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THERMAL EFFICIENCY GAINS ENABLED BY USING SUPERCRITICAL CO_2 MIXTURES IN CONCENTRATED SOLAR POWER APPLICATIONS

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ABSTRACT

Supercritical Carbon Dioxide (sCO_2) power cycles have been proposed for Concentrated Solar Power (CSP) applications as a means to increase the performance and reduce the cost of state-of-the-art CSP systems. Nevertheless, the sensitivity of sCO_2 systems to the usually hot ambient temperatures found in solar sites compromises the actual thermodynamic and economic gains that were originally anticipated by researchers of this innovative power cycle.

In order to exploit the actual potential of sCO_2 cycles, the utilization of dopants to shift the (pseudo)critical temperature of the working fluid to higher values is proposed here as a solution towards enabling exactly the same features of supercritical CO_2 cycles even when ambient temperatures compromise the feasibility of the latter technology. To this end, this work explores the impact of adopting a CO_2-based working mixture on the performance of a CSP power block, considering hexafluorobenzene (C_6F_6) and titanium tetrachloride ($TiCl_4$) as possible dopants. Different cycle options and operating conditions are studied (250-300 bar and 550-700ºC) as well as molar fractions ranging between 10 and 25%.

The results in this work confirm that CO_2 blends with 15-25%(v) of the cited dopants enable efficiencies that are well in excess of 50% for minimum cycle temperatures as high as 50 or even 55ºC. It is also confirmed that, for these cycles, turbine inlet temperature and pressure hardly have any effect on the characteristics of the cycle that yields the best performance possible. In this regard, the last part of this work also shows that cycle layout should be an additional degree of freedom in the optimisation process inasmuch as the best performing layout changes depending on boundary conditions.

INTRODUCTION

FROM THE FIRST STEPS TO SUCCESSFUL DEMONSTRATION

The sCO_2 power cycle technology has triggered a growing interest in the scientific community in the last ten years. It currently stands out as the strongest alternative to steam turbines in the next generation of Concentrated Solar Power plants. Such interest is brought about by the higher thermal efficiency of the cycle and arguably smaller footprint of the equipment, features that were already recognised in the pioneering works by Angelino and Feher in the late sixties. The former author identified 650ºC as the breakeven turbine inlet temperature (TIT) beyond which sCO_2 power cycles attain better thermodynamic performance than both air Brayton and water/steam Rankine cycles [1]. At the same time, Feher discussed the benefits of compressing sCO_2 in the vicinity of the critical point, taking advantage of the low compressibility factor in that region [2].

After a long period without interest in the technology, a large amount of research works have been published in the last fifteen years. In 2004, Vaclav Dostal's Ph.D thesis put sCO_2 in the spotlight again, identifying the *Recompression* and *Partial Cooling* sCO_2 cycles as the best candidates for IV Generation Nuclear reactors, capable of taking thermal efficiency close to 50% for a turbine inlet temperature of 650ºC [3]. A little later, the work carried out by the National Renewable Energy Laboratory explored advanced configurations of the same *Recompression* layout for CSP applications, adding intercooling and reheat and indeed confirming the potential of the cited cycle in this application [4,5]. This theoretical work received a crucial experimental support by SANDIA National Lab, whose first-of-a-kind experimental loop proved the benefits enabled by sCO_2 condensation in terms of turbomachinery design and operational flexibility [6]. This has later been confirmed by experimental activities carried out by other institutions at the small scale [7,8].

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From a commercial, larger-scale standpoint, the technology achieved a milestone when the Waste Heat Recovery Unit developed by Echogen was deployed to the market [9], becoming the first sCO_2 system to be ever commercialised. This was followed by the much larger system developed by NetPOWER and based on the Allam cycle. A 50 MWt oxy-combustion sCO_2 cycle running on natural gas started up in May 2019, demonstrating the unmatched capability of this technology to produce carbon-free electricity from fossil fuels [10].

FIRST DOUBTS AND INTRODUCTION TO sCO_2 BLENDS

Riding the wave of theoretical works developed in the first decade of the 21st century, the potential of the sCO_2 power cycle to enable thermal efficiencies higher than 50% in a variety of applications was widely acknowledged by the scientific community. Nevertheless, more detailed analyses published in recent years, and including not only thermal but also economic considerations, reveal that there are important challenges ahead of the technology.

For instance, as a common denominator, a large number of research works consider a fairly low temperature at compressor inlet, around 35 ºC, in order to perform the compression process near the critical point. This is because the low compressibility factor of sCO_2 at such conditions enables a significant reduction of compression work, hence increasing thermal efficiency. Nevertheless, this assumption is utterly unrealistic for CSP applications, since sites with the very high solar resource needed (Direct Normal Irradiation) are usually located in desertic areas with ambient temperatures much higher than 35ºC. If higher minimum cycle temperatures (~50ºC) are taken into account, thermal efficiency drops significantly and the potential gains with respect to conventional steam cycles become unclear. This is further discussed in a later section.

In the light of these considerations, the interest in the sCO_2 power cycle technology for CSP applications decreases largely as the performance gain with respect to state-of-the-art steam turbines and the technology readiness level (TRL) is reduced substantially.

Nevertheless, the addition of certain dopants to the raw carbon dioxide used in conventional sCO_2 cycles, yielding the so-called sCO_2 blends, has been identified by the SCARABEUS project as a groundbreaking route towards reverting this situation. Several authors have investigated this concept in the very last years: Invernizzi et al. (partners of SCARABEUS) studied the performance of Brayton cycles running on sCO_2 blended with various hydrocarbons [11], while Jeong et al. presented a similar study employing different gases (such as N_2, O_2 or He) as chemical dopants [12]. Bonalumi et al. (also partners of SCARABEUS) claimed that employing a binary mixture of CO_2 and $TiCl_4$ in lieu of pure CO_2 could lead to efficiency gains as high as 5% and 3% in Brayton and *Recompression* cycle respectively [13]. Along the same lines, Baik et al. investigated the performance of Brayton cycles employing CO_2/R32 and CO_2/Toluene mixtures and confirmed that these working fluids enable better performance than pure sCO_2 at high heat sink temperatures [14]. Finally, Manzolini et al. (partners of SCARABEUS) investigated the use of N_2O_4 and $TiCl_4$ as chemical dopants in order to improve the efficiency of solar tower plants and, accordingly, reduce the cost of electricity [15].

It is in this context that the SCARABEUS project started in 2019, with the aim to demonstrate that the application of supercritical CO_2 blends to CSP plants has the potential to increase thermal efficiency above 50% when the minimum cycle temperature is as high as 50ºC. This enhancement of thermal performance comes along with a reduction of CAPEX by 30%, OPEX by 35% and LCOE to 96€/MWh, which is 30% below the current state-of-the-art steam-based CSP plants in a similar location [16].

Bearing all this in mind, the present paper aims to provide an assessment of the performance gain that could be expected from the utilisation of sCO_2 blends in CSP plants under realistic boundary conditions. To this end, the main concept of the SCARABEUS project is thermodynamically reviewed first. Then, the blends considered in this study are introduced, along with a brief description of the simulation tools used and of the two reference cycle layouts: *Recuperated Rankine* and *Precompression*. Finally, a comparison between the results obtained with the different mixtures is developed, with the aim to estimate the performance gains enabled by the adoption of the sCO_2-based blends as against a similar plant using steam turbines.

SCARABEUS PROJECT - CONCEPT

The enthalpy rise across a compression stage can be calculated through integration of Eq. (1). Assuming the process to be isentropic, Eq. (1) can be simplified and so compression work can be expressed as in Eq. (2), where the specific volume of the non-ideal working fluid depends on the compressibility factor *Z*. This relates the actual specific volume of the non-ideal gas to the specific volume of the gas at the same temperature and pressure, should it behave ideally.

$$dh = Tds + vdp \qquad (1)$$
$$Wc = \int_1^2 vdp = \int_1^2 \frac{ZR_sT}{p} dp \qquad (2)$$

Equation (2) suggests that compression work can be reduced if compressibility decreases, and this could potentially have a beneficial impact on cycle efficiency (all things being equal). This idea led Feher to propose a supercritical cycle [2] where compression takes place in the vicinity of the critical point with a liquid-like specific volume (i.e. a significantly lower specific volume and compressibility factor than in the gas phase). Unfortunately, a side-effect of working near this point is the large increase of the isobaric specific heat, which leads to a larger irreversibility in the recuperative heat exchanger. This was also identified by Angelino who, nevertheless, proposed different cycle layouts to overcome these problems related to heat transfer whilst still exploiting the compression work reduction [1].

Table 1 presents the impact of minimum temperature (bounded by ambient temperature) on cycle performance for a large number of sCO_2 cycle layouts. These layouts are taken from previous work by some of the authors, which provided a systematic approach to selecting pure sCO_2 cycles for CSP applications [17]. The cycles are modelled with Thermoflex software, with the same boundary conditions as in previous works [17] and setting isentropic efficiencies to 93%, 89% and 83% for turbines, compressors and pumps respectively. The *Transcritical CO_2* configuration, a recuperated Rankine-like cycle with a pump inlet temperature of 15ºC, is added to the comparison for the sake of completeness and in spite of not being feasible at intermediate-high ambient temperature. The high thermal efficiency at lower temperatures, for which the cycle is feasible, will be further discussed in the following sections.

Cycle layout	ηth@32ºC[%]	ηth@50ºC[%]	Δη[pp]
Simple Recuperated	46.2	43.5	2.7
Precompression	50.0	46.9	3.1
Recompression	51.4	43.1	8.3
Recompr.+IC+RH	53.0	49.1	3.9
Partial Cooling	51.6	46.6	4.0
Partial Cooling+RH	53.9	48.9	5.0
Double Reheated	54	44.3	9.7
Schroder - Turner	49.0	45.3	3.7
Modified Allam	45.6	43.5	2.1
Transcritical CO_2	48.3 (15ºC)	-	-

Table 1: Thermal efficiency of selected sCO2 power cycles for compressor inlet temperatures of 32ºC and 50ºC. Turbine inlet pressure and temperature are set to 300 bar and 750ºC.

The trends observed in Table 1 come about because of the impact of compressor/pump inlet temperature on fluid compressibility, which rises rapidly when departing from the critical temperature, hence increasing compression work. For instance, for a compressor inlet pressure of 1.1 times the critical pressure, the compressibility factor increases from 0.28 to 0.65 when temperature changes from 34 to 61ºC [18]. Additionally, compressor outlet temperature increases more than proportionally due not only to the higher inlet temperature but, also, higher compressibility. This means a lower potential for heat recovery in the cycle given that both turbine inlet temperature and pressure ratio remain the same for 32 and 50ºC.

A significant efficiency drop is observed when raising this temperature from 32ºC (very close to the critical temperature) to 50ºC (more realistic for usual CSP locations), regardless of cycle layout: between 2 and almost 10 percentage points. Moreover, for some layouts, like the *Transcritical CO_2* cycle, the cycle cannot be implemented at 50ºC anymore.

In addition to the evident detrimental effect of ambient temperature on cycle performance, with efficiency drops between 2 and 10 percentages depending on cycle configurations, a twofold observation can be made. On the one hand, most of the cycles in the comparison exhibit thermal efficiencies that are just slightly higher than steam Rankine cycles under similar boundary conditions (42%). On the other hand, those layouts achieving substantially higher efficiencies in the order of 49% imply very complex layouts which, in addition to compromising operability, also lead to significantly higher capital costs. This is the case of the *Recompression+IC+RH* and *Partial Cooling +RH* cycles which have been proved not cost effective in spite of their high thermal efficiency [19].

In order to counteract the effects discussed in the previous section, the SCARABEUS project explores the opposite strategy. Rather than trying to reduce compressor inlet temperature to operate near the critical point, which is irremediably constrained by ambient conditions, the critical temperature of the working fluid is increased by adding dopants to the raw CO_2. This enables not only lower compressibility and compression work but also, and more interestingly, condensation of the working fluid at high ambient temperatures. This has already been explored preliminarily by Di Marcoberardino et al. in the context of the SCARABEUS project [20]. These authors considered a mixture of CO_2 and C_6F_{14} in a cycle with condensation at 50ºC and a turbine inlet temperature of 400ºC, proving that thermal efficiency could be increased by 3-4 percentage points with respect to pure sCO_2 if the appropriate dopant composition were used.

SIMULATION TOOLS

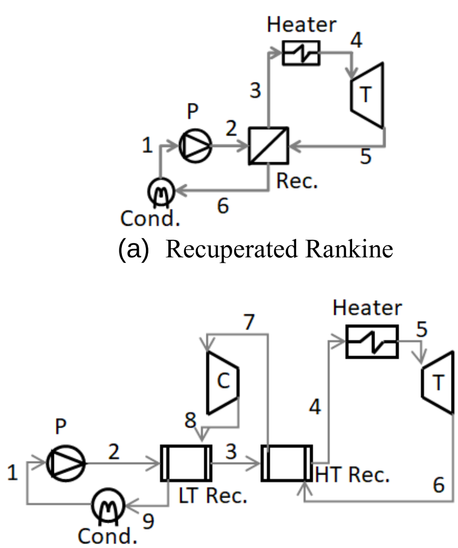
In order to study the impact of adopting sCO_2-based blends on the thermal performance of the power cycle, a series of simulations are run with the commercial software Thermoflex [21]. Two different cycles are considered, *Recuperated Rankine* and *Precompression,* whose layouts are provided in Figure 1. The former is a well-known configuration, adapted here to operate with sCO_2-blends whilst the *Precompression* layout originally proposed by Angelino [1] presents a somewhat unique and extremely interesting feature among the other sCO_2 power cycles. In contrast with other more popular configurations, such as *Recompression* or *Partial Cooling* (which present a flow-split before the low temperature recuperator in order to enhance thermal performance and avoid pinch-point problems), the potential of the *Precompression* layout lies on the addition of a compressor in the low-pressure side of the cycle, between the low and high-temperature recuperators. This particular feature overcomes the restriction imposed by the compression process on turbine exhaust pressure, thus enabling to control the compression and expansion ratios of the cycles separately. The additional degree of freedom can then be used to enhance thermal efficiency.

One of the critical tasks in SCARABEUS is to identify the optimal working fluid (dopant composition and molar fraction) that yields the largest thermal efficiency gain. To this aim, different dopants have already been studied by some of the authors [20] and some others are currently under investigation by the project partners. In this study, two of such dopants are considered: C_6F_6 (dopant D1) and $TiCl_4$ (dopant D2). The former is an organic, aromatic compound, characterised by low toxicity but high flammability and unconfirmed thermal stability at high temperatures. The latter is a low cost fluid whose thermal stability has been proven at 550 ºC, although it presents a very aggressive water reactivity, which may affect its actual feasibility at commercial scale. Further investigations regarding this particular aspect are currently undertaken by SCARABEUS consortium. A short evaluation of these two dopants in the context of NFPA 704 code is provided in Table 2.

	Health Hazard	Flammability	Chemical Reactivity	Special Hazard
sCO_2	2	0	0	SA
C_6F_6	1	3	0	-
$TiCl_4$	3	0	2	~~W~~

Table 2: Dopant hazard according to NFPA 704 [22].

With varying molar fractions of these two dopants, the blends in Table 3 are obtained, where X and YY in the blend code DXCYY stand for dopant D1/D2 and molar fraction (%) respectively. Table 3 also provides the saturation pressure of each blend corresponding to a bubble temperature of 50ºC; this latter temperature is set as the minimum cycle temperature of choice for cycle analysis. These two, 50ºC and P_{cond} are therefore the temperature and pressure at pump inlet (station 1 in both layouts in Figure 1).



(a) Recuperated Rankine

(b) Precompression

Figure 1: *Recuperated Rankine* and *Precompression* layouts.

For each blend, the thermophysical properties of the mixture have been obtained with Aspen [23], employing the Peng-Robinson equation of state calibrated on experimental data of the corresponding Vapour-Liquid-Equilibrium (VLE) conditions [24, 25].

It is worth noting that the critical conditions reported in Table 3 change significantly with blend composition, what gives room to tailoring the optimum working fluid to a given minimum cycle temperature (i.e., ambient temperature). The criterion to determine the feasible range of compositions that can be used in the cycles considered is thus based on the margin between critical temperature (T_{cr}) and temperature at pump inlet (T_1), which is set to 30ºC in this work. Accordingly, for the T_1 of choice, 50ºC, only those blends whose compositions yield critical temperatures higher than 80ºC are eligible; for instance, according to the information in Table 3, blends based on dopant D1 with a molar fraction lower than 10% do not meet this criterion and are, therefore, discarded. This possibility to adapt the composition of the blend to the desired pump inlet temperature turns out to be a very powerful feature of SCARABEUS, since different mixtures can be tailored to specific CSP locations (ambient conditions). This is highlighted in the concluding section.

Blend	Composition [% molar]	MW [g/mol]	Tcr [ºC]	Pcr [bar]	Pcond [bar]
D1C10	CO2-C6F6 [90-10]	58.21	80.28	112.4	83.51
D1C15	CO2-C6F6 [85-15]	65.32	102.1	121.3	77.52
D1C20	CO2-C6F6 [80-20]	72.42	121.9	123.6	71.83
D1C25	CO2-C6F6 [75-25]	79.52	139.8	121.1	66.36
D2C15	CO2-TiCl4 [85-15]	65.86	93.76	190.9	99.53
D2C20	CO2-TiCl4 [80-20]	73.15	149.6	243.7	97.63
D2C25	CO2-TiCl4 [75-25]	80.43	192.0	247.1	94.52

Table 3: Specifications of CO_2 blends. P_{cond} is the condensation pressure corresponding to a bubble temperature of 50ºC.

The *Recuperated Rankine* and *Precompression* cycles have been modelled for all the sCO_2 blends in Table 3, for a Turbine Inlet Temperature of 550/700ºC and a maximum cycle pressure of 250/300 bar. For the resulting twenty-eight cases, the gross output of the cycle is 100 MW and the specifications of turbomachinery (isentropic efficiency) and heat exchangers (minimum pinch-point, pressure drops) are those summarised in Table 4.

PIT [ºC]	TIT [ºC]	Pmax [bar]	η_{is} [%] Pump/Turb/Compr
50	550/700	250/300	88 / 93 / 89
ΔT_{min} [ºC]	ΔP_{HEATER} [%]	ΔP_{COND} [%]	ΔP_{REC} [%] Low P / High P
5	1.5	0	1 / 1.5

Table 4: Boundary conditions and specifications of turbomachinery and heat exchangers.

Analysis of the Results

A thorough discussion on the actual potential of CO_2-blends to improve the thermal performance of sCO_2 power cycles is presented in this section. First of all, the combinations of blend and cycle layout enabling thermal efficiencies higher than 50% are identified. Then, the performance of cycles using these selected blends is analysed in detail in order to identify the root causes of the superior thermodynamic performance; this second step of the analysis is done for the case at 700ºC and 250 bar, herein considered as the most representative of SCARABEUS. Later, the dependence of the best combination of layout and blend on the operating and boundary conditions of the cycles is discussed. Finally, the influence of working fluid composition on the characteristics of certain equipment is investigated, with a particular focus on turbine and cooler/condenser.

Best Combination of Fluid Blend and Cycle Layout

The thermal efficiencies of the *Recuperated Rankine* and *Precompression* cycles for the entire set of boundary conditions presented in Table 4 are reported in Figures 2 and 3 respectively. These are compared with the thermal efficiency of a state-of-the-art steam-based CSP plant (live steam temperature is set to 550ºC) and, for the sake of completeness, with an ultra-supercritical Rankine cycle (live steam pressure and temperature set to 300 bar and 625ºC/650ºC). These two reference values are reported in Figures 2 and 3 with solid (labelled *St.R*) and dashed (labelled *Usc.R*) lines respectively.

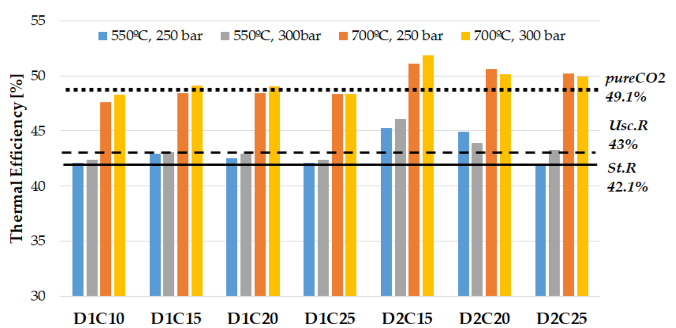


Figure 2: Thermal efficiency obtained by *Recuperated Rankine* cycle for different operating conditions and blends.

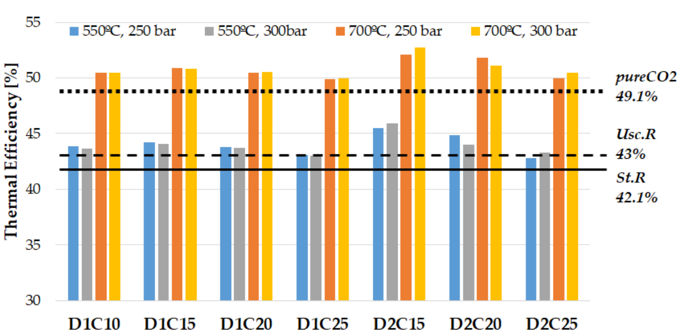


Figure 3: Thermal efficiency obtained by *Precompression* cycle for different boundary conditions and employing different blends.

The thermal efficiency of the *Recompression+IC+RH* cycle running on pure sCO_2 and a minimum cycle temperature of 50ºC is also reported in Figures 2 and 3 with a dotted line (labelled *pureCO2*). The value is taken from Table 1 and aims to represent the best case scenario of a pure-sCO_2 power cycle bounded by the same extreme temperatures.

The information in Figures 2 and 3 confirms that using sCO_2-blends enables better thermal efficiency than when pure sCO_2 or steam Rankine cycles are used. This becomes even more important in the light of the more complex (thus expensive) layout of conventional CSP plants with respect to the proposed solutions. As expected, it is also confirmed that the impact of increasing turbine inlet temperature on thermal efficiency is stronger than that of increasing maximum cycle pressure.

For the *Recuperated Rankine* cycle operating with CO_2-C_6F_6 mixtures (D1), the corresponding efficiency when TIT=550ºC is visibly higher than for the standard steam Rankine cycle, and the difference increases dramatically when this temperature increases to 700ºC, even if compared against an ultra-supercritical steam cycle working at 625ºC/650ºC. For the best case in Figure 2, given by D1C15 at 300 bar & 700ºC, the *Recuperated Rankine* cycle presents slightly better performance than the *Recompression+IC+RH* layout working with pure sCO_2, even though the latter presents a significantly more complex layout and operates with 50ºC higher TIT.

It is also interesting that CO_2-$TiCL_4$ mixtures (D2) present, for the most part, thermal efficiency higher than CO_2-C_6F_6 and, depending on operating conditions, the other technologies in Figure 2 (sCO_2 and steam). Furthermore, amongst the D2CYY cases, it is the D2C15 blend which yields the best performance, outperforming all the other candidates at 700°C by a large margin, attaining a thermal efficiency well above 50% (η_{th}=52%). This result is extremely interesting, bearing in mind that even if the complexity of the *Recuperated Rankine* cycle is similar to that of a *Simple Recuperated* (recuperated Brayton) cycle working on sCO_2, the former achieves much better performance: the efficiency of a *Recuperated Rankine* cycle working on D2C15 at 700ºC turbine inlet temperature (51.9%) is 8 percentages higher than that of a *Simple Recuperated* (Brayton) cycle running on sCO_2 at 750ºC (43.5%).

Some comments about the better performance enabled by the specific features of the *Precompression* cycle, as reported in Figure 3, are worth noting. As already highlighted for this cycle, turbine exhaust pressure is not constrained by condenser pressure, thanks to the incorporation of a compressor between the two recuperators (see Figure 1). This increases the complexity but enables a much more flexible optimisation of compressor pressure ratio, regardless of turbine expansion ratio, after which thermal efficiency can be increased substantially. Indeed, utilising D1 blends in this cycle enables a thermal efficiency gain in the order of 2 percentage points with respect to the base sCO_2, depending on the molar fraction of dopant and operating conditions. D1C10 and D1C15 yield the largest gains, 2.8pp and 2.4pp, at 250 bar & 700ºC, with the latter achieving 50.9% thermal efficiency and being the optimum mixture overall amongst the CO_2-C_6F_6 cases. Interestingly, for this combination of layout and blend, increasing the maximum pressure of the cycle has hardly any effect on η_{th} in spite of the significantly higher specific work (see Figure 4).

Using blends based on D2 in the *Precompression* cycle enables higher thermal efficiencies than the same fluid in the *Recuperated Rankine* but, in this case, the rise in η_{th} is in the order of 1 percentage point only. This happens when a D2C15 blend is used in cycles working at 250 bar and 700ºC, for which thermal efficiency increases from 51.1 to 52.1%. This depicts a situation where the *Precompression* cycle steps forward as a better performing option overall, for which all the candidate mixtures achieve thermal efficiencies in the 50-52% range when running the cycle at 700ºC. For this cycle, adding a 15-20% molar fraction of C_6F_6 yields the best performance whereas 15% is best for mixtures based on $TiCL_4$.

The heat and mass balance sheets of a *Precompression* cycle operating with pure CO_2 and D2C15 are reported in Tables 5 and 6, showing also the compressibility factors at each cycle station.

Cycle Station	T [ºC]	P [bar]	h [kJ/kg]	s [kJ/kgK]	ρ [kg/m3]	Z [-]
1	50.0	102	-128.3	-1.179	408.4	0.409
2	103	250	-95.41	-1.169	576.0	0.611
3	214	246	98.36	-0.7111	304.6	0.877
4	498.5	243	462.1	-0.1179	160.6	1.04
5	700	239	716.1	0.1774	123.3	1.05
6	546	76.5	534.1	0.1952	48.96	1.01
7	231	75.7	170.5	-0.3615	83.52	0.951
8	268	104	204.0	-0.3547	106.4	0.956
9	110	103	10.27	-0.7791	184.3	0.772

Table 5: Heat and mass balance of the *Precompression* cycle with pure CO_2. Compressor and turbine inlet temperatures are 50ºC and 700ºC. Maximum cycle pressure is 250 bar. Station numbers as per Figure 1.

Cycle Station	T [ºC]	P [bar]	h [kJ/kg]	s [kJ/kgK]	ρ [kg/m3]	Z [-]
1	50.0	99.5	-7016	-1.231	1184	0.206
2	63.9	250	-7002	-1.225	1132	0.519
3	283	246	-6689	-0.501	399.4	0.879
4	537	243	-6420	-0.099	229.1	1.04
5	700	239	-6257	0.087	183.8	1.06
6	573	84.6	-6370	0.097	78.64	1.01
7	288	83.8	-6639	-0.290	128.5	0.921
8	307	101	-6625	-0.287	148.3	0.925
9	71.6	99.5	-6938	-0.991	466.6	0.490

Table 6: Heat and mass balance of the *Precompression* cycle with D2C15. Compressor and turbine inlet temperatures are 50ºC and 700ºC. Maximum cycle pressure is 250 bar. Station numbers as per Figure 1.

The beneficial influence of working fluid composition on thermal performance is now seen to be brought about by the effect of a lower compressibility across the compression stage (stations 1-2 and, to a lesser extent, 7-8 in Figure 1).

With regard to specific work (W_s), the *Precompression* cycle presents, as expected, a significantly higher W_s than the *Recuperated Rankine* cycle, owing to the higher expansion ratio enabled by the utilisation of a compressor between turbine outlet and pump inlet. This is shown in Figure 4 and 5 where the impact of turbine inlet temperature and peak cycle pressure can also be assessed. The figure also shows that both cycles and dopants exhibit similar W_s patterns for different blends: the blends with the smallest fraction of dopant (D1C10 and D2C15) always enable the highest specific work (for a given set of boundary conditions), and this decreases progressively as higher fractions are considered. For a given dopant, this is due to the increasing molar weight of the mixture, corresponding to an increasing circulating mass flow rate in the power cycle.

Generally speaking, $TiCl_4$-based (D2) blends present lower specific work than D1 mixtures, contrary to the pattern observed earlier for thermal efficiency. For this reason, a compromise between η_{th} and W_s is mandatory when selecting the best blend for a given cycle layout, even if the weight of thermal efficiency on this decision is expectedly much heavier than that of specific work.

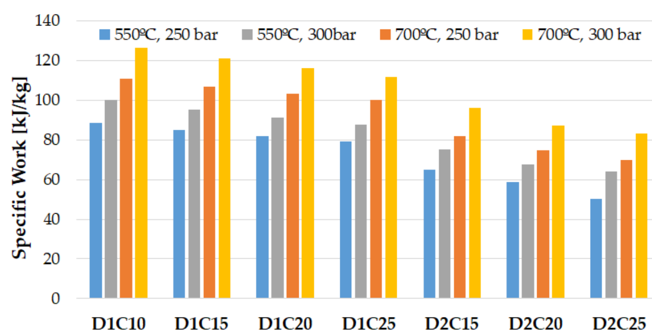


Figure 4: Specific work of the *Recuperated Rankine* cycle for different operating conditions and blends.

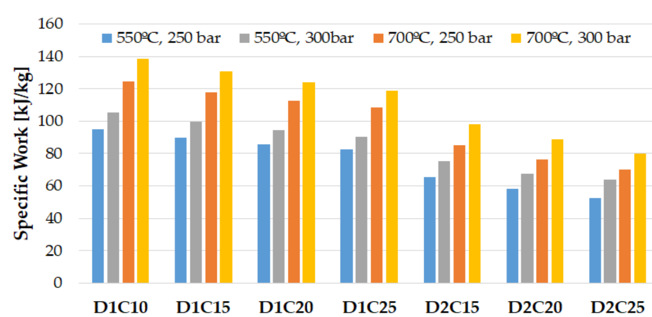


Figure 5: Specific work of the *Precompression* cycle for different operating conditions and blends.

BEST COMBINATION OF CYCLE LAYOUT AND BLEND COMPOSITION - INFLUENCE OF OPERATING CONDITIONS

Earlier sections of this work have revealed that D1C15 and D2C15 yield highest thermal efficiency for all the operating conditions taken into account and considering a minimum cycle temperature of 50ºC. This means that variations of either turbine inlet temperature or maximum cycle pressure do not have any influence on this selection; i.e., the optimum blend remains the same regardless of further changes in these parameters. This conclusion is nevertheless not applicable to the minimum temperature of the cycle (pump inlet) whose variations impact which the optimum blend choice is. Given the dependence of this temperature on ambient temperature, this sets up a tight link between the location of the plant and the composition of the optimum blend.

In order to explore this further, a parametric analysis of the impact of ambient temperature on blend selection is performed for the *Recuperated Rankine* cycle. The results are provided in Table 7, where the performance of a *Simple Recuperated* Brayton working on pure sCO_2 at 250 bar and 700ºC is added for the sake of comparison.

There are several interesting aspects in Table 7. Remarkably, CO_2-blends prove to enable higher thermal efficiency than pure CO_2, employing a cycle with similar complexity. Nevertheless, an absolute best-performing blend regardless of minimum cycle temperature cannot be identified. Indeed, for the C_6F_6-based mixtures, D1C15 is found to yield the best performance for pump inlet temperatures equal or lower than 50ºC (best cases highlighted in bold). At higher temperatures, D1C20 becomes the best mixture of choice. The pattern is similar for the mixtures based on $TiCl_4$: D2C15 yields the best performance for minimum cycle temperatures equal or higher than 50ºC whilst D2C20 becomes the best blend at lower temperature.

PIT →	30ºC	35ºC	40ºC	45ºC	50ºC	55ºC	60ºC
CO_2	-	43.69	43.15	42.60	42.06	41.51	40.96
D1C10	50.96	50.21	49.36	48.61	47.64	47.03	45.94
D1C15	**51.39**	**50.4**	**50.10**	**49.19**	**48.43**	47.99	47.02
D1C20	50.50	50.25	49.97	48.76	48.41	**48.19**	**47.05**
D1C25	50.46	49.29	48.82	48.59	48.34	47.13	46.97
D2C15	53.47	52.98	52.45	51.89	**51.14**	**50.30**	**49.42**
D2C20	**54.48**	**53.23**	**52.62**	**52.42**	50.65	50.24	48.84
D2C25	52.54	51.35	50.73	49.64	48.34	47.13	46.97

Table 7: Thermal efficiency ([%]) of the *Recuperated Rankine* for different blends and pump inlet temperatures.

According to these results, the possibility to tailor the composition of the working fluid to the ambient conditions of the plant site in order to maximise performance becomes evident. This is an extremely powerful feature of this study, which goes beyond the application of the concept to Concentrated Solar Power plants and paves the way for the further optimisation of supercritical power cycles using CO_2 blends in other applications (for instance nuclear or waste heat recovery applications).

IMPACT ON COMPONENT PERFORMANCE AND DESIGN

In this section, interesting aspects of component design and performance are discussed. For the turbine, two parameters are usually employed to preliminarily assess design and manufacturability: Volumetric Expansion Ratio (*VER*) and Size Parameter (*SP*) [26]. The former is defined as the ratio from specific volume at turbine outlet to specific volume at turbine inlet, assuming isentropic expansion, Eq. (3)a.

$$\text{a) } VER = \frac{v_{4s}}{v_3}; \qquad \text{b) } SP = \frac{\sqrt{\dot{V}_{4s}}}{\Delta h_{is}^{1/4}} \qquad (3)$$

Large values of this parameter imply large area variations across the turbine which, inevitably, lead to larger aerodynamic losses and a larger number of stages to accommodate the large density variations. Therefore, the volumetric expansion ratio provides a qualitative indication of the expected isentropic efficiency and stage count of the turbine.

The size parameter is defined as the ratio from the square root of the volumetric flow at turbine outlet to the enthalpy change across the turbine (Δh_{is}) to the power of 0.25, in both cases assuming an isentropic expansion. This parameter is linked to turbine size, thus being a suitable indicator to compare size (and cost, for a given set of boundary conditions) of turbines operating with different blends and it is also linked to turbine efficiency. Turbines with smaller size parameters are more likely to suffer from tip leakage losses and low Reynolds number effects. Therefore, all things being equal, one would be interested in cycles and blends yielding low volumetric expansion ratios and high size parameters, in order to achieve the highest turbine efficiency.

These two parameters are reported in Table 8 for the reference *Recuperated Rankine* cycle working at 250 bar and 700ºC. The *VER* values reported are low regardless of the mixture, which confirms that the aerodynamic design of the turbine is not challenging in terms of a largely three-dimensional flow. Nevertheless, in spite of this favourable *VER* overall, it is interesting to verify that the addition of larger fractions of dopant has the effect of increasing the volumetric expansion ratio due to the higher molecular weight of the resulting mixture.

The size parameter is higher values for CO_2-$TiCl_4$ than for the CO_2-C_6F_6 blends, contrary to *VER*, and it also exhibits a proportional increase with the molar fraction of dopant. In any case, the values of both *VER* and *SP* in Table 8 suggest that the aerodynamic design of turbines for the cases analysed does not pose large challenges (as far as the annulus is concerned).

Cooler design and operation stems as one of the most critical tasks to undertake in CSP plants, usually located in desertic areas with extremely high ambient temperatures. This becomes even more challenging if condensing cycles are considered and if the use of air-cooled condensers turns out mandatory due to water scarcity.

Blend	VER [-]	SP [m]
D1C10	2.410	0.1882
D1C15	2.598	0.1903
D1C20	2.800	0.1930
D1C25	3.024	0.1961
D2C15	2.026	0.2031
D2C20	2.062	0.2077
D2C25	2.121	0.2109

Table 8. Volumetric expansion ratio and size parameter for a *Recuperated Rankine* cycle operating at 250 bar and 700ºC with CO_2-$TiCl_4$ than for the CO_2-C_6F_6 blends.

In state-of-the-art CSP plants using steam turbines, the flow entering the condenser is partly condensate already. Typically, 10% of the turbine exhaust mass flow has already condensed inside the turbine. This is somewhat similar to what happens when CO_2-based blends are used, given that the fluid entering the condenser is partly in liquid state. Nevertheless, in this case, this previous condensation does not take place inside the turbine but across the low-pressure side of the low-temperature recuperator. The beneficial aspect of this condensation upstream of the condenser, which can be observed in the heat and mass balance provided in Table 6, is a reduction of the duty of this component, what lowers not only its cost but also the auxiliary power needed to reject heat to the environment.

Interestingly, the particular composition of the CO_2 blend used in the cycle has an impact on steam quality at condenser inlet and, accordingly, on condenser duty. This is shown in Figure 6 where the blue and yellow bars stand for specific and overall duty of the condenser (left axis) whereas inlet quality is reported by the black markers (right axis). The values apply to a *Recuperated Rankine* cycle operating at 250 bar and 700ºC, with 50ºC pump inlet temperature and a power output of 100 MW.

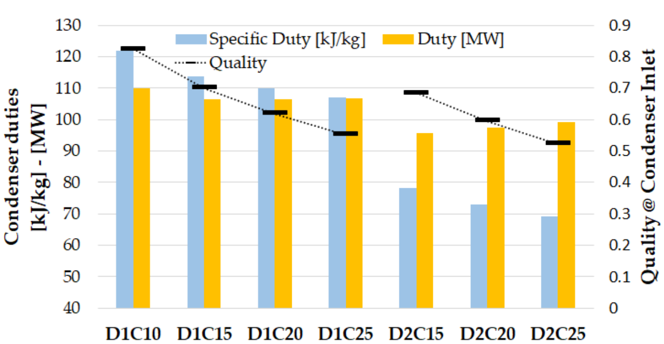


Figure 6: Specific and absolute condenser duty Duty (left axis) and fluid quality at condenser inlet (right axis) of a 100 MW *Recuperated Rankine* cycle operating at 250 bar and 700ºC.

In the chart, quality at condenser inlet and specific duty show a decreasing trend for increasing molar fraction. This pattern suggests that the use of mixtures of a higher dopant fraction could reduce the specific duty of the condenser, hence reducing the associated auxiliary power and cost. Nevertheless, a look at the absolute duty reveals that this metric is almost constant for all D1 blends whereas it increases slightly at higher molar fractions of dopant for D2 mixtures. This is, of course, due to the counteracting effect of a visibly higher mass flow rate for increasing dopant concentration, as shown in Figure 7; this could have also been deduced from the specific work patterns in Figure 4, in a context where cycle output (MW) remains constant. In summary, the reduction in condenser specific duty cannot counterbalance the effect of the increased circulating mass flow and, therefore, does not necessarily correspond to smaller equipment.

Overall, it is confirmed that peak thermal efficiency is provided by the blends for which the absolute duty of the condensers, for given gross cycle output, is minimum (as it was to be expected).

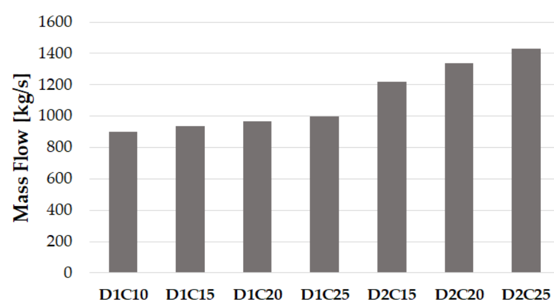


Figure 7: Circulating mass flow of a 100MW *Recuperated Rankine* cycle operating at 250 bar and 700ºC.

SCARABEUS: A PARADIGM SHIFT

It has already been stated in earlier sections that thermal efficiency of the cycle is generally enhanced when shifting from a *Recuperated Rankine* cycle to a *Precompression* cycle. However, the thermal efficiency variation experienced in this move is not homogenous; rather, it happens to depend strongly on the working fluid considered. This is clearly observed in Table 9 which has a seemingly irregular pattern. The reason for this pattern is actually found in the fundamental thermodynamic behaviour of the cycles, which depends itself on the different thermophysical properties of the various candidate mixtures.

At a macro-scale, the thermal efficiency enabled by $TiCl_4$ mixtures in a *Recuperated Rankine* cycle, Table 7, proved to be higher than when using C_6F_6. Now, Table 9 reveals that the performance gain brought about by the adoption of the *Precompression* layout is larger for C_6F_6 blends than for cases based on $TiCl_4$. From a different angle, this indicates that, despite starting from a lower efficiency, CO_2-C_6F_6 mixtures seem to have a larger margin for performance improvement out of modifications of cycle layout than CO_2-$TiCl_4$.

As a consequence of this, the more relevant conclusion of this work, second to the very high efficiencies enabled by CO_2 blends, is the new approach to the design of supercritical cycles using these mixtures. Indeed, the optimisation of working fluid composition for a given dopant and set of boundary and operating conditions does not make sense anymore or, to say it better, is incomplete. In order to really accomplish full optimisation for a given dopant and boundary conditions, leading to the attainment of the highest efficiency possible, it is mandatory to perform a simultaneous optimisation of cycle layout and fluid composition. This approach to cycle optimisation is currently under development at University of Seville for the SCARABEUS project although, at this stage, more research is still needed to fully understand the behaviour of CO_2-based blends in different cycle configurations. If confirmed, this paradigm shift would certainly pave the way for a more flexible and comprehensive understanding of sCO_2 power cycles technology development.

Blend	550ºC & 250bar	550ºC & 300bar	700ºC & 250bar	700ºC & 300bar
D1C10	+1.76	+1.28	+2.84	+2.14
D1C15	+1.25	+1.04	+2.44	+1.68
D1C20	+1.27	+0.81	+2.07	+1.53
D1C25	+0.99	+0.63	+1.53	+1.59
D2C15	+0.25	**-0.18**	+0.97	+0.84
D2C20	**-0.05**	+0.12	+1.15	+0.96
D2C25	+0.86	+0.01	**-0.22**	+0.54

Table 9: Thermal efficiency gains (pp) when shifting from a *Precompression* cycle to a *Recuperated Rankine* cycle for the given operating conditions. Figures are in percentage points.

CONCLUSIONS

This work has investigated the actual potential of CO_2-based blends to enhance the performance of sCO_2 power cycles when applied to boundary and operating conditions characteristic of Concentrating Solar Power applications. The objective of the assessment, set forth at the beginning of the paper, was to verify the performance gains that could be attained thanks to the utilisation of working fluids incorporating carbon dioxide and different dopants with the overall effect to shift the pseudocritical temperature of the resulting mixture to a value higher than the critical temperature of CO_2.

With this in mind, two different dopants have been studied, C_6F_6 and $TiCl_4$, with molar fractions ranging from 10 to 25%, and their performances have been assessed in two cycle layouts, *Recuperated Rankine* and *Precompression*. In both cases, minimum cycle temperature (temperature at pump inlet) has been set to 50ºC, corresponding to an intermediate-high ambient temperature representative of typical CSP locations. For the sake of completeness, the maximum pressure and temperature of the working fluid have been changed in a range of interest as well.

The assessment described in the afore-described framework yields the following conclusions:

- For a given minimum cycle temperature, there is a minimum molar fraction of dopant below which condensation is not feasible. This sets a lower limit of dopant concentration which is specific to each dopant composition. For the dopants considered in this analysis and a PIT of 50ºC, this lower limit is found between 10 and 15%.
- Using CO_2-based mixtures in supercritical cycle layouts proves to enable ηth well in excess of 50%, even for ambient temperatures as high as 50ºC. This is well above what state-of-the-art Rankine cycles running on steam are currently achieving in CSP plants, thus meaning an unprecedented upsurge in performance for this type of application.
- This performance of supercritical cycle layouts using CO_2-based mixtures is also much better than what conventional supercritical CO_2 can attain for the same boundary conditions. This is due to the deleterious effect of high ambient temperatures on the compression process in the latter cycles. The gain enabled CO_2-based mixtures is in the order of 5-6 percentage points (more than 10% relative performance improvement with respect to an equivalent embodiment with pure CO_2).
- The performance of supercritical cycle layouts using CO_2-based mixtures shows a weak dependence on turbine inlet pressure whereas the influence of minimum and maximum cycle temperatures is very strong. Nevertheless, regarding temperature, whilst both temperatures determine thermal efficiency, turbine inlet temperature does not have any influence on the composition of the blend yielding the best performance. This seems to be dependent on minimum cycle temperature only.
- Component design, in particular turbine design, seems to be not compromised by the utilisation of the new WFs.
- When CO_2-based mixtures are used, cycle optimisation must include WF composition and cycle layout as independent variables. This is because the layout yielding the best ηth changes as mixture composition changes.

In addition to the specific conclusions listed above, there are two main, general conclusions drawn from this work. First and foremost, the discussion in this work confirms that achieving thermal efficiencies well in excess of 50% at attainable turbine inlet temperatures is now possible. This is because the CO_2-blend concept overcomes the main Achilles' heel of conventional supercritical CO_2 power cycles. Second, CO_2 mixtures pave the way for new CSP plants which can actually be tailored to the boundary conditions that are specific to each CSP plant. In other words, fluid composition and cycle layout could be tuned specifically to these boundary conditions in order to squeeze the thermodynamic potential of the concept as much as possible.

Further research by the authors will search new dopants and cycle layouts that could bring even larger gains whilst also developing new optimisation strategies that can automate this decision making process.

NOMENCLATURE

CIT	Compressor Inlet Temperature	[ºC]
CSP	Concentrated Solar Power	
ΔT_{min}	Minimum temperature difference in HX	[ºC]
ΔP_{HX}	HX Pressure drop	[%]
ΔH_{is}	Turbine isentropic enthalpy variation	[J/kg]
$\eta$is	Isentropic Efficiency	[%]
ηth	Cycle Thermal Efficiency	[%]
h	Enthalpy	[J/kg]

MW	Molar Weight	[g/mol]
pp	Percentage point	[%]
s	Entropy	[J/kgK]
Pcr	Critical Pressure	[bar]
Pmax	Maximum Cycle Pressure	[bar]
PIT	Pump Inlet Temperature	[ºC]
R_s	Specific Gas Constant	[J/kgK]
SA	Simple Asphyxiant Gas	[-]
sCO2	Supercritical Carbon Dioxide	
SP	Turbine Size Parameter	[m]
Tcr	Critical Temperature	[ºC]
TIT	Turbine Inlet Temperature	[ºC]
TIP	Turbine Inlet Pressure	[bar]
v	Specific Volume	[m^3/kg]
V	Volumetric flow	[m^3/s]
VER	Volumetric Expansion Ratio	[-]
~~W~~	React with water	[-]
Wc	Compression Work	[J/kg]
WF	Working Fluid	[-]
Z	Compressibility Factor	[-]

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