

THE POTENTIAL OF SUPERCRITICAL CYCLES BASED ON CO₂ MIXTURES IN CONCENTRATED SOLAR POWER PLANTS: AN EXERGY-BASED ANALYSIS

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ABSTRACT

This paper, developed in the context of the SCARABEUS project funded by the Horizon 2020 programme of the European Commission, focuses on the thermodynamic comparison between pure supercritical Carbon Dioxide and blended transcritical Carbon Dioxide power cycles by means of a thorough exergy analysis. A reference power plant based on a steam Rankine cycle and representative of the current state of the art of Concentrated Solar Power plants is selected as base-case. Afterwards, four cycles are added to the comparison. Two of these cycles employ pure CO₂, with either a *Recompression* or a *Partial Cooling* layout, whereas two cycles employ CO₂-based mixtures with either Hexafluorobenzene (CO₂-C₆F₆) or Titanium Tetrachloride (CO₂-TiCl₄) with a *Precompression* and a *Recuperated Rankine*.

The figures of merit used to carry out the second-law analysis are exergy efficiency and exergy destruction in the main components of the cycle. Two different cases are identified, corresponding to two temperatures of the energy (heat) source: 575°C and 725°C. The first one is representative of the peak temperatures achieved by the molten salts used in modern Concentrated Solar Power plants. 725°C will expectedly be achieved by next generation systems and it is hence assessed with the aim to unfold the true potential of the concept proposed. The results show that at 575°C pure sCO₂ power cycles are clearly outperformed by steam Rankine cycles whilst, at 725°C, they are able to achieve higher thermal and exergy efficiencies, in the order of 49% and 72% respectively. When compared to state-of-the-art Rankine cycles using steam, blended-sCO₂ power cycles enable thermal efficiency gains of up to 1.1 and 6 percentage points at 575°C and 725°C respectively, with exergy efficiencies of up to 75.2%.

1 INTRODUCTION

The potential of supercritical Carbon Dioxide power cycles to enhance the performance and reduce the cost of state-of-the-art (SoA) CSP plants has already been recognized by the Concentrated Solar Power (CSP) industry. Nevertheless, the high ambient temperatures typically found in solar sites are extremely detrimental for sCO₂ technology, compromising its actual potential in terms of the thermodynamic and economic gains attainable in a practical case. In order to overcome this weakness whilst still retaining the thermodynamic features enabling potentially higher efficiencies, the use of blended sCO₂ has been investigated in the very last years by different authors (Invernizzi and van der Stelt, 2012; Manzolini *et al.*, 2019). It is exactly in this scenario where the SCARABEUS project is being developed, with the main idea of increasing the critical temperature of the working fluid through the addition of certain additives to the raw sCO₂, enabling its condensation even at very high ambient temperatures, hence yielding higher thermal efficiency than with either (steam) Rankine or conventional sCO₂ cycles.

Thermal efficiency is a suitable figure of merit to compare power cycles working under similar heat source and sink temperatures. Nevertheless, the comparison between steam Rankine cycles and supercritical CO₂ cycle is often misleading because different turbine inlet temperatures (TIT) are

involved: lower for steam cycles and higher for sCO₂ systems. In other words, higher energy efficiencies of the latter cycles can potentially be brought about by the higher temperatures of heat addition to the cycle and not by an inherently more efficient conversion of this energy into useful work. The utilization of the 2nd Law of Thermodynamics to carry out an exergy analysis, as opposed to the more usual energy analysis, has a twofold benefit. On the one hand, it provides meaningful information about whether or not a cycle is closer to the best thermodynamic performance attainable for given heat source/sink temperatures (Carnot cycle). On the other, it allows the identification of those component where energy losses are taking place; i.e., where cycle performance is departing from the ideal (reference) Carnot cycle. As a result, it is possible to modify the cycle layout to compensate for these losses, thus yielding a cycle performance closer to the true potential enabled by the temperatures of heat source and sink.

Several authors have carried out exergy analyses of sCO₂ cycles in the past (Angelino, 1968; Padilla *et al.*, 2015; Penkuhn & Tsatsaronis, 2020, among others), yielding the known conclusion that the main source of irreversibilities in the simple recuperated Brayton cycle operating on sCO₂ is the recuperative heat exchanger, due to the dissimilar heat capacity of the high- and low- pressure streams. This conclusion brought about a series of advanced layouts proposed by Angelino (1968), and later by other authors, including split-compression that resulted in the well-known *Recompression* and *Partial Cooling* layouts. These cycles largely improved the exergy efficiency of the simple recuperated Brayton cycle, redistributing exergy destruction and reducing the losses associated to the recuperative heat exchangers, at the expense of increasing the losses across the compression and heat rejection processes. Such advanced sCO₂ cycles exhibit a more uniform loss distribution across the different cycle components, in contrast with that of the steam Rankine cycle which concentrates most of the exergy destruction in the primary heat addition process (Angelino, 1969).

These conclusions about the most interesting cycle layouts for given boundary conditions can nevertheless change when the characteristics of the working fluid vary. Such is the case of the SCARABEUS project where the addition of additives brings about modifications of the working fluid properties (most notably the critical pressure and temperature). Previous studies, developed in the context of SCARABEUS by some of the authors, demonstrated that part-flow configurations can be of little interest for sCO₂-based blends, due to poor adaptability to compression in liquid phase (Crespi *et al.*, 2021a and 2021b). This is numerically confirmed for the additives currently under investigation in SCARABEUS - Hexafluorobenzene (C_6F_6) and Titanium Tetrachloride (TiCl₄) - and paves the way for the exploration of other cycle layouts. Amongst these, attention was paid by the authors to other cycle configurations that had been disregarded by the sCO₂ scientific community in the last years, in particular the *Recuperated Rankine* and *Precompression* cycles about which, unfortunately, only a few studies analysing the 2^{nd} Law characteristics can be found in literature.

Bearing all this in mind, the present paper aims to analyse the intrinsic 2nd Law performance of sCO₂ cycles in depth, following the footsteps of Gianfranco Angelino back in the late 1960s, with the aim to explore the performance enhancement that sCO₂ blends could potentially bring to the technology. To this end, two different heat source temperatures are considered: 575°C, representative of contemporary CSP plants using state-of-the-art technology, and 725°C, representative of next-generation receiver technologies. The work is organised as follows: in the first part of the manuscript a thorough description of the computational environment is provided, followed by a brief introduction to the fundamentals of exergy analysis as used in the paper. In the second part, sCO₂ cycles, either pure or blended, are compared against SoA CSP Rankine cycles using steam, and a series of interesting conclusions are drawn.

2 COMPUTATIONAL ENVIRONMENT

2.1 Definition of Reference Case, Candidate Cycles and Blends

Three different power cycle technologies are considered in this work: i) SoA steam-based Rankine cycles, ii) pure supercritical CO₂ cycles and iii) transcritical cycles using CO₂ blends. Due to the intrinsic differences between these technologies, in particular between the Rankine and sCO₂-based cycles (either pure or blended), it is not possible to define a complete set of common boundary

conditions to be employed in the simulations. Rather, the only common specifications are power output, set to 100 MW gross, minimum cycle temperature, set to 50°C to have a representative value applicable to a site with extreme conditions, and the two heat source temperatures, 575 and 725°C respectively.

The reference power cycle considered for contemporary CSP plants using steam turbine technology features reheat and feedwater heating. Live steam is produced at 150 bar and 550°C and the extraction pressures for the seven feedwater heaters are set so as to balance peak cycle efficiency and inventory and auxiliary power consumption of the molten salt system. Condensation is enabled by an Air-Cooled Condenser with a design pressure of 0.123 bar (50°C)¹.

For the cycles based on supercritical CO₂, either pure or blended, a total of four different layouts are considered: *Recompression* (RC) and *Partial Cooling* (PC) for pure sCO₂, *Recuperated Rankine* (RR) and *Precompression* (PrC) for CO₂ mixtures. The common set of boundary conditions applied to all cases is summarised in Table 1, where two maximum cycle temperatures are considered, 550°C and 700°C, corresponding to the two different heat source temperatures mentioned above.

P _{max} [bar]	η _{is,T} [%]	η _{is,C} [%]	η _{is,P} [%]
250	93	89	88
ΔT _{min} [°C]	ΔP_{PHX} [%]	$\Delta P_{ m HRU}$ [%] pure/blended	ΔP_{REC} [%] low/high P side
5	1.5	1.5/0	1/1.5

Table 1: Common set of boundary conditions for sCO₂-based cycles (pure or blended).

The *Recompression* and *Partial Cooling* layouts shown in Figure 1 are acknowledged to be two of the most interesting cycle layouts for sCO₂ technology (Dostal, 2004), in particular for Concentrating Solar Power applications (Crespi, 2020. Neises and Turchi, 2019). For both temperatures -550 and 700°C-, the following cycle parameters have been optimised with MATLAB's 'Global Optimisation Toolbox': split-flow fraction (mass flow circulating through the main compressor) and inlet pressures to the main compressor and pre-compressor (P_{in,MC} and P_{in,PreC} respectively). The detailed methodology cannot be included in this document, given the strict length limitation, but the complete set of parameters maximising cycle performance is provided in Table 2. The corresponding values of thermal efficiency are presented and discussed in Section 4 later.

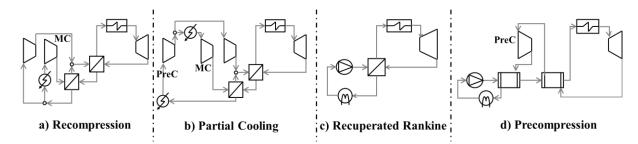


Figure 1: Layouts of sCO₂ cycles considered: pure (a, b) or blended (c, d).

Table 2: Optimum values of the main design parameters employed in pure sCO₂ cycles.

Variable	RC 550°C	RC 700°C	PC 550°C	PC 700°C
P _{in,MC} [bar]	104.5	102.0	114.8	110.9
split flow fraction [-]	0.707	0.708	0.596	0.594
Pin,PreC [bar]	-	-	70.7	64.84

¹ This power block is adapted from the cycle proposed for the *Rice Solar Energy Project* in California (Rice Solar, 2021). When the higher heat source temperature is taken into account (725°C), live steam is produced at 180 bar and 600°C, herein considered as the maximum live steam temperature enabled by SoA steam turbine technology.

For the transcritical cycles using sCO₂ mixtures (SCARABEUS technology), previous works by the authors (Crespi et al, 2021a and 2021b) identified the *Recuperated Rankine* and *Precompression* layouts as the best performers, in particular when the additives are Hexafluorobenzene (C_6F_6) and Titanium Tetrachloride (TiCL₄). Both layouts were originally proposed by Angelino in 1969 and are shown in Figure 1. The former cycle is a mere adaption of a Rankine cycle employing CO_2 -based blends whereas the latter layout features a pre-compressor in the low-pressure section of the cycle, between the high and low temperature recuperators, in order to overcome the limitation imposed by condensing pressure on turbine exhaust pressure. This provides an additional degree of freedom for further optimisation, increasing the expansion ratio achievable by the turbine. An interesting conclusion drawn from previous analyses is that the performance of each of these cycles is optimised by a different composition of the working mixture. In particular, the efficiency of the *Precompression* cycle is highest when the working fluid is comprised of $85\%CO_2$ - $15\%C_6F_6$ (termed D1C15 PrC here) whereas the *Recuperated Rankine* performs best with $85\%CO_2$ - $15\%TiCl_4$ (D2C15 RR). This sensitivity of optimum cycle performance to working fluid composition is carried out throughout the rest of the analysis, and the four possible combinations between these layouts and blends.

The main specifications of the sCO_2 mixtures considered in this work are provided in Table 3, while a brief evaluation of the additives employed is summarised in Table 4, following NFPA 704 standard. Some of the features reported in the table are currently under evaluation by the SCARABEUS consortium in order to assess how much they compromise the commercial deployment of the technology (high flammability of C_6F_6 , aggressive water reactivity for $TiCl_4$). Further information about this and other dopants being screened now will be reported by the corresponding partners in future publications.

Table 3: Specification of CO₂ blends. P_{cond} and Glide corresponding to a bubble temperature of 50°C.

Blend	Composition [% molar]	MW [g/mol]	T _{cr} [°C]	P _{cr} [bar]	P _{cond} [bar]	Glide [°C]
CO_2	CO ₂ [100]	44.01	31.0	72.8	-	-
D1C15	CO ₂ - C ₆ F ₆ [85-15]	65.32	102.1	121.3	77.52	88.4
D2C15	CO ₂ - TiCl ₄ [85-15]	65.86	93.76	190.9	96.88	174

Table 4: Additive hazard according to NFPA704, 2021.

Compound	Health Hazard	Flammability	Chemical Reactivity	Special Hazard
CO_2	2	0	0	SA
C_6F_6	1	3	0	-
TiCl ₄	3	0	2	₩

2.2 Simulation Tools

The modelling and simulation of the power cycle has been developed using the commercial software Thermoflex (Thermoflow Inc., 2020), a widely used software for power plant engineering and analysis with built-in datasets of steam and carbon dioxide properties using Refprop database (Lemmon *et al.*, 2018). Unfortunately, Thermoflex does not have a similar database of properties for CO₂ mixtures of variable composition. These properties have thus been estimated with Aspen Plus (Aspen Technology Inc., 2011) and the resulting data has been incorporated into Thermoflex through a dedicated User-defined General Fluid feature specifically developed by Thermoflow for the SCARABEUS project. Further information regarding the calculation of thermophysical properties can be found in previous papers by the authors (Crespi *et al.*, 2021a) and by other partners of the SCARABEUS consortium (Bonalumi *et al.*, 2020, Manzolini *et al.*, 2021). Finally, an in-house Matlab code has been developed to complement Thermoflex for cycle optimisation, exergy analysis and to post-process the results.

3 FUNDAMENTALS OF EXERGY ANALYSIS

Exergy can be defined as the maximum work that can be extracted from a thermodynamic system from its current state until a final state of equilibrium with the environment -the dead state- is reached, assuming that the system interacts with the environment only (Reynolds and Colonna, 2018). Flow exergy of the working fluid can be calculated using Equation 1, where H_0 and S_0 are the enthalpy and entropy at the pressure and temperature of the environment P_0 and T_0 , here set to 40°C and 1 bar. Other forms of exergy such as kinetic, potential and chemical exergy have not been considered in the analysis, and the cycles are assumed to operate in steady-state.

$$E_{flow} = (H - H_o) - T_0 (S - S_0)$$
 (1)

The approach to exergy analysis employed in this work is inspired by the work by Penkuhn and Tsatsaronis (2020), who also provide a very detailed explanation and mathematical formulation of all the parameters needed, which is not included here due to length constraints. Thermodynamic irreversibility is a consequence of the generation of entropy over a thermodynamic transformation, also called "exergy destruction" (E_D), and this can be applied to both individual the components (Equation 2 and 3) and overall power cycle (Equation 3); these are identified with the sub-index k and cyc respectively. Regarding heat rejection and addition, constant cold and hot reservoir temperatures are considered, set to 40°C and 575/725°C (depending on TIT) respectively. The definition of this parameter makes use of the concept of product exergy (E_P), fuel exergy (E_P) and Exergy losses (E_L).

$$E_{D,k} = T_0 \, \Delta S_{gen,k} = E_{F,k} - E_{P,k} - E_{L,k} \tag{2}$$

$$E_{D,cvc} = E_{F,cvc} - E_{P,cvc} - E_{L,cvc} \tag{3}$$

In addition to these parameters, the following two figures of merits are added to the analysis: *exergy efficiency* (ε) and *efficiency losses from Carnot cycle* ($\Delta \eta_k$). The first index is well-known and defined as the ratio between product exergy and fuel exergy (see Equation 4). The second metric, though, deserves a more thorough explanation. $\Delta \eta_k$ is a means to translate the irreversibility taking place in each individual component (typical of 2nd Law analysis) into an actual thermal efficiency loss (1st Law), employing Carnot cycle efficiency as a reference case (Invernizzi, 2013). With this in mind, the thermal efficiency loss brought about by a component is defined as the ratio between the exergy destruction that takes place in that particular component and the heat provided to the cycle (Q_{in}). The correlation employed to calculate this parameter is provided in Equation 4c.

a)
$$\varepsilon_k = \frac{E_{P,k}}{E_{F,k}} = 1 - \frac{E_{D,k}}{E_{F,k}} \quad \| \quad \text{b)} \quad \varepsilon_{cyc} = \frac{E_{P,cyc}}{E_{F,cyc}} = 1 - \frac{\sum_k E_{D,k}}{E_{F,cyc}} \quad \| \quad \text{c)} \quad \Delta \eta_k = \frac{T_0 \Delta S_{gen,k}}{Q_{in}} \quad (4)$$

Finally, the absolute values of thermal efficiency (η_{th}), specific work (W_s), recuperators overall conductance (UA) and temperature rise across the primary heat exchanger (ΔT_{PHX}) are taken as complementary figures of merit, eve if not strictly related to a 2nd Law analysis. It is to note that ΔT_{PHX} is of extreme importance inasmuch as it affects the temperature rise across the solar receiver and, therefore, the final size and cost of the entire solar subsystem (most notably the receiver and Thermal Energy Storage system). In particular, this size can be reduced with higher values of ΔT_{PHX} and this effect has been proven as important as the impact of η_{th} (Crespi *et al.*, 2019) to influence the overall thermo-economics of the plant. As a consequence, even if the present paper does not openly develop the thermo-economic features of the cycles considered, these parameters are still kept in the analysis as an indirect metric to account for these aspects of plant performance.

4 RESULTS

The main results obtained from the 1st and 2nd Law analyses are summarised in Table 5 for the two turbine inlet temperatures considered. At 575°C (corresponding to TIT=550°C), Rankine cycles working on steam outperform pure sCO₂ cycles for all figures of merit: >2% higher thermal and exergy efficiency, lower E_D (3-7 MW) and a >115°C higher ΔT_{PHX} . For sCO₂ mixtures, the D1C15 PrC presents performances comparable to the ones obtained by SoA Rankine, while the D2C15 RR exceeds that of steam Rankine in terms of thermal and exergy efficiency by 1.1 and 1.7 percentage points (pp) respectively, but with a significantly lower ΔT_{PHX} . This implies that a thermodynamic gain is to be expected from the SCARABEUS technology even at 550°C but how much this translates into a true techno-economic benefit is yet to be determined; further economic analysis is needed, in particular for the solar subsystem.

Considering the higher temperature case (725°C), the behaviour of the steam Rankine cycle changes significantly. Live steam temperature is set to a maximum of 600°C, representative of the current state-of-the-art of ultrasupercritical technology and widely considered as a threshold temperature for cost-effective steam-based Rankine cycle. This brings about a large turbine inlet temperature gap between the steam and sCO₂ cases which leads to a significant reduction in exergy efficiency of the steam Rankine case due to the much larger exergy destruction during heat addition. On the contrary, sCO₂-based cycles exploit the higher turbine inlet temperature successfully thereby improving the performance from a 1st and 2nd Law standpoints. Pure sCO₂ cycles achieve thermal and exergy efficiencies that are 4 and 5.5 pp higher than for the steam Rankine cycle, around 49% and 72% respectively. This performance gain is even higher for transcritical cycles working with sCO₂ mixtures, which achieve significantly higher thermal and exergy efficiencies, with maximum values of 51.6 and 75.2% respectively.

Moreover, it is to note that, as expected, the 2^{nd} Law performances of steam Rankine cycles operating at 550°C (live steam temperature) and sCO₂-based cycles operating at 700°C are closer than when a steam Rankine cycle working at 600°C is considered: pure sCO₂ leads to a slightly higher ε_{cyc} (in the order of 2pp higher) whilst the exergy efficiency gains achieved by sCO₂-mixtures increase up to 5.5pp.

	Cycle	η _{th} [%]	ε _{cyc} [%]	ΔT _{PHX} [°C]	UA [MW/K]	W_S [kJ/kg]	E _D [MW]
	SoA Rankine	43.9 / 45.6	69.7 / 66.6	309.1 / 352.1	-/-	1249 / 1344	43.3 / 50.0
	sCO2 PC	42.0 / 49.1	66.6 / 71.5	191.2 / 222.4	26.6 / 20.8	100 / 137	50.2 / 39.8
	sCO2 RC	42.7 / 49.5	67.7 / 72.1	132.8 / 150.1	49.9 / 42.1	71 / 94	47.6 / 38.7
	D1C15 RR	42.5 / 48.2	67.3 / 70.3	148.0 / 162.0	28.2 / 25.1	84 / 106	48.5 / 42.3
	D1C15 PrC	43.5 / 50.3	69.0 / 73.3	150.5 / 168.3	36.1 / 32.9	88 / 115	44.9 / 36.5
	D2C15 RR	45.0 / 51.0	71.4 / 74.3	145.0 / 165.1	50.4 / 43.5	67 / 85	40.1 / 34.7
	D2C15 PrC	44.8 / 51.6	71.0 / 75.2	144.5 / 167.5	59.8 / 50.4	66 / 87	40.8 / 33.1

Table 5: Results for the five different cycles and two energy source temperatures (575 /725°C).

The rightmost column in Table 5 shows that, for a given exergy product (set to 100MW), the largest destruction of exergy is found for pure sCO_2 and steam Rankine for energy source temperatures of 575°C and 725°C respectively. On the contrary, sCO_2 mixtures always present the lowest E_D , hence ensuring an enhanced exergy performance as compared to pure sCO_2 and even steam. In order to assess where this improvement comes from, a closer look into the constituents of E_D for each cycle is presented below. To this end, cycle components have been organised in five categories: turbine, primary heat exchanger (PHX), recuperators, compression devices and heat rejection unit (HRU). The resulting share of each category is shown in Figure 2, together with the amount of exergy destroyed in each equipment (text in labels, expressed in MW).

This information confirms the conclusions in past works such as Angelino's: in steam Rankine cycles, exergy destruction takes place mostly in the primary heat exchanger PHX (around 65%) whereas losses spread somewhat evenly across several components in pure sCO₂ cycles. If sCO₂ mixtures are used,

then the pattern sits in between the other two cases, with a higher exergy destruction in the recuperators than for a pure sCO_2 cycle; this is of course in relative terms since the losses are comparable from a quantitative standpoint. This contribution in a blended- sCO_2 cycle is nevertheless compensated by the lower exergy destruction across the compression devices and heat rejection unit. Actually, the behaviour of the latter equipment is particularly interesting given the condensing nature of the cycle that takes exergy destruction across this component closer to the steam Rankine cycle than to the pure sCO_2 case.

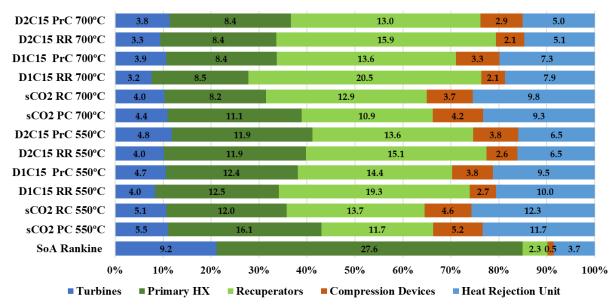


Figure 2: Breakdown of exergy destruction for different combinations of cycles, fluids and TIT. Labels indicate the amount of exergy destroyed in each component (MW).

This change of the exergy destruction pattern is enabled by the modified properties of the working fluid when additives are added to Carbon Dioxide and suggest that the SCARABEUS concept is a sound approach to inherently more efficient Concentrated Solar Power plants. This is confirmed by the very similar trends observed for the two energy source temperatures studied, which is an indication of the general applicability of the behavior observed. At the same time though, the amount of exergy destroyed across the recuperator of blended sCO₂ cycles also reveals the need for further cycle optimisation, probably figuring out new layouts where this irreversibility can be reduced without increasing exergy destruction at another component. This has already been tackled for pure sCO₂; for instance, the development of the *Recompression* and *Partial Cooling* cycles by Angelino (1968) aimed to reduce the irreversibility brought about by the recuperators in order to enhance cycle performance.

Another interesting observation for sCO₂-based cycles is that the configurations presenting higher ΔT_{PHX} experience higher relative exergy destruction reduction when increasing TIT from 550°C to 700°C. In particular, D1C15 PrC and PC, for which ΔT_{PHX} is 170 °C and >200°C respectively, experience an E_D reduction of 8.4 and 9MW. Interestingly, both configurations present a common feature in their layout -the pre-compressor PreC in Figure 1- which significantly increases turbine expansion ratio and, accordingly, the specific work of the cycle. On the negative side, a slight drop in heat recuperation is observed, brought about by a lower temperature at turbine outlet. This feature does not result particularly beneficial at low temperatures but it becomes extremely interesting at 700°C where these two contributions are well balanced and lead to a positive effect on cycle performance. This can be observed in Table 5 by merely comparing the Partial Cooling and Recompression cycles with pure CO₂ and the Precompression and Recuperated Rankine with D1C15. The addition of a pre-compressor in a pure CO₂ configuration (i.e., moving from the *Recompression* to the *Partial Cooling* cycle) leads to a 46% gain in W_s and a 48% rise in ΔT_{PHX} , with comparable thermal exergy efficiency (0.5pp). On the other hand, moving from a Recuperated Rankine to a Precompression cycle with D1C15 increases W_s by more than 8% and ΔT_{PHX} by 4%, with a resulting 2pp gain in thermal efficiency. This is a promising result for CSP plants since these configurations (Partial Cooling with pure sCO₂, Precompression with 85%CO₂-15%C₆F₆) could reduce the overall amount of exergy destroyed in the power block whilst, at the same time, limiting the installation costs of the solar sub-system and reducing the footprint of the plant.

Figure 3 compares the efficiency losses from Carnot cycle for the four different cycle configurations considered, using a similar colour code to Figure 2. This is a very useful information to identify the root causes for the thermal efficiency drop with respect to the reference Carnot cycle since η_{th} can be obtained by merely subtracting the total losses indicated in Figure 3 (also second column in Table 3) from the efficiency of a Carnot cycle working between the same heat source (725°C) and heat sink (40°C) temperatures: 68.6%. Moreover, $\Delta \eta_k$ also allows to "normalise" the results obtained previously with a common reference for energy input, hence overcoming the difference in overall fuel exergy introduced to the cycle (unavoidable, as it is brought about by the different values of ΔT_{PHX}). The results provided are in agreement with those shown earlier in this section, confirming that condensation of the working fluid leads to a considerable reduction in the thermodynamic losses (with respect to Carnot efficiency) across the compression and heat rejection processes. The six sCO₂-based configurations, in fact, concentrate roughly the same overall irreversibility in turbine, PHX and recuperators (\sim 14%) with the main differences found in the cumulative value of $\Delta \eta_k$ across the compression devices and HRU: ~5% for pure sCO₂ and 2~3.5% for blended sCO₂. It is therefore thanks to this difference that using sCO₂ mixtures enables better 2nd Law performance of both the *Recompression* and *Partial Cooling* cycles working with pure sCO₂. The only exception to this is the Recuperated Rankine cycle with D1C15, whose higher E_D in the HRU and recuperator causes a significant performance drop, comparable to the *Partial Cooling* cycle running on pure CO₂.

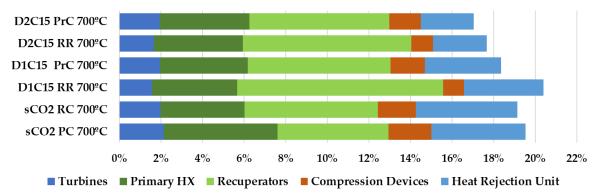


Figure 3: Efficiency losses from Carnot cycle for six different sCO₂-based cycles (TIT=700°C).

Finally, some interesting observations can be drawn comparing the performance of the *Precompression* and Recuperated Rankine cycles operating on the same mixture. Considering D1C15, the former obtains a thermal efficiency that is 2pp higher than that of the simple regenerative configuration, whilst this gain is reduced to 0.6pp when D2C15 is taken into account. This enhanced performance of D1C15 PrC is brought about by the higher E_D reduction in the recuperators (6.9 MW for D1C15, 2.9MW for D2C15), obtained at the expense of increasing E_D in turbine and compression devices by only 1.8 MW (1.3MW for D2C15). On the other hand, focusing on the *Recuperated Rankine* layout, the use of D2C15 leads to a thermal efficiency that is 2.8pp higher than for D1C15. This is due to the higher heat regeneration potential of the D2C15 mixture, revealed by the reduction in $\Delta \eta_k$ of recuperators and HRU. Interestingly, these circumstances confirm and explain from a 2nd Law perspective the results obtained in a previous work by the same authors, which identified the *Precompression* layout as the most promising layout for CO₂-C₆F₆ mixtures and the Recuperated Rankine cycle as the most adequate to exploit CO₂-TiCl₄ blends (Crespi et al., 2021b). In any case, it is worth noting that the selection of the optimum combination of blend and cycle layout cannot overlook economic metrics, and a thorough thermo-economic analysis is mandatory to assess the actual potential of blended CO₂ power cycles integrated into CSP plants.

5 CONCLUSIONS

The aim of this work is to explore the 2^{nd} Law performance supercritical power cycles working on blended Carbon Dioxide in order to assess their actual potential and the reasons for the expected performance gains with respect to either contemporary steam turbine technology or pure supercritical CO_2 cycles. To this end, the paper has presented a thorough comparison of three CSP power cycle technologies (steam Rankine, pure sCO_2 and blended sCO_2) based on exergy analysis for two different turbine inlet temperatures (550 and 700°C) and one single minimum cycle temperature (50°C). A series of interesting conclusions can be drawn, putting this technology forward as a very promising alternative for mid-term future of CSP plant:

- sCO₂ blends are a promising working fluid even at turbine inlet temperatures as low as 550°C, enabling better energy and exergy efficiencies than state-of-the-art steam Rankine (1.5 and 2.5pp higher 1st and 2nd Law efficiencies, respectively);
- At 700°C, sCO₂ mixtures clearly outperform both state-of-the-art (steam) Rankine cycles and pure sCO₂ cycles, achieving thermal and exergy efficiencies as high as 51.6 and 75.2%. This confirms that the technology is a firm candidate for next generations CSP plants;
- Compared to pure sCO₂ cycles, using sCO₂ mixtures leads to a significant drop in the amount of exergy destroyed across the compression and heat rejection processes, rounding 50% for a given cycle output. This is enabled by the possibility to condense the working fluid.
- Finally, a larger (relative) E_D is experienced in the recuperators, even if this is still comparable to pure sCO₂ cycles from a quantitative standpoint. This sets a focus area for future research of CO₂ mixtures, where solutions to tackle the larger irreversibilities of these components will have to be devised.

NOMENCLATURE

E_{D}	Exergy destruction	(MW)	\mathbf{W}_{s}	Specific Work	(kJ/kg)
E_{F}	Fuel Exergy	(MW)	ΔΡ	Pressure drops	(%)
E_L	Exergy Losses	(MW)	ΔT_{PHX}	Temperature Rise in PHX	(°C)
E_{P}	Product Exergy	(MW)	ΔT_{min}	HX Minimum Temp. differen	ce (°C)
HRU	Heat Rejection Unit		$\Delta\eta_k$	Eff. losses from Carnot cycle	(%)
$P_{in,MC}$	Main Compressor Inlet Pressure	(bar)	3	Exergetic efficiency	(%)
PC	Partial Cooling cycle		η_{is}	Isentropic efficiency	(%)
$P_{in,PreC}$	Pre-compressor Inlet Pressure	(bar)	η_{th}	Thermal efficiency	(%)
PHX	Primary Heat Exchanger		SA	Simple Asphyxiant Gas	
P_{max}	Maximum Cycle Pressure	(bar)	₩	React with Water	
pp	percentage point		UA	Overall Conductance	(W/K)
PrC	Precompression cycle				
RC	Recompression cycle		Subscr	ript	
RR	Recuperated Rankine cycle		k	generic cycle component	
TIT	Turbine Inlet Temperature	(°C)	cyc	cycle	

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