

# Investigation of CO<sub>2</sub> mixtures to overcome the limits of sCO<sub>2</sub> cycles

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**Abstract.** Supercritical CO<sub>2</sub> cycles are a promising technology, but their performance drops for hot cold source, in hot and arid environments, typical of a CSP field. The adoption of CO<sub>2</sub>-based mixtures as working fluid can turn supercritical CO<sub>2</sub> cycles into transcritical cycles even at high temperatures, with performance improvement and significant power block cost reduction. The concept is addressed within the SCARABEUS project, an EU funded Horizon 2020 project dedicated to the use of CO<sub>2</sub>-based mixtures for CSP plants. In this work, the use of the CO<sub>2</sub>+C<sub>6</sub>F<sub>6</sub> mixture as working fluid for a power cycle coupled with a solar tower is analysed. The potentiality of the mixture is presented, given its very low toxicity and its good thermal stability limits. Comparisons with the sCO<sub>2</sub> cycle is performed for some typical configurations, in order to underline the advantages of the mixture, and a preliminary design of the turbine is presented, developed in a 1D tool.

## 1 Introduction

Supercritical CO<sub>2</sub> cycles are emerging as a valid alternative to traditional steam cycles for a wide variety of applications [1]. Nevertheless, the compression step of pure CO<sub>2</sub> is quite critical, and the cycle efficiency is badly affected by the typical minimum temperature of the heat rejection unit, especially in hot and dry environment. Significant variations of the fluid thermodynamic properties are present around the critical point of CO<sub>2</sub> (31°C): operation-wise, this variability of fluid properties leads to difficulties in operating the system in off-design conditions [2]. In order to overcome these limits, an alternative to sCO<sub>2</sub> cycles can be represented by CO<sub>2</sub>-based blends: mixing CO<sub>2</sub> and a second fluid with a high critical temperature can increase the critical temperature of the overall mixture and turn a supercritical cycle into a transcritical one, at constant conditions of the cold and hot source. In this circumstance, the compressor would be replaced by a pump, with a significant reduction in compression work. Moreover, working with dopants with a higher molecular complexity can reduce the temperature differences in the recuperators, favoring simpler cycle configurations with respect to the more complex ones used in sCO<sub>2</sub> cycles, making easier to operate the cycle in all conditions and reducing the costs.

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This work focuses on the adoption of CO<sub>2</sub> blended with C<sub>6</sub>F<sub>6</sub> as working fluid for CSP application: it is part of the EU funded SCARABEUS project [3], which aims at demonstrating the technical feasibility of using innovative CO<sub>2</sub>-based binary mixtures as working fluid for CSP cycles, assuming to operate with an air cooled condenser in a hot and arid environment characterized by high ambient temperatures.

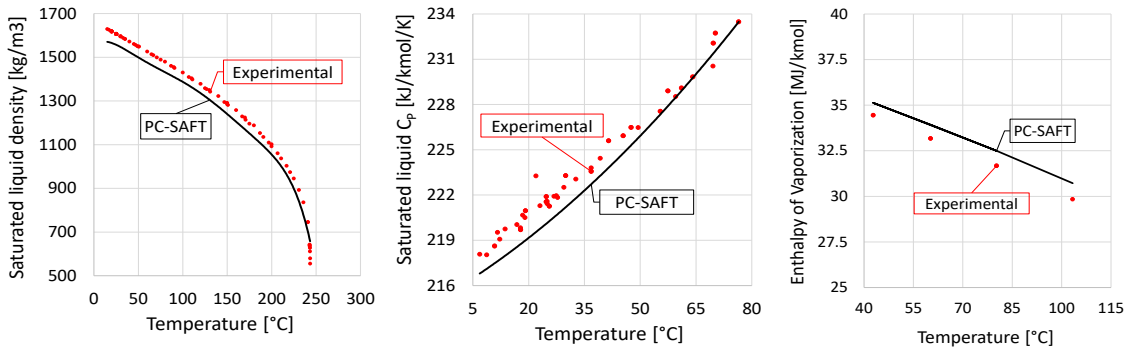
## 2 Characterization of the CO<sub>2</sub>-C<sub>6</sub>F<sub>6</sub> mixture

### 2.1 Characterization of the mixture with PC-SAFT EoS

In order to model the thermodynamic properties of a fluid, an Equation of State (EoS) is needed. In this work, the PC-SAFT EoS has been selected [4]. The parameters needed for the modeling of the pure components with the PC-SAFT EoS (embedded in the ASPEN PLUS environment, used in this work) are the segment number ( $m$ ), segment diameter ( $\sigma$ ), and segment-segment interaction energy ( $\epsilon/k$ ). They are regressed from experimental data of vapor pressure, saturated liquid density and constant pressure heat capacity at saturated liquid conditions for each of the pure components. Table 1 reports the parameters for both pure fluids. For C<sub>6</sub>F<sub>6</sub> a regression on experimental data was necessary. The results of the regression are presented in Fig 1: vaporization enthalpies were added in the optimization.

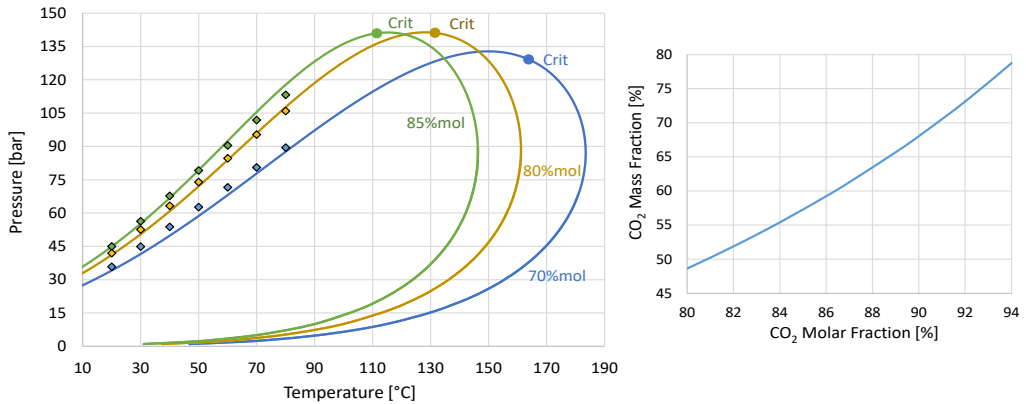
**Table 1.** PC-SAFT pure parameters  $m$ ,  $\sigma$  and  $\epsilon/k$  used in the ASPEN environment for CO<sub>2</sub> and C<sub>6</sub>F<sub>6</sub>

	$m$ [-]	$\sigma$ [-]	$\epsilon/k$ [°C]
CO <sub>2</sub>	2.569	2.564	-121.05
C <sub>6</sub> F <sub>6</sub>	3.779	3.396	-51.50



**Fig 1.** Comparison between experimental data and the modelled values by PC-SAFT of pure C<sub>6</sub>F<sub>6</sub>

Once the pure components are modelled, the EoS should be further optimized on the behavior of the mixture. Normally, vapor liquid equilibrium (VLE) data are used for the calibration of the EoS through the binary interaction parameters (BIP). For this mixture, a set of experimental VLE data (bubble points) are available in literature [5] for a wide range of temperatures and pressures. These data were useful to calibrate the BIP for this mixture with PC-SAFT EoS, resulting in a BIP of 0.04. Fig 2 reports the graphical representation of the fitted resulting bubble lines computed with PC-SAFT and optimized BIP, along with a representation of the relationship between molar content and mass content of CO<sub>2</sub> in the mixture. Once the VLE is optimized, the EoS can precisely identify the cycle minimum pressure and the phase composition along the whole condensation process.



**Fig 2.** PT curves of the CO<sub>2</sub>+C<sub>6</sub>F<sub>6</sub> mixture for various CO<sub>2</sub> molar fractions.  
Dots: Experimental data [5]. Curves and critical points: PC-SAFT, BIP=0.04 (left).  
Relationship between molar and mass fraction for the mixture (right)

## 2.2 Determination of the thermal stability of the CO<sub>2</sub>-C<sub>6</sub>F<sub>6</sub> mixture

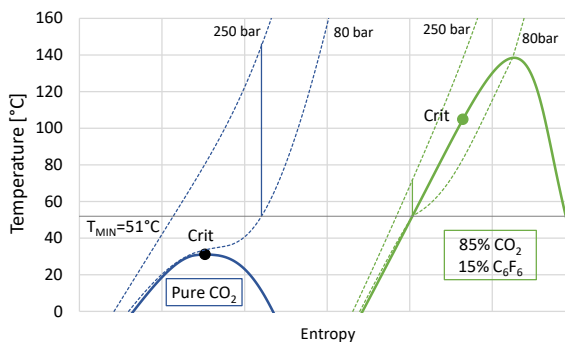
The choice of the proper working fluid to be adopted in closed cycles must take into account numerous factors: the fluid must be thermally stable up to the maximum cycle temperature, it must have a limited toxicity, it must be inert both with the metallic components of the cycle and with the environmental air in case of leakages. Moreover, a limited flammability and cost of the working fluid are positive aspects. The toxicity level of hexafluoro benzene (C<sub>6</sub>F<sub>6</sub>) is low (LC50=12488 ppm/2h), moreover it is liquid at ambient conditions and the volatility of the liquid in air is relatively low. Similarly, the flammability level of C<sub>6</sub>F<sub>6</sub> is relatively low and the fluid does not react with water, metals, CO<sub>2</sub> nor air.

The thermal stability of the fluid remains to be studied, as no references in literature are found for this fluid. For this reason, the thermal stability of various mixtures is studied within the SCARABEUS project. The resulting stability limit of the CO<sub>2</sub>+C<sub>6</sub>F<sub>6</sub> were tested successfully at least up to the maximum temperatures of interest for CSP cycle with solar salts as heat transfer fluid (HTF). The methodology used, nevertheless, can be explained referring to a previous work on the CO<sub>2</sub>+C<sub>6</sub>F<sub>14</sub> mixture [6]: the mixture is filled in a vessel and introduced in an isothermal thermostatic bath. The (P,T) conditions of the mixture are measured along an isochoric transformation, before the heating of the fluid (virgin mixture). Then, the mixture is heated for 100 hours up to the maximum temperature of interest, which covers the range of 450 to 700°C, depending on the fluid of interest, and then cooled down. The thermal stability is evaluated through a comparison between the pressures of the mixture in virgin conditions and the ones at the same temperatures after the heating phase: if the (P,T) behavior of the virgin fluid is mimicked after the heating phase, then the mixture can be considered thermally stable up to the maximum investigated temperature. From the reported experiments on CO<sub>2</sub>+C<sub>6</sub>F<sub>14</sub>, the mixture can be considered stable up to 400°C.

### 3 Influence of the mixture on the cycle compression phase

The adoption of binary CO<sub>2</sub>-based mixtures as working fluid in closed cycles, the idea developed within the SCARABEUS project, aims at overcoming the most critical aspect in the design and operation of sCO<sub>2</sub> cycle, which is the compression step. In sCO<sub>2</sub> cycles reducing the temperature at compressor inlet (minimum cycle temperature) is certainly beneficial for the cycle efficiency, but it brings the conditions at the inlet of the compressor closer to the CO<sub>2</sub> critical point (at 31°C), presenting significant difficulties both on the design and on the operation of the compressor, especially at off design conditions. In addition, considering instead higher cycle minimum temperatures (higher than 50°C, typical of the hot and arid environments of CSP power plants), the compression of CO<sub>2</sub> necessitates of a substantial power consumption, increasing drastically also the compressor outlet temperature. In order to overcome these issues, the adoption of CO<sub>2</sub>-based mixtures can represent a solution: mixing CO<sub>2</sub> and another fluid, with a higher critical temperature, can increase the critical temperature of the resulting mixture well over 50°C, thus ensuring liquid phase conditions at the inlet of the compression step. In this condition the compressor would be replaced by a pump, with a drastic reduction of the relative compression work and an increment of cycle efficiency.

Fig 3 depicts the Andrew's curve of the two different working fluids in a T-s diagram, highlighting an isentropic compression from 80 bar to 250 bar, starting from 51°C: from the figure it is possible to appreciate the position of the critical point of the innovative working fluid, well below the inlet of the compression step, which is fully in liquid conditions. If mixtures are used as working fluid, they can also be exploited to tailor the fluid behavior to the cold source: colder cold sources can exploit higher fraction of CO<sub>2</sub>, while more dopant is necessary for warmer cold sources. The research developed within the SCARABEUS project aims at finding the most suitable dopants for the CO<sub>2</sub>-based mixtures: these dopants should allow the condensation of the working fluids even for high minimum temperatures, exploit the use of the pump in the compression step, increase the cycle efficiency with respect to the one of pure sCO<sub>2</sub> cycles and, finally, reduce the specific cost of the power block due to a significant simplification of the cycle layout.



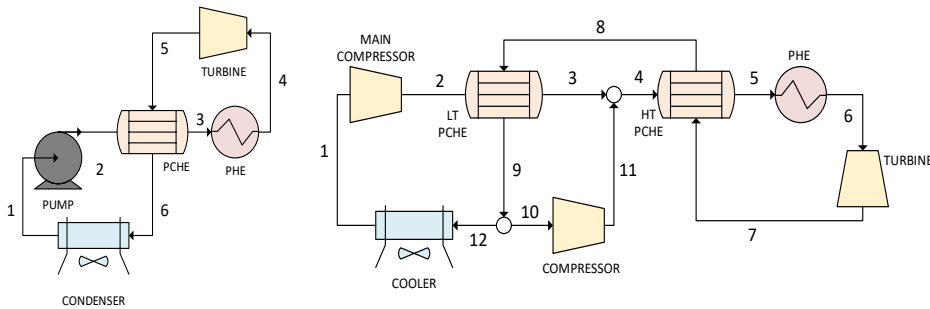
**Fig 3.** Andrew's curve for the pure CO<sub>2</sub> and the CO<sub>2</sub>-C<sub>6</sub>F<sub>6</sub> mixture with 85% of CO<sub>2</sub> molar content

## 4 Application of the innovative working fluid in a CSP plant

### 4.1 Cycle design and comparison with sCO<sub>2</sub> for a solar tower CPS plant

The research on a suitable power cycle for CSP applications has always aimed at tackling the most problematic aspects of the steam Rankine cycle: the low efficiency at high minimum temperatures, the complexity of the cycle layout, the average yearly cycle efficiency and the transient response to off design conditions. The pure sCO<sub>2</sub> cycle has improved the cycle efficiency and compactness, but still suffers from efficiency drops when no low temperature cold sinks are available. Moreover, in order to reach a significant improvement of performance with respect to steam Rankine cycles, the recompression layout for sCO<sub>2</sub> is needed [7]: the recuperator is split into two parts with different low pressure mass flow rates, and an additional compressor is added. The simple recuperative cycle, suitable for the CO<sub>2</sub> mixtures, and the recompression layout are presented in Fig 4.

In this work, the hypotheses on the plant layouts are representative of a large scale, 100MW power cycle located in arid areas. For this reason, the cycle minimum temperature is set at 51°C and an air-cooled condenser is considered. The cycle maximum temperature is fixed at 550°C, a common choice for large scale installations using solar salts as HTF. Other assumptions on the turbomachinery efficiencies and the HX pressure drops are listed in Table 2.



**Fig 4.** Simple recuperative cycle for CO<sub>2</sub> mixtures (left) and recompression cycle for sCO<sub>2</sub> (right)

**Table 2.** Cycle assumptions for the simple recuperative and recompressed plant layouts

Minimum temperature	Maximum temperature	Maximum pressure	Turbine Isentropic Efficiency	Compressor/Pump Isentropic Efficiency	$\Delta P_{LOSS}$ PHE	$\Delta P_{LOSS}$ Condenser	$\Delta P_{LOSS}$ PCHE (HP/LP)
51°C	550°C	257.5 bar	91.9%	88%	4 bar	2 bar	0.5/1 bar

The last necessary information for the cycle working with CO<sub>2</sub>+C<sub>6</sub>F<sub>6</sub> is the mixture composition: for this reason a sensitivity analysis has been developed in order to identify the most efficient composition. A CO<sub>2</sub> molar fraction of 87% resulted as the most efficient composition for the simple recuperative cycle. The cycle calculations of the sCO<sub>2</sub> cycle have been developed with the well-known EoS for pure CO<sub>2</sub> by Span and Wagner [8].

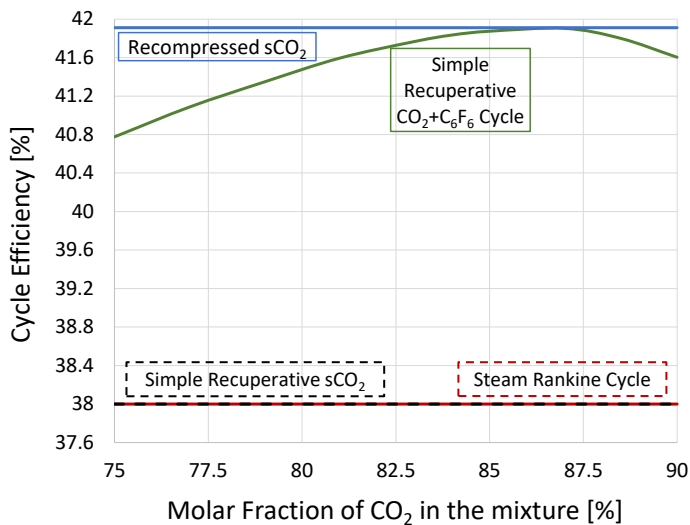
Comparing the pure sCO<sub>2</sub> cycle and the CO<sub>2</sub>+C<sub>6</sub>F<sub>6</sub> one, reported in Table 3, the cycle efficiency is not influenced by the presence of the mixture nor by the different plant layout, while the compression power in the case of the sCO<sub>2</sub> cycle is almost three times higher than the one of the mixture: for this reason the specific work of the CO<sub>2</sub>+C<sub>6</sub>F<sub>6</sub> cycle is higher.

The temperature at the inlet of the PHE is similar, with a slight edge for the mixture. The PCHE size is comparable since both the MITA (minimum internal temperature difference) and  $UA_{PCH\bar{E}}/Q_{IN}$  are in agreement. In this work, the interest in the investigation of  $UA_{PCH\bar{E}}$  is limited to the study of its impact on the power block costs, since the recuperator cost are normally considered proportional to  $UA_{PCH\bar{E}}$ . Any future developments of the SCARABEUS project will aim at the analysis of different mixtures that can reach substantially higher efficiencies than the one of  $sCO_2$ .

**Table 3.** Performances of the two reference cycles for CSP applications under hypotheses of Table 2

	Simple recuperative cycle $CO_2+C_6F_6$	Recompressed $sCO_2$ cycle
Cycle efficiency [%]	41.9	41.9
Cycle specific work [kJ/kg]	82.5	74.9
Temperature at PHE inlet [°C]	401	408
$UA_{PCH\bar{E}}/Q_{IN}$ [1/°C]	0.144	0.156
$MITA_{PCH\bar{E}}$	5	7
Cycle gross power [MW]	100	100
Compression power consumption [MW]	24.4	67.6

Fig 5 reports the trend of cycle efficiency using the  $CO_2+C_6F_6$  mixture for various molar compositions, along with the efficiency of the  $sCO_2$  cycle in simple recuperative configuration, recompressed configuration and the steam Rankine cycle, fixing the same minimum and maximum temperatures. If a higher  $CO_2$  molar fraction in the mixture is preferred, it is possible to increase it up to 90% with only a minor shift from the best efficiency point.



**Fig 5.** Gross cycle efficiency of the various solutions investigated for CSP applications

### 4.2 Economic analysis of the power block and comparison with sCO<sub>2</sub>

From the economic point of view, a simpler plant layout helps in reducing the specific costs of the power block, reported in Fig 6: in this analysis, the reference cost functions are the one reported by Weiland et al [9], analyzed for a 100MW cycle. The simple recuperative cycle working with the mixture has an overall cost of 577 \$/kW, where the recompressed sCO<sub>2</sub> cycle a cost of 741 \$/kW. The only cost function for the definition of the power block cost with a limited reliability is the one of the primary heat exchangers (PHE): for this component, the reference provides a cost function for natural gas fired PHE. In this comparison, the cost of the PHE and the condenser is constant, since the same thermal input into the cycle and the same cycle efficiency is considered. The heat rejection unit, instead, is modelled as an air-cooled HX with  $\Delta T_{ML}=15^{\circ}C$ . In the end, the adoption of the innovative mixture for the thermodynamic cycle is found to be beneficial in terms of cycle compactness, efficiency (especially at high minimum temperatures) and costs.

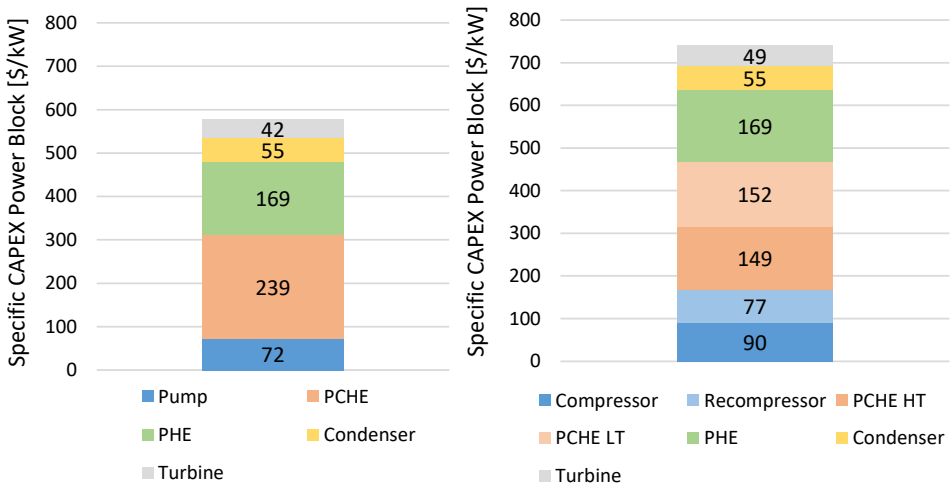
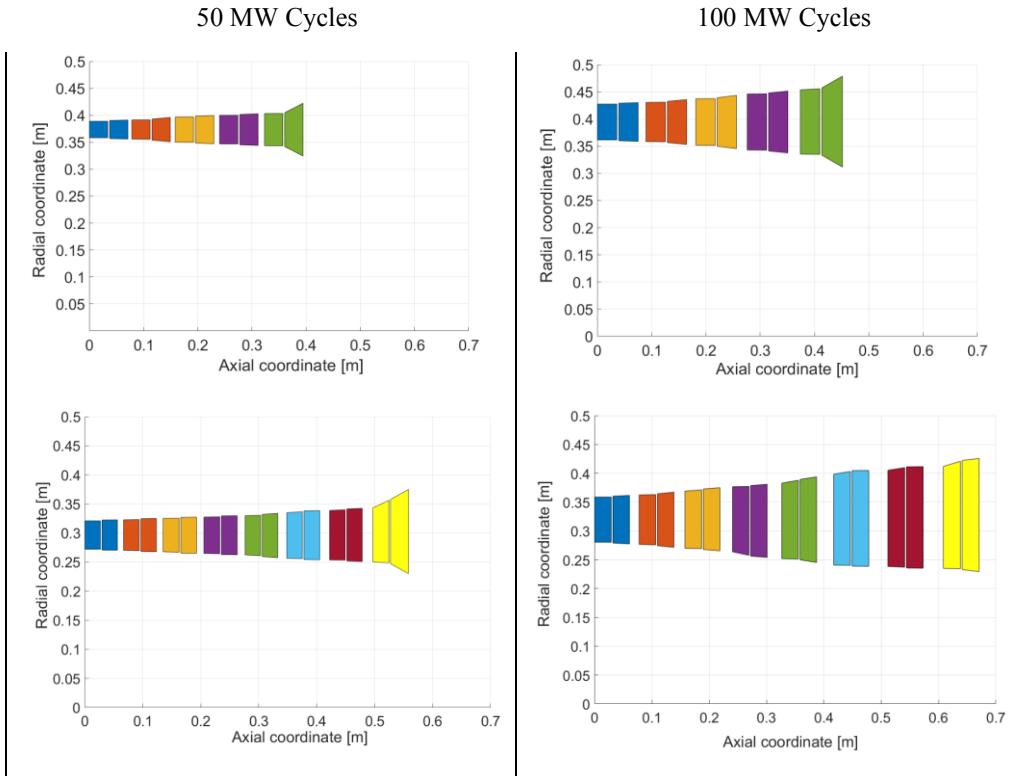


Fig 6. Specific CAPEX of the power block for the simple recuperative CO<sub>2</sub>+C<sub>6</sub>F<sub>6</sub> cycle (left) and the recompressed sCO<sub>2</sub> cycle (right) reported in Table 3

### 4.3 Design of the turbine of the cycle with the 1D tool AXTUR

In this chapter the characterization of the power block is deepened thanks to the design of the turbine of the cycle. Previous works studying sCO<sub>2</sub> cycles [10] emphasized the characterization of this component in the CSP plant using the pseudo 1-D tool AXTUR, a tool developed decades ago by researchers of Politecnico di Milano in Fortran [11]: in this work, instead, an adjourned MATLAB version is adopted [12]. The software is developed with solid and validated losses correlations, assumed valid also in case of CO<sub>2</sub> mixtures used as working fluid. Within this work, the tool has been modified in order to model CO<sub>2</sub>-based mixtures using look up tables with the necessary thermodynamic variables computed by PC-SAFT. The expansion studied in Fig 7 is the one of the simple recuperative CO<sub>2</sub>+C<sub>6</sub>F<sub>6</sub> cycle, at the optimal CO<sub>2</sub> molar composition of 87%, detailed in Table 3. Four solutions are studied, varying the number of stages and the cycle size. The sensitivity on the cycle size and number of stages aims at stressing the dependance of the turbine isentropic

efficiency on both parameters. In these simulations the rotational speed is fixed at 3000rpm, limiting the maximal peripheral speed and enabling a direct connection with the generator. Under these circumstances, no solution is optimal, since an increment of mass flow rate or number of stages always leads to an increment in the turbine efficiency.



**Fig 7.** Meridian plane of the axial turbines designed for the CO<sub>2</sub>+C<sub>6</sub>F<sub>6</sub> simple recuperative cycle reported in Table 3 at 3000 rpm. In addition, the results of a 50MW cycle are also presented.

In the analyzed cases the turbine inlet and outlet pressure are 253 bar and 86.7 bar, respectively. Moreover, considering the isentropic expansion, the overall enthalpy drop is 111.6 kJ/kg and the volume ratio 2.4. Table 4 reports a detailed characterization of the intermediate stage of the turbines (the third for the five stages expanders and the fifth for the eight stages ones) and the efficiency of the turbines designed. The peripheral speeds at midspan, instead, are around 100 m/s for the 8 stages turbines and around 120 m/s for the solutions with 5 stages. Examining various applications of axial turbines, in fact, the maximum peripheral speed at blade tip can be assumed around 400 m/s for mechanical reasons [11]. The speed of sound varies from 385 to 335 m/s along the expansion. Considering also the limited rotational speed, the resulting peripheral speed can be considered low. From the results, the trend of the isentropic efficiency is mimicked by the trend of specific speed ( $N_s$ ), optimal around 0.1 for axial stages, and the isentropic load coefficient, optimal in the range 2.5-3.0. The Mach number computed on the relative velocity ( $W_1$ ) at the inlet of the rotor is presented for the worst-case conditions (the stage with the higher value): in these calculations the reference speeds of sound are computed at



the same conditions (rotor inlet). In all the cases reported, the higher relative Mach number is found at the last stage, evidencing subsonic conditions all along the four expansions.

**Table 4.** Characteristics of the turbines designed with AXTUR

		50 MW Cycle		100 MW Cycle	
		5 Stages	8 stages	5 stages	8 stages
Isentropic efficiency	Of the turbine	89.4%	91.3%	91.6%	92.8%
Last rotor velocity outlet		31.7 m/s	24.6 m/s	33.5 m/s	33.3 m/s
First stator velocity inlet		39.6 m/s	34.6 m/s	37.4 m/s	32.8 m/s
Mass flow rate		606.3 kg/s	606.3 kg/s	1212.6 kg/s	1212.6 kg/s
Maximum Mach <sub>w1</sub>		0.476	0.376	0.487	0.400
Ns	Of the intermediate stage	0.057	0.085	0.082	0.127
Isentropic load coefficient		3.43	3.23	2.94	2.58
Degree of reaction		59.5%	52.5%	61.7%	59.4%
Pitch between rotor blades		0.041 m	0.029 m	0.050 m	0.042 m
h/D Rotor		0.070	0.129	0.124	0.232

Finally, considering the resulting computed isentropic efficiencies, the selected value of expander isentropic efficiency (91.9%) of Table 2 can be approximately obtained with a number of stages equal to 6 for the 100MW configuration, since the target efficiency represent an intermediate value between what computed with 5 stages and 8 stages.

## 5 Conclusions

The extensive research carried in the last years developed a comprehensive and detailed knowledge of the design and operations of sCO<sub>2</sub> power cycles. Nevertheless, their complex plant layouts and the complexities in the design of the main compressor can be overtaken if CO<sub>2</sub>-based mixtures are used. The mixture can allow the employment of a transcritical cycle instead of a supercritical one, using a pump instead of a compressor, enabling condensation in the heat rejecting unit. Higher cycle efficiencies can be obtained, especially in hot and arid environment typical of CSP application, adopting air-cooled condensers. This work highlights the potential of the CO<sub>2</sub>+C<sub>6</sub>F<sub>6</sub> mixture, a deeply investigated working fluid within the SCARABEUS project as a potential candidate to replace the pure CO<sub>2</sub> in power cycles. The innovative transcritical cycle presents high cycle efficiencies, a reduced cost of the power block with respect to sCO<sub>2</sub> cycles and a significantly simpler layout. The next steps the SCARABEUS project will face revolve around the very difficult task to select another dopant for CO<sub>2</sub> who is able to withstand very high temperatures (over 600°C). Then, the cycle performance of the power plant will be determined on design and on an annual basis and an overall economic analysis to prove the advantages of using the innovative CO<sub>2</sub> mixtures with respect to sCO<sub>2</sub> cycles will be carried out.

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