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Refrigeration with eco-friendly fluids.
Development of refrigeration systems with
CO₂-based refrigerant mixtures.

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It takes something more than intelligence to act intelligently.

Fëdor Dostoevskij

Ad Angela

DECLARATION

I hereby declare that this submission is my own work and, to the best of my knowledge and belief, it contains no material previously published or written by another person, nor material which to a substantial extent has been accepted for the award of any other degree or diploma at University of Florence or any other educational institution, except where due references are provided in the thesis itself.

Any contribution made to the research by others, with whom I have been working at the University of Florence or elsewhere, is explicitly acknowledged in the thesis.

Guglielmo Vaccaro

31/10/2024

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I consider my colleagues Luca, Nicola, Lorenzo, and Claudio to be more than just colleagues; they are friends. The years we've spent together have been wonderful and filled with fun, and I believe our bond is truly unique. I sincerely hope that our connection endures, even if our paths diverge.

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These three years have been truly incredible, Angy! They started as soon as we moved in together, then, came the moment when we decided to take the big step of marriage, and, perhaps, from that day on, everything is even more beautiful. It hasn't always been easy, distance is never pleasant, but you patiently waited for me and endured this period, looking forward to the future that awaits us. We have become uncles, and a little niece will arrive soon. It's incredible to think that, after all, right at the end of these three years, we are about to become parents, and, right now, for someone, the real journey is just beginning: Life.

ABSTRACT

This thesis explores the development of sustainable and high-performance refrigeration systems using natural, non-toxic, and non-flammable refrigerants, particularly carbon dioxide (CO_2) and carbon dioxide-based mixtures. The interest towards CO_2 is dictated by the fact that many traditional refrigerants have significant environmental impacts and are nowadays banned in Europe under the F-Gas regulation. Hydro-olefins, given their low GWP, have been regarded as a promising alternative, but require careful attention due to potential environmental long-term effects.

As a first step, a general, steady-state thermodynamic model of inverse cycles was developed using Python and REFPROP 10. The model can accommodate most common cycle configurations, including regeneration and expansion work recovery through an ejector. Several fluid compositions may be implemented. Optimization algorithms were used to optimize conditions at the condenser and evaporator outlets.

Mixing CO_2 with refrigerants such as R1234yf, propylene and dimethyl ether (DME) significantly improved system performance, due to reduced critical pressure, increased critical temperature and matching between the mixture glide and imposed temperature lift at the cold heat exchanger. R1234yf achieved a Coefficient of Performance (COP) increase of up to 12.8% in the base configuration with an internal heat exchanger (IHx). The highest absolute COP was obtained with the double ejector configuration, although the relative improvement compared to pure CO_2 was only 4.3%.

A first outcome of this thermodynamic analysis was the idea of using the internal heat exchanger to complete the evaporation. In this way, a higher percentage of secondary refrigerant could be used for a given temperature lift at evaporator. This approach resulted in superior performance, with CO_2 - DME mixture achieving a COP increase of 25% while maintaining a GWP of 1. To this aim, a mere 8% of DME is needed, so that the mixture turns out to be non-flammable. Such outstanding result suggested to concentrate our effort on CO_2 - DME mixtures.

Meanwhile, a critical review and improvement of flow boiling correlations for CO_2 and CO_2 -based mixtures were conducted. A novel flow boiling correlation was proposed, achieving a mean error prediction of 28% for pure CO_2 and 37% for CO_2 -propane mixtures.

Another relevant aspect is the fluid solubility in lubricant oil. Experimental investigations revealed that DME has a greater solubility in polyalkylene glycol (PAG) oil compared to propylene. New empirical correlations may improve modelling accuracy.

Finally, an experimental validation of the most important results was conducted, using an experimental bench equipped with a CO_2 scroll compressor and high-pressure brazed plate heat exchangers.

The experimental findings confirmed the effectiveness of the CO_2 -DME mixture, showing a maximum COP increase of 15% for a mixture with 10% DME and a condensation temperature of 35°C . Uncertainties concerning the actual circulating composition were addressed using gas chromatography and Coriolis mass flow meters, confirming the accuracy of the Johansson method with an average absolute error of 0.64%. The measured evaporative

heat exchange was compared with calculated values, identifying the Silver and Bell & Ghaly method coupled with the Amalfi and Cooper correlations as the best-performing model, with a mean absolute relative error of 1.17%.

This research concludes that CO₂-based mixtures, particularly with DME, can enhance the efficiency and performance of refrigeration systems, contributing to the development of sustainable technologies with reduced environmental impact.

Keywords: Refrigeration cycle, Mixtures, CO₂, DME

PROPOSITIONS

Motivation

- COP increase
- Eco-friendly refrigerants

Original contribution

- COP increase with mixtures
- GWP = 1 and non-flammable
- Mixtures heat transfer

Open questions

- Oil- mixture interaction
- Different geometries and boundary conditions
- Compressor efficiency

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NOMENCLATURE

Acronyms

CO ₂	Carbon Dioxide
COP	Coefficient Of Performance
DME	Dimethyl Ether
GWP	Global Warming Potential
HTC	Heat Transfer Coefficient
IHX	Internal Heat Exchanger
PAG	Polyalkylene Glycol
PHE	Plate Heat Exchanger
POE	Polyolester
SBG	Silver and Bell & Ghaly correction
TCD	Thermal Conductivity Detector
TEWI	Total Equivalent Warming Impact
TS	Thome & Shakir correction

Greek symbols

α_{rec}	percentage of mass recovered at the end of life	[-]
β	chevron angle	[°]
β_{eq}	equivalent CO ₂ emission per kWh produced	[kg kWh ⁻¹]
δ	film thickness	[m]
Δ	difference	[-]
ε	void fraction	[-]
η	efficiency	[-]
θ	contact angle or generic angle with subscript	[rad]
λ	corrugation pitch	[m]
μ	dynamic viscosity or chemical potential	[Pa s] or [J mol ⁻¹]
ρ	density	[kg m ⁻³]
σ	surface tension	[N m ⁻¹]
ϕ	enlargement factor of the corrugated plates	[-]
ω	entrainment ratio	[-]
Ω	Wattelet parameter	[-]

Latin symbols

A	area	[m ²]
b	height of PHE	[m]
b_d	bubble diameter	[m]
B_d	Bond number	[-]
Bo	boiling number	[-]

C_p	specific heat capacity	$[\text{J kg}^{-1} \text{K}^{-1}]$
D	diameter	$[\text{m}]$
E_{annual}	annual electricity consumption	$[\text{kWh}]$
F	enhancement factor	$[-]$
F_c	correction factor for nucleate boiling	$[-]$
g	gravitational acceleration	$[\text{m s}^{-2}]$
G	mass velocity	$[\text{kg s}^{-1} \text{m}^{-2}]$
G_F	Gibbs free energy	$[\text{J}]$
h	heat transfer coefficient or specific enthalpy	$[\text{W m}^{-2} \text{K}^{-1}]$
i	specific enthalpy	$[\text{J kg}^{-1}]$
k	thermal conductivity	$[\text{W m}^{-1} \text{K}^{-1}]$
L	length	$[\text{m}]$
L_{annual}	percentage of annual fluid losses	$[-]$
$\dot{m}$	mass flow rate	$[\text{kg s}^{-1}]$
M	mass	$[\text{kg}]$
M_{mol}	molecular weight	$[\text{kg mol}^{-1}]$
N_{ch}	number of channels	$[-]$
Nu	Nusselt number	$[-]$
n_y	number of years	$[-]$
P	pressure	$[\text{Pa}]$
Pr	Prandtl number	$[-]$
p_r	reduced pressure	$[-]$
q	heat flux	$[\text{W m}^{-2}]$
$\dot{Q}$	heat flow rate	$[\text{W}]$
Re	Reynolds number	$[-]$
S	suppression factor	$[-]$
T	temperature	$[\text{K}]$
t	thickness	$[\text{m}]$
U	overall heat transfer coefficient	$[\text{W m}^{-2} \text{K}^{-1}]$
$\dot{W}$	power	$[\text{W}]$
W	width	$[\text{m}]$
We	Weber number	$[-]$
x	quality	$[-]$
X	mass fraction	$[-]$
X_{tt}	Martinelli parameter	$[-]$
Y	rate of sensible heat over latent heat	$[-]$

Subscripts

cb	convective boiling
de	dryout completion
di	dryout inception
dry	dry portion of the pipe
dryout	dryout region
eff	effective
eq	equivalent
g	gas phase

h	hydraulic
ht	heat transfer
ia	intermittent to annular flow
l	liquid
M	mist
nb	nucleate boiling
oil	oil
ref	refrigerant
sat	saturation
sf	secondary fluid
strat	stratified flow
tp	two phases
v	vapor
wavy	wavy flow
wet	wet portion of the pipe

SYNOPSIS

The aim of this doctoral thesis is to study environmentally friendly, non-toxic, and non-flammable refrigerant fluids to be used in energy-efficient refrigeration systems. In particular, the focus is on CO₂ and CO₂-based mixtures. This research is structured to provide a comprehensive understanding of the potential of CO₂-based mixtures in enhancing refrigeration system performance while adhering to stringent environmental regulations.

The thesis is constituted of a collection of articles. The reported papers have been published in authoritative scientific journals or have been presented to relevant international conferences. Some dedicated parts have been added to enhance the completeness and readability of the work. The thesis is organized into five main sections:

1. **State of the Art:**

- A thorough review of pure CO₂ refrigeration cycles, highlighting their issues and potential solutions.
- An overview of the state of the art for refrigerant mixtures, including experimental and theoretical studies on refrigeration plants, heat transfer coefficients, and oil-related problems.

2. **Methods:**

- Development of algorithms to solve the thermodynamic cycle under known boundary conditions.
- Implementation of an optimization algorithm to enhance operational conditions.
- Modelling of the plate evaporator to analyse heat transfer.

3. **Experimental Bench:**

- Description of the components of the experimental bench and the chosen boundary conditions.
- Measurement instrumentation used and their uncertainties.
- Considerations on the composition of mixtures and their impact on system performance.

4. **Results:**

- Presentation of the results through five papers and two appendices, structured to provide a coherent narrative that aligns with the research objectives and methodologies.
- **First Paper:** Analysis of the effectiveness of mixtures compared to pure CO₂ for different configurations and fluids, showing performance improvements without altering the use of system components.
- **Second Paper:** Continuation of the analysis with a focus on a non-conventional use of the Internal Heat Exchanger (IHX). The IHX is used to complete the evaporation process, thereby reducing the temperature lift in the evaporator. This approach allows for better temperature matching between the evaporating mixture and the fluid to be cooled, leading to promising results in terms of coefficient of performance (COP), flammability and the use of natural mixtures.

- **Third Paper:** Investigation of the effects of CO₂ and propane mixtures on boiling heat transfer, considering the reduction in heat transfer coefficient (HTC) due to glide.
- **Fourth Paper:** Examination of the different oil absorption rates for various fluids, showing how absorption characteristics affect the actual system charge and composition variations.
- **Fifth Paper:** Experimental campaign to verify the theoretical findings obtained in the second article, understanding the discrepancies between model predictions and experimental results with insights from the third and fourth articles.
- **Appendix 1:** Experimental evaluation of the circulating composition to address hypotheses left open in the fifth article.
- **Appendix 2:** Heat exchange measurements conducted on the plate heat exchanger of the test bench described in the fifth article, evaluating various correlations to identify the most accurate one.

5. Conclusions:

- A synthesis of the research findings, highlighting how CO₂-based mixtures, particularly with dimethyl ether (DME), can enhance the efficiency and performance of refrigeration systems. This research demonstrates that use of DME in CO₂ mixtures can produce significant performance improvements while maintaining non-flammability and low Global Warming Potential (GWP). Performance indicators such as the Coefficient of Performance (COP) and heat transfer efficiency were considered for comparing the mixtures with pure CO₂.

Everything considered, this thesis offers a comprehensive screening of various configurations and boundary conditions for different mixtures of natural fluids. A mixture and a configuration are singled out as the most efficient. The results are then validated experimentally. The performance is proven to be enhanced when compared to pure CO₂, while ensuring non-flammability, non-toxicity, and low Global Warming Potential (GWP), complying with current and future regulations.

Compared to previous work in the literature on this topic, this research has found improved performance in terms of COP improvement over studies with CO₂ and DME, due to the effective use of an internal heat exchanger. Additionally, it has shown better performance and reduced flammability with respect to mixtures with CO₂ and Propane, previously tested with the same experimental test-rig of this Doctoral thesis, under the same boundary conditions.

1 STATE OF THE ART

1.1 Introduction

The Paris Agreement [1], adopted by the United Nations in 2015, aims to significantly reduce greenhouse gas emissions to combat climate change. The European Union has set ambitious targets to cut emissions by 80 to 95% compared to 1990 levels by 2050[1]. Additionally, international and European regulations, such as the Kigali Amendment to the Montreal Protocol [2] and the F-gas Regulation 517/2014, focus on reducing emissions from fluorinated refrigerants.

Given these stringent targets, it is crucial to identify refrigerant fluids that have low Global Warming Potential (GWP) and high efficiency, while also ensuring safety in terms of toxicity and flammability. Carbon dioxide (CO₂) is one such refrigerant that meets many of these criteria and is currently widely used in Europe for supermarket refrigeration [3]. CO₂ is a natural fluid that is non-toxic, non-flammable, and has a GWP of 1. However, its efficiency is lower compared to fluorinated gases, flammable hydrocarbons (HC), or toxic fluids like ammonia.

A useful metric for evaluating the environmental impact of a refrigeration cycle is the Total Equivalent Warming Impact (TEWI) [4], which considers both GWP and efficiency:

$$TEWI = GWP * M_f * L_{annual} * n_y + GWP * M_f * (1 - \alpha_{rec}) + E_{annual} * \beta_{eq} * n_y \quad 1.1$$

In this formula, M_f represents the mass of fluid in the system, L_{annual} the percentage of annual fluid losses, n_y the number of years of use, α_{rec} the percentage of mass recovered at the end of life, E_{annual} the annual electricity consumption and β_{eq} the equivalent CO₂ emission per kWh produced.

This formula accounts for both the direct emissions from the release of the refrigerant and the indirect emissions from the energy consumption of the system.

By considering both direct and indirect emissions, TEWI provides a comprehensive measure of the environmental impact of refrigeration systems, making it a valuable tool for developing sustainable and efficient refrigeration technologies.

1.2 CO₂ cycle

Carbon dioxide (CO₂) is a natural refrigerant that is safe, non-flammable, environmentally friendly, inexpensive, and widely available [5]. Despite these advantages, CO₂ faces significant challenges as a refrigerant, primarily due to its critical temperature of 31°C. This low critical temperature leads to trans-critical conditions on the high-pressure side of the cycle in many applications.

Under trans-critical conditions, condensation does not occur, and heat transfer does not happen at a constant temperature. Instead, the pressure is not determined by the condensing temperature but can vary and be optimized. This high optimal pressure results in substantial losses at the throttle valve, which reduces the overall efficiency of the system.

To address these issues, various strategies have been proposed in the literature, including:

- Ejectors.
- Internal Heat Exchangers (IHX)
- Parallel compression
- Two stage compression
- Mechanical subcooling
- Dedicated mechanical subcooling

These configurations can also be applied to refrigerant mixtures, offering potential solutions to improve the efficiency and performance of CO₂ refrigeration systems. However, each of these strategies comes with its own set of challenges and trade-offs, which need to be carefully considered in the design and implementation of CO₂-based refrigeration systems.

1.2.1 Ejectors

An ejector is a fluid-dynamic device without moving parts, used for the compression of liquids or gases [6]. It operates using two fluids: a primary fluid at high pressure and temperature, and a secondary fluid at low pressure and temperature. The primary fluid passes through a convergent-divergent nozzle, exiting at low pressure and supersonic speed. In the subsequent mixing zone, the primary fluid transfers part of its momentum to the secondary fluid, mixing with it.

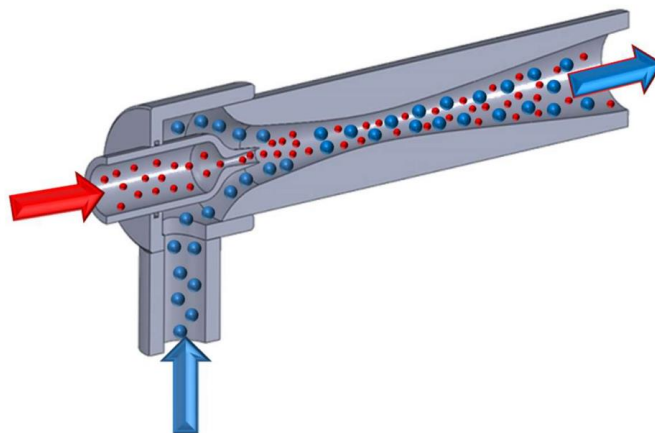


Figure 1.1: Operating principle of an ejector.

If the mixed flow is supersonic, it undergoes a shock (either straight or oblique), returning it to subsonic conditions. The divergent section then further slows the flow, bringing it to near-stagnation speeds and intermediate pressure between the initial primary and secondary pressures.

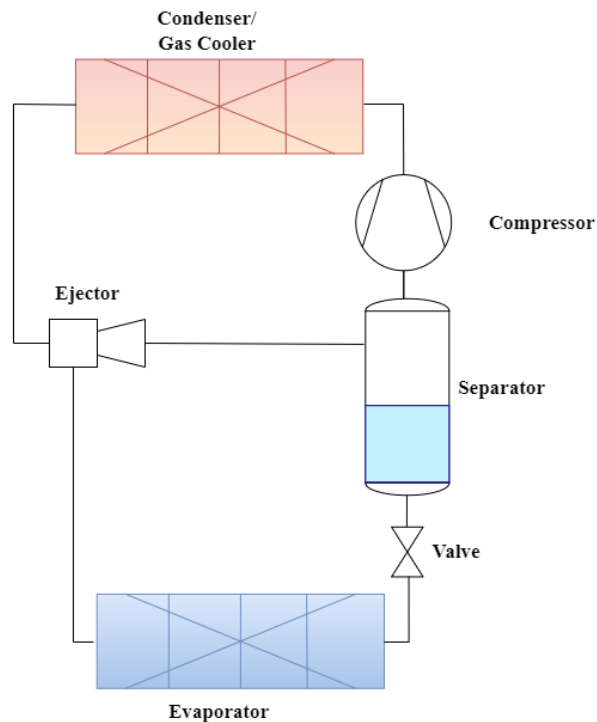


Figure 1.2: Cycle with ejector.

In CO₂ refrigeration cycles, ejectors can be particularly beneficial. They help recover energy that would otherwise be lost at the throttle valve, providing additional compression to the flow after the evaporator [7]. This process improves the overall efficiency of the system by reducing the work required from the compressor and enhancing the heat transfer in the evaporator.

The thermodynamics of the cycle with an ejector will be discussed in detail in Paper 1.

1.2.2 Internal Heat Exchangers (IHX)

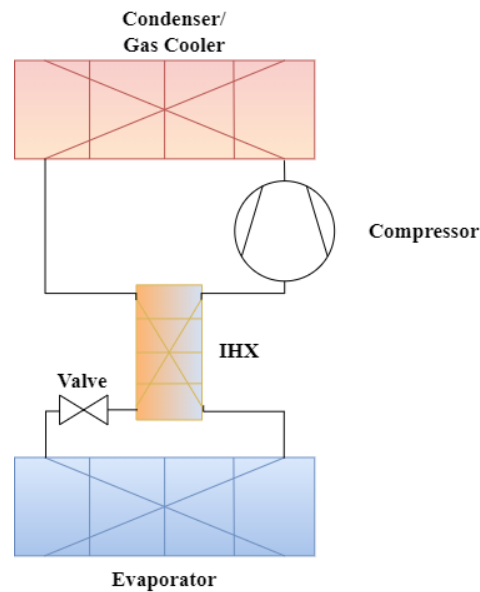


Figure 1.3: Cycle with IHX.

The use of internal heat exchangers (IHX) in refrigeration systems can significantly enhance performance. By cooling the refrigerant before it enters the throttle valve, IHXs reduce throttling losses, thereby increasing the specific cooling capacity [8]. However, this process also raises the temperature at the compressor inlet, which can decrease suction density and, consequently, the mass flow rate. Therefore, the effectiveness of IHXs can vary depending on the type of refrigerant used [9,10].

For CO₂ refrigeration systems, the use of IHXs has been shown to be particularly beneficial. Studies by Aprea and Maiorino [11], Cavallini et al. [12], and Torrella et al. [13] have demonstrated that IHXs can increase the coefficient of performance (COP) by approximately 10%. The increase in specific cooling capacity allows for a reduction in optimal working pressure. However, the higher suction temperature can lead to an increase in outlet temperature by up to 20°C.

Additionally, IHXs can improve the overall efficiency of the refrigeration cycle by ensuring that the refrigerant entering the compressor is in vapor form, which is crucial for the proper functioning of the compressor. This solution can be easily integrated with other strategies, such as ejectors, parallel compression, and two-stage compression, to further enhance the efficiency and performance of CO₂ refrigeration systems.

1.2.3 Parallel compression

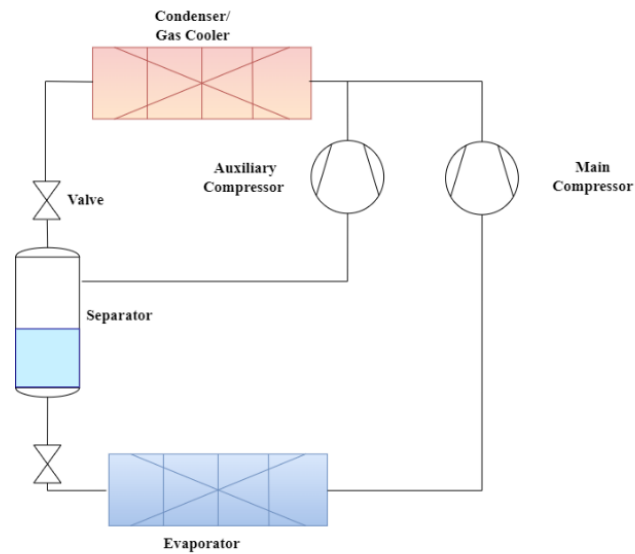


Figure 1.4: Parallel compression cycle.

The implementation of parallel compressors in CO₂ refrigeration systems offers significant benefits, as they operate at a reduced pressure ratio compared to the main compressor. This reduction in pressure ratio decreases the work required for vapor compression, making the system more efficient, especially when the amount of vapor exiting the throttle valve increases.

Research has demonstrated the advantages of parallel compression systems. Studies by Gullo et al. [14,15], and Chesi et al. [16] have shown that parallel compressors can enhance the overall efficiency of CO₂ refrigeration systems. Specifically, parallel compression helps manage the flash gas produced during the pressure reduction process, which would otherwise not contribute to cooling. By using a separate compressor to handle this flash gas, the system can achieve higher efficiency and better performance.

1.2.4 Subcooling with two stage compression

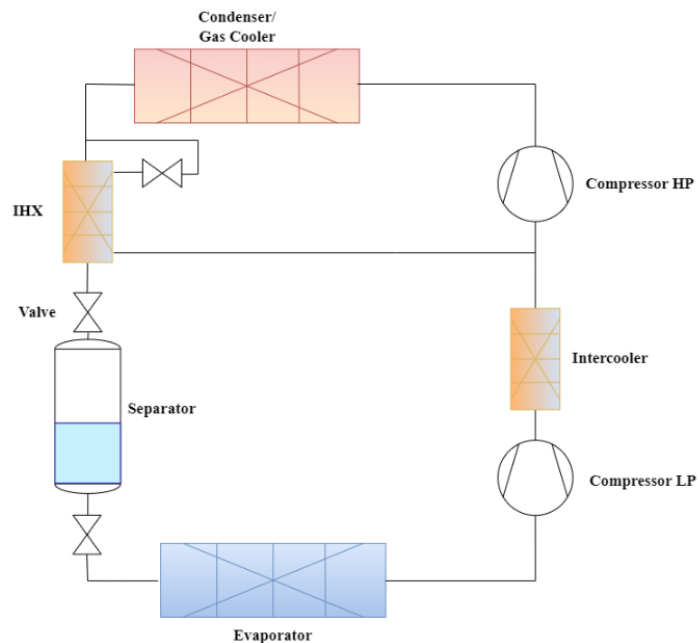


Figure 1.5: Two stage compression cycle.

Subcooling in refrigeration systems, particularly when combined with two-stage compressors, offers significant performance enhancements. This technique involves using a portion of the refrigerant mass flow to cool the remaining refrigerant, which evaporates at a medium pressure. This method is advantageous because subcooling is achieved through evaporation at a medium temperature, making it less energy-expensive for the same enthalpy change. Figure 1.5 illustrates a possible configuration with subcooling.

The medium pressure must be optimized, and an intercooler should be used after the first compressor to maximize efficiency. According to Cavallini et al. [17], this configuration can increase the coefficient of performance (COP) by approximately 25% compared to a basic cycle.

Subcooling can lead to a substantial increase in cooling capacity and a reduction in the optimal high working pressure of CO₂ systems. Subcooling helps to lower the temperature of the refrigerant before it enters the expansion valve, which minimizes energy losses and enhances system efficiency.

Overall, the integration of subcooling with two-stage compressors presents a promising solution for improving the performance and efficiency of CO₂ refrigeration systems, making them an interesting solution for a wide range of applications.

1.2.5 Mechanical subcooling

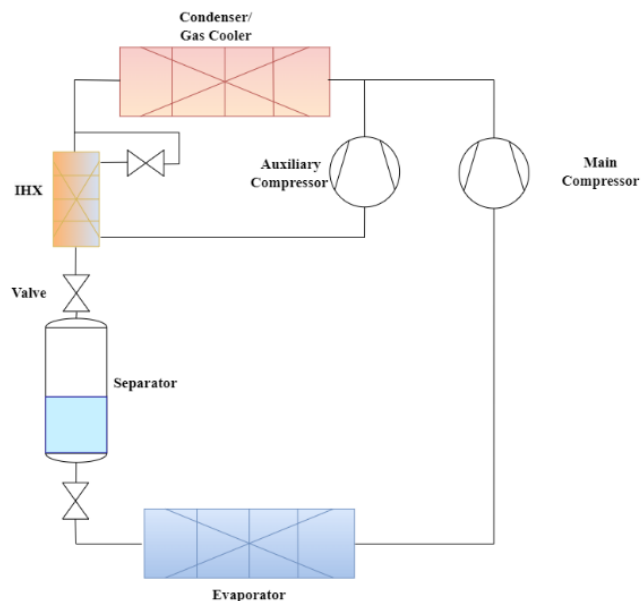


Figure 1.6: Cycle with mechanical subcooling.

Mechanical subcooling in refrigeration systems involves the use of a dedicated compressor. This allows to increase the evaporating pressure above the intermediate pressure of the two-stage compression cycle. This approach enhances the overall efficiency of the system by reducing the energy required for the same cooling effect.

Cecchinato et al. [18] found that a single-stage cycle coupled with a gas cooling circuit can achieve a 17.3% increase in energy efficiency compared to a basic single-stage cycle. This improvement is primarily due to the more effective use of energy in the subcooling process, which reduces the overall work required by the compressors.

By lowering the temperature of the refrigerant before it enters the expansion valve, mechanical subcooling minimizes energy losses and improves system efficiency. Additionally, this method helps prevent the formation of flash gas, ensuring that the evaporator receives only liquid refrigerant, which enhances its performance.

1.2.6 Dedicated subcooling

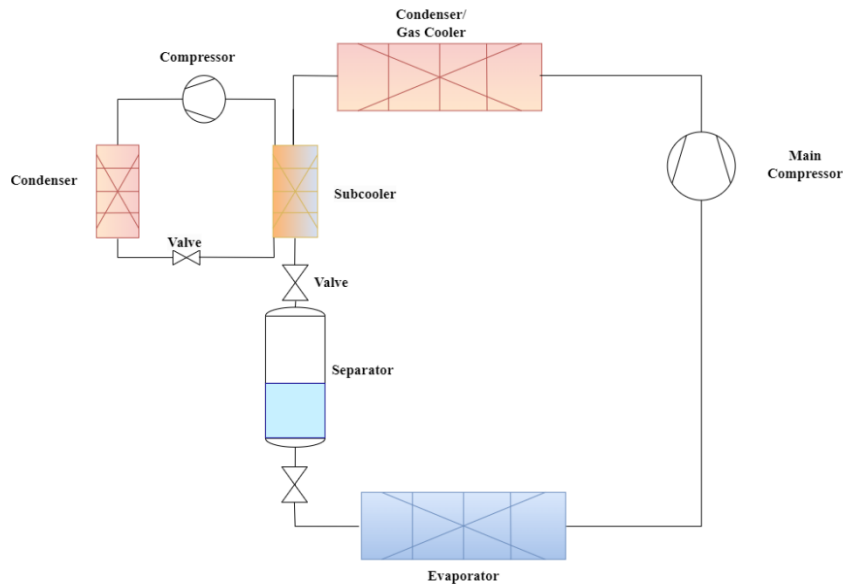


Figure 1.7: Cycle with dedicated subcooling.

Dedicated mechanical subcooling involves the use of an additional mechanical compression system to enhance the performance of refrigeration cycles. This approach allows for the use of a different refrigerant, which can be a fluid with higher performance characteristics than CO₂. Due to the small size of the dedicated subcooling cycle, it is feasible to use fluids with high Global Warming Potential (GWP) or even flammable fluids, which might not be suitable for the main cycle.

Research has shown that dedicated mechanical subcooling can significantly improve the efficiency of refrigeration systems. For instance, Hafner and Hemmingsen [19], Llopis et al. [20], and Gullo et al. [21] have studied various refrigerants and configurations, demonstrating the benefits of this approach.

1.3 CO₂ based mixtures

The use of CO₂-based mixtures in refrigeration systems offers several advantages, particularly by increasing the critical temperature of the refrigerant and reducing the cycle pressure. By mixing CO₂ with other refrigerants that have higher critical temperatures (Table 1.1), intermediate pseudo-critical conditions can be achieved. This approach combines the benefits of CO₂, such as low Global Warming Potential (GWP) and high volumetric cooling capacity, with the low operating pressure of the additive fluid, thereby reducing losses at the throttle valve.

The mixture we obtain has therefore low flammability and low GWP. In the case of zeotropic mixtures, the glide effect can be beneficial for the evaporator, especially in case of a coupling in temperature difference with the cold fluid delivered to the user. Additionally, these mixtures can lower the triple point temperature below -56.6°C, which is advantageous for certain applications.

Research has shown that CO₂-based mixtures can significantly enhance the performance and efficiency of refrigeration systems.

Table 1.1: Main fluid properties.

Fluid	T _{cr} [C]	P _{cr} [bar]	GWP	Safety class
R1234yf	94.7	33.8	4	A2L
R1233zd(E)	165.6	35.7	1	A1
R1234ze(E)	109.4	36.3	7	A2L
n-pentane	196.5	33.6	5	A3
propane	96.7	42.5	3.3	A3
Isobutane	134.7	36.4	3	A3
Dimethyl ether	127.2	53.67	1	A3
Ammonia	132.4	113.6	0	B2
Propylene	91.1	45.55	2	A3
CO ₂	30.98	73.77	1	A1

The study of CO₂-based mixtures for refrigeration and heat pump applications is well-documented in the literature, covering a variety of configurations and boundary conditions. Both experimental and theoretical studies have been conducted to explore the potential of these mixtures.

Tobaly et al. [22] experimentally analysed CO₂-propane mixtures for refrigeration, finding improvements in the coefficient of performance (COP) and reductions in gas cooler/condenser pressure. Similarly, Yu et al. [23] studied CO₂-propane mixtures for automobile air conditioning, reporting COP increases of up to 29.4% with fixed compressor speed and 22% with fixed cooling capacity. In 2019, Yu et al. [24] also investigated CO₂/R41 mixtures, observing COP increases of up to 14.5% for heating mode and 25.7% for cooling mode.

Bouteiller et al. [25,26] examined CO₂-propane and CO₂-R1234yf mixtures for central heating and domestic water heating. They found benefits in terms of COP for central heating but noted a reduction in performance for domestic water heating. Ju et al. [27] tested CO₂-propane mixtures for high sink temperature lift, identifying an optimal mass fraction of 12%/88%. This mixture was proposed as an alternative to R22, showing increased COP and heating capacity.

Sicco et al. [28] experimentally studied CO₂-R152a mixtures, finding COP improvements of up to 11.6% for a 5% mass fraction of R152a. Martínez-Ángeles et al. [29] also investigated CO₂-R152a mixtures, noting COP improvements and reductions in cooling capacity for refrigeration with an integrated mechanical subcooling cycle.

Sánchez et al. [30] explored CO₂/R1270 (92.5/7.5%) and CO₂/R32 (78/22%) mixtures for a vertical beverage cooler, achieving energy savings of up to 15.7% and 17.2%, respectively. In

2024, Sánchez et al. [31] assessed a refrigeration plant with and without an internal heat exchanger (IHX) for mixtures with propylene, R1234yf, and R32. They found the R32 mixture to be the best performing in both configurations, with COP increases of 15.3% and 22.2%, while reducing operating pressures and capacities. Sun et al. [32] also studied CO₂ and R32 mixtures, finding an optimal mass fraction of CO₂ at 0.6, which increased cooling COP by 65.2% compared to a configuration without IHX and pure CO₂.

Koyama et al. [33] tested a mixture with 10% DME, finding no significant differences in COP but noting a reduction in optimal discharge pressure by 2 MPa for heating mode and 1.9 MPa for cooling mode. Kim et al. [34] investigated propane mixtures for air conditioning, achieving a COP increase of up to 12.8%. Niu and Zhang [35] proposed CO₂-propane mixtures (71/29%, mole fraction) as an alternative to R13 for cascade refrigeration, showing benefits in terms of COP and refrigeration capacity. Sobieraj et al. [36] also explored CO₂-propane and CO₂-R32 mixtures for cascade refrigeration, achieving temperatures as low as -72°C, overcoming the CO₂ triple point temperature limit of -56.5°C.

Gómez-Hernández et al. [37] proposed acetone-CO₂ mixtures for high-temperature heat pumps, finding that a composition with 5% CO₂ had the best performance.

Numerous theoretical studies have been conducted on CO₂-based mixtures for refrigeration and heat pump applications, exploring various configurations and boundary conditions. Some of them are reported below:

Di Nicola et al. [38,39] investigated the use of mixtures in the low-temperature cycle of cascade refrigeration systems to reduce the minimum temperature compared to pure CO₂, finding only a slight reduction in COP. Massuchetto et al. [40] analysed a cascade system using a CO₂/ammonia mixture for the high-temperature cycle to better couple the two cycles. They identified CO₂/DME (10% CO₂) as the optimal mixture for the low-temperature cycle, achieving a COP increase of up to 30%.

Nasruddin et al. [41] evaluated a cascade refrigeration system with propane for the high-temperature circuit and an ethane/CO₂ mixture for the low-temperature circuit, finding a CO₂ fraction of 68% as the thermodynamic and economic optimum. Onaka et al. [42] conducted a thermodynamic analysis of a heat pump water heater operating with a CO₂/DME mixture, identifying 10% mass DME as the optimal composition for their boundary conditions, with reduced operating pressure and mass flow rate.

Sarkar and Bhattacharyya [43] explored CO₂/R600 and CO₂/R600a (0.5/0.5) mixtures for medium and high-temperature heat pumps, noting a reduction in discharge pressure but no significant improvement in COP. Fan et al. [44] studied CO₂/propane mixtures for heat pumps with large heat-sink temperature rises, finding an optimal mixture mass fraction of 20/80% and a COP increase of 12.62% compared to the reference cycle with R22. They also observed that R22 performed better for small heat-sink temperature rises. Dai et al. [45] evaluated heat pump water heaters with various mixtures, noting benefits in terms of COP and discharge pressure.

Wang et al. [46] examined the effects of a CO₂/R41 (0.5/0.5) mixture as an azeotropic refrigerant, finding high system COP and low optimal high pressure, with more than a 23% increase in exergy efficiency compared to pure CO₂ across three studied systems. Martínez-Ángeles et al. [47] studied mixtures with R-152a, R-1234yf, R-1234ze(E), and R-1233zd(E) for both single-stage cycles with IHX and parallel compression, achieving COP increases of up to 5.8% for the IHX cycle and 10.0% for the parallel compression cycle.

The literature includes numerous studies on heat transfer. While mixtures can offer advantages in terms of pressure, critical temperature, and improved coupling at the evaporator with the cold fluid, it is crucial to note that mixtures may exhibit lower heat transfer coefficients and higher pressure drops compared to pure fluids.

Onaka et al. [48] investigated the evaporation heat transfer of CO₂/DME mixtures in a horizontal tube. They observed a reduction in the heat transfer coefficient by 20% for a 10% CO₂ mixture and by 48% for a 25% CO₂ mixture. Afroz et al. [49] examined heat transfer and pressure drop during in-tube condensation for CO₂/DME mixtures with 21% and 39% CO₂. Their findings indicated that both the heat transfer coefficient and pressure drop decreased as the CO₂ concentration increased. Grauso et al. [50] conducted an experimental study on the flow boiling of CO₂/Propane mixtures in a horizontal smooth tube, revealing significant degradation in the heat transfer coefficient compared to pure CO₂. Similarly, Cho et al. [51,52] studied CO₂/Propane mixtures across different diameters and reported comparable trends.

1.4 Pure fluids and mixtures correlations

Boiling heat transfer is a critical phenomenon in various industrial applications, influencing the efficiency and performance of heat exchangers. In this study, evaporation was analysed for both horizontal tubes and a plate heat exchanger. Literature correlations for calculating the heat transfer coefficient (HTC) are primarily based on the superposition of effects:

$$h_{tp} = [(Sh_{nb})^n + (Fh_{cb})^n]^{\frac{1}{n}} \quad 1.2$$

where h_{nb} represents the nucleate boiling and h_{cb} the convective boiling.

As the quality increases, the contribution from nucleate boiling decreases, while the convective contribution becomes more significant. This trend is modelled through the suppression factor (S) for nucleate boiling and the enhancement factor (F) for convective boiling. S and F are typically correlated to the Reynolds number and the Martinelli parameter, respectively, and are calibrated using experimental data. When the exponent n equals 1, the model is linear; otherwise, n is greater than one.

For instance, the correlations by Gungor and Winterton (1986) [53] and Jung [54] are linear, whereas those by Liu and Winterton [55] and Wattelet et al. [56] have ($n > 1$). Not all correlations are based on the superposition of effects; for example, Gungor and Winterton (1987) [57] is strictly convective. Another class of correlations is based on flow pattern maps, where different correlations are applied for each flow regime as in Cheng et al. [58] and Wojtan et al. [59].

1.4.1 Pure fluids correlations for in-tube flow boiling

Various empirical and theoretical correlations have been developed to predict the HTC for different pure fluids under various conditions. In this section, several correlations for pure fluids are presented.

1.4.1.1 Gungor and Winterton 1986

The Gungor and Winterton [53] correlation for the heat transfer coefficient (HTC) in boiling heat transfer is expressed as:

$$h_{tp} = F \cdot h_l + S \cdot h_{nb} \quad 1.3$$

Where h_{nb} is the nucleate boiling heat transfer coefficient, calculated using the Cooper [60] correlation, and h_l is the liquid phase heat transfer coefficient, determined by the Dittus-Boelter [61] correlation.

The nucleate boiling heat transfer coefficient h_{nb} is given by:

$$h_{nb} = 55 \cdot p_r^{0.12} (-\log_{10} p_r)^{-0.55} \cdot M_{mol}^{-0.5} \cdot q^{0.67} \quad 1.4$$

where p_r is the reduced pressure, M_{mol} is the molecular weight, and q is the heat flux.

The liquid phase heat transfer coefficient h_l is calculated as:

$$h_l = 0.023 \cdot Re_l^{0.8} \cdot \frac{k_L}{D_{eq}} \cdot Pr_l^{0.4} \quad 1.5$$

where Re_l is the Reynolds number for the liquid phase, k_L is the thermal conductivity of the liquid, D_{eq} is the equivalent diameter, and Pr_l is the Prandtl number for the liquid phase.

The factor F is a function of the boiling number (Bo) and the Martinelli parameter (X_{tt}):

$$F = 1 + 24000 \cdot Bo^{1.16} + 1.37 \cdot \left(\frac{1}{X_{tt}} \right)^{0.86} \quad 1.6$$

While the suppression factor (S) also depends on the Reynolds number:

$$S = \frac{1}{1 + 1.15 \cdot 10^{-6} \cdot F^2 \cdot Re_l^{1.17}} \quad 1.7$$

Additionally, if the Froude number (Fr) is less than 0.05, F is multiplied by $Fr^{0.12 \cdot Fr}$ and S is multiplied by $Fr^{\frac{1}{2}}$

This correlation was developed based on over 4300 experimental data points, covering a wide range of conditions: tube diameters between 2.95 and 32.00 mm, saturation temperatures from -0.7°C to 364.9°C, mass velocities between 59.2 kg/m²s and 8179.3 kg/m²s, heat fluxes from 1.1 kW/m² to 2280.0 kW/m², and qualities ranging from 0 to 0.99.

1.4.1.2 Gungor and Winterton 1987

In 1987, Gungor and Winterton [57] proposed a simplified correlation for predicting the heat transfer coefficient (HTC) in boiling heat transfer. Unlike their 1986 correlation [53], which is based on the superposition of nucleate and convective boiling effects, the 1987 correlation [57] focuses solely on convective boiling.

The correlation is expressed as:

$$h_{tp} = F \cdot h_l \quad 1.8$$

The liquid phase heat transfer coefficient h_l is typically calculated using the Dittus-Boelter [61] correlation. The enhancement factor is given by:

$$F = 1 + 3000 \cdot Bo^{0.86} + 1.12 \left(\frac{x}{1-x} \right)^{0.75} \cdot \left(\frac{\rho_l}{\rho_v} \right)^{0.41} \quad 1.9$$

Bo is the boiling number, which represents the ratio of heat flux to the product of mass flux and latent heat, x is the vapor quality, ρ_l and ρ_v are the densities of the liquid and vapor phases, respectively.

1.4.1.3 Jung 1988

The Jung [54] correlation for the heat transfer coefficient (HTC) in boiling heat transfer is expressed as:

$$h_{tp} = F \cdot h_l + S \cdot h_{nb} \quad 1.10$$

Where h_{nb} is calculated using the Stephan and Abdelsalam [62] correlation and h_l is determined by the Dittus-Boelter [61] correlation.

The nucleate boiling heat transfer coefficient is given by:

$$h_{nb} = 207 \cdot \frac{k_l}{b_d} \cdot \left(\frac{q \cdot b_d}{k_l \cdot T_{sat}} \right)^{0.745} \cdot \left(\frac{\rho_v}{\rho_l} \right)^{0.581} \cdot Pr_l^{0.533} \quad 1.11$$

Where T_{sat} is the saturation temperature, b_d is the bubble diameter calculated as:

$$b_d = 0.0146 \cdot \theta \left(\frac{2 \cdot \sigma}{g \cdot (\rho_l - \rho_v)} \right)^{0.5} \quad 1.12$$

θ is the contact angle assumed to be 35° , σ is the surface tension and g is the gravitational acceleration.

The factor F is dependent on the Martinelli parameter X_{tt}

$$F = 2.37 \cdot \left(0.29 + \frac{1}{X_{tt}} \right)^{0.85} \quad 1.13$$

The suppression factor (S) is calculated differently depending on the value of X_{tt} :

If $X_{tt} \leq 1$:

$$S = 4048 \cdot X_{tt}^{1.22} \cdot Bo^{1.13} \quad 1.14$$

While if $1 < X_{tt} \leq 5$:

$$S = 2 - 0.1 \cdot x_{tt}^{-0.28} \cdot Bo^{-0.33} \quad 1.15$$

This correlation was developed based on over 3000 experimental data points, covering a range of conditions: tube diameters of 9.1 mm, reduced pressures between 0.08 and 0.16, mass velocities between 250 kg/m²s and 720 kg/m²s, heat fluxes from 10 kW/m² to 45 kW/m², and qualities up to 0.95.

1.4.1.4 Liu and Winterton 1991

The Liu and Winterton [55] correlation for the heat transfer coefficient (HTC) in boiling heat transfer is expressed as:

$$h_{tp} = ((F \cdot h_l)^2 + (S \cdot h_{nb})^2)^{\frac{1}{2}} \quad 1.16$$

Where h_{nb} is calculated using the Cooper [60] correlation and h_l is determined by the Dittus-Boelter [61] correlation for the liquid phase.

The factor F is a function of the Prandtl number, the quality and density ratio between the liquid and vapor phases:

$$F = 1 + x \cdot Pr_l \cdot \left(\frac{\rho_l}{\rho_v} - 1 \right)^{0.35} \quad 1.17$$

While the suppression factor S also depends on the Reynolds number

$$S = (1 + 0.55 \cdot F^{0.1} \cdot Re_l^{0.16})^{-1} \quad 1.18$$

This correlation was developed based on experimental data for tube diameters ranging from 2.95 to 32 mm, mass velocities between 12.4 kg/m²s and 8157 kg/m²s, heat fluxes from 3.5 kW/m² to 2620 kW/m².

1.4.1.5 Wattelet et al., 1993

The Wattelet et al. [56] correlation for the heat transfer coefficient (HTC) in boiling heat transfer is expressed as:

$$h_{tp} = ((R \cdot F \cdot h_l)^{2.5} + (h_{nb})^{2.5})^{\frac{1}{2.5}} \quad 1.19$$

Where h_{nb} is calculated using the Cooper [60] correlation and h_l is determined by the Dittus-Boelter [61] correlation.

The enhancement factor F is a function of a modified Martinelli parameter (X_{tt}):

$$X_{tt} = \left(\frac{1-x}{x} \right)^{0.9} \cdot \Omega \quad 1.20$$

Where x is the vapor quality and Ω is a parameter defined as:

$$\Omega = 0.551 \cdot P_r^{0.492} \quad 1.21$$

The factor F is then calculated as:

$$F = 1 + 1.925 \cdot X_{tt}^{-0.83} \quad 1.22$$

The factor R depends on the Froude number:

If $Fr_l < 0.25$:

$$R = 1.32 \cdot Fr_l^{0.2} \quad 1.23$$

Else:

$$R = 1 \quad 1.24$$

This correlation was developed based on experimental data for a tube diameter of 7.04 mm, mass velocities between 25 and 100 kg/m²s, heat fluxes from 2 kW/m² to 10 kW/m², and saturation temperatures ranging from -15°C to 5°C.

1.4.1.6 Choi et al., 2007

The Choi et al. [63] correlation for the heat transfer coefficient (HTC) in boiling heat transfer is expressed as:

$$h_{tp} = F \cdot h_l + S \cdot h_{nb} \quad 1.25$$

Where h_{nb} is calculated using the Cooper [60] correlation and h_l is determined by the Dittus-Boelter [61] correlation.

The enhancement factor (F) is a function of the Martinelli parameter (X_{tt}) and is given by:

$$F = 0.042 \cdot \phi_f^2 + 0.958 \quad 1.26$$

Where ϕ_f^2 is defined as:

$$\phi_f^2 = 1 + \frac{C}{X_{tt}} + \frac{1}{X_{tt}^2} \quad 1.27$$

The suppression factor (S) depends on the boiling number (Bo) and (ϕ_f^2):

$$S = 469.1689 \cdot (\phi_f^2)^{-0.2093} \cdot Bo^{0.7402} \quad 1.28$$

This correlation was developed based on experimental data for tube diameters ranging from 1.5 to 3 mm, mass velocities between 200 kg/m²s and 600 kg/m²s, heat fluxes from 10 kW/m² to 40 kW/m², and a saturation temperature of 10°C.

1.4.1.7 Cheng et al., (2008)

The Cheng et al. [58] correlation for the heat transfer coefficient in boiling heat transfer is based on flow pattern maps. This approach involves identifying the flow regimes and then applying specific correlations for the HTC within each regime. The correlation is an adaptation of the Wojtan et al. [59] correlation, specifically obtained for CO₂.

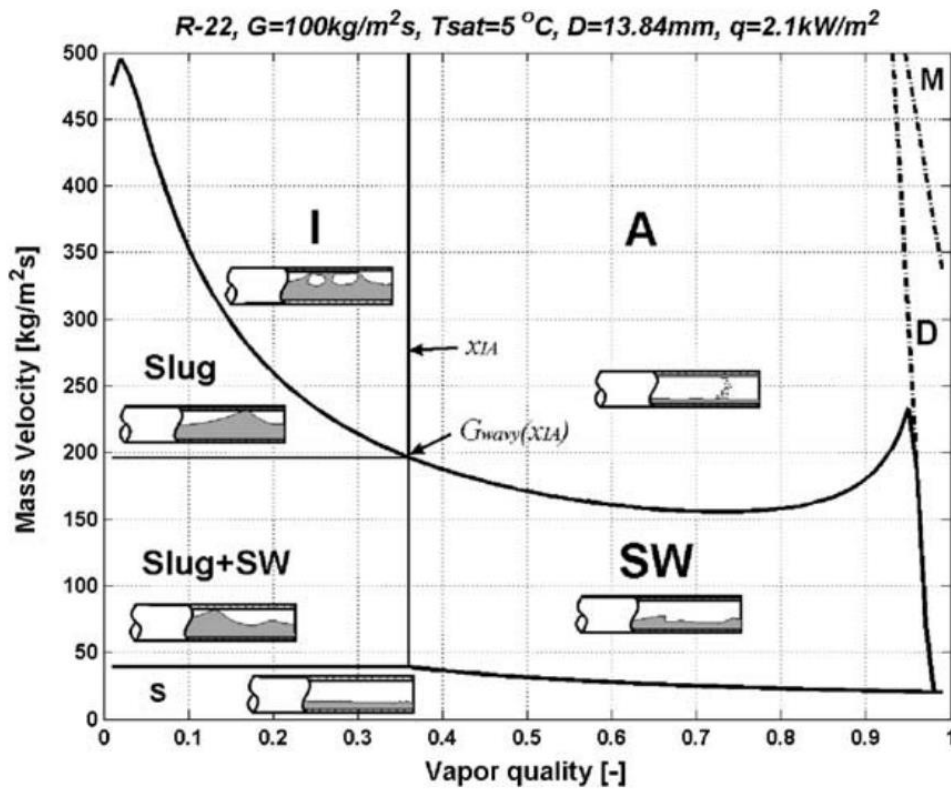


Figure 1.8: Representation of the map by Wojtan et al. [64] for R22, temperature of 5 °C, internal diameter of 13.84 mm, mass velocity of 100 kg/m²s and a heat flow of 2.1 kW/m².

Figure 1.8 shows the flow pattern map obtained for a specific condition using the Wojtan et al. [64] correlation. For example, at low mass velocities in horizontal tubes, the flow is stratified (S on the figure). For medium mass velocities and low qualities, the flow is slug plus stratified wavy, then as the vapor quality increases it becomes stratified wavy and in the last part it reaches the dry out region. For higher mass velocities and low qualities, the flow can be slug or even intermittent, increasing the quality becomes annular and then can pass to the dry out or even mist region.

The basic formulation of the overall heat transfer coefficient is represented as follows:

$$h_{tp} = \frac{\theta_{dry} h_v + (2\pi - \theta_{dry}) h_{wet}}{2\pi} \quad 1.29$$

Where θ_{dry} is the angle corresponding to the dry portion of the pipe, h_v is the heat transfer coefficient for the vapor phase, h_{wet} is the heat transfer coefficient for the wet portion.

The value of θ_{dry} varies depending on the flow regime:

For annular flow θ_{dry} is equal to zero, for stratified flow it is equal to θ_{strat} , while for stratified wavy flow:

$$\theta_{dry} = \theta_{strat} \left(\frac{G_{wavy} - G}{G_{wavy} - G_{strat}} \right)^{0.61} \quad 1.30$$

and for slug-stratified wavy flow:

$$\theta_{dry} = \theta_{strat} \frac{x}{x_{IA}} \left(\frac{G_{wavy} - G}{G_{wavy} - G_{strat}} \right)^{0.61} \quad 1.31$$

Here, θ_{strat} is calculated using the Biberg [65] correlation, and G_{wavy} and G_{strat} are obtained from the flow pattern map correlations.

The heat transfer h_v is calculated with Dittus-Boelter (1930)[61] correlation for the vapor phase, while h_{wet} is calculated using a non-linear superposition of nucleate boiling and convective boiling:

$$h_{wet} = [(Sh_{nb})^3 + h_{cb}^3]^{\frac{1}{3}} \quad 1.32$$

Where h_{nb} is calculated using the Cooper [60] correlation and h_{cb} is determined by a modified Dittus-Boelter [61] correlation

$$h_{cb} = 0.0133 Re_{\delta}^{0.69} Pr_L^{0.4} \frac{k_L}{\delta} \quad 1.33$$

Where:

$$Re_{\delta} = \frac{4G(1-x)\delta}{(1-\varepsilon)\mu_l} \quad 1.34$$

And the film thickness δ is calculated as:

$$\delta = \frac{d}{2} - \sqrt{\left(\frac{d}{2}\right)^2 - \frac{2A_1}{2\pi - \theta_{dry}}} \quad 1.35$$

The suppression factor S is equal to 1 for qualities less than x_{IA} . For higher qualities:

$$S = 1 - 1.14 \left(\frac{D_{eq}}{0.00753} \right)^2 \left(1 - \frac{\delta}{\delta_{IA}} \right)^{2.2} \quad 1.36$$

The HTC for mist and dry out region is calculated differently.

For the mist region:

$$h_M = 2 \times 10^{-8} Re_H^{1.97} Pr_V^{1.06} Y^{-1.83} \frac{k_V}{D_{eq}} \quad 1.37$$

For the dry-out region:

$$h_{dryout} = h_{tp}(x_{di}) - \frac{x - x_{di}}{x_{de} - x_{di}} [h_{tp}(x_{di}) - h_M(x_{de})] \quad 1.38$$

Where:

$$Y = 1 - 0.1 \left[\left(\frac{\rho_l}{\rho_v} - 1 \right) (1 - x) \right]^{0.4} \quad 1.39$$

This correlation was developed based on experimental data for tube diameters ranging from 0.6 to 10 mm, mass velocities between 50 kg/m²s and 1500 kg/m²s, heat fluxes from 1.8 kW/m² to 46 kW/m², and saturation temperatures between -28°C and 25°C.

1.4.2 Pure fluids correlations for PHE boiling

Plate heat exchangers (PHEs) are widely used in various industrial applications, due to their high efficiency and compact design. Although most heat transfer correlations are designed for in-tube flow boiling, they can be modified for PHEs by replacing the tube diameter with the hydraulic diameter of the channel. However, this approach is not always effective [66,67].

SPHEs consist of multiple thin plates with corrugated surfaces, which create complex flow patterns and enhance heat transfer. The hydraulic diameter in PHEs is typically smaller than in traditional tube heat exchangers, leading to higher heat transfer coefficients but also increased pressure drops. Therefore, it is crucial to use correlations that account for these unique features to ensure accurate thermal performance predictions.

Several studies have focused on developing and validating correlations specifically for PHEs. These studies take into consideration the effects of plate geometry, flow arrangement, and operating conditions on the heat transfer coefficient. The following sections present a summary on heat transfer correlations for PHEs.

1.4.2.1 Hsieh and Lin, (2003)

Hsieh and Lin [68] demonstrated that the Gungor and Winterton (1986)[53] correlation is effective for predicting the heat transfer coefficient in plate heat exchangers (PHEs) operating with R410a. Their study covered a vapor quality range of 0.1 to 0.8, mass velocities between 50 and 100 kg/m²s, heat fluxes from 10 to 20 kW/m², and pressures between 1.08 and 1.25 MPa. The results indicated that the correlation provided accurate predictions within these operating conditions, highlighting its applicability for PHEs using R410a.

1.4.2.2 Longo et al., (2015)

The Longo et al. [69] correlation for the heat transfer coefficient (HTC) in plate heat exchangers is expressed as:

$$h_{tp} = \max(h_{nb}, h_{cb}) \quad 1.40$$

Where h_{nb} and h_{cb} are calculated as follows:

$$h_{cb} = 0.122 \cdot \phi \cdot \left(\frac{k_L}{D_h}\right) \cdot Re_{EQ}^{0.8} \cdot Pr_L^{\frac{1}{3}} \quad 1.41$$

$$h_{nb} = 0.58 \cdot \phi \cdot h_0 \cdot \left(\frac{Ra}{Ra_0}\right)^{\frac{2}{15}} \cdot F_P \cdot \left(\frac{q}{q_0}\right)^{0.467} \quad 1.42$$

In these equations ϕ is the enlargement factor of the corrugated plates and Re_{EQ} is the equivalent Reynolds number, calculated as:

$$Re_{EQ} = G \cdot \left(1 - x + x \cdot \left(\frac{\rho_l}{\rho_v}\right)^{\frac{1}{2}}\right) \cdot \frac{Dh}{\mu_l} \quad 1.43$$

F_P is a function of the reduced pressure (p_{red}):

$$F_P = 1.2 \cdot p_{red}^{0.27} + \left(2.5 + \frac{1}{1 - p_{red}}\right) \cdot p_{red} \quad 1.44$$

Ra_0 is $0.4 \mu m$, q_0 is 20 kW/m^2 , and h_0 is calculated with Ra_0 , q_0 and $p_{red_0} = 0.1$.

This correlation was developed based on a set of 251 experimental data points for HFC, HC, and HFO refrigerants.

1.4.2.3 Amalfi et al., (2016)

The Amalfi et al. [70] correlation distinguishes between microscale and macroscale using the Bond number (B_d):

$$B_d = g \cdot D_h^2 \cdot \frac{\rho_l - \rho_v}{\sigma} \quad 1.45$$

For $B_d < 4$, the Nusselt number (Nu) is calculated as:

$$Nu = 982 \cdot \gamma^{1.101} \cdot We_m^{0.315} \cdot Bo^{0.32} \cdot \left(\frac{\rho_l}{\rho_v}\right)^{-0.224} \quad 1.46$$

Else the Nusselt number is given by:

$$Nu = 18.495 \cdot \gamma^{0.248} \cdot Re_v^{0.135} \cdot Re_L^{0.351} \cdot B_d^{0.235} \cdot Bo^{0.198} \cdot \left(\frac{\rho_l}{\rho_v}\right)^{-0.223} \quad 1.47$$

Where We_m is the Weber number calculated using the mean density for the homogeneous model, Bo the boiling number and

$$\gamma = \frac{\beta}{\beta_{max}} \quad 1.48$$

being β the chevron angle and β_{max} equal to 70° .

The heat transfer coefficient is then calculated as:

$$h_{tp} = Nu \cdot \frac{k_L}{D_h} \quad 1.49$$

This method was developed based on 1903 heat transfer data points for various refrigerants.

1.4.3 Zeotropic mixture correlations

For zeotropic mixtures, the heat transfer coefficient is significantly affected by the glide effect.

At the interface where bubble growth occurs, the concentration of the less volatile component in the liquid phase is higher than that in the bulk liquid, resulting in a higher temperature at the bubble interface compared to the rest of the liquid, thus increasing the effective superheat[71].

The glide increases the effective superheat between the liquid and vapor phases required for vaporization, thereby reducing the overall heat transfer efficiency. This phenomenon complicates the heat transfer process, making it essential to use correlations that accurately account for the glide effect to ensure reliable predictions.

Most correlations addressing this issue have been developed for in-tube flow boiling, where the unique characteristics of zeotropic mixtures are considered. These correlations help in understanding the impact of glide on the HTC and provide a basis for optimizing the design and operation of heat exchangers using zeotropic mixtures. Below are some of these correlations, which have been specifically made to address the challenges posed by the glide effect in zeotropic mixtures.

1.4.3.1 Thome & Shakir (1987)

The Thome and Shakir [72] correction factor was developed for pool boiling and is expressed as:

$$\frac{h}{h_{id}} = F_c = \left(1 + \left(\frac{h_{id}}{\dot{q}} \right) \cdot (T_{dew} - T_{bub}) \cdot \left(1 - \exp \left(\frac{-Bq}{\rho_l \cdot \Delta i_{lv} \cdot \beta_f} \right) \right) \right)^{-1} \quad 1.50$$

Where T_{dew} is the dew point temperature, T_{bub} is the bubble point temperature and Δi_{lv} is the latent heat.

Later, Thome [73] proposed modifications to the Gungor and Winterton (1986)[53] and Gungor and Winterton (1987)[57] correlations to account for mixture effects. For the Gungor and Winterton (1986)[53] correlation, Thome [73] introduced the correction factor for the nucleate boiling term:

$$h_{tp} = F_c \cdot S \cdot h_{nb} + F \cdot h_l \quad 1.51$$

For the Gungor and Winterton (1987)[57] correlation, Thome [73] suggested modifying the enhancement factor as follows:

$$F = 1 + 3000 \cdot (Bo \cdot F_c)^{0.86} + 1.12 \left(\frac{x}{1-x} \right)^{0.75} \cdot \left(\frac{\rho_l}{\rho_v} \right)^{0.41} \quad 1.52$$

The Thome and Shakir [72] correction factor is a general correlation that can be easily applied to any correlation based on the superposition of effects.

1.4.3.2 Shah (2015)

Shah [74] proposed a combined approach for calculating the heat transfer coefficient in boiling heat transfer. This approach integrates the correction factor on the nucleate boiling correlation proposed by Thome & Shakir [72] with the correction on the convective boiling correlation proposed by Bell & Ghaly [75]. The combined correlation is expressed as:

$$h_{tp} = F_c \cdot h_{nb} + \left(\frac{1}{h_{cb}} + \frac{Y}{h_v} \right)^{-1} \quad 1.53$$

Where F_c is the correction factor for nucleate boiling, as defined by Thome & Shakir [72], h_v is the vapor phase heat transfer coefficient. The term Y represents the ratio of sensible heat transfer to the total heat load and is calculated as:

$$Y = x \cdot C_{pg} \cdot \frac{dT}{di} \quad 1.54$$

Where C_{pg} is the specific heat capacity of the gas phase, di/dT is the apparent specific heat capacity of the mixture (dT/di is equal to zero for pure fluids).

This combined correlation effectively accounts for both nucleate and convective boiling mechanisms, providing a more comprehensive prediction of the HTC in boiling heat transfer scenarios.

1.4.3.3 Silver (1947) and Bell and Ghaly (1973)

Sardesai et al. (1982)[76] proposed another combination based on the correction by Silver [77] and Bell and Ghaly [75], resulting in the following correlation:

$$h_{tp} = \frac{1 + \frac{F_c \cdot h_{nb}}{h_{cb}}}{\frac{1}{h_{cb}} + \frac{Y}{h_v}} \quad 1.55$$

Where F_c is the correction factor for nucleating boiling, and h_v is the vapor phase heat transfer coefficient.

This correlation was named in this manner to ensure consistency with Mancini's [67] nomenclature, where the same evaporator was examined for different mixtures.

1.4.3.4 Jung (1989)

The Jung [78] correlation for the heat transfer coefficient (HTC) in boiling heat transfer is expressed as:

$$h_{tp} = \frac{S}{C_{UN}} \cdot h_{nb} + C_{me} \cdot F \cdot h_l \quad 1.56$$

Where h_{nb} is the nucleate boiling heat transfer coefficient calculated with Stephan and Abdelsalam (1980) correlation and h_l is the liquid phase heat transfer coefficient calculated using the Dittus-Boelter (1930). The mixture effect coefficient (C_{me}), is calculated as:

$$C_{me} = 1 - 0.35|\tilde{Y} - \tilde{X}|^{1.56} \quad 1.57$$

where $\tilde{Y}$ and $\tilde{X}$ are the concentrations of the most volatile component in the vapor and liquid phases, respectively.

The Ünal [79] coefficient, (C_{UN}), is calculated as follows:

$$C_{UN} = (1 + (b_2 + b_3) \cdot (1 + b_4)) \cdot (1 + b_5) \quad 1.58$$

With

$$b_2 = (1 - X) \ln \left(\frac{1.01 - \tilde{X}}{1.01 - \tilde{Y}} \right) + X \cdot \ln \left(\frac{\tilde{X}}{\tilde{Y}} \right) + |\tilde{Y} - \tilde{X}|^{1.5} \quad 1.59$$

$$b_4 = 152 \cdot \left(\frac{p}{p_{cmvc}} \right)^{3.9} \quad 1.60$$

$$b_5 = 0.92 \cdot |\tilde{Y} - \tilde{X}|^{0.001} \cdot \left(\frac{p}{p_{cmvc}} \right)^{0.66} \quad 1.61$$

Where p_{cmvc} is the critical pressure of the more volatile component.

If $\tilde{X} < 0.01$ then:

$$b_3 = \left(\frac{\tilde{Y}}{\tilde{X}} \right)^{0.1} - 1 \quad 1.62$$

Else b_3 is zero.

This correlation is designed to be used in conjunction with Jung [54]. It is derived from research into the effects of mixtures on horizontal flow boiling, specifically examining both non-azeotropic and azeotropic mixtures, such as R22/R114 and R12/R152a.

1.4.3.5 Wettermann and Steiner, (2000)

Wettermann and Steiner [80] proposed a model to determine the heat transfer coefficient for zeotropic mixtures, focusing on the impact of mass transport resistance on the nucleate boiling component. The overall heat transfer coefficient, (h_{tp}), is expressed as:

$$h_{tp} = (h_{nb}^3 + h_{cb}^3)^{\frac{1}{3}} \quad 1.63$$

Where, the convective boiling h_{cb} is calculated as:

$$h_{cb} = h_{lo} \left((1-x)^{0.01} \cdot \left((1-x) + 1.2 \cdot x^{0.4} \cdot \left(\frac{\rho_l}{\rho_v} \right)^{0.37} \right)^{-2.2} + x^{0.01} \cdot \left(\frac{h_{vo}}{h_{lo}} \cdot \left(1 + 8(1-x)^{0.7} \cdot \left(\frac{\rho_l}{\rho_v} \right)^{0.67} \right) \right)^{-2} \right)^{-0.5} \quad 1.64$$

The nucleate boiling h_{nb} is determined by:

$$h_{nb} = h_{eff} \left(1 + \frac{h_{eff}}{q} \cdot \Delta T_{bp} \right)^{-1} \quad 1.65$$

Where h_{eff} is the effective heat transfer coefficient, given by:

$$h_{eff} = h_{id} \left(1 - 0.25 \left(\frac{q}{q_{cr,nb}} \right)^{1.5} \right)^{215 \cdot \left(\frac{\Delta T_{bp}}{T_{cr,max} - T_{cr}} \right)} \quad 1.66$$

the critical heat flux $q_{cr,nb}$ is calculated as:

$$q_{cr,nb} = 2.79 \cdot q_{0,cr,nb} \cdot p_r^{0.4} \cdot (1 - p_r) \quad 1.67$$

And $q_{0,cr,nb}$ is a reference value and is to calculate as:

$$q_{0,cr,nb} = 0.13 \cdot \Delta i_{lv} \cdot \rho_v^{0.5} \cdot (\sigma \cdot g \cdot (\rho_l - \rho_v)) \quad 1.68$$

This model was obtained for mass velocities ranging from 80 kg/m²s to 400 kg/m²s, heat fluxes between 1.3 kW/m² and 70 kW/m², and temperature glides less than 30°C.

1.5 Refrigerant oil

The presence of oil is a crucial factor to consider not only for refrigerant mixtures but also for pure fluids. For flammable fluids, there are refrigerant charge limits for various applications as specified by the International Standard IEC 60335-2-40[81]. To avoid these restrictions, the refrigerant charge must be less than four times the lower flammability limit. As solubility increases, the circulating refrigerant charge decreases, which in turn limits the maximum power of the refrigeration system.

Sanchez-Moreno-Giner et al. [82] demonstrated that in a low-charge propane heat pump, up to 41% of the refrigerant can be mixed with oil in the compressor. Therefore, it is essential to minimize both the solubility and the quantity of oil.

The presence of oil alters the vapor-liquid equilibrium properties and, if it accumulates in the evaporator, can reduce heat transfer efficiency and increase pressure drops as explained by Youbi-Idrissi and Bonjour [83] and Radermacher et al.[84]. This accumulation also leads to a reduction in the coefficient of performance (COP) [85].

In mixtures of multiple refrigerants, oil may have varying affinities with the different refrigerants, causing a discrepancy between the circulating and the weighed composition [86]. The solubility ($X_{ref,L}$) indicates the mass fraction of the refrigerant in the liquid phase (liquid refrigerant plus oil) at equilibrium:

$$X_{ref,L} = \frac{M_{ref,l}}{M_{ref,l} + M_{oil}} \quad 1.69$$

This solubility can be regressed as a function of temperature and pressure using various methods based on experimental data. These methods can be purely empirical, where regression is used to calibrate polynomial coefficients (e.g., Mermond et al. [87]), or based on activity coefficients, such as the Wilson [88] model, the NRTL [89] model, and Heil's [90] model.

Generally, polyolester (POE) oil is less viscous than polyalkylene glycol (PAG) oil at low temperatures and performs better, as shown by Shi et al. [91]. However, PAG oil has lower solubility compared to POE oil [92], making it preferable for low-charge systems. This thesis investigates the solubility of PAG oil with propylene and dimethyl ether (DME). Additionally, the oil used in the refrigerator test bench is PZ-68S.

2 METHODS

2.1 Thermodynamic problem

This paragraph describes the thermodynamic resolution algorithm for the configuration present in paper two.

The steady-state model of the inverse cycles was developed in Python [93] Software, exploiting the thermodynamic properties package of REFPROP 10 [94]. The cooling and heating power calculations were based on steady-state mass and energy balances. The working fluid properties were taken from REFPROP [94]. The compressor is assumed to be an adiabatic device. Negligible pressure losses occur in the components of the cycle and its piping system. Neglecting the changes of kinetic and potential energies, the mass and energy balance equations in the steady-state condition can be applied to each component.

$$\sum \dot{m}_i = \sum \dot{m}_e \quad 2.1$$

$$\sum \dot{Q} + \sum \dot{m}_i h_i = \sum \dot{W} + \sum \dot{m}_e h_e \quad 2.2$$

The main cycle under consideration is the basic cycle featuring an Intermediate Heat Exchanger (IHx). This cycle comprises a compressor, a condenser/gas cooler, an internal heat exchanger, a valve, and an evaporator, as depicted in Figure 2.1. The system operates under constraints imposed by the ambient temperature, setting the minimum temperature of the hot heat exchanger (point 3), and by ensuring a minimum superheating at the compressor inlet (point 1) to prevent liquid ingestion. Sub-cooling from point 3 to point 4 is achieved within the internal heat exchanger (IHx), where heat is transferred from the hot liquid to the cold fluid exiting the evaporator at point 0. If the IHx does not interact thermally with the surroundings, it must adhere to the following conditions:

$$h_3 - h_4 = h_1 - h_0 \quad 2.3$$

It's important to note that point 0 can fall within the two-phase zone, with superheating ensured by the IHX. This introduces an additional degree of freedom to the system configuration, which can prove highly beneficial for optimizing the evaporator.

The efficiency of the IHX is defined as:

$$\eta = \frac{\dot{Q}}{\min(\dot{Q}_{\max,34}, \dot{Q}_{\max,01})} \quad 2.4$$

$$\dot{Q} = \dot{m}(h_3 - h_4) = \dot{m}(h_1 - h_0) \quad 2.5$$

The limit heat exchange on the two sides of the IHX is:

$$\dot{Q}_{\max,34} = \dot{m}(h_3 - h_{4(T_4=T_0)}) \quad 2.6$$

$$\dot{Q}_{\max,01} = \dot{m}(h_{1(T_1=T_3)} - h_0) \quad 2.7$$

The objective function for the optimization is the system COP:

$$COP = \frac{h_0 - h_5}{h_2 - h_1} \quad 2.8$$

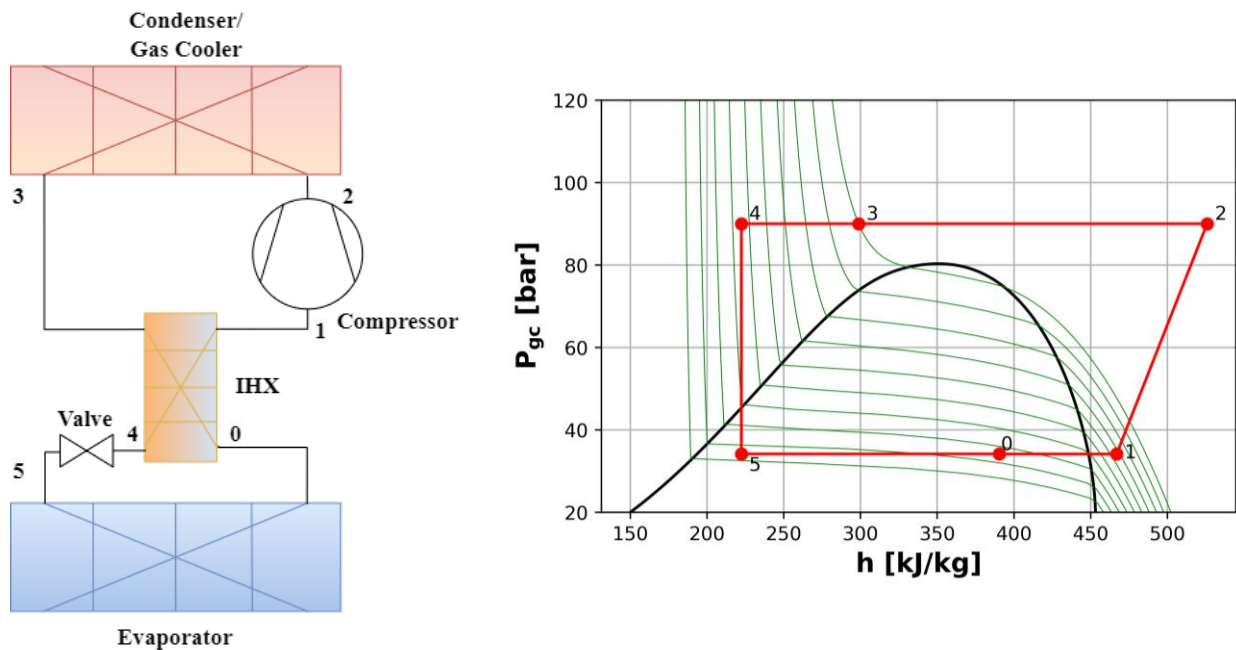


Figure 2.1: Schematic of Basic cycle with IHX.

To enhance the performance of the developed cycles, an optimization algorithm has been employed. The optimization algorithm was utilized to determine the optimal pressures at the condenser and the quality at the exit of the evaporator.

2.2 Optimization algorithm

The chosen optimization method employs a coordinate directions approach to identify local optima and a multistart technique to determine the global optimum. This method offers the advantage of optimizing functions without requiring knowledge of derivatives or the computation of numerical derivatives, which can introduce significant errors, especially when dealing with noisy functions, as is the case in our scenario.

The multistart technique can be illustrated with a simple flow diagram (Figure 2.2). Initially, the minimum and maximum values for each variable are defined and organized into minimum and maximum vectors. Subsequently, the number of local optima to be calculated (m) is determined, and the optimal solution is selected. It is important to note that for convex functions, each local minimum coincides with the global minimum, making (m) equal to one.

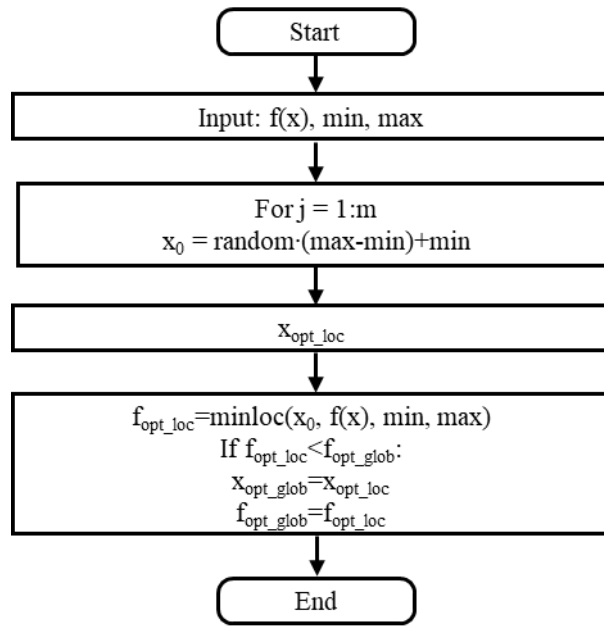


Figure 2.2: Description of multistart technique.

The Coordinate Descent method [95] is based on the principle that if a point is not a local minimum, then at least one of the coordinate directions will serve as a descent direction for a sufficiently small step. In the coordinate search method, N coordinate directions are considered, along with one additional direction that is linearly independent from the others.

With $n+1$ directions, the Coordinate Search method can be implemented. The direction matrix is structured as the identity matrix for the first n rows, and for the $n+1^{\text{st}}$ row, it is:

$$\left(-\frac{1}{\sqrt{n}}, -\frac{1}{\sqrt{n}}, \dots, -\frac{1}{\sqrt{n}}\right).$$

The algorithm performs an inexact line search to determine a step length that achieves sufficient reduction in the function (f):

$$f(x + \text{step} \cdot d) < f(x) - \rho(\text{step}) \quad 2.9$$

Where:

$$\rho(t) = Mt^{\frac{3}{2}} \quad 2.10$$

With M being a positive constant.

If this criterion is not satisfied, the step size is reduced until a specified tolerance level is reached.

In scenarios with box constraints, if any component of the vector $x_{\text{new}}[i]$ exceeds the limits of $\text{min}[i]$ or $\text{max}[i]$, then $x_{\text{new}}[i]$ is set to $\text{min}[i]$ or $\text{max}[i]$, respectively. Figure 2.3 illustrates the flowchart depicting the application of this technique.

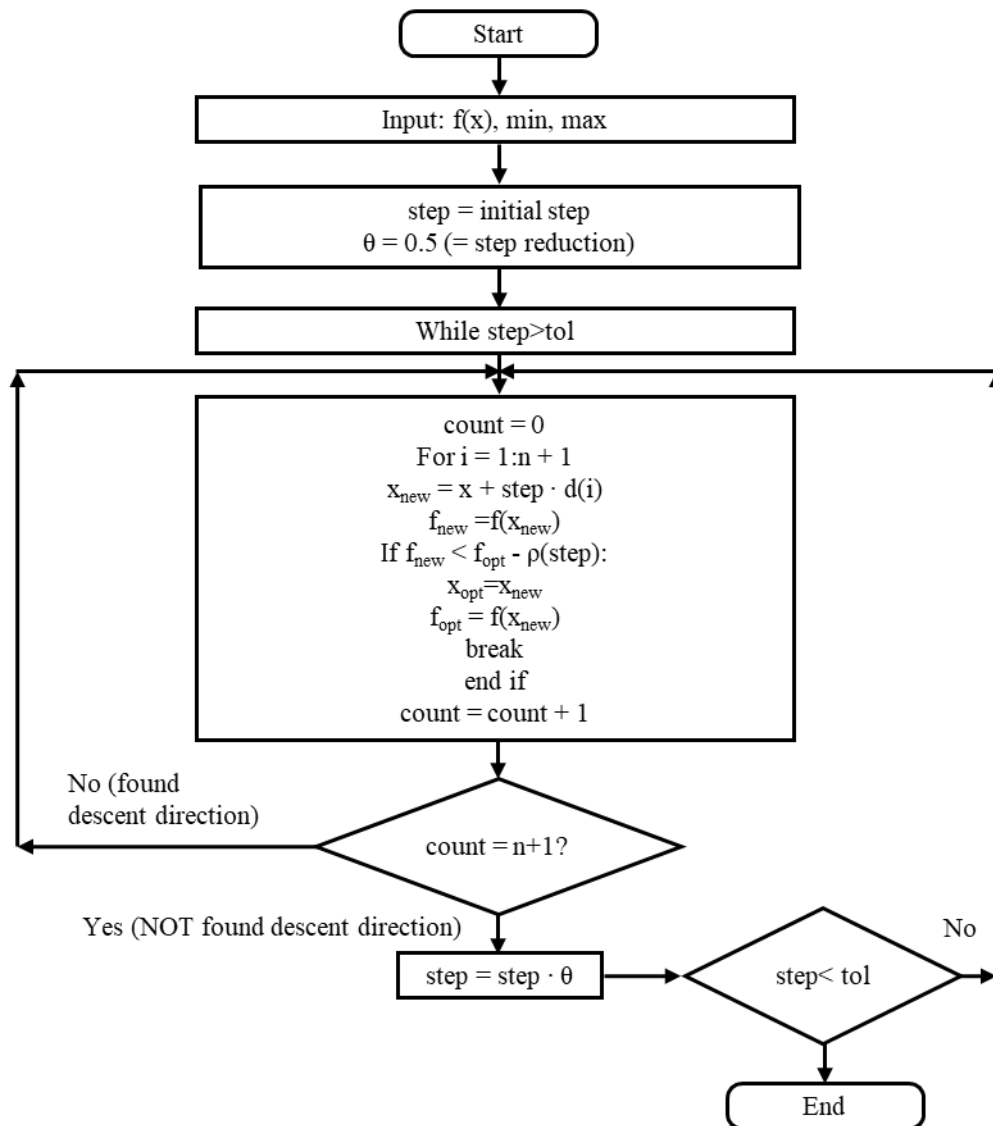


Figure 2.3: Description of Coordinate search approach.

Finally, mass and energy equations are applied to solve the base cycle with an internal heat exchanger (IHX). Table 2.1 summarizes the main input parameters for the code. The optimization algorithm determines the optimal pressure at the compressor outlet and the optimal quality at the evaporator outlet (which can also be superheated).

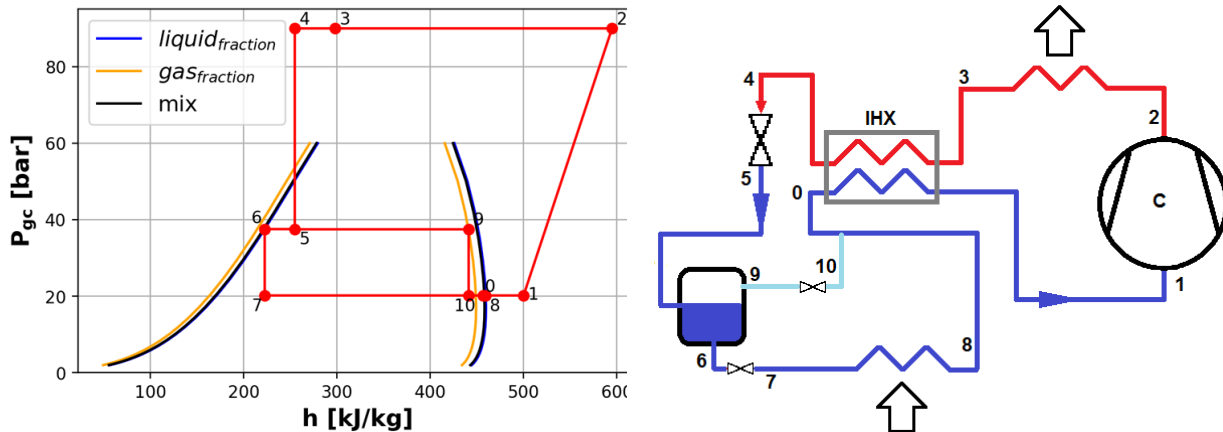
The described method is either unconstrained or subject to box constraints. If the optimal point does not ensure minimum superheating, the optimization is performed solely on the pressure at the compressor outlet. The quality at the evaporator outlet is then iteratively calculated using the Newton method to achieve the minimum required superheating. This approach ensures optimization at the boundary of the admissible domain.

Table 2.1: Main Input variables of the IHX cycle.

Parameters
Gas cooler temperature
Circulating mass fraction
Heat exchanger efficiency
Pinch point temperature
Cooled fluid inlet temperature
Cooled fluid temperature drop
Minimum superheat

2.3 Other configurations

Three additional refrigeration cycle configurations were modelled to evaluate the benefits and/or limitations of CO₂-based mixture solutions for enhancing CO₂ trans-critical systems. These configurations include (i) a separator, (ii) an ejector, and (iii) an ejector with a double evaporator. Figure 2.4 to Figure 2.6 illustrate the schematics of the evaluated cycles.

**Figure 2.4:** Refrigeration cycle with separator: P-h diagram and Scheme.

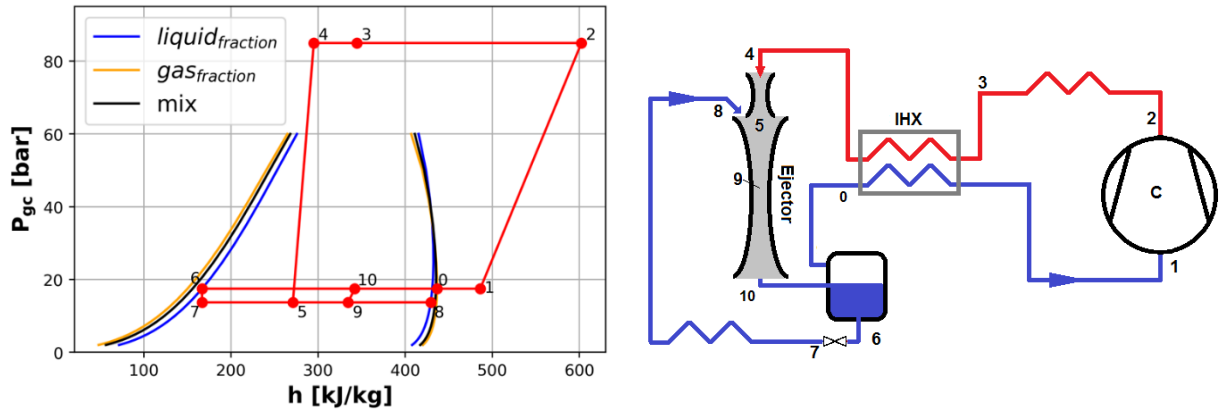


Figure 2.5: Refrigeration cycle with ejector: P-h diagram and Scheme.

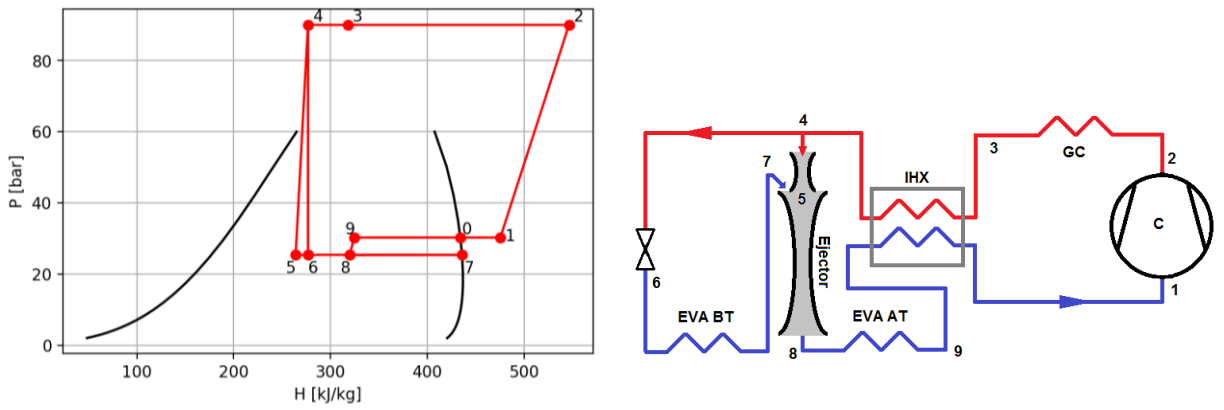


Figure 2.6: Refrigeration cycle with ejector and double evaporators: P-h diagram and Scheme.

The primary distinction in the equation set for these cycle configurations lies in the inclusion of the separator and the ejector. At the separator, two distinct compositions are present: the gas phase contains a higher concentration of the more volatile component, while the liquid phase is enriched with the less volatile component. This variation in composition affects the properties of the flow stream and, consequently, the heat exchange occurring at the evaporator.

To compute the compositions of the two streams exiting the separator, the definition of chemical potential must be applied. Under equilibrium conditions, the chemical potential of the liquid and vapor phases are equal. This implies that, while the liquid and vapor phases have differing compositions, it is possible to derive the mixture fraction that satisfies the chemical potential, assuming identical pressures and temperatures for both phases.

$$\mu_i = \left(\frac{\partial G_F}{\partial n_i} \right)_{P,T,n_j} \quad 2.11$$

$$\mu_i^{sol} = \mu_i^{vap} = \mu_i^{liq} \quad 2.12$$

The ejector is another addition to the cycle. This component enables the partial recovery of significant expansion losses experienced in high-pressure cycles through the expansion valve. The energy reclaimed from the expansion of the high-pressure stream can be utilized to compress a

low-pressure stream, such as the vapor coming from the evaporator to an intermediate pressure level. The ratio between the entrained flow rate and the motive flow rate is referred to as the entrainment ratio:

$$\omega = \frac{\dot{m}_{entrained}}{\dot{m}_{motive}} \quad 2.13$$

The algorithm used to evaluate the entrainment ratio is illustrated in Figure 2.7. The efficiencies are derived from a regression analysis of the experimental data presented in Giacomelli et al. [96].

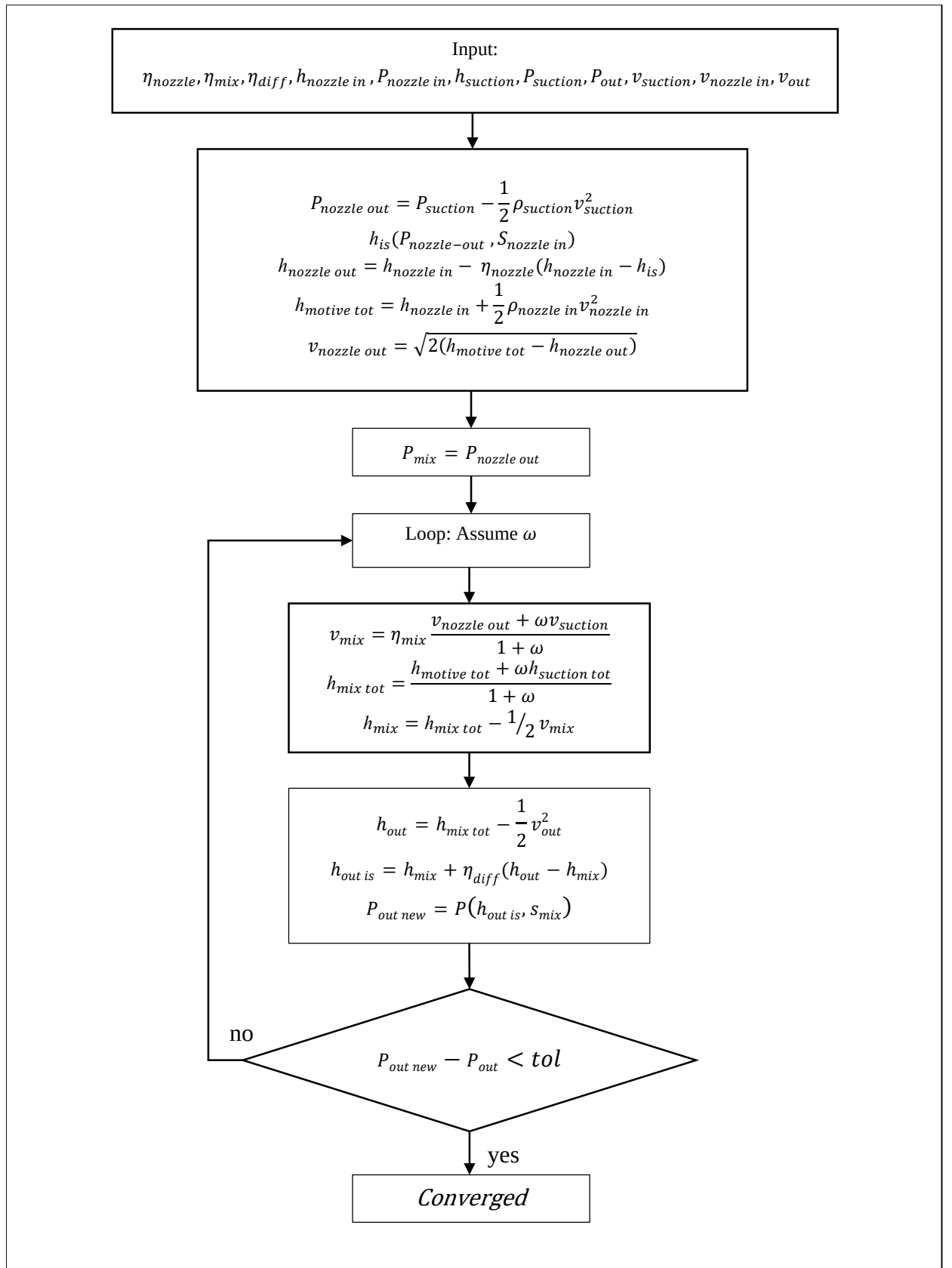


Figure 2.7: Algorithm for the ejector calculation.

2.4 PHE evaporator model

The heat exchanger used in the test bench is a plate heat exchanger (PHE) with chevron corrugations. The main geometrical parameters are depicted in Figure 2.8 and summarized in Table 2.2. The plate dimensions are defined by the width (W) and length (L), with L_{ht} representing the heat transfer length. The corrugation geometry is characterized by the chevron angle (β), the corrugation pitch (λ), the height (b), and the plate thickness (t).

The hydraulic diameter (d_h) is estimated using the formula provided by Martin [97]:

$$d_h = \frac{2b}{\phi} \quad 2.14$$

Where ϕ is the enlargement factor, representing the ratio between the effective and flat plate area (Martin, 1996):

$$\phi = \frac{1}{6} \cdot \left(1 + \sqrt{1 + \left(\frac{\pi b}{\lambda} \right)^2} + 4 \sqrt{1 + \frac{1}{2} \left(\frac{\pi b}{\lambda} \right)^2} \right) \quad 2.15$$

The total heat transfer area is calculated based on the number of channels on the refrigerant side (N_{ch}), assuming adiabatic end plates:

$$A_{ht} = 2 \cdot \phi \cdot (W \cdot L_{ht}) \cdot N_{ch,ref} \quad 2.16$$

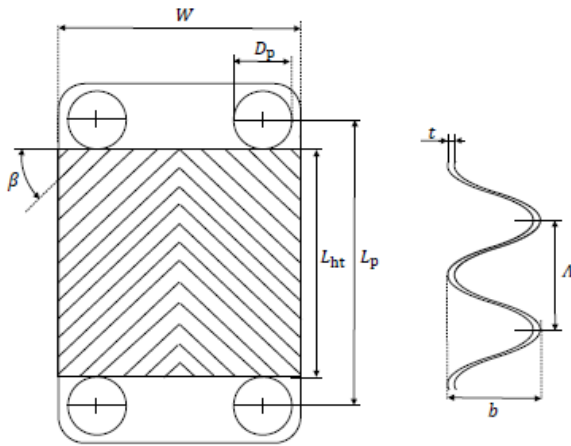


Table 2.2: Geometric parameters.

Parameter	Unit of measure
W	m
L_{ht}	m
t	m
β	°
b	m
λ	m
N_{ch}	-
d_h	m
A_{ht}	m ²

Figure 2.8: Schematic of PHE geometry [67].

The PHE is modelled [67] by discretizing the component in one dimension (1D) through the flow direction. The following assumptions are made:

- steady state conditions
- adiabatic end plates
- no longitudinal conduction
- no pressure drops in the manifolds

- vapor moves faster than liquid according to Smith [98]
- no maldistribution effects

The model is developed in Python [93] and is based on the Mancini's [67] model, it takes as input the geometry, thermodynamic inlet conditions, and mass flow rates. An initial guess for the temperature at the outlet of the secondary flow is provided to start the calculations. The iteration variable is the wall temperature, and the equations are solved until the wall temperature converges within a specified tolerance.

Beginning with the results from the previous iteration, the model solves the balance equations for the two fluids within each control volume (CV). From these results, the new wall temperature can be calculated, allowing the process to be repeated:

$$T_{wall} = \frac{U_{ref} \cdot T_{ref} + U_{sf} T_{sf}}{U_{ref} + U_{sf}} \quad 2.17$$

Where U_{ref} and U_{sf} represent the overall heat transfer coefficient for the refrigerant and secondary fluid side, respectively.

$$U = \frac{1}{\frac{1}{h} + \frac{t}{2} \cdot \frac{1}{k_w}} \quad 2.18$$

Where h is the heat transfer coefficient (HTC) and k_w is the wall conductivity. The HTC of the secondary fluid is calculated according to Martin [97], while for the refrigerant is determined using the correlation provided in section 1.4. The properties of the refrigerant and heat source are computed by REFPROP 10 [94] and CoolProp [99], respectively.

At each step, the enthalpy of the refrigerant is calculated as:

$$i_{ref,j+1} = i_{ref,j} + U_{ref,j} \cdot \frac{\delta A_{ht}}{\dot{m}_{ref}} \cdot (T_{wall,j} - T_{ref,j}); \quad 2.19$$

For the temperature of the secondary fluid:

$$T_{sf,j-1} = T_{sf,j} - U_{sf,j} \cdot \frac{\delta A_{ht}}{\dot{m}_{sf}} \cdot c_{p_{sf,j}} \cdot (T_{sf,j} - T_{wall,j}) \quad 2.20$$

The PHE is divided into $N=100$ control volumes. The algorithm starts solving the control volumes from the refrigerant inlet, i.e. the refrigerant flows in the same direction as the control volume index j . The secondary fluid side is separately computed, starting from j equal to N .

2.5 Refprop mixture model

REFPROP [94], distributed by NIST, is a software tool for calculating the physical properties of fluids. It is based on equations of state whose coefficients are adapted to extensive thermodynamic data from experimental studies and measurements [100,101].

REFPROP [94] includes mixture laws that vary depending on the mixtures considered. The coefficients for these mixture laws are determined based on available measurements in the

literature [100,101]. As noted in Bouteiller's thesis [26], no calorimetric data is considered for CO₂ and propane mixtures. However, REFPROP [94] calculates enthalpies for this mixture not too far from reality, with a maximum deviation of 2.99% [102]. On the other hand, for other binary mixtures, it is appropriate to be careful about the data used to determine the coefficients of the associated mixing rule.

In this study, the most relevant mixture is composed of carbon dioxide and dimethyl ether (DME) due to its qualities of high COP, low GWP, and low flammability, as shown in Paper 2.

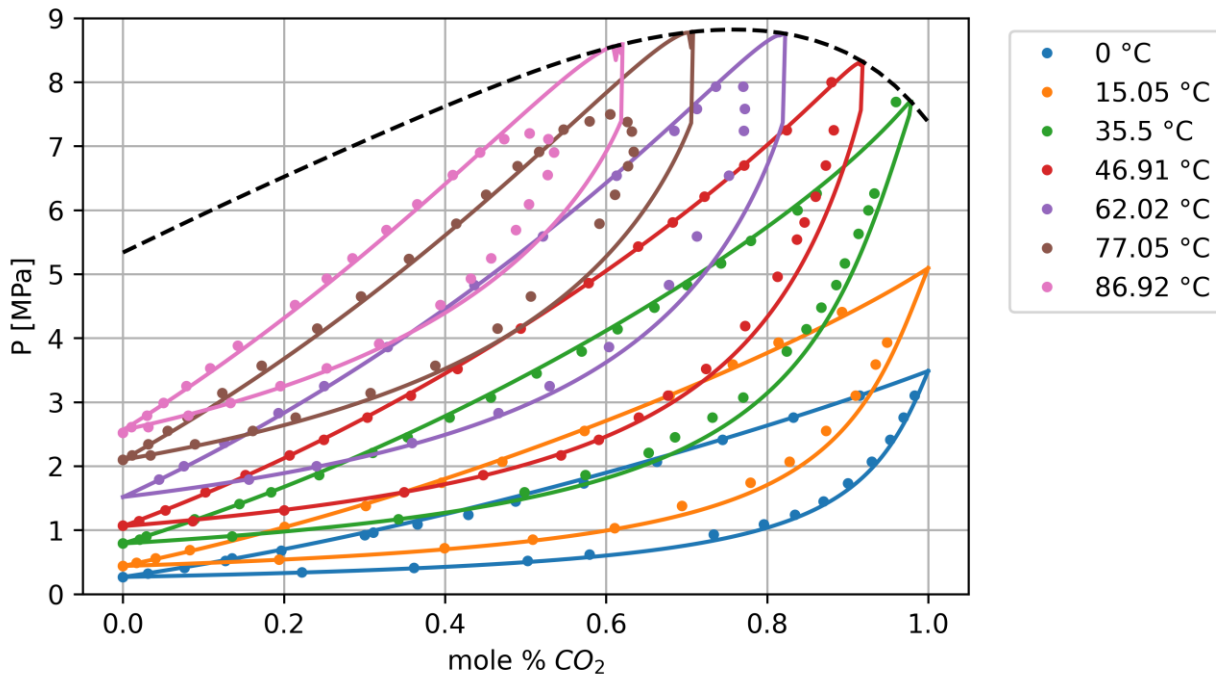


Figure 2.9: CO₂-DME VLE calculated with REFPROP[94] and measured by Tsang and Streett [103].

Figure 2.9 illustrates the differences between REFPROP[94] (continuous lines), and measured vapor liquid equilibrium points (dots) obtained by Tsang and Streett [103]. The error is acceptable for low quantities of DME and low pressures. However, as the mole fraction of CO₂ decreases and temperature increases, the error becomes unacceptable, particularly for the critical pressure and vapor equilibrium. This indicates that the model can be used for the low-pressure side of the thermodynamic cycle but may present problems when modelling the gas cooler/condenser, especially near the critical point.

The two experimental points to take into consideration are the critical points measured at 35.5°C (7.7 MPa) and at 46.91°C (8 MPa), with mole fraction of 0.96 and 0.88, respectively.

For these compositions, REFPROP [94] returns pressures of 7.93 MPa and 8.56 MPa, resulting in relative errors of 2.9% and 7.3%, respectively.

Bouteiller [26] compared the critical points of a CO₂-propane mixture calculated by REFPROP [94] and measured by Niesen and Rainwater [104], finding differences of up to five bars (7% error). This suggests that for DME mole fractions lower than 12%, REFPROP's vapor-liquid equilibrium reliability is comparable to that of the CO₂-propane mixture. Regarding enthalpy, it will be necessary to conduct heat balances on the exchangers to verify energy conservation.

3 EXPERIMENTAL BENCH

The experimental bench, situated at the Lafset laboratory of Le CNAM University in Paris, is engineered to operate under both subcritical and supercritical conditions for CO₂-based mixtures. Initially detailed in Bouteiller's [26] thesis, this bench has undergone modifications for the current research. In this study, it is employed to test mixtures of CO₂ and DME, simulating the boundary conditions typical of an air conditioning chiller, with the cold fluid experiencing a temperature lift from 12°C to 7°C and source temperatures of 30, 35, and 40°C.

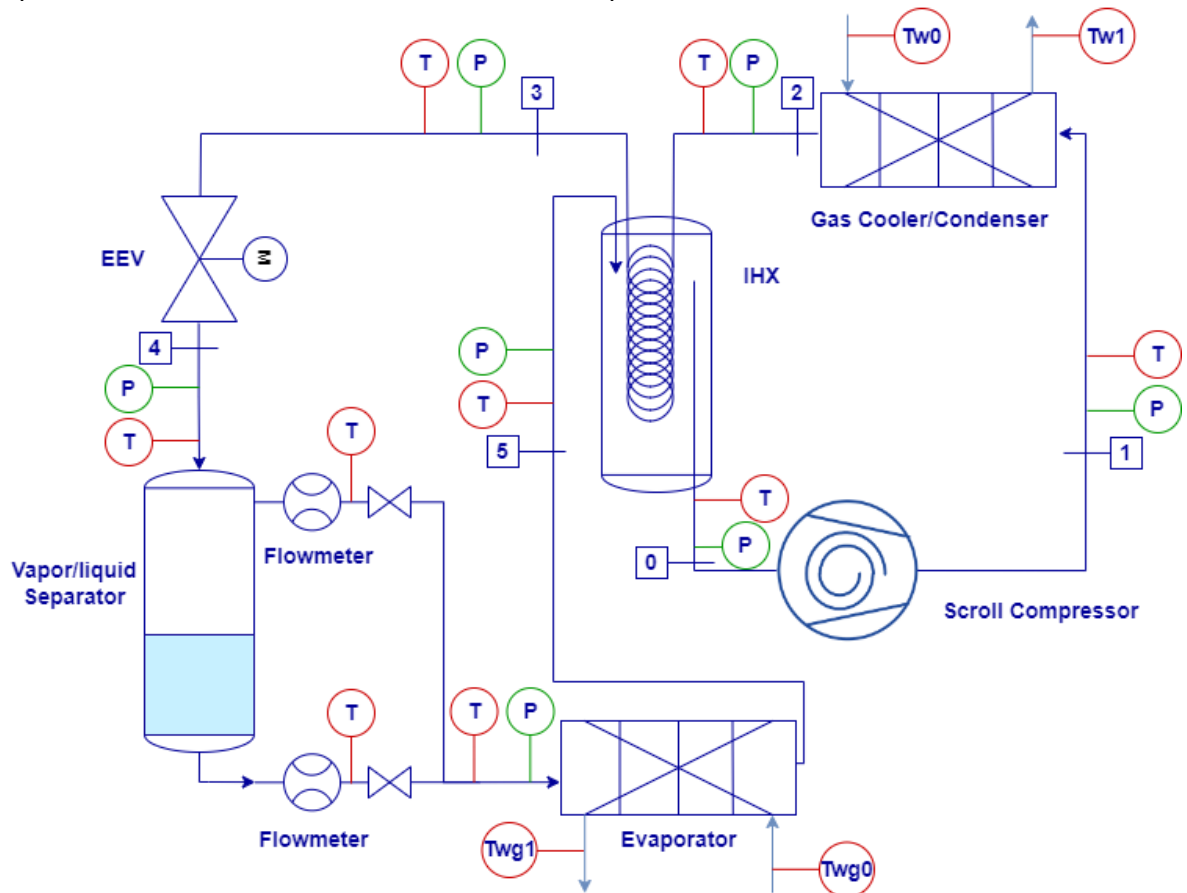


Figure 3.1: Experimental setup: P pressure transducers, T thermocouples.

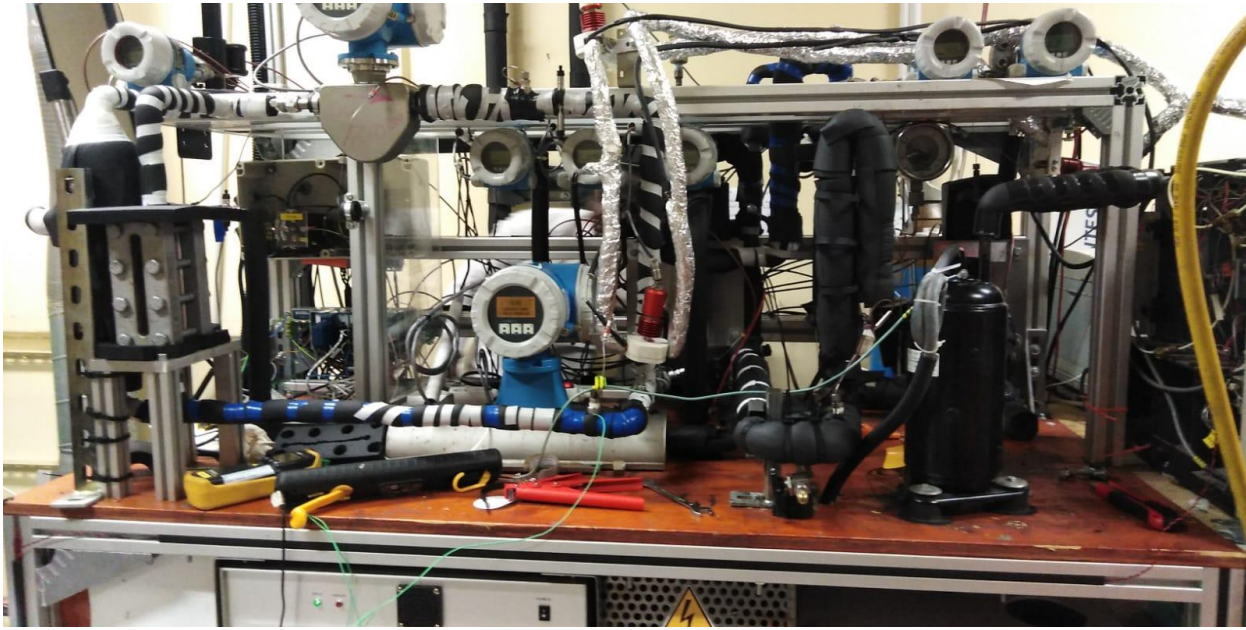


Figure 3.2: Experimental bench.

The bench is composed by five components:

- Compressor: Sanden brand. Specific CO₂ scroll type model, 4 cm³ displacement and variable speed controlled via a 0-5 V continuous signal, from 1200 to 5500 rpm.
- Gas cooler: SWEP brand, high pressure brazed plate exchanger (B9) for a maximum operating pressure of 140 bar at 110°C. 28 plates (approximately 0.75 m²).
- Internal heat exchanger: Manufactured by the Carly company based on the specifications provided in Bouteiller (2017) [26] thesis.
- Electronic expansion valve: UKV-J14D from Saginomiya. 480 steps. Motor controlled via an Arduino Uno card and Motor shield.
- Evaporator: SWEP brand, high pressure brazed plate exchanger (B17), geometry described in appendix 2.

The experimental bench is equipped with pressure and temperature sensors positioned as shown in Figure 3.1. Additionally, two Coriolis mass meters are installed after the separator, one on the vapor side and one on the liquid side. The separator serves both as an accumulator for transients and as a device for separating the liquid and gaseous phases to determine the quality at the onset of evaporation. The separated liquid and gaseous flows are then recombined to avoid changes in composition.

The boundary conditions are maintained using a hot loop with water and a cold loop with a water-glycol mixture (32% glycol). The hot circuit's delivery temperature is controlled by a thermostatic bath (LAUDA Variocool VC2000) with a cooling capacity of 2 kW at an ambient temperature of 20°C. The mass flow rate in the hot loop can be manually adjusted using a valve. For the cold loop, temperature regulation is achieved via LabVIEW, utilizing an electrical resistance of up to 3 kW, with manual adjustment of the mass flow rate through a valve.

Furthermore, heat exchange between the cold and hot circuits is possible to reduce the power consumption of the thermostatic bath. If additional cooling is required, the thermostatic bath can be cooled with tap water.

3.1 Measurement acquisition

Liquid and vapor mass flow rates are measured using two Coriolis mass flow meters, which have an accuracy of 0.15% within the range of 4 to 400 kg/h. The mass flow rates of water and water-glycol mixtures are measured with magnetic flow meters, with an accuracy of 0.5% within the range of 0.5 to 30 l/min. Power consumption at the compressor is measured with a wattmeter, accurate to 0.5% within the power range of 500 to 1500 W, while the power consumption of the pumps is not measured and is neglected.

The system includes six pressure transducers, three for high pressure and three for low pressure, each with an accuracy of 0.03% within the range of 0 to 96-78.4 bar. Temperature measurement requires a more detailed discussion. T-type class 1 thermocouples are used, which have an error margin of 0.5 K. However, this error is too high for accurately determining the COP. Therefore, the thermocouples are calibrated using a PT 100 reference probe connected to an F17 precision resistance bridge (ASL). This calibration setup was conducted based on recommendations from the Joint Metrology Laboratory (LCM LNE) of CNAM in St Denis, with a comprehensive explanation provided in Bouteiller's [26] thesis.

Temperature measurements are acquired using NI 9214 thermocouple modules and NI TB-9214 isothermal connection terminals. Calibration is performed on the entire acquisition chain. Initially, the thermocouples were placed on the experimental loop to test its tightness, then dismantled and calibrated in their final form. They were calibrated and then immersed in a copper crucible, which was itself immersed in a thermostatically controlled bath (LAUDA RP 855 C). Table 3.1 presents the errors throughout the acquisition chain.

Table 3.1: Chain elements error [26].

Chain elements	Parameters	Values
Calibration range	Temperature range	-30 °C to +130 °C (i.e. 243 K to 403 K)
NI 9214 acquisition center	Sensibility	0.01 K
	Precision of cold junction measurement	0.25 K
Thermocouples (TC Direct) Reference 12-T-150-118-1,5-2i-3P	Thermocouple type	T, jacketed
	Thermocouple class	1 (i.e. $\pm 0,5$ K on the range -40 +125 °C, or $\pm 0.4\%$ of T measured on the range 125 to 350 °C)
Bain LAUDA RP 855 C	Stability en temperature	± 0.01 °C
Resistor bridge F17 (ASL)	Resolution	10-6 on the display; 10-8 digital output
	Internal precision resistor	99.99277 Ω
	Sensibility (on PT100) at 0°C	0.00025 K
PT100 standard probe: PT-102-14H calibrated (Lake Shore)	PT 100 probe repeatability	PT 100 probe repeatability ± 0.005 K at 77 K (after repeated thermal shocks from 305 to 77 K, conducted by the supplier)
	Precision from 90 to 280 K	RMS error = 0.39 mK Max error = 0.86 mK
	Precision from 280 to 500 K	RMS error = 9.30 mK Max error = 30.6 mK

Through this calibration process, the error of the thermocouple is determined by summing the maximum error of the PT100, the repeatability of the calibration temperature probe, and the sensitivity of the data acquisition unit. Consequently, the error in temperature measurement is reduced from 0.5 K to 0.05 K. Table 3.2 details the calculation of the total error in temperature measurement.

Table 3.2: Final error on temperature.

Uncertainties	Value
Maximum error of calibration Temperature probe [K]	0.0306
Repeatability of the calibration Temperature probe [K]	0.005
Sensitivity of the data acquisition unit [K]	0.01
Total uncertainty (sum) in temperature for each thermocouple [K]	0.0456

Table 3.3 summarizes the accuracy of all measurements.

Table 3.3: Measuring instrument accuracy.

Sensors	Type / Supplier	Accuracy
Pressure transducers	Cerabar M /	0.04% on the range 0.96 – 137.7 bar.
	Endress Hauser	0.03% on the range 0.96 – 78.4 bar.
Refrigerant mass flow meters	Promag 83 /	0.15% in the range 4 – 400 kg/h (with 3/8" tube).
	Endress Hauser	0.1% in the range 4 – 90 kg/h (with 1/8" tube).
Magnetic flow meters	Promag 10H08 / Endress Hauser	0.5% on the range 0.5 – 30 l/min.
Wattmeter	μTAC300 / Sfere	0.5% on the power range 500 – 1500 W.
Thermocouples	Class 1 T type/TC	0.05°C on the range -10°C – +40°C

3.2 Circulating composition

The system is charged at first by introducing the fluid with the lowest pressure at room temperature, which in this case is DME, followed by the fluid with the highest pressure, CO₂. The mixing process is monitored using two scales: one with a 1 g error for DME and another with a 5 g error for CO₂. Tests were conducted with a total mass of 800 g. Consequently, when 5% of DME is added, the actual percentage may vary between 4.85% and 5.15%, and when 10% of DME is added, the actual percentage may vary between 9.82% and 10.18%.

However, the weighted and circulating compositions can differ due to three main factors:

- The liquid mixture stored in the separators is richer in the less volatile component (DME), resulting in vapour phase richer in CO₂.
- The oil may mix differently with the two components, preferentially absorbing one over the other.
- The vapor phase moves faster than the liquid phase in heat exchangers, potentially enriching the mixture in the more volatile compound.

These differences were also observed by Bouteiller [26] in CO₂ and propane mixtures, where gas chromatography revealed that the circulating composition was richer in CO₂ compared to the weighted composition. In our case, the differences are even more pronounced, as supported by Paper 4, which indicates that DME is more soluble in oil than propane. These issues are also reported by Youby Idrissi [86].

The circulating composition is calculated using the method by Johansson et al. [105], which involves postulating an isenthalpic transformation across the throttle valve. By knowing the pressure and temperature before and after the valve, the composition is iteratively calculated until the enthalpy upstream and downstream of the valve matches within a required tolerance.

To validate this method, Appendix 1 includes the latest work conducted at the Lafset laboratory, where three additional Coriolis mass flow meters and a new gas chromatograph (Shimadzu GC-2014) were integrated into the experimental setup.



Figure 3.3: Experimental bench with gas chromatograph.



Figure 3.4: Micro-sampler Rolsi®.

The three Coriolis meters were positioned as follows: one at the compressor inlet (point 0 in Figure 3.5), another at the compressor outlet (point 1 in Figure 3.5), and the last one before the throttle valve (point 3 in Figure 3.5). This arrangement ensures additional verification of the accuracy of the measured flow rates. The use of Coriolis meters before and after the compressor allows for the detection of any liquid at the compressor inlet. Additionally, it enables the measurement of densities, which is useful when dealing with mixtures. Gas chromatography is enabled by two Rolsi® electronic valves located in the system, one at the compressor outlet and the other before the throttle valve.

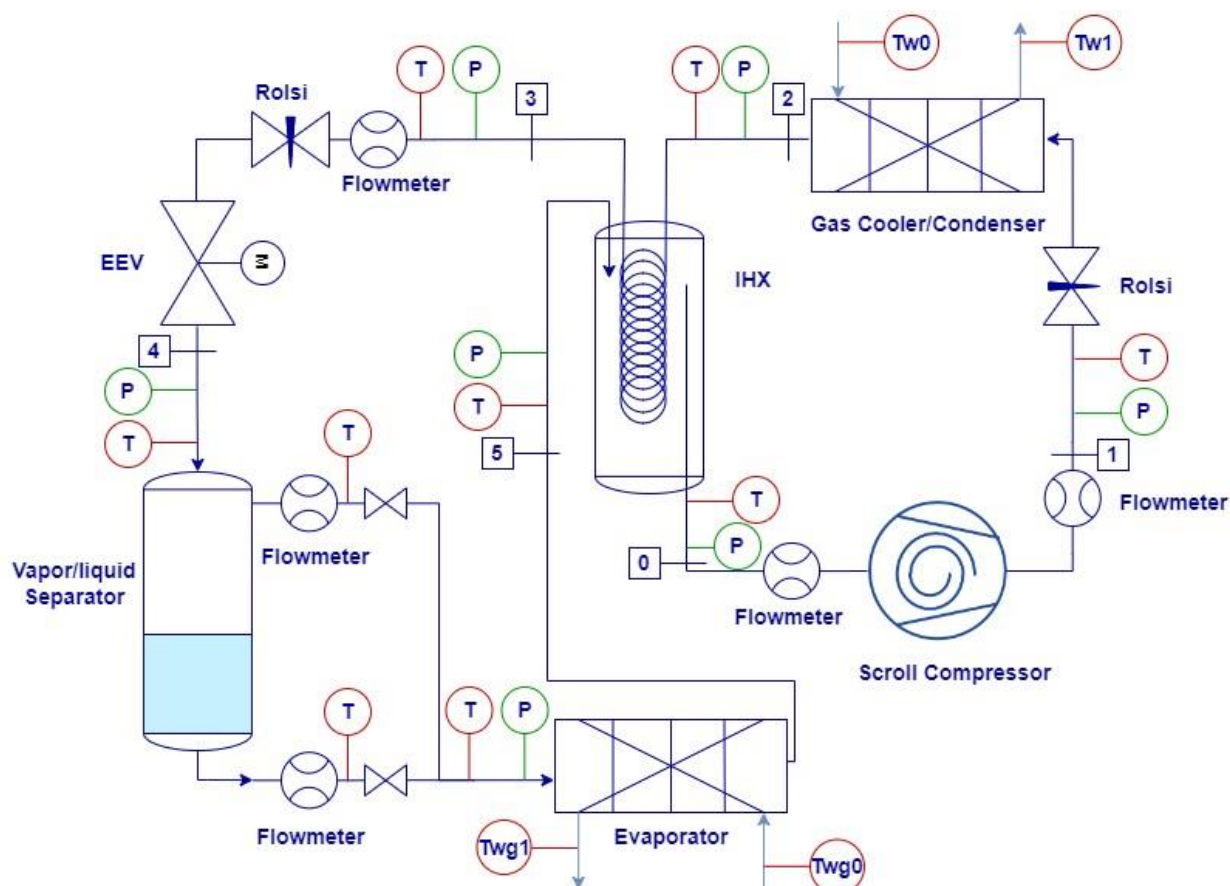


Figure 3.5: Experimental setup with micro-sampler Rolsi® and five Coriolis.

Gas chromatography is a powerful technique used to separate and analyse compounds in a mixture. This process begins with the introduction of a sample of refrigerant fluid into the system through a Rolsi® electro valve during the apparatus's operation. The sample is then carried by an inert gas, helium, which acts as the mobile phase.

The sample passes through a porous medium within a long, coiled column, where the components are separated based on their affinity with the stationary phase. Components with a higher affinity for the stationary phase move more slowly, while those with a lower affinity move more quickly. In this case, CO₂, being less retained by the stationary phase, passes through the column faster than DME.

To ensure that the sample remains in the vapor phase, both the valves and the transfer line are heated up to the separation column. The temperature of the column can be adjusted to optimize the separation and prevent overlapping of the components' passage.

After passing through the column, the separated components reach a detector. In this setup, a Thermal Conductivity Detector (TCD) is used. The TCD consists of a Wheatstone bridge with two channels: one for the sample flow and one for the reference flow (helium). As the separated components exit the column and pass through the sample channel, they cause changes in thermal conductivity compared to the reference channel. These changes unbalance the Wheatstone bridge, resulting in a voltage peak that is recorded.

The TCD detects these voltage peaks, which correspond to the presence of different components in the sample. The time it takes for each component to pass through the column

(retention time) and the size of the peaks provide qualitative and quantitative information about the sample's composition.

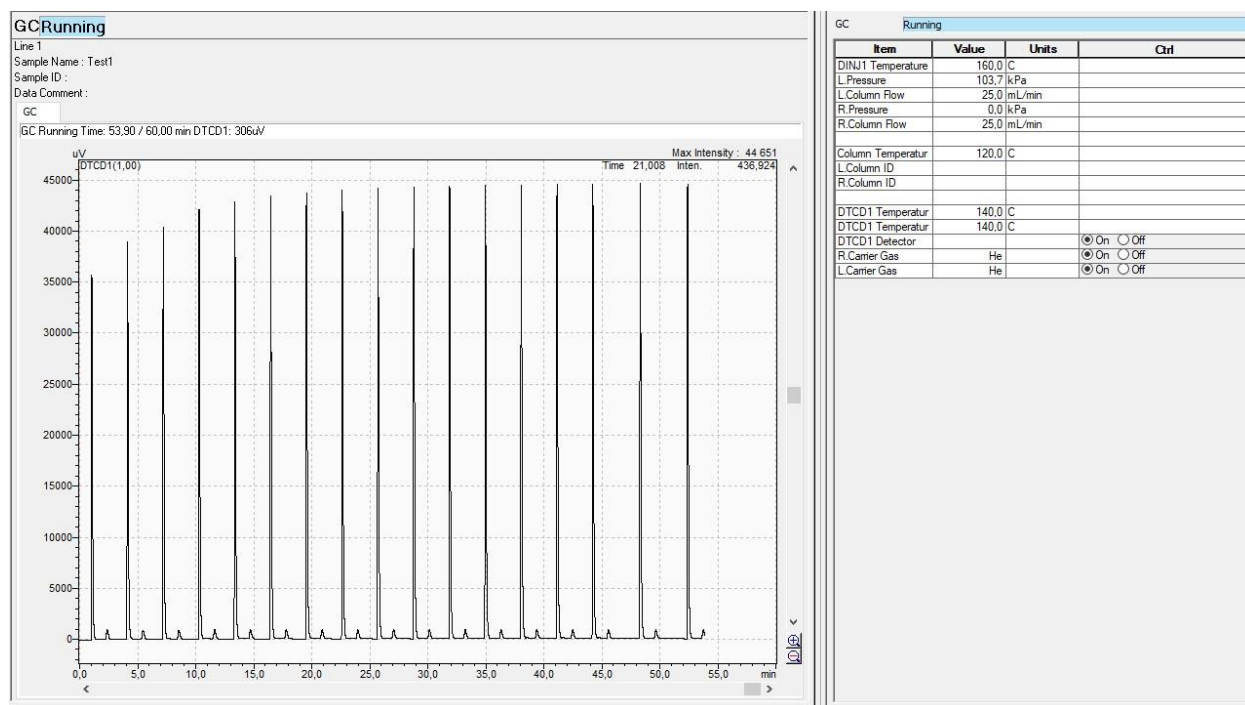


Figure 3.6: Chromatogram of CO₂ and DME.

Figure 3.6 illustrates a series of measurements under fixed thermodynamic conditions. The graph shows a succession of two peaks: the first peak corresponds to CO₂, while the second peak corresponds to DME, with measurements repeated at regular intervals. The operating conditions are tabulated on the right side: an injector temperature of 160°C, a separation column temperature of 120°C, a detector temperature of 140°C, and a helium flow rate of 25 ml/min.

The area under each peak over time is directly proportional to the molar quantity of the component. Therefore, calibration can be performed by varying the volume of gas injected to establish a regression line that correlates the peak area to the number of moles of gas for both components. Graduated syringes were used for this calibration. Both CO₂ and DME were placed in a cylinder at room pressure and a temperature of 25°C the day before. Using the volume of the syringe, the number of moles can be calculated using the ideal gas law. Since the mole fraction is of interest, the ratio between the volumes is equal to the ratio of the number of moles at the same pressure and temperature.

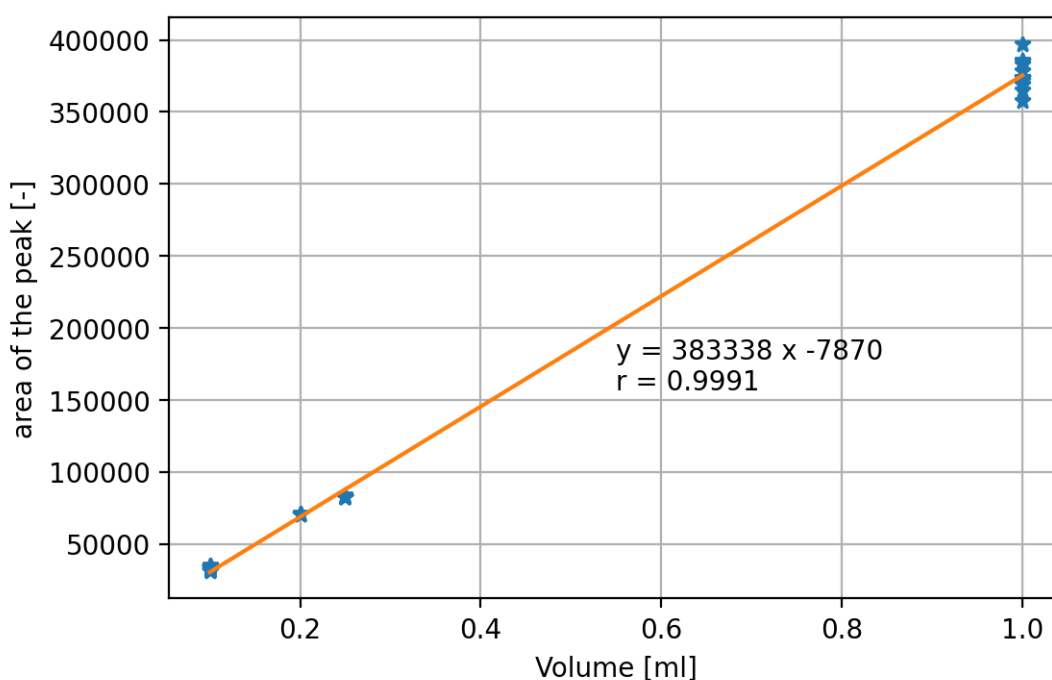


Figure 3.7: CO₂ calibration.

As illustrated in Figure 3.7, the regression line does not intersect the origin, indicating a discrepancy between the injected and measured volumes, possibly due to the volume in the syringe needle. This repeated error results in a deviation of the curve, which must be considered as an offset error. If the intercept is set to zero, the slope can range from a maximum of 397144 to a minimum of 357551.

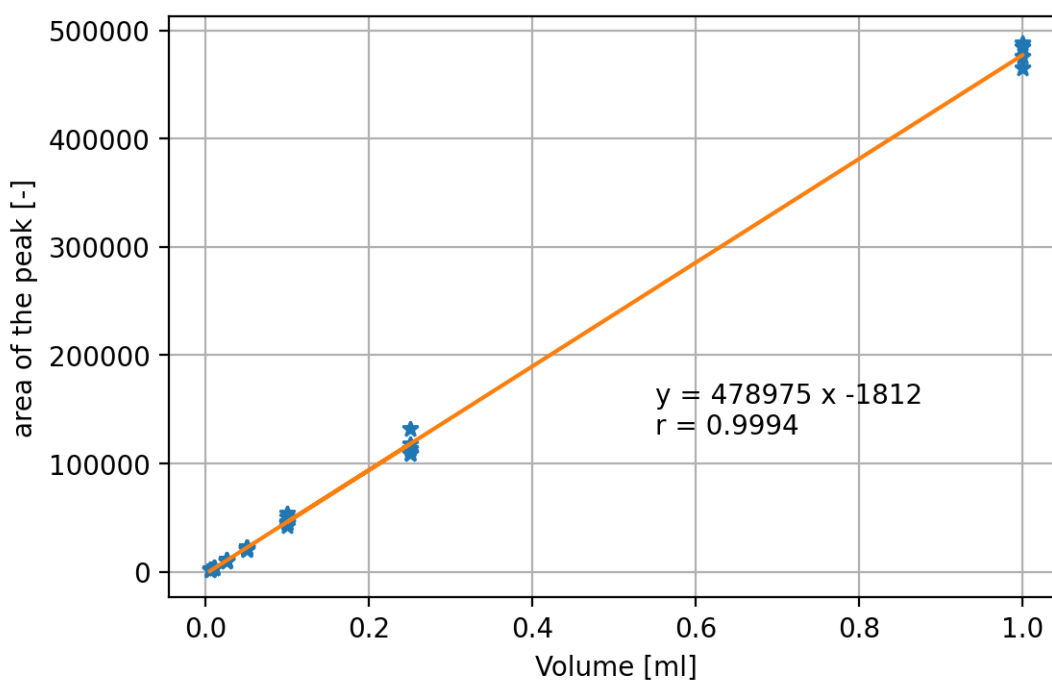


Figure 3.8: DME calibration.

Figure 3.8 displays the regression curve for DME. If the intercept is set to zero, the slope can range from a maximum of 515924 to a minimum of 465527.

The mole fraction of the mixture is calculated as follows:

$$mol\ fraction = \frac{\frac{A_{DME}}{C_{DME}}}{\frac{A_{DME}}{C_{DME}} + \frac{A_{CO_2}}{C_{CO_2}}} \quad 3.1$$

here C_{DME} can vary between 515924 and 465527, while C_{CO_2} can vary between 397144 and 357551. This means that for a mole fraction of 5%, the value can range from a maximum of 5.3% to a minimum of 4.4%. Similarly, for a mole fraction of 3%, the value can vary between 2.6% and 3.2%.

4 RESULTS

This section presents the key findings of the research, encapsulated in five articles. Four of these articles have been published in the International Journal of Refrigeration, and one has been presented as a conference paper. The order of presentation follows the structure outlined in

Figure 4.1, rather than a chronological sequence. This approach ensures a coherent narrative that aligns with the research objectives and methodologies.

At the end of this section, a study on the circulating composition has been included to validate the findings. Additionally, a second appendix on heat exchange in the evaporator has been added.

List of papers:

- Vaccaro, G., Milazzo, A., & Talluri, L. (2023). Thermodynamic assessment of trans-critical refrigeration systems utilizing CO₂-based mixtures. *International Journal of Refrigeration*, 147, 61-70.
- Vaccaro, G., Milazzo, A., & Talluri, L. (2024). A proposal for a non-flammable, fluorine-free, CO₂-based mixture as a low TEWI refrigerant. *International Journal of Refrigeration*, 158, 157-163.
- Vaccaro, G., Andreini, N., Caramaschi, M., Talluri, L., Elmegaard, B., & Milazzo, A. (2023). Numerical assessment of CO₂-based mixtures for refrigeration systems: focus on the evaporation process. In 26th International Congress of Refrigeration. International Institute of Refrigeration.
- Caramaschi, M., Notturmo, J., Vaccaro, G., Meesenburg, W., Jensen, J., Elmegaard, B., ... & Tobaly, P. (2024). Propylene and DME solubility in PAG oil: Experimental investigations and simplified modeling. *International Journal of Refrigeration*.
- Vaccaro, G., Milazzo, A., Tobaly, P., Diaby, A. T., & Talluri, L. (2024). Experimental results on a chiller using a CO₂-DME mixture. *International Journal of Refrigeration*.

In the first article, the effectiveness of the mixtures compared to pure CO₂ is analysed for different configurations and fluids, leading to performance improvements without altering the use of the system components. The second paper continues this analysis, but with a focus on using the internal heat exchanger (IHX) differently from the classic use with pure fluids. Flammability and use of natural mixtures are dealt with, yielding even more promising results.

However, these results may overestimate the system's real efficiency, as the heat exchange on the evaporator side for CO₂ and the mixtures is treated similarly, without accounting for the decrease in average temperature difference due to glide and the reduction in heat transfer coefficient (HTC). Therefore, the third paper investigates the effects of CO₂ and propane mixtures on boiling heat transfer.

The fourth paper examines the different oil absorption rates for various fluids, showing that propylene and DME have different absorption characteristics, which affect the system's actual charge. This effect can lead to composition variations, as demonstrated in the fifth paper.

The fifth paper builds on the results from the second paper, conducting an experimental campaign to verify the theoretical findings. Papers three and four help understand the discrepancies between model predictions and experimental results.

In Appendix 1, an experimental evaluation of the circulating composition has been added to this thesis, addressing the hypotheses left open in the fifth paper.

Appendix 2 presents the heat exchange measurements conducted on the PHE evaporator of the test bench described in paper 5. This appendix serves to bridge the findings of paper 2, which focuses on studying the heat transfer coefficient for mixtures, with those of paper 5. Various correlations are evaluated in this appendix to identify the most accurate one.

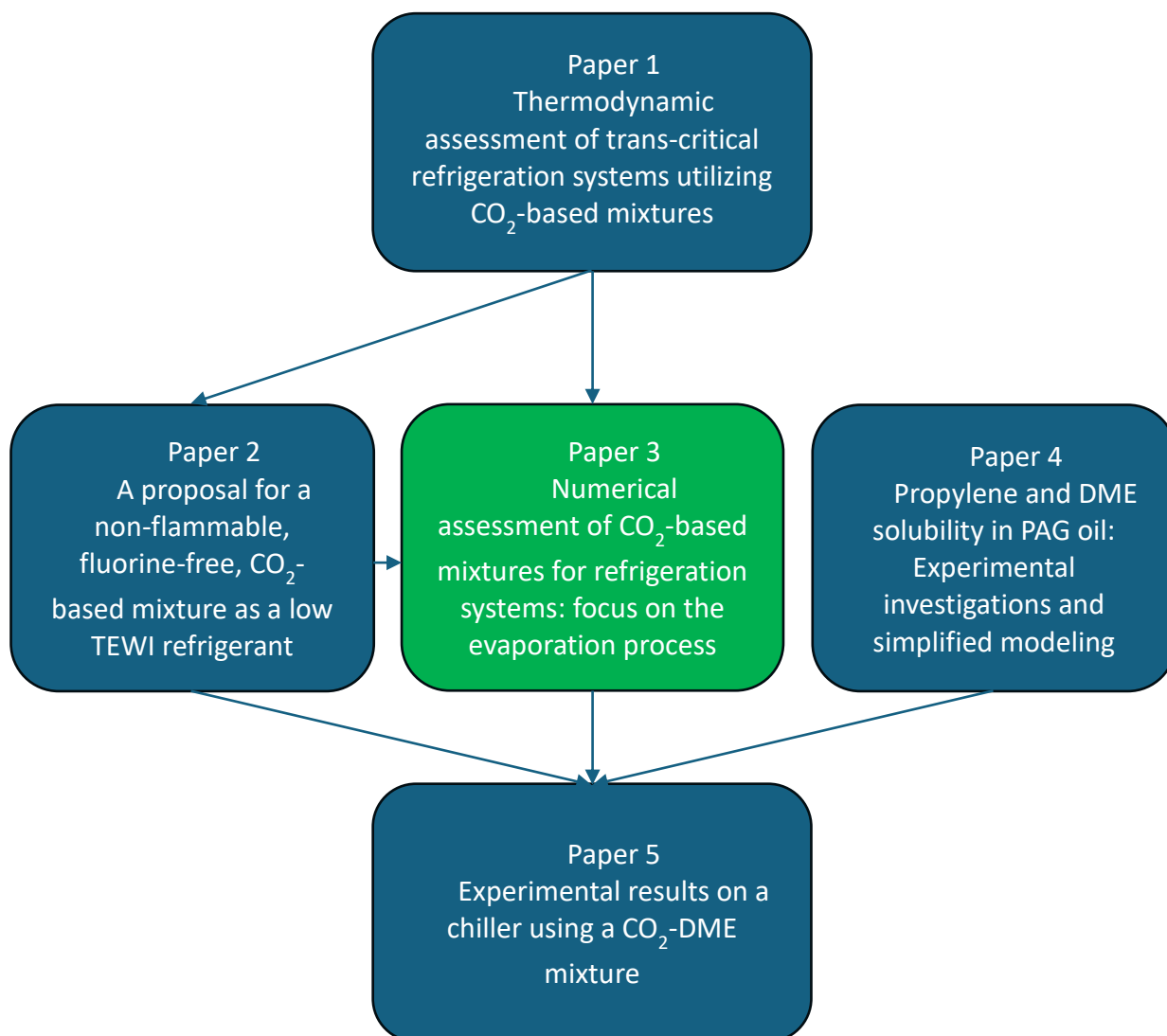
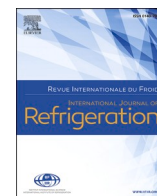


Figure 4.1: Path of the publications.

4.1 Paper 1: Thermodynamic assessment of trans-critical refrigeration systems utilizing CO₂-based mixtures

As highlighted in the introduction, numerous studies in the literature focus on CO₂-based mixtures. The objective of this research is to analyse various fluids and configurations, in order to provide a comprehensive theoretical review of the different possibilities. This analysis demonstrates that certain mixtures perform better than others and that the configuration can significantly influence the advantages of using these mixtures.

The Ph.D. candidate is the first author of this work and was mainly involved in modeling and calculation under supervision and writing of Professor Adriano Milazzo. Dr. Lorenzo Talluri provided supervision and assistance with conceptualization.



Thermodynamic assessment of trans-critical refrigeration systems utilizing CO₂-based mixtures

Évaluation thermodynamique des systèmes frigorigènes transcritiques utilisant des mélanges à base de CO₂

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ABSTRACT

Since the last decade of the 20th century, there has been increasing attention to the use of CO₂ as a working fluid in transcritical refrigeration and cooling cycles. Transcritical cycles suffer from a heavy expansion loss, requiring specific means for its mitigation. Moreover, most applications for cooling or refrigeration are cooling a stream that is not changing phase, therefore has a finite heat capacity and does not well match with the evaporation curve of any pure fluid. In this work, to overcome these limitations (low COP and poor matching of heat exchanges curves) the potential of using a second component, mixed with CO₂, has been assessed. For this purpose, several fluids have been investigated, from synthetic refrigerants, such as R1233zd(E) or R1234yf, to hydrocarbons, such as n-butane, or n-pentane and alcohols, like dimethyl ether. To investigate the effects of the addition of the second element in the CO₂ transcritical cycles, several configurations have been investigated, from the base refrigeration cycle to the double evaporator ejector cycle. All examined mixtures show a COP improvement with respect to pure CO₂. However, the mixture with R1234yf has the flattest evaporation curve and hence, in the case of a constant specific heat of the fluid to be cooled, gives the best result. The quantity of R1234yf that must be added to the mixture never exceeds 15%.

1. Introduction

Refrigerant mixtures have been studied since the early days of refrigeration and offer some advantages in specific applications. One of the most important characteristics is the “temperature glide”, i.e. the change of the boiling point with the mixture composition. This produces a variable saturation temperature for a given pressure and a different composition for the vapour and liquid phases.

A temperature glide is advantageous when the heat capacity of the load served by the refrigeration cycle is finite (Lorenz cycle). For example, Llopis et al. (2021) proposed to use zeotropic refrigerant mixtures in a dedicated mechanical subcooling system for a CO₂ cycle. The glide, for near-ideal mixtures, increases with the difference in the boiling point between the mixture components (Mulroy et al., 1994).

In Europe, a further stimulus for the formulation of new mixtures is represented by the F-gas regulation 517/2014. As an example, the

review paper of Heredia-Aricapa et al. (2020) presents a comparison between mixtures proposed as replacements for high-GWP HFCs. Some of these mixtures fulfil the limit GWP<150 imposed in many applications. In our view, a fundamental component of a promising mixture should be CO₂. This fluid may reduce the mixture GWP, cost and flammability while increasing its volumetric heat capacity. The addition of small quantities of other fluids may improve the mixture’s thermodynamic features. This approach is proposed in the present work.

1.1. CO₂-based mixtures

CO₂ low critical temperature implies that in most cases the working cycle comes out to be trans-critical. Such a cycle may be advantageous or not, depending on the application. If heat is to be reclaimed from the refrigeration cycle (e.g. heat pumps or combined cooling and heating), a gas cooler may be better suited than a condenser, due to its continuous temperature variation. On the other hand, the expansion loss is very

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Nomenclature

μ	Chemical Potential [$\text{kJ}\cdot\text{kmol}^{-1}$]
COP	Coefficient of performance [-]
EVA	evaporator
G	Gibbs free energy [kJ]
GC	Gas cooler
h	Enthalpy [$\text{kJ}\cdot\text{kg}^{-1}$]
IHX	Internal heat exchanger
n	Number of moles [-]
P	Pressure [bar]
Q	Heat [kW]
T	Temperature [$^{\circ}\text{C}$]
v	Velocity [$\text{m}\cdot\text{s}^{-1}$]
W	Work [kW]
x	Mass fraction [%]
η	Efficiency [-]
ω	Entrainment ratio [-]

high, impairing the cycle COP. Expansion loss reduction may be done by several methods, i.e. using an internal heat exchanger, an expander, a staged expansion or an ejector (Barta et al., 2021).

Another relevant feature of CO_2 is the high pressure throughout the working cycle, yielding high values of fluid density both in the liquid and in the vapour phase. This gives a volumetric cooling capacity of 3 to 10 times higher when compared to HFC or HC refrigerants (Kim et al., 2004).

The introduction of one or more fluids in a mixture containing CO_2 may aim at different objectives. For example, Kim et al. (2008) used propane in percentages from 15 to 40% within an air conditioning system. Their experimental findings show that by increasing the percentage of propane, the maximum cycle pressure and the cooling capacity decrease monotonically. The COP increases, showing a maximum for 25% of propane in the mixture (+12.8% with respect to pure CO_2) due to the good match between the chilled water and the gliding evaporation temperature. Sarkar and Bhattacharyya (2009) did a thermodynamic simulation of a heat pump using blends of CO_2 with butane and isobutene. They show that the use of blends reduces the system pressure and the throttling loss, though it reduces the volumetric heat capacity. Zhang et al. (2013) published a thermodynamic simulation and some experimental results for a transcritical cycle working with R744/R290 mixture. They found the relation between the main cycle parameters and the optimum gas cooler pressure.

Bouteiller et al. (2017) applied CO_2 mixtures with propane and R1234yf to a heat pump, aiming to raise the critical temperature of the mixture. According to their experimental results, the addition of propane to CO_2 decreases the heat pump COP when domestic hot water at 65°C is produced, while the result is not clear for central heating at 35°C . On the other hand, R1234yf increases the COP for central heating.

Heat pumps have also been studied by Wang et al. (2021) in theoretical work on mixtures of CO_2 and R32. These authors point out that the use of mixtures may avoid the complications commonly used for increasing the efficiency of CO_2 systems. The addition of R32 increases the critical temperature, but the mass fraction of R32 needed to reach a sufficient value (e.g. 55°C) is above 50%. Obviously, the mixture GWP increases linearly with the mass fraction of R32. The temperature glide at the evaporator has a maximum of 14.2°C for an R32 mass fraction of 60%. In terms of COP, an increase is registered for R32 mass fractions below 30% or above 70%, the latter case being impractical due to GWP and flammability concerns. CO_2 and R32 blends have been studied experimentally also by Sun et al. (2019) in a water-to-water heat pump. In this case, the COP trend is complicated by the switching from trans- to subcritical cycle, but at a CO_2 mass fraction of 0.6, the heating COP is

Table 1

Main characteristics of assessed fluids (NIST Refprop; ASHRAE).

Fluid	T_{cr} [$^{\circ}\text{C}$]	P_{cr} [bar]	GWP	NBP [K]	ASHRAE safety classification
R1234yf	94.7	33.8	4	243.7	A2L
R1233zd(E)	165.6	35.7	1	291.4	A1
R1234ze(E)	109.4	36.3	7	254.2	A2L
n-pentane	196.5	33.6	5	309.2	A3
propane	96.7	42.5	3.3	231.0	A3
Isobutane	134.7	36.4	3	261.4	A3
Dimethyl ether	127.2	53.67	1	248.4	A3
CO_2	30.98	73.77	1	194.7 ¹	A1

¹ In the case of CO_2 , must be intended as Normal Sublimation Point instead of Normal Boiling Point.

increased by 23.3% and cooling COP by 65.2%.

Yu et al. (2019) tested mixtures of CO_2 and R41 on an experimental heating/cooling system for automotive air conditioning. These fluids form an azeotrope. The system COP shows a steady improvement with the R41 mass fraction, while the heating capacity is reduced. The maximum cycle pressure is reduced as well, switching the cycle from transcritical to subcritical. These authors present also a discussion on the flammability, showing that for a CO_2 mass fraction above 89% the CO_2 /R41 blend is non-combustible. Wang et al. (2020) studied an azeotropic CO_2 /ethane mixture and claimed a reduction in compressor discharge temperature. However, the effect on COP was unfavourable. The azeotropic CO_2 /ethane mixture was also studied by Kravanja et al. (2018). The heat transfer performance was experimentally characterized under various operating conditions.

In our view, the previous literature offers detailed reports about one or two mixtures working in a specific refrigeration system, while a more general approach would be needed in order to highlight the relevant general trends. Therefore, we decided to use several blends containing CO_2 and relatively small amounts of a vast collection of HFOs or hydrocarbons. In this way we guarantee the following two results:

- the mixture is not flammable
- the working fluid has a high volumetric capacity.

Another objective of our work is to explicitly relate the mixture composition to the glide required by the specific application. Therefore, we decided to compare all cases on a common value of the glide.

Furthermore, we selected some representative configurations, in order to highlight the interaction between the variable mixture composition and some specific components commonly found in CO_2 refrigeration systems. To the best of our knowledge, such a general review on the behaviour of CO_2 based mixtures has not yet been presented in the literature.

1.2. Fluid selection

In this work, 7 working fluids have been considered as the secondary component of a CO_2 -based mixture for transcritical refrigeration cycles: R1234yf, R1233zd(E), R1234ze(E), n-pentane, propane, isobutane and dimethyl ether. R1234yf, R1233zd(E), and R1234ze(E) have been selected as representatives of the best-known hydro-fluoro olefins with low GWP. N-pentane, propane and isobutane are adopted as reference hydrocarbons. Dimethyl ether was taken as a reference for the category of alcohols. All selected fluids have good environmental characteristics (0 ODP, low GWP, low toxicity) and a much lower critical pressure with respect to CO_2 , as resumed in Table 1. HFOs have low flammability levels, while hydrocarbons and dimethyl ether are highly flammable. Nonetheless, as the percentage of these fluids in the mixture is lower than 15% for all cases, the obtained mixtures are expected to be non-flammable. A discussion on the flammability of CO_2 mixtures is

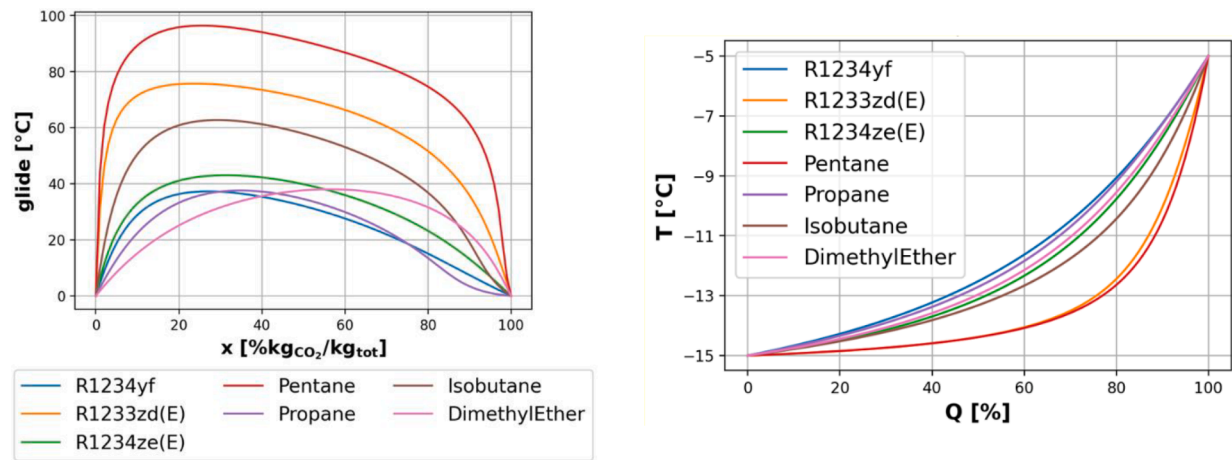


Fig. 1. Temperature glide of the mixtures as a function of the concentration ($T_{\text{sat}} = -5\text{ }^{\circ}\text{C}$) and Evaporation curve for various mixtures at fixed glide ($10\text{ }^{\circ}\text{C}$).

Table 2
Main variable assumption for all assessed cycles.

Parameter	Value
Gas cooler temperature	40°C
Separator temperature	10°C
Heat exchanger efficiency	0.8
Pinch point temperature	5 °C
Cooled fluid inlet temperature	0 °C
Cooled fluid temperature drop	10 °C

outside the scope of this paper and may be found e.g. in [Chen et al., 2009](#).

[Fig. 1](#), left side, shows the temperature glide obtained when adding a percentage (1-x) of the selected fluids to CO₂. The temperature glide is null for $x = 0$ and $x = 1$ and has a maximum in between. As expected, the maximum glide is featured by pentane, which has the highest NBP. Furthermore, the slope of the pentane curve on the right side of the diagram is very steep, suggesting that small quantities of this fluid give a high glide. On the opposite, propane has a moderate slope as x approaches 1, showing that a higher quantity of this fluid has to be mixed with CO₂ to reach a significant glide. This graph offers a first hint on the choice of the additive fluid according to the required glide for the specific application.

A better insight can be obtained by looking at [Fig. 1](#), right side, which represents the evaporation curve of each assessed mixture for a fixed glide of $10\text{ }^{\circ}\text{C}$. The blue curve of the CO₂-R1234yf mixture is the one that is closest to a straight line and therefore allows the lowest irreversibility

in the heat exchange with a constant specific heat fluid. On the other hand, the curves of the CO₂-Pentane and CO₂-R1233zd(E) mixtures are far from a straight line, indicating a poor match between the cooling curve and the refrigerant evaporation curve.

2. System configurations

Four refrigeration cycle configurations were modelled as the basis to assess the advantages and/or drawbacks of CO₂-based mixture solutions for improving CO₂ trans-critical systems.

A fixed compressor isentropic efficiency $\eta = 0.8$ has been assumed in all configurations. This choice has been made in order to compare all cases on a common basis, even if the compression ratio changes in a relatively wide range (from 2.5 to 5). The idea is that there should be the possibility to select an optimized compressor for each configuration. Obviously, the real compressor efficiency depends on the type, size, operating conditions, etc. Therefore, the results should not be taken as quantitative predictions, but rather as comparative assessments related to different configurations at an equal degree of technological refinement. The other fixed parameters are shown in [Table 2](#). Particularly, the separator temperature has been fixed at $10\text{ }^{\circ}\text{C}$, which is a typical value for the refrigeration cycle. This value could change the COP of the analysed systems but does not influence the trend, therefore it has been taken as a fixed value.

The working cycles are numerically solved with locally – evaluated real fluid properties. All simulations have been performed using Python Software linked to NIST Refprop fluid library release 10 (<https://www.nist.gov/srd/refprop>). Indeed, this is the most reliable method to assess

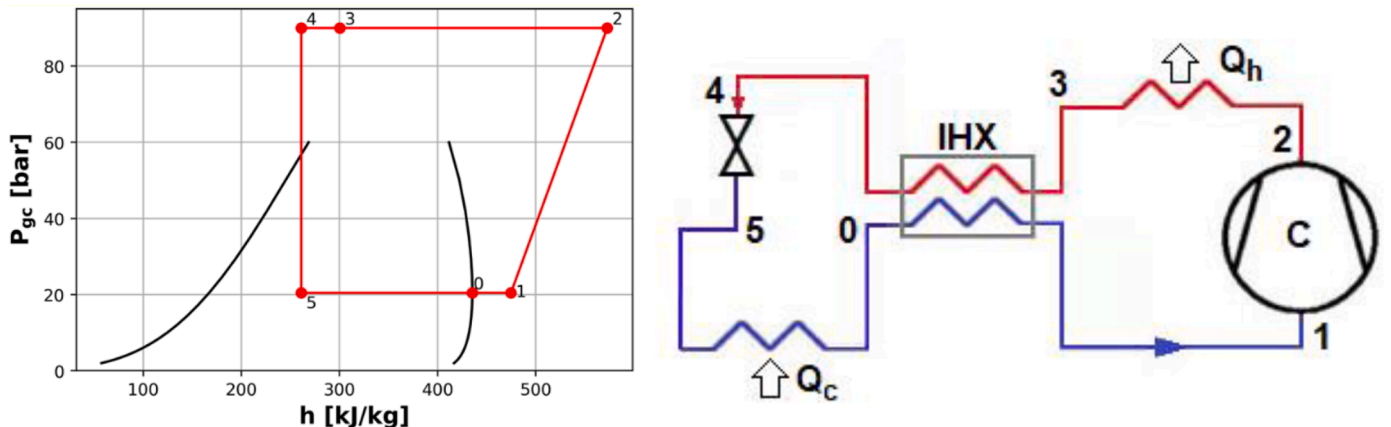


Fig. 2. Base Refrigeration cycle: P-h diagram and Scheme.

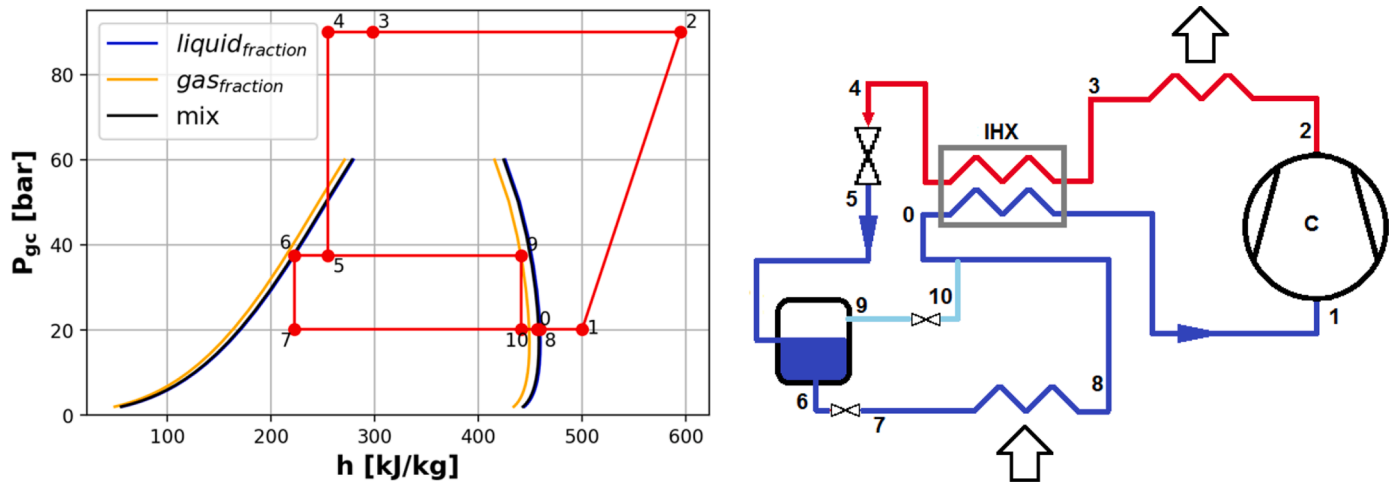


Fig. 3. Refrigeration cycle with separator: P-h diagram and Scheme.

the thermodynamic properties of CO₂-based mixtures, as highlighted in Bertini et al., 2021. The main assumptions are: refrigeration cycles operating in steady-state conditions, negligible kinetic and potential energies, and negligible pressure losses in cycle components and piping.

2.1. Base refrigeration cycle

The main components of the base refrigeration cycle (Fig. 2, right side) are a compressor, a gas cooler, an evaporator and a valve. The base cycle includes an internal heat exchanger (IHx), as it ensures a proper superheating value at the compressor inlet and increases the cooling capacity.

Starting from point 1, the fluid, at superheated vapour conditions (Fig. 2, left side) enters the compressor and is cooled through a gas cooler until point 3, where it enters the IHx. In the IHx the fluid reaches point 4, where it is laminated through a throttle valve that brings it to point 5 where evaporation starts. Even if having some residual liquid at the evaporator exit could increase the heat transferred in the IHx, point 0 has been put on the upper limit curve. This assumption is justified by the need to limit the number of design parameters and to avoid, even for low IHx efficiencies, liquid ingestion by the compressor. Then the fluid is superheated in the IHx and closes the cycle.

A typical result for the base cycle is reported in Fig. 2. As an example, a mixture containing 80% mass of CO₂ and 20% of R1234yf has been chosen. Note that, even with a fairly high efficiency of the IHx, the vapour quality at point 5 is rather high, reducing the cooling capacity. A

high void fraction is expected within the evaporator, which is likely to cause problems of poor heat exchange and fluid maldistribution in the case of multichannel evaporators. This issue is obviously related to the assumption done in the previous paragraph and could be mitigated by moving point 0 to the left (which should produce a shift to the left of point 5). However, our focus is on the effect of the mixture rather than on the cycle details.

2.2. Base refrigeration cycle with separator

The second analysed configuration includes a separator between the valve and the evaporator (Fig. 3). This component is often present in refrigeration cycles and, in the case of CO₂, it has the function to divide the expansion into a pressure-regulated part (4–5), useful for optimization of the gas cooler pressure, and a thermostatically operated part, that controls the evaporator.

Indeed, at the separator, two different compositions will be present. The gas phase will be richer in the more volatile component (CO₂), while the liquid phase will be richer in the less volatile component. This will imply a change in the property of the flow stream and therefore the heat exchanged at the evaporator.

To calculate the compositions of the two streams exiting the separator, the definition of chemical potential has to be used (Eq. (1)). At equilibrium conditions the chemical potential of liquid and vapour are equal (Eq. (2)). This implies that liquid and vapour phases have different compositions, but it is possible to derive the mixture fraction that

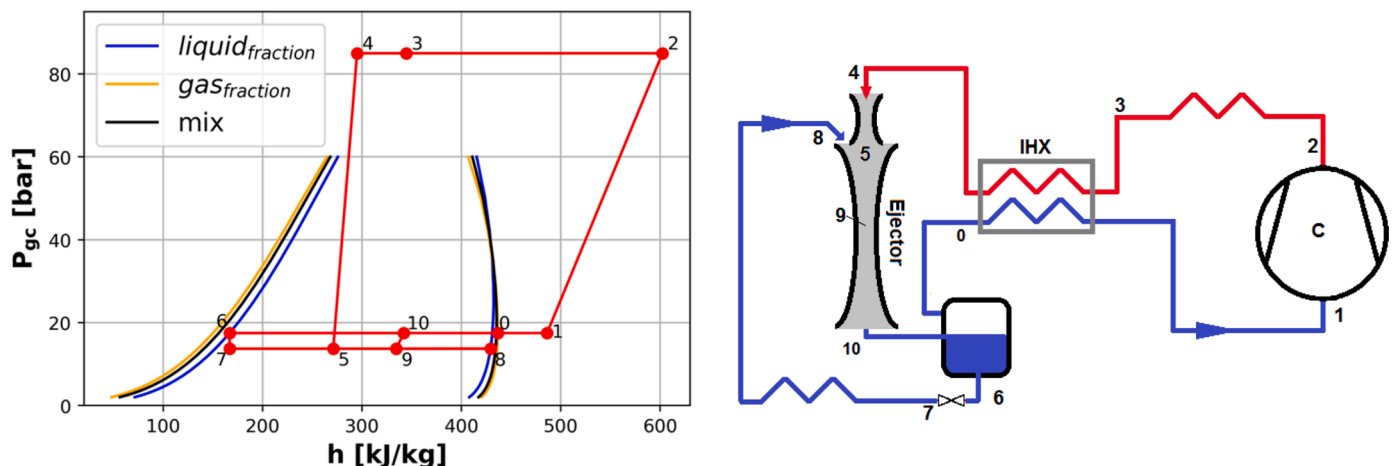


Fig. 4. Refrigeration cycle with ejector: P-h diagram and Scheme.

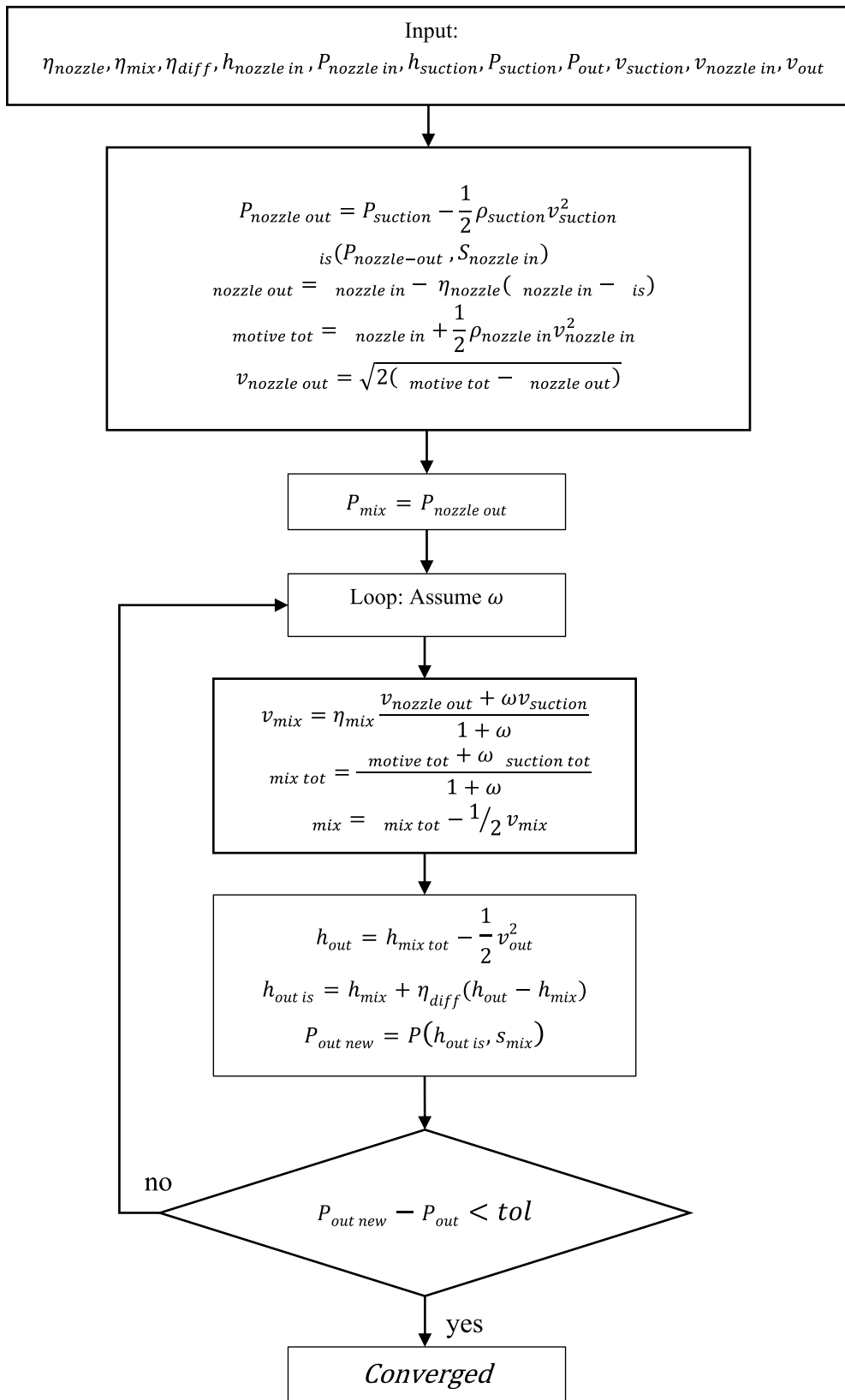


Fig. 5. Algorithm for the ejector calculation.

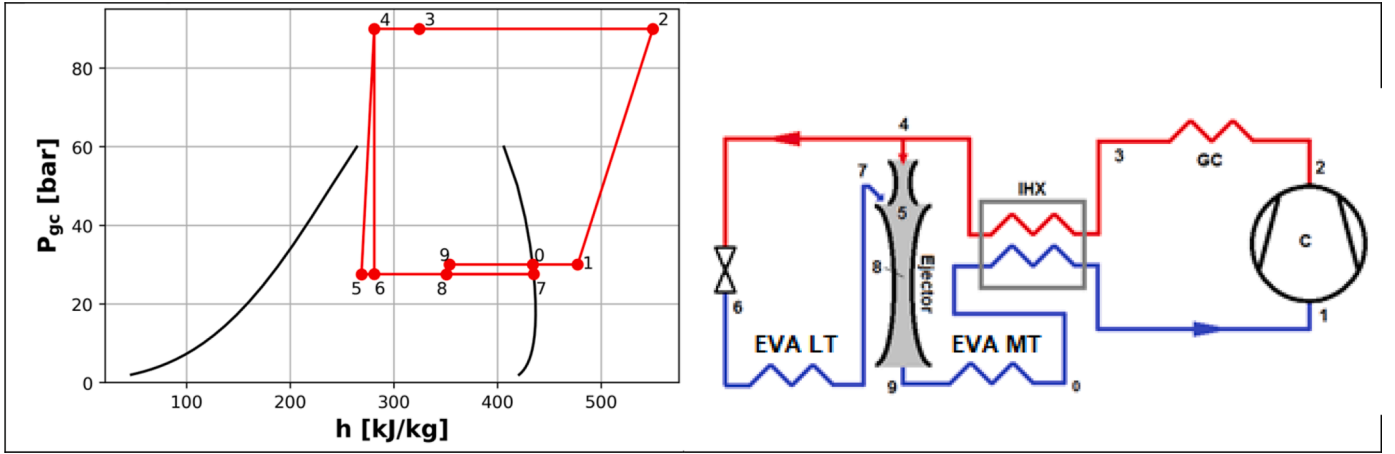


Fig. 6. Refrigeration cycle with ejector and double evaporators: P-h diagram and Scheme.

satisfies Eq. (2), assuming the same pressures and temperatures of the two streams.

$$\mu_i = \left(\frac{\partial G}{\partial n_i} \right)_{P,T,n_j} \quad (1)$$

$$\mu_i^{sol} = \mu_i^{vap} = \mu_i^{liq} \quad (2)$$

The cycle was calculated for the same composition used in the case without a separator and the result is shown in the Ph diagram in Fig. 3 (left side). Now point 7 at the evaporator inlet is moved leftwards with respect to the prosecution of line 4–5. On the other hand, the need to evacuate the flash gas from the separator introduces a source of irreversibility due to the expansion valve between points 9 and 10. The flash gas could be compressed by a “parallel” dedicated compressor back to the gas cooler pressure, but this implies a further complication. Therefore, we decided to exclude this option from the “base” configuration.

2.3. Refrigeration cycle with ejector

The third assessed configuration comprises, in addition to the separator, an ejector between the IHX and the separator (Fig. 4). This component allows to partially recover the heavy expansion loss suffered in high-pressure cycles across the expansion valve. The work recovered from the expansion of the high-pressure stream can be used to compress a low-pressure stream, e.g. the vapour coming from the evaporator to an intermediate pressure. The ratio between the entrained and the motive

flow rate is called the entrainment ratio:

$$\omega = \frac{\dot{m}_{entrained}}{\dot{m}_{motive}} \quad (3)$$

In the case shown in Fig. 4, the ejector discharges the fluid into a separator. The compressor, therefore, operates on a lower compression ratio. Moreover, the cooling capacity is increased, because the evaporator is fed with a low-quality fluid. A comparison between the Ph diagram shown in Fig. 4 and the one shown in Fig. 3 (without ejector) evidences the enthalpy recovered between points 4 and 5 and the compression operated by the ejector between points 9 and 10.

The algorithm used to evaluate the entrainment ratio is shown in Fig. 5. Fixed values are assumed for the efficiencies of the ejector nozzle, the mixing between motive and entrained flow and the diffuser. A value is guessed for the entrainment ratio and the calculation is iterated until the required pressure (i.e. the saturation pressure at the separator) is reached at the ejector discharge.

To guarantee a stable, steady-state operation of the separator, the vapour quality at the ejector should match the entrainment ratio, i.e. the liquid fraction of the flow rate entering the separator must be exactly equal to the entrained flow rate. If so, the expansion of the flash gas (path 9–10 in Fig. 3, left side) may be eliminated.

2.4. Refrigeration cycle with ejector and double evaporator

The final configuration includes an ejector and two evaporators

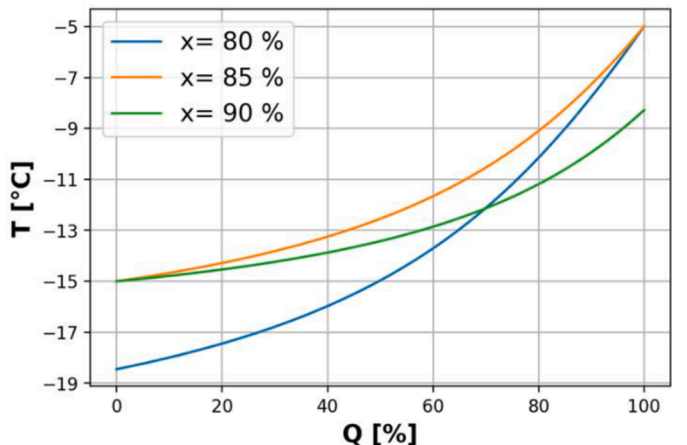
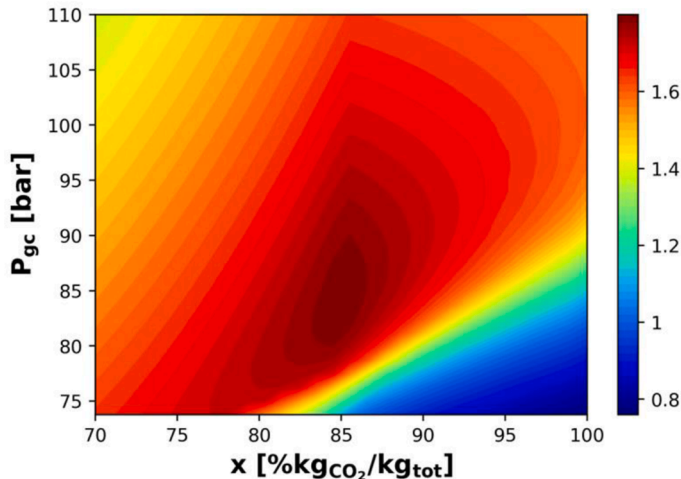


Fig. 7. Performance maps of base refrigeration cycle as a function of P_{gc} and x and temperature-heat diagram at $P_{gc} = 85$ bar for different x values.

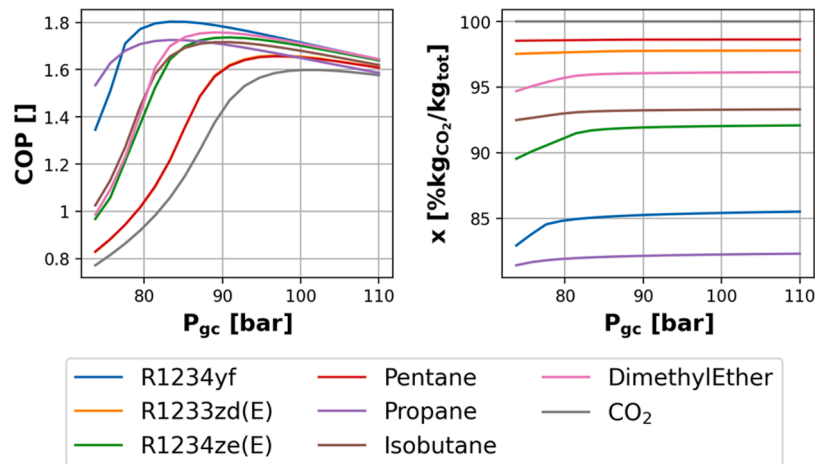


Fig. 8. COP as function of P_{gc} and optimum mixture composition as function of P_{gc} .

(Fig. 6). The separator is substituted by a medium-temperature evaporator, reducing the fluid charge and giving a further degree of freedom.

Both inlet temperatures of the evaporators can be defined independently, once the nature of the cooling service is defined. Assuming e.g. that the system is designed to cool a constant heat capacity flow, an optimization assessment can be carried out. The mixture composition may be optimized as well.

In the case of a system with only CO_2 , the low-temperature evaporator will have a temperature fixed by the pinch point, while the temperature of the medium-temperature evaporator can be optimized.

3. Results and discussion

3.1. Base refrigeration cycles

Base refrigeration cycle without separator

In order to understand the benefit of mixing a secondary fluid with CO_2 for a given temperature drop of the fluid to be cooled, the increase of the Coefficient of Performance (COP) (as defined in Eq. (4)) has been evaluated as a function of the mixture composition and of the gas cooler pressure.

$$COP = \frac{Q_{eva}}{W_c} \quad (4)$$

The evaporator is designed to cool down a fluid entering at $0^\circ C$ and undergoing a $10^\circ C$ temperature drop, allowing a temperature difference of $5^\circ C$ with the evaporating mixture. Furthermore, the mixture temperature at the gas cooler exit is fixed at $40^\circ C$. This allows a consistent comparison of the results, as the increase in COP will mainly be due to the increase of the cooling capacity caused by the decrease of the heat exchange irreversibility in the evaporator.

Fig. 7, left side, shows the COP map of the system using a mixture of CO_2 and R1234yf (this mixture has been taken as reference as it offers the best performance, due to the well-matching curves at the evaporator), as a function of the gas cooler pressure and the CO_2 mass fraction.

The map shows a maximum COP at a CO_2 mass fraction of around 85% and a gas cooler pressure around 85 bar. Setting the gas cooler pressure at 85 bar, the optimum mass fraction is the point where the glide at the evaporator coincides with the temperature difference of the fluid to be cooled, as shown by the temperature – heat exchange diagram in Fig. 7, right side.

For a CO_2 mass fraction $x = 80\%$ the glide is excessive, causing the temperature at the beginning of evaporation to be lower than necessary, while for a mass fraction $x = 90\%$ the temperature is lower than necessary at the end of evaporation.

Fig. 8, left side, introduces a comparison between the various added

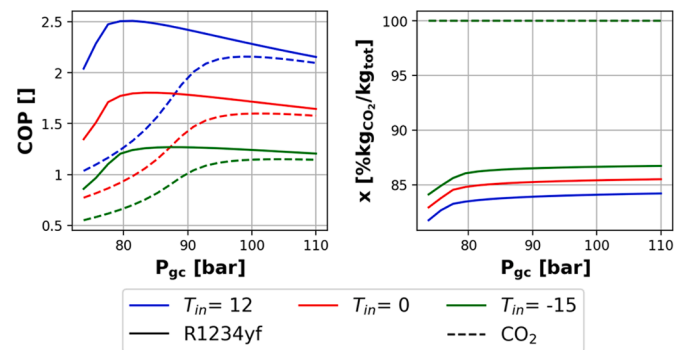


Fig. 9. Effect of the evaporator inlet temperature and effect of the temperature drop of the cooled fluid.

fluids and displays the double beneficial effect of introducing a small quantity of a secondary fluid in a CO_2 -based transcritical refrigeration system: (i) an increase of the COP and (ii) a decrease of the gas cooler pressure. All fluid mixtures present a maximum value of COP for a given P_{gc} . This is due to the counterbalancing effects of cooling capacity and compression work increase when the gas cooler pressure is raised. When compared with pure CO_2 , all mixtures provide an increase in COP and a reduction of the gas cooler pressure, but the highest increase in COP and reduction in pressure is achieved with a mixture of CO_2 and R1234yf. This can be explained because the evaporation curve of this mixture is the closest to a straight line, as shown in Fig. 1.

Fig. 8, right side, also highlights that even a small fraction of secondary fluid deeply modifies the properties of the CO_2 -based mixture.

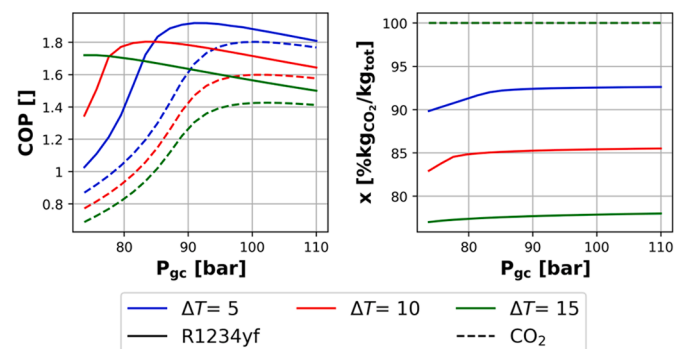


Fig. 10. Effect of the evaporator inlet temperature and effect of the temperature drop of the cooled fluid.

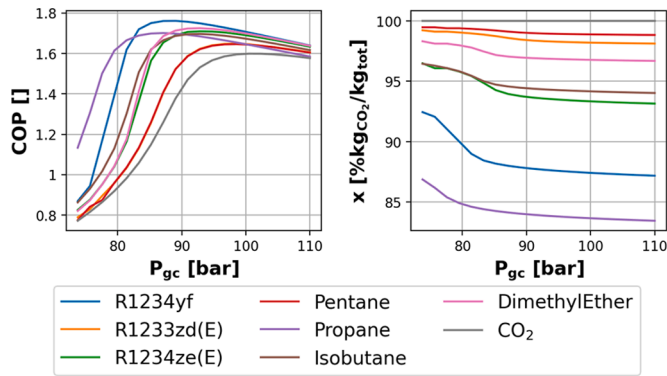


Fig. 11. Refrigeration cycle with separator: COP as a function of P_{gc} at optimum composition and optimum composition as a function of P_{gc} .

The optimum mass fraction of most fluids, for a temperature glide of 10 °C, is lower than 15% (except for the case of propane).

Once it is understood that the injection of a small quantity of secondary fluid is beneficial to the performance of the CO₂-based transcritical refrigeration system, a sensitivity analysis as function of the evaporator temperature and the glide is carried out for the most performing mixture (CO₂-R1234yf).

From Fig. 9, left side, the COP increase and the reduction of the optimal gas cooler pressure due to the introduction of R1234yf in the mixture are evident for all values of evaporator inlet temperature. An increase in the evaporator temperature produces also a reduction of the optimum gas cooler pressure. Fig. 9, right side, also shows that, as the evaporator inlet temperature increases, a greater quantity of R1234yf is required to obtain the same glide; this can be explained by referring to the bell structure of the saturation curves. As the temperature increases, an isobar has a lower enthalpy difference from the lower to the upper limit curve and therefore a lower glide.

Fig. 10 shows that the convenience of using mixtures grows as the temperature drop of the fluid to be cooled increases. While in the case of $\Delta T = 5$ °C the COP obtained with the fluid mixture increases only by 5% over the pure CO₂, for $\Delta T = 15$ °C the increase reaches 20%. Furthermore, the optimum gas cooler pressure moves to the left by 30 bars in the case of $\Delta T = 15$ °C. This can be explained considering that a higher percentage of R1234yf is required to adapt the mixture temperature glide to the increased temperature drop of the cooled fluid, as shown in Fig. 10, right side.

This result may be interesting, for example, in the case of mobile air conditioning, where the air is taken from the ambient at a very high temperature and must be brought below its dew point. Obviously, if the CO₂ percentage is brought below 80%, one should verify that the mixture does not become flammable, notably if the added fluid is highly flammable (e.g. hydrocarbons).

Base Refrigeration cycle with separator

It is worth pointing out that the separator does not raise the cycle COP at fixed evaporation temperature. The beneficial effect of a separator can be measured only by a detailed analysis of the heat exchange at the evaporator so that the possibility to increase the evaporation temperature is pointed out. Given that the separator moves the lamination (points 6 and 7 in Fig. 3) towards the left, the 10 °C glide can be obtained with a lower percentage of secondary fluid in the mixture. Furthermore, the vapour fraction that is released from the separator and mixes with the fluid coming from the evaporator (path 9–10 in Fig. 3) is rich in CO₂. These two circumstances lead to a composition richer in CO₂ at the compressor, causing an increase in compression work. As a result, the maximum COP in Fig. 11 is slightly lower than that shown in Fig. 8.

Fig. 11 right side shows the optimal mass fraction as a function of the gas cooler pressure. As this latter decreases, lamination occurs at higher enthalpies, yielding a more vapour-rich fluid at the separator. The liquid

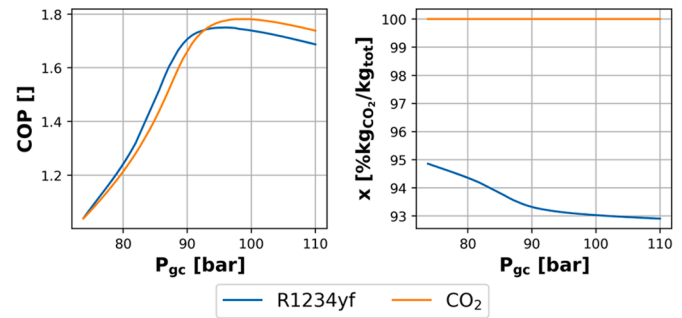


Fig. 12. COP comparison between mixture and pure CO₂ and optimum mixture composition.

fraction thus formed will therefore be smaller and leaner in CO₂. This is why a lower quantity of the added refrigerant is needed to obtain the same glide (conversely to the case without the separator) and explains why the CO₂ percentage that gives a 10 °C glide decreases with the gas cooler pressure, while in Fig. 8 we saw an opposite behaviour.

3.2. Cycles with ejector

Refrigeration cycle with ejector and separator

A comparison of the COP obtained by the cycle with ejector and separator operating with pure CO₂ and with a mixture of CO₂ and R1234yf is shown on the left in Fig. 12. Quite surprisingly, in this case, the use of a mixture yields a COP curve that is higher in the left part of the diagram, but on the right side is surpassed by the curve obtained with pure CO₂, that shows a slightly higher maximum value. This can be explained considering that the addition of R1234yf does indeed improve the heat exchange at the evaporator (due to the temperature glide), but, on the other hand, reduces the evaporator pressure. The optimum gas cooler pressure is reduced as well, but only by a small amount so that the compression ratio increases. Therefore, the compression work actually increases and, on the whole, the COP is reduced.

To understand why the gas cooler pressure shows only a moderate reduction, one should consider the effect of the separator on the composition of the mixture flowing in the various paths of the system. As shown in Fig. 4, the fluid that flows through the IHX, compressor and gas cooler is the gaseous fraction that comes out from the separator. Therefore, it is richer in the most volatile mixture component, i.e. CO₂, and behaves not so differently from pure CO₂. On the other hand, the liquid that goes to the evaporator is richer in R1234yf and hence shows a significant pressure decrease.

By the way, the increase of the compression ratio is a common feature of all cycles working with a mixture and a separator, but, in the cycle without an ejector, its negative effect has a lower impact, in comparison to the benefit given by the improved heat exchange at the evaporator.

The right side of Fig. 12 is similar to Fig. 10: as the gas cooler pressure is reduced, a larger quantity of R1234yf is required to guarantee a temperature glide of 10 °C, for the same reason explained in the previous section. Similar results are obtained with the mixtures containing other fluids.

Refrigeration cycle with Ejector and double evaporator

In this case, the composition remains constant throughout the system because there is no separator. However, it is no longer trivial to find the optimal composition since there are two evaporators.

Several possible cases are thus studied:

Pure CO₂

In the case of pure CO₂, the glide being zero, the temperature of the low-temperature evaporator is determined by its minimum temperature difference from the fluid to be cooled. The only parameters available for optimization are the gas cooler pressure and the temperature of the

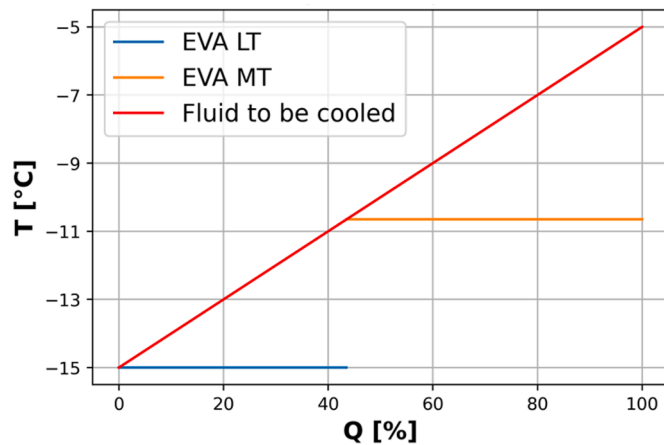


Fig. 13. Optimization of the temperature at the high-pressure evaporator for pure CO₂.

medium-temperature evaporator. The COP of a cycle with two evaporators can be defined by summing up the cooling capacities obtained at the two temperature levels, as shown in Eq. (5).

$$COP = \frac{\omega Q_{LT} + (1 + \omega) Q_{MT}}{(1 + \omega) W_c} \quad (5)$$

The ejector entrainment ratio ω , for a given amount of energy delivered by the expansion of the motive flow, is inversely proportional to the compression ratio that the ejector must overcome. Therefore, the ejector produces a variable subdivision of the cooling capacity between the two temperature levels, which may be optimized according to the heat capacity of the fluid to be cooled. The result of this optimization is shown in Fig. 13. Note that in this figure the temperature curve of the fluid to be cooled is translated vertically by the minimum temperature difference, to give graphical evidence of the optimum condition. Therefore, the isotherm of the LT evaporator touches the straight inclined line of the cooled fluid. In the optimum condition, also the MT isotherm comes in touch with the inclined line, minimizing the heat transfer irreversibility.

Mixture

As a second fluid is added to CO₂, two additional degrees of freedom are added to the cycle. The first one is the mixture composition, while the second is the temperature at the low-temperature evaporator, which now, due to the temperature glide, is not fixed anymore.

The optimum solution is the one that minimizes the area between the refrigerant mixture curves and the line of the fluid to be cooled. This goal may be pursued in two ways: 1) optimization of the heat exchange

in the medium-temperature evaporator and 2) optimization of the heat exchange in the low-temperature evaporator. In this way, we may divide the problem into two cases. In each case, the mixture composition is found by equating the temperature glide to the slope of the curve of the fluid to be cooled and the cycle may be optimized by varying the gas cooler pressure.

In the following, a mixture of CO₂ and R1234yf will be used as an example.

Optimisation of medium-temperature and low-temperature evaporator

As shown in Fig. 14 left side, the mixture composition has been optimized to adapt the temperature glide at the medium-temperature evaporator to the line of the fluid to be cooled. This produces a worsened condition at the low-temperature evaporator, i.e. a very low inlet temperature. A COP of 1.84 is reached. Again, the line of the fluid to be cooled is translated downwards by the minimum temperature difference.

Fig. 14, right side, shows the opposite case of a mixture composition that optimizes the temperature glide at the low-temperature evaporator. Now the mismatch between the curves is found at the exit from the medium-temperature evaporator. This case yields a COP of 1.83.

Comparison between the two options

The two options presented before are compared in Fig. 15. The maximum COP is almost equal (left side Fig. 15). However, the optimization of the medium-temperature evaporator requires a lower gas-cooler pressure, due to the higher quantity of R1234yf in the mixture (right side Fig. 15). Note that in any case the percentage of R1234yf is limited to 12% at optimum conditions. The percentage of R1234yf increases with the gas-cooler pressure, as for the base cycle without a liquid separator.

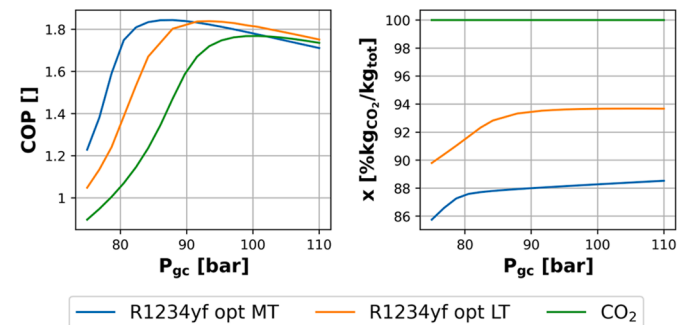


Fig. 15. COP comparison between the two optimization strategies and optimum mixture composition.

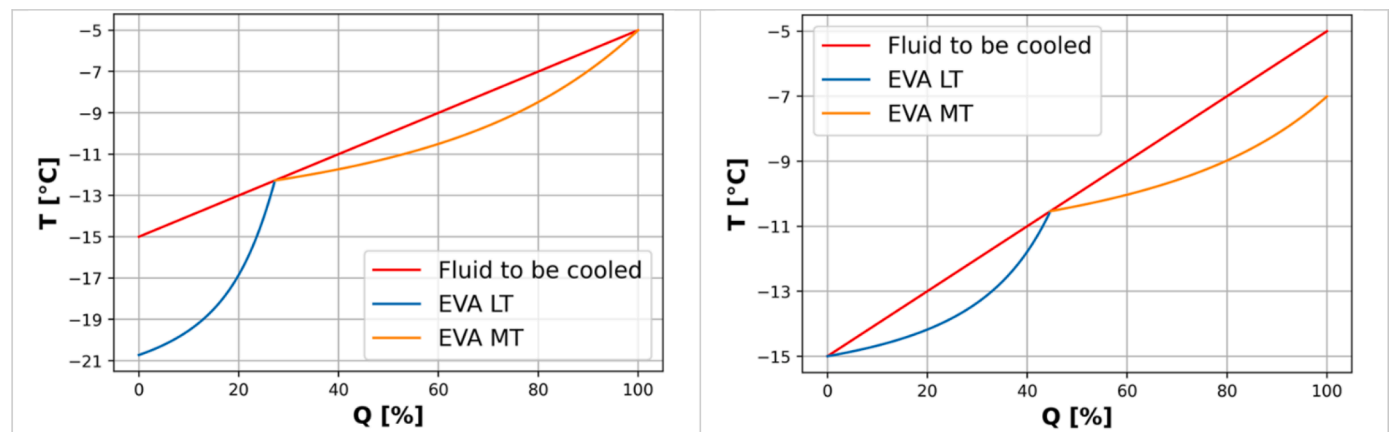


Fig. 14. Optimization of the medium-temperature (left) and the low-temperature evaporator (right).

Table 3

COP improvements by mixture and technology ($T_{gc} = 40\text{ }^{\circ}\text{C}$, $T_{eva} = -15\text{ }^{\circ}\text{C}$, glide = $10\text{ }^{\circ}\text{C}$).

	Base CO ₂	Base CO ₂ with separator	Ejector and separator	Ejector and double evaporator
Pure CO ₂	1.60	1.60	1.78	1.77
CO ₂ R1234yf (best mixture)	1.80 (+12.8%)	1.76 (+10.2%)	1.75 (−1.8%)	1.84 (+4.3%)
CO ₂ -Propane (best natural fluid)	1.73 (+7.9%)	1.70 (+6.4%)	1.74 (−2.1%)	1.77 (+2.0%)

4. Conclusions

The results presented thus far prove that the use of a mixture of CO₂ and an additional fluid may improve the performance of a transcritical refrigeration cycle. Four different configurations have been simulated, highlighting the different impacts produced by the use of a fluid mixture. Two of these configurations include an ejector, which has been assessed by a simple thermodynamic procedure.

7 non-toxic fluids with ODP=0 and low GWP have been used in our simulations. Given the prevailing fraction of CO₂, all proposed mixtures are non-flammable and offer a high volumetric cooling capacity.

As far as can be seen from our simulations, the best COP is obtained by a mixture of CO₂ and R1234yf (Table 3). However, interesting results are obtained also using a mixture of CO₂ and propane, which by the way allows a significant reduction of the gas cooler pressure. This, on one hand, would imply a reduction of the compressor outlet temperature, but the compression ratio slightly increases and, consequently, this reduction is almost negligible.

The presence of a liquid separator produces a variable mixture composition along the cycle, which may pose problems in case of fluid leakage. On the other hand, the configuration with an ejector and two evaporators shows interesting results and may be worth of further analysis.

Finally, it can be said that the highest increase in performance is reached in the base configuration cycle, proving that the use of a fluid mixture can be considered an alternative to more refined configurations.

Évaluation thermodynamique des systèmes de réfrigération transcritiques utilisant des mélanges à base de CO₂

Fluides, cycles, réfrigération

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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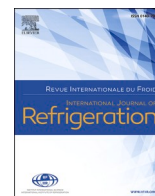
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4.2 Paper 2: A proposal for a non-flammable, fluorine-free, CO₂-based mixture as a low TEWI refrigerant

Following the evidence from paper 1, which demonstrated that the conventional use of the separator is not advantageous for mixtures, the authors investigated various natural fluids to identify the optimal performance for an air conditioning chiller. In this case the IHX is not used in the classic way but is used to complete the evaporation. This approach allows for a higher percentage of secondary refrigerant in the mixture without exceeding the temperature lift of the cold fluid, resulting in superior performance compared to the findings in paper 1. Specifically, DME achieves higher performance than other fluids while maintaining a GWP of 1 and non-flammability. This research highlights the benefits of this approach for CO₂-based mixtures, particularly the CO₂-DME mixture, yielding improved results compared to previous studies by Onaka et al.[42] and Koyama et al.[33]

Interestingly, although paper 1 indicated comparable benefits for propane and DME with the conventional use of IHX, this study reveals that DME achieves significantly better results.

The Ph.D. candidate is the first author of this work and was mainly involved in modeling and calculation under supervision and writing of Professor Adriano Milazzo. Dr. Lorenzo Talluri provided supervision and assistance with conceptualization.



A proposal for a non-flammable, fluorine-free, CO₂-based mixture as a low TEWI refrigerant

Proposition d'un mélange ininflammable, non-fluoré et à base de CO₂ comme frigorigène à faible TEWI

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ABSTRACT

A thermodynamic analysis of a simple inverse cycle is proposed as a means to evaluate mixtures of CO₂ and four organic substances (propane, iso-butane, dimethyl-ether and propylene) as working fluids. The cycle features an internal heat exchanger and is designed to cool down a finite heat capacity flow on the cold side. The analysis covers trans-critical as well as sub-critical cycles. For each organic substance, the composition is optimized. Flammability is accounted for. Dimethyl-ether (DME) turns out to be the best option, as a relatively low mass fraction of this compound is sufficient for reaching the thermodynamic optimum. In this way, a simple, sub-critical refrigeration system may be obtained featuring a non-flammable working fluid and a significant COP increase with respect to pure CO₂.

1. Introduction

CO₂ refrigeration systems are experiencing an increasing market share in some applications. For example, in Europe, trans-critical CO₂ systems have surpassed a 14% market share in the food retail sector (Dilshad et al., 2020). This success is due to the huge effort done by researchers from academia and the industry to increase the efficiency of these systems (Gullo et al., 2018). New attempts are done to extend this success to other sectors, e.g. transport refrigeration (Minetto et al., 2023). However, the improvements are often done at the expense of an increasing complication of the refrigeration system, e.g. the use of multiple ejectors (Gullo et al., 2018b).

An alternative path towards the improvement of CO₂-based systems could be sought through the use of fluid mixtures. This approach would allow performance improvements comparable to those obtained with complex cycles, as shown recently by Sánchez et al. (2023). This doesn't mean that blends would not be useful in more complex systems, as shown in Martínez-Ángeles et al. (2023), where a parallel compression system using a CO₂/R1233ze(E) mixture [90/10%] has been shown to bring a COP improvement of almost 12%.

Cycles employing mixtures, when compared to cycles using pure

CO₂, will have the following features:

- higher critical temperature (in some cases leading to sub-critical operation)
- lower operating pressure
- lower volumetric refrigeration capacity
- variable evaporation temperature (glide)

The last feature (Lorentz cycle) may be useful whenever the heat source has a finite heat capacity, as in the case of water chillers or direct-expansion air conditioners. Even in the case of a refrigerated cell in a food storage plant, a well-measurable temperature difference exists between the inlet and outlet of the evaporator, air flow rate being limited. The glide-matching between the refrigerant mixture and cooled fluid has been pursued for CO₂/propane mixtures since the work of Kim et al. (2008).

1.1. Fluid selection

Many substances may be considered possible components in a CO₂-based mixture. In our previous work on this subject (Vaccaro et al., 2023), we have examined various fluid categories and we have shown

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Nomenclature

COP	Coefficient of performance
DME	Dimethyl-ether
ε	Heat exchanger efficiency
h	enthalpy [kJ/kg]
HFO	Hydro-fluoro-olefin
IHX	Internal heat exchanger
$\dot{m}$	Mass flow rate [kg/s]
Q	Vapour quality
$\dot{Q}$	Thermal power [kW]
T	Temperature [K]
x	CO ₂ mass fraction

that, among selected fluids, the best results were obtained using a mixture of CO₂ and an HFO (R1234yf), as confirmed by [Martinez-Angelès et al. \(2023\)](#).

In this second work on the same topic, we have decided to concentrate on fluorine-free substances. This decision is partially related to the recent trend to include HFOs among PFAS (Per Fluoro Alchil Substances), as e.g. in ECHA Restriction Report (2023).

Hence we have selected a relatively small set of refrigerants: propane, isobutane, dimethyl-ether and propylene. All these substances, when mixed with CO₂, give a performance improvement with respect to pure CO₂. However, all these substances are highly flammable. Therefore, an interesting issue is the flammability of the mixture. According to ISO 817 2014, refrigerants may be divided into 4 classes; 1) non-flammable, 2 L) mildly flammable, 2) flammable and 3) highly flammable. Given that distinction between 2 and 2L classes is bound to the flame propagation velocity, we cannot specify the mixtures in this respect, due to the lack of experimental data. Therefore, in this paper, we will classify the blends into only 3 classes.

If non-flammability or mild flammability is sought, CO₂ must be the main component of the mixture. However, sometimes even low quantities of a flammable substance may make the mixture highly flammable. Therefore, a dedicated analysis must be performed for each substance.

1.2. System configuration and modelling

As already stated, the use of a mixture may be seen as an alternative to cycle complications (e.g. expansion work recovery) in the effort for improving the performance of CO₂ refrigeration systems. Therefore, a simple refrigeration system, comprising a compressor, condenser (or gas

cooler), internal heat exchanger (IHx) and evaporator, has been taken as a reference ([Fig. 1](#)). The system is constrained by the ambient temperature, that fixes the minimum temperature of the hot heat exchanger (point 3), and by a minimum superheating at the compressor inlet (point 1), to avoid liquid ingestion. The sub-cooling from point 3 to point 4 is obtained in the IHx, where heat is transferred from the hot liquid to the cold fluid exiting the evaporator at point 0. If the IHx does not exchange heat with the environment, it must be:

$$h_3 - h_4 = h_1 - h_0 \quad (1)$$

Note that point 0 can be well within the two-phase zone, being the superheating guaranteed by the IHx. This represents a departure from what was written in the previous paper by the same authors ([Vaccaro et al., 2023](#)), where a saturated state was imposed at the evaporator exit. In this way, we add a further degree of freedom to the system configuration, which may be very useful for the optimization of the evaporator. For a given mixture composition, moving point 0 to the left (i.e. reducing the vapour quality at the evaporator exit) reduces the glide. Therefore, a desired value of glide may be re-established by increasing the quantity of added fluid to the mixture. Within certain limits, this improves the COP, as will be shown later. Note also the increasing downward slope of the isotherms on the right side of the saturation zone, which makes the glide very sensitive to the position of point 0.

To show some quantitative results, a set of reference values have been fixed for the fundamental system parameters ([Table 1](#)). A system that produces chilled water at 7°C is taken as a reference, but the results apply to any other case that allows a performance improvement employing a variable evaporation temperature. The minimum temperature difference between the cooled fluid and the evaporator is 5°C.

Note that the values reported in [Table 1](#) are specified only as a common base for the sake of comparison between the various mixtures, without any reference to an existing refrigeration system. The system size is not constrained, in order to keep the analysis as general as possible. The efficiency value assumed for the compressor must be

Table 1

Main variable assumptions for all assessed cycles.

Parameter	Value
Gas cooler/condenser exit temperature	40°C
Compressor efficiency	0.8
IHX Heat exchanger efficiency	0.8
Pinch point temperature difference	5°C
Cooled fluid inlet temperature	12°C
Cooled fluid temperature drop	5°C
Minimum superheating at the compressor inlet	2°C

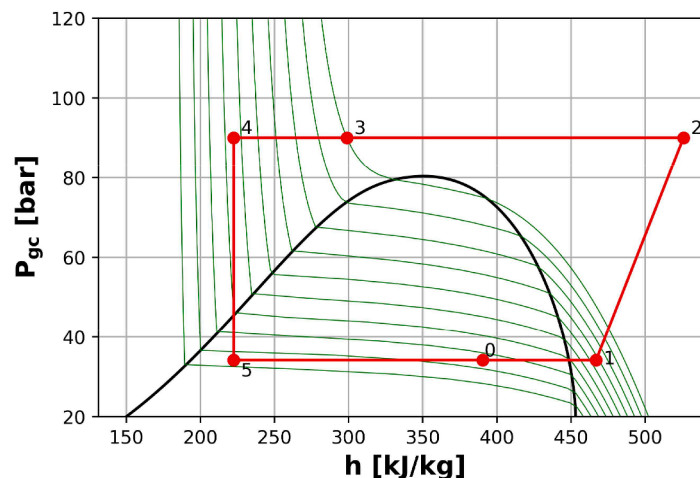


Fig. 1. Example of the cycle with IHx for a 95/5% CO₂/DME mixture.

revised once the size and degree of refinement of the case study are defined.

The thermodynamic cycle is modelled by imposing the energy balance for each component. Fluid properties are evaluated through NIST Refprop 10.0. The use of Refprop for mixtures may cause slight errors. A comparison between the experimental data published by Tsang and Street (1981) and the data calculated by Refprop has shown a maximum error on the predicted mole fraction below 5%.

The efficiency of the IHX is defined as:

$$\varepsilon = \frac{\dot{Q}}{\min(\dot{Q}_{\max_34}, \dot{Q}_{\max_01})} \quad (2)$$

where

$$\dot{Q} = \dot{m}(h_3 - h_4) = \dot{m}(h_1 - h_0) \quad (3)$$

The limit heat exchange on the two sides of the IHX is:

$$\dot{Q}_{\max_34} = \dot{m}(h_3 - h_{4(T_4=T_0)}) \quad (4)$$

$$\dot{Q}_{\max_01} = \dot{m}(h_{1(T_1=T_3)} - h_0) \quad (5)$$

The objective function for the optimization is the system COP:

$$COP = \frac{h_0 - h_5}{h_2 - h_1} \quad (6)$$

2. Results and discussion

A typical performance map is shown in Fig. 2. COP is shown as a function of the gas cooler (or condenser) pressure and of the quality at the evaporator exit. A 95/5% CO₂/DME mixture is considered (critical point at $T = 40.97^\circ\text{C}$ and $P = 80.30$ bar). The dashed black line is the locus of the optimal vapour quality as a function of the pressure, i.e. along this line the vapour quality at the evaporator exit gives a maximum COP because the glide is 5°C . The highest COP is found at 84.54 bars, i.e. for a trans-critical cycle.

Fig. 2 shows also a continuous black line that marks a limit for the quality. On the left side of this line, the heat provided to the fluid exiting from the evaporator in the IHX is insufficient to guarantee the minimum superheat imposed at the compressor inlet, i.e. 2°C . In the case of Fig. 2, all optimal points are admissible.

Fig. 3 shows a comparison between 3 cycles using the same mixture and the same quality at the evaporator exit (point 0). The maximum COP, as shown in Fig. 2, belongs to the cycle in the middle, with a gas cooler pressure of around 90 bar. If the gas cooler pressure is raised to 110 bar, the cooling capacity is practically unchanged, while the compressor work is raised. Point 1 is shifted to the left, due to the

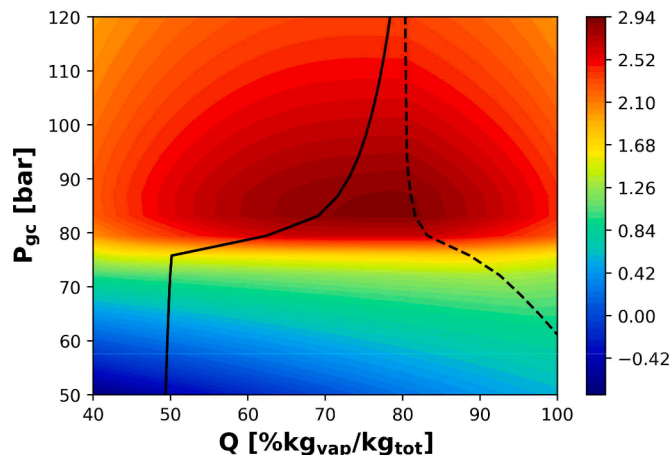


Fig. 2. Contour map of COP for a 95/5% (in mass) CO₂/DME mixture.

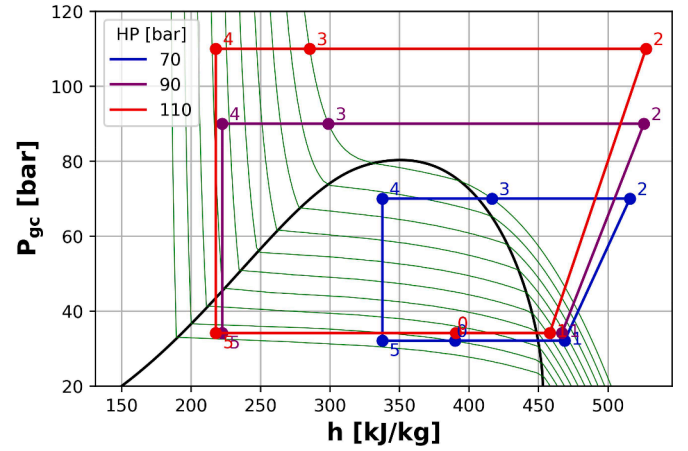


Fig. 3. Comparison of cycles with different maximum pressure for a 95/5% (in mass) CO₂/DME mixture.

reduction of the heat available at the IHX (the length of segment 3–4), due to the shape of the isotherms. The lower cycle is clearly meaningless, as the constraint on the point 3 temperature (40°C) produces a heat release to the ambient completely outside of the two-phase zone, even if the cycle is sub-critical. The IHX sees a partial condensation of the fluid, but point 5 turns out to have a high enthalpy anyway, giving a very low cooling power.

If the percentage of DME is raised to 10% in mass, the situation changes as shown in Fig. 4. The critical point is raised at $T = 49.48^\circ\text{C}$ and $P = 84.161$ bar, hence the maximum COP is reached with a subcritical cycle. Now the dashed line is on the left of the continuous line for any pressure above 73.62 bars, i.e. all points above this pressure that give maximum COP are no longer admissible in terms of superheating at the compressor inlet.

This result may be explained by noting that the increased percentage of DME gives a higher glide and vice-versa, as shown in the diagram in Fig. 5. This diagram has been built by keeping fixed the maximum cycle pressure and the vapour quality at evaporator exit. The light-brown curve, corresponding to $x = 95\%$, shows exactly a glide of 5°C , matching the temperature drop of the cooled fluid and hence giving the maximum performance. If the DME percentage is increased to 97% (blue curve), the glide increases to 7°C . The opposite happens for lower DME percentage (e.g. green curve).

For the sake of comparison, we may show the contour map obtained with pure CO₂, which is shown in Fig. 6. In this case, the maximum COP is outside the map, due to the isothermal evaporation that cannot match

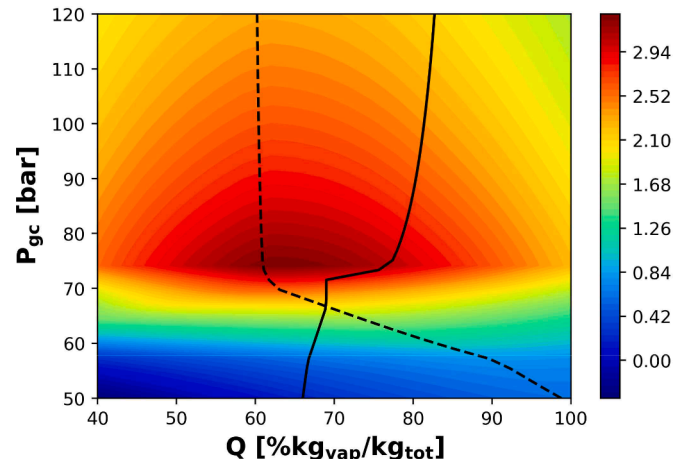


Fig. 4. Contour map of COP for a 90/10% (in mass) CO₂/DME mixture.

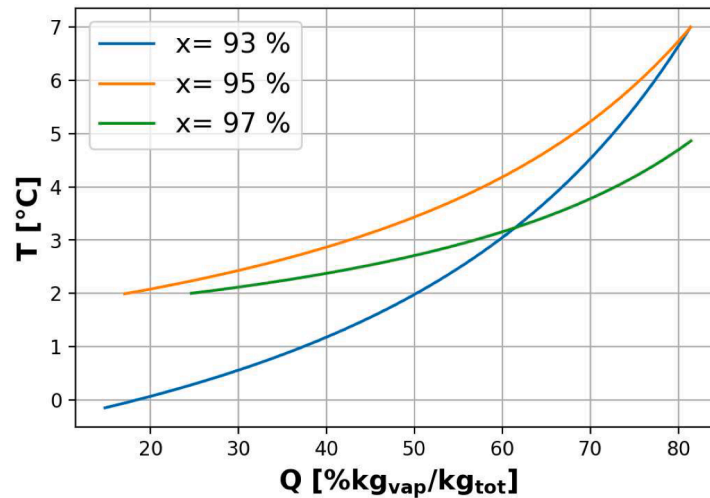


Fig. 5. Diagram of evaporator temperature for different CO₂ mass fractions at constant vapour quality at evaporator exit.

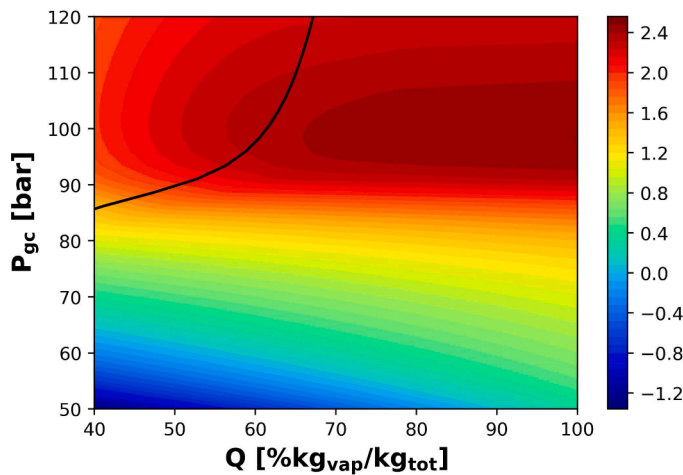


Fig. 6. Contour map of COP for pure CO₂.

the cooled fluid temperature drop even for a 100% vapour quality at evaporator exit. A better result could be obtained for a 5°C superheating within the evaporator. However, the maximum COP is significantly lower than the values found for the mixture.

All these behaviours have been summarized by collecting the optimal

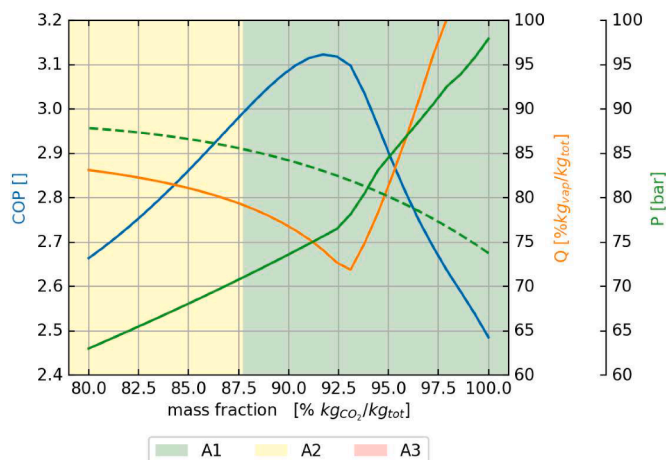


Fig. 7. Summary of results for CO₂/DME mixture.

results in the graph shown in Fig. 7. A further aspect is added, i.e. the flammability of the mixture, which has been evaluated according to Kondo et al. (2006). This paper presents a modified Le Chatelier formula, specifically applicable to mixtures of flammable and inert gases, allowing the calculation of the FIP (Fuel Inertization Point) for blends of CO₂ and several flammable substances.

The x-axis in Fig. 7 shows the mixture composition, with pure CO₂ on the right and a 80/20% mixture on the left. The mixture is non-flammable on the green zone, i.e. for a DME mass fraction below 11.8%. For higher mass fractions of DME, the mixture is mildly flammable, i.e. classified A2 according to ASHRAE Standard 34/2019.

The continuous blue line shows the maximum COP reached for a given composition by optimizing the maximum cycle pressure and the vapour quality at the evaporator exit. The highest point corresponds to a DME mass fraction of 8.08%, well within the green zone. In other words, a COP value of 3.12 may be reached with a non-flammable mixture of CO₂ and DME, while the corresponding value for pure CO₂ is 2.49. This remarkable result may be explained by considering that the mixture has an optimal pressure (continuous green line) of 75.89 bar, while pure CO₂ requires a gas cooler pressure of 97.93 bars to reach the optimum condition.

The continuous orange line shows the optimum vapour quality at the evaporator exit. The optimum COP corresponds to the minimum vapour quality. On the right of this minimum value, an increase of the mass fraction of DME produces an increased glide and hence point 0 of the cycle moves to the left on the Ph diagram in order to keep the 5°C value of glide. On the left of the minimum of the orange line in Fig. 6, the vapour quality at the evaporator exit must be increased, in order to satisfy the limit on the superheating at the compressor inlet. Hence, the glide exhibited by the mixture exceeds the 5°C value that matches the assigned temperature drop of the cooled fluid. Therefore, the COP is reduced, even if the optimum cycle pressure (and hence the compressor work) continues to decrease.

The green dashed line shows how the critical pressure decreases for decreasing the mass fraction of DME, approaching the critical pressure of pure CO₂ (73.77 bar). The intersection of this dashed line with the continuous green line shows that all optimized cycles using a CO₂/DME mixture with a mass fraction of DME higher than 6.1% are subcritical.

The cycle corresponding to the optimum condition (CO₂ mass fraction 91.9%) is shown in Fig. 8. Note that in this cycle the condenser exit (point 3) is exactly on the saturated liquid line, while the compressor inlet (point 1) is exactly at the imposed value of superheating.

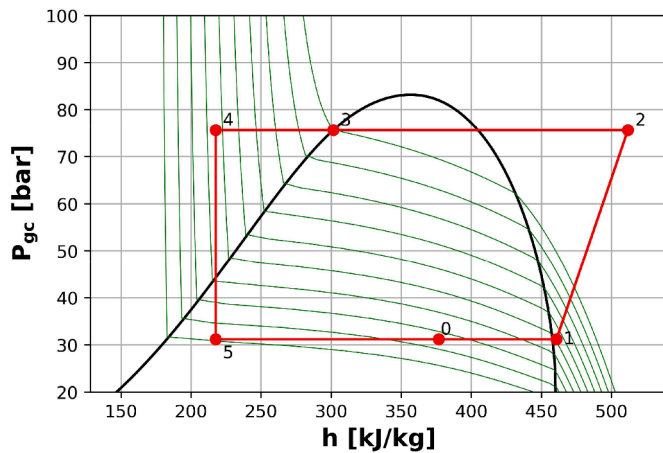


Fig. 8. Optimized cycle for CO₂/DME mixture.

2.1. Comparison of different fluids

As stated above, our objective is to explore the feasibility of a refrigeration system using a mixture of carbon dioxide and an organic compound that should improve the system efficiency, without impairing the well-known advantages of CO₂ (low GWP, high volumetric cooling capacity, absence of flammability and toxicity).

DME has been extensively dealt with in the previous part of the paper. Other fluids will be examined in this section. The first one is propane, which has been proposed by many authors as a possible candidate. The results of the calculations done with this fluid are shown in Fig. 9a.

The first point that emerges from the comparison between Figs. 9a and 7 is the maximum COP, that is 2.83 for propane against 3.12 for DME. Moreover, the optimum composition is found for a mass fraction of propane of 27.7%, which makes the mixture highly flammable (A3 ASHRAE classification).

Almost all the mass fraction range shown in the figure yields transcritical cycles, as shown by the intersection between the green dashed line (critical pressure) and the green line (optimum gas cooler pressure). The minimum vapour quality at the evaporator exit (i.e. the condition that gives a glide of 5°C) lies on the right of the maximum COP because the effect of compressor work reduction overcomes the effect of temperature matching at the evaporator.

The results gathered with CO₂/isobutane mixtures are similar (Fig. 9b), though the maximum COP is slightly higher and takes place for a lower mass fraction of the added component. The optimum composition yields a subcritical cycle. However, the optimum composition is highly flammable.

Finally, we consider CO₂/propylene mixtures (Fig. 9c), which give the highest COP among all the substances considered herein. The maximum cycle pressure is lower than 70 bar in the optimum zone. However, this good result is obtained for a mass fraction of propylene above 20%, well within the range of high flammability.

We may conclude that propane, isobutane and propylene may give a benefit in terms of performance when added to CO₂, but this result is gathered only when the added substance has a mass fraction that makes the mixture highly flammable. From a practical point of view, this makes these mixtures scarcely attractive with respect to the pure hydrocarbons, which give even higher performance.

2.2. Effects of the ambient temperature

Up to now, a fixed temperature has been set at the gas-cooler or condenser exit, i.e. the ambient condition has been left unchanged. If the ambient temperature is lowered and hence the condenser may work at a lower temperature, the results change as shown on top of Fig. 10, where

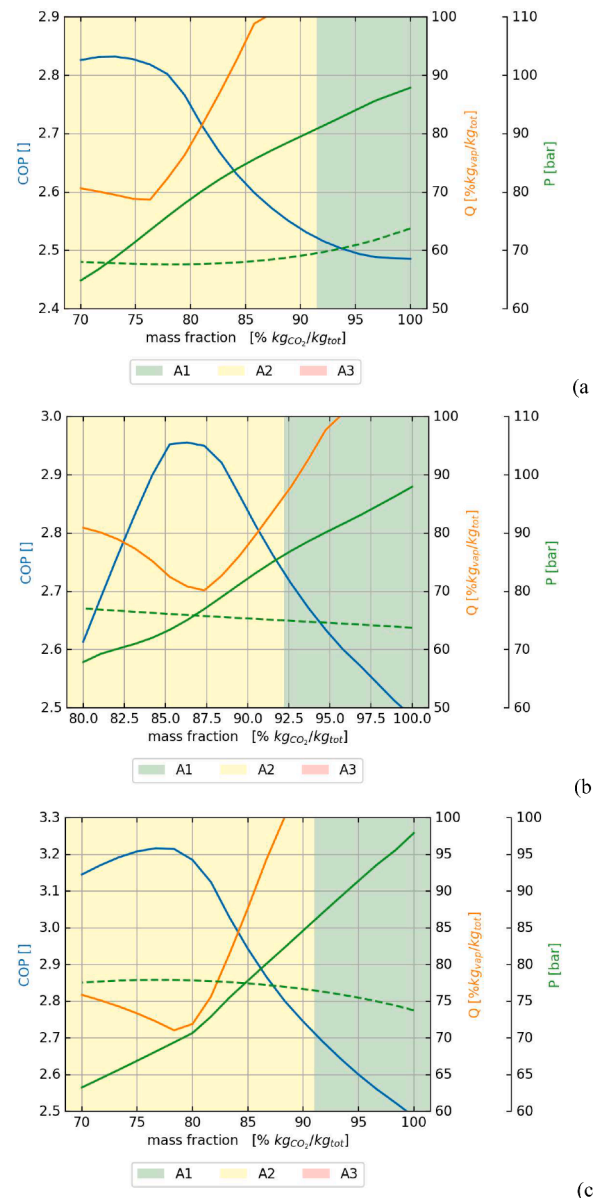


Fig. 9. Summary of results for mixtures of CO₂ and propane (a), isobutane (b), propylene (c).

a condenser exit temperature of 30°C has been chosen.

According to the findings reported in the previous section, only mixtures of CO₂ and DME are used. For an easy comparison, the results for condenser exit temperature of 40°C already shown in Fig. 7 are copied in the middle part of Fig. 10 on the same range of mass fractions. The first evident feature is the downward movement of the COP curve (the blue one) going from the top graph to the bottom one.

Moreover, the optimum mass fraction of DME moves to the left, i.e. more added fluid is required if the condenser exit temperature (i.e. the ambient temperature) is raised. This may be understood considering that, if point 3 of the cycle (exit of the condenser or gas cooler) moves upward and to the right, even considering the slight variations in the IHX operation, the whole expansion 4–5 moves rightward. Therefore, the evaporation 5–0 is shortened and a higher fraction of DME is required to give the assumed 5°C glide.

The top graph in Fig. 10 shows that all the COP curve (blue line) is higher with respect to the one shown in the middle graph. This means that, for any mass fraction of DME, the reduced temperature at point 3 is highly beneficial. For example, if the system has been optimized for T₃

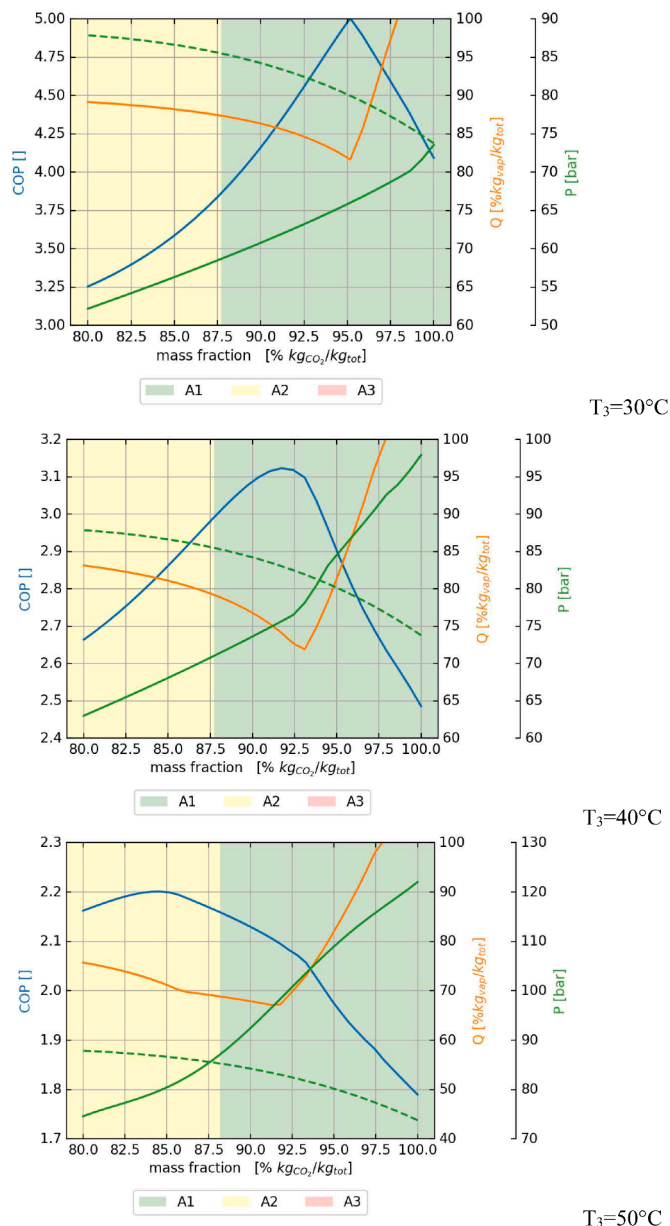


Fig. 10. Summary of results for CO₂/DME mixture as a function of condenser exit temperature.

= 40°C as in the middle graph in Fig. 10, the optimum CO₂ mass fraction is 91.92%, as already stated. If a system featuring this fluid composition is operated at T₃ = 30°C, the upper graph gives a COP of 4.46, which is not the absolute maximum (≈5) that would be reached with a mixture specifically optimized for T₃ = 30°C (i.e. CO₂ mass fraction = 95.15%), but is anyway significantly higher than any COP attainable with T₃ = 40°C.

On the opposite, as shown in the lowest graph in Fig. 10, if the condenser exit temperature is raised to 50°C, the COP lowers, showing a maximum of 2.2 for a mixture composition with about 85% of CO₂. This optimum is located in the yellow part of the diagram, which means that the mixture is flammable (A2 classification). The optimum gas cooler pressure is now around 80 bar, i.e. around 4 bar higher than that shown in the middle graph. Note that, while in the two uppermost diagrams the maximum COP is in the zone of the lowest vapour quality at evaporator exit (yellow curve), in the lowest graph the two points are located at different compositions.

As explained in the comment to Fig. 7, the minimum quality at

evaporator exit represents the optimum operation of the evaporator in terms of glide. In the case of the bottom graph in Fig. 10, this optimum corresponds to a very high condenser pressure, i.e. a very high compressor work. Apparently, this counterbalances the effect of the evaporator optimization and shifts the optimum mixture composition to the left. If the mixture is optimized for operating with T₃ = 40°C (i.e. CO₂ mass fraction 91.92%), the COP at T₃ = 50°C is further lowered to 2.1. Even so, this composition is preferable, as it gives a non-flammable working fluid. A potential drawback of this choice is that it gives a supercritical operation for high ambient temperature.

3. Conclusions

The thermodynamic analysis presented above shows that mixtures of CO₂ and organic compounds, such as propane, isobutane, DME and propylene, may increase the COP of refrigeration cycles thanks to a reduction of compression work and an improved temperature matching between the evaporating working fluid and a finite-heat-capacity heat source. The best results are obtained with a mixture of CO₂ with a 23% mass fraction of propylene, which guarantees a COP increase of 28%. However, this mixture, as well as those containing propane and isobutane, is highly flammable. Therefore, they may hardly compete with pure hydrocarbons, which give even higher performance.

On the other hand, adding CO₂ with 8% of DME gives a COP increase of 25%, but the mixture is non-flammable. Therefore, this mixture would represent a safe option, combining the advantages of CO₂ (low GWP, high volumetric cooling capacity) with good energy efficiency, even for a basic cycle comprising only an internal heat exchanger. By the way, DME has GWP=1, so that the direct emission term in the TEWI calculation for the CO₂/DME mixture is negligible. The 25% reduction in energy consumption with respect to pure CO₂ translates in an equal reduction of indirect emission (i.e. on the whole TEWI, direct emission being negligible). In other words, the proposed mixture would allow a low TEWI without requiring complicated plant layouts, even if, obviously, improved configurations may be explored. This result may be a first suggestion towards future experimental activity.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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4.3 Paper 3: Numerical assessment of CO₂-based mixtures for refrigeration systems: focus on the evaporation process

Considering the discussions presented in papers 1 and 2, which address evaporative heat exchange for both mixtures and pure fluids with a fixed pinch point, this paper aims to analyse the variations in the heat transfer coefficient on the refrigerant fluid side as the composition of a mixture changes, based on data available in the literature. For this analysis, the CO₂ and propane mixtures were selected due to the availability of experimental data in the literature [50] and [51,52]. As regards mixtures of CO₂ and DME, however, in the literature there are studies only with high quantities of DME [48].

The paper is structured into two parts: the first part compares various correlations for pure CO₂, and the second part focuses on CO₂ and propane mixtures. The objective is to elucidate the existing correlations by first evaluating their reliability using the extensive database for pure CO₂, and then assessing their predictive capability on the smaller database for mixtures through appropriate additional correlations. This comprehensive correlation analysis for pure CO₂ helps avoid errors due to the limited size of the database for mixtures, as the best correlation should perform well even for pure fluids.

This work can be useful for calculating the COP of a refrigeration system where the effects of the mixture on the evaporator are considered.

The Ph.D. candidate is the first author of this work and was mainly involved in modelling and calculation, Dr. Nicola Andreini helped with the bibliographic research and primarily wrote the paper, while the other contributors provided supervision.

Numerical assessment of CO₂-based mixtures for refrigeration systems: focus on the evaporation process

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ABSTRACT

A large number of refrigeration systems operate on a stream that is not changing phase, i.e. has a finite heat capacity. The matching between the cooled stream and the evaporation of a pure refrigerant causes therefore significant irreversibility in the heat exchange. The use of mixtures is a well-known option for the mitigation of this problem. In this work, the use of a CO₂-based mixture is proposed to allow the possibility of matching variable-temperature heat sources with the glide of the working fluid in the evaporator to minimize the heat exchange irreversibility. Modelling of a mini-channel evaporator by means of numerical techniques, accounting for the variable fluid composition, is presented. Several flow boiling correlations are assessed for pure CO₂ (170<G<900) and CO₂-propane blends (200<G<650). An optimized correlation for CO₂-propane is proposed. As a final result, a high fidelity CO₂ correlation for flow boiling is presented, which is also able to predict quite accurately the CO₂-propane mixture heat transfer coefficient.

Keywords: Refrigeration, Carbon Dioxide, COP, Evaporators, Energy Efficiency

1. INTRODUCTION

One of the most impacting losses in an inverse cycle is the heat exchange irreversibility taking place in evaporators and condensers. Usually, refrigeration cycles work with secondary fluids that do not change phase, therefore having a finite heat capacity. If the temperature profiles of the two fluids could therefore be matched, the irreversibility required for the heat exchange would be reduced to a minimum (Lorentz Cycle). Among all the possibilities, the most attractive way to minimize this irreversibility is to use zeotropic mixtures. Coupling environmental and efficiency needs, candidate mixtures should be based on a natural and safe refrigerant, such as carbon dioxide (CO₂). In the literature, the mixtures containing CO₂ have yet to be fully investigated. There are few studies in which CO₂ and Hydrocarbons (HCs) blends have been assessed. The mixing of CO₂ with HCs mitigates the shortcomings of using CO₂ and allows for lower cycle pressures, as well as an increase in the critical temperature which enables the possibility of subcritical cycles. This kind of mixture seems to be able to compete with the performance of the best HFCs, such as R32. Some investigations have been carried out both as experimental analysis Ju et al. (2018) and at system-level assessment Vaccaro et al., (2022) and Wang et al. (2021). Particularly, Ju et al. (2018) demonstrated that the achievable COP of the CO₂ – propane blend heat pump had similar values to those of an R22 heat pump. Also, Kim et al. (2008) investigated the CO₂ – propane blend, attaining interesting COP values. Wang et al. (2021) and Vaccaro et al. (2022) found that CO₂ blends could be a feasible solution to improve the efficiency of CO₂ systems. When focusing on the characterisation of such blends, even fewer studies are present in literature

that deal with CO₂ + another fluid with the aim of investigating their heat transfer properties. Only the CO₂ - propane blend has been partly assessed by Grauso et al. (2011), Cho et al. (2010) and Zhu et al. (2015) for the flow boiling.

The previous literature review highlights that the studies on CO₂-based mixtures are limited to a few other components and specific systems, while there are scarce investigations regarding the effective heat transfer characteristics of CO₂-based mixtures during evaporation. This paper aims to collect the available experimental data of CO₂ blends for flow boiling, assess the actual flow boiling correlations, both for pure and blended CO₂, and improve such correlations with a best-fitting methodology.

2. MIXTURE FLOW BOILING

Flow boiling heat transfer is composed of two main factors: nucleate boiling and convective boiling. In nucleate boiling, the heat-transfer mechanism is influenced by the vapour bubbles that form on the heat-transfer surface and then break away, grow, merge and collapse. Convective boiling is linked to the evaporation process happening at the vapor-liquid interface due to the convection heat transfer within the liquid flowing on the wall. These two driving forces of the phenomenon are hindered when zeotropic mixtures are taken into account, due to the renowned mass transfer resistance and the decline of effective superheat (Zhang et al., 2019). These issues are due to the difference in composition between vapour and liquid phases, which hinder correct evaporation of the pure fluid, due to the lower driving force which is the effective superheat of the vapour phase. Furthermore, the mass transfer resistance is due to the diffusion of the vapour phase of the more volatile component over the bubbles, which finds a higher resistance compared to the pure fluid. Moreover, the heat transfer degradation of the mixtures is also due to the reduced values of thermophysical properties compared to the ideal values and the increase of the bubble point temperature due to the different compositions of the phases. Finally, also the glide plays a role in the reduction of the HTC. Particularly, the glide is directly connected with the suppression of the nucleate boiling. Therefore, the higher the glide of the mixtures, the higher is the reduction of the nucleate boiling value and consequently lower the HTC of the mixture.

2.1. Overview of flow boiling heat transfer models

There are two main families of flow boiling heat transfer models. The first one is based on empirical correlations, which are derived from the fitting of experimental data through representative numbers that are related to the phenomena. Several correlations have been proposed by different authors, trying to properly describe the flow boiling in a wider range of parameters. Almost all of the correlations calculate the two-phase heat transfer coefficient as the sum of the nucleate boiling and convective boiling contributions. Some of the proposed correlations present in the literature have been used in this work and reported in Table 1.

Table 1. Resume of empirical correlations for pure fluids

Reference	Model		Range
Gungor and Winterton, 1986	$h_{tp} = F \cdot h_l + S \cdot h_{nb}$ $h_l = 0.023 \cdot Re_l^{0.8} \cdot \frac{k_l}{D_{eq}} \cdot Pr_l^{0.4}$ $h_{nb} = 55 \cdot p_r^{0.12} (-p_r)^{-0.55} \cdot M^{-0.5} \cdot q^{0.67}$	$F = 1 + 24000 \cdot Bo^{1.16} + 1.37 \cdot \left(\frac{1}{X_{tt}}\right)^{0.86}$ $S = \frac{1}{1 + 1.15 \cdot 10^{-6} \cdot F^2 \cdot Re_l^{1.17}}$ if $Fr < 0.05$ multiply F by $Fr^{0.12 \cdot Fr}$; $S = S \cdot Fr^{\frac{1}{2}}$	$-0.7^\circ C < T_{sat} < 364.9^\circ C$ $59.2 kg/m^2 s < G < 8179.3 kg/m^2 s$ $1.1 kW/m^2 < q < 2280.0 kW/m^2$ $2.95 mm < D < 32 mm$
Gungor and Winterton, 1987	$h_{tp} = F \cdot h_l$ $F = 1 + 3000 \cdot Bo^{0.86} + 1.12 \left(\frac{x}{1-x}\right)^{0.75} \cdot \left(\frac{\rho_l}{\rho_v}\right)^{0.41}$		Gungor Winterton 1986

Jung, 1988	$h_{tp} = S \cdot h_{nb} + F \cdot h_l$ $h_{nb} = 207 \cdot \frac{k_l}{b_d} \cdot \left(\frac{q \cdot b_d}{k_l \cdot T_{sat}} \right)^{0.745} \cdot \left(\frac{\rho_v}{\rho_l} \right)^{0.581} \cdot Pr_l^{0.533}$ $b_d = 0.0146 \cdot \theta \left(\frac{2 \cdot \sigma}{g \cdot (\rho_l - \rho_v)} \right)^{0.5} ; \theta = 35^\circ$	$h_l = 0.023 \cdot Re_l^{0.8} \cdot \frac{k_l}{D_{eq}} \cdot Pr_l^{0.4}$ $F = 2.37 \cdot \left(0.29 + \frac{1}{X_{tt}} \right)^{0.85}$ $S = 4048 \cdot x_{tt}^{1.22} \cdot Bo^{1.13} \text{ if } X_{tt} < 1$ $S = 2 - 0.1 \cdot x_{tt}^{0.28} \cdot Bo^{-0.33} \text{ if } 1 < X_{tt} < 5$	$0.08 < p_r < 0.16$ $250.0 \text{ kg/m}^2\text{s} < G < 720.0 \text{ kg/m}^2\text{s}$ $10.0 \text{ kW/m}^2 < q < 45.0 \text{ kW/m}^2$ $D = 9.1 \text{ mm}$
Liu and Winterton, 1991	$h_{tp} = ((Fh_l)^2 + (Sh_{nb})^2)^{\frac{1}{2}}$ $h_l = 0.023 \cdot Re_l^{0.8} \cdot \frac{k_l}{D_{eq}} \cdot Pr_l^{0.4}$ $F = 1 + x \cdot Pr_l \cdot \left(\frac{\rho_l}{\rho_v} - 1 \right)^{0.35}$	$h_{nb} = 55 \cdot p_r^{0.12} (-p_r)^{-0.55} \cdot M^{-0.5} \cdot q^{0.67}$ $S = (1 + 0.55 \cdot F^{0.1} \cdot Re_l^{0.16})^{-1}$	$12.4 \text{ kg/m}^2\text{s} < G < 8157 \text{ kg/m}^2\text{s}$ $3.5 \text{ kW/m}^2 < q < 2620 \text{ kW/m}^2$ $2.95 \text{ mm} < D < 32 \text{ mm}$
Wattelet J. P. et al., 1993	$h_{tp} = (h_{cb}^n + h_{nb}^n)^{\frac{1}{n}} \quad n = 2.5$ $h_{nb} = 55 \cdot p_r^{0.12} (-p_r)^{-0.55} \cdot M^{-0.5} \cdot q^{0.67}$ $h_{cb} = F \cdot h_l \cdot R$ $h_l = 0.023 \cdot Re_l^{0.8} \cdot \frac{k_l}{D_{eq}} \cdot Pr_l^{0.4}$	$F = 1 + 1.925 \cdot X_{tt}^{-0.83}$ $X_{tt} = \left(\frac{1-x}{x} \right)^{0.9} \cdot \Omega$ $\Omega = 0.551 \cdot Pr_l^{0.492}$ $R = 1.32 \cdot Fr_l^{0.2} \text{ if } Fr_l < 0.25$ $R = 1 \text{ if } Fr_l \geq 0.25$	$D = 7.04 \text{ mm}$ $25 \text{ kg/m}^2\text{s} < G < 100 \text{ kg/m}^2\text{s}$ $2 \text{ kW/m}^2 < q < 10 \text{ kW/m}^2$ $-15^\circ\text{C} < T_{sat} < 5^\circ\text{C}$
Choi et al., 2007	$h_{tp} = S \cdot h_{nb} + F \cdot h_l$ $F = 0.042 \cdot \phi_f^2 + 0.958$ $\phi_f^2 = 1 + \frac{C}{X_{tt}} + \frac{1}{X_{tt}^2}$	$X_{tt} = \left(\frac{\mu_f}{\mu_g} \right)^{\frac{1}{8}} \cdot \left(\frac{1-x}{x} \right)^{\frac{7}{8}} \cdot \left(\frac{\rho_g}{\rho_f} \right)^{\frac{1}{2}}$ $h_{nb} = 55 \cdot p_r^{0.12} \cdot (-4343 \cdot \ln p_r)^{-0.55} \cdot M^{-0.55} \cdot q^{0.67}$ $S = 469.1689 \cdot (\phi_f^2)^{-0.2093} \cdot Bo^{0.7402}$	$10 \text{ kW/m}^2 < q < 40 \text{ kW/m}^2$ $200 \text{ kg/m}^2\text{s} < G < 600 \text{ kg/m}^2\text{s}$ $1.5 \text{ mm} < D < 3 \text{ mm}$ $T_{sat} = 10^\circ\text{C}$

The second family of models is not based on empirical data, but on flow pattern maps. These models, therefore, take into account mathematical relations to describe the flow structure evolution during the flow boiling process of the fluid. In this work, the Cheng (2008) model has been considered. Table 2 resumes the main equations of the model.

Table 2. Cheng flow pattern model for pure fluids

Reference	Model		Range
Cheng et al., (2008)	$h_{tp} = \frac{\theta_{dry} h_v + (2\pi - \theta_{dry}) h_{wet}}{2\pi}$ $\theta_{dry} = 0 \text{ if anular regime}$ $\theta_{dry} = \theta_{strat} \left(\frac{G_{wavy} - G}{G_{wavy} - G_{strat}} \right)^{0.61} \text{ if stratified-wavy zone}$ $\theta_{dry} = \theta_{strat} \left(\frac{x}{x_{IA}} \left(\frac{G_{wavy} - G}{G_{wavy} - G_{strat}} \right) \right)^{0.61} \text{ if slug-stratified wavy zone}$ $h_v = 0.023 Re_v^{0.8} Pr_v^{0.4} \frac{k_v}{D_{eq}}$ $\text{if } x < x_{IA}, \quad S = 1$ $\text{else, } S = 1 - 1.14 \left(\frac{D_{eq}}{0.00753} \right)^2 \left(1 - \frac{\delta}{\delta_{IA}} \right)^{2.2}$	$h_{wet} = [(Sh_{nb})^3 + h_{cb}^3]^{1/3}$ $h_{nb} = 131 p_r^{-0.0063} (-p_r)^{-0.55} M^{-0.5} q^{0.58}$ $Re_\delta = \frac{4G(1-x)\delta}{(1-\epsilon)\mu_l}$ $h_{cb} = 0.0133 Re_\delta^{0.69} Pr_l^{0.4} \frac{k_l}{\delta}$ $h_M = 2 \times 10^{-8} Re_H^{1.97} Pr_V^{1.06} Y^{-1.83} \frac{k_V}{D_{eq}}$ $h_{dryout} = h_{tp}(x_{di}) - \frac{x - x_{di}}{x_{de} - x_{di}} [h_{tp}(x_{di}) - h_M(x_{de})]$	$0.6 \text{ mm} < D < 10 \text{ mm}$ $50 \text{ kg/m}^2\text{s} < G < 1500 \text{ kg/m}^2\text{s}$ $1.8 \text{ kW/m}^2 < q < 46 \text{ kW/m}^2$ $0.21 < p_r < 0.87$ $-28^\circ\text{C} < T_{sat} < 25^\circ\text{C}$

To apply the models developed for the pure fluids, a correction factor is added to take into account the mixture effects. Particularly, two mixture correction factors, S_{mix} and F_{mix} are introduced. The first one is to correct the nucleate boiling contribution, while the second one is to modify the convective boiling contribution. Equation 1 represents the final HTC of the mixture. The mixture correlations present in the literature that have been used in this work are reported in Table 3.

$$h_{tp} = S_{mix} \cdot Sh_{pool} + F_{mix} \cdot Fh_l \quad \text{Eq. (1)}$$

Table 3. Flow boiling mixture correction factors

Reference	Model	Range
Thome and Shakir, 1987	$\frac{h}{h_i} = S_{TS} = \left(1 + \left(\frac{h_i}{q} \right) \cdot (T_{dew} - T_{bub}) \cdot \left(1 - \exp \left(\frac{-Bq}{\rho_f \cdot \Delta i_{lv} \cdot \beta_f} \right) \right) \right)^{-1}$	glide < 30°C
Jung et al., 1989	$h_{tp} = \frac{S}{C_{UN}} \cdot h_{nb} + C_{me} \cdot F \cdot h_i$ $S = 4048 \cdot x_{tt}^{1.22} \cdot BO^{1.13} \text{ if } X_{tt} < 1$ $S = 2 - 0.1 \cdot X_{tt}^{-0.28} \cdot BO^{-0.33} \text{ if } 1 < X_{tt} < 5$ $X_{tt} = \left(\frac{\mu_l}{\mu_v} \right)^{0.1} \cdot \left(\frac{1-x}{x} \right)^{0.9} \cdot \left(\frac{\rho_v}{\rho_l} \right)^{0.5}$ $C_{me} = 1 - 0.35 \bar{Y} - \bar{X} ^{1.56}$ $F = 2.37 \cdot \left(0.29 + \frac{1}{X_{tt}} \right)^{0.85}$ $C_{UN} = (1 + (b_2 + b_3) \cdot (1 + b_4)) \cdot (1 + b_5)$ $b_2 = (1 - X) \ln \left(\frac{1.01 - \bar{X}}{1.01 - \bar{Y}} \right) + X \cdot \ln \left(\frac{\bar{X}}{\bar{Y}} \right) + \bar{Y} - \bar{X} ^{1.5}$ $b_3 = 0 \text{ if } \bar{X} \geq 0.01$ $b_3 = \left(\frac{\bar{Y}}{\bar{X}} \right)^{0.1} - 1 \text{ if } \bar{X} < 0.01$ $b_4 = 152 \cdot \left(\frac{p}{p_{cnvc}} \right)^{3.9}$ $b_5 = 0.92 \cdot \bar{Y} - \bar{X} ^{0.001} \cdot \left(\frac{p}{p_{cnvc}} \right)^{0.66}$	$250 \text{ kg/m}^2\text{s} < G < 720 \text{ kg/m}^2\text{s}$ $2^\circ\text{C} < T_{sat} < 9^\circ\text{C}$ $10 \text{ kW/m}^2 < q < 45 \text{ kW/m}^2$ $p_r < 0.08$
Wettermann and Steiner, 2000	$h_{tp} = (h_{nb}^3 + h_{cb}^3)^{\frac{1}{3}}$ $h_{cb} = h_{lo} \left((1-x)^{0.01} \cdot \left((1-x) + 1.2 \cdot x^{0.4} \cdot \left(\frac{\rho_l}{\rho_v} \right)^{0.37} \right)^{-2.2} + x^{0.01} \cdot \left(\frac{h_{vo}}{h_{lo}} \cdot \left(1 + 8(1-x)^{0.7} \cdot \left(\frac{\rho_l}{\rho_v} \right)^{0.67} \right) \right)^{-2} \right)^{-0.5}$ $h_{nb} = h_{eff} \left(1 + \frac{h_{eff}}{q} \cdot \Delta T_{bp} \right)^{-1}$ $h_{eff} = h_{id} \left(1 - 0.25 \left(\frac{q}{q_{cr,nb}} \right)^{1.5} \right)^{215 \left(\frac{\Delta T_{bp}}{T_{cr,max} - T_{cr}} \right)}$ $q_{cr,nb} = 2.79 \cdot q_{0,cr,nb} \cdot p_r^{0.4} \cdot (1 - p_r)$ $q_{0,cr,nb} = 0.13 \cdot \Delta i_{lv} \cdot \rho_v^{0.5} \cdot (\sigma \cdot g \cdot (\rho_l - \rho_v))$	$80 \text{ kg/m}^2\text{s} < G < 400 \text{ kg/m}^2\text{s}$ $D < 14 \text{ mm}$, glide < 30°C $1.3 \text{ kW/m}^2 < q < 70 \text{ kW/m}^2$
TSBG (Shah, 2015)	$h_{tp,mix} = S_{TS} \cdot S \cdot h_{nb} + \left(\frac{1}{h_{mix}} \right)^{-1}$ $S_{TS} = \left(1 + \left(\frac{h_{nb}}{q} \right) \cdot (T_{dew} - T_{bub}) \cdot \left(1 - \exp \left(\frac{-Bq}{\rho_f \cdot \Delta i_{lv} \cdot \beta_f} \right) \right) \right)^{-1}$ $\frac{1}{h_{mix}} = \frac{1}{E \cdot h_{cb}} + \frac{Y}{h_{GS}}$ $Y = x \cdot C_{pg} \cdot \frac{dT_{DEW}}{dH}$	$50 \text{ kg/m}^2\text{s} < G < 930 \text{ kg/m}^2\text{s}$ glide < 30°C $0.05 < p_r < 0.65$ $0.19 \text{ mm} < D < 14 \text{ mm}$

3. EXPERIMENTAL DATABASE COLLECTION

The development of a new correlation for the heat transfer coefficient is a multi-step process that involves the collection and analysis of data, the development of a database to store and organize the data, and the use of mathematical methods to develop a new correlation. The goal of this process is to provide a simple and accurate model that can be used to predict the heat transfer coefficient in various engineering applications. In this case, a database of experimental measurements available in the literature was collected.

For each dataset shown in Table 4, heat transfer coefficient values were extracted as a function of vapor quality x , varying: channel diameter D , flow rate G , external heat flux q , and saturation temperature T_{sat} . The constructed database was used to evaluate the accuracy, in terms of mean error and mean absolute error, of correlations found in the literature and to develop a new predictive method based on flow pattern maps. By using flow pattern maps as a basis for the predictive method, the new correlation takes into account the influence of the flow regime on the heat transfer process, which can provide a more accurate prediction of the heat transfer coefficient. The database contains 10 experimental campaigns from various research groups and consists of 1350 points. It includes channel diameters ranging from 4 mm to 7.75 mm with mass fluxes ranging from 170 kg/m²s to 900 kg/m²s, saturation temperature ranging from -5°C to 20°C, heat fluxes ranging from 5 kW/m² to 60 kW/m² and CO₂ mass fraction ranging from 25% to 100%.

Table 4. Database of experimental studies on flow boiling of CO₂ and CO₂-propane blend

Reference	Fluid	Temperature [C]	Mass Flux [kg/(m ² s)]	Heat Rate [kW/m ²]	Diameter [mm]
Yun et al., 2003	CO ₂	5, 10	170, 240, 340	10, 15, 20	6
Yoon et al., 2004	CO ₂	0, 5, 10, 15, 20	318	12.5, 16.4, 18.6	7.53
Cho and Kim, 2007	CO ₂	0, 5, 10, 20	212, 424, 656	6, 12, 16, 20	7.72, 4
Oh et al., 2008	CO ₂	-5, 0, 5	200, 300, 400, 500	10, 20, 30	7.75
Oh and Son, 2011	CO ₂	5, 10, 15, 20	400, 600, 700, 800, 900	20, 30, 40	4.57
Mastrullo et al., 2012	CO ₂	7	200, 350	20, 5	6
Grauso et al., 2013	CO ₂	7	200, 265, 354, 371, 501, 526	5, 20	6
Cho et al., 2010	CO ₂ /R290 25-75% CO ₂	-5, 0	212, 424, 530, 656	15, 30, 45, 60	5
Grauso et al., 2011	CO ₂ /R290 70-83.2% CO ₂	7, 9.4, 12, 14	200, 350	10, 20	6

4. Proposed improved model

To develop a general flow boiling heat transfer prediction method, it is necessary to consider not only numerical accuracy but also the ability to follow the trends in data. Two approaches can be used to construct a one-dimensional evaporator model, the first involving the use of empirical correlations that are based purely on experimental data and do not provide a physical explanation for the underlying mechanisms of flow boiling. Empirical correlations are often limited in their accuracy and are only applicable over a limited range of conditions. The second approach involves the use of models built on flow pattern maps. These models can provide a more general and physically-based description of the flow boiling process, thanks to them it is possible to predict the transitions between different flow patterns, such as annular flow, intermittent flow, and mist flow, based on the fluid properties, channel dimensions, and inlet conditions. We considered as a starting point the model developed by Cheng et al. (2008), in which three modifications were introduced to make it efficient and accurate for channels larger than 3mm in diameter:

- Starting from the flow pattern maps obtained from the experimental set, it was seen that in all cases the value of heat transfer contribution due to convective boiling was overestimated so a suppressive coefficient was introduced.
- We then postponed dry out point by changing the curves of the dry-out and mist region, in accordance with the flow pattern maps of the dataset
- S_0 coefficient responsible for the starting value of nucleate boiling was changed. This is because, from comparison with experimental data, Cheng's model tends to overestimate the heat transfer coefficient in the early part of the annular evaporation regime for diameters larger than 3 mm.

The heat transfer coefficient on the wet perimeter, h_{tp} , is calculated as a third-order averaging combination of the two contributions, the nucleate boiling and the convective boiling properly corrected with two suppression factors S and F .

$$h_{tp} = [(Sh_{nb})^3 + Fh_{cb}^3]^{1/3} \quad \text{Eq. (2)}$$

where h_{nb} , S and h_{cb} , F are respectively nucleate boiling heat transfer coefficient, nucleate boiling heat transfer suppression factor, convective boiling heat transfer coefficient, and convective boiling heat transfer suppression factor. The suppressive coefficient F was introduced to limit the growth of convective heat transfer h_{cb} . The suppressive coefficient S was introduced to limit the growth of convective heat transfer

h_{nb} , which has exponential behavior as vapor quality increases. For diameters greater than 3mm, the formation of vapor along the channel walls creates a thermal barrier that inhibits heat transfer. For F , the correlation of Jung, (1988) was chosen.

These terms are defined as resumed in Equations 3-5. Particularly, Eq. 4 is the Dittus-Boelter equation, different from the one used in Cheng et al., 2008, because the dependency from the void fraction would greatly increase the h_{cb} when the quality is high, bringing inaccuracy to the correlation.

$$h_{nb} = 131(-p_r)^{-0.615} \log(p_r)^{-0.55} M^{-0.5} q^{0.55} \quad \text{Eq. (3)}$$

$$h_{cb} = 0.023 \cdot Re_l^{0.8} \frac{k_l}{D_{eq}} Pr_l^{0.4} \quad \text{Eq. (4)}$$

$$F = 2.37 \cdot \left(0.29 + \frac{1}{x_{tt}}\right)^{0.8} \quad \text{Eq. (5)}$$

In the region before the transition from intermittent to annular, the nucleate boiling suppression term was imposed as 0.8, as suggested by Wojtan et al., (2005). This is because it is observed, from the experimental data taken as reference, that the heat transfer in the first phase of boiling is less than that predicted by Cheng's correlation. The heat transfer coefficient in mist flow was not calculated through the equation proposed by Cheng et al., 2008, but the one proposed by Wojtan et al., (2005).

$$\text{if } x < x_{IA}, S = 0.8$$

$$x \geq x_{IA}, S = 0.8 - 1.14 \left(\frac{D_{eq}}{0.00753}\right)^2 \left(1 - \frac{\delta}{\delta_{IA}}\right)^{2.2} \quad \text{Eq. (6)}$$

Subsequently, to the modification of the heat transfer coefficients, a revision of the boiling regime curves proposed by Cheng et al., (2008) was performed. The reconstruction of the flow pattern maps on the experimental dataset showed that the dry-out and mist curves constructed by Cheng et al. (2008) for geometries smaller than 3 mm, greatly anticipate the transition point of the dry-out. This leads to high errors and poor predictive results for the geometries treated in this work. For this reason, the dry-out and mist curves were recalculated and the values follow these correlations:

$$q_{crit} = 0.131 \cdot \rho_v^{0.5} \cdot \Delta i_{lv} \cdot [g \cdot \sigma \cdot (\rho_l - \rho_v)]^{0.25} \quad \text{Eq. (7)}$$

$$G_{dryout} = \left\{ \frac{1}{0.08} \left[\ln\left(\frac{0.58}{x}\right) + 0.52 \right] \left(\frac{D_{eq}}{\rho_v \sigma}\right)^{-0.17} \left[\frac{1}{g D_{eq} \rho_v (\rho_l - \rho_v)} \right]^{-0.17} \left(\frac{\rho_v}{\rho_l}\right)^{-0.25} \left(\frac{q}{q_{crit}}\right)^{-0.27} \right\}^{1.471} \quad \text{Eq. (8)}$$

$$G_M = \left\{ \frac{1}{0.3} \left[\ln\left(\frac{0.61}{x}\right) + 0.57 \right] \left(\frac{D_{eq}}{\rho_v \sigma}\right)^{-0.16} \left[\frac{1}{g D_{eq} \rho_v (\rho_l - \rho_v)} \right]^{-0.15} \left(\frac{\rho_v}{\rho_l}\right)^{0.09} \left(\frac{q}{q_{crit}}\right)^{-0.72} \right\}^{1.613} \quad \text{Eq. (9)}$$

The coefficients of terms G_{dryout} , G_M , h_{cb} were obtained through gradient-based optimization to reach a smaller mean error over the whole dataset.

Starting from the correlation developed for CO₂ alone, we introduced modifications to account for the composition of the mixture and the glide effect. In particular, the study focused on CO₂ propane mixtures, and the data obtained by correlation were compared with 2 datasets found in the literature (unfortunately, to the best of our knowledge, other data regarding CO₂-based mixtures are not available in the literature). The dataset developed by Zhu et al., (2015) was not assessed due to the excessively small dimension of the channel (2 mm), while in this study we focus on mini-channels ($d_e > 4$ mm).

The calculation method proposed in this paper involves modification of the Shah (2015) model in which two terms are combined, respectively: the Thome-Shakir term for the nucleate boiling contribution and the Bell-Ghaly term for the convective boiling contribution. Two significant corrections have been proposed:

- The dry-out region was removed because, in the experimental data concerning the mixtures, there was no clear evidence of the dry-out zone;

- Although the TSBG correlation proposed by Shah, (2015) returns better values in terms of mean trend, it tends to underestimate the contributions of nucleate boiling and convective boiling in certain regions. For this reason, we proposed to use a weighted average (Eqns. 10-12) for the reduction rates of the two boiling contributions mentioned above.

$$c = \frac{Sh_{nb}}{Sh_{nb} + Fh_{cb}} \quad \text{Eq. (10)}$$

$$F_c = \left(1 + c \left(\frac{h_{nb}}{\dot{q}} \right) \cdot (T_{dew} - T_{bub}) \cdot \left(1 - \exp \left(\frac{-Bq}{\rho_f \cdot \Delta t_{lv} \cdot \beta_f} \right) \right) \right)^{-1} \quad \text{Eq. (11)}$$

$$Y = (1 - c) \cdot x \cdot C_{pv} \cdot \frac{dT_{dew}}{dH} \quad \text{Eq. (12)}$$

5. Results

5.1. Pure CO₂

The first step to understanding the effectiveness of the proposed modification to the correlation is to compare the predicted results from the proposed model with experimental data. This has been done, not only for the proposed model but also for every correlation implemented within the code. Fig. 1 displays the discrepancy between the predicted HTC and the experimental one, for the proposed model (a), for the modified Gungor and Winterton, (1987) (b), for Jung (1988) (c), and for Cheng et al., (2008) (d) models. A different symbol is provided for each experimental dataset. As can be seen in Fig. 1a and 1b for the proposed model and the modified Gungor and Winterton (1987) one, almost all data are within the $\pm 30\%$ “fork” normally used as an acceptance criterion in the literature. The modification that has been proposed for Gungor and Winterton, (1987) is quite simple and consists in multiplying such model by a 1.3 factor. This has been proposed due to the analysis of data which allowed us to understand that, for this dataset, the Gungor and Winterton, (1987) model had an offset that required a correction. It is interesting to note how Cheng et al. (2008) predicts also quite well the experimental dataset, but there are several points outside the $\pm 30\%$ “fork”, mainly due to the incorrect early prediction of dry-out.

Table 2 displays the comparison of all of the assessed correlations, from a statistical point of view. Particularly, the relative error ε , the absolute relative error $|\varepsilon|$, the percentage of points with a relative error between $\pm 30\%$, λ_{30} and the standard deviation of relative errors σ_{st} , have been chosen as representative parameters to understand the effectiveness of the correlations. As can be noted, the proposed model is the one with the lowest absolute relative error of about 28% and is also the one with the highest number of points within the $\pm 30\%$ “fork”, with a value of 64%. Following the proposed model, the modified Gungor and Winterton, (1987) provides very accurate results, while, without the modification, it loses in accuracy, increasing the absolute relative error from 30% to about 39%. The correlations with the highest absolute relative error resulted to be the Wetterman and Steiner, (2000). This can be justified as this correlation has been developed specifically for mixtures and it does not perform well with pure fluids.

The final step to check the accuracy of the correlation is to compare the predicted results with the experimental one, not only from a statistical mean but also by looking at the effective trend during an evaporation process. Figure 2 shows four different experimental dataset points where the trend of the best correlation is compared to the trend of the experimental data. As can be seen, the proposed model (purple line) has a similar trend to the original Cheng et al., (2008), but with a better prediction of the trend, thanks to the improvement in the dry-out region and the introduced nucleate boiling suppression factor. Through this correction, the proposed model seems to follow well the experimental data trend.

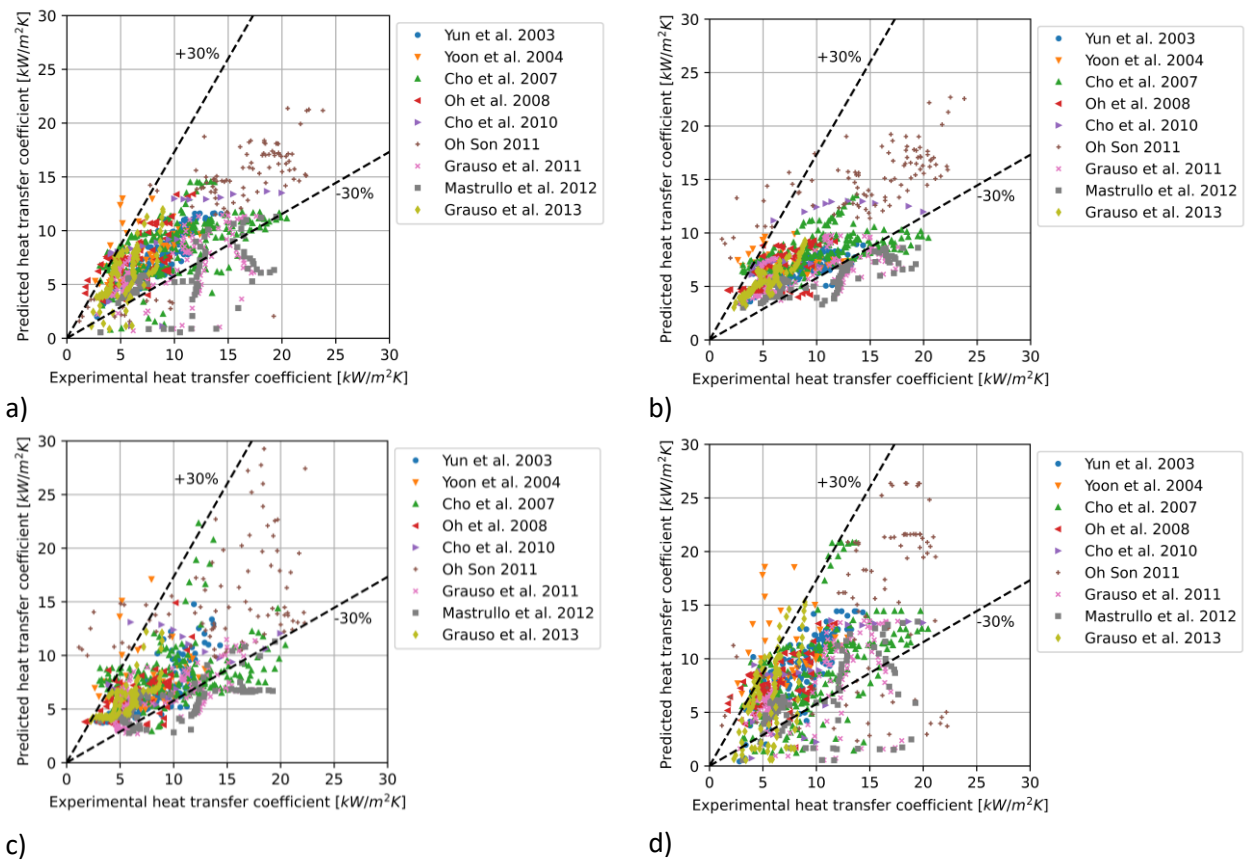


Figure 1: Comparison of the predictions and experimental data: a) Proposed Model, b) Modified Gungor and Winterton (1987) multiplied for a 1.3 factor, c) Jung, (1988), d) Cheng et al., (2008).

Table 5. Comparison of the predictions and experimental data of all implemented correlations.

	ε	$ \varepsilon $	λ_{30}	σ_{std}
Proposed model	-0.029	0.279	0.644	0.378
Modified Gungor and Winterton, 1987	-0.022	0.309	0.623	0.509
Gungor and Winterton, 1986	-0.017	0.359	0.521	0.595
Cheng et al., 2008	-0.249	0.365	0.399	0.391
Jung, 1988	0.207	0.375	0.612	0.629
Gungor and Winterton, 1987	0.086	0.386	0.534	0.544
Liu and Winterton, 1991	0.305	0.478	0.570	0.983
Choi et al., 2007	0.241	0.511	0.510	1.236
Wattelet J. P. et al., 1993	0.565	0.644	0.489	1.215
Wetterman and Steiner, 2000	0.510	0.639	0.448	1.191

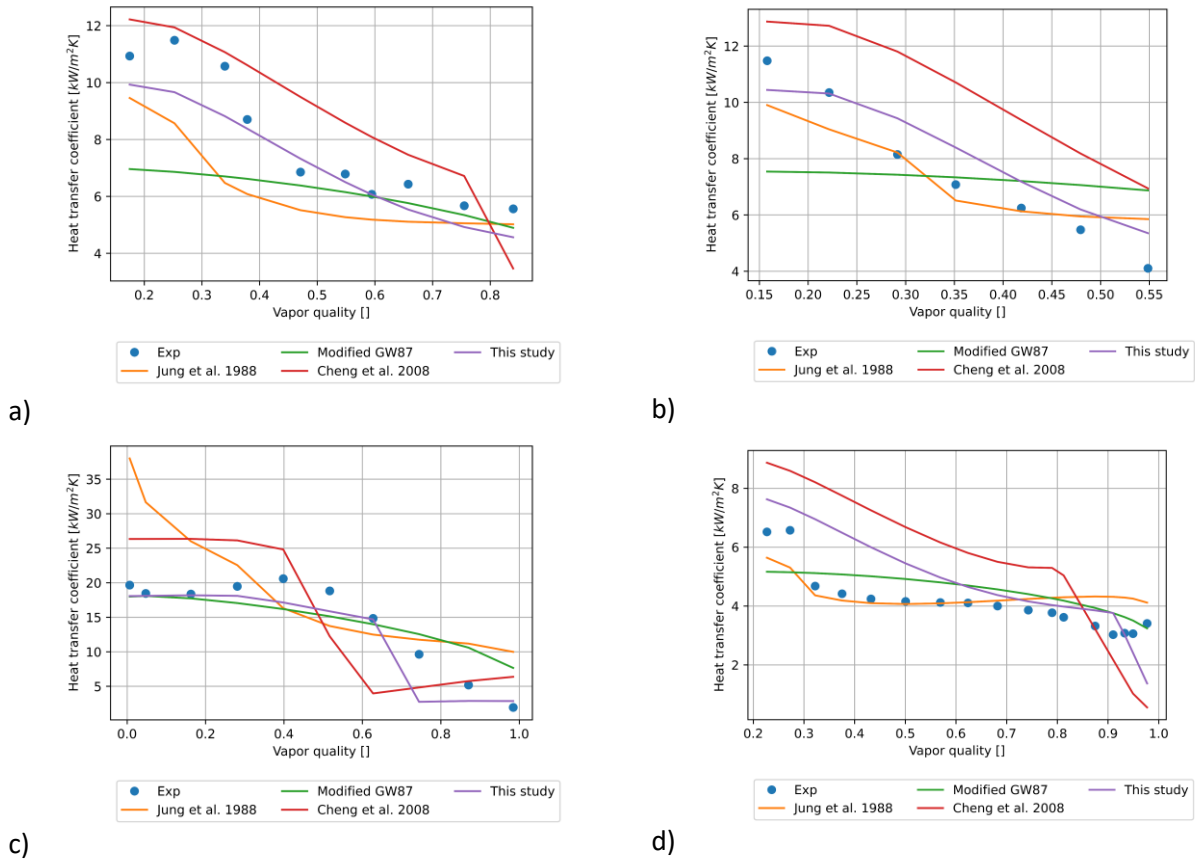


Figure 2: Comparison of the trend of predictions and experimental data:

- a) Data from Yun et al., 2003, $T=10^{\circ}\text{C}$, $G=240 \text{ kg/m}^2\text{s}$, $q=15 \text{ kW/m}^2$, $D_{eq} = 0.006 \text{ m}$, $\%CO_2 = 100\%$,**
- b) Data from Yoon et al., 2004, $T=10^{\circ}\text{C}$, $G = 318 \text{ kg/m}^2\text{s}$, $q=16.4 \text{ kW/m}^2$, $D_{eq} = 0.00753 \text{ m}$, $\%CO_2 = 100\%$,**
- c) Data from Oh et al., 2008, $T=20^{\circ}\text{C}$, $G = 800 \text{ kg/m}^2\text{s}$, $q = 40 \text{ kW/m}^2$, $D_{eq} = 0.00457 \text{ m}$, $\%CO_2 = 100\%$,**
- d) Data from Grauso et al., 2013 $T=7^{\circ}\text{C}$, $G = 201 \text{ kg/m}^2\text{s}$, $q = 10.1 \text{ kW/m}^2$, $D_{eq} = 0.006 \text{ m}$, $\%CO_2 = 100\%$.**

5.2. CO_2 -Propane Mixture

Once the comparison with the pure fluid was performed, the next step was to add a further piece to the correlation that would be able to accurately predict also the mixture heat transfer coefficient. The first step was to add the mixture corrections proposed by Thome and Shakir (TS) and Thome Shakir Bell-Ghaly (TSBG), as discussed in Shah, (2015). These corrections have been applied both to the proposed model and to the modified Gungor and Winterton, (1987). The TS correction is good in terms of average deviation, however, it provides a high decrease in the nucleate contribution without affecting the convective one. This leads to a decrease in the HTC only for low-quality values, while for high-quality values the HTC rises. The TSBG correction, although it returns improving trends, overall underestimates the results, therefore the use of a weighting coefficient for the reduction of the 2 contributions has been introduced. With this new modification, the proposed model with the TSBG-M correction provides results that are in line with the best-performing correlations, which are the Wetterman and Steiner, (2000) and the modified Gungor and Winterton, (1987). However, as can be noted from Table 5, the absolute relative error for all correlations is quite higher if compared with the pure fluid results. It is interesting to note how the best correlation, in this case, is the Wetterman and Steiner, (2000), which was the worst for the pure fluid. Finally, also for the mixtures, the comparison of the predicted HTC with the experimental trend during an evaporation process was evaluated. Figure 3 shows four different experimental dataset points where the trend of the best correlation is compared to the trend of the experimental data. As can be noted, the proposed model follows quite well the experimental data of the Grauso et al., (2013) dataset, while (similarly to all other correlations), does not manage to properly match the experimental data trend. It is indeed to quote that there are several uncertainties in the datasets, especially the ones with mixtures. It is therefore difficult to provide a consistent reliable correlation able to match all datasets.

Table 6. Comparison of the predictions and experimental data of all implemented correlations for the CO₂-Propane Dataset.

	ε	$ \varepsilon $	λ_{30}	σ_{std}
Wetterman and Steiner, 2000	-0.075	0.355	0.443	0.411
Modified Gungor and Winterton, 1987 - TSBG	-0.211	0.365	0.376	0.382
Proposed model TSBG-M	-0.142	0.370	0.394	0.412
Jung, 1989	0.038	0.383	0.437	0.494
Proposed model TSBG	-0.302	0.394	0.385	0.355
Modified Gungor and Winterton, 1987 - TS	0.086	0.401	0.420	0.498
Proposed model TS	0.001	0.429	0.372	0.521

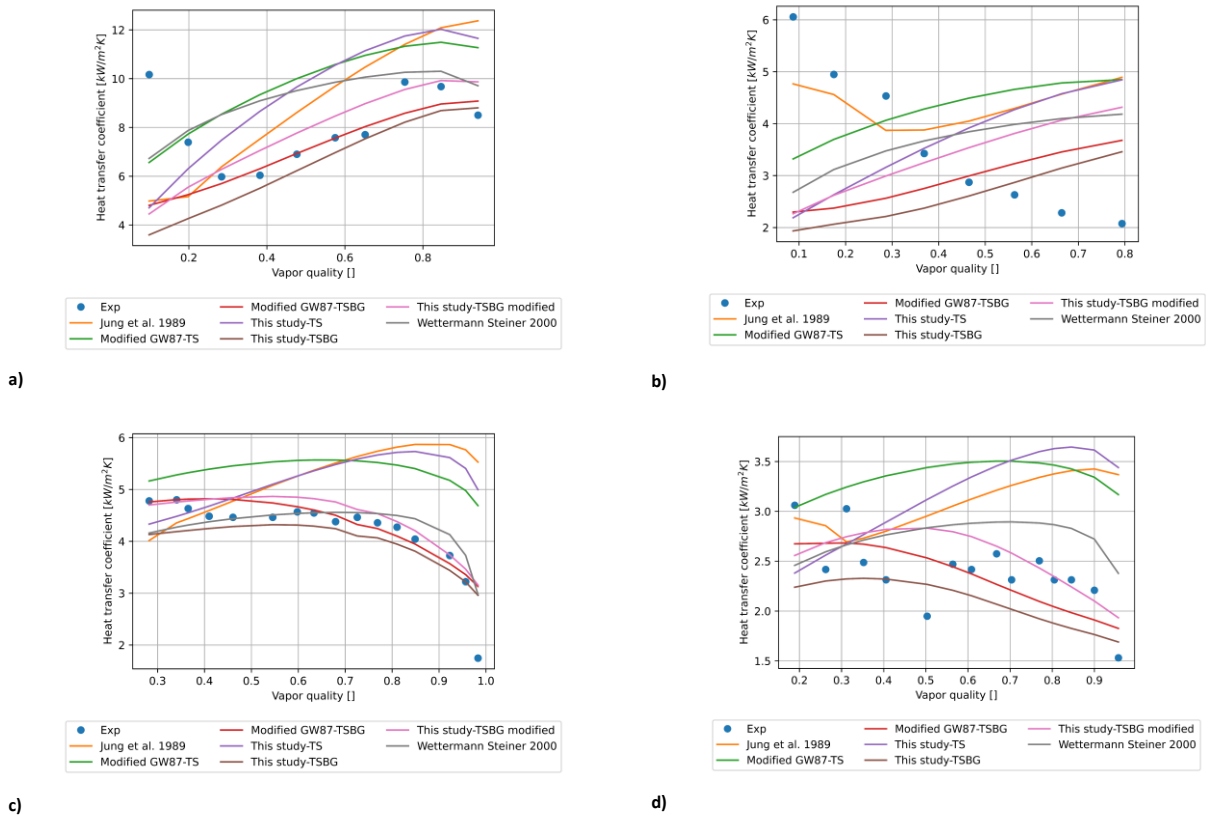


Figure 3: Comparison of the trend of predictions and experimental data:

- a) Data from Cho et al., 2010, T=-5°C, G = 656 kg/m²s, q = 30 kW/m², D_{eq} = 0.004 m, %CO₂ = 25%,
- b) Data from Cho et al., 2010, T=-5°C, G = 212 kg/m²s, q = 30 kW/m², D_{eq} = 0.004 m, %CO₂ = 25%
- c) Data from Grauso et al., 2013, T= 7.7°C, G = 350 kg/m²s, q = 10 kW/m², D_{eq} = 0.006 m, %CO₂ = 83%,
- d) Data from Grauso et al., 2013, T= 9.4°C, G = 200 kg/m²s, q = 10 kW/m², D_{eq} = 0.006 m, %CO₂ = 70%

6. CONCLUSIONS

A critical review and improvement of flow boiling correlations for CO₂ and CO₂-based mixtures were carried out in this work. A pivotal point of this research was the proper tuning procedure of the CO₂ pure fluid flow boiling model compared to the current literature: it did not only consider the flow pattern and empirical correlation models separately but tried to merge them, taking from the former one the physical phenomenon interpretation and from the latter one the required correction factors. Therefore, the key outcomes of the present work have general value and may be summarised as follows:

- A novel flow boiling correlation for CO₂ and CO₂ mixture has been proposed. The model tries to accurately predict the experimental data points of the dataset available in the literature.
- A weighting factor for the mixture correction coefficient was also proposed. Starting from an existing literature approach (Shah, 2015), the new one was generalized, considering the offset introduced by the “simple” addition of the Bell-Ghaly correction factor to the Thome-Shakir.
- Not only the overall fidelity of the prediction has been assessed, but also the trend of the data has been pursued as a characteristic to represent the effectiveness of the model.

As a final remark, the proposed model allowed for a mean error prediction for the pure CO₂ dataset of 28% and for the CO₂-propane dataset of 37%. For this reason, the present research might represent a significant contribution to improving the correlations for CO₂-based mixture.

NOMENCLATURE

Nomenclature

C_p	Specific heat at constant pressure
Bo	Boiling number
D_{eq}	Diameter (m)
F	Convective boiling enhancement factor
Fr	Froude number
G	Refrigerant mass flux (kg/(m ² s))
h	Local heat transfer coefficient (W/(m ² K))
k	Thermal conductivity (W/(m K))
M	Molecular weight (kg/kmol)
Pr	Prandtl
p_r	Reduced pressure
q	Heat flux (W/m ²)
Re	Reynolds number
S	Nucleate boiling suppression factor
T	Temperature (°C)
X_{tt}	Martinelli's parameter
x	Vapor quality
$\tilde{X}$	Liquid phase composition based on mole
$\tilde{Y}$	Vapor phase composition based on mole
Y	Factor in Bell-Ghaly method

Greek

ε	Cross-sectional vapor void fraction
---------------	-------------------------------------

ε_r	Relative error %
$ \varepsilon $	Mean error %
$\lambda_{30\%}$	Percentage of experimental points predicted within 30%
δ	Liquid film thickness (mm)
θ	Angle of tube perimeter (rad)
μ	Dynamic viscosity (Pas)
ρ	Density (kg m ³)
σ	Surface tension (N m ⁻¹)
σ_{std}	Standard deviation

Subscripts

A	annular
cb	convective boiling
$crit$	critical
de	dryout completion
di	dryout inception
I	intermittent
nb	nucleate boiling
l	liquid
M	mist flow
sat	saturation
tp	two-phase flow
v	vapor

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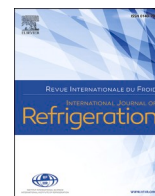
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4.4 Paper 4: Propylene and DME solubility in PAG oil: Experimental investigations and simplified modelling

This paper experimentally investigates the solubility of dimethyl ether (DME) and propylene in PAG oil. The experimental analysis revealed that DME has a greater solubility compared to propylene. Following this, the accuracies of various correlations were examined.

The Ph.D. candidate is the third author of this work and contributed to the post-processing of the data. He proposed an empirical correlation with six coefficients, which, for zero oil quantities, returns the value calculated by Refprop and has a derivative equal to zero. Empirical observations have shown that the derivative for zero oil concentrations tends to be zero.

These two properties ensure a monotonic trend of the curves and prevent significant errors for small oil concentrations. If we want to compare a refrigeration circuit without oil, calculated with Refprop, to one with small quantities of oil, a correlation that does not return Refprop results for zero oil concentrations would introduce errors. Additionally, if we could not guarantee a monotonic concentration curve around zero, the results could be contrary to expectations.



Propylene and DME solubility in PAG oil: Experimental investigations and simplified modeling[☆]

Solubilité du propylène et du diméthyle éther dans l'huile polyalkylène glycol : études expérimentales et modélisation simplifiée

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ABSTRACT

This work experimentally investigated the solubility of Propylene and Dimethyl Ether (DME) in polyalkylene glycol (PAG) oil. The solubility experimental data were used to fit different local composition models from the literature, the Wilson and Heil equations, and the Non-Random Two-Liquid (NRTL) model. Two new empirical correlations were proposed to decrease the deviation between experiments and the models. The first correlation used six fitting coefficients and resulted in an average deviation of 1.2 % for Propylene and 2.8 % for DME. The second empirical correlation was proposed with a single solubility coefficient (SSC) and a compact form, which allows solubility to be determined explicitly. The correlation resulted in average deviations from experimental data of 1.6 % for Propylene and 2.5 % for DME. Moreover, the SSC correlation showed performance robustness against the decrease of available data points. The correlation was used to compare the solubility of Propylene and DME with the solubility of Propane. At the same conditions, Propane showed the lowest solubility while DME resulted in the most soluble refrigerant.

1. Introduction

The developments of the F-gas regulation and the regulation on the registration, evaluation, authorisation and restriction of chemicals (REACH) are accelerating the adoption of natural refrigerants such as Propane, Isobutane, and CO₂ in heat pump and refrigeration applications. Hydrocarbons are increasingly being adopted in refrigeration and heat pump applications, also thanks to their good thermophysical properties and low Global Warming Potential (GWP). Their main drawback is flammability, which introduces limits to the allowed refrigerant charge in indoor applications, according to [International](#)

[Standard IEC 60335-2-40 \(2022\)](#). Maintaining the charge amount below four times the lower flammability limit of the refrigerant allows to avoid installation restrictions and additional safety measures. These charge limits are 152 g for Propane, 184 g for Propylene, and 256 g for Dimethyl Ether (DME).

[Fernando et al. \(2004\)](#) investigated the refrigerant solubility of propane in different oils in the oil sump of a Propane compressor. Propane and hydrocarbons were found to be highly soluble in most lubricants, and careful oil selection and oil quantity minimisation are fundamental to reducing the amount of refrigerant in the oil. [Sánchez-Moreno-Giner et al. \(2023\)](#) presented the results of the performance and refrigerant distribution of a Propane low-charge

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Nomenclature		(dimensionless or J/mol)	
<i>Symbols</i>		α	NRTL's non-randomness coefficient
p	Pressure (MPa)	r	Refrigerant
T	Temperature (K or °C)	φ	Fugacity coefficient
ρ	Density (kg/m ³)	<i>Acronyms and initialisms</i>	
σ	Standard deviation	NRTL	Non-Random Two-Liquid
B	Second virial coefficient (m ³ /kg)	COP	Coefficient of Performance
M	Mass (kg)	LFL	Low Flammability Limit
x	Molar concentration (mol/mol)	FS	Full Scale
X	Mass concentration (kg/kg)	GWP	Global Warming Potential
l	Liquid	SCC	Single Solubility coefficients
v	Vapor	MAPE	Mean Absolute Percentage Error
a	Coefficients for empirical correlations	RMSPE	Root Mean Squared Percentage error
a_1	Single solubility coefficient (1/K)	REACH	Regulation on the registration, evaluation, authorisation, and restriction of chemicals
R	Molar gas constant (8.314472 J mol ⁻¹ K ⁻¹)	sat	Saturation
V	Volume (m ³)	exp	Experimental
v	Molar volume (m ³ mol ⁻¹)	tot	Total
Λ	Interaction parameter		
τ	NRTL's binary adjustable interaction parameter		

brine-to-water heat pump. 41 % of the refrigerant was found in the compressor, mainly dissolved in the oil. One of the study's conclusions was that further charge reduction had to be focused on the charge stored in the oil, reducing solubility or oil quantity. Compressors designed with low oil amounts for use in low-charge Propane units were proposed by Gao et al. (2014) to reduce the refrigerant quantity absorbed by the lubricant. The adoption of polyalkylene glycol (PAG) oil allowed the reduction of solubility, as investigated by Ginies and Dewitte (2014). The solubility, viscosity and miscibility characteristics were compared with those of other lubricants. Polyolester (POE) oil has often been preferred to PAG thanks to its lower viscosity at low temperatures, lower film thickness and better performance, as investigated by Shi et al. (2022). Moreover, the same study found that under any condition, the oil sump solubility was uniform and was close to the oil sump inlet saturation solubility. PAG and POE lubricants are both synthetically produced. However, in general, the specific price of PAG oil is expected to be higher compared to POE oil. On the other hand, since PAG oil is usually adopted in low-charge systems, its quantity is often minimised. This may result in a reduction of the impact of the oil on the overall compressor cost. Nevertheless, PAG oil has been increasingly adopted by manufacturers of compressors for applications with low refrigerant charge.

The non-fluorinated refrigerants Dimethyl Ether (DME or R-E170) and Propylene (R-1270) were proposed by Granryd (2001) as long-term solutions among other hydrocarbons. DME is characterised by a high coefficient of performance (COP) and Propylene by a relatively high volumetric heating capacity. Another attractive characteristic of DME is the relatively high lower flammability level (LFL), when compared to Propane, allowing higher refrigerant charge limits. DME solubility in squalane was experimentally investigated by Sun et al. (2021). The author adopted the local composition Non-Random Two-Liquid model (NRTL) from Renon and Prausnitz (1968) and fitted it to experimental data. Wang et al. (Wang et al., 2021) adopted a similar experimental and modeling approach for Propane in mineral oils. Different thermodynamic local composition models were compared for multiple binary refrigerant-oil mixtures by Martz and Jacobi (1994) and Youbi-Idrissi (2003). Local composition models from Wilson and Wilson (1964), Heil and Prausnitz (1966) and Renon and Prausnitz (1968) were found to be able to reach a good level of accuracy.

As previously discussed, due to its lower solubility, PAG oil is particularly suitable for systems which aim to minimise refrigerant charge. This is an essential requirement of refrigeration equipment that

uses flammable refrigerants. PAG oil has also been adopted for CO₂ applications. Ikeda et al. (2004) evaluated the chemical and physical properties of different lubricants for CO₂. The study found that PAG was the most suitable oil for CO₂ applications. The reasons were suitable miscibility, higher chemical stability and improved lubricity under high pressure. While PAG was investigated and adopted for Propane and CO₂ applications, there is a lack of available experimental data on the interaction of PAG oils with other non-fluorinated refrigerants.

Despite the good accuracy, local composition models, commonly used for modeling refrigerant-oil solubility, also encounter some drawbacks. (i) They are semi-empirical models and rely on multiple coefficients. (ii) Their fitting requires refrigerant-lubricant solubility data that is time-consuming to obtain. (iii) The formulation of solubility is implicit. The coefficient fitting procedure, as well as the utilization of the fitted model, requires the adoption of iterative numerical methods. To incentivize the adoption of refrigerant-lubricant solubility models, the development of simplified and robust models with low implementation and execution time requirements may be needed.

This study is an extension of the work by Caramaschi et al. (2023). It investigated experimentally the solubility of the non-fluorinated refrigerants Propylene and DME in PAG oil. The newly obtained datasets were presented in tabular and graphical form. Local composition methods from Wilson and Wilson (1964), Renon and Prausnitz (1968) and Heil and Prausnitz (1966) were applied to fit the experimental data. Two new empirical correlations to characterize solubility as a function of pressure and temperature were proposed. A first correlation using six coefficients and a second simplified correlation using a single solubility coefficient (SSC) were developed. The SSC correlation was tested on other datasets available in the literature and its performance was assessed. At last, the solubility of Propylene and DME in PAG oil was evaluated and compared against the solubility of Propane in PAG oil, and the implications on the refrigerant charge in compressors of a heat pump were discussed.

2. Methods

The methods of this study are divided into six subsections. The investigated media are initially introduced in Section 2.1. Then, the experimental set-up is presented in Section 2.2 followed by the calculation of the solubility in Section 2.3, as part of the experimental procedure. The solubility data obtained were then fitted by different models, as described in the last three subsections. In Section 2.4, the

semi-empirical models from the literature are introduced. They are followed by the presentation of a new empirical correlation based on six fitting coefficients in Section 2.5. The method section concludes with the presentation of a new user-friendly correlation with a single fitting coefficient.

2.1. Media

The characteristics of the refrigerants investigated in this study are described in Table 1. Information about the PAG oil density follow in Table 2. The oil investigated was characterized by a kinematic viscosity at 40 °C of 64 mm²/s and 10 mm²/s at 100 °C.

2.2. Experimental setup

An experimental setup at the refrigeration laboratory (Lafset) of Conservatoire National des Arts et Métiers (CNAM) described also by Ginies and Dewitte (2014) and Notturmo et al. (2023) allowed to measure the solubility of refrigerant in PAG oil. The studied oil was a PAG66 oil and had similar characteristics to the PAG40 investigated by Shi et al. (2022). The test stand was composed of (i) a temperature-controlled oil bath; (ii) two sealed test cells equipped with a pressure transducer and a temperature sensor; and (iii) the sensors were connected to a computer for data collection. The volumes of the test cells were of 64.95 cm³ and 64.72 cm³. A simplified schematic of the test installation is in Fig. 1.

The experimental procedure, described in Fig. 2, started with the preparation of the cell, air removal (i), and weighing (ii). Oil density was measured using a densimeter. The results are presented in Table 2 (iii). A polynomial characterized the oil density as a function of temperature. After selecting the wanted refrigerant composition (iv), the refrigerant and oil quantities necessary for the tests were determined (v). Oil was then added to the cell (vi), and residual air was removed from the cell with a vacuum pump (vii). The cell containing oil was weighed to determine the exact quantity of oil introduced. Refrigerant was introduced in the cell and weighed (viii). At this point, the mixture in the cell was composed of three zones. One in vapour phase and two in the liquid phase. The cell was then manually shaken to reach only one zone in vapour phase and one zone in liquid phase. A first miscibility check was then made (ix). The desired bath temperature set-point was selected (x) and the solubility tests were carried out by immersing the test cell in the oil bath (xi).

The time required to reach steady state was at least two hours and it varied depending on the conditions and the refrigerant tested (xii). When a steady-state condition was achieved, the pressure and temperature of the cell were measured for 20 min or more (xiii). The measurements were taken every 5 s. At the end of the measurement, miscibility was visually checked (xiv). From the measurement of pressure and temperature, knowing the internal volume of the cell and the quantity of oil and refrigerant, it was possible to first calculate the quantity of vapour refrigerant, and then the solubility (xv) defined as the liquid refrigerant in the oil. It was assumed that given the low vapour pressure of oil, no oil is contained in the vapour phase. The refrigerant concentrations tested were between 8 % and 50 %, with temperatures varying from -10 °C to 90 °C for Propylene and to 100 °C for DME. The temperature and concentration ranges were selected with the goal to cover the typical operating conditions of compressors for heat pump applications. The test range was also determined by the safety

Table 2
Oil density measurements.

Density [g/cm ³]	Temperature [°C]
1.0018	20.0
0.9920	30.0
0.9824	40.0
0.9737	50.0
0.9659	60.0
0.9589	70.0
0.9528	80.0

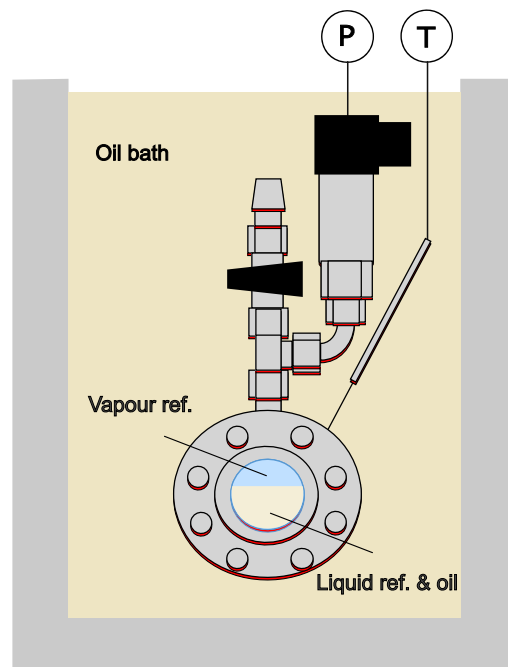


Fig. 1. Schematic of the experimental setup.

requirements and physical limitations of the test bench, which constrained the maximum cell pressure.

The methods of this work were implemented in the Python (Van Rossum and Drake, 2009) programming language using an object-oriented approach. The modelling work was divided into five parts: (i) calculation of solubility from the measured temperatures and pressures; (ii) uncertainty analysis using Monte Carlo simulations; (iii) local-composition models; (iv) empirical correlations; (v) the utilization of the solubility models for solubility prediction.

2.3. Calculation of the refrigerant solubility

The extended derivation of the method applied to determine the solubility was described by Youbi-Idrissi (2003). The main equation to calculate solubility $X_{r,l}$ was given:

$$X_{r,l} = \frac{M_{r,l}}{M_{oil} + M_{r,l}} = \frac{M_r - M_{r,v}}{M_{oil} + M_r - M_{r,v}} \quad (1)$$

Where $X_{r,l}$ is the mass concentration, r stands for refrigerant, l for

Table 1

Characteristics of the refrigerants considered in this study. The data are from ISO 817 (ISO 817, 2014), EN 378-1 (EN 378, 2016) and ASHRAE 34 (ASHRAE 34, 2022). GWP is the global warming potential, LFL is the lower flammability level, AIT is the autoignition temperature, NBP is the normal boiling point.

Name	R number	Chemical formula	Safety class	GWP	Molar mass [g/mol]	LFL [g/m ³]	AIT [°C]	NBP [°C]
Propylene	R-1270	C ₃ H ₆	A3	2	42.1	46	455	-48
DME	R-E170	C ₂ H ₆ O	A3	1	46.0	64	235	-25

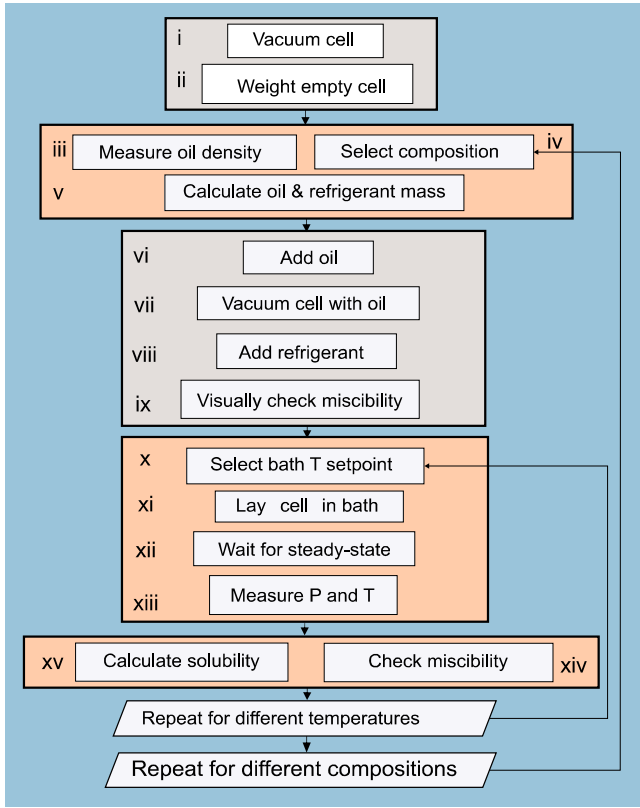


Fig. 2. Test procedure steps.

liquid, and v for vapour. Neglecting excess volume, the vapour volume $V_{r,v}$ was calculated in Eq. (2) as the difference between the total cell volume V_{tot} and the liquid volume, composed by refrigerant volume $V_{r,l}$ and the oil volume V_{oil} . The mass of refrigerant vapour $M_{r,v}$ is the only unknown and it can be calculated in Eq. (5) by combining Eqs. (2), (3), and (4):

$$V_{r,v} = V_{tot} - V_{r,l} - V_{oil} \quad (2)$$

$$M_{r,v} = V_{r,v} \rho_{r,v} = (V_{tot} - V_{r,l} - V_{oil}) \rho_{r,v} \quad (3)$$

$$V_{r,l} = \frac{M_{r,l}}{\rho_{r,l}(P)} = \frac{M_r - M_{r,v}}{\rho_{r,l}(P)} \quad (4)$$

$$M_{r,v} = \frac{\left(V_{tot} - \frac{M_{oil}}{\rho_{oil}(T)} - \frac{M_r}{\rho_{r,l}(P)} \right) \rho_{r,l}(P) \rho_{r,v}(P, T)}{\rho_{r,l}(P) - \rho_{r,v}(P, T)} \quad (5)$$

V_{tot} is the total volume of the cell and ρ is the density, calculated as a function of the cell temperature T and/or of the equilibrium pressure P . The main assumptions taken for the calculations were the following.

- The vapour was assumed to contain only refrigerant and no oil, due to the negligible oil vapor pressure.
- The refrigerant dissolved into the oil was assumed to be in liquid phase.
- The excess volume of the refrigerant-oil mixture was neglected, assuming ideal refrigerant-oil mixing.
- Full miscibility of the refrigerant-oil mixture.

An uncertainty analysis on the measurement of solubility was carried out using the standard uncertainties of Table 3 and propagating the uncertainties using Latin Hypercube sampling (Helton and Davis, 2003) and Monte Carlo simulations. The uncertainty distribution was assumed to be normal for all parameters.

Table 3

Uncertainties. FS stands for Full Scale and σ is the standard deviation.

Parameter measured	Uncertainty (2σ)
Mass of oil	0.03 g
Mass of refrigerant	0.03 g
Pressure	0.4 % FS
Temperature	0.25 K
Oil density	0.5 kg/m ³

2.4. Semi-empirical local composition models

Different solubility models in the literature were adopted to fit the experimental data. The activity coefficient of the refrigerant was calculated using the Wilson equation (Wilson and Wilson, 1964), the NRTL model from Renon and Prausnitz (1968) and Heil's equation (Heil and Prausnitz, 1966). Their parameters were fitted to the experimental data using an optimization procedure to minimize the difference between experimental data and measurements. For each component i of a binary mixture, the equilibrium between the two phases is characterized by the equality of fugacities of the vapour and liquid phases:

$$x_{i,v} \varphi_{i,v} p = x_{i,l} \varphi_{i,l} p \quad (6)$$

Where v and l are the vapour and liquid phases, x is the molar concentration, p is the equilibrium pressure and φ are the fugacity coefficients. Due to the assumption of negligible oil vapour pressure, $x_{oil,v} = 0$ and $x_{r,v} = 1$. It was possible to determine the activity coefficient of the refrigerant γ_r following Van Ness and C.H. (1982) as:

$$\gamma_r = \frac{p \varphi_r}{x_{r,l} p_{sat}} \quad (7)$$

The fugacity coefficient of the refrigerant φ_r , despite having a value very close to 1, was calculated by using Eq. (8) as adopted by Wang et al. (2021):

$$\varphi_r = \exp \left(\frac{(B_1 - V_l)(p_{sat} - p)}{RT} \right) \quad (8)$$

Where B_1 is the second virial coefficient in [m³/mol], V_l is the molar liquid volume in [m³/mol] from REFPROP 10 by Lemmon et al. (2018).

The activity coefficients were calculated using three different local composition models from the literature. The Wilson semi-theoretical equation (Wilson and Wilson, 1964) derived from Flory-Huggins's equation introduced an equal interaction energy parameter between two components. The Non-Random Two-Liquid model (NRTL) developed by Renon and Prausnitz (1968) model adopts an equation composed of three interaction parameters.

$$\text{Wilson} \ln \gamma_r = -\ln(x_r + \Lambda_{r,oil} x_{oil}) + x_{oil} \left(\frac{\Lambda_{r,oil}}{x_r + \Lambda_{r,oil} x_{oil}} - \frac{\Lambda_{oil,r}}{x_{oil} + \Lambda_{oil,r} x_r} \right) \quad (9)$$

$$\text{NRTL} \ln \gamma_r = x_{oil}^2 \left(\tau_{r,oil} \left(\frac{\Lambda_{oil,r}}{x_r + x_{oil} \Lambda_{oil,r}} \right)^2 + \frac{\tau_{r,oil} \Lambda_{r,oil}}{x_{oil} + x_r \Lambda_{oil,r}} \right) \quad (10)$$

Where $\Lambda_{r,oil}$ and $\Lambda_{oil,r}$ are interaction parameters related to the local composition of refrigerant around oil and vice versa. The NRTL model adopts two binary adjustable interaction parameters τ and a third fitting coefficient α , which can be set to a fixed value. This study also adopted the Heil equation (Heil and Prausnitz, 1966) which is a combination of the Wilson equation and the NRTL model.

For the Wilson and Heil models:

$$\Lambda_{r,oil} = \frac{V_r}{V_{oil}} \exp(-\tau_{r,oil}) \quad (11)$$

$$\Lambda_{oil,r} = \frac{V_{oil}}{V_r} \exp(-\tau_{oil,r}) \quad (12)$$

For the NRTL model:

$$\Lambda_{r,oil} = \exp(-\alpha\tau_{r,oil}) \quad (13)$$

$$\Lambda_{oil,r} = \exp(-\alpha\tau_{oil,r}) \quad (14)$$

For the NRTL and Heil models, the interaction parameters were modelled using two different approaches. In the first case, a conventional formulation was found in [Renon and Prausnitz \(1968\)](#).

$$\tau_{r,oil} = \frac{\tau_{r,oil}(1) - \tau_{r,oil}(2)}{RT} \quad (15)$$

$$\tau_{oil,r} = \frac{\tau_{oil,r}(1) - \tau_{oil,r}(2)}{RT} \quad (16)$$

Where $\tau_{r,oil}(1)$, $\tau_{r,oil}(2)$, $\tau_{oil,r}(1)$ and $\tau_{oil,r}(2)$, typically defined as energy parameters, were set as four fitting coefficients in J/mol. α is a fifth coefficient, the non-randomness parameter, available only for the NRTL.

In a second approach, aimed to reduce the deviation between the models and the experimental data, the binary interaction parameters were formulated as function of temperature, similarly to part of the Antoine equation ([Antoine, 1888](#)) as suggested by [Leon Poesy \(1996\)](#) and adopted by [Wang et al. \(2021\)](#).

$$\tau_{r,oil} = \tau_{r,oil}(1) + \frac{\tau_{r,oil}(2)}{T} \quad (17)$$

$$\tau_{oil,r} = \tau_{oil,r}(1) - \frac{\tau_{oil,r}(2)}{T} \quad (18)$$

In the result section, the NRTL and Heil models adopting this alternative formulation of the interaction parameters were called NRTL 2 and Heil 2, respectively.

2.5. Empirical correlation with 6 coefficients

This work proposed two empirical correlations. The first proposal came from the commonly used correlation from [Mermond et al. \(1999\)](#) adopted by [Wu et al. \(2018\)](#), written below as a reference:

$$\log_{10}\left(\frac{P}{10^5}\right) = a_1 + \frac{a_2}{T} + \frac{a_3}{T^2} + \log_{10}(X_{r,l})\left(a_4 + \frac{a_5}{T} + \frac{a_6}{T^2}\right) + \log_{10}^2(X_{r,l})\left(a_7 + \frac{a_8}{T} + \frac{a_9}{T^2}\right) \quad (19)$$

Some modifications were implemented to the existing correlation:

- The first three coefficients were removed and substituted by the calculated saturation pressures at solubility $X_{r,l} = 1$.
- The first-degree term in [Eq. \(11\)](#) was substituted with a term of the third degree.

This allowed us to obtain an equation with a derivative equal to 0 at $X_{r,l} = 1$, hence assuring a monotone curve with a horizontal tangent. The equation had six, instead of nine, parameters a_i and it determined pressure as a function of solubility, temperature, and the calculated saturation pressure. The proposed correlation resulted in:

$$\beta = \ln^2(X_{r,l})\left(a_1 + \frac{a_2}{T + a_3}\right) + \ln^3(X_{r,l})\left(a_4 + \frac{a_5}{T + a_6}\right) \quad (20)$$

$$p = p_{sat}(T)e^\beta \quad (21)$$

In the initial study from [Caramaschi et al. \(2023\)](#) for the case of DME, the term $-1e^{-4/X_{r,l}^2}$ was added to the polynomial β to improve the behaviour at low refrigerant concentrations. In the current study instead, the additional term was removed. The formulation of the correlation changed from $a_i + \frac{a_{i+1}}{T} + \frac{a_{i+2}}{T^2}$ to a form that resembles Antoine's equation $a_i + \frac{a_{i+1}}{T + a_{i+2}}$. The final form of the first proposed correlation can

be rewritten as:

$$\ln\left(\frac{P}{p_{sat}(T)}\right) = \ln^2(X_{r,l})\left(a_1 + \frac{a_2}{T + a_3}\right) + \ln^3(X_{r,l})\left(a_4 + \frac{a_5}{T + a_6}\right) \quad (22)$$

2.6. Empirical correlation with a single solubility coefficient (SSC)

Empirical correlations with multiple coefficients, as the one developed in the previous section, require a high amount of experimental data in order to be accurate. To simplify the understanding and the application of refrigerant-oil solubility models, and reduce the need for experimental data, a new user-friendly correlation was proposed.

The correlation characterized the equilibrium pressure as function of temperature and solubility and a single coefficient.

$$p = p_{sat}(T) - \frac{p_{sat}(T)}{\exp\left(\frac{X_{r,l}}{a_1 T}\right)} \quad (23)$$

Where p is the pressure of the refrigerant-oil mixture in MPa, p_{sat} is the saturation pressure of the pure refrigerant, T is the equilibrium temperature in Kelvin, $X_{r,l}$ is the solubility and a_1 is a single fitting parameter. The simple form of the equation allows to determine solubility $X_{r,l}$ explicitly as:

$$X_{r,l} = a_1 T \ln\left(\frac{p_{sat}(T)}{p_{sat}(T) - p}\right) \quad (24)$$

At raising pressure p , solubility increases. At increasing difference between saturation pressure and equilibrium pressure $p_{sat}(T) - p$ solubility instead drops. The effect of temperature on solubility depends also on how pressure is affected, and it is not trivial. On the other hand, the coefficient a_1 was found proportional to solubility. In this work a_1 was named single solubility coefficient (SSC).

All models were fitted to the experimental data through an optimization procedure which applied the global optimization algorithm Basin-Hopping first described by [Wales and Doye \(1997\)](#) and implemented in the Scipy library by [Millman et al. \(Virtanen et al., 2020\)](#). The objective function to minimize was the mean absolute percentage error (MAPE) between modelled and measured pressures:

$$MAPE = \frac{1}{n} \sum_{i=1}^n \left| \frac{P_{exp,i} - P_{model,i}}{P_{exp,i}} \right| \cdot 100 \quad (25)$$

Where P_{exp} are the measured pressures, P_{model} the predicted pressures and n is the number of data points.

The deviations between experimental data and modelled data were compared for different models. Moreover, for the single-coefficient correlation, it was evaluated how the number of available data points can affect the accuracy of the correlation. Finally, the correlation's accuracy was tested on datasets in the literature.

3. Results

3.1. Miscibility

After the refrigerant filling process in the cell containing oil, it was possible to observe three phases: a vapour phase containing refrigerant and a negligible amount of oil, a liquid phase rich in liquid refrigerant, and another liquid phase rich in oil. An example can be seen in [Fig. 3](#). After shaking the cell and mixing the two components, full miscibility could be obtained. The miscibility of the refrigerant-oil mixture was visually confirmed for all the test points, for both Propylene and DME. For the tested compositions, no color change, and no phase separation were observed. An example can be observed in [Fig. 4](#).



Fig. 3. Refrigerant not fully miscible in oil, immediately after refrigerant filling.



Fig. 4. Example of Propylene miscible in PAG oil.

3.2. Solubility

The propagated uncertainty on the measurement of solubility resulted in between 0.2 % and 1.6 % of the calculated value. Pressure had the highest sensitivity on refrigerant solubility in oil. The experimental data for Propylene and DME are presented in Tables 4. and 5. respectively.

All the studied models were fitted to the experimental data through an optimization procedure. Table 6 summarizes the resulting coefficients.

The fitted correlations were used to predict the Pressure-Temperature-Solubility curves, also outside of the experimental range. Results were presented in Figs. 5–8. The curves are monotone and as it can be expected, the lower the refrigerant concentration, the lower the measured equilibrium pressure.

As depicted in Figs. 5 and 6, for Propylene the empirical correlations show a generally satisfactory match with the experimental results. The mean absolute percentage error (MAPE) for the correlation with 6 coefficients and the one with a single coefficient is found to be 1.2 % and 1.6 % respectively. At conditions of pure refrigerant, with a mass fraction of 1, the pressures were calculated using REFPROP through

Table 4

Experimental data Propylene.

Temperature [K]	Pressure [MPa]	Refrigerant solubility [-]
263.78	0.238	0.095 ± 0.001
263.88	0.397	0.295 ± 0.001
264.01	0.342	0.196 ± 0.001
264.10	0.409	0.396 ± 0.001
283.19	0.401	0.093 ± 0.001
283.26	0.596	0.193 ± 0.001
283.57	0.693	0.291 ± 0.001
283.59	0.743	0.392 ± 0.001
303.33	0.978	0.189 ± 0.001
303.36	0.638	0.092 ± 0.001
303.43	1.244	0.386 ± 0.001
303.48	1.157	0.286 ± 0.001
313.02	1.200	0.187 ± 0.001
313.12	1.550	0.383 ± 0.001
313.13	0.767	0.091 ± 0.001
313.21	1.424	0.283 ± 0.001
323.07	1.926	0.378 ± 0.002
323.07	1.475	0.184 ± 0.001
323.19	1.752	0.280 ± 0.001
323.2	0.930	0.090 ± 0.001
333.03	1.775	0.181 ± 0.001
333.03	2.362	0.373 ± 0.002
333.18	2.120	0.276 ± 0.002
333.22	1.098	0.089 ± 0.001
342.98	2.871	0.366 ± 0.003
343.00	2.097	0.178 ± 0.002
343.15	2.540	0.271 ± 0.002
343.21	1.276	0.088 ± 0.001
352.92	2.444	0.175 ± 0.002
353.20	1.464	0.087 ± 0.001
362.88	2.808	0.172 ± 0.002
363.19	1.661	0.086 ± 0.001

Table 5

Experimental data DME.

Temperature [K]	Pressure [MPa]	Refrigerant solubility [-]
263.57	0.072	0.097 ± 0.001
263.60	0.169	0.498 ± 0.003
263.73	0.143	0.299 ± 0.001
283.68	0.345	0.496 ± 0.001
283.69	0.143	0.096 ± 0.001
283.72	0.292	0.298 ± 0.001
293.33	0.394	0.297 ± 0.001
293.35	0.458	0.495 ± 0.001
293.55	0.217	0.095 ± 0.001
303.28	0.517	0.296 ± 0.001
303.36	0.613	0.494 ± 0.001
303.55	0.255	0.095 ± 0.001
313.33	0.673	0.295 ± 0.001
313.40	0.799	0.493 ± 0.001
313.47	0.331	0.094 ± 0.001
323.11	0.853	0.294 ± 0.001
323.11	0.411	0.094 ± 0.001
323.17	1.017	0.492 ± 0.001
333.07	1.069	0.293 ± 0.001
333.08	0.510	0.093 ± 0.001
333.14	1.278	0.490 ± 0.001
343.02	1.320	0.291 ± 0.001
343.03	0.617	0.092 ± 0.001
343.12	1.583	0.489 ± 0.001
352.98	1.609	0.289 ± 0.001
352.99	0.742	0.091 ± 0.001
353.02	1.945	0.486 ± 0.001
362.92	0.877	0.091 ± 0.001
362.92	1.938	0.288 ± 0.001
362.99	2.362	0.484 ± 0.001
372.82	1.022	0.090 ± 0.001
372.88	2.302	0.286 ± 0.001
372.94	2.838	0.482 ± 0.002

Table 6
Fitting coefficients for the local composition models and empirical correlation.

Local composition semi-empirical models – 4 and 5 coefficients						
Refrigerant	Model	α	$\tau_{r,oil}(1)$	$\tau_{r,oil}(2)$	$\tau_{oil,r}(1)$	$\tau_{oil,r}(2)$
Propylene	Wilson	–	-36,581	24,607	7979	5099
	NRTL	0.010	-1,000,000	1,000,001	-5532	6442
	NRTL 2	0.807	13.2	-3045	-2.55	304
	Heil	–	-9721.9	1881	1518	196
	Heil 2	–	-10.7	4278	4.81	-4471
DME	Wilson	–	-3710	-1055	-10,930	-11,730
	NRTL	0.750	-1706	-3116	-779	4028
	NRTL 2	1.276	1705	-10,300	-2.2	287
	Heil	–	-2715	-1110	181.6	-229
	Heil 2	–	0.988	151	-16.5	-241
Empirical correlation six coefficients						
	a_1	a_2	a_3	a_4	a_5	a_6
Propylene	-0.0462	216	-16,770	-0.219	-286	-1461
DME	-0.204	460	-19,355	-0.022	24	9559
Empirical correlation single solubility coefficient						
	SSC a_1					
Propylene	$4.588 \cdot 10^{-4}$					
DME	$6.530 \cdot 10^{-4}$					

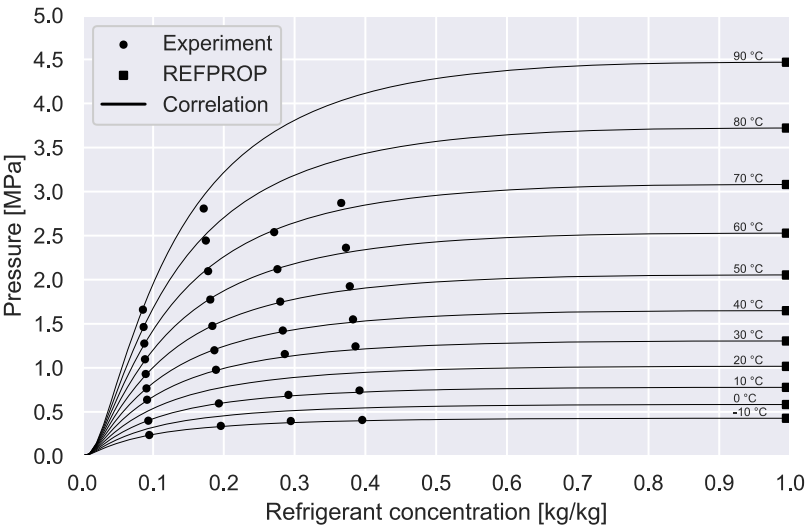


Fig. 5. Propylene data and correlation 6 coefficients. Average deviation 1.2 %.

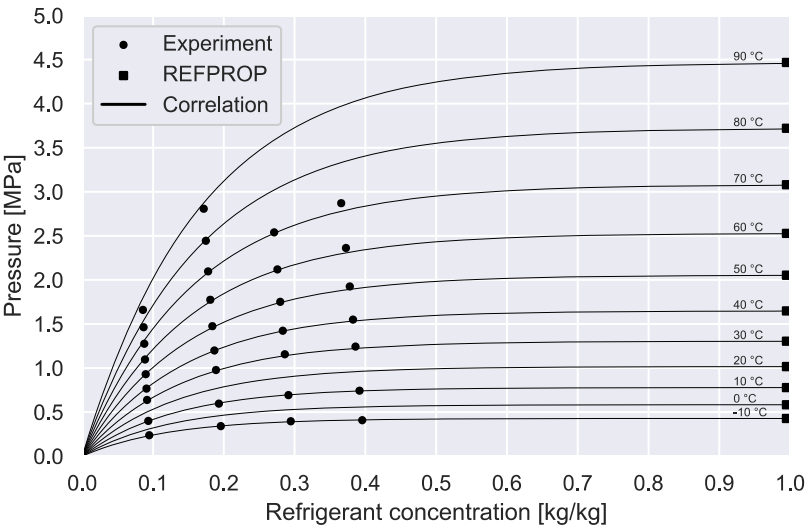


Fig. 6. Propylene data and correlation single coefficient. Average deviation 1.6 %.

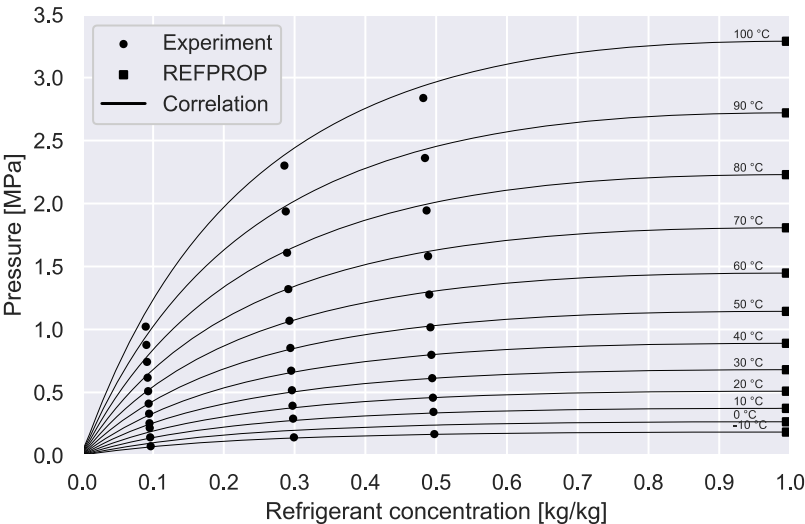


Fig. 7. DME data and correlation 6 coefficients. Average deviation 2.8 %.

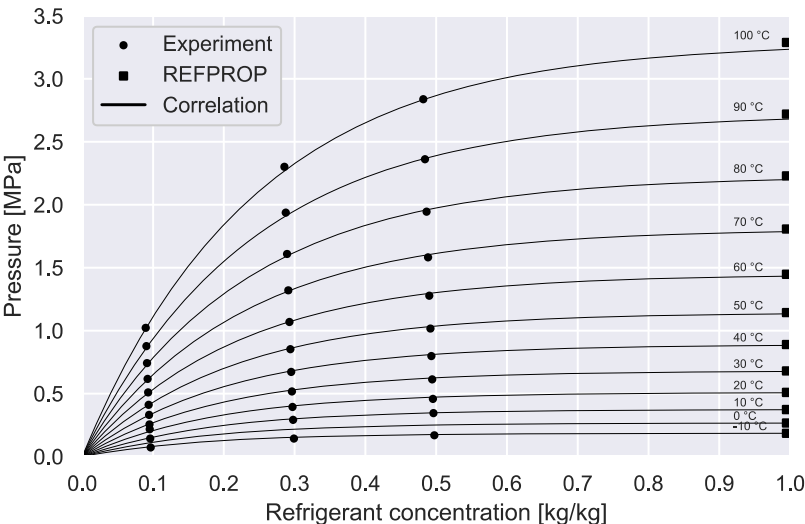


Fig. 8. DME data and correlation 1 coefficient. Average deviation 2.5 %.

CoolProp (Bell et al., 2014). These data points were excluded from the calculation of the average deviation. However, it can be stated that for Propylene, both correlations successfully predict the pressure behavior

of the pure refrigerant conditions, at all temperatures. Moreover, pressure tends to zero when no refrigerant is in the system.

The two empirical correlations matched DME data with an average

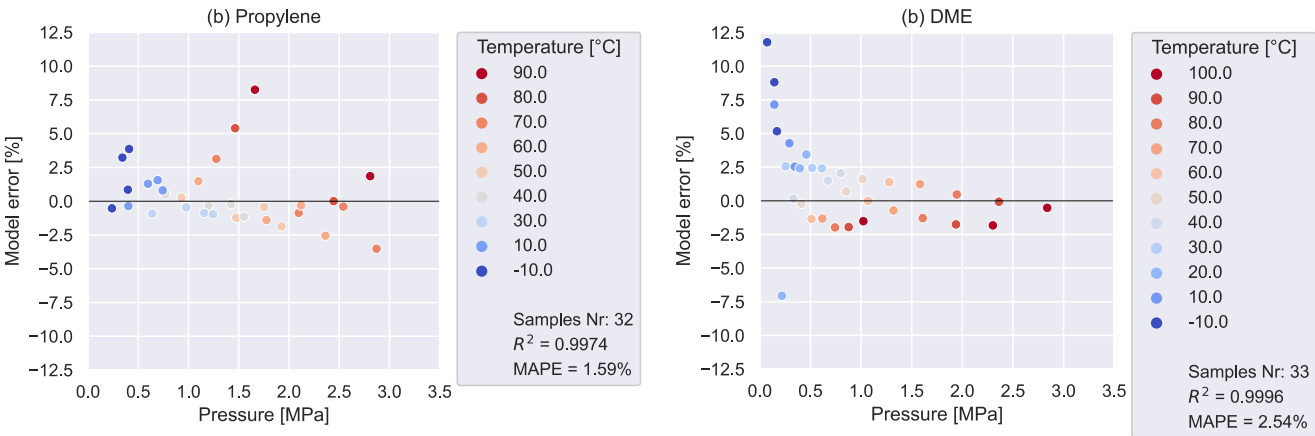


Fig. 9. Deviation for each datapoint using the single-coefficient correlation vs measured pressures, at different temperatures, for Propylene (a) and DME (b).

deviation of 2.8 % when 6 coefficients were adopted, and 2.5 % with the SSC correlation. For DME, in Fig. 7, the 6-coefficient correlation predicted well the points with pure refrigerant and tends to overestimate pressures at high temperatures. The SSC correlation, in Fig. 8 introduces a slight deviation at a refrigerant concentration of unity and high temperatures while reducing the deviation at lower concentrations.

In Fig. 9, the errors of the correlation with a single coefficient were plotted versus pressures and temperatures. The two refrigerants present different trends. For Propylene, in Fig. 9a, the maximum deviations occur between 1 MPa and 2 MPa, and the highest error of 8.2 % was found at the temperature of 90 °C. For DME, in Fig. 9b, the maximum deviations occur at low pressures and low temperatures, with the largest value being 11.7 %.

Furthermore, additional error analysis was performed to evaluate the effect of the number of data points used for fitting the model on the error. The data points selected for training were kept in consecutive order and tested $n_{data,tot} - n_{data,training}$ times. As shown in Fig. 10a, it was found that for Propylene, reducing the number of data points used during model fitting to only two data points increased the percentage error, on average, from 1.6 % to 2 %. Moreover, in light blue, it is possible to observe that depending on the chosen data points, the average error can vary between 1.6 and 4.5 %. The maximum error, on average, remained stable and slightly decreased from 8.2 % to 8 %. Using three data points, the possible error variation increased, ranging from about 4.8 % to 19 %. For DME, the average error increase was more pronounced when the number of data points decreased to two (Fig. 10b). With two data points, the average error increased from 2.5 % to 3.8 %, and the maximum error moved, on average, from 12 % to 13.9 %. On the other hand, using two and three data points increased the uncertainty significantly, with the average error ranging between 2.5 % and 9 % and the maximum error varying between 9 and 21 %. Overall, while the mean values of the average and maximum errors only slightly increased with the reduction of data points, their uncertainty was raised significantly for all the cases, especially when the number of data points used for training was reduced below four.

3.3. Model comparison

The accuracy of the seven models considered in this study were compared for both Propylene and DME. The results are reported in Fig. 11. For both refrigerants the local composition models (Wilson, NRTL and Heil) adopting conventional formulation of the binary interaction parameters resulted in the highest deviations, in the range between 4.2 % and 9 %. The alternative form of the binary interaction parameters, $\tau_{ij} = \tau_{ij}(1) + \frac{\tau_{ij}(2)}{T}$ resulted in a significant improvement of the performance. NRTL 2 lowered the error to 1.1 % for Propylene and Heil 2 reached an error of 1.3 % for DME. The empirical correlations

outperformed the local composition models, while tend to underperform compared to one model between NRTL 2 and Heil. The empirical correlations ranked among the top three models for Propylene and among the top four options for DME.

3.4. Test of the SSC correlation with other datasets in the literature

The correlation with a single fitting coefficient was tested on other datasets, and its performance was evaluated. As can be observed from Table 7, the mean average percentage error (MAPE) was between 1.6 and 6.2 %, the model performed better than the existing models for 3 datasets of the 7 tested. While the correlation introduces a lower performance for the majority of the models it was compared with, a performance improvement of 1.7 % points was obtained on the dataset from Stöckel et al. (2023), which however is only composed of 8 data points. The worst case was instead for DME-Squalane where MAPE increased by 3.9 % compared to the NRTL model applied by Sun et al. (2021), similar to the NRTL 2 model applied in this work. Here the minimum value for R^2 was reached at 0.9928.

At last, the solubilities of different refrigerants in PAG oil were calculated with the proposed SSC correlation. In Fig. 12, data on the solubility of different refrigerants were compared, at the saturation temperature of 0 °C and 60 °C. Compared to the data presented by Caramaschi et al. (2023) which applied an empirical correlation with 6 coefficients, in this study the solubility curves were obtained by applying the correlation with a single coefficient. As expected, solubility increases at higher saturation temperatures (pressures) and at decreasing superheat temperature differences. DME resulted in having the highest solubility values, especially at higher saturation temperatures, with a solubility of 33 % at a superheat value of 10 K and a saturation temperature of 0 °C. At the same conditions, Propylene showed a lower solubility, with a value of about 26 %. Propane, used as a reference, showed the lowest solubility of 19 %. At the saturation temperature of 60 °C and 20 K of superheating, DME had a solubility of 35 %, followed by Propylene at 27 % and Propane at 19 %.

4. Discussions

Despite miscibility being visually checked in all the test points, it could not be guaranteed in the entire composition range. The study had a limited solubility range, from about 9 % to a maximum of 50 %, in the case of DME, and to a maximum of about 40 % for Propylene. Immiscibility at higher refrigerant concentrations could not be excluded, especially when considering that the PAG oil studied by Shi et al. (2022), with similarities to the one in the current study, was found to be partially miscible with Propane. The choice of the testing range was made to cover solubility levels typically found in compressors of residential heat

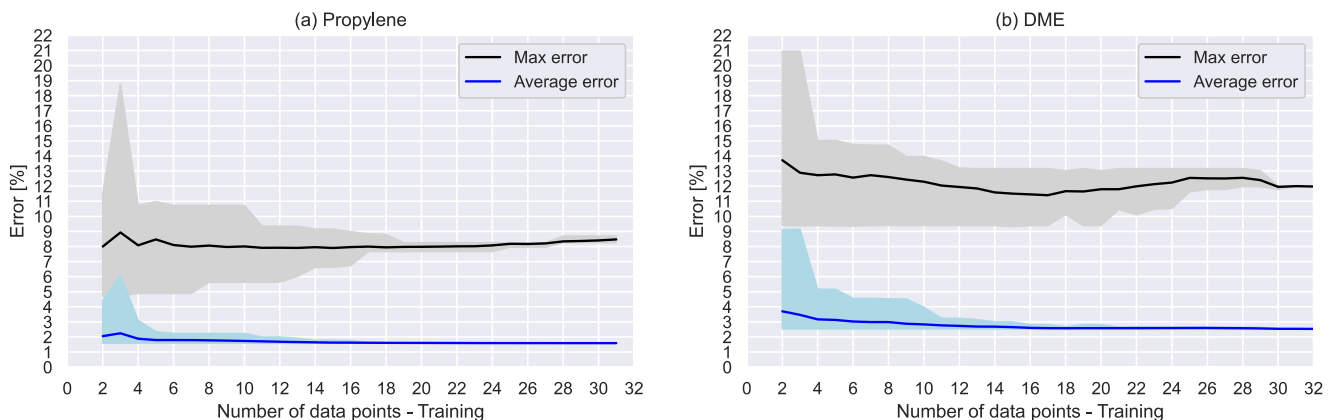


Fig. 10. Average and maximum model deviations as a function of the number of data points used for fitting the single solubility coefficient (SSC) a_1 . The two lines represent the mean values. The areas in grey and light blue show the ranges of the maximum and average errors, respectively.

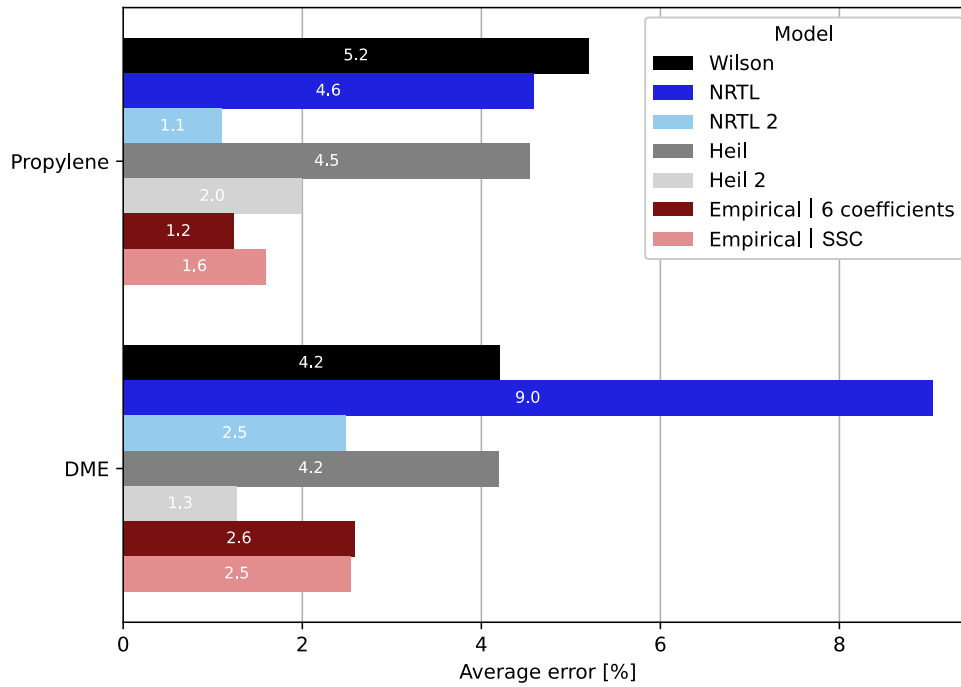


Fig. 11. Average deviation comparison between different models and correlations for refrigerant-oil solubility.

Table 7

Evaluating the performance model with one fitting parameter using other datasets. Solubility is considered Low for SSC $a_1 < 4 \cdot 10^{-4}$, high for SSC $a_1 > 6 \cdot 10^{-4}$, and Medium in between.

Oil	Ref	Source	Data points	SSC correlation						Model in literature		Δ MAPE [%]
				Solubility	SSC a_1 [1/K]	R^2	Max E [%]	RMSPE [%]	MAPE [%]	Model name	MAPE [%]	
PAG	Propylene	This work	32	Medium	$4.59 \cdot 10^{-4}$	0.9974	8.2	2.8	1.6	NRTL	1.1	+0.5 %
PAG	DME	Stöckel et al. (2023)	33	High	$6.53 \cdot 10^{-4}$	0.9996	11.7	1.7	2.5	Heil	1.3	+1.2 %
POE	DME		8	High	$6.378 \cdot 10^{-4}$	0.9980	6.7	3.1	2.4	Empirical	4.1	-1.7 %
Squalane	DME	Sun et al. (2021)	56	Medium	$5.613 \cdot 10^{-4}$	0.9928	20.8	6.6	6.2	NRTL	2.3	+3.9 %
Squalane	Isobutane	Sun et al. (2021)	49	High	$7.697 \cdot 10^{-4}$	0.9994	5.4	1.8	1.7	NRTL	0.8	+0.9 %
MO 3GS	Propane	Wang et al. (2021)	49	Medium	$5.461 \cdot 10^{-4}$	0.9980	9.8	4.5	3.0	NRTL	1.9	+1.1 %

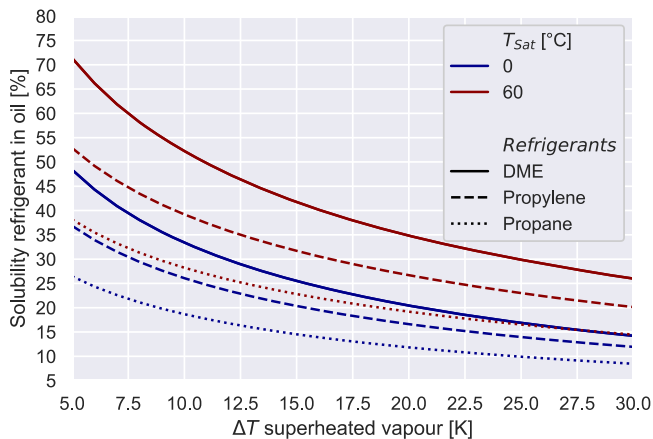


Fig. 12. Solubility as a function of the level of superheated vapour for different refrigerants.

pumps.

For the NRTL methods, the formulation of the interaction parameters was found to be critical for the minimisation of errors. The temperature-dependent form similar to Antoine's equation (Antoine, 1888) as suggested by Leon Poesy (1996) was found to be best. The form of the interaction parameters was adopted also by other studies, such as the one by Wang et al. (2021).

The simple and explicit form of the developed SSC correlation may incentivize refrigerant-oil solubility characterization also in those models where computational power or allowed running time is limited. Existing semi-empirical models in the literature were found to reach a high level of accuracy, however, their implementation may be considered complicated. Moreover, existing models, both semi-empirical and empirical, are formulated in implicit form, which requires solubility to be determined iteratively. The proposed SSC correlation, on the other hand, thanks to its compact and explicit formulation allows for a simple implementation and a fast execution. The latter may be a requirement in screening and parametric analysis or dynamic simulations. Overall, refrigerant-oil solubility is more likely to be included in the modelling of heat pumps and refrigeration equipment.

Moreover, for the tested datasets, the SSC correlation was found to be

robust and maintained an acceptable mean accuracy also at a very low number of data points. On the other hand, the rising uncertainty of the errors at the low amount of data points suggests that the choice of the data points may be critical to error minimization. Further analysis of the most effective selection criteria is recommended. Furthermore, particular care shall be taken when using the SSC to predict solubility at high refrigerant concentrations and low operating pressures and temperatures. Further testing and efforts to improve the SSC correlation are suggested.

The SSC correlation may also find use in the early design of new refrigerants and oils. Knowing the single coefficient of a specific refrigerant-oil combination with satisfactory solubility characteristics, the coefficient can be used as a reference or target for the design of new oils and refrigerants. For instance, thanks to this study it was found that Propane with the same PAG oil was able to reach an SSC a_1 equal to $3.34 \cdot 10^{-4}$ with the lowest resulting solubility. For the development of oils which offer low DME solubility, a similar a_1 target could be set. The existing DME-PAG single solubility coefficient a_1 is $6.53 \cdot 10^{-4}$, 95 % higher than Propane suggesting significant efforts may be required.

The difference between solubility levels of DME and Propylene compared to Propane was found to be significant. At the saturation temperature of 60 °C, DME would require about an additional 26.5 K in superheated vapour to match the same solubility of Propane. Propylene instead would require 7 K to 11 K additional superheating. From the results, it might be obvious to deduct that higher refrigerant solubility is expected in heat pump compressors using DME and Propylene compared to Propane. However, heat pumps using DME, and Propylene are expected to also operate with higher discharge temperatures at the same condensing temperatures. Since the superheated vapour level on the compressor high-pressure side is expected to be larger, a negative effect on solubility is expected. Solubility data are not enough to determine the refrigerant quantity in a compressor. Operating temperatures, pressures, densities, volumes, and kinetics may also play an important role. For having a realistic picture of the quantity of refrigerant dissolved in compressor oil for heat pumps, the modelling of a compressor and a full heat pump analysis was recommended.

The obtained results do not give information on the charge levels to be expected in the compressor. However, they may give insights into the solubility levels at the low- and high-pressure side. While the temperature on the suction side of a rotary compressor is close to the evaporator outlet condition, higher temperature uncertainties can be expected for the oil sump on the high-pressure side. The developed solubility models could be further integrated into a compressor or evaporator model that determines the amount of refrigerant contained by the single component.

The study did not investigate the effect that solubility has on viscosity and lubricity. Great care shall be dedicated to this aspect for the development of reliable and efficient compressors and vapour-compression cycles. Particularly for conditions at high discharge temperatures and high pressures, where both high solubility and low viscosity can be expected to be the most critical. These challenges may be expected for refrigerants with high solubility in oil, such as DME. Moreover, despite the foamy mixtures were not experienced in the experiments, it cannot be excluded in the case experiments are carried out on a compressor.

As discussed in the study from [Fernando et al. \(2004\)](#), the minimization of solubility should be a priority, especially for compressors in low-charge applications. The PAG oil tested was developed for Propane and small charge systems. For the future investigation and development of DME as a refrigerant, the custom design of an oil optimized for use with DME can be considered.

5. Conclusions

This study investigated the solubility and miscibility of Propylene and Dimethyl Ether (DME) in polyalkylene glycol oil for Propane

compressors. The solubility experimental data were used to fit different local composition models from the literature, the Wilson and Heil equations, and the Non-Random Two-Liquid model. It was found that the formulation of the binary interaction parameters of the NRTL and Heil models had a high influence on the accuracy of the models. NRTL with the second formulation of interaction parameters reduced deviations to an average of 1.1 % for Propylene. On the other hand, The Heil model achieved the best accuracy for DME, with an average error of 1.3 %.

Two new empirical correlations were introduced, and they were fitted to the experimental data. The first empirical correlation used six fitting coefficients and resulted in an average deviation of 1.2 for Propylene and 2.8 % for DME.

The second empirical correlation, formulated in a compact form and with a single solubility coefficient, was performed with an average deviation between experiments and the models of 1.6 % for Propylene and 2.5 % for DME. The fitted coefficient was found to be proportional to the solubility of the refrigerant.

Moreover, the SSC correlation showed performance robustness against the decrease of available data points. For Propylene, reducing the number of data points used during model fitting to only two data points, increased the percentage error, on average, from 1.6 % to 2 %. The maximum error, on average, remained stable, and slightly decreased from 8.2 to 8 %. For DME using only two data points, the average error increased from 2.5 % to 3.8 %, and the maximum error changed from 12 to 13.9 %. On the other hand, it was found that, when the amount of training data points were reduced below four, error uncertainties increased significantly. The results suggest that data points selection may have an important role on error minimization and further analysis on effective selection methods is recommended. The proposed SSC correlation, thanks to its compact and explicit formulation, may allow a simple implementation and a fast execution. It may incentivize the characterization of refrigerant-oil solubility in those applications where computational power or allowed running time are limited.

The same correlation allowed for comparing the solubility of Propylene and DME with the reference refrigerant Propane, at different temperatures, pressures, and compositions. It was found that at the same conditions, Propane had the lowest solubility while DME had the highest, and that the difference between solubility levels increased at growing pressures. For the potential future adoption of DME in low-charge heat pumps, the design of new low-solubility lubricants might be needed.

CRedit authorship contribution statement

Matteo Caramaschi: Conceptualization, Data curation, Formal analysis, Funding acquisition, Investigation, Methodology, Software, Validation, Visualization, Writing – original draft, Writing – review & editing. **Jonathan Notturmo:** Conceptualization, Formal analysis, Methodology, Supervision, Writing – review & editing, Data curation, Investigation, Software. **Guglielmo Vaccaro:** Conceptualization, Data curation, Methodology, Software, Writing – original draft, Writing – review & editing. **Wiebke Meesenburg:** Conceptualization, Methodology, Supervision, Writing – review & editing. **Jonas Jensen:** Conceptualization, Methodology, Project administration, Writing – review & editing, Supervision. **Brian Elmegaard:** Conceptualization, Funding acquisition, Methodology, Project administration, Resources, Supervision, Writing – review & editing. **Brice Treméac:** Project administration, Resources, Supervision, Writing – review & editing. **Pascal Tobaly:** Conceptualization, Project administration, Resources, Supervision, Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence

the work reported in this paper.

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4.5 Paper 5: Experimental results on a chiller using a CO₂-DME mixture.

This work connects to all previous works. The first two articles identify the most suitable configurations for the mixtures and the optimal fluids. In this Paper, therefore, the choice of fluid is justified by a previous theoretical analysis and the cycle of Paper 2 for an air conditioning chiller is analysed from an experimental point of view. Papers 3 and 4 help to understand some reasons for the discrepancy between the predicted improvements in paper 2 and the measured improvements. This study demonstrates the actual effectiveness of the CO₂ and DME mixture, yielding better results compared to the literature, where Koyama et al. [33] did not achieve significant benefits on the COP with the same fluid mixture.

The Ph.D. candidate is the first author of this work and was mainly involved in measuring, modelling and calculation. Dr. Ahmadou T. Diaby helped in the experimental investigation with the supervision of Professor Pascal Tobaly, while Professor Adriano Milazzo co-wrote and supervised the work.



Experimental results on a chiller using a CO₂-DME mixture

Résultats expérimentaux sur un refroidisseur utilisant un mélange CO₂-DME

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ABSTRACT

CO₂-DME (Carbon Dioxide-Dimethyl Ether) mixtures raised our interest in the last year as they promise to increase the COP with respect to pure CO₂ while maintaining GWP = 1. The mixture can be non-flammable, as far as the percentage of DME is low. This study presents experimental findings obtained from a chiller system utilizing CO₂-DME mixtures as the working fluid. The experimental investigation aims to analyse the performance and behaviour of the chiller under varying operating conditions. Key parameters, such as coefficient of performance, cooling capacity, and thermodynamic behaviour are examined to assess the suitability and efficacy of the CO₂-DME mixture in chiller applications. The experimental results shed light on the thermodynamic characteristics and operational considerations of the chiller system, providing valuable insights into the potential of CO₂-DME mixtures for environmentally friendly, safe and energy-efficient cooling technologies. The experimental findings indicate a maximum increase in COP of 15 % for a mixture comprising 10 % DME, with a condensation temperature of 35 °C. Furthermore, the cooling capacity is reduced only by 7 % in the worst case.

1. Introduction

The literature on CO₂-based mixtures as working fluids in refrigeration systems is rapidly increasing. These mixtures may combine the high volumetric cooling capacity and low GWP of CO₂ with a reduced pressure at the gas cooler (or condenser, if the mixture allows a subcritical working cycle) and a temperature glide at the evaporator, which may be beneficial in order to improve the heat exchange with the cold fluid delivered to the user. This concept has been discussed since the first decade of this century. Experimental results on CO₂ and propane mixtures have been published for example by Tobaly et al. (2018).

A very recent experimental work on a mixture of CO₂ and R152a has been presented by Sicco et al. (2024), showing that a maximum COP improvement of 11.6 % can be achieved with a mixture featuring a 5 % of R152a. Mixtures with R152a have been used also by Martínez-Ángeles et al. (2024).

Yu et al. (2018) investigated CO₂/propane mixtures for automobile air conditioning. They obtained a COP increase up to 29.4 % with fixed compressor speed and of 22 % with fixed cooling capacity. The same

authors (Yu et al., 2019) also investigated CO₂/R41 mixtures obtaining a COP increase of 14.5 % and 25.7 % respectively for heating and cooling mode.

Sanchez et al. (2023) investigated a CO₂ vertical beverage cooler using binary mixtures of CO₂/R1270 (92.5/7.5 %) and CO₂/R32 (78/22 %) in a configuration with an IHX. Their findings indicated energy savings of up to 15.7 % and 17.2 % respectively, under class III climate conditions (25 °C, 60 %).

Sanchez et al. (2024) examined a refrigeration plant in two configurations, with and without an IHX, using three different mixtures. They found that the mixture with R32 performed best in both configurations, achieving COP increases of 15.3 % and 22.2 %.

The works on CO₂-DME mixtures are less numerous. Onaka et al. (2008) did a thermodynamic analysis of a heat pump cycle using CO₂/DME mixture, and found 10 % mass DME as the local optimal composition for their boundary conditions.

Koyama et al. (2007) did an experimental analysis with 10 % DME, both in cooling and heating mode, for a cycle without IHX. They found almost the same maximum COP for pure CO₂ and mixture. When using the mixture, the optimal discharge pressure is reduced by 2 and 1.9 MPa

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Nomenclature		DME	Dimethyl ether
c_p	Specific heat capacity (kJ/kgK)	EVA	Evaporator
h	Enthalpy (kJ/kg)	GC	Gas Cooler
$\dot{m}$	Mass flow rate (kg/h)	HP	High Pressure
P	Pressure (bar)	IHX	Internal Heat Exchanger
Q_{ref}	Cooling capacity (W)	<i>subscripts</i>	
ρ	Density (kg/m ³)	f	refrigerant fluid
T	Temperature (K)	in	inlet
$\dot{V}$	Volumetric flow rate (l/min)	liq	Liquid
W	Work (W)	vap	Vapour
x	Mass concentration (kg kg ⁻¹)	w	Water
COP	Coefficient of performance [-]	wg	Water-glycol

and the discharge temperature is increased by 16 and 13 K for heating and cooling mode respectively.

Di Nicola et al. (2011) did an analysis for a cascade refrigeration system with the low temperature cycle employing different mixtures of natural refrigerants. They found that the addition of small quantities of CO₂ brings a little reduction of COP, but also a reduction of GWP and flammability, maintaining the possibility to evaporate below the CO₂ triple point.

Starting from the same idea, Massuchetto et al. (2019) did an analysis for a cascade system and decided to use a mixture of CO₂/ammonia for the high temperature cycle, in order to decrease the heat exchanger losses. For the low temperature cycle, they found that the best mixture was CO₂/DME (10 % CO₂), which brought an efficiency increase up to 30 %

Onaka et al. (2010) also did an experimental study on evaporation heat transfer of a CO₂/DME mixture in a horizontal smooth tube. Starting from pure DME they obtained a reduction of HTC of 20 % for 10 % CO₂ and of 48 % for 25 % CO₂

Afroz et al. (2008) did an experimental study on heat transfer and pressure drop during in-tube condensation for 21 % and 39 % mass of CO₂, finding a decrease of HTC and pressure drop when increasing CO₂.

A recent review of several mixtures working on various cycle configurations has been presented by Vaccaro et al. (2023). Soon after, the same authors have decided to concentrate on mixtures of CO₂ and hydrocarbons (Vaccaro et al. 2024), showing that DME (Dimethyl ether) may be the best option in terms of performance and safety.

The present work is mainly intended to verify the theoretical results presented by Vaccaro et al. (2024). To this aim, the experimental facility used by Tobaly et al. (2018) is particularly well suited. The scroll compressor is quite robust with respect to liquid ingestion, and this has allowed to explore low superheating values at compressor inlet. A favourable consequence of this choice is the reduction of the compressor exit temperature. With respect to the other experimental work on CO₂/DME mixture (Koyama et al., 2007), the introduction of a IHX has proven fundamental and has produced a significantly higher COP. Moreover, the extensive discussion about the IHX and its role in the cycle forms another important contribution of this paper. In the previous literature the IHX receives the fluid in superheated state from the evaporator, while in our experiments the temperature glide featured by zeotropic mixtures is split between the evaporator and the IHX, in order to optimize the low temperature side of the cycle as a whole.

The experimental results presented herein enlarge those described by Tobaly et al. (2018). As suggested by the calculations performed by Vaccaro et al. (2024), low quantities of DME are used as additive in the CO₂ mixture. In this way, a low-GWP, non-flammable refrigerant, featuring improved performance over pure CO₂, is obtained.

2. Experimental details

2.1. Experimental setup

The experiments have been carried on a refrigeration system comprising a scroll compressor, brazed-plate heat exchangers, an electronic expansion valve, a liquid separator and an internal heat exchanger IHX. The experimental apparatus has been first described in Bouteiller et al. (2015) and is shown in Fig. 1. The circuit is based on a 3.5 kW water-to-water heat pump. A Sanden hermetic scroll compressor with 4 cm³vol is used. The compressor speed may be varied from 1200 to 5500 rpm through a continuous 0 - 5 V signal. In order to maintain homogeneity in the measurements, the entire experimental campaign presented herein was carried out at 2.5 V.

The test bench was specifically designed for tests with refrigerant mixtures. The apparatus has been used for tests in heat pump configuration till 2017 (Bouteiller et al., 2017). Later, its use has been extended to refrigeration and air conditioning (Tobaly et al., 2018). External working conditions are set by means of two auxiliary water loops. On the gas cooler side, the inlet water temperature is regulated by a thermostatic bath and the flow rate is adjusted by a valve. On the evaporator side, a 32 % water/glycol mixture is used and its inlet temperature is regulated using an electrical heater. The flow rate in this loop can be adjusted to reach the targeted outlet temperature. Flow rates in the auxiliary loops are given by electromagnetic flow meters.

The system is controlled by a high-pressure electronic valve and two manually operated valves fitted at the separator liquid and vapour exits. In this way, the maximum cycle pressure P_1 and the superheat at the compressor inlet can be controlled.

The internal heat exchanger should also act as a liquid reservoir/separator at compressor inlet. However, in some cases, the liquid level has changed significantly, either exposing the coil to dry vapour (and hence reducing the heat exchange) or overcoming the entrance of the exit pipe (and hence causing liquid ingestion by the compressor).

2.2. Measurement instrument

The circuit is fully instrumented for the complete characterization of the refrigerant state throughout the cycle. Two Coriolis flow meters (0.15 % accuracy in the range 4 - 400 kg/h) are installed after the liquid vapour separator, one on the liquid line and one on the vapour line. A wattmeter measures the electric input to the compressor. The thermodynamic conditions are measured by T-type thermocouples (copper and constantana wires, measuring range between -200 °C and 200 °C, with a maximum error of ± 0.5 K), and piezo resistive pressure transducers (Endress Hauser, 0.03 % in the range 0 - 96–78.4 bar). The thermocouples have been specifically calibrated in a narrow range (-10 °C to

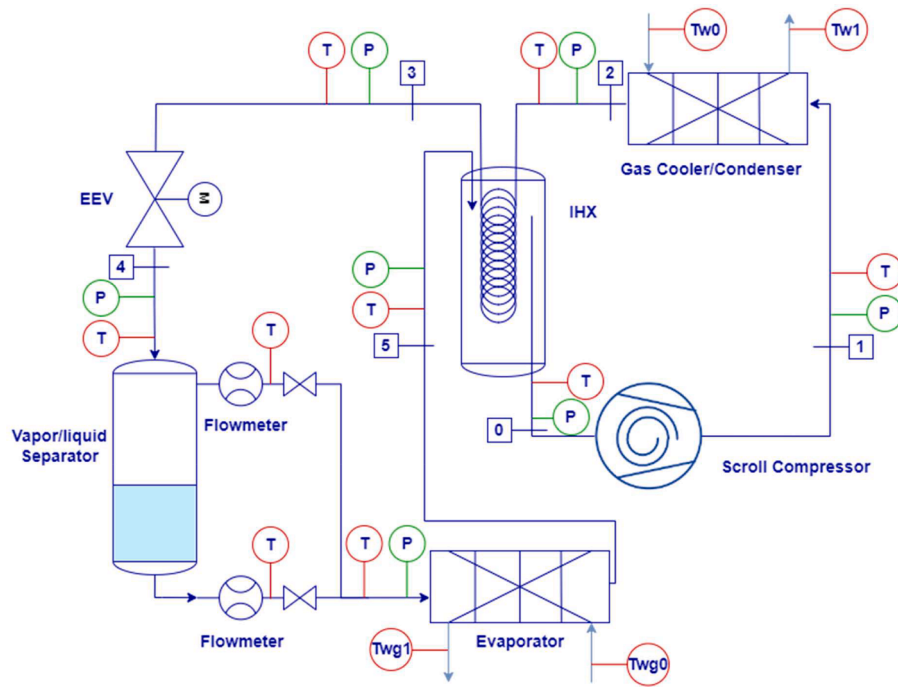


Fig. 1. Experimental setup: P pressure transducers, T thermocouples.

Table 1
Measuring instrument and accuracy.

Sensors	Type / Supplier	Accuracy
Pressure transducers	Cerabar M / Endress Hauser	0.04 % on the range 0.96 – 137.7 bar. 0.03 % on the range 0.96 – 78.4 bar.
Refrigerant mass flow meters	Promag 83 / Endress Hauser	0.15 % in the range 4 – 400 kg/h (with 3/8" tube). 0.1 % in the range 4 – 90 kg/h (with 1/8" tube).
Magnetic flow meters	Promag 10H08 / Endress Hauser	0.5 % on the range 0.5 – 30 l/min.
Wattmeter	μTAC300 / Sfere	0.5 % on the power range 500 – 1500 W.
Thermocouples	Class 1 T type/TC	0.05 °C on the range –10 °C – +40 °C

+40 °C), in order to increase their accuracy, with a PT100 (PT-102–14H) that has maximum error of 30.6 mK and a repeatability of 0.005 K Bouteiller (2017). The calibration has been performed according to the advice of the Joint Metrology Laboratory (LCM LNE) of the CNAM in St Denis. The PT100 is inserted in a copper cylinder to protect it from shocks and limit temperature gradients. The inside of the cylinder was flushed with nitrogen to remove humidity and filled with thermal paste (Apiezon N). A thin stainless-steel tube is brazed onto one end of the cylinder to protect the probe cables and allow handling. The metal body and probe stem are grounded. The sensibility of the data acquisition NI 9214 is 0.01 K. The resulting error of the calibrated thermocouple is:

$$e = 0.0306 + 0.005 + 0.01 = 0.0456 \text{ K} \quad (1)$$

All signals were acquired by a National Instruments compact DAQ platform 9174 (combined with NI9214 thermocouple modules, NI9203 current module for pressure transducers, NI9263 for signal output of compressor inverter) and processed by a software specifically developed in LabView environment. Table 1 summarizes the measurements ranges and accuracy of the measuring instruments.

2.3. Coefficient of performance

The COP of the refrigeration system is defined as:

$$COP = \frac{\dot{m}_{wg} c_{pwg} \Delta T_{wg}}{P_{comp}} \quad (2)$$

where $\dot{m}_{wg}$ is the water/glycol mass flow rate, c_{pwg} is its specific heat, ΔT_{wg} is its temperature difference and P_{comp} is the electrical power input of the compressor. The error on the calculated COP (see below) may therefore be estimated as follows:

$$\frac{dCOP}{COP} = \frac{dW}{W} + \frac{dc_{pwg}}{c_{pwg}} + \frac{d\rho_{wg}}{\rho_{wg}} + \frac{d\dot{V}_{wg}}{\dot{V}_{wg}} + \frac{d\Delta T_{wg}}{\Delta T_{wg}} \quad (3)$$

Given the measurement uncertainties reported in Table 1, the maximum error comes out to be 3.04 %. As a further proof of the accuracy of data, the COP for pure CO₂ has been calculated in two ways, one relying on the cooling power evaluated on the water/glycol flow and the other evaluated on the refrigerant side. The results obtained are quite close, with an average difference between the two of only 2.5 % and a maximum of 4.8 %.

3. Results

This work presents results for various compositions and water temperature at gas-cooler exit T_{w0} . All results are obtained for a water-glycol inlet and outlet temperature in the evaporator of 7 and 12 °C respectively.

The percentage of DME has been obtained by mixing with utmost care the due masses of CO₂ and DME during the filling of the circuit. The scales have an error, which may be pessimistically evaluated in 5 g for the one weighting the CO₂ and 1 g for the one weighting the DME. Therefore, considering that the total mass of refrigerant is 800 gs, when

5 % of DME is added, the real percentage may vary between 4.85 % and 5.15 %. When 10 % of DME is added, the real percentage may vary between 9.82 % and 10.18 %.

The differences found, however, are much bigger. Significant discrepancies between weighted and circulant compositions have been reported also by other authors. For example, Bouteiller (2017) has found the same problem for mixtures of CO₂ and propane. A possible reason may be the fact that the liquid mixture stored in the separators is richer in the less volatile compound (DME), leaving the vapour phase richer in CO₂. A second issue is related to the absorption of refrigerants by the lubricant oil. Caramaschi et al. (2024) have shown that DME is even more soluble in oil than propane. This issue is hence surely present also in our case. A third issue is the velocity difference between the liquid and vapor phase in heat exchangers. If liquid and vapor have different compositions, this may further enrich the mixture in the most volatile component. Experimental results on the mixture composition problems have been published also by Youby Idrissi (2003).

3.1. COP analysis

Fig. 2 shows the COP of the different compositions of mixtures studied for various experimental conditions. In all cases, the addition of DME increases the system COP. Obviously the COP increases for decreasing T_{w0} . The three curves on the lower part of the diagram, referred to $T_{w0} = 40^\circ\text{C}$, are rather flat around the optimum and clearly show a best result for a 10 % of DME in the mixture. By the way, the optimum is reached for a significantly lower value of the maximum cycle pressure P_1 (below 85 bars), which is >10 bars lower than the optimum for pure CO₂. The three curves referred to $T_{w0} = 35^\circ\text{C}$ are shorter, i.e. the system is more sensitive to small variations in the maximum cycle pressure. However, the convenience of the 10 % DME mixture is very evident and on average reaches a 15 % improvement over pure CO₂. The optimum value of P_1 is as low as 75 bars. A difference is evident between the results on top of the diagram and the others: these results are obtained with a subcritical cycle, being $T_{w0} = 30^\circ\text{C}$. The trend in terms of COP is more difficult to read. Moreover, the best results in this case are obtained for a mixture with 5 % DME at maximum cycle pressure around 72 bars. In the following section, we analyze all cases in further detail. The Ph digrams shown in the following sections are all referred to the

optimum condition, i.e. the one that gives the highest COP for a given set of boundary conditions, marked with a star in Fig. 2.

In order to have a further insight in these results, we have used the model presented in Vaccaro et al. (2024). A comparison has been carried on between the parameters calculated using the Refprop version 10 database (Lemmon et al. 2018) and those measured in each point. This comparison shows a significant difference between the composition of the mixture introduced in the circuit and the one that must be used within the model in order to reproduce the experimental measurements.

3.2. Thermodynamic analysis

The experimental results shown above have been used to calculate the thermodynamic cycle of the system. Points 0, 1, 2 and 3 are directly calculated from measured temperature and pressure. Point 4 is calculated from the measured pressure and from the quality, which is calculated from the mass flow rates measured by the Coriolis flow meters shown in Fig. 1. This quality has been checked imposing a constant enthalpy transformation between points 3 and 4. Fig. 3 shows that the agreement between the two methods is very good. The average absolute difference is 0.88 % with pure CO₂ (Fig. 3a). In the case of mixtures, the average absolute difference is 0.92 % (Fig. 3b).

Point 5 has been calculated by adding the heat exchanged on the water/glycol side in the evaporator to the enthalpy of point 4.

A further validation has been performed on the heat exchangers, comparing the measurements obtained on the water and water/glycol sides with those obtained on the refrigerant side. The results for pure CO₂ are shown in Fig. 4a and 4b, showing that all points are within $\pm 5\%$. The only exception is the blue point below the -5% line, which is related to a $P_1 = 74.37$ bar. In this condition, the gas cooler exit (point 2) is located on a rather flat isotherm and hence a small error in pressure translates in a large enthalpy difference.

On the gas cooler/condenser side, the relative error averaged on all data points, in absolute value,

$$e_{gc} = \left| \frac{\dot{m}_w c_{pw} \Delta T_w - \dot{m}_f (h_1 - h_2)}{\dot{m}_w c_{pw} \Delta T_w} \right| \quad (4)$$

comes out to be 1.9 % for pure CO₂.

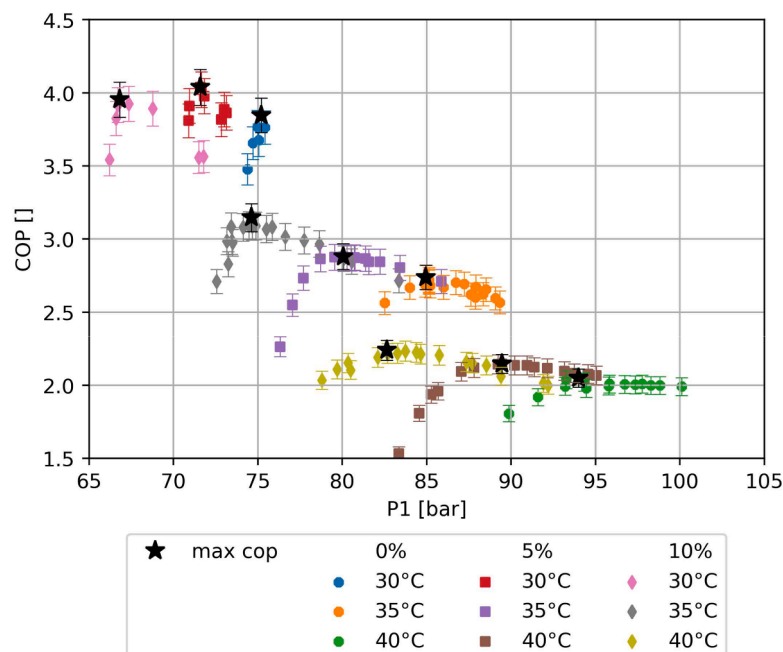


Fig. 2. Synopsis of the COP results.

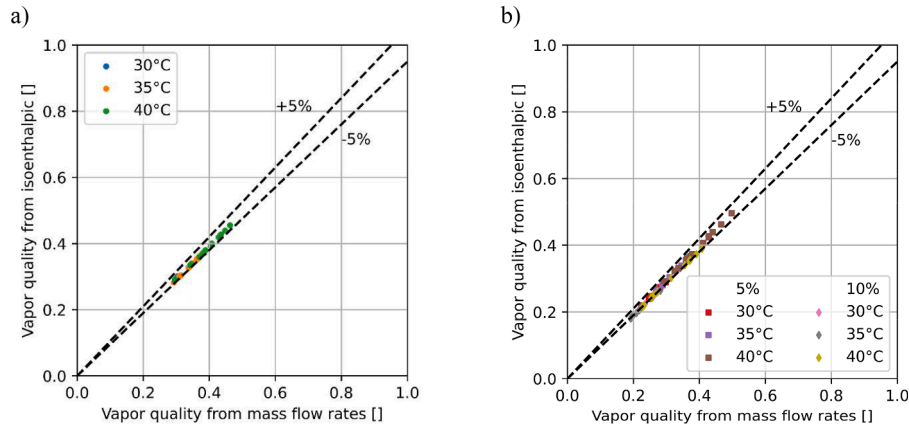


Fig. 3. Vapor quality validation: a) Pure CO₂, b) Mixtures.

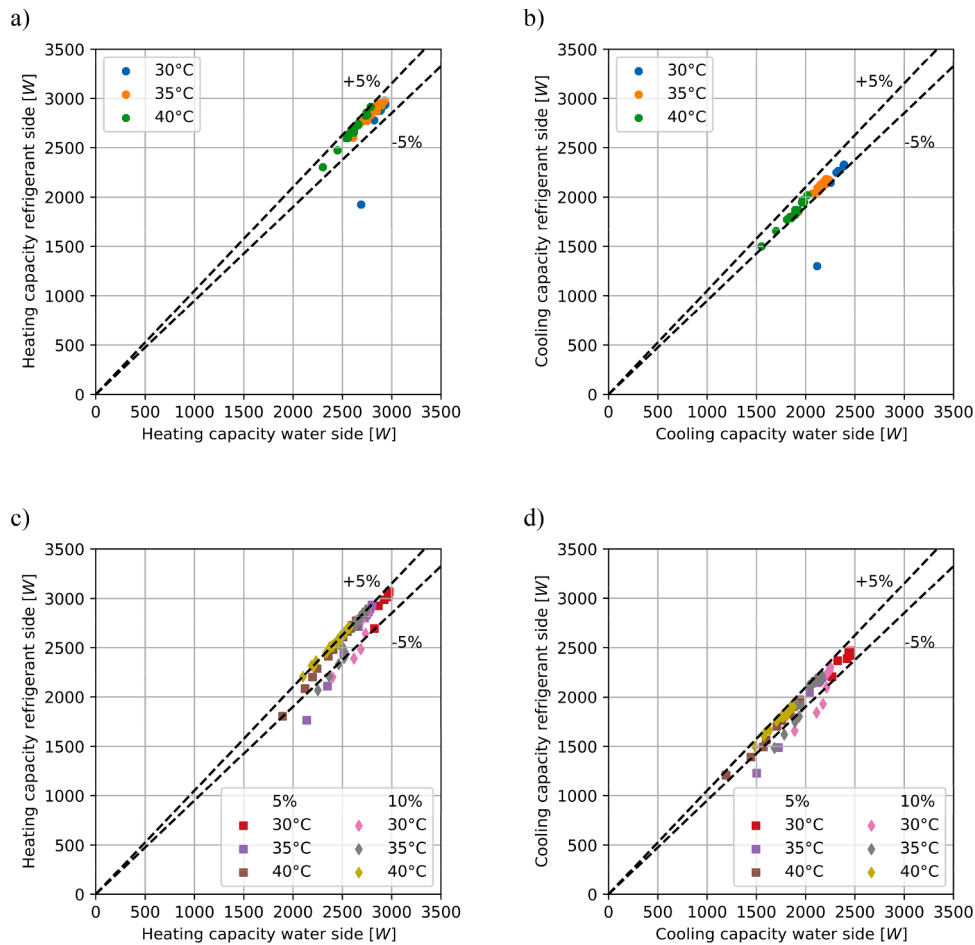


Fig. 4. Heat transfer validation: a) Heating capacity pure CO₂, b) Cooling capacity pure CO₂ c) Heating capacity mixtures, d) Cooling capacity mixtures.

For what concerns mixtures, the results are affected also by the uncertainty in composition. Anyway, results of heating capacity validation are shown in Fig. 4c, and the relative error averaged on all data points, in absolute value, is 4.4 %.

On the cold side, the heat exchanged with the water/glycol may be compared with the heat received by the working fluid, being point 5 obtained by starting from point 0 and subtracting the heat exchanged in the IHX.

$$e_{eva} = \left| \frac{\dot{m}_{wg} c_{p_{wg}} \Delta T_{wg} - \dot{m}_f [h_0 - (h_2 - h_3) - h_4]}{\dot{m}_w c_{p_w} \Delta T_{wg}} \right| \quad (5)$$

The average relative error in absolute value is 2.5 % for pure CO₂ (Fig. 4b) and 3.0 % for mixtures (Fig. 4d).

For what concerns the mixture composition, we have used the iterative method proposed by Johansson et al. (2001) that postulates an isenthalpic expansion and modifies the circulating composition until convergence.

Fig. 5 shows that tests performed with a measured DME percentage of 5 % and 10 % actually have a circulating composition around 2 % and 5 % respectively. Obviously, these are not the precise compositions of the mixture circulating within the system, but undoubtedly show that the

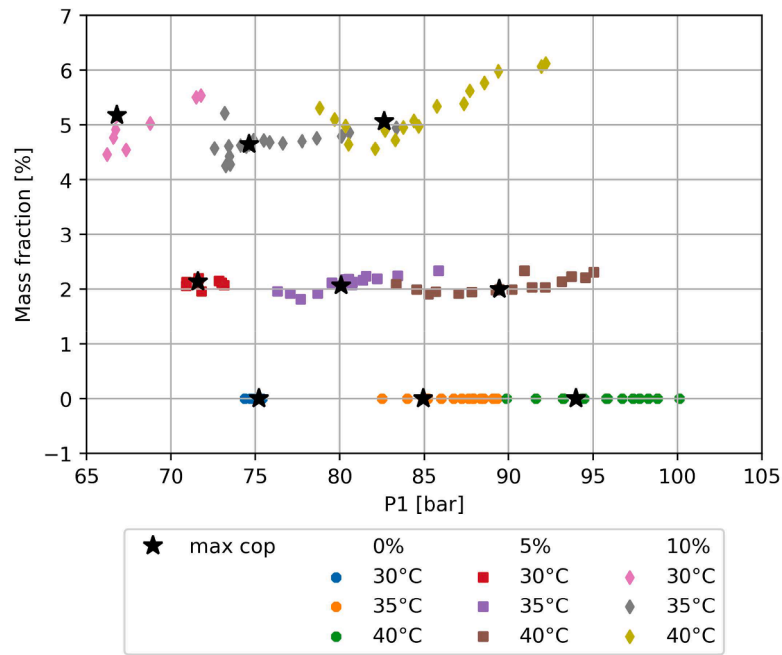


Fig. 5. Calculated circulating composition.

DME percentage during the system operation is significantly lower than expected. Once more, it is proven that DME is able to change significantly the properties of CO₂, even when added in very small quantities.

When dealing with mixtures, REFPROP introduces an additional source of error by overestimating the critical pressure of the mixture (note that the term “pseudo-critical pressure” should be used for mixtures, but the shorter version has been used here for the sake of simplicity). The results calculated by REFPROP may be compared to the experimental results for CO₂ and DME obtained by Tsang and Streett (1981), showing evident discrepancies. Luckily, the temperatures and DME concentrations used in our experiments are moderate, and hence the error is acceptable. Furthermore, as shown by Caramaschi et al. (2022), REFPROP is more robust than other options when modeling

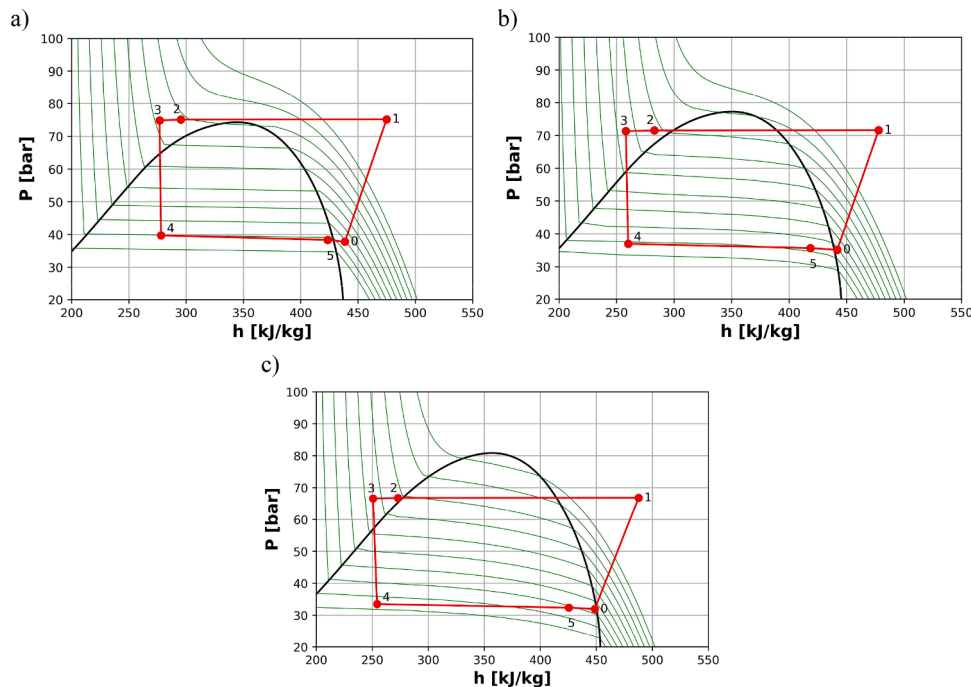
mixtures of CO₂ and other fluids.

3.2.1. Case $T_{w0} = 30^\circ\text{C}$

As a reference, let's first consider the Ph diagram of the cycle operating with pure CO₂ (Fig. 6a). The maximum cycle pressure is practically equal to the CO₂ critical pressure.

In this case, there is obviously no glide on the lower side of the cycle. The condenser pressure is 75 bar. The electric power absorbed by the compressor is 620 W, while the cooling power is 2390 W, giving a COP of 3.85. This result is obtained when the fluid condition at evaporator exit is saturated vapour. The superheating at compressor inlet, i.e. 4.3 °C, is completely given by the IHX.

The IHX heat transfer capacity is weak, as can be seen by the short Δh

Fig. 6. Ph diagram for $T_{w0} = 30^\circ\text{C}$; a) pure CO₂, b) mixture with 5 % DME c) mixture with 10 % DME.

between point 5–0 and 2–3. This may be due to the fact that the IHX in this case does not contain significant quantities of liquid.

When a 5 % of DME is added, the cycle changes significantly (Fig. 6b). The COP rises to 4.04. The condensation pressure lowers to 71.5 bar. Another fundamental difference is evident from the graph: point 5 (end of evaporation) is now well within the two-phase region. This circumstance stems from the optimization of the temperature glide at the evaporator, i.e. this position of point 5 gives a good match between the temperature rise of the water/glycol mixture (5 °C) and the variable evaporation temperature of the CO₂/DME mixture. Furthermore, the residual latent heat available between points 5 and 0 improves the heat transfer within the IHX and hence contributes to the performance improvement.

When a 10 % of DME is added, the results change as shown in Fig. 6c. As already seen in Fig. 2, the increase of DME percentage does not give an improvement in terms of COP. In the case of the cycle depicted in Fig. 6c, the COP is 3.96, i.e. very close, but slightly lower than that obtained with 5 %.

The marginal decrease in COP could be attributed to the increased proportion of DME, which expands the cycle and shifts points 3 and 4 to the left. While this enhances the cooling capacity, it also widens the temperature glide to 6.9 °C, surpassing the temperature differential of the water-glycol mixture. Consequently, this elevates the heat-transfer irreversibility at the evaporator. The reduction in condensation pressure to 66.8 bar is insufficient to compensate this issue.

3.2.2. Case $T_{w0} = 35^\circ\text{C}$

For the case $T_{w0} = 35^\circ\text{C}$, pure CO₂ produces the cycle shown in Fig. 7a. The cycle is clearly transcritical and rather “narrow”, i.e. vapour quality at evaporator inlet is high. Consequently, the IHX has a limited effectiveness because it is empty of liquid. Correspondingly, the COP is as low as 2.74. The gas cooler pressure must now be optimized, and in this case it is as high as 84.9 bar. When a 5 % of DME is added, the critical temperature of the mixture increases to 36.1 °C and hence the cycle becomes wider and passes very close to the critical point, as shown in Fig. 7b. The COP increases to 2.88, while the temperature glide is 2.2 °C. Finally, a mixture with 10 % DME has a critical temperature of 39.9 °C, so that the cycle becomes clearly subcritical and widens even more,

as shown in Fig. 7c. The COP raises to 3.15.

3.2.3. Case $T_{w0} = 40^\circ\text{C}$

The cycle pure CO₂ at $T_{w0} = 40^\circ\text{C}$ shown in Fig. 8a is not dissimilar from the one shown in Fig. 8a, but the optimum gas cooler pressure raises to 94 bar with a COP of 2.05. Adding a 5 % of DME produces the modifications shown in Fig. 8b. The COP is raised to 2.15. Finally, adding a 10 % of DME gives a cycle as shown in Fig. 8c. The COP is further raised to 3.09. The temperature glide is exactly 5 °C, giving a perfect match with the water-glycol mixture.

3.3. Parametric study

Fig. 9a shows the electric power consumed by the compressor as a function of maximum cycle pressure P_1 . A definite, practically linear trend is evident. More precisely, the lower line groups together the points referring to pure CO₂ and 5 % DME at 35 and 40 °C, while the points referring to 10 % DME and 5 % DME at 30 °C are slightly higher. In any case, the vertical distance between the points is so small that, when a reduction of P_1 of the order of 10 bars is considered, the addition of DME surely reduces the power consumption.

The system cooling capacity is shown in Fig. 9b. As can be seen, the 9 curves are grouped as the COP curves in Fig. 2, but the cooling capacity always increases with the gas cooler (or condenser) pressure. The combination of this trend with the one of the power consumed by the compressor gives rise to the maximum COP points shown in Fig. 2. Pure CO₂ exhibits a cooling capacity comparable to that of the mixtures. Only in the case of $T_{w0} = 40^\circ\text{C}$ does the CO₂ cooling capacity consistently surpass that of the mixtures. However, when comparing the maximum COP points, the disparities are not so pronounced: the cooling powers are 1892, 1833, and 1774 W, respectively, for pure CO₂, 5 % DME, and 10 % DME. In other words, only a 6 % is lost in terms of cooling power. Apparently, the loss in volumetric heating capacity is compensated by the improved efficiency, and hence the system may basically satisfy the same cooling load with lower energy consumption.

Fig. 10a shows that for a given pressure P_1 , the compression ratio increases as the DME percentage increases. However, Fig. 9a shows that

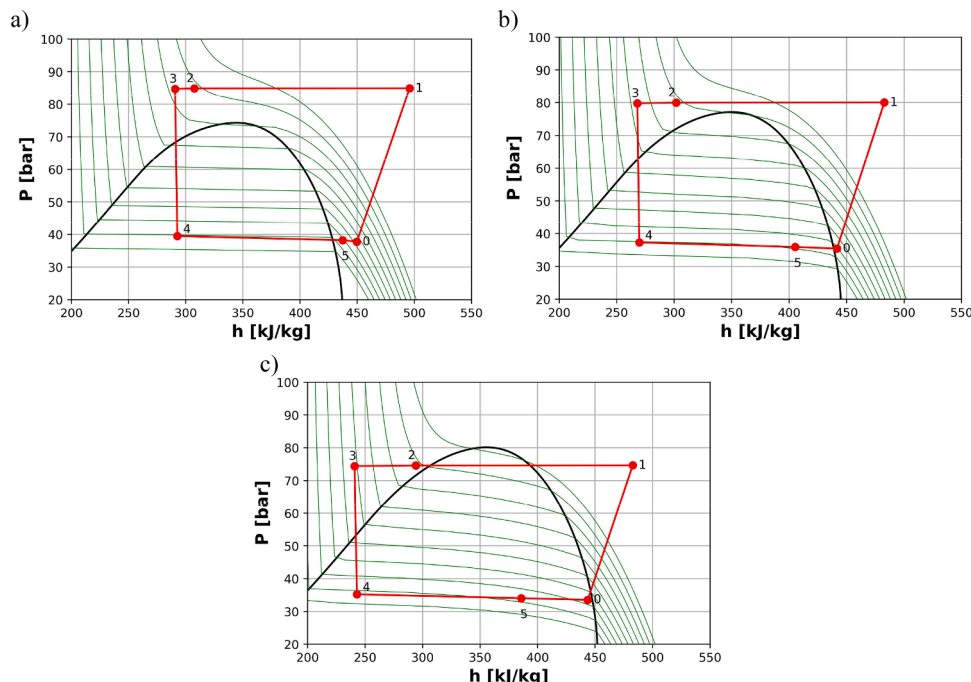


Fig. 7. Ph diagram for $T_{w0} = 35^\circ\text{C}$: a) pure CO₂, b) 5 % DME, c) 10 % DME.

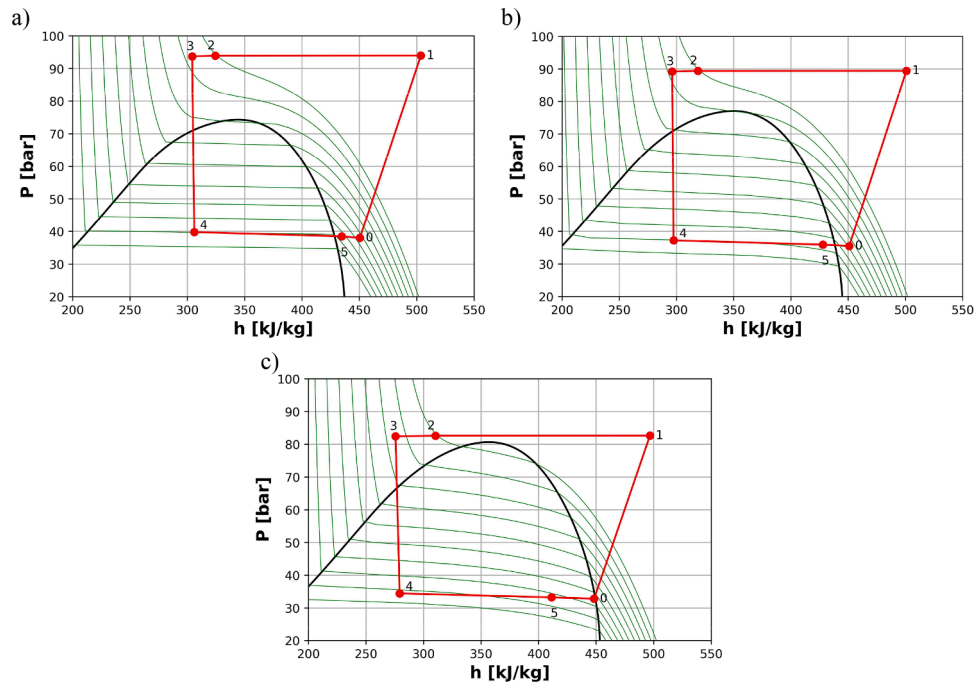


Fig. 8. Ph diagram for $T_{w0} = 40^{\circ}\text{C}$: a) pure CO₂, b) 5 % DME, c) 10 % DME.

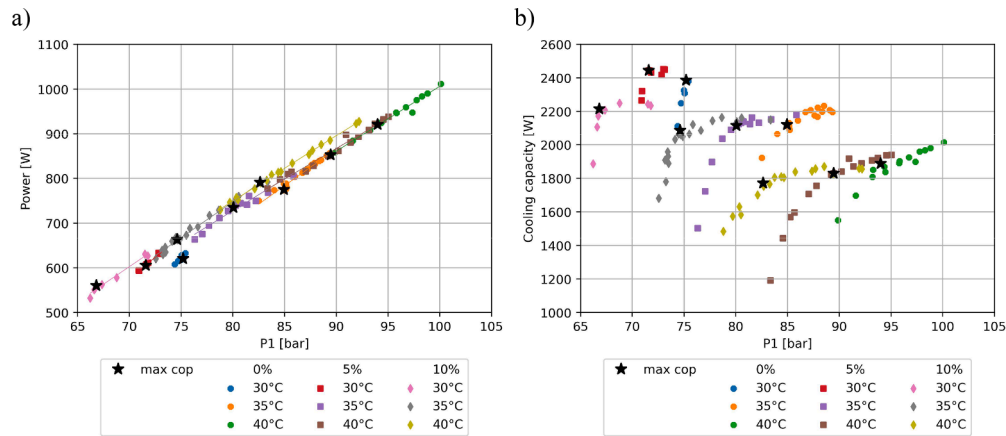


Fig. 9. Compressor: a) Electric power consumed, b) Cooling capacity.

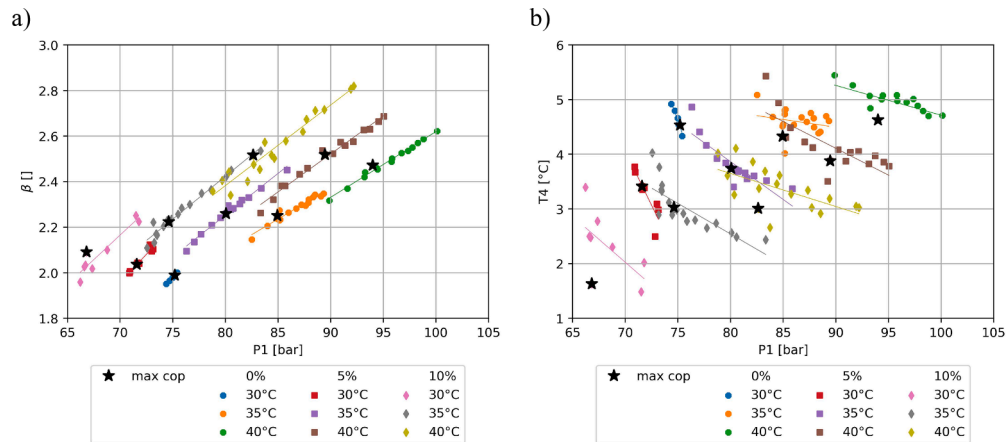


Fig. 10. a) Compression ratio, b) Evaporator inlet temperature.

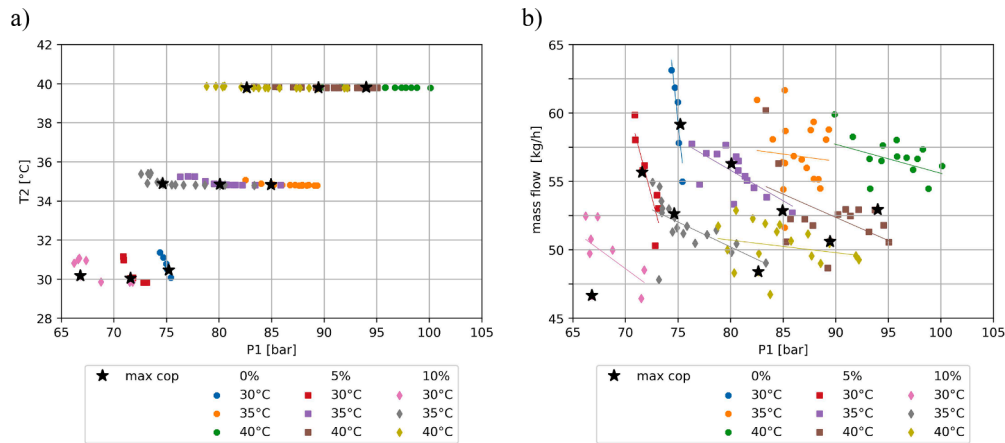


Fig. 11. a) Condenser/gas cooler exit temperature, b) Mass flow rate.

actually input work does not increase that much. This is due to the mass flow rate decrease, which is due to the reduced compressor inlet pressure. The black stars show the optimum conditions in terms of COP and quite evidently are located at roughly the same compression ratio for a given water inlet temperature. An exception is registered in the case marked as 30 °C, as will be explained later.

Another evidence in Fig. 10a is that curves at constant composition and P_1 , (e.g. yellow, grey or pink curves) have a higher compression ratio as temperature T_{w0} decreases. This may be explained from Fig. 10b, where the evaporator inlet temperature T_4 is seen to decrease as T_{w0} decreases. The reason of this behaviour is related to the heat exchange at the evaporator. The enthalpy difference available at the evaporator increases, causing an increased temperature glide and hence an increased pinch point temperature difference between the evaporating fluid and the water/glycol. Henceforth the compressor inlet pressure decreases, increasing β .

Fig. 11a shows the condenser/gas cooler exit temperature (T_2) as a function of pressure P_1 . The dots on top of the figure are all aligned and very close to the water inlet temperature $T_{w0} = 40$ °C. The intermediate series refers to $T_{w0} = 35$ °C. The temperature of the working fluid shows

some variations at low P_1 .

The variations for $T_{w0} = 30$ °C are much more evident. This variability is due to the fact that the gas-cooler/condenser works differently in these cases. For the case at 40 °C, the cycle is transcritical and the coupling between the working fluid temperature and the water temperature is better. Therefore the dots are all aligned and very close to the water temperature (the gas cooler has a huge heat exchange surface). In the case of the dots in the middle of the figure (which correspond to $T_{w0} = 35$ °C), when the pressure decreases, the temperature T_2 increases slightly. In the case of the dots on the lower left corner, the situation is more complex. An explanation can be proposed referring to the blue dots (pure CO₂). If we open the throttle valve and the high-pressure P_1 decreases, the superheat is reduced and the density at the inlet of the compressor is increased. Hence, the increased mass flow rate (Fig. 11b) produces a worse heat exchange at the gas cooler, the water mass flow rate being constant. Fig. 11b shows that increasing the DME concentration, the mass flow rate decreases, as expected due to the lower density.

Fig. 12 illustrates the vapor quality at the evaporator inlet. Within each group of experimental points (same shape and color), we

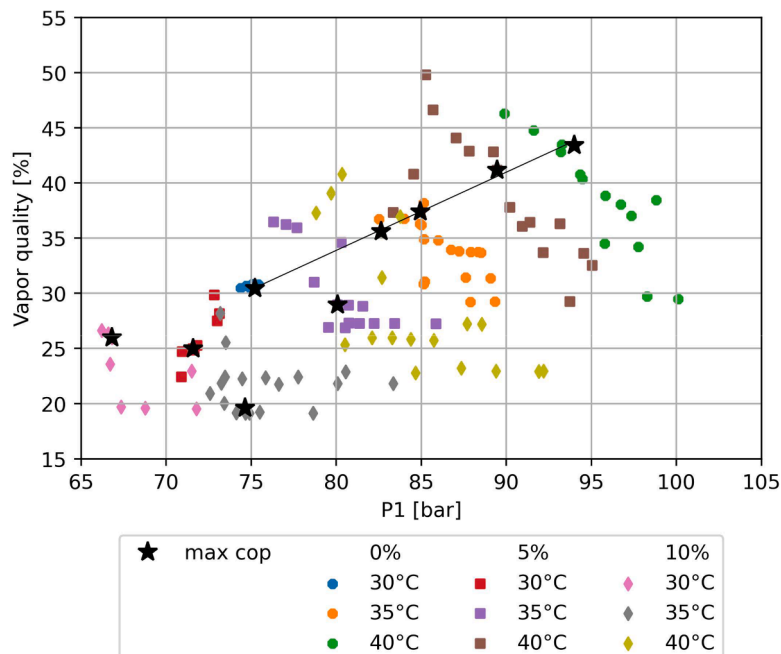


Fig. 12. Vapor quality.

Table 2
Experimental data.

	0 %	0 %	0 %	5 %	5 %	5 %	10 %	10 %	10 %
T_0 [°C]	8.4	15.2	16.1	8.1	8.1	14.2	10.7	10.6	11.3
T_1 [°C]	65.9	85.9	96.4	66.2	75.2	92.5	70.1	72.5	86.8
T_4 [°C]	4.5	4.3	4.6	3.4	3.7	3.9	1.6	3.0	3.0
T_5 [°C]	4.1	6.7	5.8	6.2	5.9	7.0	8.5	6.6	8.0
T_{w0} [°C]	29.8	34.8	39.8	29.8	34.8	39.8	29.9	34.8	39.8
T_{w1} [°C]	34.0	38.7	43.5	34.1	38.8	43.3	33.7	38.6	43.2
T_{wg0} [°C]	12.4	12.1	12.1	12.6	12.0	11.9	12.1	12.0	12.0
T_{wg1} [°C]	7.0	7.0	7.0	7.0	7.0	7.0	7.0	7.0	7.0
T_2 [°C]	30.5	34.8	39.8	30.0	34.8	39.8	30.2	34.9	39.8
T_3 [°C]	27.5	32.3	36.8	24.4	28.2	36.3	24.5	21.4	33.3
m_{liq} [kg/h]	41.2	33.1	29.9	41.8	40.0	29.8	34.5	42.3	31.2
m_{vap} [kg/h]	18.0	19.8	23.0	13.9	16.3	20.8	12.1	10.3	17.2
$\dot{V}_w$ [l/min]	10.1	10.1	10.1	10.1	10.1	10.1	10.1	10.1	10.1
$\dot{V}_{wg}$ [l/min]	6.9	6.6	5.8	6.9	6.7	5.9	6.8	6.6	5.6
P_4 [bar]	39.0	38.8	39.1	36.3	36.6	36.5	32.9	34.6	33.8
P_5 [bar]	38.4	38.2	38.5	35.7	35.9	35.9	32.4	34.0	33.3
P_0 [bar]	37.8	37.7	38.0	35.1	35.4	35.5	32.0	33.6	32.8
P_1 [bar]	75.2	84.9	94.0	71.6	80.1	89.5	66.8	74.6	82.6
P_2 [bar]	75.1	84.9	93.9	71.5	80.0	89.4	66.8	74.6	82.6
P_3 [bar]	74.9	84.8	93.7	71.3	79.8	89.2	66.6	74.4	82.4
W [W]	620.2	774.7	920.9	605.2	734.3	852.4	560.1	663.2	790.6
COP [-]	3.85	2.74	2.05	4.05	2.88	2.15	3.96	3.15	2.24
ΔCOP [%]	0	0	0	+5.2 %	+5.1 %	+4.9 %	+2.9 %	+15.0 %	+9.3 %
Q_{ref} [W]	2389.9	2124.3	1891.5	2448.5	2118.6	1832.6	2218.2	2090.1	1774.4
ΔQ_{ref} [%]	0	0	0	+2.5 %	-0.3 %	-3.1 %	-7.2 %	-1.6 %	-6.2 %

experimented different qualities for each P_1 . By using the two valves positioned after the separator, we can control the superheat at the IHX exit. By reducing superheat, the IHX efficiency is increased, because the liquid volume inside it increases. For a given P_1 , enhancing IHX efficiency leads to a decrease in vapor quality at the evaporator inlet.

For pure CO₂, the optimal condition occurs when the evaporator exit is superheated. Hence the Internal Heat Exchanger (IHX) has a low efficiency, and the quality at the evaporator inlet tends to be high. The graph shows that for a subcritical condition (light blue dots) the quality at the evaporator inlet is constant, while for transcritical cycles (orange and green dots) the quality decreases as P_1 increases.

For mixtures, the data is more varied because we experimented with different superheat levels at the IHX exit for the same P_1 . Interestingly, connecting the optimal points (black stars) of each group reveals a linear trend for both pure CO₂ and mixtures at 40 °C.

However, the results for mixtures at 35 °C (purple and grey symbols) exhibit a different trend. As T_{w0} decreases, the enthalpy difference at the evaporator increases. Therefore, in order to match the water-glycol temperature difference, the quality at evaporator inlet that gives the best COP is reduced.

Finally, for the mixtures at 30 °C (pink and red groups), the optimal vapor quality stops decreasing, because it must be high enough to avoid a two-phase fluid at compressor inlet. Figs. 6b and 6c have already shown that, in both cases, the fluid at compressor inlet is saturated vapor.

Table 2 summarizes all the experimental data obtained for the nine cases discussed in the preceding analysis. Additional points were obtained during the experimental campaign; however, for the sake of brevity, they were not included in this study, but are available as supplementary material.

4. Conclusion

The experimental findings outlined in this paper validate the potential of the CO₂/DME mixture as a viable working fluid for cooling systems. In reference to air conditioning applications, calculations reported in Vaccaro et al. (2024) assert a 25 % enhancement in COP compared to pure CO₂. However, the experimental results demonstrate a maximum COP increase of 15 % (for a mixture containing 10 % DME, with a condensation temperature of 35 °C).

The discrepancy of the experimental result with respect to the calculations may be explained taking in account the differences in boundary conditions, the simplifying assumption used in the modelling and the measurement error on the composition of the mixture used in the experiments. Combining experimental data with thermodynamic analysis, our work suggests that the real DME percentage in the circuit was lower than the one introduced during the charge. This may be due to the preferential absorption of DME in the lubricant and to the different composition of the liquid and vapour phase in the separators. If the gaseous refrigerant is considered, considering that the DME concentration in the gaseous phase is lower than in the liquid phase, more DME can be used and an increased performance may be obtained, without surpassing the flammability level.

Furthermore, the performance of the IHX is not always optimal. For instance, the scenario involving 10 % DME at 30 °C is penalized by a glide of 6.9 °C, exceeding the 5 °C temperature drop of the water-glycol. If the performance of the IHX could be improved, this glide would be reduced, resulting in a higher cycle COPs.

In any case, the result seems interesting and deserves further analysis. It is worth to recall that this mixture is non-flammable, non-toxic and has a GWP of 1. Furthermore, the advantages of CO₂ in terms of high volumetric cooling power, low pressure losses and high heat transfer coefficient, given the low quantity of DME added, change by a small amount.

Declaration of competing interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at [doi:10.1016/j.ijrefrig.2024.10.002](https://doi.org/10.1016/j.ijrefrig.2024.10.002).

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4.5.1 Appendix 1 to paper 5: Analysis of the circulating composition

This appendix aims to address the uncertainties left unresolved in paper 5 concerning the actual circulating composition. Thanks to gas chromatography, the test bench used in Paper 5 was complemented with the possibility to measure the composition under the most relevant thermodynamic boundary conditions, thereby validating the error made in paper 5 when using the Johansson [105] method. Furthermore, thanks to the addition of 3 Coriolis mass flow meters, we attempted to calculate the circulating composition based on the measurements of density, pressure, and temperature.

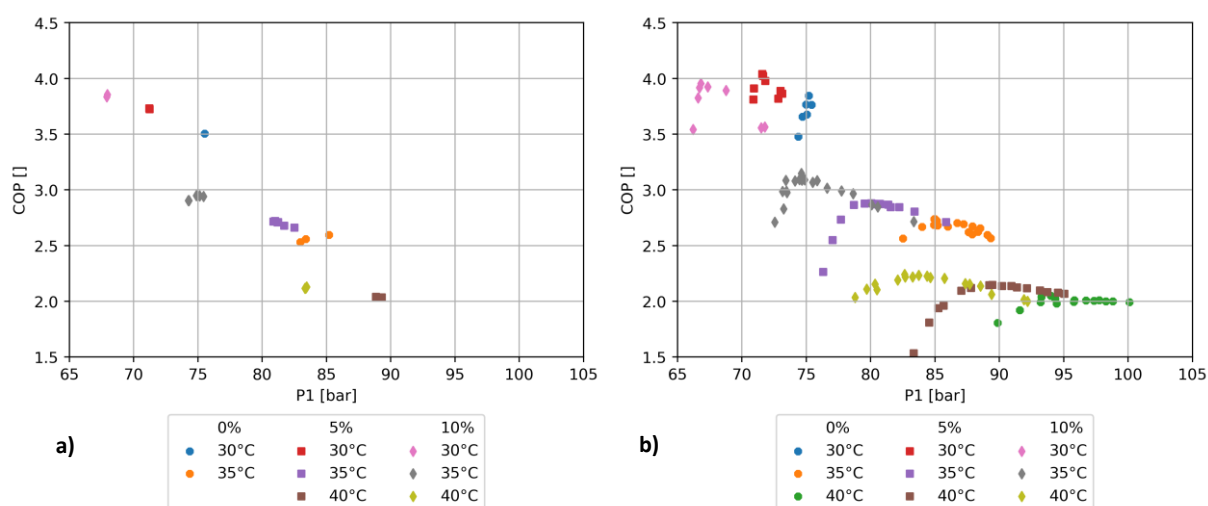


Figure 4.2: COP a) for the second dataset, b) for the dataset of Paper 5.

The measured thermodynamic points were selected to reflect the optimal boundary conditions identified through the COP study in Paper 5. Figure 4.2 presents the COP obtained from the new measurement (Figure 4.2a, new configuration) and from the measurement depicted in Paper 5 (Figure 4.2b, old configuration). A reduction in performance is observed, which is attributed to the addition of the three Coriolis flow meters, introducing pressure losses. However, the overall trends remain consistent with the old configuration, except for the case with 10% DME at 30°C, where the evaporator glide is 5.5°C, therefore insufficient to reduce efficiency.

The compositions measured through the gas chromatograph at point 1 (Figure 4.3a) and point 3 (Figure 4.3b) are consistent. However, the DME fraction at the compressor outlet (point 1) is slightly higher, with an absolute average difference of 0.20%. This is probably due to the fact that the mixture is in the vapor phase at the compressor outlet, making the quantity present in the oil negligible. Conversely, upstream of the throttle valve, the fluid is in the liquid phase, and the higher solubility of DME results in a reduced DME fraction in the measured sample. As illustrated in Figure 4.4 (Fig. 12 in Paper 4), at the same saturation temperature and pressure, solubility decreases with superheat.

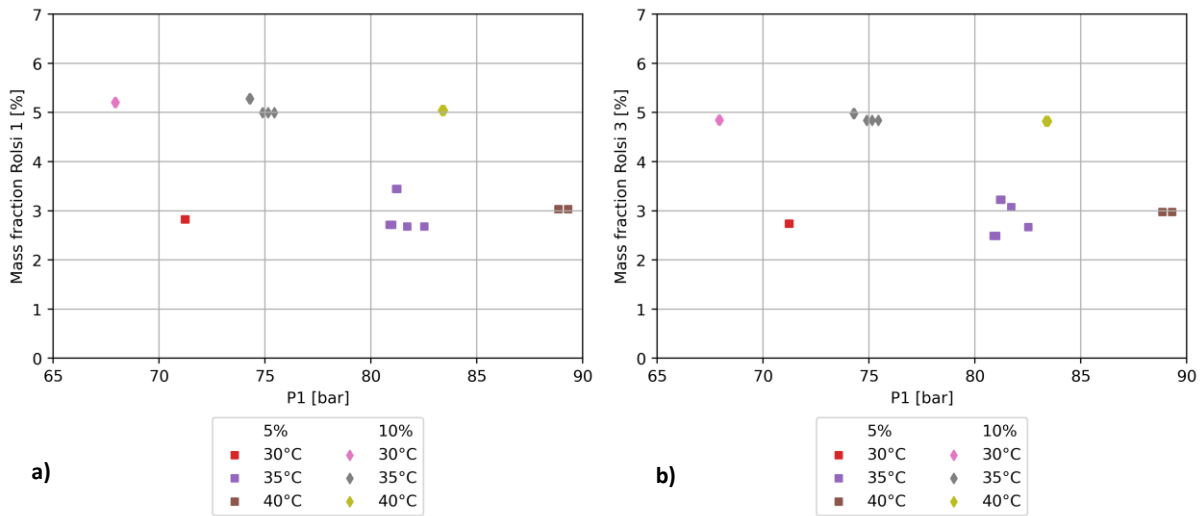


Figure 4.3: Mass fraction measured at: a) Rolsi 1, b) Rolsi 2.

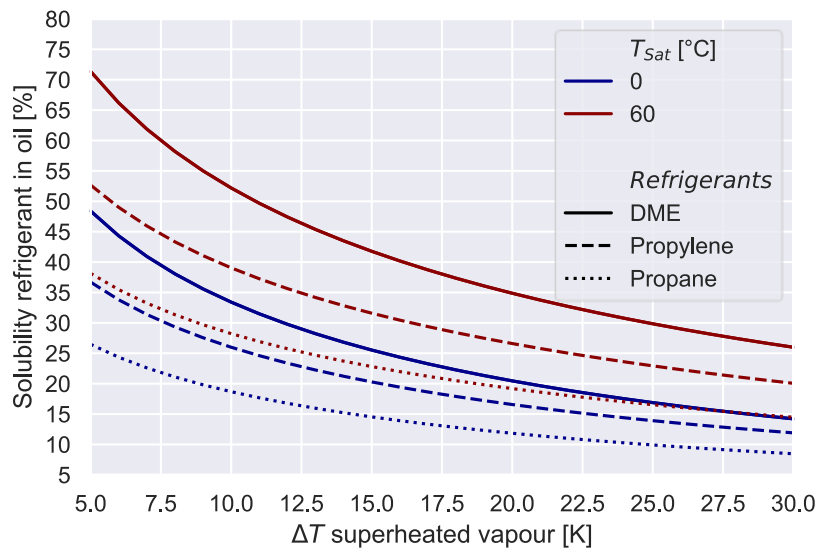


Figure 4.4: Solubility as a function of the level of superheated vapor for different refrigerants.

The Johansson [105] method (Figure 4.5) qualitatively predicts the trend of the mass fraction as the weighted mass fraction varies, correctly for all points. However, the prediction appears to underestimate the circulating composition measured by gas chromatogram in point 3, with an average absolute error of 0.64% and a maximum error of 0.78%.

It is more appropriate to compare this method with the measurement taken upstream of the valve, rather than at the compressor outlet, as it utilizes the temperature and pressure measurements from the same position.

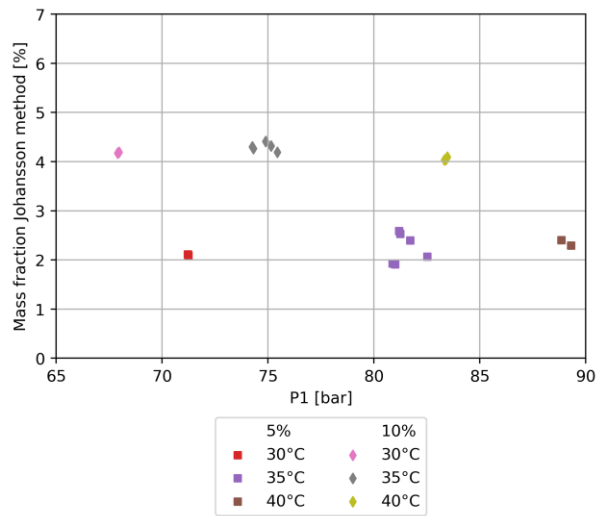


Figure 4.5: Mass fraction calculated with Johansson method.

Thanks to the addition of the three Coriolis, a check was carried out on the measured flow rates.

The figure below (Figure 4.6) shows the error between the mass flow measurement carried out at the compressor inlet (point 0) compared to the measurements carried out at the compressor outlet (point 1), before the throttle valve (point 3) and finally through the sum of the measurements of liquid and gaseous flow.

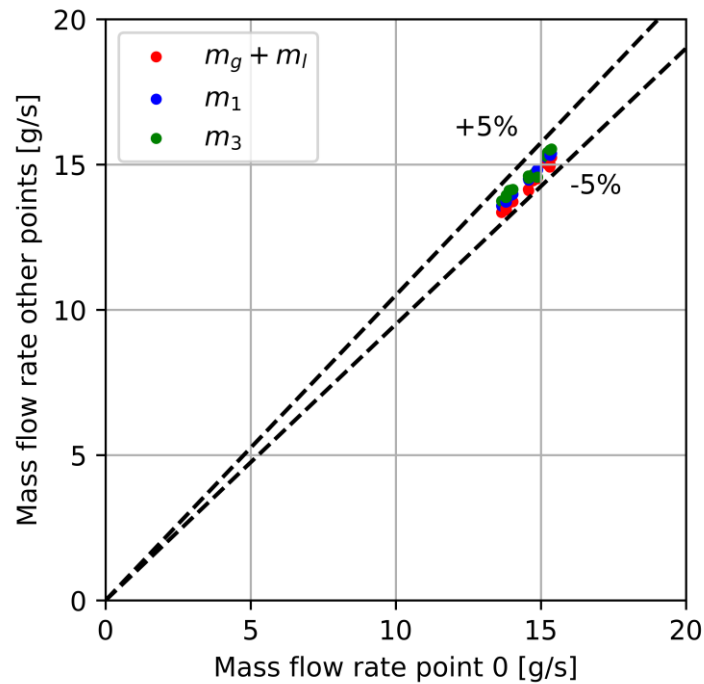


Figure 4.6: Mass flow rate validation.

Coriolis mass flow meters have also been utilized for density measurements, enabling the calculation of composition through an iterative process. Indeed, given the temperature, pressure, and density at a thermodynamic point, only one composition can satisfy these parameters.

The figures below (Figure 4.7) illustrate the composition calculated using this method for the three thermodynamic points. The graphs qualitatively show an increase in the quantity of DME as its weighted fraction rises. However, there are significant discrepancies compared to the values measured with the gas chromatograph. This is likely because small differences in density measurement can lead to large variations in composition. Additionally, density measurements can be affected by gas bubbles or liquid droplets, and the presence of oil can increase the mixture's density. In all three cases, for a weighted fraction of 5% and at 40°C, the mass fraction is qualitatively overestimated.

Among the various measurements, the best prediction is attributed to the Coriolis meter positioned at the compressor inlet, with an average absolute difference of 0.55% and a maximum difference of 1.87% compared to the mass fraction measured with the gas chromatograph at point 3. Although the compressor inlet density method shows a better average error compared to the Johansson [105] method, the repeatability of the Johansson method makes it more robust. The error of the Johansson [105] method is primarily due to an offset, with all points exhibiting similar trends, having a maximum error of 0.78% and an average error of 0.64%.

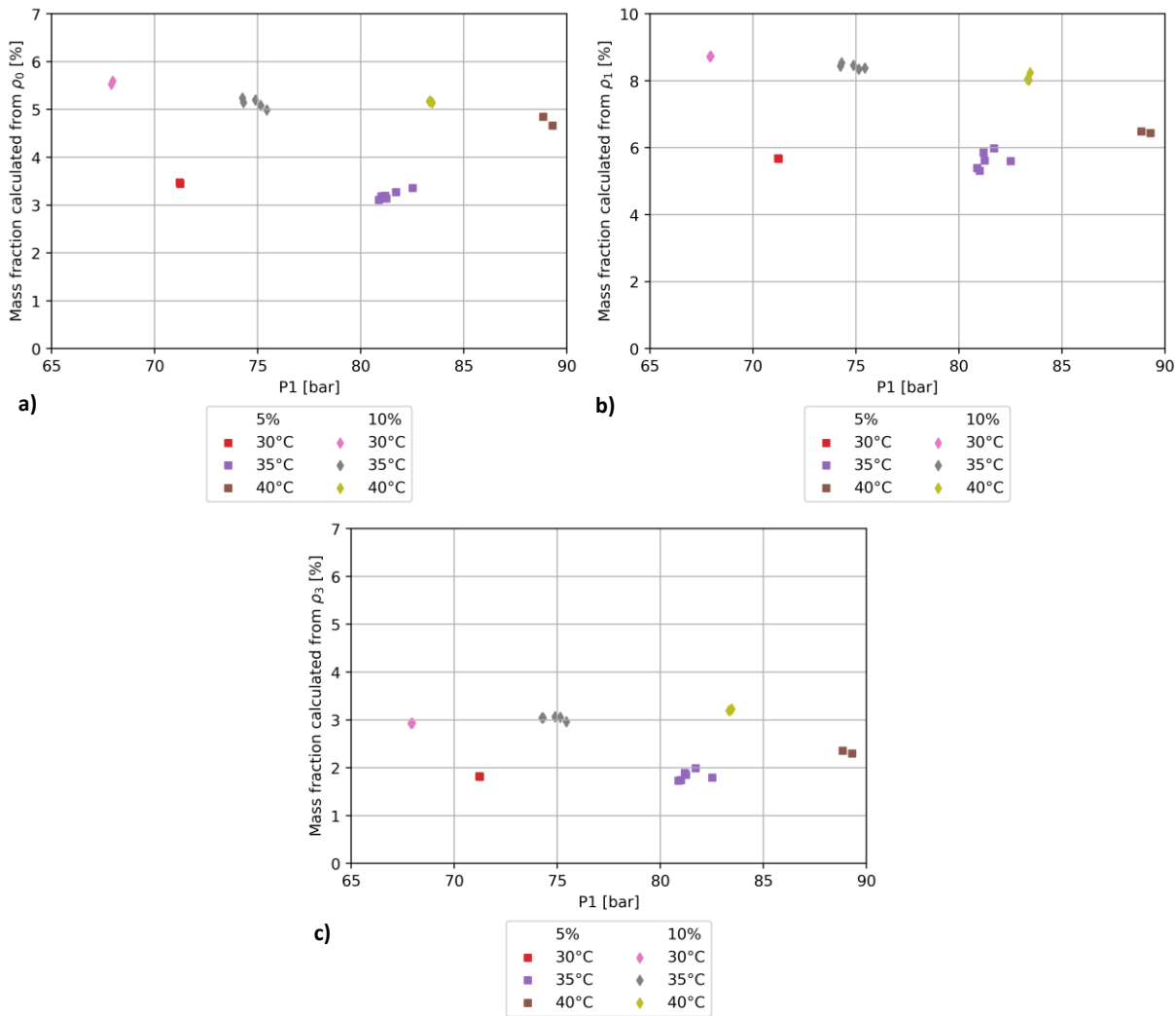


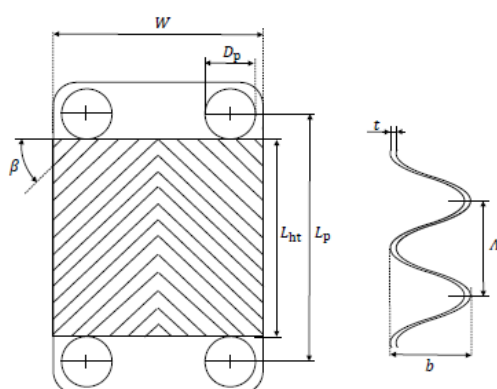
Figure 4.7: Mass fraction calculated with density method at: a) compressor inlet (point 0), b) compressor outlet (point 1), c) throttle valve inlet (point 3).

4.5.2 Appendix 2 to paper 5: Analysis of the evaporative heat exchanger

Based on the results presented in Appendix 1, which detail the actual composition of the circulating mixture, we can compare the measured evaporative heat exchange with the heat exchange calculated using the correlations provided in section 1.4. This comparison is crucial for understanding the actual HTC reduction caused by the introduction of the mixture.

Figure 4.8 and Table 4.1 present the main parameters of the tested evaporator. Similar calculations for the same evaporator were conducted in Roberta Mancini's PhD thesis [67] for CO₂-propane mixtures, yielding similar results. The method used is described in Section 2.4, and the results below show the relative error between the experimentally obtained heat exchange from the water and glycol side and the heat exchange calculated through the model for different correlations on the refrigerant side. It is important to note that the measurements were conducted for mass velocities in the channels ranging from a minimum of 18.8 kg/m²s to a maximum of 21.4 kg/m²s, which are outside the range of many correlations.

Table 4.1: Geometric parameters [67].



Parameter	Unit of measure	Value
W	m	0.120
L_{ht}	m	0.329
t	mm	0.5
β	°	35
b	mm	2.0
λ	mm	7.0
N_{ch}	-	3
d_h	mm	3.4
A_{ht}	m ²	0.28

Figure 4.8: Schematic of PHE geometry.

The Amalfi [70] correlation provides a good prediction for pure CO₂ (Figure 4.9a), with a slight overestimation of heat transfer for mixtures (Figure 4.9b). Figure 4.9c shows the error in heat exchange using the Amalfi [70] correlation with Thome and Shakir [72] (TS) correction, indicating a slight underestimation of the heat exchanged. The Amalfi [70] correlation calculates the HTC without separating it into the convective boiling (CB) and nucleate boiling (NB) contributions. Consequently, applying the TS correction to the entire HTC, rather than just the NB contribution as proposed by Thome and Shakir [72], results in an underestimation.

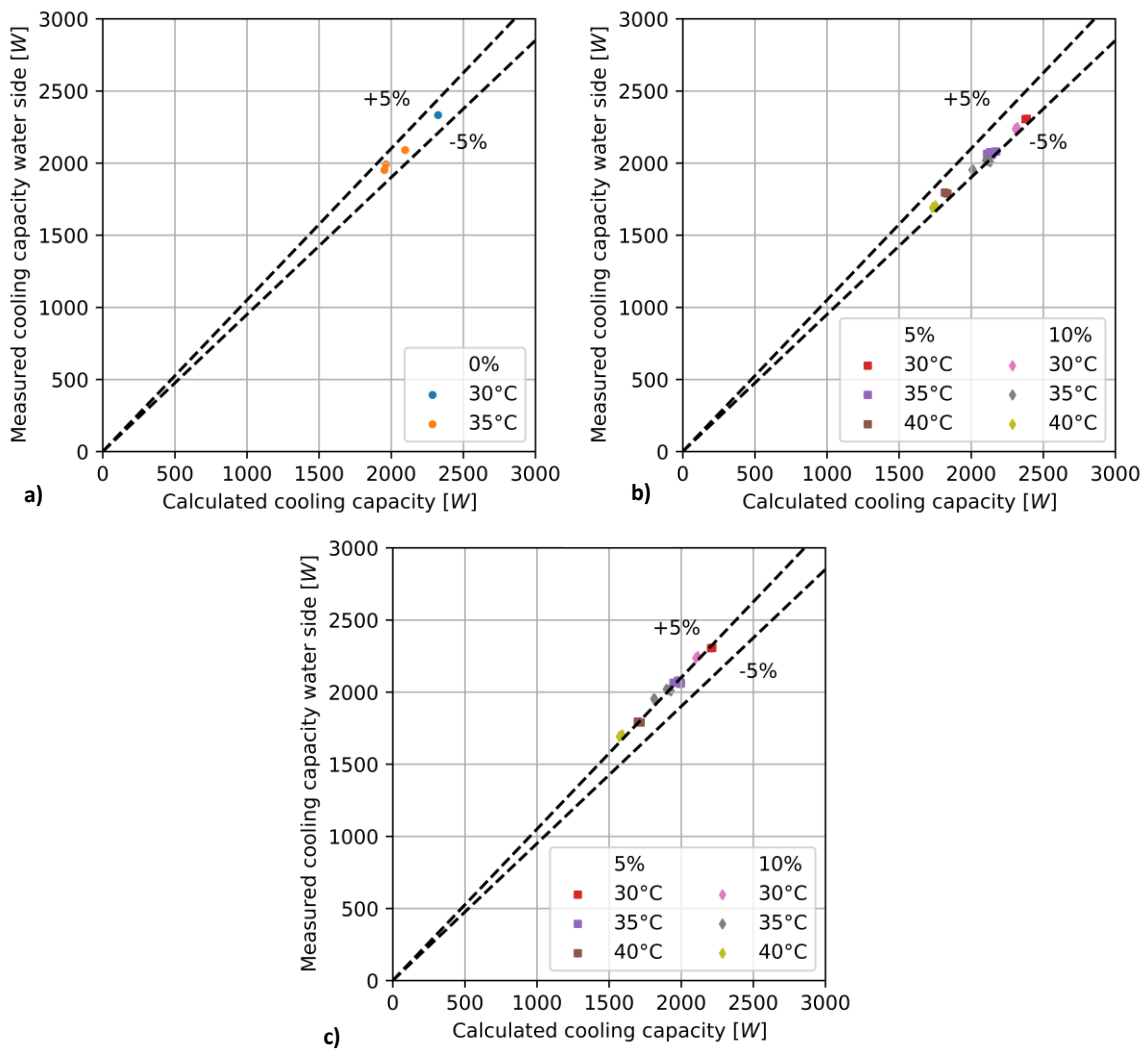


Figure 4.9: Measured and calculated cooling capacity a) for pure CO₂ with Amalfi [70] correlation, b) for mixtures with Amalfi [70] correlation c) for mixtures with Amalfi [70] correlation and TS [72] correction.

The Longo [69] correlation overestimates heat transfer for mixtures (Figure 4.10b). However, Figure 4.10c shows the results with TS [72] correction, achieving a good prediction with a mean absolute relative error of 1.93%.

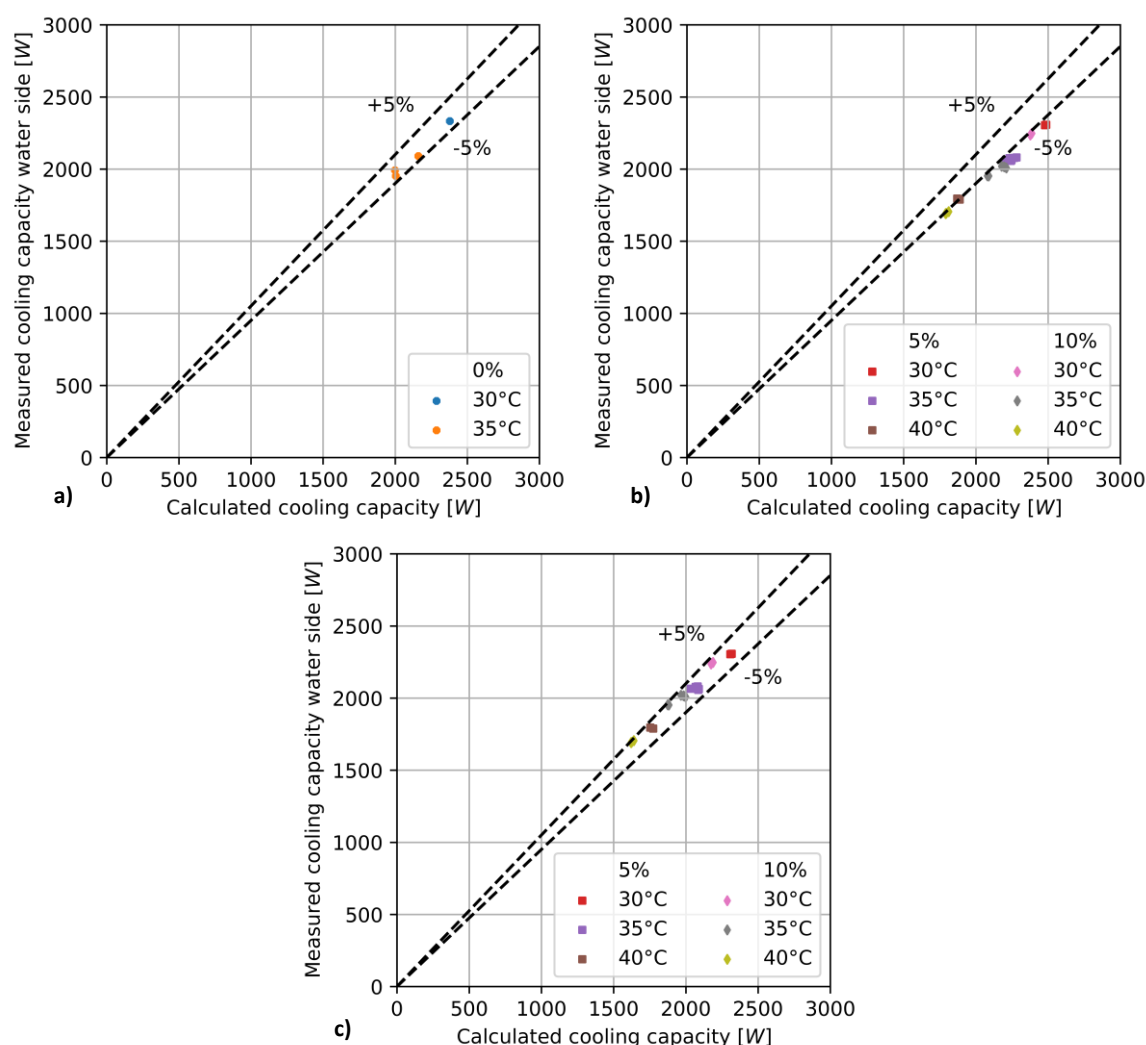


Figure 4.10: Measured and calculated cooling capacity a) for pure CO₂ with Longo [69] correlation, b) for mixtures with Longo [69] correlation c) for mixtures with Longo [69] correlation and TS [72] correction.

The theoretical method by Silver [77] and Bell & Ghaly [75] (SBG) was applied using Amalfi et al. [70] correlation for convective boiling, Cooper [60] correlation for nucleate boiling, and Martin [97] correlation for vapor heat transfer, as suggested by Mancini [67]. In this case, the mean relative error is approximately 3% for both pure CO₂ and mixtures (Figure 4.11), indicating consistency between pure fluids and mixtures. This indicates that the correction factor is effective, despite an overestimation of heat transfer. This overestimation occurs because Amalfi's [70] correlation is designed for the total HTC, not specifically for convective boiling.

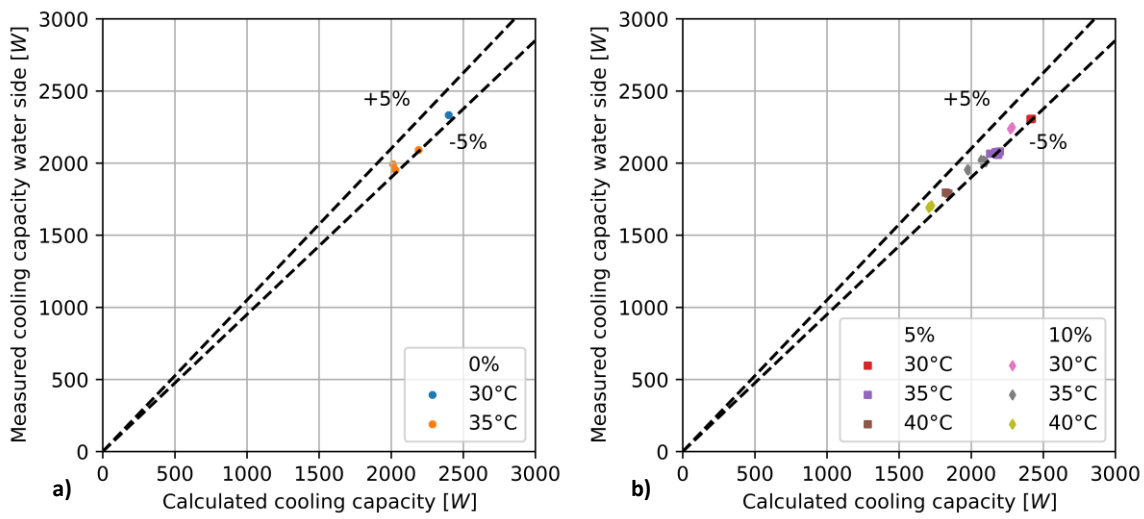


Figure 4.11: Measured and calculated cooling capacity a) for pure CO₂ with SBG [75,77] correlation, b) for mixtures with SBG [75,77] correlation.

Figure 4.12a and b illustrate the error in heat exchange calculated using the Gungor and Winterton (1986)[53] method, as proposed by Thome [73]. Figure 4.12b includes the TS [72] modification for nucleate boiling. For this correlation, the mean absolute relative error is 0.62% for pure fluids and 1.34% for mixtures. Figure 4.12c, which incorporates the modification proposed by Shah [74], shows, as observed in Paper 3, that this method underpredicts the HTC, with a mean relative error of 11.1%.

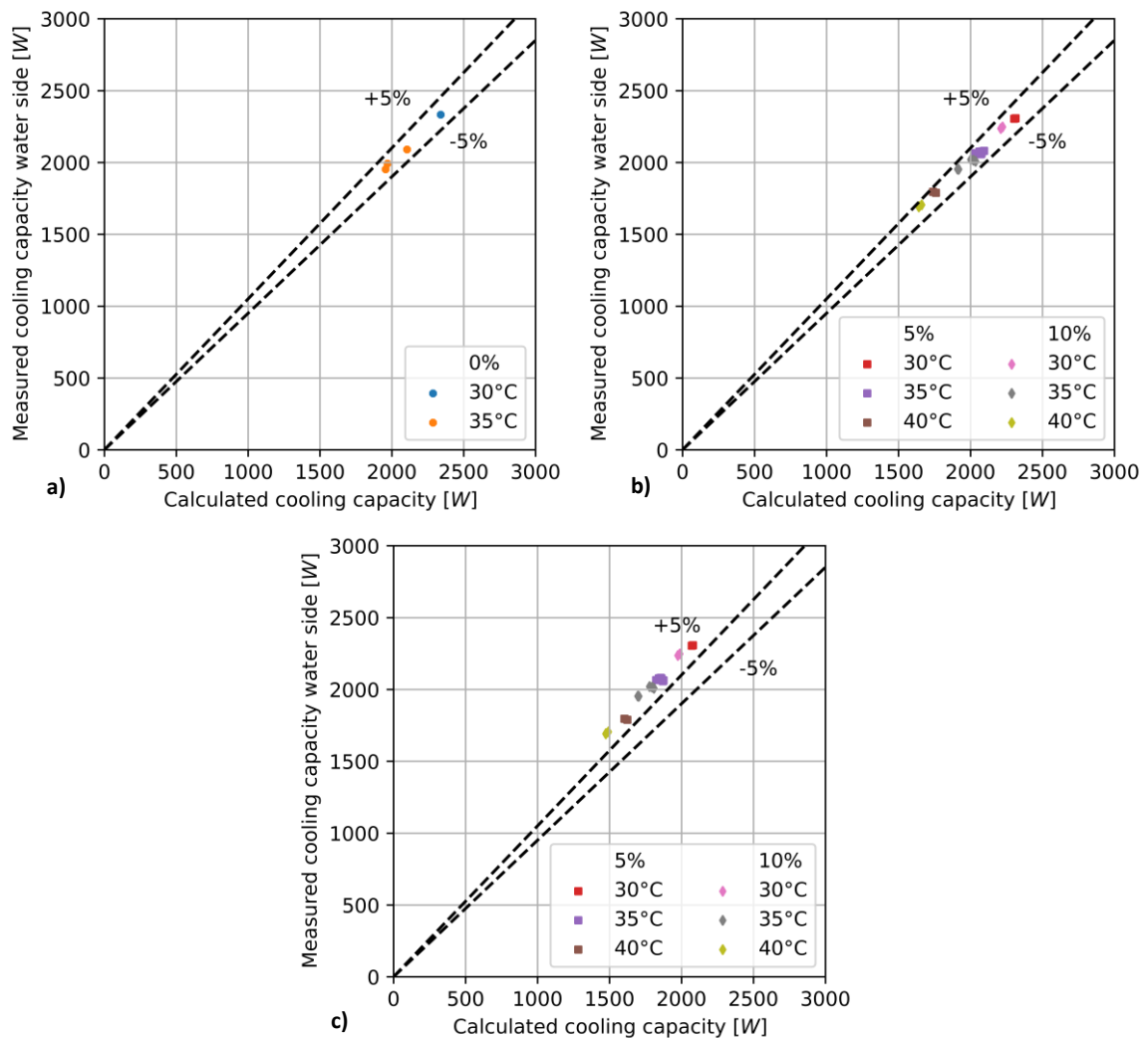


Figure 4.12: Measured and calculated cooling capacity a) for pure CO₂ with Gungor and Winterton 1986 [53] correlation, b) for mixtures with Gungor and Winterton 1986 [53] correlation and TS [72] correction c) for mixtures with Gungor and Winterton 1986 [53] correlation and Shah [74] correction.

Figure 4.13a and b illustrate the error in heat exchange calculated using the Gungor and Winterton (1987) [57] method with the correction proposed by Thome [73]. As observed in Paper 3, the Gungor and Winterton (1987) [57] correlations with TS [72] correction tend to underpredict the HTC. This is likely because the correlation is too simple and does not account for the distinct effects of nucleate and convective boiling.

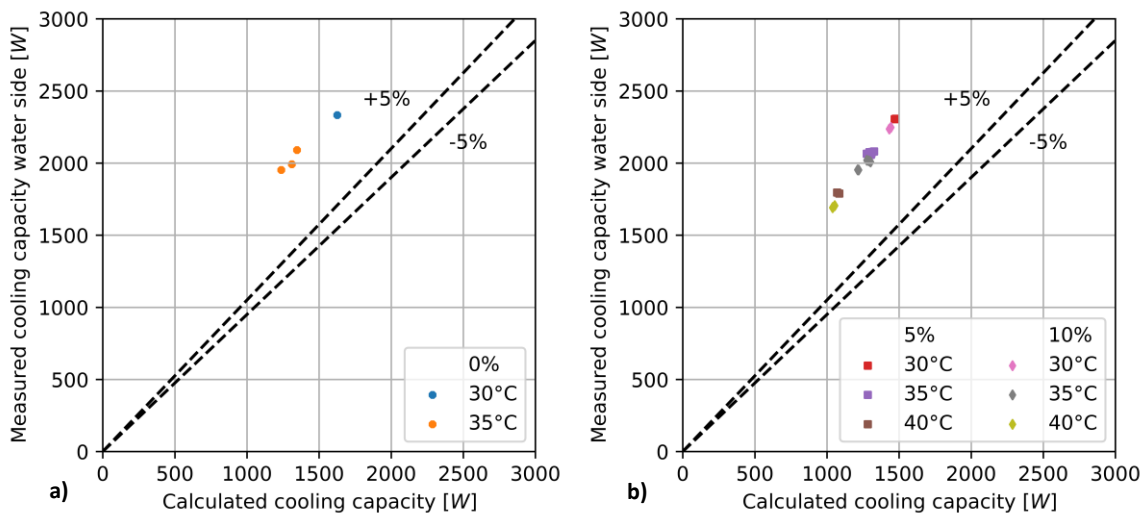


Figure 4.13: Measured and calculated cooling capacity a) for pure CO₂ with Gungor and Winterton 1987 [57] correlation, b) for mixtures with Gungor and Winterton 1987 [57] correlation and TS [72] correction.

Figure 4.14a and b illustrate the error in heat exchange calculated using the Wettermann and Steiner [80] correlation. The HTC for pure fluids is estimated quite accurately, with an average relative error of 2.18%. However, the HTC for mixtures is underestimated, likely because the correlation is designed for high glides, whereas in this study, the glide is approximately 5°C.

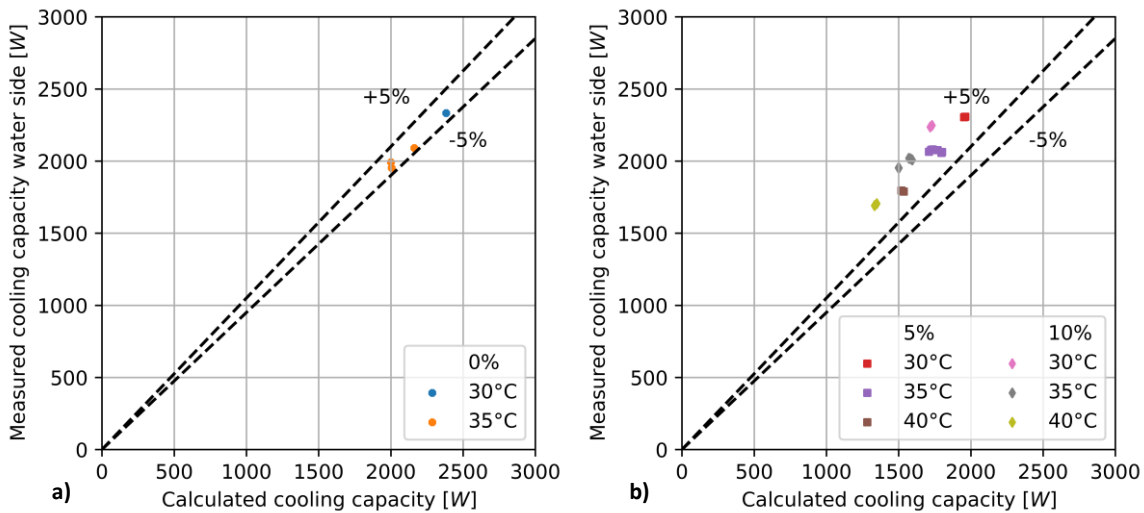


Figure 4.14: Measured and calculated cooling capacity with Wettermann and Steiner [80] correlation a) for pure CO₂, b) for mixtures.

Figure 4.15a and b illustrate the error in heat exchange calculated using the Jung [78] correlation. In this case, the HTC is underestimated for both mixtures and pure fluids. This discrepancy may be attributed to the fact that the correlation for pure fluids is designed for in-tube flow boiling with mass velocities between 250 and 720 kg/m²s, whereas in the present study, the mass velocities range from a minimum of 18.8 kg/m²s to a maximum of 21.4 kg/m²s.

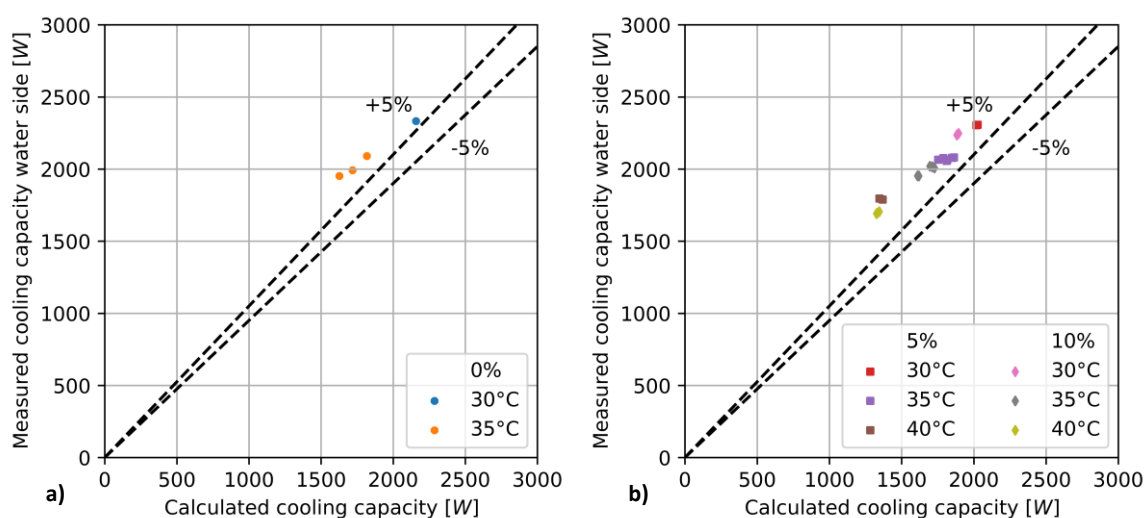


Figure 4.15: Measured and calculated cooling capacity with Jung [78] correlation a) for pure CO₂, b) for mixtures.

To address the issue with the SBG [75,77] correlation using the Amalfi [70] correlation for the convective boiling contribution, one approach could be to subtract the nucleate boiling component from the Amalfi [70] correlation to obtain the convective boiling. For pure fluids, this method ensures that the sum of convective and nucleate boiling matches the Amalfi [70] HTC, which is the best-performing correlation for pure CO₂. For mixtures, the Silver [77](1947) and Bell & Ghaly [75](1973) correlation can then be applied to both nucleate and convective boiling. This approach results in a mean absolute relative error of 1.17%, providing the best performance.

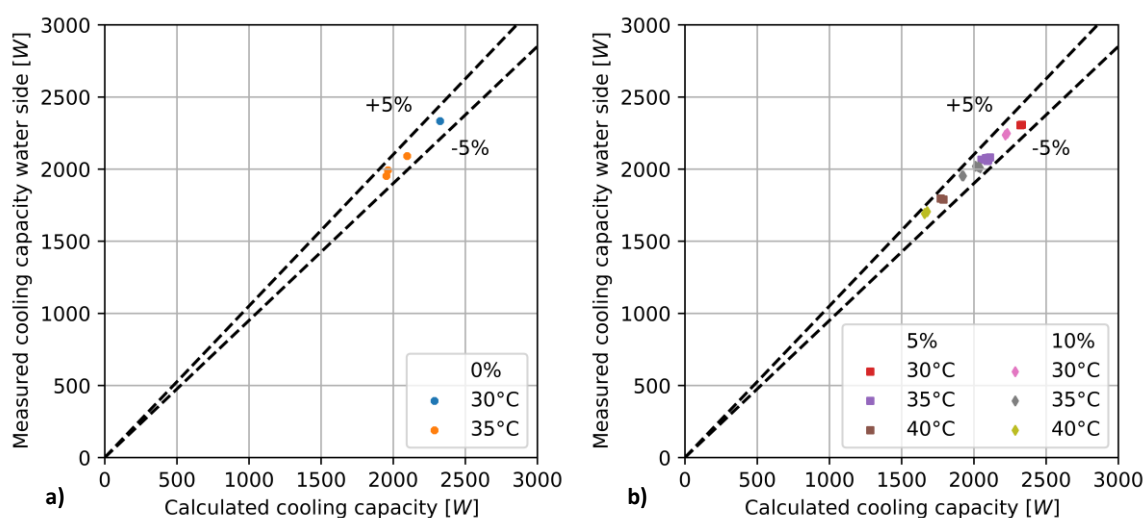


Figure 4.16: Measured and calculated cooling capacity with modified SBG [75,77] correlation a) for pure CO₂, b) for mixtures.

Table 4.2 presents the mean absolute relative error of the studied correlations compared to the measured heat exchange on the water-glycol side. The best correlation is the Silver [77] and Bell & Ghaly [75] method coupled with the Amalfi [70] and Cooper [60] correlations, incorporating the proposed modification. The second-best correlation is the Gungor and Winterton (1986) [53] with TS [72] modifications. These methods effectively represent the heat

transfer degradation due to mixture effects, with mean errors of 1.17% and 1.34%, respectively, and provide good predictions for the pure fluid, with mean errors of 0.53% and 0.62%, respectively. The Amalfi [70] and Longo [69] correlations are specifically designed for PHEs, while the Gungor and Winterton (1986) [53] correlation has been demonstrated by Hisien & Lee [68] to perform well on PHE evaporators. All these correlations offer good predictions, considering the measurement error on the heat exchange on the water-glycol side is about 3%.

It is not recommended to use correlations specifically designed for zeotropic mixtures, such as Wettermann and Steiner [80] or Jung [78]. These correlations are intended for in-tube flow boiling with high glides, whereas in the present case, the glide is around 5°C. Consequently, these correlations underpredict heat transfer by overestimating the glide effects. Additionally, these correlations are designed for higher mass velocities.

Table 4.2: Relative error in absolute value for the analysed correlations.

Correlation	Pure CO ₂ ε %	Mixture ε %
Amalfi [70]	0.53	3.34
Amalfi [70] Ts [72]	0.53	5.25
Amalfi [70] SBG [75,77]	3.14	3.23
Amalfi [70] SBG [75,77] modified	0.53	1.17
Longo [69]	2.07	7.38
Longo [69] TS [72]	2.07	1.93
Gungor and Winterton 1986 [53] TS [72]	0.62	1.34
Gungor and Winterton 1986 [53] shah [74]	0.62	11.10
Gungor and Winterton 1987 [57] TS [72]	34.14	37.21
Wettermann and Steiner [80]	2.18	18.52
Jung [78]	12.73	16.13

5 CONCLUSIONS

This doctoral thesis explores the use of binary mixtures containing CO₂ and small quantities of other fluids in refrigeration applications. The research includes both theoretical/modelling and practical/experimental approaches. It collects a series of scientific publications in international journals produced during the three-year doctoral period, supplemented with additional studies and in-depth analyses.

The starting point was the selection of the refrigerant to be added to CO₂. After a careful literature search, a thermodynamic model incorporating the most common features of a transcritical refrigeration cycle was built. A specific sub-model was devoted to the ejector for expansion work recovery. A large number of compounds were evaluated. A synthesis of this work has been published in the first paper, where a set of mixtures is proven to significantly enhance the performance of trans-critical refrigeration cycles. Simulations of four different configurations, including those with ejectors, reveal that mixtures like CO₂/R1234yf and CO₂/propane offer notable improvements in COP and gas cooler pressure reduction. CO₂/R1234yf achieved a COP increase of up to 12.8% in the base configuration, including only an internal heat exchanger. The highest absolute COP was obtained with a double ejector configuration, although the relative improvement compared to the same configuration operating with pure CO₂ was only 4.3%.

In this first phase, for the sake of simplicity, a saturated vapour condition was fixed at the evaporator exit. When this constrain was removed, as shown in the second paper, the results were even more promising. Specifically, the CO₂/DME (8% DME) mixture has shown a 25% increase in COP, while remaining non-flammable and maintaining the GWP of pure CO₂. At this point, a more detailed analysis was deemed necessary, particularly for what concerns the heat exchange on the low-temperature side of the cycle.

Therefore, in the third paper, a critical review and improvement of flow boiling correlations was carried out, showing how different correlations predict the HTC of pure CO₂ and the degradation of the HTC for CO₂-propane mixtures. This study may help to reduce the error in HTC prediction and understand the benefits and limits of diverse types of correlations.

Another issue may arise from the interaction of the proposed mixtures with the lubricant oil. The fourth paper examines the solubility and miscibility of propylene and DME in POE oil. Solubility experimental data were used to fit different models, and two simple empirical correlations were proposed. Moreover, this paper shows that DME has higher solubility compared to other natural refrigerants.

Finally, thanks to the cooperation with the “Laboratoire du froid et système énergétiques et thermiques (Lafset)” at Cnam, in Paris, an experimental validation of the results obtained thus far has been attempted. The fifth paper reports the experimental results gathered along a large number of experiments along a ... months of lab activity. Despite discrepancies due to IHX efficiency, heat transfer degradation, and mixture composition, the experiments validate the potential of the CO₂/DME mixture. The findings suggest that the circulating DME percentage in the circuit may be lower than the weighted one, possibly due to preferential absorption in the lubricant and phase separation issues.

This issue has been dealt with in an extended period at Lafset, after some improvements in the test bench. Appendix 1 reports the results of this further activity and shows the actual circulating composition measured using gas chromatography. Future research should investigate not only the interaction between DME and oil, as in Paper 4, but also the interaction between the CO₂/DME mixture and oil.

Appendix 2 connects Paper 3 and Paper 5, obtaining promising results for mixtures HTC prediction of PHE evaporator, achieving a relative error in the absolute value of 1.17% between calculated and measured cooling capacity. These correlations should be tested for different geometries and boundary conditions.

The CO₂/DME mixture remains non-flammable, non-toxic, and has a GWP of 1, making it a viable option for refrigeration systems. The advantages of CO₂, such as high volumetric cooling power and low-pressure losses, are maintained with minimal changes due to the small amount of DME added. Our experimental results show a COP increase of up to 15%, with a maximum decrease of 7.2% in cooling power.

To further advance the understanding and application of CO₂-based mixtures, several areas require additional research. One key area is the investigation of compressor behaviour when operating with mixtures of refrigerants and oil. This includes studying the impact on lubrication, wear, and overall efficiency. Developing models to predict the performance of compressors with different refrigerant mixtures is essential, considering factors such as solubility, miscibility, and viscosity of the refrigerant-oil mixtures.

Another important aspect is exploring advanced cycle configurations that can further enhance the performance of CO₂-based mixtures. This includes the use of ejectors, IHX, and other innovative components. Conducting experiments to validate the performance of these advanced configurations under various operating conditions will provide valuable insights into their practical applications.

Additionally, detailed experimental studies are needed to measure the thermophysical properties of refrigerant-oil mixtures, including density, viscosity, and heat transfer coefficients. Developing and validating models to predict the behaviour of these mixtures in real-world applications will ensure accurate and reliable performance predictions.

Overall, fluid mixtures present a promising alternative to pure CO₂, offering enhanced efficiency for refrigeration applications. This study provides a foundation for future experimental work to further optimize these mixtures and explore their practical applications in various cooling systems.

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AI TOOLS USAGE

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