Proceedings of ASME Turbo Expo 2021: Turbomachinery Technical Conference and Exposition
GT2021
June 7-11, 2021, Virtual, Online,

GT2021-60293

INFLUENCE OF WORKING FLUID COMPOSITION ON THE OPTIMUM CHARACTERISTICS OF BLENDED SUPERCRITICAL CARBON DIOXIDE CYCLES

F. Crespi, G. S. Martínez, P. Rodriguez de Arriba, D. Sánchez*, F. Jiménez-Espadafor
Department of Energy Engineering, University of Seville
Camino de los descubrimientos s/n, 41092 Seville, Spain
crespi@us.es, gsm@us.es, prdearriba@us.es, ds@us.es, fcojjea@us.es

ABSTRACT

The supercritical Carbon Dioxide power cycle technology has attracted growing interest from the scientific community, becoming one of the most important options currently considered for CSP applications. This is thanks to its high thermal efficiency, even at moderate turbine inlet temperatures, and small footprint. Nevertheless, sCO_2 power cycles require a fairly low compressor inlet temperature to exploit their full thermodynamic potential. When this cannot be achieved, as it is usually the case for Concentrated Solar Power plants where ambient temperatures are high, the interest of the technology is compromised. To compensate for this effect, the SCARABEUS project is working on the development of certain chemical dopants that could be added to the raw CO_2, obtaining new working fluids with the same or even better performance than pure CO_2 even at higher minimum cycle temperatures.

This paper studies the impact of using CO_2 mixtures blended with Hexflurorobenzene (C_6F_6) and Titanium Tetrachloride ($TiCl_4$). It is found that these mixtures enable thermal efficiencies that are higher than if pure CO_2 were used. The efficiency gain can be as high as 3 percentage points, depending on the dopant used and the operating conditions considered.

In addition to this absolute performance gain, the paper reveals that there are additional degrees of freedom that enable more effective cycle optimisation. These are the dopant molar content, not only its composition, and the cycle layout used. When this is studied, it is found that the optimum molar content ranges from 10 to 20% and that the layouts of interest when using mixtures are simpler than if plain CO_2 were used. These results open the way for a significant performance enhancement of Concentrated Solar Power plants.

Nomenclature

ΔP_{HX}	HX Pressure drop [%]
ΔT_{min}	HX minimum temperature difference [ºC]
η_{is}	Isentropic Efficiency [%]
η_{th}	Cycle Thermal Efficiency [%]
C_6F_6	Hexafluorobenzene
CIT	Compressor Inlet Temperature [ºC]
$Cond.$	Condenser
$HTRec.$	High Temperature Recuperator
IC	Inter-cooling
$LTRec.$	Low Temperature Recuperator
MW	Molar Weight [g/mol]
P_{cond}	Condensation Pressure [bar]
P_{cr}	Critical Pressure [bar]
P_{Max}	Maximum Cycle Pressure [bar]
PIT	Pump Inlet Temperature [ºC]
pp	Percentage point
RH	Re-heating
T_{cr}	Critical Temperature [ºC]
$TiCl_4$	Titanium Tetrachloride
TIT	Turbine Inlet Temperature [ºC]

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*Address all correspondence to this author. Email: ds@us.es

INTRODUCTION

Origins and short history of the Supercritical CO_2 cycle

Supercritical Carbon Dioxide cycles have been attracting a lot of attention since a decade ago or so, owing to the excellent performance characteristics in comparison with Rankine and Brayton cycles using steam or air/combustion gases at intermediate temperatures (600-1000ºC). This has been confirmed by numerous research works in recent years and, as a consequence, a significant amount of cycle layouts have been proposed in literature with the aim to investigate the actual potential of sCO_2 technology for different applications. Amongst such layouts, which are thoroughly reviewed in a previous work by the authors [1], two configurations have usually been considered most interesting: *Recompression* cycle and *Partial Cooling*. Firstly proposed by Angelino in a transcritical, condensing embodiment [2], these cycles have become widely well-known by the scientific sCO_2 community thanks to the widespread dissemination of Vaclav Dostal's Ph.D. thesis [3], where they were adapted to supercritical conditions (both minimum cycle temperature and pressure above the critical point) for application to Generation IV Nuclear applications. Considering a minimum cycle temperature of 32ºC (T_{CR,CO_2}=31ºC) and setting Turbine Inlet Temperature and Pressure to 550ºC and 25 MPa respectively, the *Recompression* and *Partial Cooling* cycles were found capable to achieve thermal efficiencies in the order of 46-47% [4].

More recently, Allam et al. proposed an extremely recuperative oxy-fired cycle, declaring thermal efficiencies significantly higher than 50% [5] thanks to the very high Turbine Inlet Temperature (1200ºC) enabled by the oxy-combustion process. Interestingly, this same combustion of natural gas with pure oxygen also enables carbon capture in pipeline-ready conditions without any chemical reaction downstream of the combustor (postcombustion CCS), hence adding a unique environmental performance which complements the low fuel consumption. Out of these outstanding thermal and environmental performance for base load applications, the *Allam* cycle has already been taken to demonstration at a larger, pre-commercial scale (50 MW_{th}, [6]).

Applicability to CSP and Supercritical CO_2 blends as a key enabling technology

The works by Turchi et al. and Neises et al. investigated inter-cooled and re-heated versions of both the *Recompression* and *Partial Cooling* layouts applied to Concentrated Solar Power plants [7, 8]. It was concluded that, for cases with high turbine inlet temperatures (650-700ºC) and the minimum cycle temperature of 32ºC, these cycles can expectedly achieve thermal efficiencies on the order of 50%, which is much higher than state-of-the-art Rankine steam cycles (41-42%). Also in the context of CSP, another study published by authors of the present paper indicates that the *Partial Cooling* and *Allam* cycles achieve the best compromise between thermal and economic performances of a solar tower plant [9].

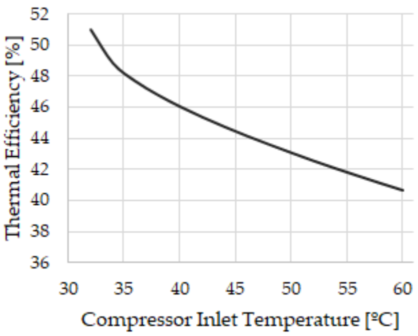

FIGURE 1. Thermal efficiency drop of a *Recompression* cycle as a function of Compressor Inlet Temperature.

Unfortunately, in spite of the overly optimistic performance quoted by several early researchers of the technology, it was soon realised that it was mandatory to perform the compression process at low temperature, close to the critical point in order to fully exploit the advantageous features of these cycles. Whilst this could be feasible in some applications, it is certainly not the case for CSP since these facilities are typically found in arid or semi-arid areas, characterised by high ambient temperatures throughout the year. This makes it impossible to reduce pump/compressor inlet temperature to values close to the critical temperature of CO_2, bringing about a significant performance drop of the cycle, Figure 1.

In order to overcome this limitation, the possibility to blend carbon dioxide with certain dopants, in order to shift the pseudocritical temperature of the mixture to a higher value, has been investigated by various authors recently. Amongst them, the works by Invernizzi et al. [10], Binotti et al. [11] and Valencia et al. [12] are worth noting. This modification of the working fluid makes it possible to have the compressor working very close to the critical point or, even more, to perform compression in liquid state at temperatures that are significantly higher than the critical temperature of Carbon Dioxide[1]. According to some preliminary estimates, the resulting modified supercritical cycle operating on blended CO_2 is expected to experience significant thermal efficiency gains, as clearly stated by McClung et al. [13] and Manzolini et al. [14].

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[1] As a matter of fact, being able to condensate such CO_2 mixture would mean taking the supercritical cycle back to the original transcritical embodiment presented by Angelino.

Scope and Organisation of Work

The concept set forth in previous paragraphs is matured by the SCARABEUS project, funded by the Horizon 2020 programme of the European Commission, where different European institutions work on identifying new CO_2 mixtures, on assessing their impact on cycle performance and on demonstrating their thermal stability at high temperature [15]. Within this context, the present paper looks into the performance gains enabled by different mixtures and on how the nature and composition of these mixtures impacts the particular cycle layout that manages to achieve the highest efficiency.

The reference power plant is presented first along with a brief description of the simulation tools used to assess the performance of each cycle and working fluid. The boundary conditions and specifications of major equipment are also provided in the same section. Then, the sCO_2 cycle configurations proposed in literature are screened thoroughly in order to identify those with the highest thermodynamic potential in CSP applications. The performance of these cycles is assessed for the reference operating and boundary conditions and compared against the performance that could be obtained from the same cycle operating on pure sCO_2. This analysis includes the impact of increasing turbine inlet temperatures and varying ambient condition with a focus on how these determine the optimum cycle configuration and working fluid composition dynamically.

COMPUTATIONAL ENVIRONMENT

The analysis presented in this work considers two dopants, as suggested by other researchers in the consortium[2]: Hexafluorobenzene -C_6F_6- and Titanium Tetrachloride -$TiCl_4$- [14, 20]. These dopants are used to produce CO_2 blends, whose characteristics come determined by the type and molar fraction of dopant used. This is shown in Table 1 where the following nomenclature is used for each mixture/blend: DXCYY where X stands for dopant composition and YY for molar fraction of dopant. Accordingly, D1C10 would be a mixture contaning 90% CO_2 and 10% C_6F_6 whilst D2C20 would be a mixture made up of 80% CO (C_6F_6) and 20% $TiCl_4$.

The impact of adding dopants on the some key properties of the resulting working fluids is shown in Table 1 through some exemplary cases. Most importantly, the table confirms that an increasing fraction of either C_6F_6 or $TiCl_4$ brings about an increasing (pseudo)critical temperature of the working fluid. For instance, for Hexafluorobenzene, every 5% additional molar fraction of C_6F_6 implies some 20ºC higher critical temperature of the mixture, in almost linear fashion. For Titanium Tetrachloride, the impact is stronger but the dependence of critical temperature on dopant fraction is visibly non-linear.

Blend	Composition [% molar]	MW [g/mol]	T_{cr} [ºC]	P_{cr} [bar]	P_{cond} [bar]
D1C10	CO_2-C_6F_6 [90-10]	58.21	80.28	112.4	83.51
D1C15	CO_2-C_6F_6 [85-15]	65.32	102.1	121.3	77.52
D1C20	CO_2-C_6F_6 [80-20]	72.42	121.9	123.6	71.83
D2C15	CO_2-$TiCl_4$ [85-15]	65.86	93.76	190.9	99.53
D2C20	CO_2-$TiCl_4$ [80-20]	73.15	149.6	243.7	97.63

TABLE 1. Specifications of sample CO_2 blends. P_{cond} is the condensation pressure corresponding to a bubble temperature of 50ºC.

The aim of this research is to demonstrate that it is possible to raise the critical temperature of the mixture to values that enable condensation of the working fluid at temperatures as high as 50ºC. This implies searching for compositions with critical temperatures higher than 80ºC, assuming a 30ºC margin between T_{cr} and the temperature at pump inlet. With this constraint, Table 1 confirms that CO_2-blends with less than 10%(v) C_6F_6 or 15%(v) $TiCl_4$ do not meet these requirements and are therefore not considered in the analysis. Moreover, this opens the way for working fluid compositions that are specifically tailored for given ambient conditions.

The thermo-physical properties of the mixtures have been obtained with Aspen [21], employing Peng-Robinson's Equation of State (EoS) calibrated on experimental data of the corresponding Vapour-Liquid-Equilibrium (VLE) conditions [22, 23]. All cycle simulations are run with the commercial software Thermoflex [24], where the aforecited fluid properties are incorporated through the novel *User-defined General Fluid* feature released specifically for this project. Except where noted, all the results presented in the next sections are produced for the common set of boundary conditions presented in Table 2.

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

TABLE 2. Set of boundary conditions and specifications used throughout the analysis.

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[2] Within SCARABEUS, the characterization of thermo-physical properties of the working fluids is carried out by University of Brescia and Politecnico di Milano, under supervision of Prof. Costante Invernizzi. Detailed information about the procedures and results can be found in publications by this team [16–19].

SCREENING OF SUPERCRITICAL CYCLE LAYOUTS

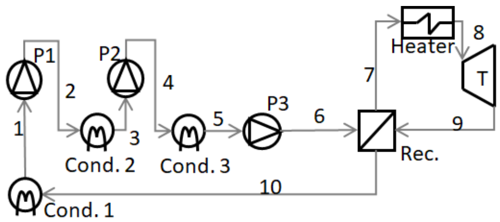
As a first step aimed at having an initial sense about how much cycle performance is affected by the composition of the working fluid, the best-performing sCO_2 cycle layouts identified by the authors in previous works are considered [25]. Table 3 shows the efficiency of these cycles, optimised following the methodology described in [25], when operating on D1C20, D2C15 and pure sCO_2 with the boundary conditions provided in Table 2. When results are not provided, it means that the cycle cannot be realised, either because it is not possible to achieve the low temperatures needed at compressor/pump inlet or because the boundary conditions of certain heat exchangers are inconsistent. The following observations can be made:

1. A significant number of cycles are barely realisable when CO_2 mixtures are used; for instance, *Partial Cooling* and *Modified Allam*. Moreover, when they are feasible, a noteworthy thermal efficiency drop is observed (*Recompression* cycle).
2. For specific layouts though, both *Recuperated Rankine* and *Precompression*, CO_2-blends seem to attain thermal efficiencies higher than 50% in spite of the very high minimum cycle temperature. This is a remarkable result in the context of CSP plants, as these particular combinations of layout and working fluid composition largely outperform any conventional pure-sCO_2 configuration.

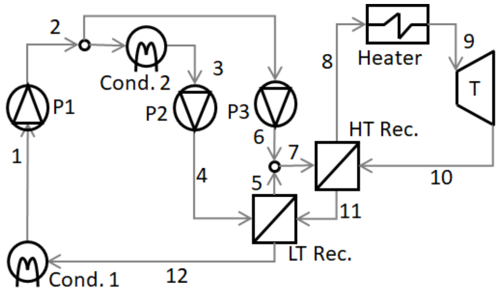
Cycle Layout	Thermal Efficiency [%]		
	D1C20	D2C15	sCO2
Simple Recuperated *Recuperated Rankine*	48.7	51.5	42.1
Precompression	50.4	51.9	45.5
Recompression	41.1	32.6	43.1
Recompression + IC + RH	42.1	34.3	48.3
Partial Cooling	-	-	46.5
Partial Cooling + RH	-	-	48.2
Schroder-Turner	-	-	44.8
Modified Allam	-	-	43.2

TABLE 3. Thermal efficiency of selected supercritical power cycles operating on pure-sCO_2 and two different CO_2-based mixtures. Temperature at compressor/pump inlet is set to 50ºC whilst turbine inlet pressure and temperature are 250 bar and 700ºC.

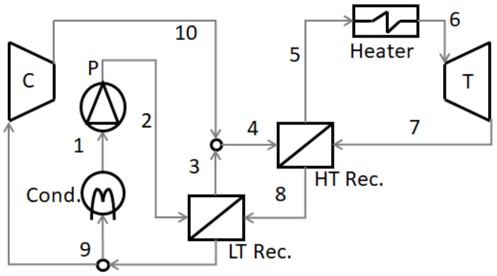
This first set of results is indeed interesting, even if some results could have been anticipated. For instance, the characteristic multi-stage, inter-cooled compression of the *Modified Allam* and *Partial Cooling* cycles (and related configurations), Figure 2(a-b), seem meaningless once condensation of the working fluid is enabled.



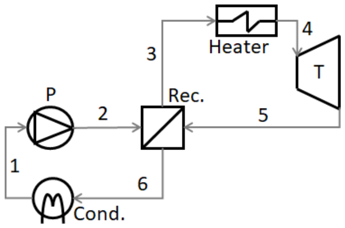
(a) *Modified Allam*



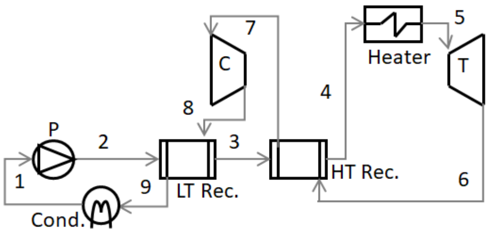
(b) *Partial Cooling*



(c) *Recompression*



(d) *Recuperated Rankine*



(e) *Precompression*

FIGURE 2. Layouts of the *Modified Allam*, *Partial Cooling*, *Recompression*, *Recuperated Rankine* and *Precompression* cycles, adapted to a transcritical embodiment.

They all incur in far more complexity than layouts such as the *Recuperated Rankine* cycle but without bringing any thermal efficiency gain. On the other hand, the very low pressures at turbine outlet considered in the *Modified Allam* cycle (30 bar [5]) are not compatible with the condensation/ambient temperatures required in the analysis; i.e., the condensation pressures at 50ºC provided in Table 1 are indeed higher than the rated minimum cycle pressure of the *Modified Allam* cycle. It is to note also that an increase of this latter pressure to resolve the incompatibility would actually change the topology of the cycle, making it very similar to a standard *Recuperated Rankine + IC* layout whose thermal efficiency is reported in Table 4.

Cycle Layout	Thermal Efficiency [%]	
	D1C20	D2C15
a) *Recuperated Rankine*	48.7	51.5
b) *Recuperated Rankine + IC*	48.7	51.5
c) *Recuperated Rankine + RH*	49.4	51.9
d) *Split-expansion*	47.9	50.2
e) *Inter-recuperated*	49.0	48.2
f) *Precompression*	50.4	51.9
g) *Recompression*	41.1	32.6
h) *Recompression + IC + RH*	42.1	34.3
i) *Turbine Split Flow I*	42.2	44.4

TABLE 4. Thermal efficiency of several supercritical cycle layouts using C_6F_6 and $TiCl_4$ based CO_2 mixtures. The associated boundary conditions are summarised in Table 2.

Interestingly, the *Recompression* cycle yields the worst performance when CO_2 blends are considered, hardly reaching 33% when D2C15 is used. The reason for such poor performance is found in the flow distribution across the compression process. When pure-sCO_2 is used, peak efficiency is achieved when roughly 65% of the flow is sent to the cold side of the low-temperature (LT) recuperator(stations 1-2-3 in Figure 2(c)) whilst the remaining 35% is compressed in the re-compressor (station 10). Nevertheless, if a similar mass balance is employed with the proposed blends, the low-pressure outlet from the LT recuperator (cycle Station 9) falls within the liquid-vapour two-phase region, hence preventing the operation of the recompressor. In order to counteract this and have this stream moving out from the two-phase area, the fraction of fluid sent to the recompressor must increase, hence reducing the flow through the high-pressure side of the LT recuperator. Globally, this leads to a substantial reduction of thermal efficiency owing to the higher power consumption of the recompressor and lower effectiveness of the LT recuperator.

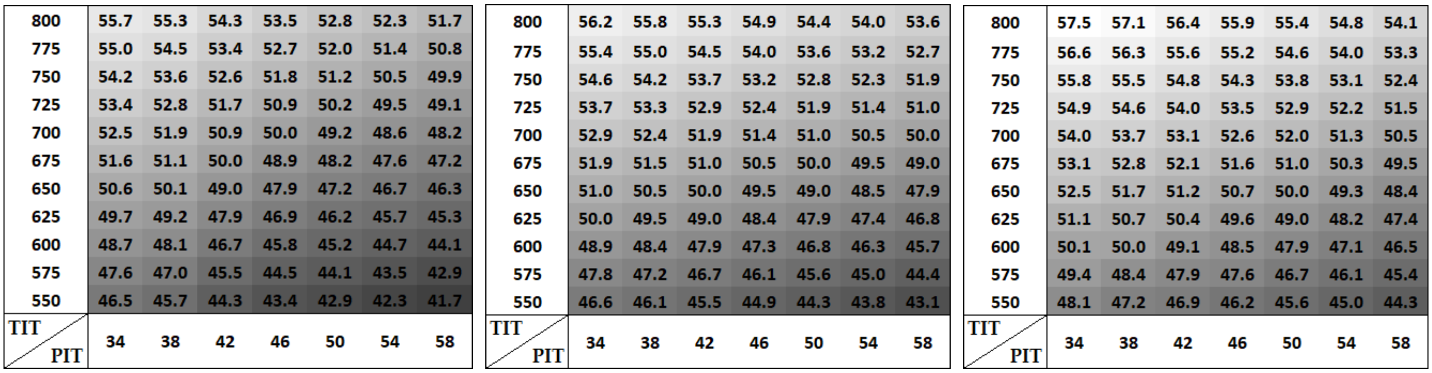
With the information obtained in Table 3, a second round of screening of a very large database of sCO_2 cycle layouts produced by the authors, see Crespi et al. [1], is carried out. These cycles are tested for the reference CO_2 blends and the results are presented in Table 4. The *Recuperated Rankine* and *Precompression* layouts presented in Figure 2(d-e) still attain the best performance, enabling thermal efficiencies in the range of 50% or higher with D1C20 and close to 52% when D2C15 is used. On the other hand, the more complex versions of the *Recuperated Rankine*, cases b) to e) in Table 4, seem to yield marginal efficiency gains at the cost of a significantly higher complexity and therefore disregarded. These are therefore not reported in the remainder of the paper although a more detailed analysis for pure-sCO_2 applications can be found in other works by the authors, for instance [1].

THERMAL EFFICIENCY GAINS ENABLED BY CO_2-BLENDS

Comparing the thermal efficiency attained by the best supercritical cycles for pure Carbon Dioxide at high minimum cycle temperature (50ºC) yields the conclusion that the *Recuperated Rankine* and *Precompression* layouts using the proposed CO_2-blends outperform their pure-CO_2 counterpart by a large margin. Hence, the efficiency of the former layout increases 6.5/9.5 percentage points when employing D1C20/D2C15 respectively whilst this gain decreases to 5/6.5 pp if a *Precompression* cycle is considered. In either case, this is a very large performance enhancement indeed.

Tables 3 and 4 show that the most efficient layouts operating on pure-sCO_2, *Recompression+IC+RH* and *Partial Cooling+RH*, attain thermal efficiencies that are similar to that of the *Recuperated Rankine* and only 2-3 percentage points lower than of the *Precompression* layout. The root cause for these narrow differences could be found in the particular set of boundary conditions considered, possibly favourable to the blended working fluids and, therefore, bringing about misleading conclusions. A deeper analysis to verify that the operation on blended-CO_2 actually outperforms the most efficient CO_2 configurations is therefore mandatory.

In order to confirm the results obtained so far, a series of systematic runs are performed in Thermoflex, setting the maximum cycle (turbine inlet) pressure to 250 bar. These runs consider a wide range of maximum (turbine inlet) and minimum (pump inlet) cycle temperatures. Hence, turbine inlet temperature is varied from 550ºC (state-of-the-art solar tower plants) to 800ºC, representative of long-term CSP plants with next-generation, higher-temperature salts); the target value of the SCARABEUS project, 700ºC, lies well within this range. Pump inlet temperature is, on the other hand, varied between 32ºC,



800	55.7	55.3	54.3	53.5	52.8	52.3	51.7
775	55.0	54.5	53.4	52.7	52.0	51.4	50.8
750	54.2	53.6	52.6	51.8	51.2	50.5	49.9
725	53.4	52.8	51.7	50.9	50.2	49.5	49.1
700	52.5	51.9	50.9	50.0	49.2	48.6	48.2
675	51.6	51.1	50.0	48.9	48.2	47.6	47.2
650	50.6	50.1	49.0	47.9	47.2	46.7	46.3
625	49.7	49.2	47.9	46.9	46.2	45.7	45.3
600	48.7	48.1	46.7	45.8	45.2	44.7	44.1
575	47.6	47.0	45.5	44.5	44.1	43.5	42.9
550	46.5	45.7	44.3	43.4	42.9	42.3	41.7
TIT / PIT	34	38	42	46	50	54	58

(a) *Pure CO_2 (Partial Cooling+RH, Recompression+IC+RH)*

800	56.2	55.8	55.3	54.9	54.4	54.0	53.6
775	55.4	55.0	54.5	54.0	53.6	53.2	52.7
750	54.6	54.2	53.7	53.2	52.8	52.3	51.9
725	53.7	53.3	52.9	52.4	51.9	51.4	51.0
700	52.9	52.4	51.9	51.4	51.0	50.5	50.0
675	51.9	51.5	51.0	50.5	50.0	49.5	49.0
650	51.0	50.5	50.0	49.5	49.0	48.5	47.9
625	50.0	49.5	49.0	48.4	47.9	47.4	46.8
600	48.9	48.4	47.9	47.3	46.8	46.3	45.7
575	47.8	47.2	46.7	46.1	45.6	45.0	44.4
550	46.6	46.1	45.5	44.9	44.3	43.8	43.1
TIT / PIT	34	38	42	46	50	54	58

(b) *D1 blends (Precompression)*

800	57.5	57.1	56.4	55.9	55.4	54.8	54.1
775	56.6	56.3	55.6	55.2	54.6	54.0	53.3
750	55.8	55.5	54.8	54.3	53.8	53.1	52.4
725	54.9	54.6	54.0	53.5	52.9	52.2	51.5
700	54.0	53.7	53.1	52.6	52.0	51.3	50.5
675	53.1	52.8	52.1	51.6	51.0	50.3	49.5
650	52.5	51.7	51.2	50.7	50.0	49.3	48.4
625	51.1	50.7	50.4	49.6	49.0	48.2	47.4
600	50.1	50.0	49.1	48.5	47.9	47.1	46.5
575	49.4	48.4	47.9	47.6	46.7	46.1	45.4
550	48.1	47.2	46.9	46.2	45.6	45.0	44.3
TIT / PIT	34	38	42	46	50	54	58

(c) *D2 blends (Recuperated Rankine, Precompression)*

FIGURE 3. Heat maps representing the peak thermal efficiency obtained with pure CO_2 and with C_6F_6 (D1) and $TiCl_4$ (D2) blends for different maximum and minimum cycle temperature (TIT and PIT respectively). Maximum cycle pressure is set to 250 bar.

very close to the critical temperature of CO_2, to 60ºC, a value that is more appropriate for typical locations of CSP plants. It is to note that the lower end of this range corresponds to the best performance of conventional sCO_2 technology whereas it does not bring any advantage for CO_2 blends.

The analysis is performed studying three different cases, corresponding to each of the working fluids considered: pure CO_2, CO_2-C_6F_6 mixtures and CO_2-$TiCL_4$ mixtures. For each of these three cases, the performance of supercritical cycles depending on pump and turbine inlet temperatures (PIT,TIT) is assessed. Two degrees of freedom are considered in this analysis, in addition to the pair of independent variables (PIT,TIT) being assessed: molar fraction of dopant, only for CO_2 blends (D1C10, D1C15, D1C20, D1C25 for CO_2-C_6F_6 and D2C15, D2C20, D2C25 for CO_2-$TiCl_4$), and layout of the cycle. For each (PIT,TIT), different cycle layouts are tested to identify which of them provides the highest efficiency.

The results of the analysis are presented in Figure 3, showing three heat maps with the same colour scale: dark grey areas correspond to lower efficiencies whereas the most efficient combinations are shown in lighter shades of grey. The highest value achieved, in the top left corner of Figure 3(c), is shown in white. The caption of each map reports the working fluid and the numerical value reported for each (TIP,PIP) corresponds to the peak efficiency obtained by any of the (cycle layout, dopant molar fraction) combinations studied. It is worth remarking that the cycle layout enabling peak performance for the pure CO_2 case is either *Partial Cooling + RH* or *Recompression + IC + RH*, depending on the particular (PIT,TIT) pair. On the other hand, peak efficiency is always attained by the *Precompression* cycle if blends based on C_6F_6 are taken into account, and by either the *Recuperated Rakine* or the *Precompression* layouts if blends based on $TiCl_4$ are considered; this information is also reported in brackets in the captions of Figure 3. Finally, another remarkable point is that, in cases b) and c), the molar fraction of dopant may change between adjacent cells or from one region of the map to another. This is discussed in the following paragraphs.

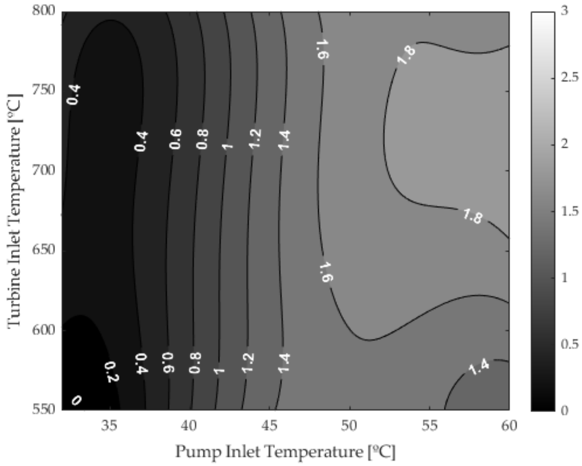
As expected, the three maps in Figure 3 present a similar pattern overall, with efficiency reaching the maximum and minimum values for (maximum TIT, minimum PIT) and (minimum TIT, maximum PIT) respectively. The highest efficiency is achieved by CO_2 blends using $TiCl_4$ (D2), regardless of pump and turbine inlet temperatures. This is deduced from the lighter grey colour of the upper region of the corresponding map. Hexafluorobenzene mixtures follow close behind with pure CO_2 yielding the worst performance. This provides an unequivocal answer with respect to the superior thermal performance of supercritical cycles using blended-CO_2. Nevertheless, this is not the only interesting qualitative conclusion to be drawn from the analysis. When cycle complexity is factored in, it is found that this superior performance of CO_2 mixtures is achieved with cycles whose layout is far simpler than that of the competing pure sCO_2 cycles: fewer turbomachinery and fewer heat exchangers will expectedly help drive installation costs down and enable a more flexible operation of a future power plant.

From a quantitative standpoint, the peak efficiency enabled by CO_2-$TiCl_4$ mixtures at high PIT and low TIT (bottom, right corner of the map) is 44+% approximately, clearly outperforming state-of-the-art steam Rankine cycles with the same boundary conditions. If more favourabe conditions are considered, high TIT and low PIT (top, left corner of the map), efficiency is boosted to values as high as 57.5%, even if this applies to ambient conditions significantly lower than the values expected in usual CSP sites. For C_6F_6, maximum efficiencies in Figure 3 range from 43+% to 56.2%, which is 0.5-1.5 percentage points higher than if pure CO_2 were used.

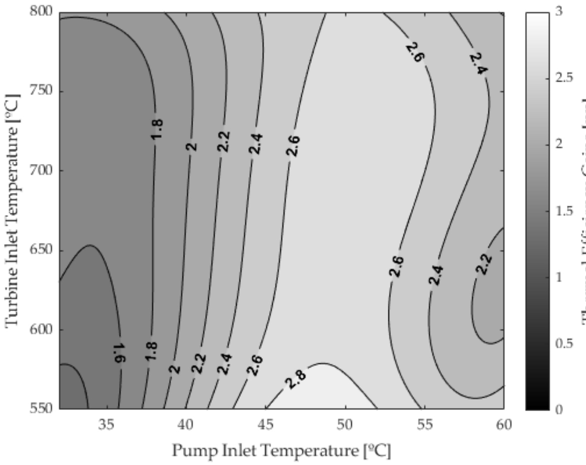
The operating temperatures of the reference CSP plant in the SCARABEUS project are 50ºC at pump inlet and 700ºC at turbine inlet. This translates into the following attainable efficiencies: 49.2% for pure CO2 on a *Partial Cooling + RH* cycle, 51% for CO_2-C_6F_6 on a *Precompression* cycle and 52% for CO_2-$TiCl_4$ on a *Precompression* cycle. The leap in efficiency and potential for installation cost reduction is self-evident from these figures.

Further manipulation of the colour maps in Figure 3 provides some additional observations. Indeed, Figure 4 reports, for each category of blends (CO_2-C_6F_6 and CO_2TiCl_4), the peak efficiency increase when the these working fluids are used with respect to the case operating with pure CO_2, hence revealing the thermal efficiency gains enabled by the mixtures. The results are represented by means of a contour chart, identifying areas characterised by the same efficiency change; iso-$\Delta\eta_{th}$ are added for convenience.

As expected, the efficiency gains reported in Figure 4 are smallest in the vicinity of the critical temperature of CO_2, confirming the interest and potential of sCO_2 in applications where operation near these conditions (P_{cr},T_{cr}) is feasible. Yet, even in the latter operating conditions, there is margin for improvement if CO_2-blends are used, though this is not a general statement for all dopants. For instance, while D1 blends present a moderate η_{th} gain (less than 0.2 pp), falling within the uncertainty of the calculations, mixtures based on D2 seem to clearly outperform pure-CO_2 even at pump inlet pressures and temperatures near the critical point of Carbon Dioxide, enabling an efficiency gain of around 1.5 percentage points. On the other hand, $\Delta\eta_{th}$ can be as high as 1.8 pp for CO_2-C_6F_6 or even 3 pp for CO_2-$TiCl_4$ at higher pump inlet temperature. Moreover, for CO_2-$TiCl_4$, the peak efficiency gain is found at moderate turbine inlet temperature (550-600ºC), which is an extremely interesting result suggesting that the utilisation of sCO_2 blends somehow reliefs the need for increasing turbine inlet temperatures if higher efficiencies are sought. This last observation is of great interest for Concentrated Solar Applications, in particular regarding the need to develop molten salts operating at higher temperatures than today's technology.



(a) *Thermal efficiency gains enabled by D1 blends*



(b) *Thermal efficiency gains enabled by D2 blends*

FIGURE 4. Thermal efficiency gains enabled by CO_2-C_6F_6 (D1) and CO_2-$TiCl_4$ (D2) mixtures with respect to pure CO_2. Contour plots based on data presented in Figure 3.

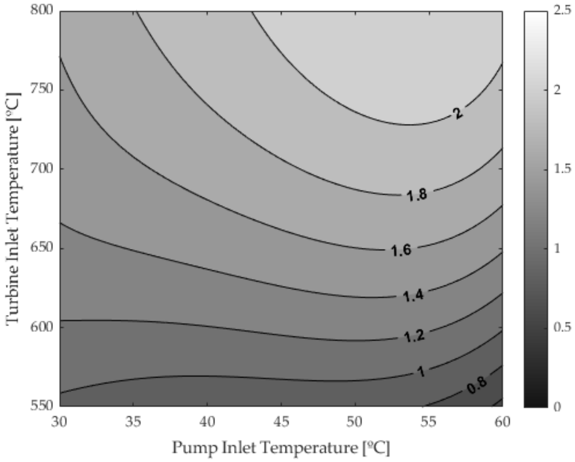
INFLUENCE OF BLEND COMPOSITION ON CYCLE PERFORMANCE

In the previous section, the peak thermal efficiency achieved by the two different groups of blends has been investigated without any reference to the impact of the actual molar composition of the mixture employed. Reference to the layouts yielding highest efficiency for a given (PIT,TIT) combination has neither been made, in order to improve the readability of the heat maps provided and to focus the discussion on the peak thermal efficiency actually achievable by the working fluids proposed. Nevertheless, the question about the influence of adding a larger molar fraction of dopant on the thermodynamic performance of the cycle is relevant for a twofold reason. On the one hand, the patterns followed by the optimum dopant molar fraction must be understood to optimise the design process. On the other, the composition of the working fluid plays a critical role not only in the thermodynamic performance of the power cycle but also on the design and performance of major equipment in the plant. This is currently investigated by Original Equipment Manufacturers of turbomachinery and heat exchangers in the SCARABEUS consortium.

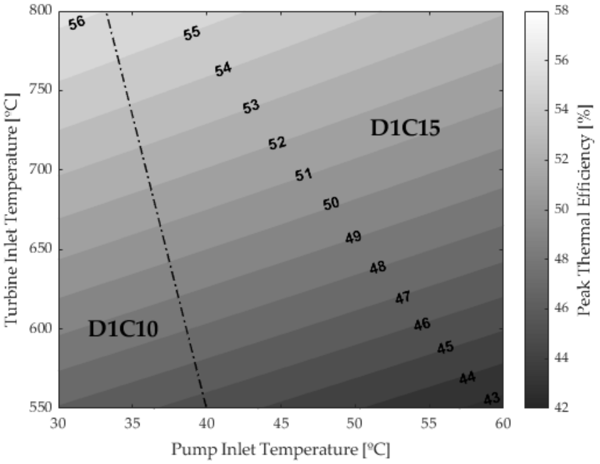
Figures 5 and 6 are aimed at shedding more light on the influence of these two design aspects: molar fraction of dopant and cycle layout. For each dopant, they show again a colour map of efficiency depending on pump and turbine inlet temperatures but adding information about the composition of the mixture providing peak efficiency. To a large extent, this is a different representation of the information already presented in Figure 3. It is to note that the same colour scales have been employed for Figures 5(a)-6(a) and Figures 5(b)-6(b) in order to enable a more direct comparison between the two dopants.

For the mixtures using CO_2-C_6F_6, Figure 5(a) shows the thermal efficiency gain (percentage points) of the *Precompression* cycle with respect to the *Recuperated Rankine* cycle for each (PIT,TIT) pair. $\Delta\eta_{th}$ is always positive and increases towards the top, right corner of the plot where ambient (pump inlet) temperature is highest. Numerically, $\Delta\eta_{th}$ ranges from 0.5-2.5 pp what suggests that, when CO_2-C_6F_6 mixtures are used, it is worth to adopt a *Precompression* cycle in spite of the more complex layout than the *Recuperated Rankine* cycle, Figure 2.

Regarding blend composition, Figure 5(b) reports the peak thermal efficiency achieved by the *Precompression* cycle operating on the best molar fraction of C_6F_6 molar. The plot is divided in two neatly defined regions. At low pump inlet temperatures, adding 10% Hexafluorobenzene yields the best cycle performance whereas, as pump inlet (ambient) temperature increases, the molar content of C_6F_6 must increase if thermal efficiency is to be maximised. The transition region between D1C10 and D1C15 at around 35-40ºC is shown for reference and applies to the 5% incremental molar fraction considered in this assessment. In a more refined analysis, a continuous transition towards a higher dopant content would be seen instead, although this would not change the main conclusion of the study regarding the variation of working fluid composition with design conditions.



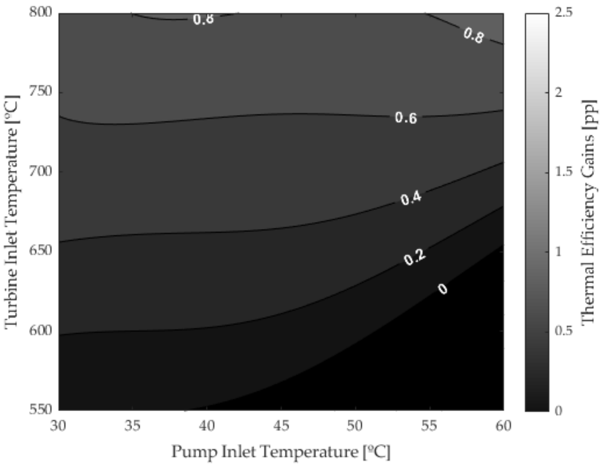
(a) *Thermal efficiency gains of a Precompression cycle with respect to a Recuperated Rankine cycle*



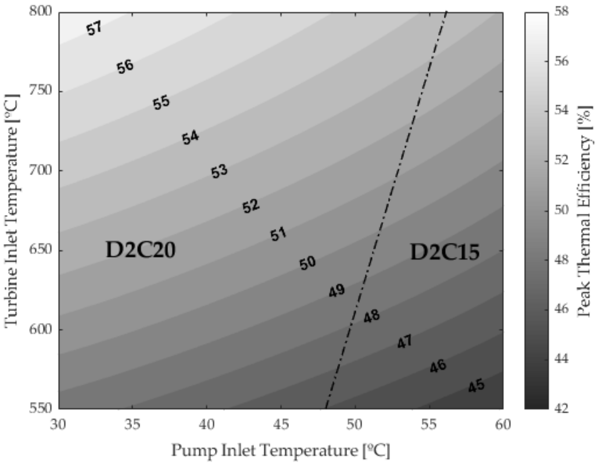
(b) *Peak Thermal Efficiency obtained by a Precompression cycle*

FIGURE 5. Impact of cycle layout and working fluid composition on the performance of a supercritical cycle operating on CO_2-C_6F_6 mixtures.

The scenario changes significantly when Titanium Tetrachloride is considered. First of all, the best performance for a given (PIT,TIT) pair is not attained by one single cycle layout anymore, as shown in Figure 6(a). At high temperatures at pump and turbine inlet (top, right corner of the plot), the *Precompression* cycle yields better performance whereas the *Recuperated Rankine* layout is more interesting if either turbine or pump inlet temperature is moderate or low. Moreover, in either case, the performance difference ($\Delta\eta_{th}$) between these two cycles is not as large as in the previous case (C_6F_6), remaining below one percentage point regardless of boundary conditions and with an average value of 0.2 pp (within the uncertainty of the calculations). This is easily deduced from the much darker colours in Figure 6(a) than in Figure 5(a). Actually, the black region in Figure 6(a), bottom right corner) corresponds to negative values of $\Delta\eta_{th}$ where the *Recuperated Rankine* cycle exhibits better performance than the *Precompression* layout. With this in mind, given the limited thermal efficiency gain provided by the *Precompression* cycle and the added complexity that is needed to attain this marginal benefit, it is concluded that this latter layout would not be of interest in an actual power plant. The *Recuperated Rankine* cycle seems to be a more balanced solution if Titanium Tetrachloride is the dopant of choice.



(a) *Thermal efficiency gains of a Precompression cycle with respect to a Recuperated Rankine cycle*.



(b) *Peak Thermal Efficiency obtained by a Precompression cycle*

FIGURE 6. Impact of cycle layout and working fluid composition on the performance of a supercritical cycle operating on CO_2-$TiCl_4$ mixtures.

The conclusion about the layout of interest is accompanied by the absolute thermal efficiency attainable by CO_2-$TiCl_4$ mixtures in a *Recuperated Rankine* cycle shown in Figure 6(b). This plot confirms the existence of an optimum dopant molar fraction depending on the operating conditions of the cycle, but this now shows a somewhat mirrored pattern to Figure 5. Indeed, the map is divided in two regions where different molar compositions yield highest efficiency but, in this case though, reducing the molar content of the dopant is beneficial when pump inlet (ambient) temperature increases. This is in contrast to the pattern exhibited by C_6F_6 mixtures in Figure 5, favoured by a higher dopant molar fraction at increasing pump inlet temperatures. Finally, a higher sensitivity of the optimum dopant molar fraction to pump inlet temperature than to turbine inlet temperature is common to both dopants, as this is brought about by cycle thermodynamics.

SAFETY CHARACTERISTICS

Health and safety aspects of the dopants considered must not be overlooked when evaluating the feasibility of the concept proposed. Therefore, some comments in the context of the NFPA 704 code of the National Fire Protection Association (*Standard System for the Identification of the Hazards of Materials for Emergency Response*) are presented here. This code provides immediate information about the hazards of a material, and the associated severity, in order to facilitate an immediate emergency response. Four concepts are considered: health hazard, flammability, chemical reactivity and special hazard [26].

Regarding health hazard (toxicity) and flammability, C_6F_6 and $TiCl_4$ show opposite trends: whereas the former is highly flammable and has low toxicity, $TiCl_4$ is non-flammable but it can cause serious or permanent health injuries. On the other hand, C_6F_6 stands out from $TiCl_4$ regarding chemical stability given that tests with $TiCl_4$ during the experimental activities carried out in SCARABEUS have shown violent chemical changes at high temperature and pressure as well as aggressive reactions with water, even with moisture in air [16].

With this information, CO_2-C_6F_6 mixtures are expected to be more appealing from a commercial standpoint than CO_2-$TiCl_4$ in spite of the better performance that is attainable by the latter mixtures. This is nevertheless to be assessed in later stages of the SCARABEUS project and more information will be reported in the public domain once available.

SUMMARY AND CONCLUSIONS

This paper has looked into the thermodynamic interest of adding certain dopants to Carbon Dioxide to enhance the performance of supercritical power cycles, with a focus on Concentrated Solar Power applications. To this end, and as a first step, the first part of the paper provided a thermodynamic assessment of the thermal performance obtained from different supercritical CO_2 cycles when CO_2 mixtures are substituted for pure CO_2. Two dopants were considered: Hexafluorobenzene (C_6F_6) and Titanium Tetrachloride ($TiCl_4$). The results showed that using CO_2 mixtures in cycles widely acknowledged for their very good thermodynamic performance yield lower thermal efficiency than when pure CO_2 is used.

Further investigations with other cycle configurations, reportedly less appealing than those considered initially, showed much better performance of CO_2 blends: the *Recuperated Rankine* and *Precompression* cycles achieve 50% efficiency when 20% C_6F_6 or 15% $TiCl_4$ is added. In order to confirm this potential, a parametric analysis for varying minimum and maximum cycle temperatures was undertaken, comparing the peak thermal efficiency achieved by each of the three working fluid considered: pure CO_2 and CO_2 mixtures of Hexafluorobenzene and Titanium Tetrachloride. CO_2 mixtures showed consistently better efficiency than pure CO_2, with thermal efficiency gains as high as 2 (CO_2-C_6F_6) or 3 (CO_2-$TiCl_4$) percentage points with respect to the reference standard sCO_2 case. Moreover, this performance enhancement was attained with simpler cycle layouts than when standard sCO_2 is employed.

In the last part of the paper, the attention was focused on the influence of both dopant content, given a particular dopant composition, and cycle layout. A first remarkable conclusion is the fact that the *Precompression* layout yields the most balanced option for CO_2-C_6F_6 mixtures in terms of performance and cycle complexity, hence stepping forward as the option of choice for future analysis. On the other hand, when CO_2-$TiCl_4$ mixtures are used, it is the *Recuperated Rankine* cycle which stems as the most leveraged solution with very good performance and low cycle complexity.

Finally, the optimum molar content of the dopants considered (i.e., the molar fraction of dopant yielding the highest efficiency) depends on the design operating conditions of the cycle: turbine inlet temperature and, in particular, pump inlet temperature. In general, the molar content oscillates between 10 and 20%. It is also been observed that, very interestingly, the trends followed by the optimum molar content for increasing pump inlet (ambient) temperature are very different for each dopant. Thus, when CO_2 is blended with Hexaflurobenzene, higher ambient temperatures call for high dopant content, whereas the opposite holds true if Titanium Tetrachloride is used.

In addition to these particular conclusions, the following general conclusions are drawn for the paper:

- Blending the working fluid of supercritical CO_2 cycles with a certain fraction of other species (10-20% molar) increases thermal efficiency by as much as 2-3 percentage points, thus enabling values of η_{th} higher than 50% for ambient temperatures well above 30-35ºC.
- The utilisation of CO_2 blends brings in three additional degrees of freedom: dopant composition and molar content, and cycle layout. This implies that it is now possible to tailor the power cycle to the particular boundary conditions of the power plant.
- Not only does the utilisation of CO_2 blends enable higher cycle efficiency but it also reduces the complexity of the cycle layout yielding best thermodynamic performance. This brings about additional benefits in the form of reduced capital costs and larger flexibility, which are critical features towards cost effectiveness of the technology.
- On the negative side, some dopants might present issues regarding health and safety. Therefore, in spite of the moderate content of this compound, it is mandatory to perform an assessment of the possible implications of these features in terms of safety and degradation.

Further work by the authors and by other partners in the SCARABEUS consortium will look into other candidate dopants in order to further enhance the performance of supercritical cycles. Also, the additional benefits that these working fluids and simpler layouts could bring about in terms of part-load efficiency will be assessed. This, nevertheless, requires further investigation with regards to component design and performance.

ACKNOWLEDGEMENTS

The SCARABEUS project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement Nº814985.

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