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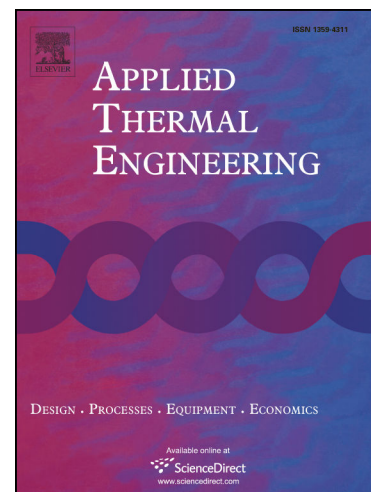
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Experimental and analytical procedure for the characterization of innovative working fluids for power plants applications

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Abstract

In the last years, several fluids have been proposed to replace steam as working fluid in power cycle for converting thermal power into electricity. This paper describes the procedure to be adopted for the selection of any innovative fluid which can be even mixtures of fluids. The first step consists of the working fluid characterization in terms of thermodynamic properties through equations of state. The equations of state have to be calibrated on experimental Vapour-Liquid Equilibrium measurements while, in the second step, the maximum operating temperature is identified through thermal stability tests. Finally, the impact of the fluid thermodynamic properties on the performance of the power cycle in which it is implemented must be assessed through modelling tools. In this work, the procedure is discussed for the mixture of CO₂ and C₆F₁₄ as a potential working fluid for gas thermodynamic cycles with liquid phase compression. Results of the application of this mixture in a closed cycle show the benefit of using a CO₂/C₆F₁₄ mixture which provides 3% points efficiency increase at 400°C with respect to the pure CO₂ together with a preliminary design of the expander.

1 Introduction

The thermodynamic conversion from heat to mechanical energy can be achieved exploiting either internal combustion gas cycles or external combustion cycles. The main advantage of the latter solution is its adaptability to a large variety of fuels and heat sources, as it is the case of the engines based on the well-known Rankine cycle [1]. The Rankine cycle was conceived with steam as working fluid and this solution still represents the reference technology for multi-MW power plants. Nonetheless, the (i) high critical temperature, (ii) small molar mass and (iii) rather simple molecular complexity of H₂O, result in a quite complicated configuration plant scheme and plant equipment design, particularly in case of the turbine and the high number of feedwater heaters. This can be the case of the recovery of the medium-high temperature heat available from many industrial processes such as glass and ceramics factories, foundries and cement plants where ORCs with size lower than 1 MW becomes a more cost-effective choice rather than the classical steam cycles [2-4].

In addition, the growing exploitation of renewable energies is calling for engines operating in a wider spectrum of power output, maintaining the highest conversion efficiency compatible with the plant size and the temperature of the heat source. This requires the evaluation of thermodynamic solutions alternative to the steam Rankine cycle, as well as the research of new working fluids, whose physical and thermodynamic properties allow a more cost-effective design of the power cycle given the thermal power and temperature of the heat supplied to the engine [5-7]. For low temperature applications, Organic Rankine Cycles (ORC) were introduced around 30 years ago [1] providing more convenient commercial solutions than the steam Rankine cycle in particular at small scale applications (power output below 20-30 MW).

Nowadays, ORC research activity focuses on the selection and optimization of the working fluid, considering various families such as organic and inorganic compounds as well as recently synthesized refrigerants. For instance, [8] provides a systematic thermodynamic optimization methodology for the selection of ORC fluids for heat recovery from large internal combustion engines, while [9-11] present a working fluid screening applied to ORCs for the exergy recovery from regasification of liquefied natural gas and waste heat in refineries. It is worth noting that one limit of ORCs is that they cannot be adopted in high temperature applications because of the organic fluid decomposition.

As an alternative to Rankine cycles, closed Brayton cycles using ideal gases have been proposed in the recent past and are today considered in niche applications at high temperature (800°C) [12]. Closed Brayton cycles with real gases as working fluid are also considered in applications with reduced maximum temperature (below 600°C) thanks to the relevant real gas effects in the compression phase which reduce the compression work [13]. In [14], the dependence of cycle performance and characteristics on the thermodynamic closed cycle location with respect to the limit curve are discussed. Brayton cycles exploiting condensation are presented in [15-17]. Real gas cycles using CO₂ were also extensively analysed in [18-20]. In [21], for example, the authors examined the potential applicability of a carbon dioxide supercritical cycle of about 150 kW in advanced nuclear power systems and develop the design of many components. Supercritical carbon dioxide cycles are today seriously reconsidered for high temperature applications in nuclear and solar plants [22-24]. The frontier of the research activity consists in the adoption of mixture of working fluids [25-27]. Within this context, the use of carbon dioxide mixtures as working fluids deserves to be investigated [28]. The identification of promising mixtures in concentrated solar power applications is the goal of the SCARABEUS project funded by the EU within the H2020 research programme.

Considering this evolution of thermal cycles from steam based to mixture-based fluids, a procedure for the selection of the optimal fluid must be adopted. This is even more relevant when the fluid properties are not available, which is typically the case of novel mixtures proposed as working fluids due to the lack of experimental data. Based on these considerations, this paper aims at defining a comprehensive procedure for selection and characterization of innovative working fluids for power plant applications. The procedure is firstly presented and then applied to the working mixture of carbon dioxide and perfluorohexane (CO₂+C₆F₁₄), a suitable working fluid for gas (Brayton) cycles with compression in the liquid phase. As the procedure requires different steps both from experimental and modeling point of view, some of the experimental tests reported in this work summarise results developed in previous works on the mixture.

2 Working fluid desiderata and procedure identification

The selection of the working fluid is crucial for an appropriate design of the power plant. The level of the working temperatures, the characteristics of the heat source, the power size and the ambient conditions are the main parameters affecting the selection of the working fluid. This section briefly summarizes the desiderata of an ideal working fluid so to identify the correct procedure for its selection in case of a Brayton cycle with condensation for a condensing temperature T_{cond} of 50 °C, and a corresponding reduced temperature (T_{cond}/T_c) of about 0.8-0.9:

- As the compression is in liquid phase, the critical temperature should be around 100 °C;
- As the operating pressures affect directly the power density and the mechanical design, the critical pressure of the working fluid should be not too high;
- The molecular fluid complexity has a strong effect on the heat capacities differences between the high-pressure and the low-pressure streams in the heat recuperator. So,

for the peculiar thermodynamic cycles here considered, in general, a relatively high molecular complexity is appropriate;

- The heat exchanger sizes, especially the recuperator, can have a significant impact on the plant cost. Thus high heat transfer coefficients are beneficial.

Obviously, the ideal fluid which has all the above mentioned characteristics does not exist. In Table 1, examples of potential pure working fluids with critical temperature of about 100°C that can be adopted in a supercritical cycle are reported. The resulting condensing pressure which is rather high leads in these cases to power plants with high power density.

In addition to the thermodynamic properties, also safety and toxicity aspects should be considered together with fluid cost and environmental impact in terms of global warming and ozone depletion potential. Therefore, some of the fluids which can be considered interesting in Table 1, i.e. the highly toxic hydrogen sulphide, cannot be implemented in a real plant. On the other hand, perfluorocarbons are very expensive fluids and with a high global warming potential, but, they are not flammable, not toxic and show a high thermal stability [29]

Table 1 - Physical properties of some potential working fluids [33]. (°) values for 100 years time horizon. (*) relative to R11

Chemical species	T_c (°C)	P_c (bar)	MM (kg/kmol)	T_b (°C)	Global Warming Potential(°)	Ozone Depletion Potential(*)
Hydrogen sulfide, H_2S	100.25	89.63	34.08	-60.31	N.A.	N.A.
R227ea, C_3HF_7	102.85	29.25	170.03	19.85	3350	0
R134a, $C_2H_2F_4$	101.11	40.56	102.03	-26.11	1300	0
Octafluorocyclobutane, C_4F_8	115.22	27.78	200.03	-5.98	9540	0
Cyclopropane, C_3H_6	125.1	55.75	42.08	-32.81	86	0
Propane, C_3H_8	96.68	42.48	44.10	-42.13	3	0

The adoption of mixtures provides an additional opportunity in the selection of the working fluid: mixing two fluids is an effective method to change the critical point and thermodynamic properties according to the requested ambient conditions, [28,30]; the mixture will have the critical points in between the two pure fluids, depending on the concentrations, hence this characteristic can be properly tuned by varying its composition. Recently, mixtures using carbon dioxide as the main component have been considered as working fluids in thermodynamic cycles [26,27]. The fluid to be added to the CO_2 must be miscible and must improve the thermodynamic characteristic of CO_2 with: (i) the increase of critical temperature, (ii) the exploitation of the temperature glide on the condenser side and (iii) the design of the turbomachines modifying the compression ratio. For example, due to their substantial immiscibility, mixture of carbon dioxide and water cannot be adopted [31], while fluids presented in Table 1 can be considered as candidates for the CO_2 rich mixture.

Once preselected a working fluid or mixture with good potentialities, a procedure to validate the fluid must be defined.

The procedure must include:

1. Definition of the thermodynamic properties and fluid behaviour at different pressure and temperatures including the two-phase region;
A comprehensive characterization of the working fluid requires a reliable Equation of State (EoS) for the evaluation of its thermodynamic properties and the consequent assessment of the cycle performance as well as the design of the equipment (the

pump or the compressor, the expander, the heat exchangers). Many EoS have been proposed in literature in the past years (see, for example, [32], [33], [34] and [35]). In general, the multi-parameter EoS have a good accuracy but require a deep validation and parameters optimization on experimental fluid volumetric behaviour or on Vapour-Liquid Equilibrium (VLE) data. In the selection of any new working fluid, one of the main goals is the identification of the bubble and dew lines; the adopted thermodynamic model has to correctly describe the Vapour-Liquid equilibria. From this point of view, the cubic equation of state (i.e. Peng Robinson or Redlich Kwong Soave) gives generally accurate results and can be easily extended to mixtures introducing the most appropriate mixing rules and calibrating the binary interaction parameters by experimental VLE data. In any case, the thermodynamic description of the critical region of the fluid is challenging and relatively inaccurate also when more complex models are adopted [36];

2. Thermal stability to identify the maximum operating temperature of the fluid before it starts substantially deteriorating;
the thermal stability is assessed through experimental tests where the fluid (or the mixture) are heated up to increasing temperatures for a predeterminate period of time. The fluid deterioration is assessed by comparing the behaviour of the fluids along curves at constant specific volume (isochoric lines) before and after thermal stress tests at high temperature, measuring two main thermodynamic properties, pressure and temperature. The deviations of the isochoric line with respect to the reference obtained from the virgin fluid, caused by the thermal decomposition, are evaluated both at high temperatures, during the thermal stress tests, and at temperature close to ambient conditions;
3. Cycle design to assess the energy performance of the innovative fluid when integrated in a power block;
The performance of the working fluid when integrated in a power block is assessed through a cycle design performed either with commercial process simulation software or by developing in-house tools with proper EoS implemented. The purpose of this activity is the assessment of the net electric efficiency as function of the cycle maximum and minimum temperatures. Typical turbomachinery efficiencies and heat exchangers minimum temperature differences are adopted in this phase;
4. Preliminary sizing of the main components;
The preliminary design of the main components (expander, pump, recuperative heat exchanger, condenser and the primary heat exchanger) is relevant to assess the potentiality of the fluid as well as the cycle performance. The main characteristics of the components can be determined starting from the optimal conditions identified in the cycle design phase. In this phase, other thermodynamic properties such as kinematic and dynamic viscosity and thermal conductivity must be derived from literature or from specific software.

The following sections detail the procedure for the evaluation of an innovative working fluid applied to defined mixture of CO₂ and perfluorocarbons (see Table 2). This choice is justified by the relatively high thermal stability and good miscibility with CO₂ of such components. Moreover, the mixing of perfluorocarbons with carbon dioxide mitigates their detrimental high Global Warming Potential. Among the suggested perfluorocarbons, perfluorohexane (C₆F₁₄) is considered in this work due to its relatively high critical temperature and molecular complexity

Table 2 – Some physical properties of perfluorocarbons and CO₂ [33]. (°) values for 100 years time horizon. (*) relative to R11.

Chemical species	T_c (°C)	P_c (bar)	MM (kg/kmol)	Global Warming Potential ^(*)	Ozone Depletion Potential ^(*)
Carbon dioxide, CO ₂	31.06	73.83	44.01	1	0
Perfluorobutane, C ₄ F ₁₀	113.20	23.23	238.03	9200	0
Perfluorohexane, C ₆ F ₁₄	176.40	18.02	338.04	7910	0
Perfluorobenzene, C ₆ F ₆	243.58	32.75	186.06	N.A.	0

3 Characterization of the working fluid

3.1 Equation of State definition

The study and the development of EoS is continuous and, in recent years, it has attracted considerable attentions. Generally speaking, an EoS should be easy to be extended and improved when experimental data become available. It should also be able to predict, with a reasonable precision, the thermodynamic behaviour outside the domain where experimental data are available. Although for carbon dioxide, the standard method to calculate its thermodynamic properties is now the NIST Reference Fluid Thermodynamic and Transport Properties Database (REFPROP) [37], this is not the case for other fluids as perfluorocarbons. Therefore, another set of EoS must be adopted. In this work, the classic cubic Peng-Robinson equation [38] is considered for the purpose of a preliminary comparison between the fluids (pure and mixtures), given its good accuracy in the prediction of a fluid behaviour [26,27]. Furthermore, when applied to mixtures, it is able to predict also the retrograde condensation. The basic and simpler original version of the equation, without any volume translation and with the classical (van der Waals) mixing rules for mixtures is implemented. Certainly, more complex models can also be adopted which require additional steps for the calibration of the additional parameters included in the equation.

As a good description of VLE data is a reasonable assurance to an acceptable evaluation of the thermodynamic behaviour [39], we use the simple selected EoS for all the following calculations.

3.2 VLE experimental apparatus

The experimental VLE data on the CO₂+C₆F₁₄ mixture, considered in this paper and presented in [40], are collected by using the experimental apparatus designed and manufactured in 2012 by ARMINES and installed at LEAP laboratory. The test rig, schematically represented in Figure 1 and already described in [40,41], is based on a static-analytical method [42]. It allows measuring the thermodynamic properties of working fluids and mixtures for different fields of application.

Experiments to obtain VLE data for the binary system of CO₂+C₆F₁₄ are performed by following this procedure described in [40]. Isothermal measurements are usually performed during the tests. By removing fluid from the cell or adding CO₂ in it, different equilibrium points at the same temperature can be evaluated. Temperature and pressure operating range of the apparatus extend respectively from -60°C to 200°C and from 10 bar to 199 bar. At least five analyses are performed for each phase and the last is considered to correspond to the equilibrium values. Considering the uncertainty margin of all measuring devices, including the GC, it is possible to evaluate the total uncertainty of the mole fraction for both liquid and vapour phases [40].

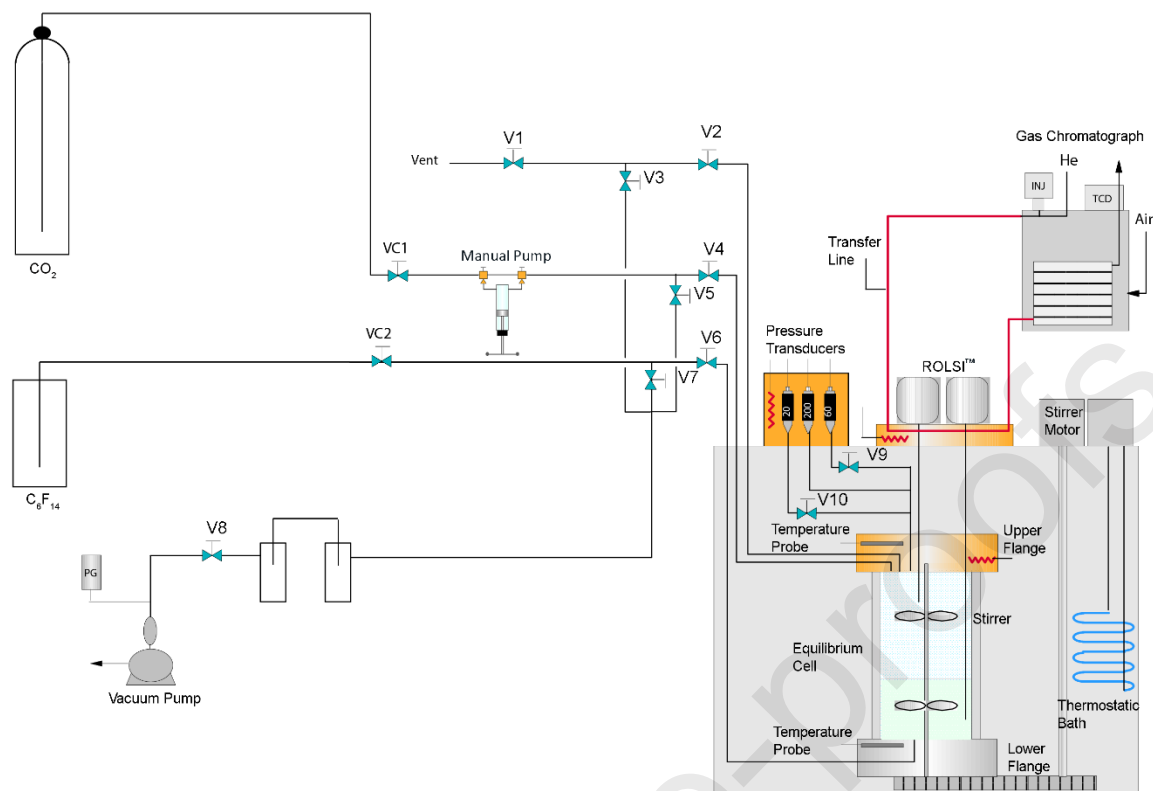


Figure 1 - Schematic diagram of the experimental apparatus. More details of all its main components are described in [41].

3.3 EoS and thermodynamic properties

The VLE experiments can be used to calibrate the coefficients of the EoS. In this work, Aspen Plus® v9.0 [43] is used to determine the coefficients $k_{i,j}$ for the considered mixtures of carbon dioxide with the selected perfluorocarbons starting from available experimental VLE data [40,44,45]; the calculated $k_{i,j}$ are shown in Table 3. Examples of obtained VLE results and a comparison with the corresponding experimental data are reported in Figure 2 for the investigated mixture $\text{CO}_2 + \text{C}_6\text{F}_{14}$.

Table 3 - Binary interaction parameters $k_{1,2}=k_{2,1}$ for the considered mixtures of carbon dioxide (subscript 1) and some perfluorocarbons (subscript 2).

Chemical species in the CO_2 rich mixture	$k_{1,2}=k_{2,1}$	Standard Deviation
Perfluorobutane, C_4F_{10}	0.1011	0.0038
Perfluorohexane, C_6F_{14}	0.0176	0.0028
Perfluorobenzene, C_6F_6	0.0312	0.0181

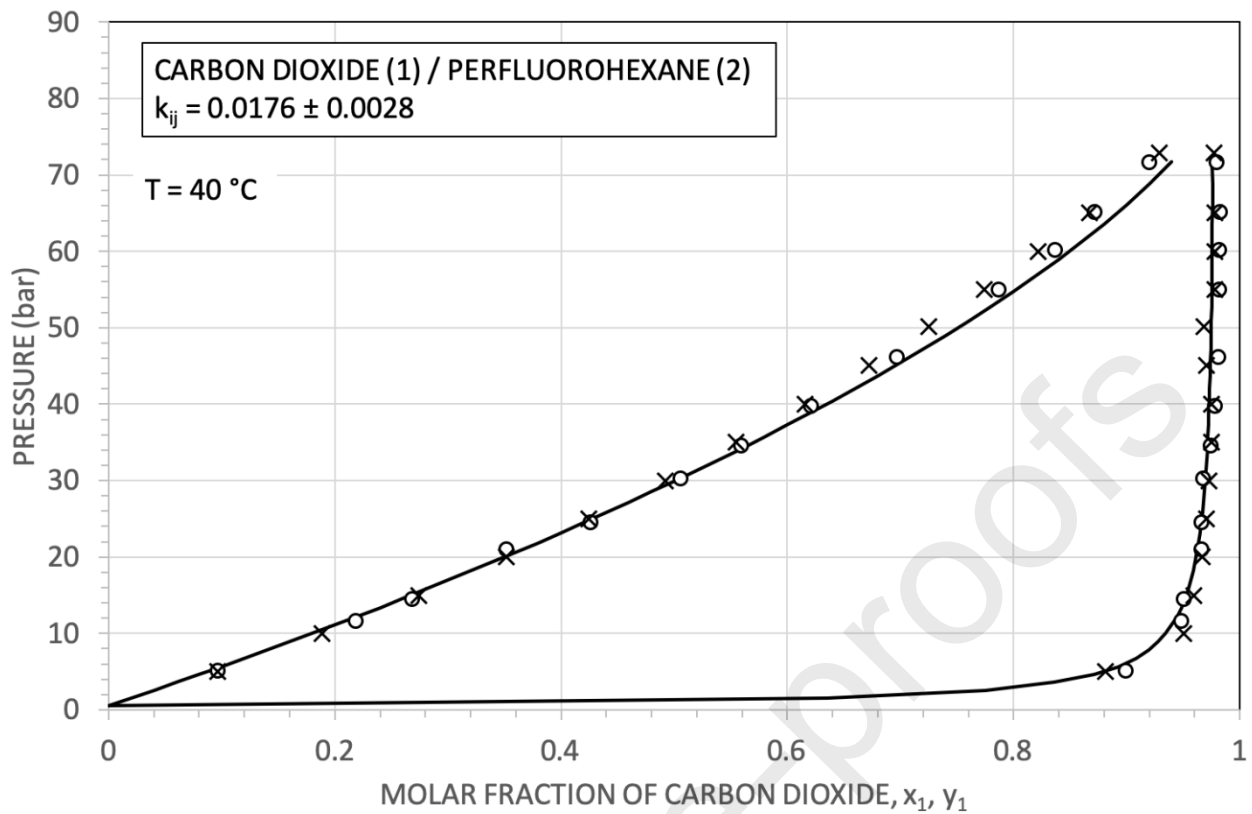


Figure 2 - P-xy VLE results for the mixture of carbon dioxide and perfluorohexane at $T=40^{\circ}\text{C}$. Circles are from experimental data reported in [40], crosses are from Aspen Plus® v9.0 database [43]. The uncertainties associated with temperatures and with pressures measurements (with coverage factor 2) are $\pm 0.08^{\circ}\text{C}$ and $\pm 0.06\text{ MPa}$ (maximum) respectively. The mean uncertainties in the measured molar fractions are about $4.0\text{e-}03$ for x_{CO_2} , and $5.0\text{e-}04$ for y_{CO_2} [40].

In addition, when dealing with mixture of working fluids, it is useful to identify the critical point as function of the composition. Since the critical temperature and pressure for mixtures do not correspond to the maximum values on the saturation curve, a tool to calculate the actual critical point of binary mixtures has to be developed. In fact, this can be estimated by an EoS applying the Gibbs criteria [46]. A successful numerical method, based on the use of the Helmholtz free energy, was proposed in [47] and in [48]; this method was adapted to the cubic equation of state and expressed in a generalized non-linear system of equations with intensive variables. The solutions of this highly non-linear system are the critical temperature and the critical volume of the mixture.

The critical point code developed in this study is based on the approach described in [48], and implemented in MATLAB version R2019a with the help of INTLAB toolbox [49]. INTLAB toolbox is specifically designed for interval arithmetic for real and complex data and is compatible with MATLAB version R2016a and onwards. The efficient root finding capability of INTLAB is exploited to solve the non-linear system of equations of critical point. The code requires pure components critical points, molar composition of each component, acentric factors and binary interaction parameter corresponding to the considered EoS as input information to compute the critical points of a binary mixture. In addition, the initial estimate of the solutions is also required. The code is capable to compute both stable and metastable critical points at given composition of any binary mixture without any initial guesses.

In Figure 3, the P-T envelopes and the critical locus for a binary mixture of carbon dioxide and perfluorohexane are reported. It can be observed that adequate thermodynamic

properties of the mixture can be obtained for instance with a CO_2 content of 0.75 (molar fraction), resulting in a bubble pressure (at 50°C) of about 55 bar and a temperature glide of about 70°C .

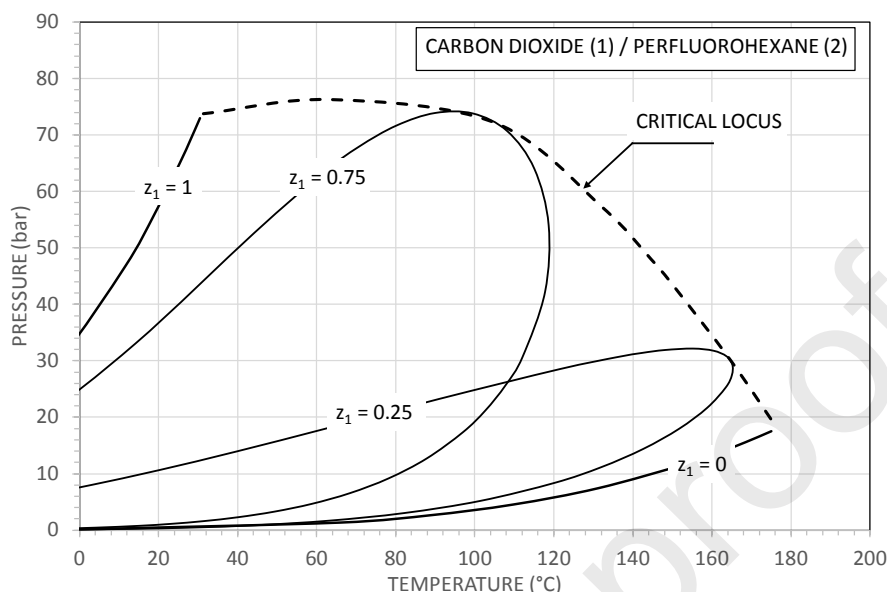


Figure 3 - Pressure-Temperature envelope for a binary mixture of carbon dioxide and perfluorohexane.

4 Thermal stability of pure fluids and mixtures

The thermal stability analysis aims at the evaluation of the maximum operating temperature range of the working fluid to be adopted in a power cycle. Experimental tests are carried out first on the two pure fluids, and then on the mixture.

The experimental apparatus consists of a cylinder of 75 cm^3 (material: AISI 304L) containing the fluid to be analysed, a thermocouple (type K) and a pressure transmitter that cover a wide range of pressure from 1 to 50 bar and some block valves to charge and isolate the investigated fluid. More details on the experimental apparatus together with the accuracy of the measurements are discussed in [50-52].

In this work, the thermal stability tests for both pure CO_2 and for the mixture of $\text{CO}_2 + \text{C}_6\text{F}_{14}$ with CO_2 content of 80% are performed while results of pure C_6F_{14} are collected from a previous experimental campaign [53], where a different procedure and approach, suitable for pure fluids was implemented.

Carbon dioxide, supplied by Sol, has a purity of 99.99% while the perfluorohexane (CAS: 355-42-0) has been supplied by Alfa Aesar with a purity level higher than 98%. For all the tests, the mass of the sample fluid is defined on the requirement of keeping the system pressure below the safety value of 50 bar.

After charging the sample of fluid at temperature close to ambient conditions, the experimental procedure consists of a thermal stress in an electric oven at high temperatures for a typical time span of 80-100 h, followed by the measure of the isochoric line (or vapour pressure for pure C_6F_{14}) in a thermostatic bath. In particular, the experimental test conditions of the investigated fluids are summarized in Table 4.

Table 4 - Thermal stability tests conditions

Fluid	Isochoric line ^(a) / Vapour pressure ^(b)		Thermal stress		
	T (°C)	ΔT_{step} (°C)	T (°C)	ΔT_{step} (°C)	Time _{step} (h)
^(a) CO ₂	-20 ÷ 40	10	400 ÷ 500	100	100
^(b) C ₆ F ₁₄ [53]	-20 ÷ 30	10	200 ÷ 450	50	80
^(a) CO ₂ +C ₆ F ₁₄	10 ÷ 140	20 for T ≤ 100 5 for T > 100	250 ÷ 500	50	100

Figure 4 shows the results of the thermal stability test for pure carbon dioxide where the reference p-T measurements correspond to the virgin fluid behaviour: the CO₂ density, equal to 32.7 kg/m³, is fixed during the tests, and it is determined by the ratio of the weighted mass loaded in the circuit and the internal volume of the sample cylinder. The upward shift of the isochoric lines for the two tests at higher temperature revealed fluid decomposition at 500°C due to the well-known interaction of the CO₂ with the stainless steel [54,17].

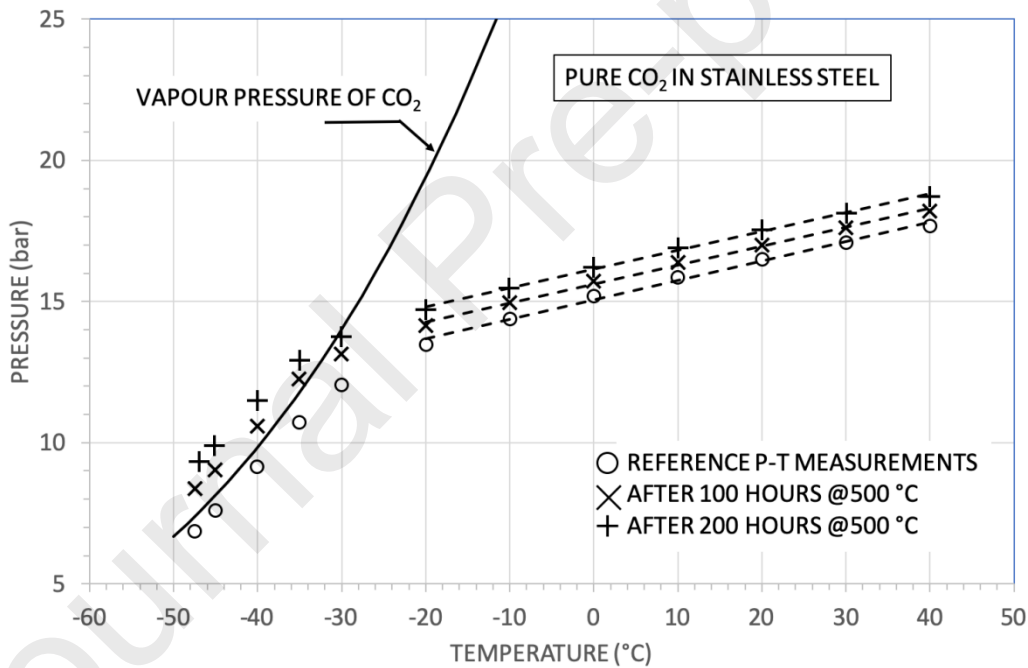


Figure 4 - Results of p-T measurements for pure carbon dioxide at 500°C.

Even if a chemical analysis could be useful to have a full picture of the decomposition phenomenon, the numerical analysis of the p-T measurements, discussed below, is enough to identify a fluid degradation signal.

The method proposed in this work lies on the study of the thermodynamic behaviours of the working fluid from the variation of the van der Waals coefficients. The simpler equation of state, accounting qualitatively the real gas effects of a fluid, is the van der Waals equation [55]:

$$P = \frac{RT}{V_m - b} - \frac{a}{V_m^2} \quad (1)$$

where V_m (m^3/kmol) is the molar volume ($V_m = V/MM$), R (kJ/kmolK) is the gas constant and the coefficients a and b can be found for each substance from the following equations at the critical point.

$$P_c = \frac{a}{27b^2} \quad (2)$$

$$V_c = 3b \quad (3)$$

$$T_c = \frac{8a}{27Rb} \quad (4)$$

The comparison of the estimated coefficients a , b and the molar mass (MM) from the regression of the experimental data (in the gas phase), starting from the virgin fluid isochoric line, and after each thermal stress test, can be representative of potential decomposition of the investigated fluid¹. As a consequence of the thermal stress, the substance decomposes in a mixture of different unknown species that, for simplicity, is assumed as a pure fluid characterised by different coefficients a , b and MM .

Pure CO_2 case is discussed below as an example of the proposed procedure. The corresponding parameters of the van der Waals equation of state, obtained by the non-linear regression of the experimental values for a density equal to $32.7 \text{ kg}/\text{m}^3$ are reported in Table 5. Decomposition of the sample produces a variation of the isochoric lines and, as a consequence, of the parameters a , b and MM . These results can be assumed as an indirect indication of the extent of the decomposition.

Table 5 - Parameters a , b and MM of the van der Waals equation of state for carbon dioxide for the thermal stability test at 500°C .

	a ($\text{MPa}\cdot\text{m}^6/\text{kmol}^2$)	b (m^3/kmol)	MM (kg/kmol)
Virgin fluid	0.607	0.060	41.452
After 100 h	0.457	0.065	42.775
After 200 h	0.355	0.069	43.080

Moreover, starting from the obtained parameters, the isothermal compressibility k_T , defined in Eq.5, can be used as a proper index to highlight the impact of the thermal degradation on the power cycle. As shown in Table 6, after 200 h at 500°C , the compressibility k_T decreases by about 18% (at the same volume and temperature).

$$\frac{1}{k_T} = -V_m \left(\frac{\partial P}{\partial V_m} \right)_T = -V_m \left[2\frac{a}{V^3} - \frac{RT}{(V-b)^2} \right] \quad (5)$$

Table 6 – The estimated isothermal compressibility k_T of carbon dioxide at 10°C for the virgin and the decomposed fluid using the van der Waals coefficients and MM of Table 5.

	$1/k_T$ (MPa)	$u(k_T)$ (MPa)
Virgin fluid	1.292	0.021
After 100 h	1.458	0.015
After 200 h	1.582	0.012

¹ Since the van der Waals fluid is not a real fluid, the coefficients a , b and MM have to be optimised also for the virgin fluid isochoric line.

Regarding the pure perfluorohexane, a previous experimental campaign [53] revealed that C_6F_{14} can be considered stable up to 350°C , showing early signs of decomposition after the thermal stress test at 400°C .

Finally, the reference isochoric and dew line for a mixture of carbon dioxide and perfluorohexane, with molar fractions of 80% and 20% respectively, is shown in Figure 5. The virgin fluid measurements are along mixture density value of 99.4 kg/m^3 , in the gas phase. Furthermore, measured p-T points after each thermal stress are represented. The best fit of the experimental values using the van der Waals equation of state, according to the procedure previously described, gives the values in Table 7, assuming a pure fluid behaviour of the mixture, while Table 8 shows the resulting isothermal compressibility k_T at different temperature. Since measurements at 250°C and 300°C are in agreement with the fresh mixture, the values were included for the calculation of the virgin mixture parameters. Although the van der Waals parameters are slightly different after the thermal stress tests at 350°C and 400°C , the mixture can be considered thermally stable up to 400°C : this behaviour is also confirmed from the parameter k_T . Decomposition phenomena occur from 450°C where not only the isothermal compressibility increases by more than 50% with respect to the virgin mixture but also a strong deviation of the van der Waals parameters from initial values can be observed.

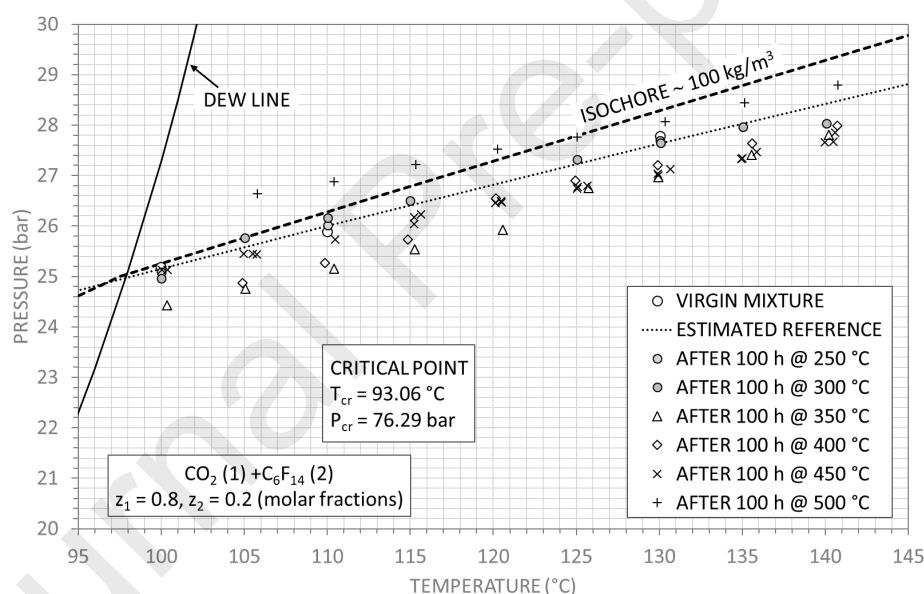


Figure 5 . Results of P-T measurements for the mixture $\text{CO}_2 + \text{C}_6\text{F}_{14}$.

Table 7 - Parameters a , b and MM of the van der Waals equation of state of the mixture carbon dioxide and perfluorohexane.

	a ($\text{MPa m}^6 \text{ kmol}^{-2}$)	b ($\text{m}^3 \text{ kmol}^{-1}$)	MM (kg kmol^{-1})
Virgin mixture	0.818	0.086	102.4
350°C	0.901	0.087	102.9
400°C	0.924	0.088	101.0
450°C	0.016	0.360	158.7
500°C	0.004	0.584	176.1

Table 8 - The estimated isothermal compressibility k_T of carbon dioxide and perfluorohexane at 120°C for the virgin and the decomposed mixture using the van der Waals coefficients and MM of Table 7.

	$1/k_T$ (MPa)	$u(k_T)$ (MPa)
Virgin mixture	2.25	0.052
350°C	2.08	0.054
400°C	2.07	0.057
450°C	3.43	0.122
500°C	4.15	0.247

5 Modelling of the thermodynamic cycle

Performance of a simple recuperative cycle working with the $\text{CO}_2 + \text{C}_6\text{F}_{14}$ mixture are investigated in Aspen Plus® v9.0 [43]. The Peng-Robinson EoS [38] with the binary parameter defined in Section 3.1.2 is adopted for all thermodynamic properties.

As shown in Figure 6, the power cycle consists of a compression step (from 1 to 2), followed by a pre-heating section (2-3), also called recuperator, and a primary heat exchanger (3-4), where the maximum operating temperature is achieved; afterwards, the working fluid is expanded in a turbine (4-5), cooled in the recuperator (5-6) and, finally, in a dry cooler, also called condenser (6-1).

Table 9 summarizes the main design parameters adopted for the cycle modelling. The minimum operating pressure is set by the minimum working temperature: a condensing cycle means that the compression step starts from saturated liquid phase, so the saturation pressure at 50°C, for each mixture composition, is the minimum cycle pressure. The maximum temperature is the minimum between the thermal stability results and the heat source.

The turbomachinery components are modelled with isentropic efficiency approach. Pressure drops in the heat exchangers are for simplicity neglected, even if they can be easily implemented. The typical pinch point of heat exchanger operating with gaseous-condensing phases is adopted in this preliminary analysis (10°C). As the minimum temperature difference can occur inside the recuperative heat exchanger, this parameter is named Minimum Internal Temperature Approach (MITA).

As the analysis is in relative terms (for example innovative fluid vs. CO_2), and considering that the cycle design is not optimized to fully exploit the potentialities of the new fluid, but as go/no-go stage gate for deeper investigations, the adoption of typical component performance and neglecting the pressure drop is reasonable in this phase.

Table 9 - Power cycle assumptions.

Maximum temperature, °C	400
Minimum temperature, °C	50
Recuperator minimum internal temperature approach (MITA), °C	10
Turbine inlet pressure, bar	150 ÷ 350
Compressor/Pump isentropic efficiency, %	0.85
Turbine efficiency, %	0.90

Examples of the T-s (Temperature-Entropy) diagrams for three mixtures at different compositions are reported in Figure 6 (right). The increasing of the C_6F_{14} molar fraction leads to a high critical temperature and an isentropic dew line. In parallel, the higher the CO_2 concentration in the mixture, the higher is the temperature variation along the expansion.

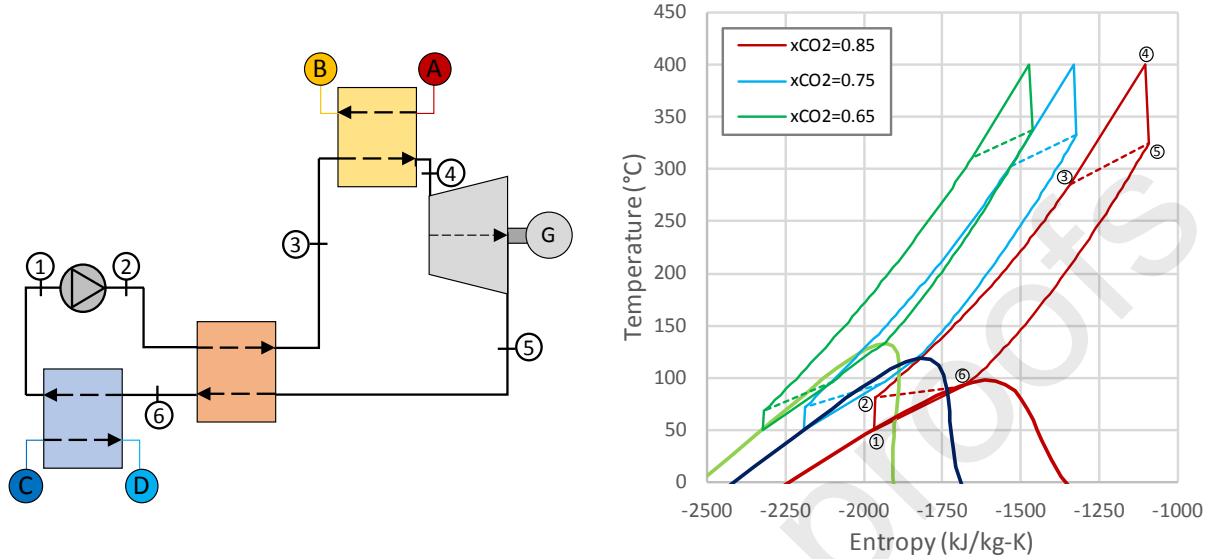


Figure 6 - (left) schematic of a simple recuperative condensing supercritical cycle and (right) T-s diagrams of the simple recuperative condensing supercritical cycle for different fractions of CO_2 and C_6F_{14} . The dashed lines represent the inlet-outlet conditions of the recuperative heat exchanger. Thermodynamic properties of points are reported in Table 10

The influence of different $CO_2+C_6F_{14}$ mixture composition is investigated in terms of power cycle efficiency which is defined as:

$$\eta_{cycle} = \frac{P_{turbine} - P_{compressor}}{Q_{in,cycle}} \quad (6)$$

where $P_{turbine} - P_{compressor}$ is the net electric power (P_{net}) generated by the recuperative cycle and $Q_{in,cycle}$ is the thermal power input to the power cycle.

Figure 7 shows the power cycle efficiency as function of the mixture composition expressed in terms of CO_2 molar fraction and the maximum cycle pressure. The highest power cycle efficiency (around 34%) is obtained for a C_6F_{14} molar fraction between 0.175 and 0.2. Notably these efficiency values are significantly higher than those obtainable adopting CO_2 as pure fluid for a Brayton recompression cycle, as shown in Figure 7. For instance, the recompression pure sCO_2 cycle [22,56] with a minimum pressure of 100 bar and assumptions consistent with those in Table 9 results in a maximum cycle efficiency of about 31% obtained with turbine inlet pressure of 190 bar.

Table 10 – Thermodynamic properties of the mixture (CO_2 80%_{mol}, C_6F_{14} 20%_{mol}) with a maximum pressure of 250 bar.(+) Enthalpy and entropy values are calculated using stream 1 (saturated liquid) as reference state

Stream	T (°C)	p (bar)	h (kJ/kg) ⁽⁺⁾	s (J/kgK) ⁽⁺⁾	Vapour fraction
1	50	61.85	0	0	0
2	75.7	250	19.7	4.7	0
3	295.1	250	308.3	647.6	1
4	400	250	442.0	863.5	1
5	329.3	61.85	377.1	875.6	1
6	92.1	61.85	88.5	258.6	0.59

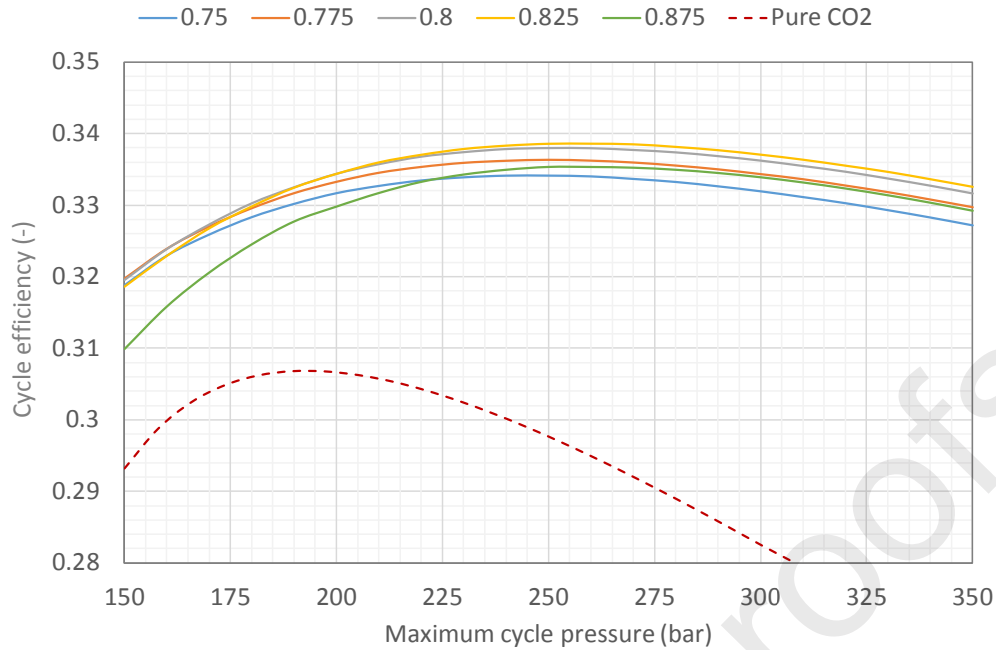


Figure 7 - Cycle efficiency as function of the turbine inlet pressure for different molar fractions of CO_2 and C_6F_{14} and for pure sCO_2 recompression cycle.

6 Preliminary considerations about heat exchangers and turbomachinery design

Once confirmed the potentialities of the innovative fluid through the cycle design, some preliminary considerations about the components must be drawn to anticipate some critical aspects in the main components (i.e. low heat transfer coefficients, volumetric expansion ratios).

Between the supercritical cycle components, the turbine, the recuperative heat exchangers and the condenser play a key role. In this section, some notes about their preliminary design and a comparison between the cycle with pure CO_2 and the innovative one with the mixture $\text{CO}_2 + \text{C}_6\text{F}_{14}$ with a molar fraction of 80% of carbon dioxide are discussed. The values used for the comparison, corresponds to the maximum cycle efficiency for both the cycle.

The cycle requires three different heat exchangers: the primary heat exchanger where the heat is transferred to the fluid, the condenser where the heat is rejected to the ambient and the recuperative heat exchanger where the fluid is preheated recovering heat from the turbine outlet flow. A detailed heat exchanger design requires the estimation of the fluid or mixture transport properties (i.e. molecular dynamics method is proposed in [57] while other methods are presented in [33]) and the definition of a certain geometry that require further analysis which are beyond the scope of this work. Even the bi-phase mixture behaviour in the condenser has to be explored in a dedicated study, considering that the mixture convective heat transfer coefficients in two-phase flow are basically lower than that of the pure fluids [58]. In particular, the effects of the relatively high condensation pressure, should be further investigated for trans-critical cycle.

In general, the primary heat exchanger and the condenser are based on shell-and-tube configuration, while the recuperator is typically based on a printed circuit heat exchanger (PCHE) configuration. The PCHE maximizes the surface to volume ratio hence minimizing the component volume/weight and it can tolerate the typical pressures of these applications. In literature there are several studies on PCHE for pure CO_2 to rely on [22,23] which can be extended to CO_2 -based mixtures.

As can be noted in Table 10, for the investigated mixture, the exchanged thermal power in the recuperator is twice the thermal power input and more than three times higher than the exchanged thermal power in the condenser. This implies that the recuperator design will considerably affect the cycle capital cost. The resulting $UA_{\text{rec}}/P_{\text{net}}$ of the recuperator (rec) is 0.36 K^{-1} with a ratio of 6.4 between the exchanged thermal power and the produced net power. These values are significantly lower than the corresponding ones for pure CO_2 which are equal to 0.53 K^{-1} and 13 respectively, meaning that the mixture would require smaller surface areas per unit of net power.

The turbomachinery design can be performed adopting a preliminary approach based on the similarity rules and assuming the thermodynamic conditions determined in the cycle design step (see Table 10).

A preliminary sizing of the turbine can be developed assuming ideal turbine stages, without considering the traditional fluid-dynamic losses, resorting to the free-vortex theory and assuming a total admission. The rotational speed N can be selected assuming ω_s and D_s close to the usually accepted optimal values, [59], and a ratio h/D (where h is the mean blade height and D the mean diameter for the stage) in a reasonable range ($0.025 < h/D < 0.4$), compatibly with a small kinetic energy loss (below 10% of the Eulerian work).

An example of the preliminary results for the considered mixture are reported in Table 11 where the main characteristics of the resulting turbine stages are summarized. Although the two stages have almost the same dimensions, the higher molar mass of the mixture involves a lower peripheral speed. Fixing the rotor reaction degree equal to 0.5, the greater volumetric expansion ratio of the mixture case could have, as a consequence, an excessive flaring angle, compared to the pure CO_2 case. For this reason, the reaction degree of the mixture has to be reduced, resulting in this case with supersonic conditions for the nozzles. The turbines do not present particular critical issues in both cases: the final design, the final design solution could require more than one stage due to the relatively high temperature but this parameter depends also on the plant power size. For a complete evaluation of the design characteristics of the turbine, the different turbine losses have to be considered.

Table 11 – Thermodynamic conditions assumed for the expander design and resulting preliminary stage design parameters.

Working fluid	Pure CO_2	$80\%\text{CO}_2+20\%\text{C}_6\text{F}_{14}$
Assumptions		
Initial expansion temperature ($^{\circ}\text{C}$)	400	400
Initial expansion pressure (bar)	190	250
Final expansion pressure (bar)	100	62.5
Isentropic power (kW)	10000	10000
Preliminary estimated design parameters		
Rotation speed (rpm)	20000	15000
Reaction degree at the mean diameter	0.5	0.25
Overall volume expansion ratio	1.673	3.587
Inlet volume flow rate (m^3/s)	0.874	0.323
Tip diameter (cm)	33.5	28.9
Mean diameter (cm)	32.47	27.2
h/D	0.031	0.062
Tip peripheral velocity (m/s)	351	227

7 Conclusions

The exploitation of renewable energy sources and the possibility to recover heat from industrial processes call for the selection of new working fluids in power cycles. This paper presented the procedure for the identification of innovative working fluids to replace the more conventional steam and pure CO₂ for heat sources at relatively high temperature (greater than 350-400 °C). The main rationale behind the adoption of an innovative fluid relies in the improvement of the conversion efficiency, reduction of the power block complexity and size, while keeping the same reliability.

Once the fluid or the mixture are selected, the procedure consists of (i) the identification and calibration of the thermodynamic properties of the innovative fluid through proper Equation of State with experimental Vapour-Liquid Equilibrium measurements, (ii) the identification of the maximum operating temperature through thermal stability tests, (iii) the assessment of the power cycle performance at different mixture compositions and (iv) the design of the main plant equipment particularly focusing on the expander and the recuperative heat exchanger.

The procedure is applied to a promising mixture of CO₂+C₆F₁₄ showing the potentialities of the mixture to replace pure CO₂ as working fluid: the cycle efficiency adopting the CO₂+C₆F₁₄ mixture is close to 34% assuming a maximum operating temperature of 400°C which is 3-4% points higher than the performance of a recompression cycle implementing pure CO₂. The preliminary evaluation of the recuperator, and the turbine confirmed the potentiality of the investigated mixture: the ratio UA_{rec}/P_{net} results about the 60% lower than the corresponding value required by pure carbon dioxide and the design of the turbine is not particularly critical.

Some crucial aspects of the described general procedure are about thermal stability investigations, particularly critical and difficult to develop, but essential. In addition to thermal stability in a (relatively) inert environment, it could be also necessary to evaluate the fluid compatibility with the usual materials involved in the manufacture of the engine.

As the use of carbon dioxide mixtures (as here proved), at least for the specific considered application, is potentially beneficial from the thermodynamic point of view, and as the thermodynamic behaviour of mixtures are not easily predictable, measures of VLE are necessary. Many other topics have to be explored (for example the transport properties necessary for a detailed design of the heat exchangers), but certainly the thermodynamic evaluations and the thermochemical stability are the most important in a preliminary study.

The final design of heat engines using new working fluids is demanding, but the results here presented and discussed show that, at least from the thermodynamic point of view, there is room for significant improvements in the resulting efficiencies.

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Nomenclature

a EoS parameter accounting for attraction between molecules

b	EoS parameter accounting for volume occupied by molecules
D	Stage mean diameter, m
D_s	Specific diameter, -
EoS	Equation of state
GC	Gas chromatograph
h	Mean blade height, m
$k_{i,j}$	Peng-Robinson EoS binary interaction parameter
k_T	Isothermal compressibility factor, MPa
MITA	Minimum Internal Temperature Approach, °C
MM	Molar mass, kgkmol ⁻¹
N	Rotational speed, rpm
ORC	Organic Rankine Cycle
P	Pressure, bar
P_{turbine}	Turbine power, kW
$P_{\text{compressor}}$	Compressor power, kW
P_{net}	Net electric power produced, kW
PCHE	Printed circuit heat exchanger
$Q_{\text{in,cycle}}$	Inlet thermal power, kW
R	Gas constant (kJkmol ⁻¹ K ⁻¹)
s	Entropy, kJkg ⁻¹ K ⁻¹
T	Temperature, °C
T_b	Normal boiling temperature, °C
$\text{Time}_{\text{step}}$	Thermal stability test duration, h
V and V_m	Mass and molar volume, m ³ /kg and m ³ /kmol
$V_{\text{out,S}}$	Stage isentropic outlet volume flow, m ³ /s
VLE	Vapour-Liquid Equilibrium
x	Species molar fraction in gas phase, -
y	Species molar fraction in liquid phase, -
z	Mixture molar fraction, -

Greek symbols

α	Peng Robinson EoS Alpha-function
ΔH_s	Static isentropic enthalpy variation of the stage, kJ/kg
ΔT_{step}	Isochoric line data acquisition step, °C
η_{cycle}	Cycle efficiency, -
ω_s	Specific rotational speed, -

Subscripts

c	Critical
i,j	Species
m	Mixture

r Reduced
rec Recuperator

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A comprehensive procedure for innovative fluid identification is proposed
Thermodynamic properties must be assessed through Equation of state
Equation of State must be calibrated with VLE experiments for innovative fluids
Maximum operating fluid temperature is identified through thermal stability tests

Journal Pre-proofs

Declaration of 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.

☐ The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: