The 7th International Supercritical CO_2 Power Cycles Symposium
February 21 – 24, 2022, San Antonio, Texas
Paper 191

Potential and challenges of the utilization of CO_2-mixtures in supercritical power cycles of Concentrated Solar Power plants

D. Sánchez[1], F. Crespi[1], P. Rodríguez de Arriba[1], A. Muñoz[1], G. Manzolini[2], C. Invernizzi[3], G. Di Marcoberardino[3], Martin White[4], Pierre-Luc David[5]

[1]University of Seville (Spain), [2]Politecnico di Milano (Italy), [3]University of Brescia (Italy),
[4]City University of London (United Kingdom), [5]Kelvion Thermal Solutions (France)

ABSTRACT

The potential of supercritical Carbon Dioxide power cycles to supersede subcritical steam turbine technology in Concentrated Solar Power applications is widely acknowledged. Some differential features of the former are higher efficiency at similar temperatures (in the range from 600 to 750ºC), smaller footprint, higher flexibility and lower cost. Several theoretical and experimental R&D projects are currently working on aspects such as component development (turbomachinery and heat exchangers), system integration into the solar subsystem (receiver and thermal energy storage system), operability, materials…

Nevertheless, whilst progress is being made at a very high pace, there is still a great deal of uncertainty regarding how much sCO2 technology will be able to reduce the cost of solar thermal electricity with respect to contemporary CSP technology. This is mostly caused by the sensitivity of cycle performance to ambient temperature, bringing about a large efficiency drop when this temperature exceeds 35ºC. The root cause for this performance drop is the unfeasibility of compression near the critical point, where the very high density of the fluid reduces density and, therefore, compression work.

The SCARABEUS project is based on the addition of certain dopants to carbon dioxide in order to yield a working mixture with higher critical pressure and temperature. As a consequence of these modified critical properties of the fluid, compression near the critical point is enabled even at ambient temperatures as high as 40-45ºC. Moreover, at these high temperatures, condensation and compression in liquid state are still possible. The characteristics of the new working fluids have been proved to enable thermal efficiencies higher than 50% for minimum cycle temperatures as high as 60ºC, hence boosting the performance of CSP plants well beyond of the capabilities of systems based on steam turbines. This implies a substantial reduction of the cost of the plant.

Nevertheless, whilst the thermal and economic performances are more favourable for CO2-mixtures, new technical challenges must be faced if the technology is to be mature: thermal stability and potential hazards of the dopants, new turbomachinery and heat exchanger designs adapted to the composition of the mixture, phase separation, materials (selection, compatibility and degradation) and others.

This paper introduces the main advantages and technical potential of the SCARABEUS technology along with a discussion of the main challenges faced by the consortium in order to

demonstrate the technology and beyond.

LIMITATIONS OF THE SCO2 CYCLES IN CSP

Supercritical CO_2 technology has attracted increasing interest in the scientific community over the last 20 years, thanks to its outstanding characteristics such as high thermal efficiency at intermediate-high temperatures and low footprint. Numerous studies have shown that this technology stands out as a very promising alternative, capable of replacing Rankine steam cycles in a large number of different applications including nuclear, Concentrating Solar Power (CSP), Waste Heat Recovery (WHR) or fossil fuels (pulverized coal or oxy-combustion of coal syngas). The potential of Carbon Dioxide power cycles to replace steam turbines was already highlighted by Angelino in his seminal work back in the late sixties (Angelino, 1968), where different sCO_2 cycle layouts were proposed. Nevertheless, Angelino noted that the true potential of sCO_2 cycles could only be developed at intermediate to high turbine inlet temperatures (TIT), usually above 600-650 ºC (see Figure 1). This threshold would apply if a Recompression sCO_2 cycle (probably the most representative layout for this technology) were considered, labelled as *Cycle A* in Figure 1. For more complex cycles, sCO_2 technology would be more efficient than a reheated Rankine cycle even at lower turbine inlet temperatures but, at the same time, the opposite would be true if less efficient sCO_2 layouts had been selected. Overall, for an appropriate cycle selection, it is widely acknowledged that 600-650ºC would be the breakeven temperature above which supercritical Carbon Dioxide cycles would outperform other options available (steam or organic Rankine, air Brayton).

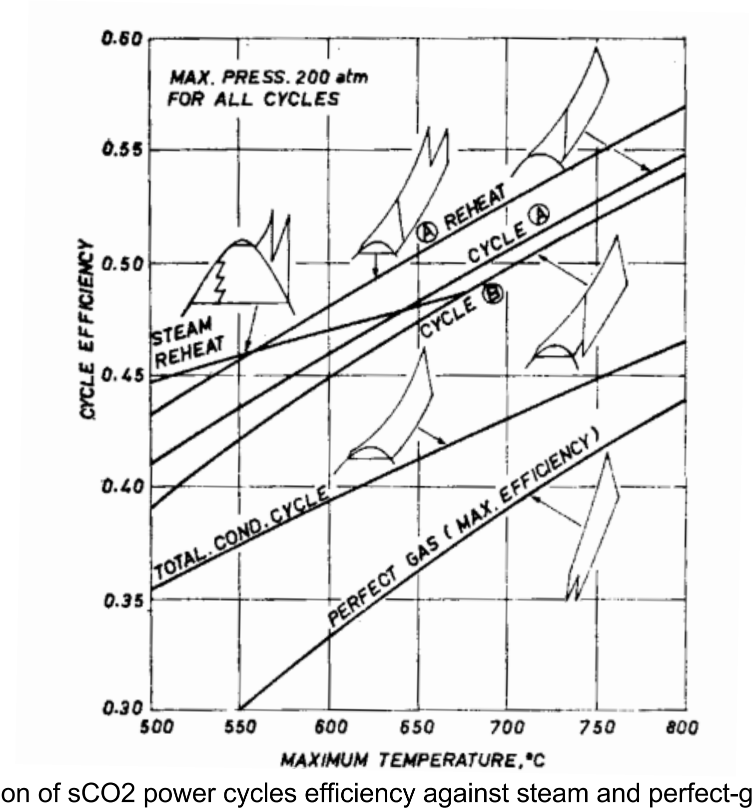

Figure 1. Comparison of sCO2 power cycles efficiency against steam and perfect-gas cycles (Angelino, 1968)

Project Name	Location	Capacity [MW]	Status	Technology	T_{amb} [ºC]
DEWA CSP Tower	Dubai (UAE)	100	Under Construction	ST	33.2
Planta Solar 10 & 20	Seville (Spain)	11+20	Operational	ST	25.4
Ivanpah Solar	Mojave Desert (US-CA)	392	Operational	ST	26.9
Cerro dominador	Acatama Desert (Chile)	110	Operational	ST	23.2
Noor III	Ouarzazate (Morocco)	150	Operational	ST	26.9
SunCan Dunhuang	Dunhuang (China)	100	Operational	ST	17.9
Khi Solar One	Upington (South Africa)	50	Operational	ST	28.5
Ashalim Plot B / Negev Energy	Negev Desert (Israel)	121	Operational	ST	31.5
SEGS VIII-IX	Mojave Desert (US-CA)	2x80	Operational	PTC	26.9
Solana Generating Station	Gila Bend (US-AR)	250	Operational	PTC	30.4
Genesis Solar Energy Project	Blythe (US-CA)	250	Operational	PTC	30.4
Solaben	Cáceres (Spain)	4x50	Operational	PTC	21.9
Bokpoort	Upington (South Africa)	50	Operational	PTC	28.5
Godawari Solar Project	Nokh (Rajhastan, India)	50	Operational	PTC	33.2
Noor I & II	Ouarzazate (Morocco)	160+200	Operational	PTC	26.9
Ashalim Plot A / Negev Energy	Negev Desert (Israel)	110	Operational	PTC	31.5

Table 1. Literature survey of Tower and Parabolic Trough CSP plants (PTC: parabolic trough collectors. ST: solar tower with central receiver).

The analysis carried out by Angelino, shown in Figure 1, set the minimum cycle temperature to a value of around 15ºC c achieved, which is possible only if wet cooling technology is adopted. The viability of this hypothesis is therefore disputable in practice, given that CSP plants are usually found in semi-arid regions characterized by high Direct Normal Irradiance (DNI) and high ambient temperatures. This is confirmed by the information in Table 1, showing a selection of CSP plants currently in operation with either central receiver (tower) or parabolic trough collector technologies (NREL, 2021). The last column shows a reference ambient temperature for the respective location of each plant, yielding an average value overall of around 25-35ºC.

The key to attaining the very good performance offered by a supercritical CO_2 cycle is the ability to carry out the compression process close to the critical point, where the low specific volume of the fluid helps reduce the work needed to overcome the pressure difference:

$$W_S = \int_{in}^{out} v \cdot dp = \int_{in}^{out} Z \cdot v_i \cdot dp$$

where W_s and v_i stand for isentropic compression work and ideal specific volume (i.e., specific volume at the same pressure and temperature if the fluid behaved as an ideal gas). The critical temperature of Carbon Dioxide is ~31ºC so, for an air-cooled condenser making use of ambient air at 25ºC or higher, it is just not possible to achieve the low cycle temperatures required. When compressor inlet temperature departs from the critical value, specific volume (or compressibility Z) increases and so does compression work, bringing about a substantial thermal efficiency drop and losing the competitive advantage of sCO_2 technology over steam Rankine cycles. Accordingly, the high ambient temperatures that are inherent to CSP stem as a fundamental limitation to the application of these cycles to solar thermal power generation.

To quantify the detrimental effect of minimum cycle temperature of sCO_2 power cycles in comparison with that of steam turbines, multiple scenarios have been studied with the commercial software Thermoflex. Two ambient temperatures were considered: ISO conditions (15ºC, 60% RH) and 35ºC as a more realistic value of CSP locations. The former suggests using wet cooling, thus a minimum cycle temperature of 25ºC is reasonable. On the other hand, water scarcity in the second scenario requires dry cooling, with a higher approach temperature which, in this study, is set to 15ºC (yielding 50ºC minimum cycle temperature). These two sets of boundary conditions have been applied to three CSP technologies, each one translating into different maximum cycle temperatures: Parabolic Trough (400ºC), State-of-Art Solar Tower (550ºC) and Advanced Solar Tower (700ºC). It is noted that steam turbines have not been considered in the latter case, since they have already been proven not cost effective at such higher temperatures (Klotz et al., 2009, Purgert et al., 2016, Liu et al., 2019).

All sCO_2 cases make use of a Recompression layout, since this is representative of the technology and used for multiple demonstration projects across the world, whilst the reference steam turbine cycle features one reheat and multiple feedwater heaters. In particular, for the latter, the general laoyut of the Rice Solar Energy Project was adapted to the various boundary conditions by changing condensation pressure and live steam conditions. Finally, the columns referring to the SCARABEUS technology in Tables 2 and 3 will be discussed later in the paper but they are added here for the sake of clarity.

The values in Table 2 confirm that the superiority of sCO_2 becomes evident in the Advanced Tower Plant (700ºC TIT) only. On the contrary, the thermal efficiency gain enabled by sCO_2 with respect to steam turbines is limited to 1 percentage point at lower TITs. Indeed, if high ambient temperatures are taken into account, sCO_2 performs even worse than the current steam technology.

	ISO (Tamb = 15ºC)			Tamb = 35 ºC		
	Steam	**sCO2**	**SCARABEUS**	**Steam**	**sCO2**	**SCARABEUS**
Parabolic Trough	38.4	39.6	38.8	35.0	33.8	34.9
SoA ST	47.0	48.7	48.3	43.7	42.9	44.4
Advanced ST	-	55.3	54.9	-	49.6	51.0

Table 2. Thermal efficiency of Steam, sCO_2 and SCARABEUS cycles for two ambient temperatures (ISO and 35ºC) and three CSP technologies (Parabolic Trough, SoA Solar Tower, Advanced Solar Tower).

Generally speaking, the thermal efficiency gain brought about by a higher turbine inlet temperature is followed by a reduction in the aperture area of the solar field and, also, the size of the thermal energy storage system (in terms of total energy stored). Nevertheless, higher temperatures also involve advanced (more expensive) materials and the development of new technology, entailing also new risks and challenges. Accordingly, the preliminary techno-economic analyses available in literature express doubts about the actual potential of the sCO_2 concept to reduce the specific cost and Levelized Cost of Electricity (LCOE) below those of state-of-art steam turbines. For example, Alfani et al. calculated an optimum specific cost of 6630 $/kW for a Recompression Cycle with Intercooling (2.5 SM, 15 hours TES) (Alfani et al., 2020). Similarly, Crespi et al. (2020a) estimated 5907 $/kW for the Partial Cooling cycle and 6867 $/kW for the Recompression Cycle (2.4 SM, 10 hours TES), values that are comparable to those of state-of-art Tower Plants based on steam turbines. According to Turchi et al. (2019), commercial Tower Plants have specific costs ranging from 3300 to 6200 $/kW, with TES sizes from 6 to 15 hours. For example, Noor III has a specific cost of 5847 $/kW with 7 hours TES and the Shouhang Dunhuang Phase II plant sits at 4581.5 $/kW with 11 hours storage capacity. The same report also states that the Tower Plant under-development will have a specific cost lower than 5500 $/kW.

The authors of this work have calculated the specific cost of the main subsystems of a SoA Tower Plant (solar field, TES and Power Block) using either steam turbines or sCO_2 technology, for two sets of minimum and maximum cycle temperatures: for two levels of 25/50ºC and 550/700ºC respectively. The cost of the solar field have been obtained from Crespi et al. (2020b), the cost of the solar receiver and tower from Meybodi et al. (2017), the cost of the TES for the SoA case from Crespi et al. (2020b) and from Alfani et al. (2020) for the advanced plant. Cost correlations for the various equipment in the CO_2 power block are taken Carlson et al. (2017) and Weiland et al. (2019), the cooling tower for the ISO case from Crespi et al. (2020b), and the power block using steam turbines from Solar Advisor Model (2021). A solar multiple of 2.4 and 15 hours TES capacity have been assumed in all cases, which are foreseeable values in future CSP plants.

With regard to the primary economic drivers, the cost of the solar field depends strongly on thermal efficiency. The higher this is, for a set solar multiple, the lower aperture area (number of heliostats) is needed. Again, at 550ºC TIT, the benefits of adopting sCO_2 cycles are quite limited or, as it can be seen for the high ambient temperature case, even detrimental. If advanced Tower

Plants with sCO_2 are compared to SoA steam turbines, the cost savings in the solar field achieved by sCO_2 cycles are 17.6% and 13% for the ISO and 35ºC cases, respectively. This confirms the decreasing interest in sCO_2 technology as ambient temperature increases.

The cost of the Thermal Energy Storage is driven mostly by the volume of Heat Transfer Fluid (HTF) stored, which in turn depends on cycle efficiency, temperature difference between hot and cold tanks (a conventional, two-tank system is assumed) and, obviously, the thermophysical properties of the storage medium. For SoA Tower plants, the use of Solar Salt is extended. In steam turbine power plants using central receiver technology, the temperature difference between tanks is standardized to 284ºC (575ºC minus 290ºC). For sCO_2 cycles, this parameter is approximated to the temperature rise across the solar receiver and it is significantly smaller than in a steam turbine. Therefore, a balance between thermal efficiency and temperature rise across the solar receiver must be found in sCO_2 systems, as a consequence of which more efficient systems may require more expensive storage systems. This is seen in the ISO case, whose TES is 8% more expensive for sCO_2 than for steam turbines in spite of the higher thermal efficiency.

The situation depicted in the paragraph above becomes more interesting when advanced Tower Plants are studied, since conventional Solar Salts cannot be employed for they degrade at temperatures higher than 575ºC or so. A new storage medium that is thermally stable at 700-800ºC is therefore needed, which in this work is the ternary salt $MgCl2/KCl/NaCl$ (Wang et al., 2021), able to reach 720ºC and with a moderate cost also (0.22$/kg (Turchi et al., 2018)[1]).

The change in the HTF has nevertheless a negative impact on the economics of the thermal energy storage system, whose cost almost doubles in spite of the higher cycle efficiency and temperature rise across the receiver. The TES cost increases from 855 $/kW to 1539 $/kW and from 1327 $/kW to 2234 $/kW in the ISO and high-temperature cases respectively, an increase that threatens to offset the cost reduction achieved in the solar field. Actually, from a global standpoint, the development of new and affordable technologies for the solar and energy storage subsystems is one of the major challenges faced by advanced, high temperature Solar Tower plants.

The results obtained for the Power Block for sCO_2-based CSP plants in locations with high ambient temperatures are not promising either. When minimum cycle temperature rises, the Recompression Cycle suffers from a lower specific work and higher energy recovery, both of which have a negative impact on component size (and cost). Furthermore, the situation does not improve either with higher turbine inlet temperatures: despite the increase in specific work, the high material requirements raise the cost of the high temperature recuperator and, more importantly, the turbine, both equipment leading to a similar or slightly higher specific cost than in the 550ºC case. Of course, this is based on the cost correlations used and is subject to change in the future as more information about component cost becomes available; nevertheless, still with these caveats, the need for cost-effective, higher-grade materials stems as another major challenge faced by sCO_2 technology in general.

---

[1] Other solar subsystems based on falling particles or gas receivers are also actively being researched but they are not considered in this work.

The main conclusion of this discussion is therefore that the superiority of sCO_2 cycles over steam turbines for CSP applications is still unclear. This is not only because the current economic estimates yield costs that are similar to those of SoA steam plants -since these costs are expected to fall as the technology develops further, in particular in terms of market deployment- but because the thermal efficiency gains under realistic boundary conditions are not that high; i.e., the potential limits found by CSP-sCO_2 plants are intrinsic to sCO_2 technology.

		ISO (Tamb = 15ºC)			**Tamb = 35-40ºC**		
		Steam	**sCO2**	**SCARABEUS**	**Steam**	**sCO2**	**SCARABEUS**
Solar Field	SoA Tower Plant	1534	1482	1486	1655	1690	1631
	Advanced Tower Plant	X	1263	1273	X	1441	1396
Thermal Energy Storage	SoA Tower Plant	790	855	750.4	827.8	1327	895
	Advanced Tower Plant	X	1539	1422	X	2234	1745
Power Block	SoA Tower Plant	1000 - 1300	867.1	818.7	1000 - 1300	1110	958.4
	Advanced Tower Plant	X	933.5	910.2	X	1269	953.3

Table 3. Cost breakdown ($/kW) of each CSP plant concept into Solar Field, TES and Power Block of SoA and Advanced Tower Plants. Two ambient temperatures (ISO conditions and 35ºC) and three power block technologies (steam turbine, Recompression sCO_2 and SCARABEUS) are considered.

NEED FOR NEW TECHNOLOGIES RESISTANT TO AMBIENT TEMPERATURE

The SCARABEUS project aims to develop an innovative sCO_2 power cycle able to achieve high efficiencies even in environments with high ambient temperature, specifically tailored to Concentrated Solar Power plants. The underpinning idea of such concept is to revert the trend followed by conventional sCO_2 for increasing ambient temperatures, as described in the foregoing section. To this end, the working fluid is modified through the addition of specific dopants/additives to the raw sCO_2 stream, thereby shifting the critical temperature of the resulting mixture to higher values. This enables operating the compressor near the critical point, hence with much lower energy consumption, or even condensing the working fluid and performing compression in liquid state.

The concept is illustrated in Figure 2, showing the saturation line of pure Carbon Dioxide in orange. When the minimum cycle temperature is higher than 31ºC (orange dot on the curve), condensation with phase equilibrium is not possible anymore. However, by adding 20%(v) of hexafluorobenzene (C_6F_6), the saturation line of the resulting mixture shifts upwards (blue) and the new critical temperature of the working fluid is 122ºC. With this customized working fluid, highly-efficient supercritical cycles with compression near the critical point at ambient temperatures as high as 40-45ºC are again possible.

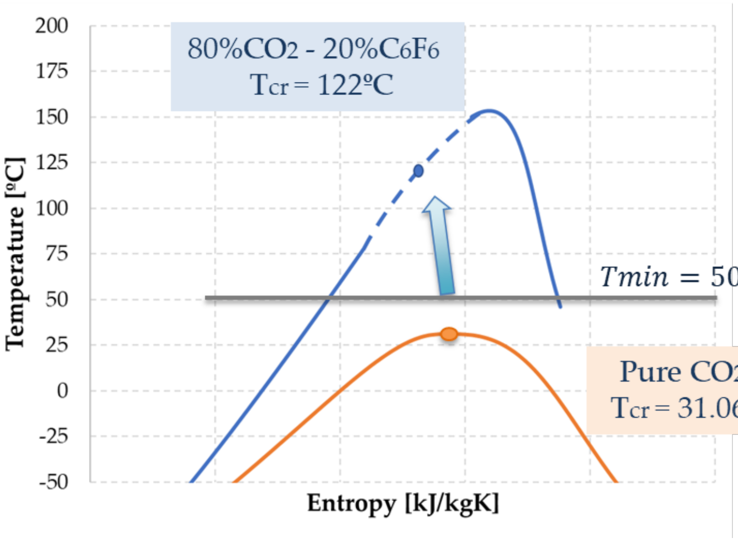

Figure 2. Changes in the saturation line of raw carbon dioxide and a mixture of 80%(v) sCO_2 and 20%(v) C_6F_6.

POTENTIAL OF sCO_2 MIXTURES

The adoption of the SCARABEUS concept in Concentrated Solar Power plants has been studied in recent years. Manzolini et al. (2019) studied two different CO_2 mixtures, CO_2-$TiCl_4$ and sCO_2-N_2O_4, in a Recuperated Rankine embodiment. They concluded that this innovative technology outperformed the Recompression Cycle with pure CO_2 both in terms of cycle efficiency (>2 p.p.) and specific cost of the power block (20% reduction). Crespi et al. (2021a, 2021b, 2022) investigated these and other mixtures -CO_2-C_6F_6, CO_2-$TiCl_4$ and CO_2-SO_2- considering different concentrations of the additives and multiple advanced transcritical cycle configurations. The authors found that (i) there exists a minimum dopant molar fraction to enable condensation, setting a lower bound for the optimization of molar composition; (ii) the cycle layout that brings about larger thermal efficiency gains depends only on the dopant considered; (iii) if the right cycle configuration is selected, thermal efficiencies higher than 50% for the reference boundary conditions (minimum/maximum cycle temperatures set to 50ºC/700ºC) are achievable for the three dopants studied; and (iv)the optimum molar fraction does not depend on maximum cycle temperature but on minimum cycle temperature only.

This information is shown numerically in Tables 2 and 3, under the header SCARABEUS, for a power cycle using a Recompression Cycle with a working mixture comprised of 70% CO_2 and 30% SO_2. Two comments are noteworthy in Table 2. First, the thermal efficiency of the SCARABEUS concept in a plant running at 400ºC or 550ºC maximum cycle temperature is not higher than that of steam turbines. Second, the SCARABEUS cycles perform worse than a conventional Recompression cycle with pure sCO_2 in ISO conditions but better than the latter at high ambient temperature. This last observation confirms that pure sCO_2 cycles are inherently better at lower ambient temperature whereas the customized working mixture is a better option in warm environments. Moreover, for a given ambient temperature, a tailored working fluid can be developed so as to enable the largest efficiency gains possible.

Regarding the economic analysis in Table 3, the SCARABEUS concept in advanced Tower Plants and high ambient temperatures benefits from a very high thermal efficiency and from a relatively high temperature rise across the solar receiver (higher than a Recompression with pure sCO_2). The former metric enables a reduction of 15.7% in the cost of the solar field with respect to a power plant using SoA steam turbines, which is in contrast with the 12% achieved by the pure sCO_2 option. The second metric helps reduce the size of the TES system, thus compensating for the impact of the more expensive, higher temperature storage medium. Also, it has to be pointed out that thermal efficiencies higher than 50% can only be achieved with pure CO_2 if reheating and/or intercooling are added to the standard Recompression Cycle. On the contrary, high efficiency systems with simpler layouts are possible when the SCARABEUS concept is used. All the foregoing comments, supported by the calculated specific costs -and conscious of the large uncertainty inherent to the available cost correlations-, anticipates that the SCARABEUS technology can significantly improve the economic figures of merit of CSP plants in arid locations.

CHALLENGES IN THE DEVELOPMENT OF CYCLES RUNNING ON CO_2 MIXTURES

CO_2 blend development

The selection of dopants and the characterization of the properties of the resulting mixtures is the core of this technology. The activities carried out by the SCARABEUS consortium in this area are (i) to identify the most promising additives, (ii) determine the thermodynamic properties of the CO_2 mixtures and (iii) demonstrate the thermal stability at high temperatures. The ideal mixture must comply with the following desired attributes:

- Miscibility with carbon dioxide.
- High enough critical temperature to enable condensation at high ambient temperature.
- Long-term thermal stability at maximum operating temperatures up to 700ºC.
- Not too high critical pressure as this has a direct impact on operating pressures and, therefore, system cost.
- Safety in terms of toxicity, flammability and reactivity, as well as environmentally friendliness.
- Positive impact on cycle efficiency (performance enhancement).
- Cost-effectiveness (positive impact on system economics).

It is of course highly unlikely for a dopant to fulfill such a large and diverse list of requirements. Therefore, the selection of the most promising fluid results from the analysis of multiple criteria and this is not a trivial process. For instance, the potential thermal performance attained by each dopant (more precisely, the corresponding mixture with CO_2) cannot be evaluated for a reference cycle like Recuperated Rankine. Rather, different dopants would yield large performance gains when used in different layouts, thus opening up a wider design space (more on this in the following subsection). Moreover, not only are the aforementioned attributes difficult to evaluate, but they are subject to a large uncertainty too. To assess the thermodynamic suitability of the studied mixture, a fluid model (i.e., Equation of State) is required. Unfortunately, though, the catalog of possible EoS is large, thus the best-fitting model cannot be deduced beforehands. Furthermore, as the working fluid is comprised of more than one substance, a Binary Interaction Parameter (BIP) accounting for the interaction between both components has also to be calibrated based on experimental VLE data, which are not always available. For these reasons, the fluid model for each candidate working fluid can only be determined with certainty through experimental tests (Di Marcoberardino et al., 2020), and this is a costly methodology for a first selection (screening) of dopants. This yields a critical chicken-and-egg problem in the development of the SCARABEUS technology where accurate thermodynamic properties are needed in order to evaluate the thermodynamic performance of a candidate working fluid, hence to enable the selection of the most interesting dopants, but, at the same time, these experimental data can only be generated (economically) for mixtures that have already been selected. The only way to break this loop is to make some reasonable assumptions about the fluid models to enable preliminary calculations; for instance, simple cubic Equations of State such as Peng-Robinson or Soave-Redlich-Kwong are adequate for this purpose. Also, the impact of binary interaction parameters cannot be overlooked, but this can be solved preliminarily through simple uncertainty analysis in the absence of optimized values (Di Marcoberardino et al., 2022).

In addition to the aspects raised in the previous paragraph, other trade-offs that are hard to balance refer to the conflicts between toxicity, flammability, reactivity and environmental impact. With all this, six candidate dopants were originally selected within the SCARABEUS consortium, as a result of a thorough literature review: C_6F_6, $TiCl_4$, SO_2, HCl, N_2O_4 and C_4F_{10}. Amongst this, those substances known to be not thermally stable beyond 300-400ºC were directly ruled out from the study, reducing the list to C_6F_6, $TiCl_4$ and SO_2. For these, experimental data were obtained in specific facilities able to perform measurements in the Vapor-Liquid Equilibrium (VLE) region, which enable the construction of the Andrew's curve of each mixture. Then, multiple fluid models (Standard Peng-Robinson, Lee-Kesler Plöcker, PC-SAFT and Refprop's Helmholtz free energy methods to cite some) were calibrated and compared.

Thermal stability of the dopant is of primary importance. This is represented by the temperature above which, the main characteristics of the fluid start to change irreversibly. This is usually accompanied by partial decomposition, which may eventually harm cycle performance and, very importantly, bring about mechanical integrity (materials) problems within the main components of the power block, such as heat exchangers and fluid machinery. Unfortunately, the information available in open literature for these innovative working fluids is scarce and scattered. This means that thermal stability can only be evaluated through experimental tests, which may involve some risk due to the reactivity and other hazards of the candidate dopants.

The thermal stability test is assessed through experimental tests where the mixture sample, confined in a vessel, is heated up in steady-state conditions at different operating temperatures for a limited period of time. The fluid degradation is then assessed by comparing the behaviour of the fluids along curves at constant specific volume (isochoric lines) before and after each thermal stress tests at high temperature, measuring two main thermodynamic properties, pressure and temperature. The deviations of the isochoric line with respect to the reference obtained from the fresh fluid, caused by the thermal decomposition, are evaluated both at high temperatures, during the thermal stress tests, and at temperature close to ambient conditions.

The test circuit for the SCARABUES project is shown in Figure 3 together with a picture of the Fluids test lab facility. The test circuit consists of one sample cylinder (A), 4 needle valves (B), 2 pressure transmitter (C), one fitting (D) for the connection with the fluid or helium bottles or with the vacuum pump and 1 thermocouple (it is not shown in the figure) that is put in contact with the sample cylinder externally. The needle valves position (on/off) allows to: (i) loading the sample and close the circuit during the tests (valve B4), (ii) use or not the pressure transmitter C1 (valve B2) with a maximum full scale of 10 bar, (iii) use or not the pressure transmitter C2 (valve B3) with a maximum full scale of 10 bar, (iv) disconnect the sample cylinder (valve B1) with the investigated sample at the end of the test. The test circuit is enveloped by the electric heaters (and thermally insulated with mineral wool) as represented with a dashed red line in Figure 3.

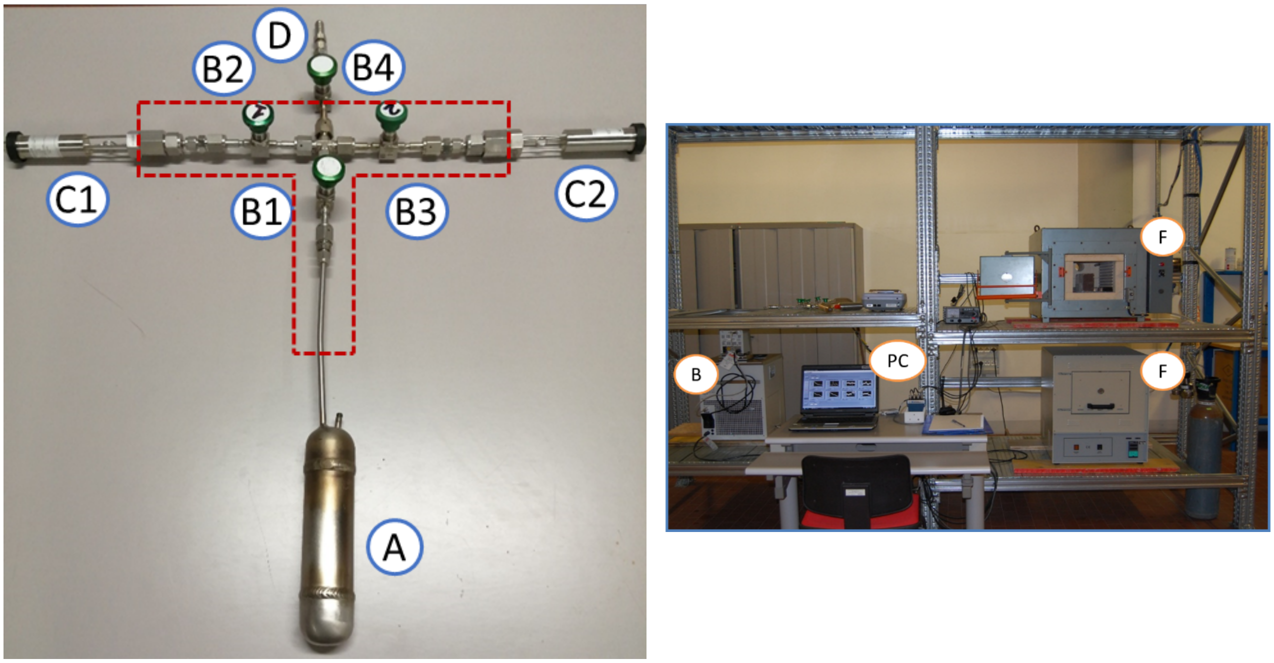

Figure 3. Test circuit and Fluids test lab picture: (F) muffle furnace, (B) thermostatic bath, Julabo FP 40, (PC) personal computer for the data acquisition and the system control.

As an example, preliminary results of thermal stability test for a fresh mixture of CO_2 + $TiCl_4$ with a CO_2 content of 85% are discussed. The dopant was charged in the sample cylinder, at sub-atmospheric pressure, thanks to a calibrated syringe, then the test circuit was placed in the thermostatic bath at 0°C and connected to the CO_2 bottle for the loading phase. The experimental procedure starts with the analysis of the mixture behaviour at different operating temperature defining the reference isochoric line. After that, different thermal stress tests at steady-state condition are carried out in an electric oven at high temperatures, followed by the measure of the isochoric line. In particular, the experimental test conditions of the investigated mixture are summarized in Table 4. At the end of each activity, no change on test circuit weight was detected.

Table 4. CO_2+ $TiCl_4$: Thermal stability test conditions

Isochoric Lines			**Thermal Stress**		
T [°C]	ΔT_{step} (°C)	$Time_{step}$ (min)	T (°C)	ΔT_{step} (°C)	$Time_{step}$ (h)
25 ÷ 295	15	15	450 ÷ 500	50	100

The comparison of the new isochoric line after each thermal stress test with respect to the reference curve allows the identification of potential decomposition phenomena. The qualitative method can reveal if the deviation of one or more p,T points after each thermal stress test (including its uncertainty) stands outside the reference isochoric limits that are calculated by fitting the experimental data with both uncertainties in x data and y data (gray dashed lines in Figure 4). The uncertainty takes into account both the systematic error due to the instrument accuracy (Type B standard uncertainty) and the statistical error due to the experimental standard deviation of the mean value (Type A standard uncertainty). Small pressure deviations, within the reference isochoric line region, can be noticed for some p,T points after the two thermal stress test at 450 and 500 °C in the two-phase region (in the range 50 – 130 °C), as shown in the bottom part of Figure 4, and at high temperature in the gas phase region. These results suggested that the investigated mixture can be considered thermally stable at least up to 500 °C. Further thermal stress tests at higher temperature will reveal if the thermal stability could be extended to higher temperatures.

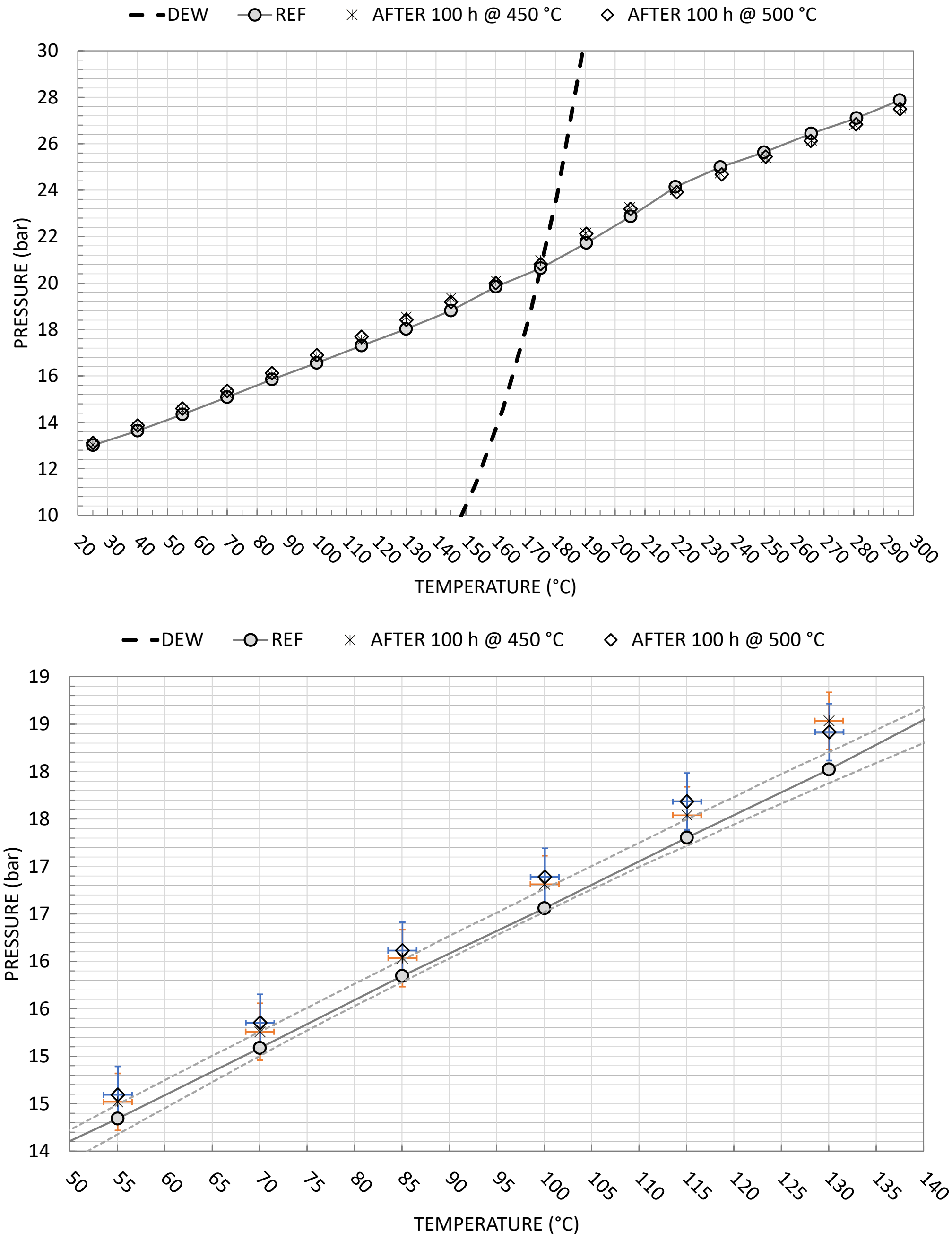

Figure 4. CO2+ TiCl4 mixture: Isochoric behaviour reference & after each thermal stress test (top) – Two phase phase behaviour zoom (bottom). Dashed grey lines represent the uncertainty of the reference isochoric line.

Cycle analysis

The objective of cycle analysis is to produce the specifications of the optimum power plant balancing multiple figures of merits such as thermodynamic performance, economics or environmental impact, hence accomplishing the different targets of the projects. The study of the innovative power cycles based on CO_2 mixtures requires for specific tools able to consider new working fluids and to have sensitivity to changes in the molar fraction of each component. This limits the number of commercial software available to study such systems. In the SCARABEUS project, a new functionality for the Thermoflex Software was developed in collaboration with Thermoflow Inc. to enable the creation of user-defined fluids, whose characteristics were incorporated through look-up tables (LUT) collating the information obtained in the aforesaid test campaign. The utilization of look-up tables overcomes the limitation set by the selection of one particular EoS, since LUTs can be adopted with different fluid models. The results obtained from Thermoflex were compared against similar simulations performed on Aspen Plus, showing satisfactory results.

The body of scientific knowledge in the field of supercritical CO_2 power cycles is quite broad. In the main, the Recompression Cycle is acknowledged as the most interesting option, both for thermal efficiency and feasibility, at least when pure Carbon Dioxide is used. Nevertheless, the analysis carried out by the consortium confirmed that, when CO_2 mixtures are used, other cycle layouts yield higher efficiency. Actually, the cycle layout of interest depends on the composition of the dopant, what means that the optimization of cycle topology has to be performed individually for each dopant since the location and magnitude of cycle irreversibility differ from one CO_2 mixture to another (Crespi et al., 2021b). In general, the changing nature of the working fluid (multiple dopants with variable molar composition) adds a new dimension (degree of freedom) to cycle analysis in comparison with the sCO_2.

The optimum molar composition of mixtures based on different dopants is also tightly linked to ambient temperature, according to findings by some of the authors in previous works (Crespi et al., 2021a). This opens the gate for the tailorability of this technology to different locations even though, at the same time, this can also be a major shortcoming for industrial deployment and standardization. Indeed, contrary to the optimization of power blocks operating on pure sCO_2, which only affects operational variables like pressures or mass flow rates, the optimization of the SCARABEUS power blocks takes into consideration the composition of the working fluid itself. In other words, technology development is potentially case-specific for each location since changes in the molar composition, even for the same dopant, have an impact on the design of turbomachinery and heat exchangers.

Turbomachinery Design

The development of innovative turbomachinery designs, able to operate on CO_2 mixtures with high efficiency, is a mandatory requirement of SCARABEUS, given that cycle efficiency is sensitive to turbomachinery performance, especially the turbine. Unfortunately, the range of possible dopants is very wide and their natures are largely different. This implies that turbomachinery designed for pure CO_2 would perform poorly with CO_2 mixtures, setting a need to develop detailed models in order to accurately design these machines and also to estimate the associated cost, crucial for the techno-economic optimization of the plant. Indeed, recent publications by the team at City University of London demonstrate the very strong dependence of turbine geometry on dopant composition and molar fraction (Aqel et al., 2021b). With this regard, Figure 5 compares the sizes of optimum turbine design, obtained with a preliminary mean-line design model, for four different working fluid: pure CO_2, CO_2-$TiCl_4$, CO_2-SO_2 and CO_2-C_6F_6. This figure evinces very large discrepancies in terms of turbine diameter and length between the three mixtures against the CO_2 case, especially for mixtures formed with Titanium Tetrachloride and Hexafluorobenzene, up to 90% higher length and 24% smaller diameter. Furthermore, Figure 6 shows the influence of varying the dopant molar fraction on the rotor blade profile of a four-stages axial turbine. An impact on blade height and blade chord length is notorious for the three mixtures.

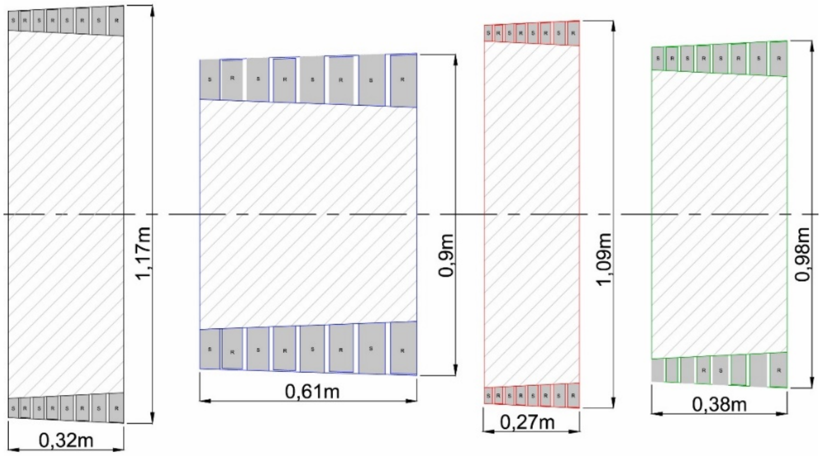

Figure 5. Comparison of optimum turbine flow path meridional view for pure CO_2, CO_2-$TiCl_4$, CO_2-SO_2 and CO_2-C_6F_6 mixtures (left to right). Retrieved from Aqel et al. (2021b).

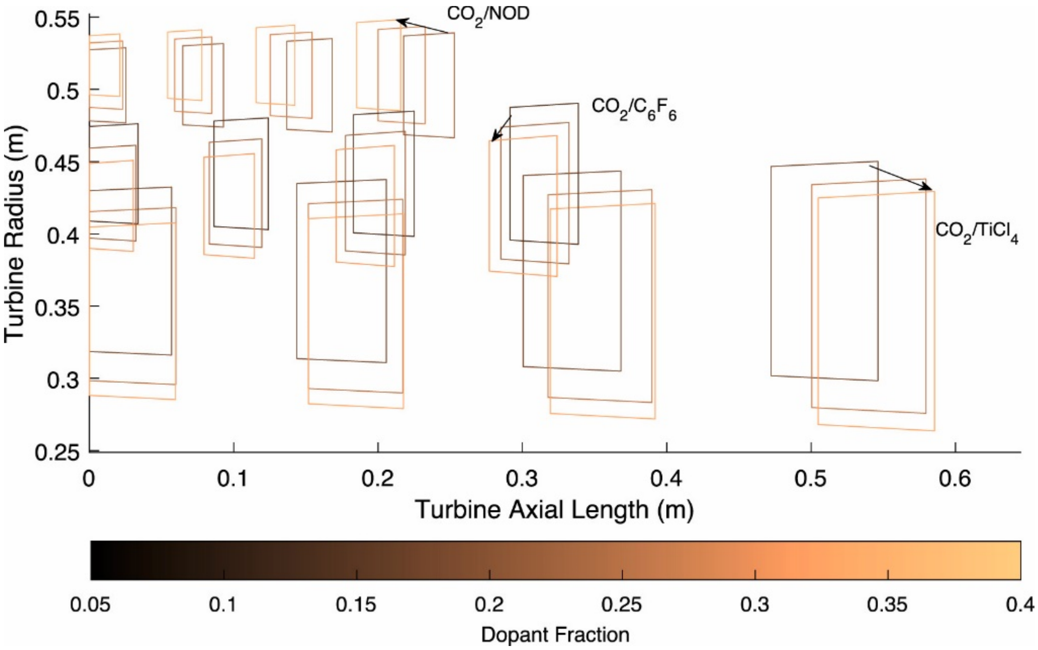

Figure 6. Changes in rotor blade profiles with molar fraction. Retrieved from Aqel et al. (2021b). NOD (Non-organic dopant) refers to SO_2.

Based on this, the interconnection between turbomachinery design and cycle analysis becomes self-evident, giving way to an iterative problem where cycle analysis provides the boundary conditions for turbomachinery design and turbomachinery design provides efficiencies of the pump, compressors and turbines that, in turn, determine cycle performance. This is complemented by the molar composition of the working mixture which has a strong impact on cycle performance and turbomachinery design at the same time. Moreover, this optimization problem is even more complex if the uncertainty regarding fluid model is also taken into account since the optimum molar composition changes when the Equation of State or the Binary Interaction Parameter vary. This is illustrated in a sensitivity analysis of turbine design to the characteristics of the EOS and BIP, recently published by City, University of London for SCARABEUS (Aqel et al., 2021a).

The foregoing considerations are very relevant for the analysis of cycle performance and turbomachinery design in rated conditions. Nevertheless, the production of performance maps sensititive to changing inlet conditions is critical to obtain accurate estimates of off-design performance. This is critical for the compressors operating near the critical point given the (potentially) wild variation of fluid properties across the machine, and also at the inlet to it when ambient conditions change. Fortunately though, the SCARABEUS concept raises the critical temperature of the working mixture and alleviates this problem, ensuring that inlet conditions to the compressor can be kept fairly constant throughout the year. Moreover, this feature of SCARABEUS also enables condensation of the working fluid, in which case, a pump and not a compressor is needed downstream of the heat rejection unit. Pumps for pure CO_2 are, unlike compressors, commercially available as they are frequently used by the O&G industry. Therefore, the challenge remains to select/design the appropriate pumping equipment from the currently available portfolio, or based on the current design rules used by the industry, but new knowledge does not seem to be needed. Final tuning/modification does nonetheless seem to be unavoidable.

Heat Exchanger design

The low enthalpy change across the compressor and turbine of a sCO_2 cycle offers a large potential for internal heat recovery, hence thermal efficiency increase. Nevertheless, this sets a need for highly effective, low cost heat exchangers (recuperator) which can take advantage of said potential without compromising the economics of the plant. Amongst the various heat exchanger technologies that can be used, Printed Circuit Heat Exchangers (PCHEs) are suitable for pure sCO_2 and for sCO_2 mixtures, owing to their capacity to withstand high pressures and temperatures. Diffusion bonded heat exchangers offer probably the most compact solution using very small channels (hydraulic diameter of approximately 1mm) and extreme resistance for high pressure applications. They are composed of plates integrally welded by diffusion bonding, which is a solid state joining process (pressing at high temperature). The manufacturing process of printed circuit heat exchangers also involve photochemical etching which uses strong chemical etchants to remove unwanted work piece material by controlled dissolution. PCHE are highly compact heat exchangers and are capable to operate in a temperature range of 200 – 900 ºC and can cope with pressures up to 1000 bar. Several technologies as shell and tube heat exchangers, propose densities of 700 m^2/m^3, while the diffusion bonded heat exchangers can even reach 1400 m^2/m^3.

In order to develop PCHEs with these features (high effectiveness and low cost), the internal geometry of the HX must be optimized either with existing designs or with advanced designs bringing about higher heat transfer coefficients. In order to evaluate the influence of new shapes on thermal-hydraulic performances, CFD simulations have been performed to create Design of Experiments (DOE). An example is provided in Figure 7. Then, initial surrogate models have been created based on inputs and results from the DOE. A surrogate model is a compact scalable analytic model that approximate the multivariate input/output behaviour of complex systems. This model mimics the complex behaviour of the underlying simulation model, and can be used for parametric studies, optimization and sensitivity analysis. The Multi-Objective Genetic Algorithm method (MOGA) is used for the optimization because it is possible to define multiple objectives (as surface reduction, heat exchange surface, pressure losses, etc.) to find the best suited configuration with the created surrogate models. Till the objectives criteria is not reached, this iterative method updates the surrogate models. A total of 3000 initial samples and a maximum of 20 iterations are used for optimising the Recuperative Heat Exchanger in order to find the best cost-effective solution. The recuperator specifically tailored and manufactured for Scarabeus project, designed to operate with pure sCO_2, is shown in Figure 8. Its dimensions are 890mm length and 580mm width, for an empty weight of approximately 130 kg.

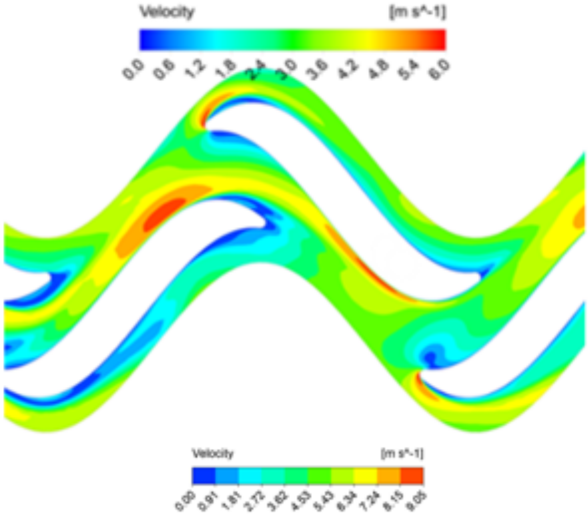

Figure 7. Example of CFD simulation employed to design a S-shape PCHE.

Figure 8. Photo of the SCARABEUS heat recuperator for pure sCO_2, designed and manufactured at Kelvion Thermal Solutions laboratories.

Whichever the case, the utilization of sCO_2 mixtures brings about a large amount of uncertainty, for the reasons discussed above with regard to the modelling of fluid properties. Indeed, according to some analysis, the difference between theoretical and actual (cooling) heat transfer coefficients (Nusselt number) on a horizontal plate in contact with sCO_2 can be higher than 60%, depending on the correlation and reference temperature used, and this can only get worse when the properties of the working fluid are not known accurately (Kruizenga, 2012).

The nature of the innovative working fluids considered in SCARABEUS entails several challenges for heat exchanger design. Contrary to supercritical CO_2 cycles, an air-condenser instead of an air-cooler may be needed for heat rejection. As the working fluid is formed by a mixture of two species, phase change occurs in a range of temperatures called temperature glide (i.e., temperature difference between dew and bubble points). Consequently, the composition of the vapor and condensate vary during condensation, with the former having a higher concentration of the more volatile species. This brings about some concerns regarding the operability of these components, which will have to be addressed during the development of the technology. Indeed, the large glide of some mixtures results in thermodynamic cycles where condensation starts inside the low temperature recuperator. This is very challenging for recuperator design but, at the same time, it helps alleviate the irreversibility inherent to the internal heat recovery: the rise in heat capacity taking place in the high pressure stream due to the vicinity of the critical point is counterbalanced by a rise in that of the low pressure stream thanks to condensation.

System Integration

Challenges entailed by closed power cycles running on sCO_2 mixtures are similar to those found in pure sCO_2 systems. That does not mean this is not an issue for further research and development but, on the contrary, it highlights that the list of open questions does nothing but increase in length. For instance, the best arrangement of turbomachinery and heat exchangers to enhance flexibility (operability) and reliability. Additionally, the integration with the solar subsystem (i.e., power block atop of the solar tower or at ground level, receiver technology, direct coupling or intermediate heat transfer fluid, number of hours of storage to minimize start-ups and shutdowns) is still an open discussion. Balance of Plant cannot be overlooked either as it brings the most salient challenges with regard to the handling and management of the working fluid. The subsystem ensuring constant composition of the working mixture and/or making up for the working fluid that leaks into the atmosphere, or that compensating for the effects of using pure CO_2 in the dry gas seals of turbines and compressors are yet to be defined. Along the same lines, the configuration of the auxiliary system and the procedures followed to keep the turbine warm during shutdown, to avoid CO_2 condensation if the time before startup becomes too long (sCO_2 cooling down to room temperature at potentially supercritical pressure) or to pressurize and purge the system in case internal pressure is let to fall well below the critical pressure have not been studied yet.

For regular off-design operation, control strategies are also included within the scope of System Integration. sCO_2 power plants are very interesting (in general, all closed cycles gas turbines) for their potentially high part load efficiency, therefore the same behavior is expected for sCO_2 mixtures. Nevertheless, the optimum operating strategies are still unclear since they largely depend on the integration layout and the configuration followed to drive compressors and pumps. Multiple control strategies have been reported in literature to manage different characteristics of the cycle, including part-load efficiency and also safe operation of components: compressor inlet temperature can be controlled through the cooling flow rate at the condenser/cooler, a cooler bypass or both; compressor surge margin can be guaranteed by the compressor flow split (in configuration with split-compression), or compressor bypass; turbine output can be control by means of a turbine flow bypass, turbine flow throttling, inventory control or speed control (White et al., 2021). All these operating strategies are, at the same time, inherently linked to the cycle layout. For pure CO_2, the main body of research has focused on the Recompression Cycle but, within the scope of SCARABEUS and as indicated before, the best-performing layout depends on the CO_2 mixture selected, thus the development of such strategies is case-specific, exacerbating (again) the challenges on technology development and standardization.

SUMMARY AND CONCLUSIONS

This paper has presented a summarized discussion of the main challenges that are faced by the utilization of Carbon Dioxide mixtures in supercritical power cycles. This concept is specific to applications in warm/hot environments since, as already discussed by the authors elsewhere, there are no benefits to using such working fluids in applications where the cycle can be cooled to very low temperatures. In these cases, supercritical power cycles using pure CO_2 are more efficient.

Concentrated Solar Power is of interest in locations with a high availability of solar energy throughout the year (more specifically, Direct Normal Irradiance). Unfortunately, these locations are mostly found in places with high to very high ambient temperatures and little availability of cooling water. In these conditions, sCO_2 cycles experience a dramatic performance drop and, in practice, steam turbines turn out more cost-effective and reliable. The addition of certain dopants to sCO_2 shifts the critical temperature of the resulting mixture to a higher value, hence counteracting the previous effect of ambient temperature on the performance of sCO_2 cycle. Two main benefits arise from this:

- Supercritical Power Cycles running on sCO_2 mixtures are able to attain higher than 50% thermal efficiency for ambient temperatures as high as 35-40%.
- The composition of the working mixture, and the associated cycle layout, can be tailored to the boundary conditions of the plant, hence maximizing the efficiency at that particular location.
- The large efficiency gain enables reducing the aperture area of the solar field, hence the main contribution to total plant cost.

These opportunities do nevertheless not come without a cost. The paper has highlighted some of the most visible challenges faced by the consortium developing the concept. At the core of this development, the lack of accurate tools to characterize the working fluid brings about a large amount of uncertainty with respect to which the most interesting working mixture is for each case. This applies to both composition and concentration of the dopant. Further to this, the very large flexibility of the SCARABEUS concept enables attaining the maximum efficiency for each specific project but, at the same time, it poses two additional challenges, namely (i) standardization of the technology is compromised, since different locations may have different optimum configurations and component designs; (ii) the uncertainty about the characterization of the working fluid is carried over to the definition of cycle specs and component design, highlighting the critical importance of an experimental support of technology development.

NOMENCLATURE

BIP	Binary Interaction Parameter
CSP	Concentrated Solar Power

EoS	Equation of State
DNI	Direct Normal Irradiance
LCoE	Levelized Cost of Electricity
PCHE	Printed Circuit Heat Exchanger
SoA	State-of-Art
TES	Thermal Energy Storage
TIT	Turbine Inlet Temperature
Tmin	Minimum Cycle Temperature

REFERENCES

Alfani, D., Neises, T., Astolfi, M., Binotti, M., & Silva, P (2020). Techno-economic Analysis of CSP Incorporating sCO2 Brayton Power Cycles: Trade-off Between Cost and Performance.

Angelino, G. (1968). Carbon dioxide condensation cycles for power production.

a) Aqel, O., White, M., & Sayma, A. I. (2021). Binary interaction uncertainty in the optimisation of a transcritical cycle: Consequences on cycle and turbine design.

b) Aqel, O. A., White, M. T., Khader, M. A., & Sayma, A. I. (2021). Sensitivity of transcritical cycle and turbine design to dopant fraction in CO2-based working fluids. *Applied Thermal Engineering*, *190*, 116796.

Binotti, M., Marcoberardino, G. D., Iora, P., Invernizzi, C., & Manzolini, G. (2020). SCARABEUS: Supercritical carbon dioxide/alternative fluid blends for efficiency upgrade of solar power plants. In *AIP Conference Proceedings* (Vol. 2303, No. 1, p. 130002). AIP Publishing LLC.

Carlson, M. D., Middleton, B. M., & Ho, C. K. (2017). Techno-economic comparison of solar-driven SCO2 Brayton cycles using component cost models baselined with vendor data and estimates. In *Energy Sustainability* (Vol. 57595, p. V001T05A009). American Society of Mechanical Engineers.

Concentrating Solar Power Projects. NREL, 2021. Available online on: https://solarpaces.nrel.gov/ (accessed 24 Nov 2021)

a) Crespi, F., Sánchez, D., Martínez, G. S., Sánchez-Lencero, T., & Jiménez-Espadafor, F. (2020). Potential of supercritical carbon dioxide power cycles to reduce the levelised cost of electricity of contemporary concentrated solar power plants. *Applied Sciences*, *10*(15), 5049

b) Crespi, F. M. (2020). Thermo-economic assessment of supercritical CO2 power cycles for concentrated solar power plants.

a) Crespi, F., Martínez, G. S., Rodriguez de Arriba, P., Sánchez, D., & Jiménez-Espadafor, F. (2021). Influence of Working Fluid Composition on the Optimum Characteristics of Blended Supercritical Carbon Dioxide Cycles. In *Turbo Expo: Power for Land, Sea, and Air* (Vol. 85048, p. V010T30A030). American Society of Mechanical Engineers.

b) Crespi, F. Rodríguez de Arriba, P., Sánchez, D., Muñoz, A., & Sánchez, T. (2021). The Potential of Supercritical Cycles Based on CO2 Mixtures In Concentrated Solar Power Plants: An Exergy-based Analysis. In ORC Power Systems.

Crespi, F., de Arriba, P. R., Sánchez, D., Ayub, A., Di Marcoberardino, G., Invernizzi, C. M., ... & Manzolini, G. (2022). Thermal efficiency gains enabled by using CO2 mixtures in supercritical power cycles. *Energy*, *238*, 121899.

Di Marcoberardino, G., Invernizzi, C. M., Iora, P., Ayub, A., Di Bona, D., Chiesa, P., ... & Manzolini, G. (2020). Experimental and analytical procedure for the characterization of innovative working fluids for power plants applications. *Applied Thermal Engineering*, *178*, 115513.

Di Marcoberardino, G., Morosini, E., & Manzolini, G. (2022). Preliminary investigation of the influence of equations of state on the performance of CO2+ C6F6 as innovative working fluid in transcritical cycles. *Energy*, *238*, 121815

Klotz, H., Davis, K., & Pickering, E. (2009). Designing an ultrasupercritical steam turbine. *Power (New York)*, *153*(7).

Kruizenga, A., Li, H., Anderson, M., & Corradini, M. (2012). Supercritical carbon dioxide heat transfer in horizontal semicircular channels. *Journal of Heat transfer*, *134*(8).

Liu, M., Zhang, X., Yang, K., Wang, B., & Yan, J. (2019). Comparison and sensitivity analysis of the efficiency enhancements of coal-fired power plants integrated with supercritical CO2 Brayton cycle and steam Rankine cycle. *Energy Conversion and Management*, *198*, 111918.

Manzolini, G., Binotti, M., Bonalumi, D., Invernizzi, C., & Iora, P. (2019). CO2 mixtures as innovative working fluid in power cycles applied to solar plants. Techno-economic assessment. *Solar Energy*, *181*, 530-544.

Meybodi, M. A., Beath, A., Gwynn-Jones, S., Veeraragavan, A., Gurgenci, H., & Hooman, K. (2017). Techno-economic analysis of supercritical carbon dioxide power blocks. In *AIP Conference Proceedings* (Vol. 1850, No. 1, p. 060001). AIP Publishing LLC.

Purgert, R., Shingledecker, J., Saha, D., Thangirala, M., Booras, G., Powers, J., ... & Hendrix, H. (2015). *Materials for advanced ultrasupercritical steam turbines*. Energy Industries Of Ohio Inc., Independence, OH (United States).

Turchi, C. S., Vidal, J., & Bauer, M. (2018). Molten salt power towers operating at 600–650 C: Salt selection and cost benefits. *Solar Energy*, *164*, 38-46.

Turchi, C. S., Boyd, M., Kesseli, D., Kurup, P., Mehos, M. S., Neises, T. W., ... & Wendelin, T. (2019). *CSP Systems Analysis-Final Project Report* (No. NREL/TP-5500-72856). National Renewable Energy Lab.(NREL), Golden, CO (United States).

Wang, X., Rincon, J. D., Li, P., Zhao, Y., & Vidal, J. (2021). Thermophysical properties experimentally tested for NaCl-KCl-MgCl2 eutectic molten salt as a next-generation high-temperature heat transfer fluids in concentrated solar power systems. *Journal of Solar Energy Engineering*, *143*(4), 041005.

Weiland, N. T., Lance, B. W., & Pidaparti, S. R. (2019). SCO2 power cycle component cost correlations from DOE data spanning multiple scales and applications. In *Turbo Expo: Power for Land, Sea, and Air* (Vol. 58721, p. V009T38A008). American Society of Mechanical Engineers.

White, M. T., Bianchi, G., Chai, L., Tassou, S. A., & Sayma, A. I. (2021). Review of supercritical CO2 technologies and systems for power generation. *Applied Thermal Engineering*, *185*, 116447.

ACKNOWLEDGEMENTS

The SCARABEUS project has received funding from the European Union’s Horizon 2020 research and innovation programme under grant agreement Nº814985. The University of Seville is also gratefully acknowledged for supporting this research through its Internal Research Programme (Plan Propio de Investigación), under contract Nº 2019/00000359. Junta de Andalucía is gratefully acknowledged for sponsoring the contract of Pablo Rodríguez de Arriba under the Programme for Youth Employment 2014-2020 (Phase 4).