

## ENCIT-2018-XXXX CHARACTERISTICS OF THE USE OF CO<sub>2</sub> IN CASCADE REFRIGERATION SYSTEMS AND FOR POWER GENERATION IN BRAYTON CYCLES

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**Abstract.** CO<sub>2</sub>(R744) is used on refrigeration systems since the end of the 19th century, but after the introduction of chlorofluorocarbons, it lost space. With the protocol of the Montreal, it got the scientific community's attention once again, due to low Ozone Depletion Potential (ODP) and Global Warming Potential (GWP). The following work presents the possibilities of the utilization of CO<sub>2</sub>(R744) in low-pressure cascade refrigeration systems and energy generation on Brayton cycles. However, the use of CO<sub>2</sub> for these applications requires the knowledge of the heat transfer coefficient, pressure drop and saturation temperature among others. This is demanding great efforts from the scientific community on controlled flow studies. This analysis presents mathematical correlations involving CO<sub>2</sub>, which presented low mean deviations if compared to the experimental data. With more robust results, there is rising trend toward the use of CO<sub>2</sub> in commercial thermodynamic systems.

**Keywords:** CO<sub>2</sub>, R744, cascade refrigeration, Brayton cycle.

### 1. INTRODUCTION

The objective of this paper is to present the possibility of using CO<sub>2</sub> in cascade refrigeration systems and in Brayton cycles for energy generation, and also to show current studies related to the categorization of the CO<sub>2</sub> properties during the change of phase. For this purpose, a bibliographic review was done on the recent and substantial works on this area, which differed from the conclusions of studies published on scientific journals and magazines.

### 2. CO<sub>2</sub> AS A REFRIGERANT

CO<sub>2</sub> was first introduced as a refrigerant in 1850, by the scientist Alexander Twining and was among the widely used refrigerants in the infancy of refrigeration. It became very popular with the increasing use of refrigeration systems in the beginning of the 20th century. In 1881, Carl Lind built the first machine that used R744 (carbon dioxide), and, in the next year, the company J&E Hall acquired the patent for the system and began manufacturing it in 1890 (Pereira, *et al.*, 2010). It was used for several applications, but in 1930, with the introduction of Freon gases, the use of R744 declined and it began being replaced by chlorofluorocarbons (CFCs).

In 1987, after the Vienna Convention and the increasingly concern with the damage caused by the CFCs on the Ozone layer, the Montreal Protocol was created, forcing member countries to progressively eliminate the use of substances that may damage this layer. In this context, CO<sub>2</sub> resurged as an alternative to the synthetic refrigerants (Lorentzen, 1989), because it not only has zero Ozone Depletion Potential(ODP) and negligible Global Warming Potential(GWP), but if obtained through the Carbon Capture and Storage(CCS) technique, its use can alleviate the contribution of fossil fuels to global warming (Gibbins and Chalmers, 2008). Studies involving the use of CO<sub>2</sub> on subcritical and supercritical states, whose difference is shown on Tab. 1, are being widely studied by the scientific community in the recent years.

Table 1. Comparison of CO2 cycles.

	Subcritical cycle	Transcritical cycle	Supercritical cycle
Critical point	31,06°C / 73,8 MPa		
Discharge pressure	Bellow critical point	Around critical point	Above critical point
Condensation	The same as conventional refrigerants; Condensation temperature < 31°C; Isobaric and isothermal	Condensation above critical point, with isobaric expansion device not isothermal	The fluid doesn't return to liquid state

### 1.1 Advantages and disadvantages of using CO2 as a refrigerant

The advantages and disadvantages of using R744 as refrigerant are listed in Tab. 2:

Table 2. Advantages and disadvantages of R744. Source: (Emerson Climate, 2015)

Advantages	Disadvantages
<p>High refrigeration capacity due to high volumetric cooling capacity. This has a positive impact on compressor displacement and the sizing of heat exchangers and pipe work.</p> <p>Lower pressure drops in pipework and heat exchangers. For example, the impact of long suction and liquid lines is less.</p> <p>High heat transfer rate in evaporators and condensers due to the high pressure and density. This will either allow lower temperature differences between the refrigerant and the air improving efficiency or the use of smaller evaporators and condensers. Tubing wall thickness may need to be increased to handle the higher pressures, so careful design is required to take advantage of the R744 properties.</p> <p>The pressure drop across an expansion valve is greater than with other refrigerants, so the minimum setting for head pressure control can be lower. This improves efficiency.</p> <p>Lower compression ratios leading to higher compressor isentropic efficiency.</p> <p>Good miscibility with compressor lubricants for oil return.</p> <p>Low toxicity and non-flammable.</p> <p>Negligible GWP so that, in the event of a leak, the direct impact on climate change is very low.</p> <p>Inexpensive to produce and widely available, although the purity of the R744 should be 99.99% to use it in refrigeration.</p> <p>High discharge temperatures due to the high compression index. This provides good potential for heat recovery.</p> <p>There is no impending legislation phasing down or phasing out, so R744 can be viewed as a long-term refrigerant.</p>	<p>High operating and standstill pressures are more hazardous and increase the leak potential. Specially designed components are required.</p> <p>Special compressors are required because of the higher refrigeration capacity.</p> <p>R744 systems are more complex. This leads to higher components and installation costs.</p> <p>Pipe working on-site potentially includes steel or stainless steel, the need for specially licensed welders, and different jointing techniques due to the higher pressure and different materials.</p> <p>The greater complexity also increases the probability of poor performance and reliability, particularly if commissioning is not done well.</p> <p>R744 transcritical systems are less suited for high ambient temperature areas (e.g., Southeast Asia), where the system will always operate above the critical point, because of the inefficiency of transcritical operation.</p> <p>R744 is not controlled by any regulation such as the European Fluorinated Gas Regulation, so its use is not as carefully monitored as HFCs and leak detection is not as rigorous. However, the high pressures make the system leak prone, and performance will be affected by leaks.</p> <p>R744 systems are very sensitive to water contamination and can form unusual compounds when there is a leak in a cascade heat exchanger.</p>

### 3. PROPERTIES OF R744

The properties of a refrigerant affect the efficiency of a refrigeration system. Table 3 compares the properties of R744 with other common refrigerants.

Table 3. Comparison of R744 properties with other refrigerants. Source: (Padalkar and Kadam, 2010)

Property	R22	R134a	R410A	R407C	HC290	R717	R744 (CO <sub>2</sub> )
ODP/GWP	0.05/1700	0/1300	0/1900	0/1600	0/3	0/0	0/1
Critical temperature (°C)	96	101.1	70.2	86.1	96.7	133	31.1
Critical Pressure(bar)	49.7	40.7	47.9	46.4	42.5	114.2	73.8
Volumetric heat capacity (kJ/m <sup>3</sup> )	4356	2868	6763	4029	3907	4382	22545
Ratio of vapor to liquid density at boiling temperature 7.2°C kJ/(kg.K)	47.4	68.84	29.79	50.23	40.66	141.7	7.155

R744 has the lowest GWP/ODP values after ammonia, which is toxic for human beings (NCBI, 2013), making it a very safe option. It is also widely available in the environment, while hydrocarbons are scarcer. R744 has a high volumetric heat capacity, with 22,545 kJ/m<sup>3</sup>, which is three to five times higher than the other listed refrigerants, reducing considerably the quantity of refrigerant, the compressor size and the pipework needed to achieve the same refrigeration effect of the other refrigerants (Padalkar and Kadam, 2010). The low ratio of vapor to liquid density of R744 results in a more homogenous refrigerant distribution in the channels, which increases the heat transfer rate, thus reducing the size of the heat exchangers needed for the same refrigeration effect (Maina and Huan, 2015).

R744 operates in higher pressures than other refrigerants, has a higher triple point pressure, and its critical point is at a lower pressure and temperature, this results in a short range of operating temperatures for subcritical systems if compared to other refrigerants, as shown in Fig. 1.

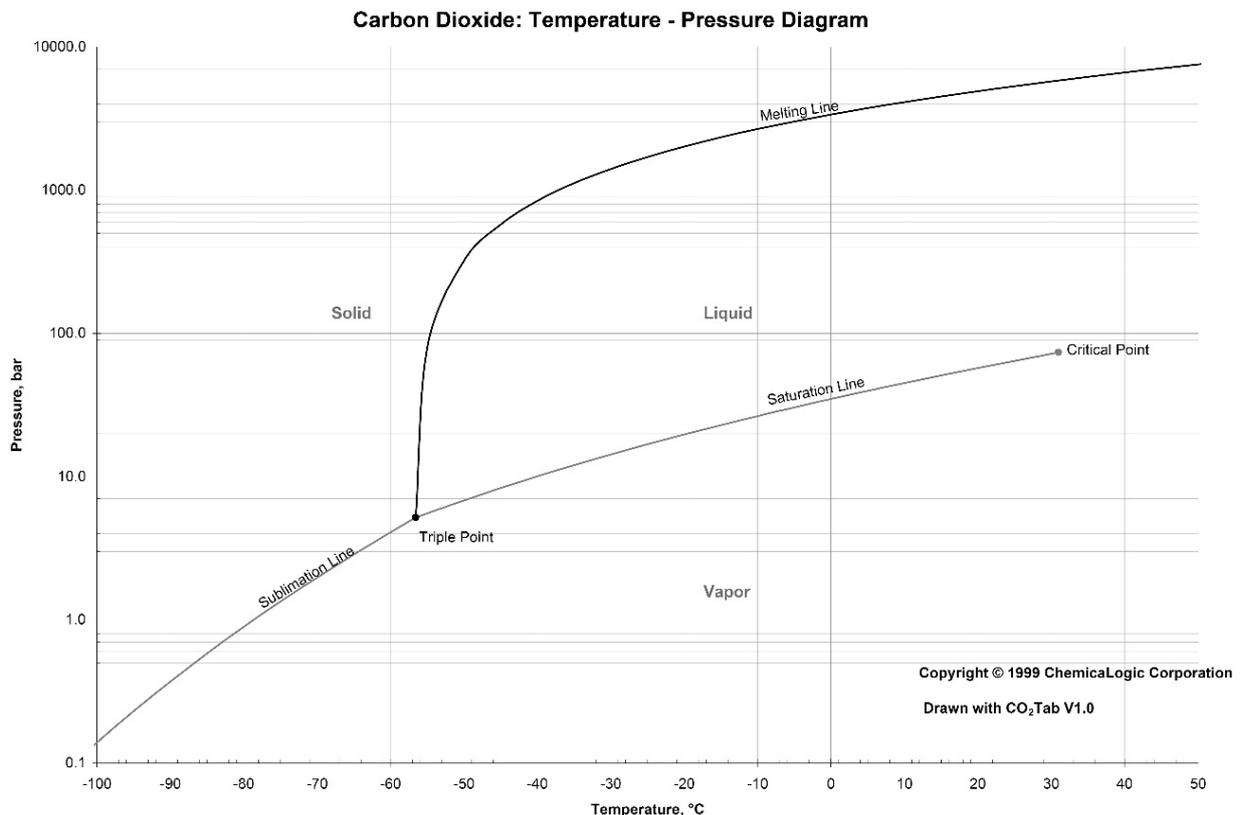


Figure 1. R744 Temperature – Pressure diagram.

#### 4. R744 ON CASCADE SYSTEMS

A cascade refrigeration system, as shown in Fig. 2, utilizes two refrigerants with different thermodynamic properties in two separate circuits connected by a heat exchanger called cascade condenser (Sharma, *et al.*, 2014). Its advantage come from the fact that the system uses each refrigerant at its more adequate temperature, thus reducing the necessary

compressor work and improving the heat transfer rate. In a cascade system, R744 is generally used in the low-temperature stage, that besides improving the system's efficiency, also results in a lower operating pressure, allowing the use of commercially available compressors and control valves (Vestergaard, 2003). In the high-temperature stage, NH<sub>3</sub>, R134a, R404A, R290 or R1270 can be used (Bansal, 2012).

In this system, R744 always operates subcritically, and, because of this, the high suction vapor specific mass results in a better heat exchange between the R744 suction line and the liquid line of the high-pressure stage, that not only improves the efficiency of the high-pressure stage, but also provides a more stable control of the suction vapor overheating in the R744 compressor, preventing the dissolution in oil (Bellé, 2017). A cascade system with R744 is generally more efficient than a transcritical R744 system, because even though R744 has an excellent performance on heat exchangers and on the compressor, it is not enough to compensate the thermodynamic losses that occur on the transcritical process (Pearson, 2005), therefore, transcritical CO<sub>2</sub> systems won't be covered in this paper.

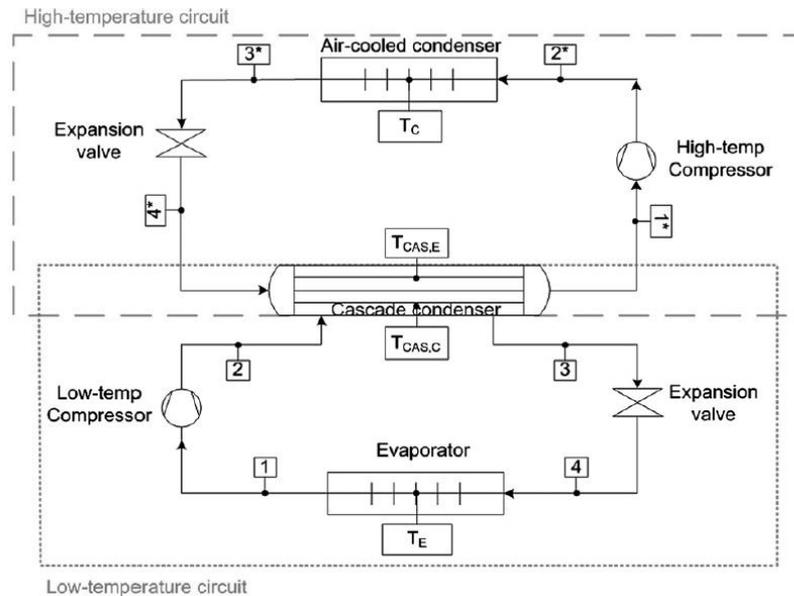


Figure 2. Example of a cascade system. Source: (Emerson Climate, 2015)

A study by Emerson Climate (2015) showed that a subcritical R744 system has a COP (coefficient of performance) better than a medium temperature (MT) HFC system, while for the transcritical R744 systems it is assumed to have an average COP of 10% for warm climates, such as Southern Europe, shown in Fig. 3. It is also possible to notice that the performance of R744, disregarding the state, is more sensible to the outdoor ambient temperature than the HFC MT system.

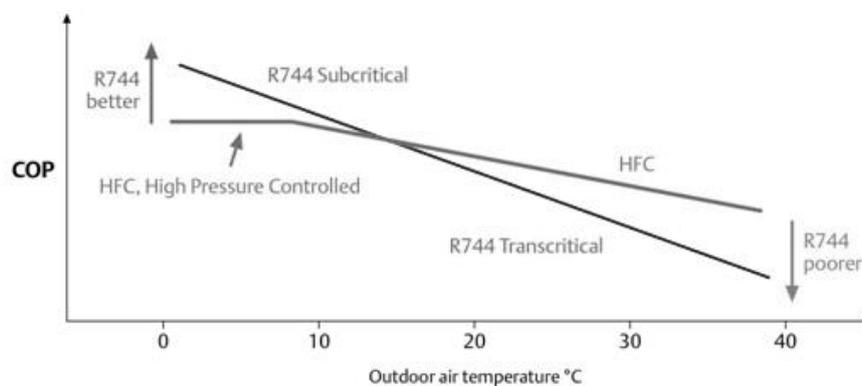


Figure 3. COP of R744 and HFC(R404A) according to outdoor temperature. Source: (Emerson Climate, 2015)

Da Silva, *et al.*, 2011 compared the cascade system using R744 and R404A with a two single-stage conventional systems, one with R22, and another with R404A, and concluded that the cascade system, for the same refrigeration effect: (i) had an equipment cost 18.5% higher than the conventional systems (ii) required 20% less area to achieve the same refrigeration effect, (iii) used 47 kg of refrigerant (15kg of R404A and 32kg of R744) while the other two racks

using R404A and R22, required 125 kg and 115 kg, respectively, (iv) used smaller piping diameter sizes, (v) was 22,3% and 13,7% more efficient than the systems with R404A and R22, respectively, as shown in Fig. 4. Pereira (2010) studied the same cascade system and achieved a COP 7,6% better than the R-22 system and 29,8% better than the R404A system. A reduction of piping diameters, heat exchangers and a lower compression ratio, which increases the useful life of the R744 compressor, was also observed.

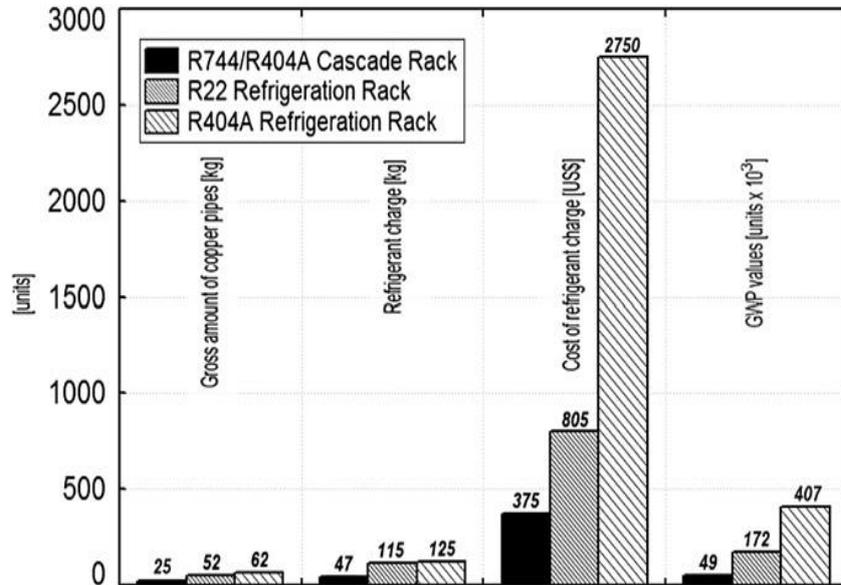


Figure 4. Comparison of three refrigeration systems. Source: (Da Silva, *et al.*, 2011)

An experiment by Likitthammanit (2007), obtained for a cascade system with R744 and NH<sub>3</sub> a COP of 2.16, while the conventional systems with R404A had a COP of 1.39 for the same cooling water temperature (30°C). Souza (2016) compared the use R744 with R131a, R438A e R404A on a cascade configuration and concluded that the pair R744/R438A was the most efficient with a COP between 1.46 and 1.49, while the maximum COP of the pairs R744/R134a and R744/R404A was 1.22, and 1.35, respectively.

## 5. BRAYTON CYCLE WITH SUPERCRITICAL CO<sub>2</sub> (S-CO<sub>2</sub>)

The Brayton cycle is a gas cycle for power generation, and its simplest plant consists by a compressor, a heat exchanger and a turbine on an open system, and, with a second heat exchanger on a closed system. More components can be added to improve its efficiency (e.g., regenerator, reheater, precooler), as shown in figure 5.

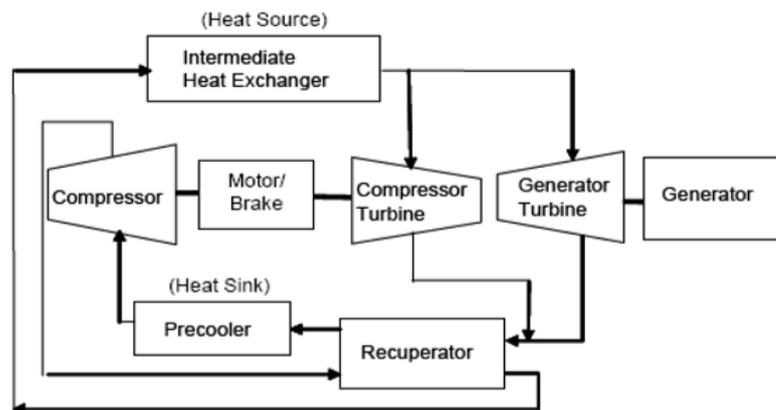


Figure 5. Brayton Cycle. Source: (Kimball, *et al.*, 2013)

The supercritical carbon dioxide (S-CO<sub>2</sub>) Brayton cycle is considered to be one of the most promising power cycles for the future (Zhou, *et al.*, 2017). The use of S-CO<sub>2</sub> was, at first, considered as an alternative on power generation researches, due to the increasing concern with climatic changes, followed by the growing global demand for energy. This cycle presented itself as a possibility of improvement for nuclear power generation. However, its use was not

restricted to this, it is also used on other energy generation systems as solar concentrators and in power plants using fossil fuels (Ahn, *et al.*, 2013). The first studies related to the utilization of supercritical Brayton cycles are authored by Angelino and Feher, at the end of the 1960s (Rinaldi, *et al.*, 2013).

Cardemil and da Silva (2016) did a thermodynamically study on the thermal performance of power cycles using CO<sub>2</sub> as the working fluid. They did a relative performance assessment with four other working fluids, ethane, toluene, D4 siloxane and water. They concluded that while the CO<sub>2</sub>'s 1st Law efficiency, thermal performance, might be lower than other fluids, its exergetic efficiency can be significantly higher (Cardemil and da Silva, 2016) in a Brayton cycle, with and without a recuperator. The Relative efficiency of CO<sub>2</sub> with respect to water, ethane, toluene and D4 siloxane for the 2nd law ratio can be seen in Fig. 6.

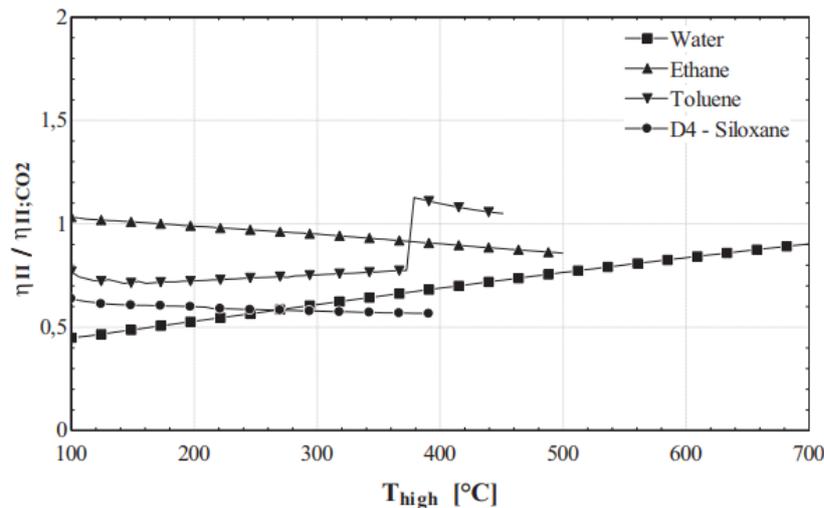


Figure 6. The Relative efficiency of CO<sub>2</sub> with respect to water, ethane, toluene and D4 siloxane for the 2nd law ratio. Source: (Cardemil and da Silva, 2016)

Zhao and Jin (2017) compared S-CO<sub>2</sub> with NaCl–KCl–ZnCl<sub>2</sub> Eutectic Salts for Solar S-CO<sub>2</sub> Brayton Cycle while Javanshir, *et al.* (2018) did a thermodynamic analysis of simple and regenerative Brayton cycles, for the concentrated solar power applications, where they aimed to select the best work fluid(s) for the cycle. They concluded that for the thermal efficiency either N<sub>2</sub> or CO<sub>2</sub> are the best choices, depending of the operating conditions but, considering the net specific work output, CO<sub>2</sub> would be the best choice.

The supercritical Brayton cycle had a higher efficiency if compared to the Rankine cycle (Fleming, *et al.*, 2013), and unites the efficiency improvement characteristics of both cycles, Brayton and Rankine, it operates with a lower pumping power and high temperatures in the turbine inlet, therefore increasing its thermodynamic efficiency (Ahn, *et al.*, 2013). CO<sub>2</sub> becomes the choice as working fluid because of the possibility to compress it near the critical point, this reduces the compressor size and work if compared to the compression of air (Rinaldi, *et al.*, 2013), and also greatly improves the capacity of the plant's reversibility (Wright, *et al.*, 2013). The S-CO<sub>2</sub> cycle operates with moderate temperatures in the turbine inlet, between 500 and 750°C (Ahn, *et al.*, 2013).

Another advantage of the supercritical Brayton cycle is the compact machinery (Dyreby, *et al.*, 2013), due to the high density of the supercritical CO<sub>2</sub> (Cha, *et al.*, 2009), and, because of this property, the S-CO<sub>2</sub> becomes attractive for small-sized and low-cost applications (Brun, *et al.*, 2017) as seawater desalinization, energy generation for districts and propulsion (Yoon, *et al.*, 2012). Even though the S-CO<sub>2</sub> Brayton cycle requires more complex components if compared to the Rankine cycle, as compressors instead of feedwater pumps, besides the need for higher heat load in the recuperators in relation to the heat source (Brun, *et al.*, 2017).

The Brayton cycle with supercritical CO<sub>2</sub> also stands out if compared to the Rankine cycle on the utilization of air for the cooling system, so in places where water availability is low this cycle becomes an alternative (Conboy, *et al.*, 2015), with the main example being the solar power plants on dry locations (e.g., deserts). This happens because the working fluid on the Brayton cycle requires less air flux for the cooling process if compared to the air-cooled condenser, with the same refrigeration system on the Rankine cycle. However, this benefit has been questioned since the reduction of the driving force for heat transfer, which requires a great increase on the heat transfer area (Moisseytsev and Sienicki, 2014).

## 6. DETERMINATION OF THE BOILING HEAT TRANSFER COEFFICIENT OF CO<sub>2</sub>

The utilization of CO<sub>2</sub> as a refrigerant in cascade refrigeration systems or for energy generation in Brayton cycles requires the knowledge of the heat transfer coefficient, pressure drop, saturation temperature among others. Many papers in the recent years tried to determine these data, more than twenty regarding this study.

In controlled flow situations the physical quantities of the process are measured, and then the elementary thermodynamic coefficients are empirically determined to quantify the heat transfer. The experimental methodology of Oh, *et al.*, (2011), Yun, *et al.*, (2005) and Chien, *et al.* (2017) basically consists on developing and constructing and instrumentalized workbench for CO<sub>2</sub> circulation, as shown in Fig. 7, where the circulation through a positive displacement pump, with the intention of keeping an uniform flow; the pressure difference between the pump suction and discharge is measured with a pressure transmitter; the verification of the mass flux on a Coriolis flow meter; the fluid then goes inside the test section where it is directed through holes of different formats and dimensions; the test section has heating sources, so that there is a change of phase of CO<sub>2</sub> and consequently its expansion a pressure increase. In this phase of the process, temperatures in various points along the section are measured, inlet, outlet and differential pressures are also measured; the fluid, after tested, goes to the heat exchangers and the circulation pump at the same initial conditions of the cycle.

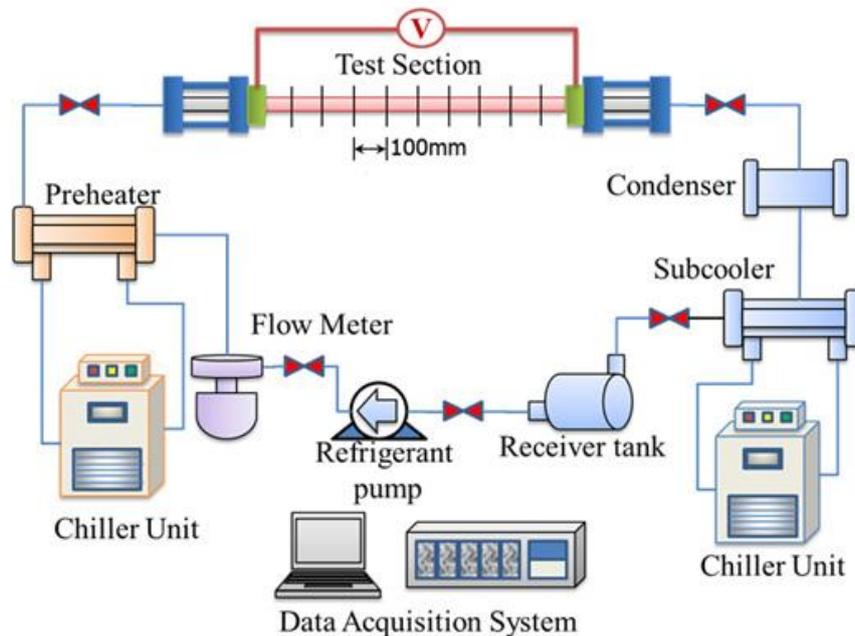


Figure 7. Experimental apparatus. Source: (Chien, *et al.*, 2017)

With the measurement of physical quantities using the workbench instruments, it is possible to determine the local heat exchange coefficient in the "h", where  $T_w$  is the wall temperature,  $T$  is the refrigerant temperature and  $q$  is the measured heat flux. This is shown in the Equation (1).

$$h = \frac{q}{(T_w - T_r)} \quad (1)$$

In the evaporator project using CO<sub>2</sub>/R744 as working fluid, it is necessary to know the heat transfer characteristics and the pressure drop during the boiling process of CO<sub>2</sub>, as well as the effects of the physical properties effects on the heat transfer. Studies by Oh, *et al.*, (2011), Yun, *et al.*, (2005) and Chien, *et al.*, (2017) showed that the boiling heat transfer of CO<sub>2</sub> is affected by the heat flux and the saturated temperature.

The pressure drop of CO<sub>2</sub> during the boiling process is highly dependent on the mass flow and the saturation temperature. Among the existing correlations for the pressure drop on boiling processes in microchannels using CO<sub>2</sub>/R744, the one that closest approaches the experimental results as stated by Oh, *et al.*, (2011) is the Choi, *et al.*, (1999) correlation, shown in Eq. (2), with a mean deviation of 16,5% on the results. The factor  $f_n$ , is shown in Equation (3.)

$$\Delta P = \left[ f_n + \frac{(x_{out} - x) \cdot d_i}{x_{in} \cdot L} \right] \frac{G_{re} \cdot L \cdot V_{TP}}{d_i} \quad (2)$$

Where,

$$f_n = 0.05R e^{0.095} k_f^{0.155} \quad (3)$$

Between the correlations of Jung, *et al.*, (1989), Thome and El Hajal, (2004) and Cheng, *et al.*, (2006) which predict the heat transfer on the boiling process, according to Oh, *et al.*, (2011), the one that approaches the experimental results more accurately is the Cheng, *et al.*, (2006) process, shown in Eq. (4), with a mean deviation varying from 12.64% to 14.68% on the results. Note that in the correlation from Cheng, *et al.*, (2006), the reduced pressure term was correlated based on the nucleate boiling heat transfer data of CO<sub>2</sub> by keeping the logarithmic and molecular terms in the Cooper (1984) correlation unchanged.

$$h_{nb} = 131 p_r^{-0.0063} (-\log_{10} p_r)^{-0.55} M^{-0.5} q^{0.58} \quad (4)$$

Nomenclature	
$c_p$	specific heat ( $J.kg^{-1}K^{-1}$ )
$d_i$	internal tube diameter $m$
$M$	molecular weight ( $kg/kmol$ )
$\Delta P$	pressure drop ( $Pa$ )
$Re$	Reynolds number
$k_f$	Pierre boiling number
$q$	heat flux ( $W/m^2$ )
$x$	vapor quality
$p_r$	reduced pressure ( $p/p_{cr}$ )

## 7. CONCLUSION

CO<sub>2</sub> resurges as an excellent alternative to chlorofluorocarbons refrigerants due to its negligible indexes of ODP and GWP among other advantages. With the increasing number of studies about CO<sub>2</sub> being published, new empirical correlation propositions about the boiling and condensation processes of subcritical CO<sub>2</sub> will be developed. With that, the uncertainty associated with such equations will be minimized, facilitating with greater reliability the dimensioning of the systems for the applications studied in this paper. With more robust results, there is growing trend towards the use of CO<sub>2</sub>/R744 in cascade refrigeration systems and in Brayton cycles for energy generation.

## 8. ACKNOWLEDGEMENTS

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