



Analysis of the CO₂ + C₂Cl₄ mixture in high temperature heat pumps: Experimental thermal stability, liquid densities and cycle simulations

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ABSTRACT

Transcritical heat pumps working with CO₂-based mixtures with a low-volatility dopant are found to achieve good performances in thermally integrated heat pumps, especially when sensible heat sources and heat sinks are considered. This paper introduces in literature tetrachloroethylene, C₂Cl₄, as CO₂-dopant for the mixture to be adopted as working fluid in high temperature heat pumps. To calibrate the thermodynamic model used in the cycle simulations, an experimental characterization on the mixture is proposed: liquid densities of the mixtures are measured, in a wide range of concentration, optimizing the binary interaction parameter of the Peng Robinson equation of state. Moreover, the thermal stability of pure C₂Cl₄ is experimentally evaluated, identifying the maximum allowable compressor outlet temperature between 200 °C and 250 °C, with a decomposition rate below 1 %/year if the fluid is kept at temperatures around 200 °C. Then, the potentialities of this very high temperature heat pump are assessed in spray dryer applications: a coefficient of performance around 3.38 is obtained for a conventional spray dryer plant, corresponding to 73 % of second law efficiency, considering an air flow heated from ambient temperature to 200 °C as the sink, while cooling the sensible heat source, available at 76 °C, below 30 °C. As term of comparison, the same system adopting propane, instead of the CO₂ + C₂Cl₄ mixture, would achieve a coefficient of performance and second law efficiency of 2.94 and 64 %, respectively.

1. Introduction

Within the heat pump research field, fast-growing interest is given to very high temperature heat pumps (VHTHP) with maximum temperatures above 150 °C, and high temperature heat pumps (HTHP) with maximum temperatures above 100 °C [1,2], considered crucial to decarbonize many industrial sectors that may be otherwise “hard to abate” with respect to the carbon emissions [3,4]. As shown in literature by Chua [5], various industrial processes can be decarbonized with thermal power from HTHP, such as the paper, food or textile manufacturing, or the space heating in the civil sector with district heating networks.

When the system is analyzed at component-level, according to a literature review from Arpagaus [6], screw compressors are largely adopted for HTHP, whereas oil-free centrifugal compressors are also mentioned for their importance in increasing the cycle efficiency [7]. Limiting the problems of the fluid contact with the lubricant oil, there

are few solutions available on the market for temperature levels above 150 °C exploiting refrigerants such as R-245fa or R-1336mzz(Z).

Detailed reviews are available in literature for screening refrigerants for HTHP [8]: in general, families of working fluids such as hydro-fluoro-olefins (HFO) and hydro-chloro-fluoro-olefins (HCFO) are considered as valid alternatives to hydro-fluoro-carbons (HFC) due to their limited global warming potential (GWP) and ozone depletion potential (ODP) effects [9].

Given the relatively low critical temperature of commercial refrigerants (the refrigerant with the highest critical temperature is R-1336mzz(Z), at 171 °C), a paradigm shift from subcritical layouts to transcritical ones is necessary if the HTHP is coupled with high sink temperatures. As a matter of fact, carbon dioxide (CO₂) is one of the most considered working fluid for transcritical HTHP, as it is already a commercial solution for HTHP with cold sources at ambient temperature [10]. For example, a possible application for the recovery of low temperature heat sources with transcritical CO₂ heat pumps investigated in literature can be identified in the waste heat from data centers [11],

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Nomenclature		VHC	Volumetric Heating Coefficient
<i>Acronyms</i>		VR	Volumetric Ratio across the compressor
AAD	Average Absolute Deviation	VTD	Vibrating Tube Densimeter
BIP	Binary Interaction Parameter of a mixture	<i>Symbols</i>	
CEEP	Centre for Energy Environment Processes	h	Enthalpy [kJ/kg]
COP	Heat pump Coefficient of Performance	\dot{m}	Mass flow rate [kg/s]
EoS	Equation of State	P	Pressure [bar]
GWP	Global Warming Potential of a fluid	ΔP	Pressure drop [bar]
HCFO	Hydro-Chloro-Fluoro-Olefins	\dot{Q}	Thermal power [MW]
HFC	Hydro-Fluoro-Carbons	T	Temperature [°C]
HFO	Hydro-Fluoro-Olefins	ΔT	Temperature difference [°C]
HTHP	High temperature heat pump	ρ	Density of the mixture [kg/m ³]
VHTHP	Very high temperature heat pump	τ	Oscillation period of the VTD [Hz]
HX	Heat Exchanger	k^*	Decomposition rate of the fluid [% _{mol} /s]
ODP	Ozone Depletion Potential of a fluid	\dot{W}	Mechanical power [MW]
sCO ₂	Supercritical Carbon Dioxide		
VLE	Vapor Liquid Equilibrium of a mixture		

available within the 25–35 °C temperature range. Similarly, simple layouts of transcritical CO₂ heat pumps can be also exploited for the simultaneous space heating and cooling in the civil sector [12]. Nevertheless, due to the low critical temperature of CO₂ (31 °C) cold sources at temperatures higher than 40–50 °C would induce significant irreversibility in the evaporator of the transcritical HTHP: under this perspective, the use of CO₂ binary mixtures with a higher critical temperature allows for the optimal exploitation of low-grade sensible heat by tuning the temperature profile at the evaporator, minimizing the average temperature difference between the heat source and the working fluid.

The adoption of CO₂ mixtures as working fluids can play an important role to improve the HP coefficient of performance (COP) by exploiting sensible and low temperature heat sources, in the 70–90 °C range, consistently above the CO₂ critical temperature: this category of HP, thermally integrated into a heat source at a temperature higher than the ambient one, can be in fact considered in waste heat upgrading processes. As the waste heat can be recovered from many applications [13], such as flue gases at the stack of conventional systems or waste by-product of industrial processes, at this low temperature range it is not always techno-economical advantageous to exploit the waste heat in a power cycle for electricity production [14]. According to reviews of waste heat availability in literature, a share of waste heat can be classified as technically recoverable but not interesting from an economical point of view, as proposed by Brückner [15]. In this context, thermally integrated heat pumps can also unlock the techno-economic potential that was originally not foreseen for a direct use of the available low temperature waste heat.

In addition to the effects of the heat source temperature profile on the HP, transcritical HTHP are proved to be effective also for applications with sensible heat sinks. This configuration of HTHP are studied in literature exploiting CO₂ as working fluid: Carnot batteries [16] (already developed by ABB [17], MAN-Energy Solutions [18] and Echogen [19]), advanced drying processes (as discussed in many literature works as by Abedini [20] and Vieren [21]), and high temperature pressurized water production useful both for industrial processes and for district heating are a few examples of possible applications. Regarding CO₂-mixtures, recent studies of HTHP with sensible heat sources evidenced promising configurations in terms of obtainable COP for various applications, such as thermally integrated Carnot batteries [22,23], upgrade of waste heat up to 90 °C as proposed by Liu [24] or low temperature drying processes as in the work of Dai, where the mixing of a dopant with CO₂ helps in reducing the cycle maximum pressure [25].

Among the many possible working fluids for this wide category of thermodynamic cycles, this work proposes tetrachloroethylene (i.e.

C₂Cl₄, CAS number: 127-18-4) as dopant for CO₂ to be used in cycles with maximum temperatures up to around 250 °C. Tetrachloroethylene is a non-flammable, non-reactive fluid with a limited toxicity level. It is liquid at ambient temperature, since its normal boiling point is 121 °C, it can be put in contact with the skin without causing permanent damage and it has an ethereal odour that can be detected by humans at concentrations above 1 ppm (7 mg/m³). It is cheap and it has plenty of commercial applications, such as being a dry-cleaning agent for textiles and an excellent solvent for organic materials: in fact, it is still massively produced and sold worldwide [26]. Its ODP approaches zero [27], as the compound is classified as a very short-lived substance, differently than other substances, like chlorofluorocarbons, that were banned by the Montreal protocol in 1987. The thermodynamic characteristics of the fluid are well known, and experimental data of this pure fluid are available in literature [28,29]. Nevertheless, even if C₂Cl₄ was historically present at high concentrations in dry-cleaning facilities in 1970 s and 1980 s (it was measured with average concentrations around 100 to 200 mg/m³ in the 1980 s in the US and Nordic European countries [30,31]), nowadays an accurate management of the leakages from the HTHP loop into the environment must be foreseen, considering that the fluid was categorized by the World Health Organization in 2017 as carcinogenic agent in class A2 (defined as “probably carcinogenic”). To do so, a series of technical solutions (such as dry gas seals for the turbomachinery leaks) are nowadays commonly adopted in the turbomachinery industry to avoid the dispersion of the working fluid in the external environment, allowing to deal with extremely problematic fluids.

C₂Cl₄ is considered of interest as dopant for a CO₂ mixture, since a very small amount of the dopant in the mixture (even below 1 % on molar basis, i.e. below 5 % on mass basis) is sufficient to drastically move the critical temperature of the resulting CO₂ + C₂Cl₄ mixture above 70 °C, allowing for large glides during the evaporation process, hence permitting favorable conditions for recovering heat from sensible sources. The dominant fraction of CO₂ in the mixture, finally, drastically reduces any effect related to the limited toxicity of the fluid and the GWP of the resulting working fluid.

Very few pieces of information are available in literature regarding C₂Cl₄ thermal stability, and no information about the thermodynamic behavior of the mixture can be found: according to a literature source the fluid starts decomposing within a narrow timespan below 400 °C, determined experimentally by flowing vapors into quartz tube [32]. However, quartz tube is an inert environment, and the residence time considered in literature is too limited to understand the actual thermal resistance of the fluid, making the outcome of this test not relevant for

real applications.

Consequently, this work adopts a robust methodology to experimentally determine the fluid thermal stability, with the experimental procedure presented in literature [33], closing the research gap on the thermal stability of the selected fluid. In addition, in order to close the gap on the lack of available data for the $\text{CO}_2 + \text{C}_2\text{Cl}_4$ mixture, a set of liquid densities of the mixture on the high-pressure region are collected: the data are exploited as a basis for a preliminary selection of the proper equation of state (EoS) for this mixture, necessary for the cycle calculations and the identification of the HTHP performances. The methods developed in this work can be reposed and extended in future works to other CO_2 -mixtures with heavy dopants, characterized by a high normal boiling point, that can be of interest for the same application.

2. Methodology and overview of the work

The schematic of the full methodology adopted to assess the potentialities of the $\text{CO}_2 + \text{C}_2\text{Cl}_4$ mixture as working fluid for VHTHP is depicted in Fig. 1.

Experimental data on the specific mixture are necessary to have a preliminary characterization of the thermodynamic behavior of the fluid in a wide range of temperatures, pressures and compositions. In this work, an experimental campaign was carried out to measure liquid density of the mixture at high pressure and low temperature, using a validated methodology with a vibrating tube densimeter at the CTP experimental platform of Mines Paris, PSL University, Centre for Energy Environment Processes (CEEP), in Fontainebleau, France.

The measurement of the liquid densities of the mixture allowed the calibration of the Peng Robinson EoS, by fitting the binary interaction parameter on the collected experimental data. Focusing on the application of the mixture in HPs, an accurate characterization of the density across the whole range in temperatures and pressures can be valuable to have a confident characterization of the compressor volumetric ratio and the volumetric heating capacity of the cycle, two crucial parameters.

As a second step, it is important to define the maximum temperature at which the fluid can be operated. To do so, stability tests are conducted on C_2Cl_4 , according to a validated methodology for pure fluids at the Fluid Test Laboratory of the University of Brescia (Italy): the CO_2 -dopant is charged in a vessel and kept for one hundred hours at a predefined temperature, in an oven. Quantitative analyses are performed before and after the thermal stress, determining the eventual decomposition rate of the fluid. The simulations proposed in this work on HTHP will be coherent with the experimental campaign on thermal stability, in particular by limiting the maximum temperature of the working fluid in the HTHP at a value that leads to an almost negligible decomposition of the working fluid along the plant lifetime (below 2 % per year).

Once the thermal stability analysis and the calibrated EoS are

available, the modelling of the innovative VHTHP using $\text{CO}_2 + \text{C}_2\text{Cl}_4$ as working fluid can start and the potentialities for a specific application assessed. In particular, the temperature range of both the sink and the source of the HP should be defined to identify the mixture composition which maximizes the COP. In addition, with respect to literature works on subcritical heat pumps with mixtures that present good performances in subcritical configurations with low temperature lifts [34], in this work excellent cycle performances are evidenced with large temperature lifts and in transcritical cycle configurations, closing this research gap.

Finally, a comparison between the HTHP performance proposed by the mixture and the one obtainable with conventional pure fluids for the same application is shown, fully demonstrating the interesting effectiveness of the innovative solution. The comprehensive analysis proposed to assess the potentialities of the innovative working fluid in commercial application can be extended and applied to any other fluid and other conditions, providing a relevant contribution to the HTHP development.

3. Experimental analysis on the $\text{CO}_2 + \text{C}_2\text{Cl}_4$ mixture liquid densities

Density measurements of the $\text{CO}_2 + \text{C}_2\text{Cl}_4$ mixture have been obtained at the CTP experimental platform of Mines Paris, PSL University, Centre for Energy Environment Processes (CEEP), in Fontainebleau (France), through a Vibrating Tube Densimeter (VTD) manufactured by Anton Paar (model DMA HPM). The test rig is already described in literature by Nazeri [35] and presented by the authors of this work for the experimental analysis of a different CO_2 -based mixture in literature [36]. The mixture is prepared in a variable volume cylinder by gravimetric method as described in [supplementary materials](#).

The layout of the apparatus is depicted in Fig. 2: the mixture is kept under pressure in liquid condition within the variable volume cylinder by a piston controlled with pressurized nitrogen. Afterwards, it flows into the VTD immersed into a thermostatic bath (opening the valves V4 and V5): when temperature and pressure reach equilibrium, the density can be measured. In order to modify the pressure of the fluid inside the VTD, a portion of liquid mixture can be accommodated in the variable volume cell, before the venting system, at constant temperature and composition. The uncertainties of the measured quantities (density, temperature and pressure) are computed as reported in [supplementary materials](#), coherently with the use of the same VTD apparatus as reported in literature [36]. The thermostatic bath allows to keep a constant temperature along the measurements. A detailed description of the working principle of the measurements carried out in the VTD is reported in [supplementary materials](#).

The densities of the $\text{CO}_2 + \text{C}_2\text{Cl}_4$ mixture are measured correlating

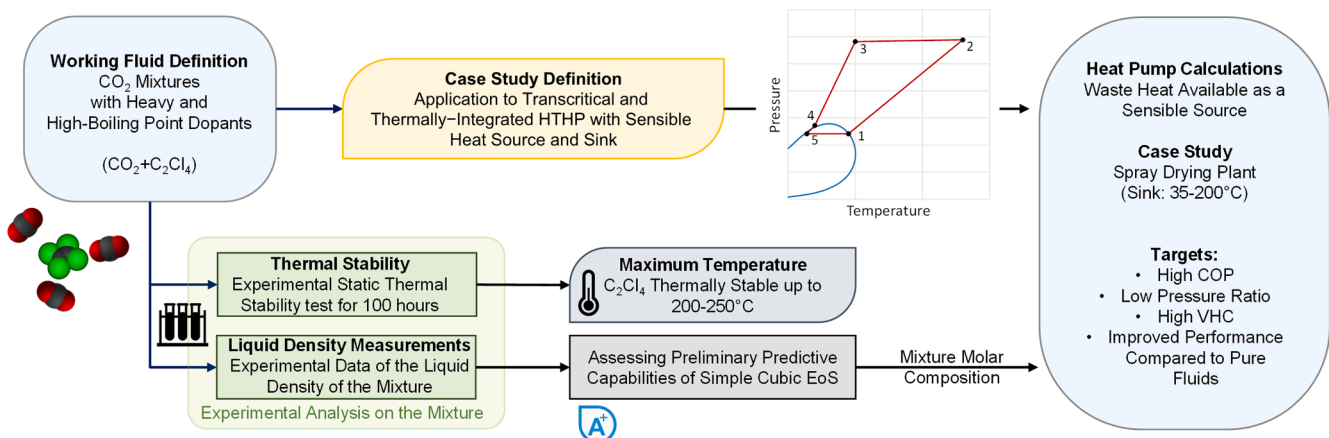


Fig. 1. Overview of the methodology adopted in this work.

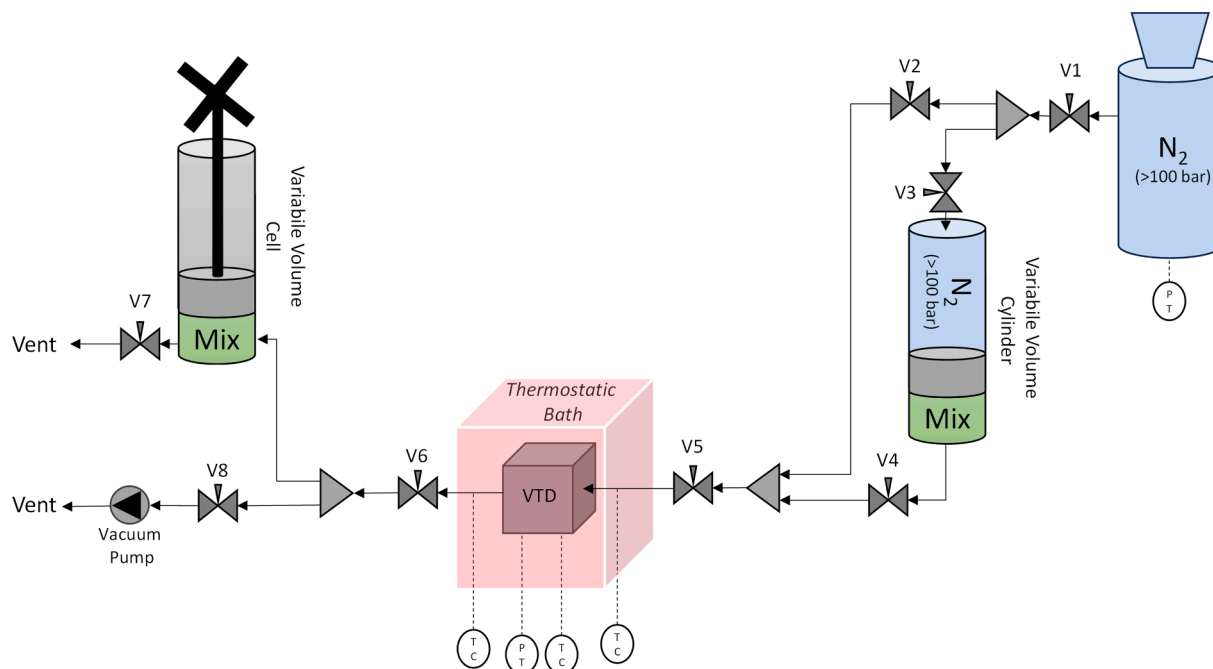


Fig. 2. Schematization of the test rig to measure the mixture liquid density.

the period of vibration of the tube (τ) with the density of a reference fluid (pure CO₂ in this work) at 40 °C, 60 °C and 80 °C (temperature conditions compatible with the thermostatic bath operative range), through a linear correlation as reported in Equation (1):

$$\rho|_T = f(\tau)_T = A \cdot \tau + B \quad (1)$$

To define the calibration curve of Equation (1), finding the numerical values of A and B at each temperature, a calibration of the VTD with pure CO₂ was carried out. The Span and Wagner reference EoS [37] is used for calculating the density of CO₂ at each measured temperature and pressure.

Density of the mixture has been measured from subcooled liquid down to a condition slightly above the bubble point, at each temperature. The results are graphically represented in Fig. 3: composition with a molar fraction of CO₂ from around 70 % to 93 % have been measured. Measurements are reproduced in a narrow range of compositions (close to 70.4 % molar in CO₂) with a different subsequent freshly charged mixtures to validate the experimental measurements. The coherency between the measured values of density at 70.47 % and 70.31 % molar content of CO₂ at two different temperatures confirms the consistency of the overall experimental procedure adopted for the preparation of the mixture. The experimental data collected and plotted in Fig. 3 are gathered, along with the respective uncertainties, in Appendix A.

3.1. Preliminary optimization of the Peng Robinson EoS on liquid densities

To preliminary estimate the performance of the selected mixture as working fluid in HTHP, an evaluation of the predictive behavior of the Peng Robinson EoS is presented in this work. The analysis is based on the fitting with the EoS of the experimental densities, as they are currently the only available set of experimental data in literature for this mixture.

The Peng Robinson EoS adopted for the simulations of this work is the one originally proposed in 1976 with the original Soave alpha function [38], embedded in ASPEN Plus v.11 [39], with Van der Waals mixing rules.

The binary interaction parameter (BIP), also known as k_{ij} for cubic EoS, of the selected PR EoS for this mixture is therefore optimized by minimizing the average absolute deviation percentage (AAD%),

proposed in Equation (2), between the density experimental data from this work and the computed values by the model.

$$AAD_{\rho_{mix}} [\%] = \frac{100}{N} \cdot \sum_{i=1}^n \left| \frac{\rho_{exp,mix} - \rho_{calc,mix}}{\rho_{exp,mix}} \right| \quad (2)$$

A sensitivity analysis is performed on the k_{ij} of the EoS, varied between -0.1 and 0.25 and assumed as independent from the temperature. According to this preliminary binary interaction parameter optimization procedure, a value of $k_{ij} = 0.10$ is found to be corresponding to the lowest $AAD_{\rho_{mix}}$ (at about 2.2 %), whereas the maximum deviation between the measured and computed density is 5.3 %. The comparison between the predicted values of the PR EoS with $k_{ij} = 0.10$ and the experimental liquid density data is graphically shown in Appendix A, evidencing the very good match between the two sets of data.

Moreover, it has been found that the resulting value of the binary interaction parameter introduces no deviations in the phase envelope of the CO₂ + C₂Cl₄ mixture for any CO₂ molar concentration above 95 %, while at the same time providing a good approximation of its densities: in that composition range the cricondenbar of the mixture is over 95 bar and its cricondenthm higher than 85 °C, not representing conditions of interest for the HTHP investigated in this study. Therefore, even if VLE data are theoretically necessary for a conclusive definition of the binary interaction parameter of the cubic EoS, in the composition range of interest in this work for this specific application the k_{ij} does not influence the prediction of the VLE conditions for this mixture.

A more detailed evaluation of the EoS performances and a more accurate selection of the available EoS is considered out of the scope of this work, given the limited amount of available experimental data, but it can be carried out in future works, when experimental data on the VLE of the mixture will be collected. Under this future scenario, the thermodynamic models can be optimized through binary interaction parameters on those experimental data, providing a good approximation of the phase-behaviour for any mixture composition. In conclusion, to estimate the mixture properties (including the enthalpies and entropies of the mixture) when adopted in a thermodynamic cycle as proposed in Section 5 of this work, the PR EoS with a k_{ij} of 0.10 is then preliminary adopted.

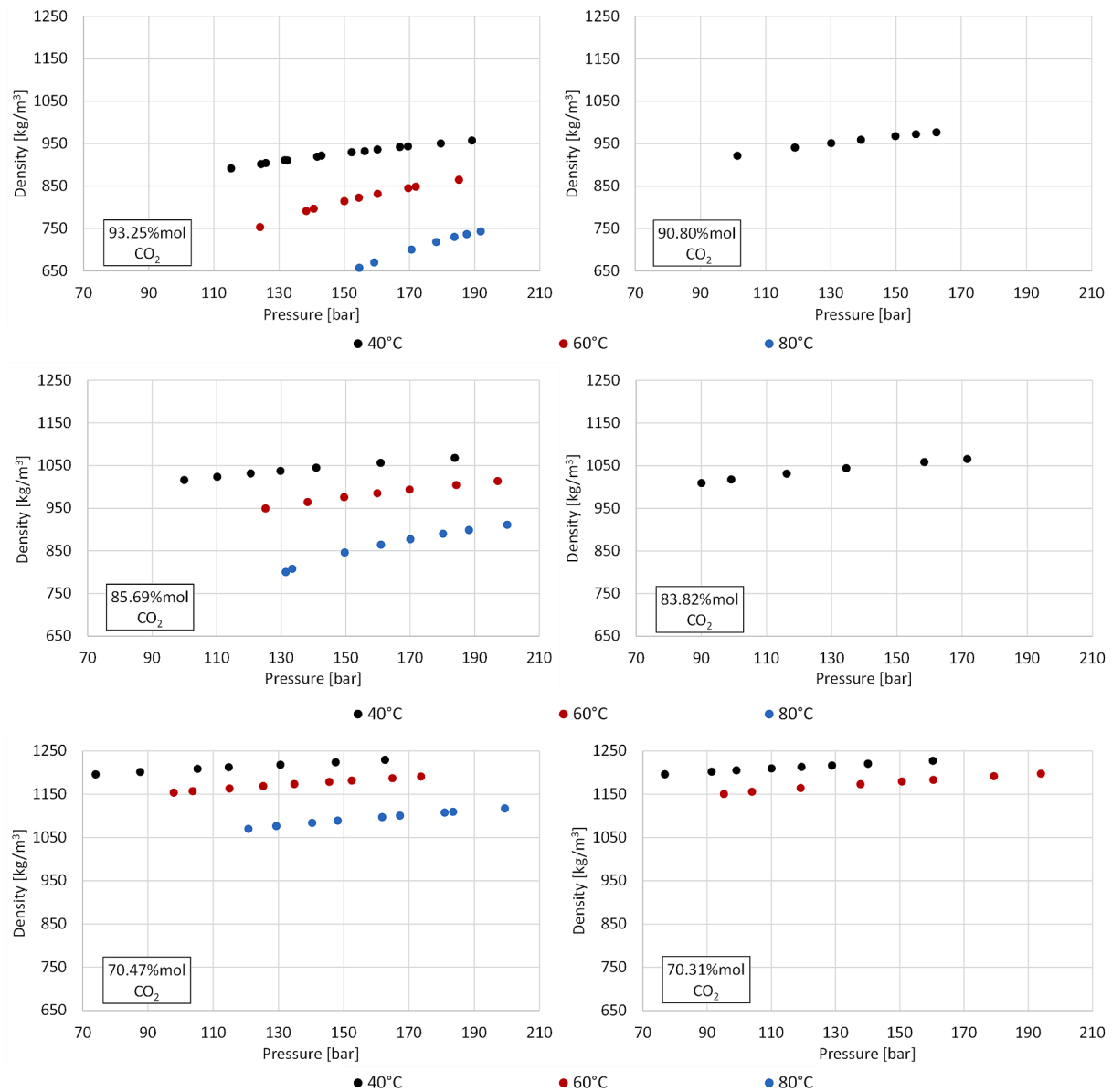


Fig. 3. Densities of the $\text{CO}_2 + \text{C}_2\text{Cl}_4$ liquid mixture measured in the VTD proposed in this work.

4. Thermal stability of tetrachloroethylene

An experimental campaign to determine the thermal stability threshold of C_2Cl_4 is carried out in this work, which is an essential information for its application as working fluid in high-temperature applications, both for heat pumps and power cycles. CO_2 is excluded from the investigation due to its recognized stability at the temperatures of interest for the HTHP application. In particular, the analysis on the thermal stability allows to determine the allowable range of compressor outlet temperature (i.e. maximum temperature of the heat pump).

The methodology adopted to evaluate the thermal stability of C_2Cl_4 is a static isochoric method originally developed in the Fluid Test Laboratory of the University of Brescia [40], to assess the thermal stability

of organic fluids adopted in Organic Rankine Cycles. The methodology assumes that even a small presence of thermal decomposition products, typically lighter and more volatile, can be identified by measuring the vapor pressure of the fluid after thermal stress. The partial pressure of non-condensable decomposition products can be recognized from the deviation of the measured fluid pressure from the vapor pressure of the fresh fluid (before thermal stress). This deviation becomes notably evident when measuring sub-atmospheric or low values of the vapor pressure, and for this reason it was decided to exclusively test C_2Cl_4 , rather than the overall mixture: decomposition products are more evident when testing C_2Cl_4 , due to the fluid high boiling point (121 °C), compared to vapor–liquid pressure conditions of a $\text{CO}_2 + \text{C}_2\text{Cl}_4$ mixture.

The core of the experimental apparatus adopted for the thermal



Fig. 4. Main components of the thermal stability test: the AISI 316L cylinder (A), the housing of the temperature probe (B), the low-pressure scale pressure transducer (PT1), the high-pressure scale pressure transducer (PT2), the main valve isolating the cylinder (V1), the valve protecting the PT1 from overpressure (V2), the valve connecting the circuit to the environment (V3). Figure adapted from authors previous work [41].

stability test is represented in Fig. 4, while more details are outlined in the previous work of Pasetti [40]. The main component is the sample cylinder (“A”) manufactured in AISI 316L by Swagelok, a material commonly utilized in high-temperature applications. To ensure precision across the measured pressure range, two pressure transducers are integrated into the system. The reference vapor pressure is measured using a Klay 2000-SAN pressure transmitter (“PT1” in Fig. 4) with an adjustable span from 1 to 10 bar and an accuracy of 0.1 % of the adjusted span. During the 100-hour thermal stress in the muffle furnace, the valve “V2” is kept closed to shield the low-pressure transmitter from overpressure. In this scenario, pressure is recorded using the high-pressure

transmitter (“PT2” in Figure X), a Klay 2000-SAN with an adjustable span from 20 to 100 bar. A TC-Direct thermocouple (tolerance class I) is inserted into the cylinder through its welded housing (“B” in Fig. 4).

The cylinder is initially loaded with a mass of liquid C_2Cl_4 of about 42 g: the fluid is supplied by Merck, with a reported purity level exceeding 99 %.

The methodology to assess the thermal stability of C_2Cl_4 involves the following preliminary steps: (i) the evacuation of the system using a vacuum pump by opening valve V3, (ii) the introduction of the pure fluid into the cylinder, and (iii) the operation of the vacuum pump to remove air traces that may have entered the system. Afterwards, the cylinder is disposed vertically in a thermostatic bath to measure the reference vapor pressure within a predetermined temperature range. Finally, the vessel is placed horizontally in the muffle furnace for a 100-hour thermal stress at a selected constant temperature: after the thermal stress, the system is replaced into the thermostatic bath to measure the fluid vapor pressure within the same temperature range of the reference test. The overview of the procedure followed is proposed in Fig. 5.

If the fluid has not deteriorated after the thermal stress, the procedure can be repeated by placing again the cylinder in the furnace at a higher temperature: the test can be considered concluded when either a target temperature is achieved during the thermal stress or when a significant divergence in the behavior of the fluid is noticed compared to the reference behavior.

4.1. Results of the thermal stability analysis on tetrachloroethylene

For this fluid, the reference vapor pressure and the pressures measured along all thermal stresses are measured in the temperature range 60–120 °C, to focus on sub-atmospheric conditions. Following the methodology described in the previous section, the experimental campaign consists of three thermal stresses from 200 °C up to 300 °C with a temperature step of 50 °C for the investigated fluid.

The results shown in Fig. 6 indicate that, based on the deviation of the fluid behavior with respect to the reference condition, C_2Cl_4 can be considered thermally stable at 200 °C, as pressure variations are insignificant compared to the reference vapor pressure. However, evidence of thermal degradation becomes apparent after exposure to thermal stress at 250 °C, with substantial degradation observed in the final 100 h at 300 °C.

To better quantify the degradation of the fluid at different temper-

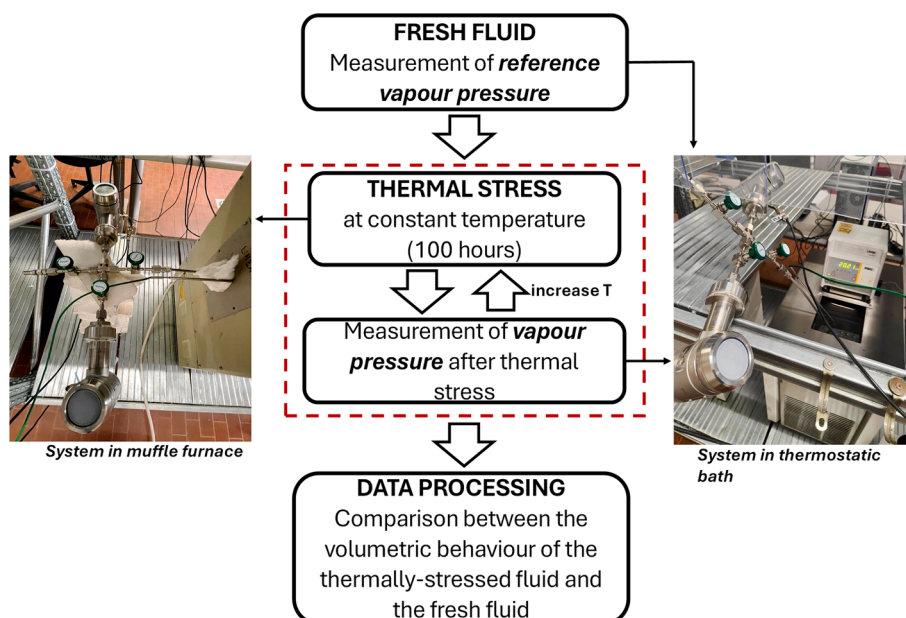


Fig. 5. Methodology adopted for the thermal stability test as already proposed in literature [41].

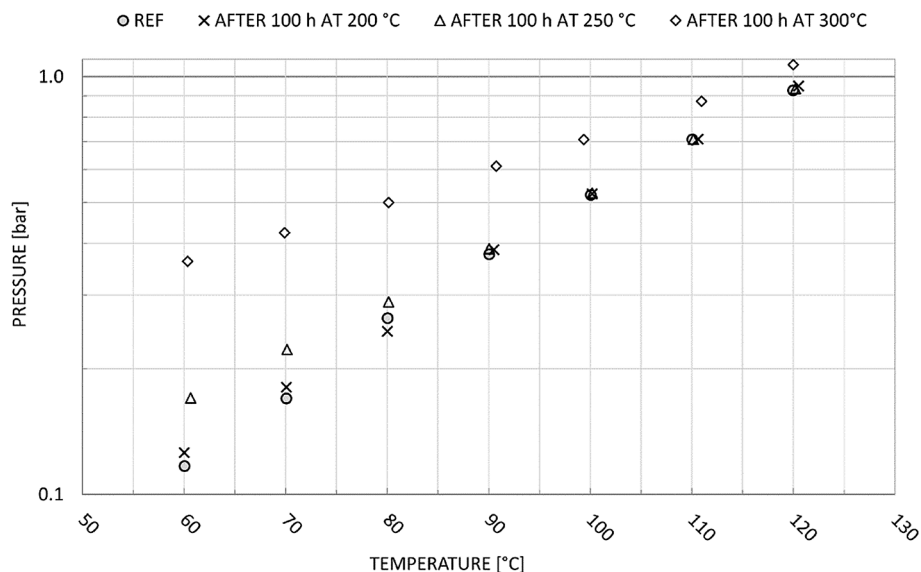


Fig. 6. Measured saturation pressure of C_2Cl_4 before ("REF") and after subsequent 100-hours thermal stress at different temperatures.

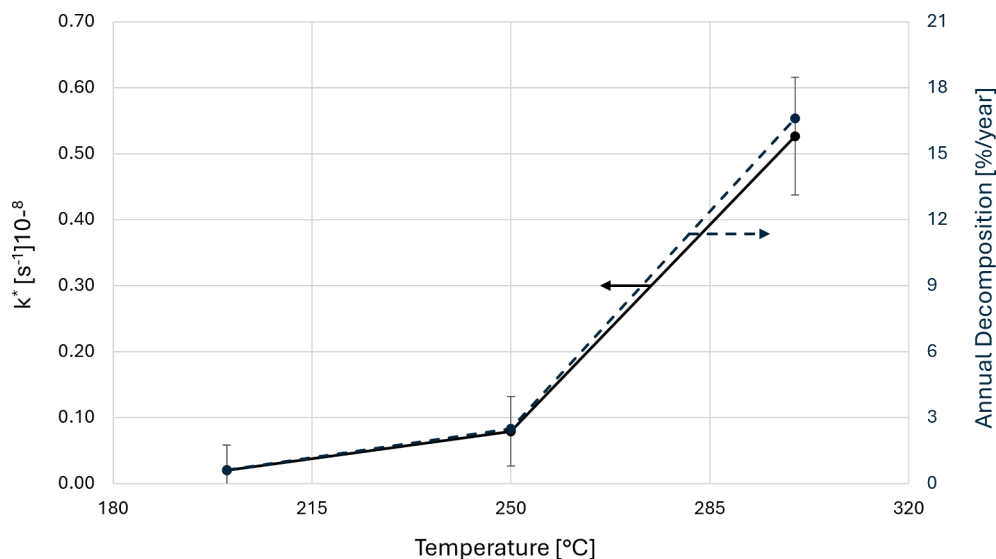


Fig. 7. Unimolecular decomposition rate k^* (black solid line) at the investigated temperature range. Corresponding annual decomposition rate of the fluid (dark blue dotted line).

atures, the rate of unimolecular decomposition, k^* , has been calculated adopting the same methodology detailed in Invernizzi [42] (equations 1–8 of the reference work) and in the work of Doninelli [43], that is not re-proposed for sake of brevity. The resulting value k^* is defined and computed as the frequency of decomposition of the fluid investigated. From k^* it can be also univocally computed the annual decomposition rate, expressed as percentage of C_2Cl_4 moles in the vessel that decomposes every year due to the high temperature conditions, under the assumption that the fluid remains at constant temperature for 8760 h per year.

The calculated k^* from the experimental data of the thermal stability stress and the associated annual degradation rate are presented in Fig. 7, along with the associated error band.

To extend the analysis on the thermal stability of the fluid, in this

work it is proposed also a comparative analysis between C_2Cl_4 and other already investigated fluids in literature under the same experimental setup and methodology [44]. Excluding fluids adopted in high-temperature ORC units (such as toluene, cyclopentane, pentane), the thermal stability of butanol and trifluoroethanol is reported in comparison with the stability of C_2Cl_4 , as these two fluids are experimentally investigated in the literature work within a similar temperature range. The results of the comparison are underlined in Fig. 8.

From the comparison presented in the figure, the degradation rate of tetrachloroethylene results to be similar to trifluoroethanol ($C_2H_3F_3O$) decomposition, and much lower than that of butanol ($C_4H_{10}O$). At 250 °C, the degradation rate of C_2Cl_4 is seven times lower than that of butanol.

From the results presented in this section, it is concluded to reasonably suggest using C_2Cl_4 up to a maximum application

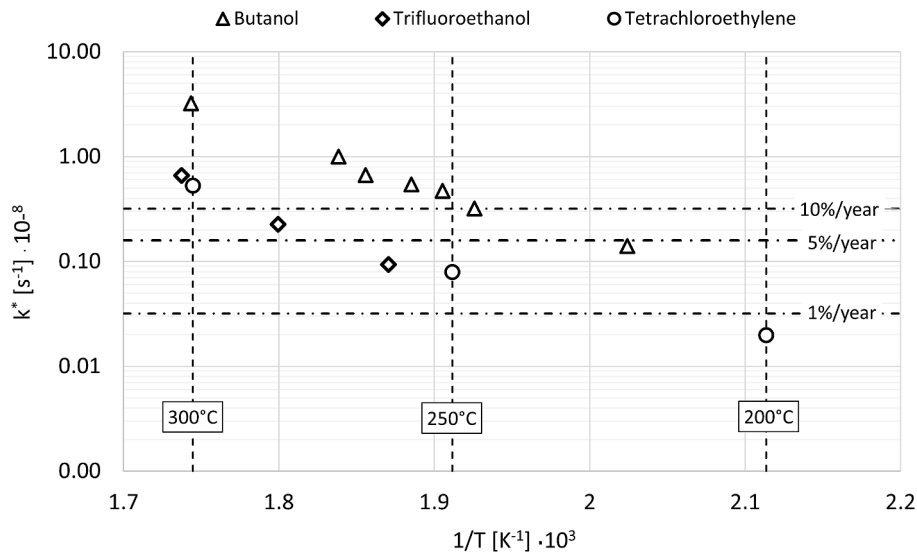


Fig. 8. Rate of decomposition of tetrachloroethylene compared to other fluids previously tested with the same methodology.

temperature in the range between 200 and 250 °C.

5. Performance of the CO₂ + C₂Cl₄ mixture for high temperature heat pumps

After the experimental characterization of the innovative CO₂-mixture, the performances of HTHP adopting this working fluid are evaluated in this chapter presenting a case study for a specific industrial application.

The performance of the mixture in a thermally integrated HTHP will be investigated for a spray drying plant, adopted mainly in the food industry and in other sectors, such as the chemical and pharmaceutical. As mentioned by Zühlsdorf [3], spray dryers in the food industry are typically in the MW-scale and are operated with a large number of equivalent hours. Spray dryers are used to turn liquid solutions (or slurry) into dried powders of the materials fed to the system. To do so, the feed is pressurized and atomized passing through nozzles, increasing the surface area per unit of volume: then, the flow is invested by hot air, evaporating the water.

Various literature studies identify the temperature range of the heat source and the sink for such application: a study of Wang [45] discussed a case study of spray drying plants in the dairy industry, where the waste heat is available at 76 °C, released by the dryer itself, whereas hot thermal power must be produced to heat dry air from ambient conditions up to 200 °C. Another case study described by Zühlsdorf [3] pointed at the temperature range of the sink to be between 60° to 210 °C, whereas a literature work by Vieren [21] also investigated an HTHP with the same heat sink of Wang. Moreover, Schlosser investigated high temperature processes, including heat pumps, to provide heat to a spray dryer for the dairy industry, identifying the same target temperature range [46].

Considering the information available in literature, the cold source of the heat pump studied in this work is assumed to be the high-humidity air at the outlet of the drying process, at a temperature of 76 °C according to the literature reference of Wang [45]. To ensure this target, the maximum temperature of the working fluid is set in this work at 210 °C at compressor outlet, a value compatible with the experimental results of the thermal stability analysis, while the minimum temperature of the working fluid in the high-pressure HX is set at 60 °C, enabling the heating of the ambient air at any reasonable value of ambient temperature. The calculations will be performed by maximizing the heat source exploitation, ensuring a target temperature difference of the heat source above 40 °C, marking a difference between a heat pump based on

mixtures with one adopting a pure fluid.

Once the heat source and sink are defined, these impose a set of boundary conditions on the cycle parameters. As a matter of fact, the cycle maximum pressure is determined by the compressor isentropic efficiency and the target value of its outlet temperature (210 °C), and it is computed on a case-by-case basis. On the other hand, the minimum pressure of the system is evaluated at the dew point of the mixture for a compressor inlet temperature of 71 °C, a value chosen to ensure a 5 °C pinch point temperature difference with the cold source available at 76 °C. As thoroughly discussed in literature by Fu [47], the proposed configuration of heat pump for drying plants is extremely effective, since the heat source of the HTHP is the by-product at the outlet of the dryer itself, exploited in a closed-cycle process.

The calculations of the HTHP are carried out considering a non-recuperative transcritical cycle layout, chosen for its simplicity. The necessity to operate the cycle in transcritical conditions arises from two major factors: i) to reach high-pressures in the hot side, leading to a high reduced pressure (easily above 2), thus ensuring a near constant heat capacity of the working fluid across the gas cooler, avoiding problems related to the pinch-conditions in the high temperature heat rejection section, and ii) to recover most efficiently, boosting the cycle performance, the pressure difference from the high to low pressure side of the cycle using an expander operating only in single phase, avoiding any mechanical issue of the turbomachinery. Additionally, a transcritical heat pump also leads to very favorable trends of the main technical key parameters of the cycle, with a limited pressure ratio and volumetric ratio across the compressor, easing its manufacturing and operation even withstanding at very high nominal pressures.

Considering a non-recuperative layout, the HTHP can be characterized by the key performance parameters commonly defined and proposed in literature, reported in Equations (3) to (8):

$$COP = \frac{\dot{Q}_{SINK}}{\dot{W}_{Compressor} - \dot{W}_{Expander}} \quad (3)$$

$$\Delta T_{Heat Source} [^{\circ}C] = T_1 - T_5 \quad (4)$$

$$PR_{Compressor} = \frac{P_2}{P_1} \quad (5)$$

$$VR_{Compressor} = \rho_2 / \rho_1 \quad (6)$$

$$VHC \left[\frac{MJ}{m^3} \right] = \rho_1 \cdot (h_2 - h_3)_{SINK} \quad (7)$$

Table 1
Characteristics and non-idealities of the transcritical HTHP of this work.

Parameter	Assumption at Design
Compressor Isentropic Efficiency	80 %
Expander Isentropic Efficiency	80 %
Pressure drops at Sink HX (supercritical cooler)	2 bar
Compressor Inlet	At Saturated Condition, at 71 °C
Expander Outlet	At Saturated Condition
Electromechanical losses	Neglected
Equation of State	Peng Robinson ($k_{ij} = 0.1$, as in this work)
Heat sink Temperature range	35–200 °C
Working fluid Temperature range across Sink HX (supercritical cooler)	60–210 °C
Heat source Temperature	76 °C

$$COP_{II\ Law} = \frac{COP}{COP_{Lorenz, mixture}} \quad (8)$$

While the thermal power and mechanical power across the HTHP components are defined as in Equations (9) to (11):

$$\dot{W}_{Compressor} = \dot{m} \cdot (h_2 - h_1) \quad (9)$$

$$\dot{W}_{Expander} = \dot{m} \cdot (h_3 - h_4) \quad (10)$$

$$\dot{Q}_{SINK} = \dot{m} \cdot (h_2 - h_3) \quad (11)$$

Finally, the main assumptions of the HTHP non-idealities simulated in this work with the CO₂ + C₂Cl₄ mixture are proposed in Table 1: it is noticeable that the relatively high values of the isentropic efficiencies of the turbomachinery points to simulations for medium-to-large scale heat pump. In addition, for an intuitive representation of the results, the ideal coefficient of performance of the heat pump is computed in this work on the basis of the temperatures of the working fluid, making this value independent from the pinch between the CO₂-mixture and both the heat sink and the cold source. As mentioned in the table, the EoS used in this analysis on the CO₂ + C₂Cl₄ mixture (hence for the calculation of the enthalpies and entropies of the mixture) is the Peng Robinson EoS, implemented as proposed in ASPEN Plus v.11 with the binary interaction parameter computed in this work. Analogously, also the HTHP is simulated in ASPEN Plus.

To properly evaluate the technical performance and effectiveness of the system, the results of the innovative HTHP with the CO₂-mixture are compared with different HTHP adopting conventional working fluids. To do so, ten different pure fluids are considered, simulating the HTHP for the same application: n-pentane, R-134a, R-1234yf, R-1234ze, propane, iso-pentane, R-245fa, R-365mfc, R-236ea, R-236fa. The performance of these pure-fluids HTHP are evaluated with the EoS provided by Refprop v.10.0 [48]. The boundary conditions on the temperature range of both the heat sink and the heat source are the same as the one previously mentioned for the CO₂ + C₂Cl₄ mixture HTHP, along with the cycle simple non-recuperative layout, and the main assumptions reported in Table 1, thus ensuring a fair comparison depending only on the thermodynamic of the working fluid selected. Similarly to this work, analogous simulations of transcritical HTHP with pure refrigerants and simple cycle layouts, heating air up to 200 °C, have been already proposed by Zhao [49], even though different boundary conditions were assumed, since in the literature work of Zhao it was assumed to thermally integrate the heat pump with an external heating network at 88 °C, evaporating the refrigerants at 85 °C.

Finally, for the calculations of the pure fluid HTHP, the compressor inlet temperature is univocally determined at 71 °C, as for the CO₂-based heat pump, and the cycle maximum pressure is defined with the same methodology as for the mixture. The comparison is proposed at constant thermal power from the cold heat source, with different useful power to the dryer depending on the COP computed.

5.1. Case study results: HTHP with CO₂ + C₂Cl₄ mixture for spray drying applications

The calculations of the HTHP with the CO₂ + C₂Cl₄ mixture are carried out by finding the composition of the mixture that can ensure a large heat source exploitation, without compromising the system efficiency, fixing the compressor inlet temperature at 71 °C: accordingly, a massic CO₂ composition of the mixture of 96 % is found (a value approximately corresponding to 99 % on molar basis), ensuring a heat source cooling degree of 47 °C (with an outlet temperature of the heat source of 29 °C) and maximizing the heat introduction in the system. This specific condition is selected as the COP is maximized by presenting an expander outlet pressure, at saturated liquid, as close as possible to the cycle minimum pressure, therefore by minimizing the pressure difference in the expansion valve. Considering the HTHP with this molar composition of the fluid, the cycle minimum pressure is 62 bar and the maximum pressure 245 bar, with a compression pressure ratio of 3.93 and a volumetric ratio of 2.40. Different simulations, with a mixture massic composition richer in CO₂, above 96 %, resulted in a glide not sufficiently extended to have saturated vapor conditions at 71 °C, moving the compression inlet condition in the superheated region, compromising the COP. On the other hand, with a CO₂ massic compositions below 96 %, the compression inlet pressure at saturated vapor increases over 62 bar and, in order to achieve the target compressor outlet temperature, the cycle maximum pressure would be higher than 250 bar, a technological threshold value adopted in literature. Secondly, in this circumstance with lower CO₂ content, the cold heat source exploitation is compromised, as the temperature difference at the evaporator decreases.

The investigated configuration of heat pump in this application is extremely promising: the COP of the cycle is computed to be 3.39 and the second law efficiency is around 74 %, a very high value considering the 80 % isentropic efficiency of the compression process. Finally, the VHC of the HTHP is computed at 36.2 MJ/m³, proving the relevant compactness of the cycle, boosted by the reduced volumetric rates (with a density at compression inlet of 131 kg/m³). According to a literature correlation for the estimation of the compressor efficiency proposed by Romei for sCO₂ cycles [50], extended in this work to the CO₂ + C₂Cl₄ mixture as a highly CO₂-dominant working fluid, the isentropic efficiency assumed in this work at 80 % for a radial compressor can be representative of a compressor mechanical power between 4 and 6 MW, with a thermal power delivered to the dryer in the range of 8 to 15 MW. These considerations are based on the predicted volumetric flow rate and computed pressure ratio of the compressor of the HTHP, being a consequence of the thermodynamic characteristics of the CO₂ + C₂Cl₄ mixture at the composition and conditions investigated in this work.

The cycle thermodynamics is represented clearly in the P-T and T-Q diagrams of Fig. 9, along with the plant layout of the simple recuperative cycle. In these circumstances, the mixture conditions at the inlet of the evaporator are computed with a highly dominant mass fraction of the liquid phase, limiting possible problems of two-phases maldistribution at the inlet of the evaporator manifolds. Moreover, in the T-Q diagrams it is visible that an internal pinch of around 5 °C is found at the heat sink HX (the supercritical cooler), while the evaporator is pinched both at the cold end and the hot end, with the working fluid absorbing most of the heat at a temperature below 40 °C. In conclusion, the investigated mixture is found to be perfectly suitable as working fluid of very high temperature heat pumps for applications, such as spray dryers, characterized by a marked temperature variation of both the sink and the cold source and a large temperature lift.

5.2. Case study results: Comparison with HTHP working with pure fluids

The case study proposed in the previous section demonstrates that the CO₂ + C₂Cl₄ mixture can achieve high efficiencies with an effective exploitation of the heat source, available at 76 °C and cooled down by

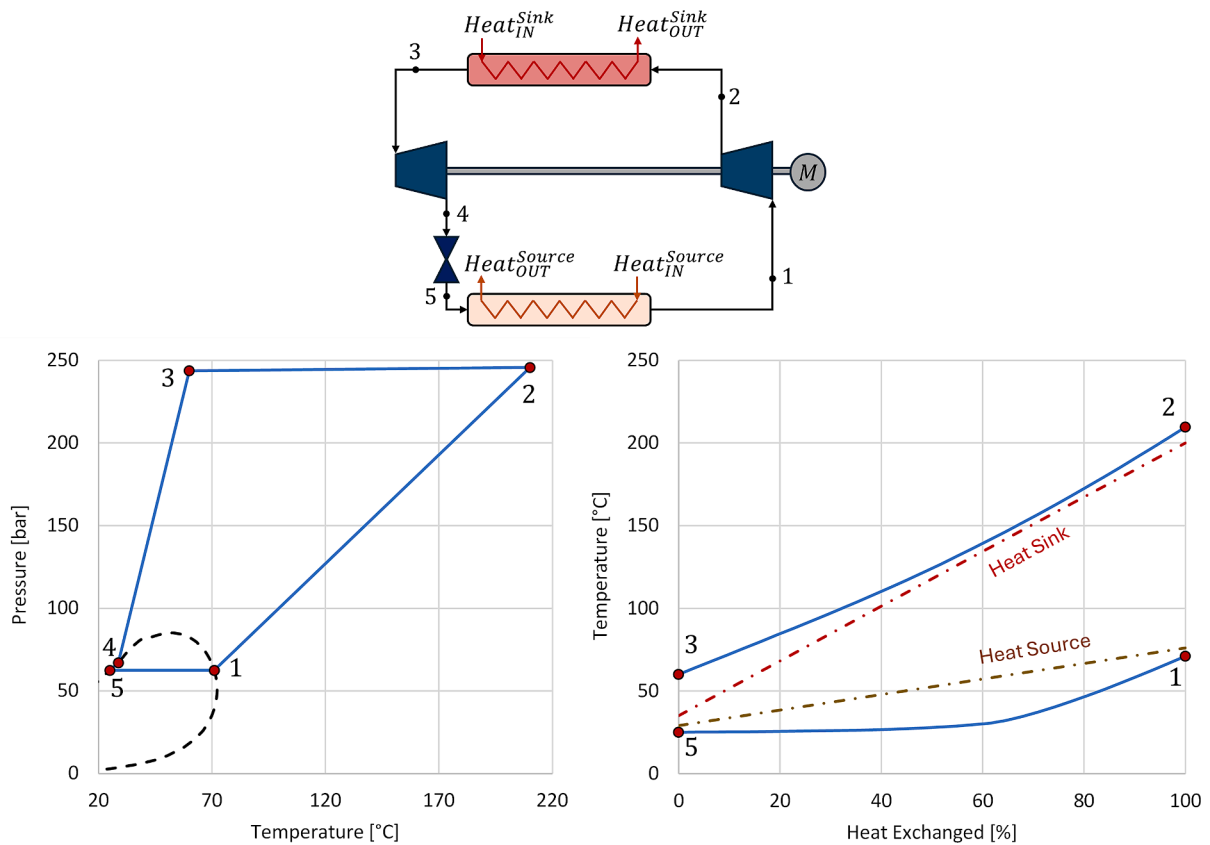


Fig. 9. Plant layout, Pressure-Temperature and Temperature-Heat Exchanged diagrams of the transcritical HTHP with the $\text{CO}_2 + \text{C}_2\text{Cl}_4$ mixture (96 %wt CO_2) proposed in this work for a spray drying plant. The T-Q diagrams evidence both the heat exchange process in the gas cooler and in the evaporator.

47 °C, to 29 °C.

The comparative analysis between the results of the HTHP with the mixture and the conventional working fluid is carried out for each of the pure-fluid HTHP by fixing the cycle minimum pressure as the evaporation pressure at 24 °C, coherently with the HTHP adopting the $\text{CO}_2 + \text{C}_2\text{Cl}_4$ mixture, with a 5 °C temperature difference at the cold end of the evaporator.

Results are listed in Table 2 for all fluids considered: it is evident that the most promising pure fluid for this plant can be considered propane, mainly for the limited compressor pressure ratio, the attractive VHC and the good COP. Consequently, for this case study, the CO_2 -mixture shows

the most promising results: with highest values of COP and second law efficiency, a minimum pressure above the atmospheric value, a compressor ratio around 4 and volumetric ratio below 3. Additionally, the fluid has also favorable characteristics in terms of flammability, toxicity and environmental impact. Accordingly, a visualization of the T-s diagrams of the heat pumps with the two working fluids, propane and the mixture, is also shown in Fig. 10, evidencing the temperature profile of both the source and the sink of the cycle. In the diagrams the cold source and the heat sink are clearly marked: a visible difference between the two cycles is the different matching of the temperature profile of the working fluid in the evaporator. Most importantly, while the compressor

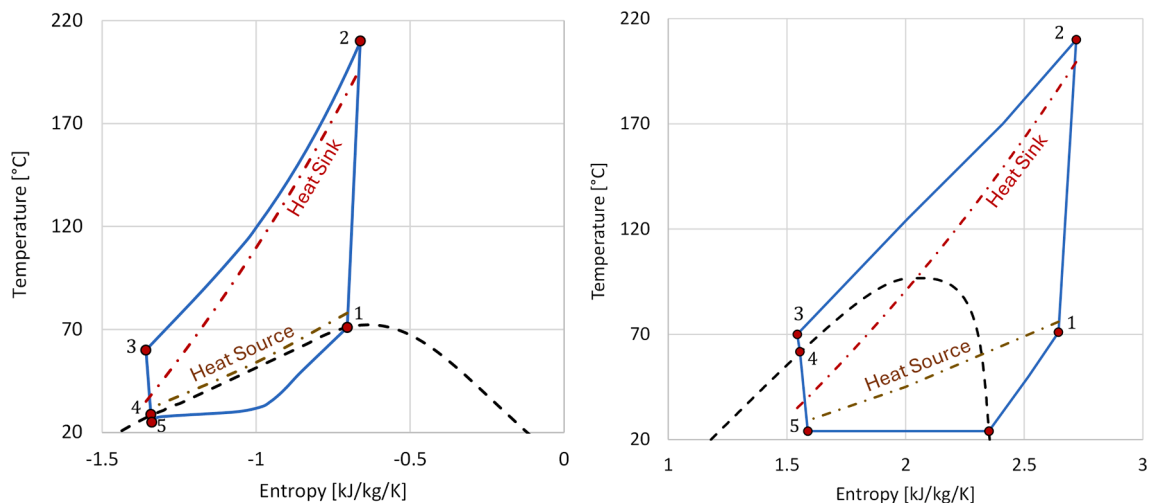


Fig. 10. Comparison between the transcritical HTHP proposed in this work for a spray dryer plant with the $\text{CO}_2 + \text{C}_2\text{Cl}_4$ mixture (left) and propane (right).

Table 2

Performance comparison between the HTHP with the CO₂ + C₂Cl₄ mixture and a conventional configuration for HTHP working with commercial refrigerants for a spray dryer plant.

Fluid	Heat Source	Heat Sink	COP	COP II Law	P _{min} [bar]	P _{max} [bar]	β_{Comp}	VR _{Comp}	$\rho_{Comp,IN}$ [kg/m ³]	VHC [MJ/m ³]	Flammable	GWP
CO ₂ + C ₂ Cl ₄ (96 % mass CO ₂)			3.39	0.738	62	245	3.93	2.40	131	36.2	No	–
n-Pentane			2.86	0.623	0.7	37	55.7	81.8	2	0.9	Yes	20
R134a			2.99	0.652	6.5	103	15.9	15.0	25	6.2	Yes	1430
R1234yf			3.01	0.657	6.6	146	22.0	19.6	29	6.2	Yes	<5
R1234ze			2.97	0.648	4.8	103	21.2	21.4	21	4.8	Yes	6
Propane	76–29 °C	35–200 °C	2.94	0.641	9.3	115	12.4	11.7	16	7.7	Yes	<5
Iso-Pentane			2.90	0.631	0.9	43	48.2	78.1	2	1.1	Yes	11
R245fa			2.94	0.640	1.4	58	40.5	47.3	7	1.8	No	1030
R365mfc			2.91	0.635	0.5	43	79.6	129.5	3	0.8	No	804
R236ea			2.98	0.650	2.0	84	42.1	52.8	11	2.4	No	1330
R236fa			2.98	0.648	2.6	106	40.4	44.9	15	3.0	No	9810

inlet for the CO₂-mixture is defined univocally at saturated vapor conditions, by properly varying the mixture composition, for the pure fluid a large superheating is necessary, from the two-phase conditions, reaching the desired compressor inlet temperature.

Comparing the mixture performance to the one of all the pure fluids, including propane, it is possible to notice that pure fluids allow for HTHP with VHC of an order of magnitude lower than the one computed for the cycle with the CO₂ + C₂Cl₄ mixture. Moreover, all pure fluids present pressure and volumetric ratios of the compressor around one order of magnitude higher than the one of the mixture, drastically compromising the manufacturing, the operation and the achievable efficiencies of the compressor, that in this case study are assumed constant for all working fluids, as a conservative choice.

In conclusion, the adoption of CO₂-mixtures with large glides during evaporation (as the CO₂ + C₂Cl₄ mixture) is proven to be an effective choice for HTHP that must operate with highly sensible heat sources and heat sinks, outperforming conventional pure fluids in terms of COP and the characteristics of the compression process. On the other hand, any different case study of HTHP with heat sources at constant temperature could not efficiently match the evaporation process of the CO₂-mixtures, resulting in poorer performance of the heat pump if compared to a pure-fluid HTHP. The outcome of this comparison hence depicts a subtle but crucial dependency between the characteristics of the sources and sinks of the heat pump for a given application and the thermodynamic characteristics of the most favorable working fluids.

6. Conclusions

This work proposes an insight into an innovative working fluid for high temperature heat pumps, the CO₂ + C₂Cl₄ mixture, suitable for both current and next-generation heat pumps.

The peculiarity of the working fluid for these systems is to allow the exploitation of a low temperature sensible waste heat, expanding the operative conditions with respect to applications of heat pumps with pure fluids, normally driven by isothermal latent heat at the cold source. To support the analytical considerations on the HTHP with this mixture, an experimental analysis of the working fluid is proposed, providing encouraging evidence for the adoption of this mixture. Long-term static thermal stability stresses demonstrated a good thermal resistance of C₂Cl₄, that in a high temperature heat pump can operate above 200 °C.

The case study investigated of a CO₂ + C₂Cl₄ mixture heat pump for an industrial application (a spray dryer plant) can demonstrate that the

working fluid, and in general the family of CO₂-based mixture with large glides adopting a dopant with a low volatility, can achieve optimal results in the main key performance parameters of a high temperature heat pump. The configuration of heat pump shown, with a heat source representative of low-temperature waste heat that is sensibly cooled by around 50 °C, shows very high COP (with second law efficiencies around 74 %), a low value of pressure ratio between the two pressure sides (below 4) and a very limited volumetric ratio across the compressor (below 2.5), with a volumetric heating capacity above 36.2 MJ/m³. The work also shows that across a pool of common refrigerants, such promising values in performance parameter are not achievable, as they are only possible due to the mixing of two pure fluids with different volatility.

As the innovative CO₂ dopant does not pose relevant issues in terms of toxicity, flammability, OPD and it is liquid at ambient conditions, it can be considered an interesting choice for industrial applications of closed thermodynamic cycles, where the working fluid does not enter in contact with the environment under normal operating conditions. Future works on the CO₂ + C₂Cl₄ mixture must include an experimental analysis of the vapor–liquid equilibrium of the mixture, to properly define a more accurate thermodynamic model. Future works on innovative working fluids with large glides for heat pumps must include a sensitivity analysis on possible mixtures and their performances, along with the characterization of the system performances on a case-by-case basis, depending on the sensible heat sources from which the waste heat is recovered, and the sensible heat sinks to provide upgraded heat.

CRedit authorship contribution statement

Ettore Morosini: Writing – review & editing, Writing – original draft, Visualization, Software, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Michele Doninelli:** Writing – review & editing, Writing – original draft, Visualization, Software, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Gioele Di Marcoberardino:** Writing – review & editing, Supervision, Methodology, Investigation, Conceptualization. **Paolo Iora:** Supervision, Resources, Formal analysis. **Mauro Riva:** Writing – review & editing, Supervision, Resources, Formal analysis, Data curation. **Paolo Stringari:** Supervision, Resources, Formal analysis. **Giampaolo Manzolini:** Writing – review & editing, Supervision, Project administration, Funding acquisition, Conceptualization.

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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Appendix A. – Liquid densities of the CO₂ + C₂Cl₄ mixture experimental data and comparison with the proposed EoS results

The liquid densities of the CO₂ + C₂Cl₄ mixture, proposed in Fig. 3, are collected in Table A1 in this appendix, along with the expanded uncertainties on temperature, pressure and density, with a coverage factor of 2.

Table A1

Experimental liquid densities collected on the CO₂ + C₂Cl₄ mixture.

x_{CO_2}	T	P	ρ_{Mix}	$u_{Expanded}(T)$	$u_{Expanded}(P)$	$u_{Expanded}(\rho)$	
[%]	[°C]	[bar]	$\frac{kg}{m^3}$	[°C]	[bar]	$\frac{kg}{m^3}$	
93.25	40.27	189.19	957.6	0.06	0.04	5.9	
		167.09	942.1	0.06	0.05	5.9	
		143.02	921.9	0.06	0.05	5.9	
		131.75	910.6	0.06	0.04	5.9	
		115.23	891.7	0.06	0.04	5.9	
		124.48	901.8	0.06	0.05	5.9	
		132.52	910.4	0.06	0.05	5.9	
		141.71	919.5	0.06	0.04	5.9	
		156.30	932.4	0.06	0.04	5.9	
		179.62	950.4	0.06	0.05	5.9	
		169.56	943.6	0.06	0.04	5.9	
		160.20	936.5	0.06	0.08	5.9	
		152.26	929.8	0.06	0.06	5.9	
		125.91	904.3	0.06	0.04	5.9	
93.25	59.98	185.20	864.8	0.06	0.08	2.4	
		169.63	845.3	0.06	0.06	2.4	
		160.23	831.6	0.06	0.05	2.4	
		150.00	814.5	0.06	0.05	2.4	
		138.32	791.1	0.06	0.04	2.4	
		124.14	753.4	0.06	0.05	2.4	
		140.62	796.9	0.06	0.04	2.4	
		154.49	822.7	0.06	0.06	2.4	
		171.99	848.6	0.06	0.05	2.4	
		191.86	743.4	0.06	0.06	2.5	
93.25	79.84	170.63	700.5	0.06	0.05	2.5	
		159.19	670.1	0.06	0.05	2.5	
		79.99	154.63	657.1	0.06	0.05	2.5
			178.24	718.5	0.06	0.04	2.5
			187.58	736.7	0.06	0.04	2.5
		183.82	730.2	0.06	0.05	2.5	
83.82	40.08	171.61	1065.6	0.06	0.05	5.9	
		158.41	1058.4	0.06	0.05	5.9	
		134.50	1044.1	0.06	0.05	5.9	
		116.23	1031.3	0.06	0.05	5.9	
		99.21	1017.6	0.06	0.04	5.9	
90.80	40.22	90.08	1009.3	0.06	0.06	5.9	
		162.38	977.0	0.07	0.05	5.9	
		149.77	967.8	0.07	0.04	5.9	
		139.22	959.3	0.07	0.04	5.9	
		118.93	941.0	0.07	0.04	5.9	
		101.31	921.8	0.07	0.05	5.9	
		130.06	951.4	0.07	0.05	5.9	
85.69	40.17	156.08	972.4	0.07	0.04	5.9	
		160.87	1056.5	0.06	0.05	5.9	

(continued on next page)

Table A1 (continued)

x_{CO_2}	T	P	ρ_{Mix}	$u_{Expanded}(T)$	$u_{Expanded}(P)$	$u_{Expanded}(\rho)$
85.69	59.96	140.88	1045.1	0.06	0.05	5.9
		120.58	1031.9	0.06	0.05	5.9
		99.97	1016.4	0.06	0.04	5.9
		110.20	1024.0	0.06	0.07	5.9
		129.81	1037.6	0.06	0.05	5.9
		183.83	1068.1	0.06	0.11	5.9
		197.11	1013.8	0.06	0.05	2.4
		169.79	993.9	0.06	0.09	2.4
		149.54	976.1	0.06	0.05	2.4
		125.13	949.4	0.06	0.05	2.4
		138.22	964.7	0.06	0.05	2.4
		159.80	985.3	0.06	0.04	2.4
85.69	79.95	184.28	1004.5	0.06	0.12	2.4
		220.43	929.7	0.09	0.05	2.5
		200.09	911.5	0.09	0.07	2.5
		180.18	890.4	0.09	0.12	2.5
		170.03	877.6	0.09	0.05	2.5
		149.72	846.4	0.09	0.05	2.5
		160.92	864.7	0.09	0.04	2.5
		188.22	899.0	0.09	0.04	2.5
		133.41	808.0	0.09	0.04	2.5
		131.43	800.8	0.09	0.04	2.5
		160.30	1227.3	0.06	0.13	5.9
		140.07	1220.5	0.06	0.04	5.9
70.31	40.18	119.36	1213.1	0.06	0.26	5.9
		99.15	1205.3	0.06	0.08	5.9
		76.84	1196.1	0.06	0.11	5.9
		91.41	1202.1	0.06	0.23	5.9
		110.05	1209.5	0.06	0.22	5.9
		128.87	1216.4	0.06	0.12	5.9
		193.95	1197.5	0.07	0.05	2.4
		179.32	1191.7	0.07	0.05	2.4
		150.66	1179.5	0.07	0.07	2.4
		119.12	1164.1	0.07	0.04	2.4
		95.24	1150.7	0.07	0.04	2.4
		103.96	1155.6	0.07	0.10	2.4
70.47	40.28	137.78	1172.9	0.07	0.08	2.4
		160.41	1183.2	0.07	0.12	2.4
		147.49	1224.2	0.06	0.23	5.9
		130.59	1218.2	0.06	0.16	5.9
		105.17	1208.8	0.06	0.27	5.9
		73.95	1195.9	0.06	0.14	5.9
		87.61	1201.7	0.06	0.07	5.9
		114.76	1212.4	0.06	0.06	5.9
		162.66	1229.3	0.06	0.09	5.9
		164.90	1187.0	0.06	0.05	2.4
		145.58	1178.6	0.06	0.05	2.4
		125.33	1168.8	0.06	0.13	2.4
70.47	59.97	97.89	1153.9	0.06	0.12	2.4
		103.68	1157.2	0.06	0.11	2.4
		115.00	1163.4	0.06	0.18	2.4
		134.86	1173.5	0.06	0.14	2.4
		152.43	1181.6	0.06	0.07	2.4
		173.68	1190.8	0.06	0.04	2.4
		199.36	1117.2	0.06	0.07	2.5
		180.92	1107.8	0.06	0.04	2.5
		161.74	1097.3	0.06	0.13	2.5
		140.29	1084.0	0.06	0.08	2.5
		120.79	1069.9	0.06	0.05	2.5
		129.32	1076.3	0.06	0.04	2.5
70.47	79.91	148.13	1089.1	0.06	0.05	2.5
		167.22	1100.5	0.06	0.05	2.5
		183.50	1109.3	0.06	0.08	2.5

The densities are also reported along with the calculations of the Peng Robinson EoS with $k_{ij} = 0.10$ in Figure A1, as discussed in Chapter 3.1: the comparison between the modelled values and the experimental data demonstrate the effective capability of the EoS to properly compute the densities of the mixture in the liquid region.

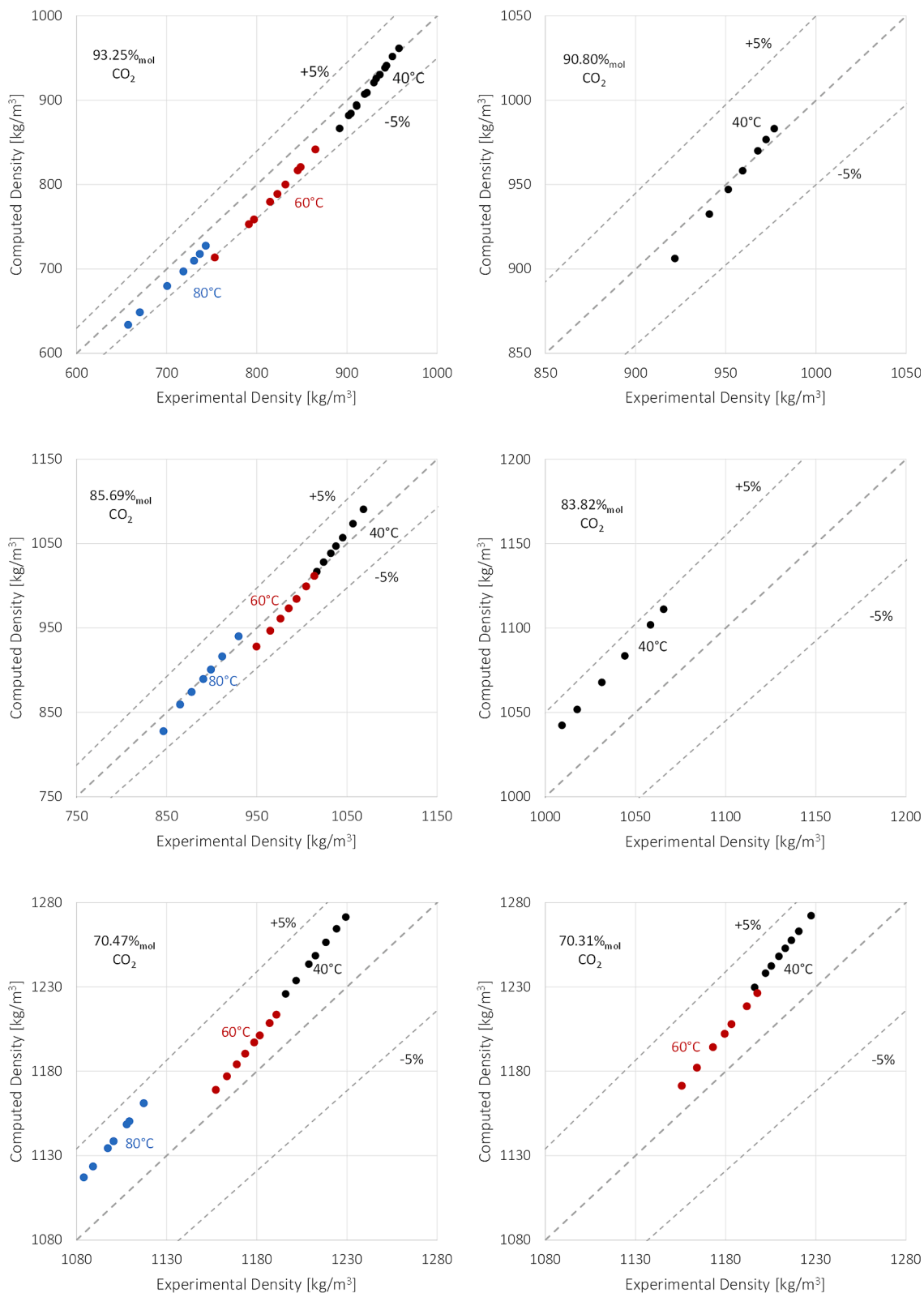


Fig. A1. Comparison between the experimental liquid densities of the CO₂ + C₂Cl₄ mixture and the values predicted by the EoS in this work (PR EoS with $k_{ij}=0.1$).

Appendix B. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.enconman.2024.119145>.

Data availability

Data will be made available on request.

References

- Hassan AH, Corberán JM, Ramirez M, Trebilcock-Kelly F, Payá J. A high-temperature heat pump for compressed heat energy storage applications: Design, modeling, and performance. *Energy Rep* 2022;8:10833–48. <https://doi.org/10.1016/J.EGYR.2022.08.201>.
- El Samad T, Żabnieńska-Góra A, Jouhara H, Sayma AI. A review of compressors for high temperature heat pumps. *Thermal Sci Eng Prog* 2024;51:102603. <https://doi.org/10.1016/J.TSEP.2024.102603>.
- Zühlsdorf B, Bühler F, Bantle M, Elmegaard B. Analysis of technologies and potentials for heat pump-based process heat supply above 150 °C. *Energy Convers Manage*; X 2019;2:100011. <https://doi.org/10.1016/J.ECMX.2019.100011>.
- Marina A, Spoelstra S, Zondag HA, Wemmers AK. An estimation of the European industrial heat pump market potential. *Renew Sustain Energy Rev* 2021;139:110545. <https://doi.org/10.1016/J.RSER.2020.110545>.
- Chua KJ, Chou SK, Yang WM. Advances in heat pump systems: A review. *Appl Energy* 2010;87:3611–24. <https://doi.org/10.1016/J.APENERGY.2010.06.014>.
- Arpagaus C, Bless F, Uhlmann M, Schiffmann J, Bertsch SS. High temperature heat pumps: Market overview, state of the art, research status, refrigerants, and application potentials. *Energy* 2018;152:985–1010. <https://doi.org/10.1016/J.ENERGY.2018.03.166>.
- Jaatinen-Varri A, Tiainen J, Honkatukia J, Uusitalo A, Turunen-Saaresti T. Design considerations for a high-temperature heat pump centrifugal compressor, in. *Proceedings of 15th European Conference on Turbomachinery Fluid Dynamics & Thermodynamics ETC.* 2023.
- Mateu-Royo C, Arpagaus C, Mota-Babiloni A, Navarro-Esbrí J, Bertsch SS. Advanced high temperature heat pump configurations using low GWP refrigerants for industrial waste heat recovery: A comprehensive study. *Energy Convers Manage* 2021;229:113752. <https://doi.org/10.1016/J.ENCONMAN.2020.113752>.
- Liu J, Zhou L, Lin Z, Zhang X. Performance evaluation of low GWP large glide temperature zeotropic mixtures applied in air source heat pump for DHW production. *Energy Convers Manage* 2022;274:116457. <https://doi.org/10.1016/J.ENCONMAN.2022.116457>.
- MAN Heat Pump, (n.d.). https://www.man-es.com/docs/default-source/document-sync/man-heat-pump-hpu328c592b5d584f9eba47f4b6bed3574e.pdf?sfvrsn=9bd416fb_3 (accessed February 20, 2024).
- Li J, Yang Z, Li H, Hu S, Duan Y, Yan J. Optimal schemes and benefits of recovering waste heat from data center for district heating by CO₂ transcritical heat pumps. *Energy Convers Manage* 2021;245:114591. <https://doi.org/10.1016/J.ENCONMAN.2021.114591>.
- Wang J, Belusko M, Liu M, Semsarilar H, Liddle R, Alemu A, et al. A comprehensive study on a novel transcritical CO₂ heat pump for simultaneous space heating and cooling – Concepts and initial performance. *Energy Convers Manage* 2021;243:114397. <https://doi.org/10.1016/J.ENCONMAN.2021.114397>.
- Luberti M, Gowans R, Finn P, Santori G. An estimate of the ultralow waste heat available in the European Union. *Energy* 2022;238:121967. <https://doi.org/10.1016/J.ENERGY.2021.121967>.
- Macchi E, Astolfi M. Organic Rankine Cycle (ORC) Power Systems - Technologies and applications. Elsevier 2017. <https://doi.org/10.1016/C2014-0-04239-6>.
- Brückner S, Liu S, Miró L, Radspieler M, Cabeza LF, Lävemann E. Industrial waste heat recovery technologies: An economic analysis of heat transformation technologies. *Appl Energy* 2015;151:157–67. <https://doi.org/10.1016/J.APENERGY.2015.01.147>.
- Shamsi SSM, Barberis S, Maccarini S, Traverso A. Large scale energy storage systems based on carbon dioxide thermal cycles: A critical review. *Renew Sustain Energy Rev* 2024;192:114245. <https://doi.org/10.1016/J.RSER.2023.114245>.
- Mercangöz M, Hemrle J, Kaufmann L, Z'Graggen A, Ohler C. Electrothermal energy storage with transcritical CO₂ cycles. *Energy* 2012;45:407–15. <https://doi.org/10.1016/J.ENERGY.2012.03.013>.
- Sanz Garcia L, Jacquemoud E, Jenny P. Thermo-economic heat exchanger optimization for Electro-Thermal Energy Storage based on transcritical CO₂ cycles. In: 3rd European Conference on Supercritical CO₂ (SCO₂) Power Systems 2019: 19th-20th September 2019; 2019. p. 353–62. <https://doi.org/10.17185/DUEPUBLICO/48917>.
- ETES System Overview | Echogen Power Systems, (n.d.). <https://www.echogen.com/energy-storage/etes-system-overview> (accessed February 13, 2024).
- Abedini H, Vieren E, Demeester T, Beyne W, Lecompte S, Quoilin S, et al. A comprehensive analysis of binary mixtures as working fluid in high temperature heat pumps. *Energy Convers Manage* 2023;277:116652. <https://doi.org/10.1016/J.ENCONMAN.2022.116652>.
- Vieren E, Demeester T, Beyne W, Arteconi A, De Paeppe M, Lecompte S. The thermodynamic potential of high-temperature transcritical heat pump cycles for industrial processes with large temperature glides. *Appl Therm Eng* 2023;234:121197. <https://doi.org/10.1016/J.APPLTHERMALENG.2023.121197>.
- Wu D, Ma B, Zhang J, Chen Y, Shen F, Chen X, et al. Working fluid pair selection of thermally integrated pumped thermal electricity storage system for waste heat recovery and energy storage. *Appl Energy* 2024;371:123693. <https://doi.org/10.1016/J.APENERGY.2024.123693>.
- E. Morosini, D. Alfani, M. Renzoni, G. Manzolini, Thermally integrated innovative Carnot batteries to upgrade and dispatch low temperature sensible waste heat, in: *ATI Annual Congress (ATI 2024)*, Under Review, IOP Publishing, 2024.
- Liu J, Zhou F, Lyu N, Fan H, Zhang X. Analysis of low GWP ternary zeotropic mixtures applied in high-temperature heat pump for waste heat recovery. *Energy Convers Manage* 2023;292:117381. <https://doi.org/10.1016/J.ENCONMAN.2023.117381>.
- Dai B, Zhao P, Liu S, Su M, Zhong D, Qian J, et al. Assessment of heat pump with carbon dioxide/low-global warming potential working fluid mixture for drying process: Energy and emissions saving potential. *Energy Convers Manage* 2020;222:113225. <https://doi.org/10.1016/J.ENCONMAN.2020.113225>.
- Tetrachloroethylene | The Observatory of Economic Complexity, (n.d.). <https://oec.world/en/profile/hs/tetrachloroethylene-perchloroethylene> (accessed February 20, 2024).
- Claxton T, Hossaini R, Wild O, Chipperfield MP, Wilson C. On the Regional and Seasonal Ozone Depletion Potential of Chlorinated Very Short-Lived Substances. *Geophys Res Lett* 2019;46:5489–98. <https://doi.org/10.1029/2018GL081455>.
- Dreisbach RR, Martin RA. Physical Data on Some Organic Compounds. *Ind Eng Chem* 1949;41:2875–8. <https://doi.org/10.1021/IE50480A053>.
- Krishnaiah A, Surendranath KN. Densities, Speeds of Sound, and Viscosities of Mixtures of Oxolane with Chloroethanes and Chloroethenes. *J Chem Eng Data* 1996;41:1012–4. <https://doi.org/10.1021/JE950304E>.
- Lynge E, Tinnerberg H, Rylander L, Romundstad P, Johansen K, Lindbohm ML, et al. Exposure to Tetrachloroethylene in Dry Cleaning Shops in the Nordic Countries. *Ann Occup Hyg* 2011;55:387–96. <https://doi.org/10.1093/ANNHYG/MEQ101>.
- Gold LS, De Roos AJ, Waters M, Stewart P. Systematic Literature Review of Uses and Levels of Occupational Exposure to Tetrachloroethylene. *J Occup Environ Hyg* 2008;5:807–39. <https://doi.org/10.1080/15459620802510866>.
- Yasuhara A. Thermal decomposition of tetrachloroethylene. *Chemosphere* 1993;26:1507–12. [https://doi.org/10.1016/0045-6535\(93\)90218-T](https://doi.org/10.1016/0045-6535(93)90218-T).
- Di Marcoberardino G, Morosini E, Di Bona D, Chiesa P, Invernizzi C, Iora P, et al. Experimental characterisation of CO₂ + C6F6 mixture: Thermal stability and vapour liquid equilibrium test for its application in transcritical power cycle. *Appl Therm Eng* 2022;212. <https://doi.org/10.1016/J.APPLTHERMALENG.2022.118520>.
- Guo H, Gong M, Qin X. Performance analysis of a modified subcritical zeotropic mixture recuperative high-temperature heat pump. *Appl Energy* 2019;237:338–52. <https://doi.org/10.1016/J.APENERGY.2018.12.094>.
- Nazeri M, Chapoy A, Valtz A, Coquelet C, Tohid B. New experimental density data and derived thermophysical properties of carbon dioxide – Sulphur dioxide binary mixture (CO₂ - SO₂) in gas, liquid and supercritical phases from 273 K to 353 K and at pressures up to 42 MPa. *Fluid Phase Equilib* 2017;454:64–77. <https://doi.org/10.1016/j.fluid.2017.09.014>.
- Doninelli M, Morosini E, Di Marcoberardino G, Invernizzi CM, Iora P, Riva M, et al. Experimental investigation of the CO₂-SiCl₄ mixture as innovative working fluid for power cycles: Bubble points and liquid density measurements. *Energy* 2024;299:131197. <https://doi.org/10.1016/j.energy.2024.131197>.
- Span R, Wagner W. A New Equation of State for Carbon Dioxide Covering the Fluid Region from the Triple-Point Temperature to 1100 K at Pressures up to 800 MPa. *J Phys Chem Ref Data* 1996;25:1509–96. <https://doi.org/10.1063/1.555991>.
- Peng DY, Robinson DB. A New Two-Constant Equation of State. *Ind Eng Chem Fundam* 1976;15:59–64. <https://doi.org/10.1021/i160057a011>.
- Aspen Plus | Leading Process Simulation Software | AspenTech, (n.d.). <https://www.aspentech.com/en/products/engineering/aspen-plus>.
- Pasetti M, Invernizzi CM, Iora P. Thermal stability of working fluids for organic Rankine cycles: An improved survey method and experimental results for cyclopentane, isopentane and n-butane. *Appl Therm Eng* 2014;73:764–74. <https://doi.org/10.1016/J.APPLTHERMALENG.2014.08.017>.
- Doninelli M, Di Marcoberardino G, Iora P, Gelfi M, Invernizzi CM, Manzolini G. Silicon Tetrachloride as innovative working fluid for high temperature Rankine cycles: Thermal Stability, material compatibility, and energy analysis. *Appl Therm Eng* 2024;249:123239. <https://doi.org/10.1016/J.APPLTHERMALENG.2024.123239>.
- Invernizzi CM, Iora P, Manzolini G, Lasala S. Thermal stability of n-pentane, cyclopentane and toluene as working fluids in organic Rankine engines. *Appl Therm Eng* 2017;121:172–9. <https://doi.org/10.1016/J.APPLTHERMALENG.2017.04.038>.
- Doninelli M, Di Marcoberardino G, Alessandri I, Invernizzi CM, Iora P. Fluorobenzene as New Working Fluid for High-Temperature Heat Pumps and Organic Rankine Cycles: Energy Analysis and Thermal Stability Test. *Energy Convers Manage* 2024.
- C. Invernizzi, M. Binotti, P. Bombarda, G. Di Marcoberardino, P. Iora, G. Manzolini, Water Mixtures as Working Fluids in Organic Rankine Cycles, *Energies* 2019, Vol. 12, Page 2629–2642 (2019) 2629. doi: 10.3390/EN12132629.
- Wang JF, Brown C, Cleland DJ. Heat pump heat recovery options for food industry dryers. *Int J Refrig* 2018;86:48–55. <https://doi.org/10.1016/j.ijrefrig.2017.11.028>.
- Schlösser F, Zysk S, Walmsley TG, Kong L, Zühlsdorf B, Meschede H. Break-even of high-temperature heat pump integration for milk spray drying. *Energy Convers Manage* 2023;291:117304. <https://doi.org/10.1016/J.ENCONMAN.2023.117304>.
- Fu H, Shi J, Yuan J, Zhang X, Sun L. Heat recovery scheme design and thermodynamic analysis of closed-cycle heat pump drying system. *Energy Convers Manage* 2023;286:117034. <https://doi.org/10.1016/J.ENCONMAN.2023.117034>.

- [48] NIST - National Institute of Standards and Technology, REFPROP - Reference Fluid Thermodynamic and Transport Properties, (n.d.).
- [49] Zhao A, Pecnik R, Peeters JWR. Thermodynamic analysis and heat exchanger calculations of transcritical high-temperature heat pumps. *Energy Convers Manag* 2024;303:118172. <https://doi.org/10.1016/J.ENCONMAN.2024.118172>.
- [50] Romei A, Gaetani P, Giotri A, Persico G. The Role of Turbomachinery Performance in the Optimization of Supercritical Carbon Dioxide Power Systems. *J Turbomach* 2020;142. <https://doi.org/10.1115/1.4046182>.