CO2 As An Alternative Refrigerant For Applications Below -50°C

Robin Langebach
TU Dresden, Germany, robin.langebach@tu-dresden.de

Ullrich Hesse
TU Dresden, Germany, ullrich.hesse@tu-dresden.de

Yixia Xu
TU Dresden, Germany, purdueherrickconf16@gmail.com

CO_2 as an Alternative Refrigerant for Applications Below -50°C

Robin LANGEBACH[1*], Ullrich HESSE[1], Yixia XU[1]

[1] Bitzer-Professur für Kälte-, Kryo- und Kompressorentechnik,
TU Dresden, Germany
Robin.Langebach@tu-dresden.de
Ullrich.Hesse@tu-dresden.de

* Corresponding Author

ABSTRACT

Carbon dioxide (CO_2) is a well-known and established refrigerant with many advantageous properties and therefore used in many applications. However, the lowest achievable temperature is usually limited by the triple conditions at approximately 217 K and a corresponding pressure of 5.2 bar. Below these triple conditions CO_2 only exists is gaseous and solid state. Commonly, the occurrence of solid particles in vapour compression cycles is carefully avoided and hence CO_2 in solid state no option at all. With respect to increasing legal restrictions and upcoming bans for fluorinated refrigerants CO_2 might be also a reasonable alternative in low temperature refrigeration – despite the obstacles with the solid phase. In this paper we give an overview on previous research activities with CO_2 sublimation cooling in literature. Further, the theoretical efficiency of a CO_2 cycle with a sublimation temperature of 198 K is compared to a conventional R404A/R23 cascade. It can be shown that a CO_2 sublimation cycle can exceed the cycle efficiency of conventional systems. Finally, a closer look to the heat transfer of solid-gaseous flow in the sublimation heat exchanger is given and challenges are discussed.

1. INTRODUCTION

With respect to refrigeration the year 2015 most probably will be of certain historical importance worldwide. In Europe the new F-gas regulation went into force. In the US, president Obama's Climate Action Plan (CAP) was brought substantially forward by announcing the EPA/SNAP programme. China as well adopted several actions with respect to refrigerant use. Even if the national activities partly differ substantially, all of them follow the goal to reduce the contribution to global warming by refrigerants released to atmosphere.
The EU F-gas regulation includes indisputable the most fundamental changes for refrigerants use in Europe since the Montreal Protocol in 1989. By law, fluorinated refrigerants with significant contribution to the greenhouse effect are intended to be driven out of the market. This is going to be realized by a chronological phase-down or even phase-out of the fluorinated refrigerants based on their GWP value or CO_2 equivalent. With this very strict roadmap it is the declared aim to reduce the GWP-weighted amount of fluorinated refrigerants about 80% by the year 2030.
Refrigerants for application below -50°C (223K) are currently not affected by the regulation due to an exemption clause. The reason is that for those applications only two safety refrigerants are available - the rarely used Tetrafluoromethane (R14) and the most commonly used Trifluoromethane (R23). Both refrigerants would be instantly banned by the EU F-gas regulation due to their substantial GWP values (GWP_{R14}=7390; GWP_{R23}=14800).
Most likely, the EU F-gas regulation will be amended in future and this exemption abolished - particularly when reasonable alternatives for safety refrigerants are available.
Carbon dioxide (CO_2) is widely used natural refrigerant for application down to a temperature of approximately 230K or slightly below. CO_2 is non-flammable, under typical conditions non-toxic and therefore an advantageous natural alternative for a lot of applications. Due to its triple temperature of ≈ 217K pure CO_2 is present below exclusively in solid and gaseous phase. This natural barrier currently limits the application range of CO_2.
In case one could exceed this natural barrier - apart from the involved obstacles and challenges - CO_2 would have an excellent substitution potential with respect to the currently used fluorinated refrigerant R23. At a pressure of ≈1bar CO_2 has a sublimation temperature of ≈195K. In comparison with that, R23 has a normal boiling temperature of ≈191K. Moreover, sublimation and evaporation line of both refrigerants are quite similar.

Within this paper we firstly discuss relevant literature sources and patents in order to give a brief overview on the available facts and data about sublimation cooling. Further, we try to estimate the theoretical efficiency of a sublimation cycle with CO_2 as the refrigerant in comparison to a conventional R404A/R23 cascade. Finally, we give a closer look to operation modes of the sublimator and relevant heat transfer considerations.

2. LITERATURE AND PATENTS

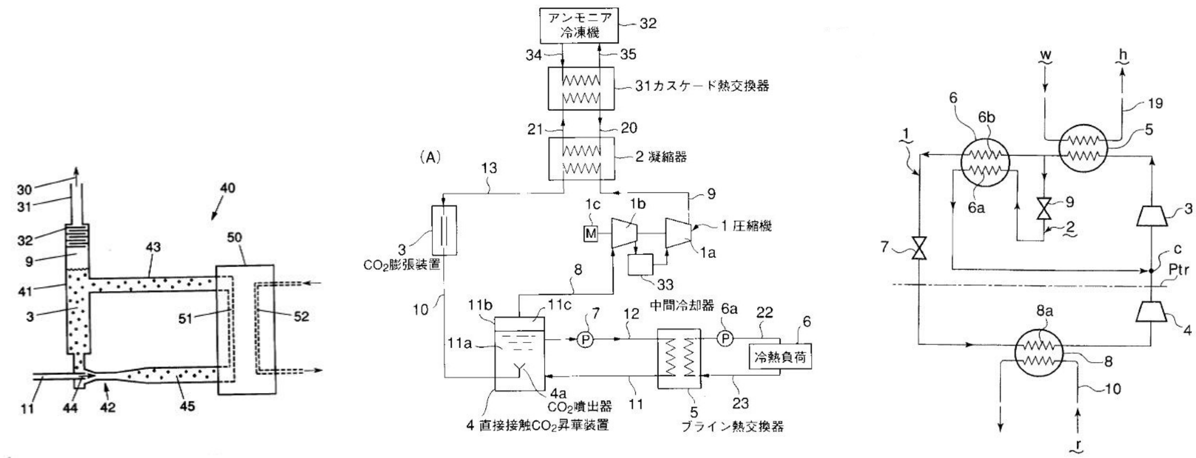
2.1 Literature

In principle, it has to be mentioned that the application of CO_2 as an at least partially solid refrigerant in a closed cycle is well known for some time. However, the number of publications related to this topic is very limited.
The first determined publications in our survey are from the early 1960th and do have their roots in cryogenics and space engineering. Weinstein et al. (1964) investigated the sublimation cooling in a closed vessel with the help of various cryogens under different pressures.
Weinstein et al. (1964) proved the practical applicability of this cooling method and investigated different structures and shapes of the sublimator.
Ostroumov (1991) later investigated the mechanism of sublimation at surfaces theoretically with respect to porosity of the solid layer. His publication is representative for a couple of publications regarding phase change solid to gas at surfaces.
Naer et al. (1995) published an article about the application of CO_2 sublimation cooling in a so called "bottle sublimation cooler". Within this device CO_2 is expanded to the solid/gaseous phase and the solid particles accumulate onto a perforated sublimation surface. The effect of sublimation was used to provide cooling of certain electronics, for instance in space application.
With respect to CO_2 safety valves a PhD thesis was carried out at TU Dresden in order to clarify the impact of solid CO_2 existence in safety valve while discharging Huang (2006). It could be shown that solid particles in CO_2 discharge flow lead to certain accumulation but do not decrease safety due to inherent self-cleaning mechanism by pressure fluctuations. Coupled to these investigations Huang et al. (2008) proposed a new concept for a CO_2 sublimation cycle. Other publications followed with direct link to CO_2 sublimation cycles, e.g. in Yamaguchi et al. (2008); Yamaguchi and Zhang (2009). On a laboratory scale sublimation experiments in a closed cycle were performed. However, a practical application in refrigeration plants never became known to the authors. The publications mainly focus on concepts and first tests (Zhang & Yamaguchi, 2011).
A first overview of previous activities in the field of CO_2 sublimation cooling is given in the review paper of Chen and Zhang (2014). Both authors indicate that the topic of sublimation cooling still needs deeper investigation but provides promising opportunities.
Beside the publications on general CO_2 sublimation cycles there are a number of publications regarding sublimation heat transfer. Even if there is only a little number available we try to give an overview on published heat transfer coefficients in section 4.2.

2.2 Patent applications

Within an extensive patent survey together with the Patent Information Centre of TU Dresden we could figure out a number of relevant patents or patent applications with regard to CO_2 sublimation cycles. Partly, these records gave clear indications for technology developments also by companies. In the end we found approximately 20 relevant records[1]. In the following we want to reflect the content of three patents or applications with interesting information content:
In the patent application NL9401324A (1996), see Fig. 1(a), made by Urenco Netherlands, a cooling process with CO_2 below the triple point is described. Basic idea is to inject the expanded CO_2 into another carrier fluid. The sublimation process takes places during and after injection in interaction with the carrier fluid. The kinetic energy of the expansion is used to drive the flow of the carrier fluid through the heat exchanger. In a later section of this paper 4.1 we discuss this idea further in terms of sublimator design. Although the patent was never granted the idea behind indicates a basic principle for CO_2 sublimation cooling - the "wet" operation of the sublimator.
Similar to the above mentioned application is JP2004308972A (2004), see Fig. 1(b), made by Mayekawa and Seisakusho. Here, the CO_2 is also expanded into a carrier fluid. The injection takes place in a liquid receiver in order to instantly

[1] Multiple applications or patent extensions to other countries not included.



(a) NL9401324A (1996). (b) JP2004308972A (2004). (c) US7818971B2 (2010).

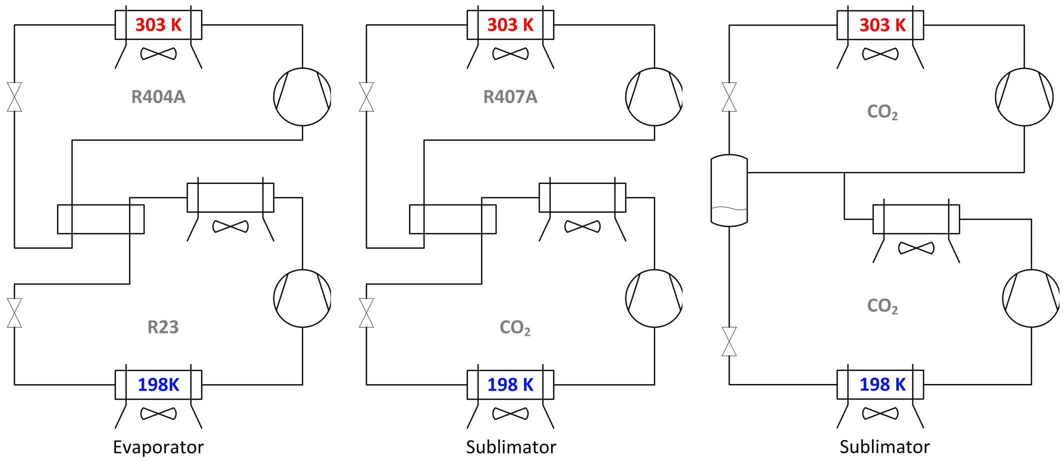
Figure 1: Selected drawings of relevant patent applications regarding CO_2 sublimation cycles.

separate gaseous CO_2 from the carrier fluid. The cooled fluid is circulated between the vessel and the heat exchanger by an additional pump. This method indicates the need for separation of CO_2 gas out of the carrier fluid.
In patent US7818971B2 (2010), see Fig. 1(c), made by Mayekawa and Doshisha we see the contrary approach. Here the sublimator is fed with pure CO_2 without the help of any additional carrier fluid. The idea behind indicates the other basic principle for CO_2 sublimation cooling - the "dry" operation of the sublimator.
Finally, it has to be mentioned that a significant number of patent applications never were granted and also granted patents expired for different reasons. Therefore, the technical solutions may be used by everybody and are no longer protected by patents.

3. THEORETICAL ANALYSIS OF TWO CO_2 SUBLIMATION CYCLES

3.1 Introductive remarks and description of the cycles

Typical refrigeration applications in the temperature range between -50°C (223K) and -100°C (173K) can be found in the chemical industry (distillation, freeze-drying,...) and in environmental simulation systems (test chambers and cells). A commonly used principle for cooling is a refrigeration cascade. Thereby, at least two refrigeration cycles are coupled in a way that an upper stage provides the necessary cooling for condensation of a lower stage. The thermal coupling of both stages is realized by a cascade heat exchanger, typically a plate fin or tube-in-tube type.
For efficiency reasons every single stages of a refrigeration cascade has its own, thermodynamically fitting refrigerant. For applications below -50°C (223K) and -75°C (198K) commonly a two stage refrigeration cascade with refrigerant R404A in the upper stage and R23 in the lower stage is used. However, other pairs of refrigerant are possible - depending on the application.
Due to the prevalence of R404A/R23 cascade systems we want to use such a system as state-of-the-art benchmark and hence for comparison. A flow chart of the R404A/R23 cascade system (baseline cycle) is given in Figure 2(a).
The first CO_2 cycle with sublimation is also a cascade system (sublimation cycle 1) which uses an evaporating refrigerant in the upper stage and CO_2 in the lower stage with sublimation for the cooling provision. Principally, R404A is a possible refrigerant option for the upper stage - as in the baseline cycle. But, R404A will be phased-out due to its GWP value of 3922 - in Europe as well as in the US. Alternative refrigerants are available and currently under extensive testing. A clear favourite for R404A substitution is not yet found. Most probably a number of alternatives will be announced depending on the different applications. One possible option is refrigerant R407A. With its GWP value of 2107 it is a widely discussed alternative but comes with certain temperature glide (e.g. 6K @ 1.6bar and 240K initial evaporation temperature). In order to compare a sustainable cycle to the baseline system we will apply R407A for the upper stage in sublimation cycle 1. The corresponding flow chart is given in Figure 2(b).
The second CO_2 cycle with sublimation (sublimation cycle 2) is based on a typical CO_2 system for application above the triple point. We have a first expansion of the re-cooled CO_2 into a liquid receiver on an intermediate pressure level.



(a) Cascade cycle with refrigerants R404A and R23 (Baseline cycle).

(b) Sublimation cascade cycle with refrigerants R407A and CO_2 (Sublimation cycle 1).

(c) Sublimation cycle with intermediate pressure level and refrigerant CO_2 (Sublimation cycle 2).

Figure 2: Flow charts of the baseline cascade and the two variations of the sublimation cycle for comparison.

The liquid phase is further expanded below the triple conditions where later the sublimation takes place for cooling provision. The sublimated gas is compressed in a first compressor to intermediate pressure and mixed with the gas from the liquid receiver at intermediate pressure. The corresponding flow chart is given in Figure 2(c).
For both sublimation cycles we disregard any obstacles with respect to the sublimation process in the sublimator for the moment. The technical realization and possible problems will be discussed later.

3.2 Used fluid properties databases

The calculation of a classical refrigeration cascade with refrigerants in the liquid/gaseous state is usually possible without constraints. Once the equation of state for a certain substance is formulated commonly used databases, e.g. Refprop by Lemmon et al. (2010), provide access to almost all fluid properties needed via comfortable interfaces to several calculation programs.
The calculation of properties of CO_2 below the triple point is still coupled to some hurdles to overcome - especially when consistent data is needed. The first equation for consistent description of CO_2 properties in all three states (liquid, gas, solid) was formulated by Jäger and Span (2012) and recently implemented to the fluid properties database TREND 2.0 by Span et al. (2015). With the help of this database and its interface to calculation programs it is possible to carry out extensive theoretical investigations for sublimation cycles including optimization.

3.3 Boundary conditions for calculation

The calculations for all three cycles were carried out with the following boundary conditions:

- Condensation temperature T_C=303K
- Evaporation-/sublimation temperature T_0=303K
- Superheating at evaporator/sublimator T_{sh}=5K
- Subcooling at condenser T_{sc}=3K
- Isentropic efficiency compression η_{is}=0.7
- Minimum temperature difference at cold end of any heat exchanger ΔT=10K (further reduced by refrigerant glide at evaporation point - R404A ≈ 0.6K, R407A ≈ 6.2K)

The coefficient of performance of the ideal and reversible Carnot cycle with the given boundary conditions was evaluated with

$$COP_C = \frac{T_0}{T_C - T_0} = \frac{198K}{303K - 198K} = 1.88\,. \tag{1}$$

The derived Carnot efficiency is calculated by

$$\eta_C = \frac{COP}{COP_C}\,. \tag{2}$$

The calculations we carried out with the help of MS Excel using both, Refprop (Lemmon et al., 2010) and Trend (Span et al., 2015) for fluid properties call. The COP of any cycle was optimized by variation of the evaporation temperature in the cascade heat exchanger (baseline and sublimation cycle 1) or by variation of the intermediate pressure (sublimation cycle 2).

3.4 Results and discussion

The results and further relevant data regarding the calculation can be found in Table 1. The discussion of each cycle is done individually in the paragraphs below.

Baseline cycle
With the above mentioned boundary conditions we calculated a COP for the baseline cycle of 0.806. This corresponds to a Carnot efficiency of 42.7% at best. The related temperatures after compression as well as the pressure ratios of both compressors are approximately in the same range as we know from field systems and therefore can be withstood by standard components available off-the-shelf.

Sublimation cycle 1
For sublimation cycle 1, the cascade with R407A/CO_2, we calculated an optimized COP of 0.742 which corresponds to a Carnot efficiency of 39.3%.
A first analysis of this result allows the conclusion that a pure substitution of the lower stage to CO_2 leads to a slightly lower expectable efficiency of the cycle - compared with the baseline cycle. However, this slight drawback so far is based on theoretical calculations. Whether the reduced performance will also be noticeable in real systems or not needs to be clarified.
Further, the compressor outlet temperature in the lower CO_2 stage give a value of about 440K. This value usually exceeds the limit given in most compressor data sheets. Most probably, the evaporation temperature in the cascade heat exchanger has to be elevated slightly to reduce the compressor outlet temperature. This will further decrease the above mentioned efficiency since the cycle is operated not at optimum.
It has to be mentioned that the obtained deficiencies cannot be equalized just by using another refrigerant instead of R407A. All other alternative refrigerants we checked theoretically have shown a similar performance as R407A and could not fully compensate the lower efficiency. This brings us to believe that in possible future cascade systems with sublimation slightly lower system efficiency is likely but might be compensated with the help of other performance enhancing measures.

Sublimation cycle 2 For sublimation cycle 2, the CO_2 cycle with intermediate pressure level and liquid receiver, we calculated an optimized COP of 0.87 which corresponds to a Carnot efficiency of 46.2%. At a first view, we can obtain a 3.5%-points better theoretical efficiency for a sublimation system in comparison with the baseline cycle representing state-of-the-art systems. This motivates to have a deeper look into the results. Similar to sublimation cycle 1 the rather high intermediate pressure at optimized conditions lead to a pressure ratio of about 16.8 and a maximum corresponding compressor outlet temperature of 455K. These high values can most probably not safely withstood by available off-the-shelf components. This is why we performed another calculation with limited pressure ratio (max. value = 12) and hence reduced corresponding compressor outlet temperature of 420K. Both values are from our experience fully in the range of state-of-the-art components. Even with this changed boundary conditions we can calculate a COP of 0.85 and a corresponding Carnot efficiency of 44.9%. Although these results are slightly lower, they are still above the ones of the baseline cycle. Hence, we can calculate a 2.2%-points higher COP of the sublimation system with CO_2.
This is indeed a very promising result. We can conclude that a sublimation cycle under the given boundary conditions and under consideration of technical restrictions can most likely compete with a state-of-the-art refrigeration cascade

Table 1: Specific details and results of the theoretical cycle comparison.

	Cascade cycle R404A/R23 (baseline cycle)	Cascade cycle R407A/CO2 (sublimation cycle 1)	CO_2 cycle with intermediate pressure (sublimation cycle 2)	
Condensation level Upper stage	303K/14.3bar	303K/14.3bar	303K/72.1bar	303K/72.1bar
Evaporation level Upper stage	250K/2.7bar glide R404A ≈0.6K	240K/1.6bar glide R407A ≈6.2K	-	-
Condensation level Lower stage	260K/18.8bar	250K/19.8bar	-	-
Intermediate Pressure	-	-	285K/22.6bar	247K/16.1bar
Evaporation/ Sublimation	198K/1.5bar	198K/1.3bar	198K/1.3bar	198K/1.3bar
Pressure ratio Upper stage	5.4	8.9	3.2	4.4
Compressor outlet temperature Upper stage	328K	354K	370K	394K
Pressure ratio Lower stage	12.5	14.7	16.8	12
Compressor outlet temperature Lower stage	360K	440K (!)	455K (!)	420K
COP	0.806	0.742	0.87	0.85
Carnot efficiency	42.70%	39.30%	46.20%	44.90%

using R404A/R23 in terms of cycle efficiency. The additional environmental advantage of such sublimation systems using CO_2 makes it a valuable option for R23 substitution.
Whether this advantage of efficiency can be proven at field systems cannot be predicted so far by the authors.

4. THE SUBLIMATOR - DESIGN AND HEAT TRANSFER

4.1 Design considerations

The sublimator is obviously the core component of a sublimation cycle and has to fulfil the same task as an evaporator - ensure appropriate heat transfer. The main difference is that now a gas-solid flow is entering into the system. So far, we can derive two main working principles of the sublimator which shall be discussed individually in the following.

"Dry" operation In this operation mode pure solid and gaseous CO_2[2] is provided at the inlet of the sublimator. The solid particles are carried by the dominant gas flow and partly settle down at the walls where usually sublimation takes place. This process is depending on different influence factors, e.g. CO_2 quality, tube geometry, surface quality and flow conditions.
The specific behaviour of solid particles in a gas flow typically leads to accumulation of solid CO_2 at mostly unwanted regions, e.g. stagnation or recirculation areas. In other words, the homogeneous particle distribution and hence balanced heat transfer is one of the main challenges for sublimator design.
With respect to the fluid properties of CO_2 at sublimation temperature and atmospheric pressure we can derive a minimum vapour quality of about $x_{s,min} = \frac{m_g}{m_s} \approx 0.4$. Out of this we can further derive the minimum volume quality of

[2]Slight impurities of the feed stream, e.g. refrigerant oil, are neglected.

$\varphi_{s,min} = \frac{V_g}{V_s}_{@x_{s,min}} = 0.9973$. In other words, even if a technically maximum fraction of solid CO_2 is fed to the sublimator the volume fraction of the gas is still higher than 99.73%.
However, the existence of solid particles in refrigeration cycle with partly narrow cross sections is often discussed as a safety problem. In case of CO_2 it might probably be one reason why sublimation cycles did not succeed so far. Solid CO_2 can cause uncontrolled accumulation or even blocking at critical cross sections. This topic was investigated by Huang (2006) at TU Dresden with respect to CO_2 safety valves. It could be proven that blocking of CO_2 safety valves is not as critical as often expected. However, for sublimator geometries with parallel arrangement of refrigerant paths further investigation is needed in order to ensure stable operation conditions.
In summary, a "dry" operating sublimator has certain similarities to a classical evaporator - at least on a first view. Internal test have shown that for small vapour quality x_s standard single path evaporators perform as sublimators, which further emphasizes the feasibility of this approach. However, when complex geometries and multiple refrigerant paths are applied, no design guidelines exist so far.

"Wet" operation In case the sublimator is operating in "wet" mode, solid and gaseous CO_2 are mixed with an additional carrier fluid before entering the sublimator. This mixing can be realized in two ways: Firstly, injection of CO_2 into the carrier fluid (see Fig. 1(a)) after expansion. And secondly, mixing of high pressure CO_2 with pumped carrier fluid and joint expansion. Both ways show individual advantages. During expansion into the fluid no additional pumping is required since the kinetic energy of the expanded CO_2 can be used. A joint expansion of both CO_2 and the carrier fluid prevents unwanted agglomeration due to fluid spray. However, in any case we have a mixture of three phases (solid, gaseous and liquid) out of two substances.
The most challenging issue is to find an appropriate carrier fluid. Ideal properties would be a low viscosity, non-flammable and non-toxic, extremely low vapour pressure and low miscibility with CO_2. Obvious candidates like methanol or ethanol turned out to be not ideal. On the one hand, both are flammable and partially toxic, on the other hand both are substantially miscible with CO_2 and do have still too high vapour pressure. The gas leaving the sublimator is therefore substantially enriched with carrier fluid. In order to keep this fraction low further treatment - at least of the vapour - is necessary. With all these facts in mind only a few fluids remain, for instance out of the group of perfluoropolyethers (PFPE). These fluids show more convenient properties with respect to miscibility and vapour pressure. However, they are extremely expensive and contain fluorine as main component.
As a result, for typical cooling applications with additional requirements such as non-flammability of the refrigerant the quest for the carrier fluid will always be a compromise tailored to the specific application.
The heat transfer in "wet" operation is depending on the carrier fluid fraction. In small quantities no assured data are available regarding the heat transfer coefficient. For larger quantities, e.g. injection into carrier fluid vessel, in a first assumption pure forced convection of the brine can be assumed (see section 4.2).
In summary, the "wet" operation mode of the sublimator has certain advantages with respect to CO_2 distribution and homogeneity of heat transfer, but also brings a couple of problems along. The elaborative process for separation of CO_2 as well as the quest for the ideal carrier fluid are clear drawbacks which have to be taken into account.

4.2 Heat transfer

A main point for sublimator design is the estimation of heat transfer coefficients in order to predict the required size. A general correlation for heat transfer estimation as for evaporation is so far not available. However, some publications at least give ranges for the heat transfer coefficient under specific boundary conditions and partly with different fluids. In table 2 we compiled all references for heat transfer coefficients in the field of sublimation with published heat transfer coefficients. Additionally, other prominent heat transfer cases are also shown for comparison reasons. All data can be found as well in Fig. 3(a) as bar chart.
In order to have a common basis for all convection or boiling correlations we used a pipe with an inner diameter D_i of 10mm. All other necessary boundary conditions were carefully chosen within reasonable ranges.
As a result of this comparison we can conclude that all cases of sublimation can most probably not compete with the well-known flow boiling in terms of the heat transfer coefficient. In order to estimate the size of a sublimator in comparison to a R23 evaporator we want to calculate out of the heat transfer coefficients a representative k-value for the whole heat exchanger. For this, we assume the heat exchanger to be a fin-tube type with air flow outside. An estimation based on the correlation of Wang et al. (1997) for the air side of the heat exchanger gives heat transfer coefficients in the range of 50...500 $\frac{W}{m^2K}$ for reasonable boundary conditions. When we further assume the reference

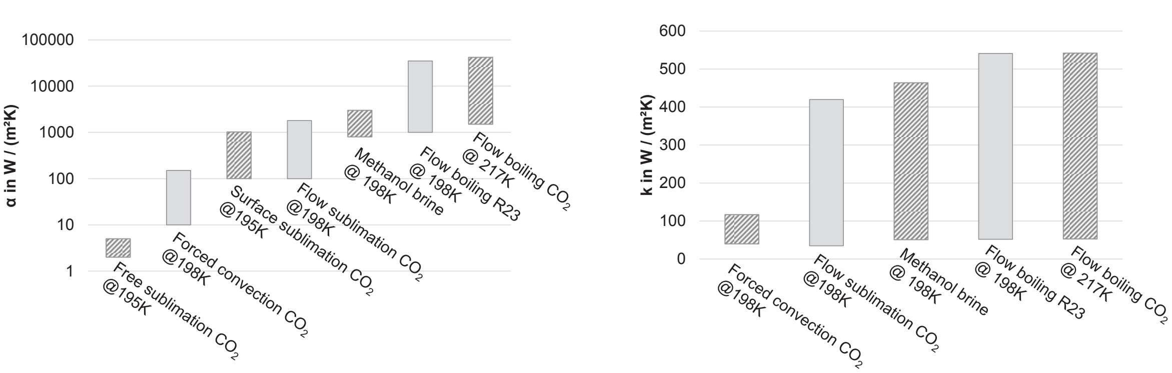
Table 2: Overview on heat transfer coefficients for different cases.

	Heat transfer coefficients in W/m^2 K	References
Free sublimation CO_2 at 195K and 1bar	2...5	Veiga and Meyer (2002)
Forced convection CO_2 gas at 195K and 1bar, 1...20 m/s	10...150	Dittus and Boelter (1985)
Surface sublimation CO_2 at 195K and 1bar	100...1020	Druzhinets et al. (1991) Dvornitsyn et al. (2006)
Flow sublimation CO_2, N_2 ("dry" sublimation)	100...1800	Balduhn and Engelhorn (1991) Balduhn and Engelhorn (1994) Zhang and Yamaguchi (2011)
Forced convection Methanol brine ("wet" sublimation) at 195K and 1bar, 1...5 m/s	800...3000	Dittus and Boelter (1985)
Flow boiling R23 at 198K and 1.5bar	1000...35000	Gungor and Winterton (1986)
Flow boiling CO_2 at 217K and 5.2bar	1500...42000	Gungor and Winterton (1986)

pipe to be made of copper ($\lambda_{Co} = 300 \frac{W}{m\,K}$) and the outer diameter D_o to be 11mm, we can calculate the k-value with reference to the inner wall area of the pipe by:

$$k = \frac{1}{\frac{1}{\alpha_i} + \frac{D_i}{2\lambda_{Co}} \ln \frac{D_o}{D_i} + \frac{D_i}{\alpha_o D_o}}. \tag{3}$$

In Fig. 3(b) the calculated k-value is shown for all cases. Contrary to Fig. 3(a) the difference for the overall k-value is very much smaller. The reason for this can be found in the heat transfer coefficient for the air side. Even if boiling occurs in the tubes, the transport through the chain of thermal resistances is dominated by the lowest value.
In order to achieve the same heat to be transferred in comparison with the maximum value of R23 flow boiling as reference, a heat exchanger with forced convection of CO_2 gas would be at least approximately 4 times larger in size - which is for sure not competitive. For CO_2 flow sublimation the size difference is not as large as expected. The heat exchanger size has to be approximately 30% larger in size. This is still in an acceptable range and therefore technically competitive. In case of the Methanol brine, which was chosen to represent the "wet" operating sublimator, we can observe a slightly higher k-value as for CO_2 flow sublimation but still lower than for R23 flow boiling. Hence, a



(a) Heat transfer coefficients

(b) k-values

Figure 3: Comparison of heat transfer coefficients for forced convection, sublimation and flow boiling.

sublimator operating with carrier fluid will need approximately 15% larger heat transfer surface.
However, is has to be clarified that this estimation was carried out for a fin-tube type heat exchanger with air flow outside. In case of other types of heat exchangers (plate fin, tube-in-tube, ...) with a liquid outside the conclusions given above would differ. An increase of the outer heat transfer coefficient will involve also a substantial increase of the k-value and coupled to this the size difference. Therefore, the sublimator will most probably be a competitive option for cooling gases such as air at low temperatures. For all other mediums no clear estimation can be made.

5. CONCLUSION

The EU F-gas regulation as well as the EPA/SNAP programme in the US are prominent examples for legislative measures for reduction or ban of fluorinated refrigerants with substantial impact on the global warming.
So far in the EU F-gas regulation refrigerants for application below -50°C (223K) are currently not affected by the regulation due to a lack in technically reasonable alternatives. CO_2 is one interesting substitution to the mostly applied fluorinated refrigerant R23 but will occur inevitably in solid state due to the exceptional high triple point. Sublimation will take place instead of evaporation.
Within this paper we carried out a theoretical comparison of two possible CO_2 sublimation cycles in comparison with the widely used R404A/R23 cascade cycle. We could show that a CO_2 sublimation cycle can compete with the cycle efficiency of the R404A/R23 cascade system or even exceed it.
We further discussed the challenges and obstacles which need to be taken into account when CO_2 sublimation technology is considered. The sublimator can be operated in "dry" mode (pure CO_2 feed) or in "wet" mode (carrier fluid added). Both operation modes show individual advantages and disadvantaged but so far no clear trend can be estimated which of both will prevail.
With respect to heat transfer coefficients in sublimating CO_2 flow we compared the rarely available literature data to conventional boiling of R23. It can be concluded that sublimation heat transfer is much less effective compared with boiling - as a rule of thumb roughly at least one order of magnitude lower with respect to heat transfer coefficient. However, for air/CO_2 heat exchangers in fin-tube-design we could estimate the additionally needed size with respect to the k-value to be approximately 15...30% larger which seems to be still competitive.
We can conclude that the CO_2 sublimation technology is a promising approach for substitution of high-GWP fluorinated refrigerants even below the triple point of CO_2. However, there is still a lot of development and testing needed in order to confirm theoretically calculated efficiency and make the cycle competitive also for practical application.

NOMENCLATURE

COP_c	coefficient of performance of ideal Carnot cycle	(W/W)
$D_{i,o}$	inner/outer diameter of the pipe	(mm)
GWP	Global warming potential	(-)
k	heat transition coefficient	(W/m^2 K)
$m_{g,s}$	mass of the gas/solid	(kg)
T_c	condensation temperature	(K)
T_0	evaporation/sublimation temperature	(K)
$T_{sh,sc}$	superheating/subcooling temperature	(K)
ΔT	minimum temperature difference at the outlet of the heat exchanger	(K)
T_{sc}	subcooling temperature	(K)
$V_{g,s}$	volume of the gas/solid	(m^3)
$\alpha_{i,o}$	inner/outer wall heat transfer coefficient	(W/m^2 K)
λ_{Co}	thermal conductivity of Copper	(W/m K)
η_{is}	isentropic efficiency of compression	(-)

REFERENCES

Balduhn, R., & Engelhorn, H. (1991). Zum Wärmeübergang von Festkörperoberflächen an kryogengem CO2 und N2. *KI Luft und Kältetechnik*, *19*(5), 216 - 218.

Balduhn, R., & Engelhorn, H. (1994). Untersuchung des Wärmeübergangs bei kryogenem CO2 und N2. *KI Luft und Kältetechnik*, *30*(7), 334 - 337.

Chen, L., & Zhang, X.-R. (2014). A review study of solid-gas sublimation flow for refrigeration: From basic mechanism to applications. *International Journal of Refrigeration*, *40*, 61 - 83.

Dittus, F., & Boelter, L. (1985). Heat transfer in automobile radiators of the tubular type. *International Communications in Heat and Mass Transfer*, *12*(1), 3 - 22.

Druzhinets, V., Levchenko, N., & Ostroumov, S. (1991). Study of porous-sublimational cooling. *Journal of engineering physics*, *60*(5), 566 - 572.

Dvornitsyn, A., Naer, V., & Rozhentsev, A. (2006). Experimental investigation of a bottle-sublimation cooler. *International Journal of Refrigeration*, *29*(1), 101 - 109.

Gungor, K., & Winterton, R. (1986). A general correlation for flow boiling in tubes and annuli. *International Journal of Heat and Mass Transfer*, *29*(3), 351 - 358.

Huang, D. (2006). *Experimental investigation and theoretical analysis of blockage in co2 safety valves and their downstream pipes*. Unpublished doctoral dissertation, TU Dresden.

Huang, D., Ding, G., & Quack, H. (2008). New refrigeration system using CO2 vapor-solid as refrigerant. *Frontiers of Energy and Power Engineering in China*, *2*(4), 494 - 498.

Jäger, A., & Span, R. (2012). Equation of state for solid carbon dioxide based on the gibbs free energy. *Journal of Chemical & Engineering Data*, *57*(2), 590 - 597.

JP2004308972A. (2004). *Maekawa, Seisakusho, patent application.*

Lemmon, E. W., Huber, M. L., & McLinden, M. O. (2010). Nist standard reference database 23: Reference fluid thermodynamic and transport properties - refprop (9.0 ed.) [Computer software manual]. Gaithersburg.

Naer, V., Roszentzesev, A., & Rybnikov, M. (1995). Eine Kältemaschine mit Drossel-Sublimation. *DIE Kaelte und Klimatechnik*, *11*, 940 - 944.

NL9401324A. (1996, 10). *Urenco Nederland, patent application.*

Ostroumov, S. (1991). Choice and optimization of the parameters of a porous-sublimation cooler. *Journal of engineering physics*, *60*(6), 697 - 701.

Span, R., Eckermann, T., Herrig, S., Hielscher, S., & Jäger, A. (2015). Thermodynamic reference and engineering data - TREND (2.0 ed.) [Computer software manual].

US7818971B2. (2010). *Mayekawa and the Doshisha, patent.*

Veiga, W. D., & Meyer, J. (2002). Heat transfer coefficient of a snow bag. *International Journal of Refrigeration*, *25*(8), 1043 - 1046.

Wang, C., Fu, W., & Chang, C. (1997). Heat transfer and friction characteristics of typical wavy fin-and-tube heat exchangers. *Experimental Thermal and Fluid Science*, *14*(2), 174 - 186.

Weinstein, A., Friedman, A., & Gross, U. (1964). Cooling to cryogenic temperatures by sublimation. In K. Timmerhaus (Ed.), *Advances in cryogenic engineering* (Vol. 9, p. 490 - 495). Springer US.

Yamaguchi, H., & Zhang, X.-R. (2009). A novel CO2 refrigeration system achieved by CO2 solid-gas two-phase fluid and its basic study on system performance. *International Journal of Refrigeration*, *32*(7), 1683 - 1693.

Yamaguchi, H., Zhang, X.-R., & Fujima, K. (2008). Basic study on new cryogenic refrigeration using CO2 solid-gas two phase flow. *International Journal of Refrigeration*, *31*(3), 404 - 410.

Zhang, X.-R., & Yamaguchi, H. (2011). An experimental study on heat transfer of CO2 solid-gas two phase flow with dry ice sublimation. *International Journal of Thermal Sciences*, *50*(11), 2228 - 2234.