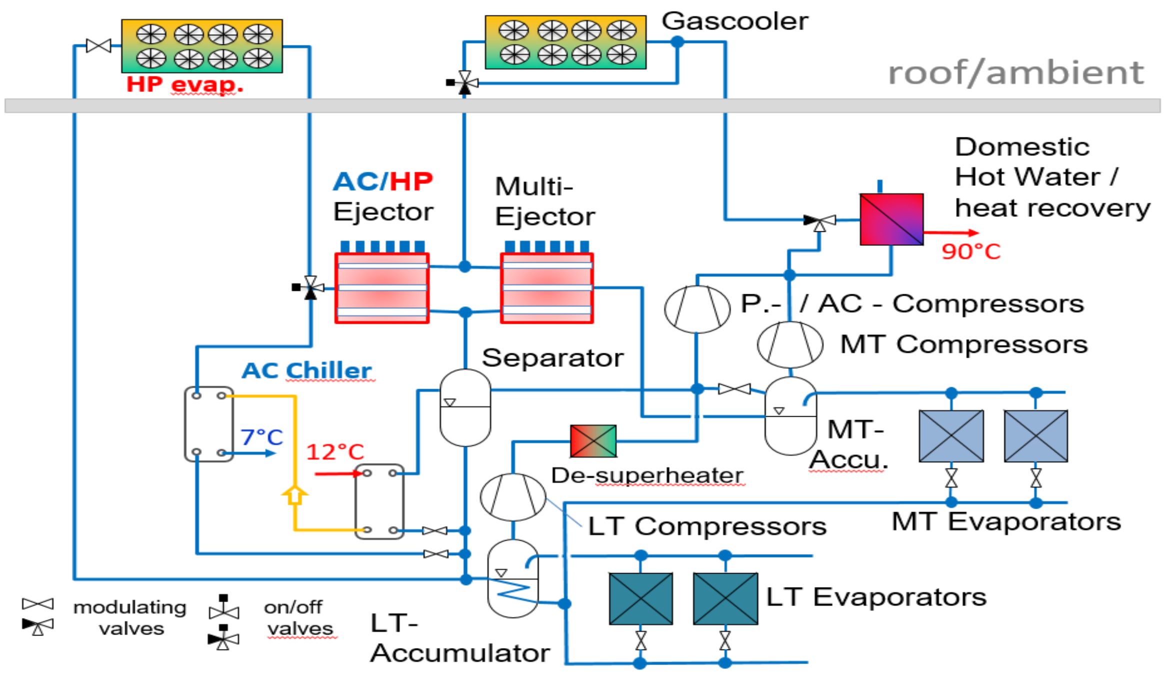

Figure 2: MultiPACK unit design with integrated AC chiller device and heat pump function.

3. DISCUSSION

The preferred working fluid, when developing and introducing HVAC and refrigeration units should have:

- a long term prospective,
- a well-known and understood environmental impact,
- enable an energy efficient operation of the units,
- highest possible safety class

This means that the working fluid should not be restricted under the F-gas regulation. Therefore, none of the current HFC blends mentioned above are suitable choices. The safety classification is also of critical importance when the refrigeration systems are intended to be in the public domain, a part of mobile applications, e.g. marine vessels. Therefore, the use of R-152A, R-1234yf and R-1234zeE are unlikely and only possible when thorough risk analysis and mitigations have been made. The group of blends like R-513A and R-450A might have a potential short period in medium temperature applications due to the relatively low GWP and A1 safety classification. However, as indicated in the safety data sheet of the fluid suppliers, the '*hazardous decomposition products may include: Hydrogen fluoride, Carbon oxides Fluorinated hydrocarbons, Carbonyl fluoride*'. The question is if the end-user is willing to take the risk. Another problem is the complex chemical blend and composition, the global availability, and the higher GWP relative to R-744 that makes these non-natural working fluids less economical.

3.1. Recommendation to estimate the environmental impact of the HVAC&R units

Total Equivalent Warming Impact (TEWI) is an established method within the refrigeration sector. TEWI measures the global warming impact of a HVAC&R system by quantifying the amount of greenhouse gasses a unit emits. TEWI does not account for the energy embodied in product materials, greenhouse gas emissions from chemical manufacturing and end of life disposal of the unit.
Therefore, a life cycle climate performance (LCCP) approach should be established for all refrigeration applications. LCCP is well established for commercial HVAC&R units and mobile air conditioning (MAC) units. This transparent method describing the environmental impact of systems allows an evaluation of alternative systems. LCCP can also account for minor emission sources that are not accounted for in TEWI such as transportation leakage, manufacturing leakage and refrigerant manufacturing emissions. LCCP is calculated as the sum of direct and indirect emissions generated over the lifetime of the refrigeration system. Direct emissions include all effects from the release of refrigerants into the atmosphere. This includes annual

leakage and leakage during the disposal of the unit. The indirect emissions include emissions from the manufacturing process, energy consumption during operation and disposal of the system. LCCP allows to describe the environmental impact of the HVAC&R units based on transparent input parameters like system performance data at various load conditions and heat rejection temperatures. A single focus on GWP values doesn't inform the end-user about the real environmental impact of a working fluid and system configuration.

3.2. Natural working fluids

Ammonia (R-717) is an approved natural working fluid for industrial and maritime refrigeration system. The system architectures for ammonia units are understood, challenges with suction pressures below atmospheric pressure at low evaporation temperatures (> -33.5 °C) are known, while handling safety issues (classified as B2L) is standard.
Home appliances, like fridges and freezers and light commercial refrigeration equipment should only apply hydrocarbons as the working fluid. A fast market introduction of hydrocarbon based split AC and heat pumping units should be promoted, eliminating the dependency of local markets to import HFCs as most countries do have sources and the ability to handle hydrocarbons. This would significantly improve the energy efficiency within these sectors and eliminate any Fluor emission with all they unknown decomposition products.
Previously CO_2 refrigeration equipment was not available in the capacity range required for fishing vessels, however, the component manufactures do see the market potential and more large capacity equipment enters the market. For maritime refrigeration applications globally CO_2 should become the preferred choice, whenever ammonia units cannot be applied.

4. SUMMARY AND CONCLUSION

Safety of service people and end-users should have the highest priority, followed by the total environmental impact when evaluation alternative working fluids within the refrigeration and heat pumping sector. A low GWP values does not necessarily mean that fluids are superior and the best available choice. As Gustav Lorentzen said, it is not logical to replace a harmful substance with another substance which total environmental impact is still unknown. Therefore, the refrigeration society has to take responsibility and phase in natural working fluids whenever it is possible.

Ammonia is one option mainly for large industrial applications. In addition due to packaged designs, low charge systems are state of the art, enabling to apply these units as chillers and refrigeration units in many locations. In combination with CO_2, as the working fluid in the low temperature part of a cascade unit, such units are superior when storage or process temperatures below -45 °C are required in high ambient temperature regions.

Propane will play an important role, within the next years, replacing most of the HFCs applied in split AC and heat pumps units today.

A remarkable development of CO_2 refrigeration technology has taken place since the revival of the refrigerant in the late 1980s. The development has led to efficient CO_2 systems and their successful introduction into the market. Additionally, it inspired the development of other innovative technologies that focus on improving the energy efficiency and reducing the total cost of ownership.

The integration of expansion work recovery devices like ejectors allows today's CO_2 commercial refrigeration systems to outperform HFC units on annual energy consumption in any climate region. The integration of further functions like chilling of process water or direct evaporation for AC purpose into the centralised refrigeration unit is a key success factor for these sustainable vapour compression systems replacing HCFC and HFC systems globally. CO_2 chillers can be applied where units with flammable refrigerants cannot be used.

The designers and engineers spreading CO_2 technology should remember when designing all of the integrated functions, that the fluid properties are an asset, not a hindrance. Therefore, all CO_2 evaporators should be operated without superheat, heat recovery should be employed whenever there is a heat demand and domestic hot water production should be a natural feature of the systems. The described innovations will further simplify CO_2 systems in the near future.

Training and knowledge transfer is the key for a successful and fast phase in of CO2 refrigeration units globally. Therefore, also World Bank and multi-lateral funds should support global education, training and certification as well as covering additional first costs with affordable loans (no interest rate), so the end-users can return the loan during the operational phase, since the new energy efficient system gives them a significant energy / cost saving.

ACKNOWLEDGEMENTS

The research leading to these results has received funding from the European Union under the programme H2020-EU.3.3.1. - Reducing energy consumption and carbon footprint by smart and sustainable use (Grant Agreement number: 723137).

REFERENCES

Banasiak, K.; Hafner, A., Kriezi, E.E.; Madsen, K.B.; Birkelund, M.; Fredslund, K.; Olsson, R. (2015), Development and performance mapping of a multi-ejector expansion work recovery pack for R744 vapour compression units, International Journal of Refrigeration, Volume 57, 1 September 2015, pp. 265-276

Ciconkov R., 2018. Refrigerants: There is still no vision for sustainable solutions. International Journal of M.D.Refrigeration, Volume 86, February 2018, Pages 441-448

Girotto, S., 2016. Direct space heating and cooling with refrigerant CO_2. ATMOsphere Europe, Barcelona. http://www.atmo.org/media.presentation.php?id=754.

Greenpeace 1992. https://www.greenpeace.org/international/story/15323/how-greenpeace-changed-an-industry-25-years-of-greenfreeze-to-cool-the-planet/

Hafner, A., Claussen, I.C., Schmidt, F., Olsson, R., Fredslund, K., Eriksen, P.A., Madsen, K.B., 2014, Efficient and integrated energy systems for supermarkets. Proceedings of the 11th IIR Gustav Lorentzen Conference on Natural Refrigerants, Hangzhou, China.

Hafner, A., Banasiak, K., 2016. Full scale Supermarket Laboratory R744 Ejector supported & AC integrated parallel compression unit. Proceedings of the 12th IIR Gustav Lorentzen Natural Working Fluids Conference, Edinburgh, Scotland.

Hattori K., Arimoto R., Terashima I. 2019. Development of a high efficient NH_3/CO_2 refrigeration system. Proceedings of the 8th IIR Conference: Ammonia and CO_2 Refrigeration Technologies, Ohrid, 2019

Hurley M.D., Wallington T.J., Javadi M.S., Nielsen O.J., 2008. Atmospheric chemistry of CF3CF=CH2: Products and mechanisms of Cl atom and OH radical initiated oxidation. Chemical Physics Letters, Volume 450, Issues 4–6, Pages 263-267

Jensen S., Gerstenberger E. 2018. Einsatz von NH_3 DX Systemen für energieeffiziente und zukunftssichere Analgen. Proceedings of the DKV meeting 2019 in Aachen. JSRAE, 2017. Risk Assessment of Mildly Flammable Refrigerants, Report from The Japan Society of Refrigerating and Air Conditioning Engineers, March 2017

Lamb R. 2017. Low Charge Packaged Ammonia Refrigeration Systems. Proceedings of the 7th IIR Conference: Ammonia and CO_2 Refrigeration Technologies, Ohrid, 2017

Lorentzen, G., Pettersen, J., 1992. New possibilities for non-CFC refrigeration. IIR Int. Symp. on Refrigeration, Energy and Environment, Trondheim, Norway, June 22-24, pp.147-163.

Lorentzen, G, 1995. The use of natural refrigerants: a complete solution to the CFC/HCFC predicament. Int. Journal of Refrigeration 9. Vol. 18, No. 3, pp 190 197, 1995

Montzka S.A., Dutton G.S., Yu P., Ray E., Portmann R.W., Daniel J.S., Kuijpers L., Hall B.D., Mondeel D., Siso C., Nance J.D., Rigby M., Manning A.J., Hu L., Moore F., Miller B.R. & Elkins J.W., 2018. An unexpected and persistent increase in global emissions of ozone-depleting CFC-11. Nature, volume 557, pages413–417.

Pardiñas, Á.Á., Hafner, A., Banasiak, K., Kvalsvik, K.H., Larsen, L., 2018. Strategy for the control of two groups of ejectors operating in parallel in integrated R744 refrigeration systems. Refrigeration Science and Technology, 2018-June, pp. 1069-1076.