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## The design of CO<sub>2</sub>-based working fluids for high-temperature heat source power cycles

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### Abstract

The application of CO<sub>2</sub> power cycles is advantageous to exploit high-temperature sources (500-800°C) in the case of available low-temperature heat sinks (15-25°C). However, their efficiency is strongly reduced for higher heat sink temperatures. At these temperatures, due to the low-critical temperature of CO<sub>2</sub> (about 31°C), CO<sub>2</sub> is in fact compressed in the supercritical vapor phase rather than in the liquid phase, thus increasing energetic demand for compression. One of the solutions envisaged to overcome this problem is the addition of one or more chemicals that allow having a mixture with a higher critical temperature than the one of pure CO<sub>2</sub>. This preserve the working fluid compression in its liquid phase, even in the case of heat sinks with temperatures greater than 25°C.

This research shows that the addition to CO<sub>2</sub> of a properly selected chemical component enables to increase the critical temperature up to 45°C with relevant improvements of cycle efficiency with respect to pure-CO<sub>2</sub> power cycles. In particular, it summarizes the most relevant criteria to be accounted for when selecting CO<sub>2</sub>-additives. Moreover, the paper warns of the thermodynamic effects deriving from adding to CO<sub>2</sub> a second characterized by a much more high critical temperature, such as the occurrence of infinite-pressure critical points and multiple-phase liquid-liquid and vapor-liquid critical points. Finally, the paper analyses the thermodynamic properties of a high-critical temperature CO<sub>2</sub>-based mixture, suitable for these applications, that presents multiple phase critical points. In this regard, it is specified that the paper also aims at filling a knowledge gap in the study of thermodynamic properties of mixtures presenting how do enthalpy and specific volume change in response to pressure variations in the event of liquid-liquid and vapour-liquid critical points. Finally, we present the comparison between performances of power cycles which use, as working fluid, either pure CO<sub>2</sub> or the novel designed higher temperature CO<sub>2</sub>-based mixture.

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*Keywords:* CO<sub>2</sub>-based mixtures; Critical points; Power cycles; High-temperature heat source

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## 1. Introduction

The ever-increasing necessity to reduce the environmental impact of industrial and urban energy conversion processes has led engineers to consider the use of mixtures as working fluids of thermodynamic power and refrigeration cycles. Mixing different fluids in different amounts, in fact, allows enhancing specific thermodynamic characteristics of the mixture that may lead cycle performances to improve; moreover, the use of multicomponent fluids enables the reduction of the environmental impact and hazardous properties of some of the basic pure fluids under mixing.

For example, performances of real-gas-Brayton-cycles may significantly increase if the working fluid is compressed in the liquid phase, rather than in the gaseous one. However, when cooling sources are only available at temperatures higher than the critical temperature of the pure working fluid, the liquid-phase compression of that fluid cannot evidently take place. To allow the achievement of subcritical conditions, it has been proposed [2, 3] to increase the critical temperature of the working fluid by adding a small amount of a high-critical temperature second component. Vapor-liquid critical temperatures of resulting mixtures lie, in fact, between the critical temperatures of the two pure components.

This paper focuses on the design of working fluids for closed power cycles that exploit a high temperature heat source comprised between 500 °C and 800 °C to convert the thermal input into electricity. Possible high-temperature heat sources are, for example, nuclear and solar technologies or high-temperature waste thermal sources recovered from industrial processes. The amount of thermal energy made available by these sources is, in general, not sufficient to enable the application of efficient steam power cycles of which minimum commercial size is 10 MW<sub>el</sub> [4]. Moreover, mainly due to the thermal decomposition of organic working fluids, that for the most stable organic molecules occurs around 300 - 400 °C [5], the high-grade of these heat sources does not allow the application of ORC especially above 400°C.

CO<sub>2</sub> cycles represent potential reliable candidates for these applications. When water at about 15°C is available to cool these cycles, CO<sub>2</sub> may be favourably pumped in subcritical liquid conditions. However, the efficiency of these cycles is highly affected by the temperature of the cooling source: the low-critical temperature of CO<sub>2</sub> (about 31°C) entails the necessity of using entirely supercritical CO<sub>2</sub> Brayton cycles when temperature of the available cooling source is above 25°C, rather than the less - compression power consumer transcritical CO<sub>2</sub>-cycle.

This paper aims at showing how to increase the efficiency of CO<sub>2</sub> cycles, used in the event of high-temperature cooling sources, by adding to CO<sub>2</sub> a properly selected second component. To this aim, section 2 presents the main criteria that should be accounted for when selecting such a fluid. Furthermore, section 3 presents the thermodynamic analysis of a promising mixture under patenting. This section also shows how do enthalpy and specific volume change in response to pressure variations across the critical region, in the event of multiple vapour-liquid and liquid-liquid critical points that characterize this system. Finally, section 4 compares performance results of a power cycle operating either with pure CO<sub>2</sub> or with the designed CO<sub>2</sub>-based working fluid.

### Nomenclature

T	temperature [K]	P	pressure [bar]
h	specific enthalpy [kJ/kg]	v	specific volume [m <sup>3</sup> /kg]
s	specific entropy [kJ/kgK]	Q	heat [kJ/kg]
LL	liquid-liquid equilibrium	VL	vapor-liquid equilibrium
x, y, z	mole fractions of liquid, vapor and global composition, respectively	η	efficiency

## 2. Criteria for CO<sub>2</sub>-additive selection

The selection of CO<sub>2</sub>-additives should be performed so that their addition to CO<sub>2</sub> leads to a mixture being (1) thermally stable; (2) characterized by a critical temperature greater than 45 °C; (3) moderate mixture critical pressure; (4) environmental benign (low-GWP and zero-ODP); (5) non-toxic and non-flammable. Since pure CO<sub>2</sub> already fulfills

all the mentioned – not exhaustive – requirements, it is evident that the non-compliance with them would be associated to the selected additive.

The simultaneous compliance with all these criteria is currently a challenge. For this reason, it is worth distinguishing between necessary and preferable conditions to be fulfilled: criteria (1-3) must be necessarily satisfied to guarantee the correct working of the power cycle, while the other mentioned criteria (4-5) generally represent a desiderata which could lead to the preferential selection between additives.

Moreover, considering criterion (1), it is specified that, in the absence of experimental and modelling results, the thermal stability of the mixture could be ensured, at an earlier stage, providing additives being non-reacting with CO<sub>2</sub> and thermally stable (in their pure form) at the operating conditions of interest. In the following, further details are provided on criteria (2) and (3), that actually represent the only criteria on the basis of which the amount of additive is defined.

The addition of a small amount of a high-critical temperature component to CO<sub>2</sub>, to allow the desired moderate increase in the mixture critical temperature, could be accompanied by an extreme increase in critical pressure that, for some classes of mixtures, may achieve indefinitely high values [6]. In other cases, the addition of a second component might lead to the emergence of multi-phase equilibria (e.g., Vapour-Liquid-Liquid Equilibrium) that could give rise to the coexistence of two critical points: one vapour-liquid and one liquid-liquid critical point.

These thermodynamic singularities in the critical region of specific binary mixtures started to be classified by van Konynenburg and Scott [6]. A first classification level discerns between binary mixtures characterized either by a continuous or discontinuous locus of vapour-liquid equilibrium critical points.

To visualize the three types of critical loci that could be encountered in the context of this work, we present, in the following, three CO<sub>2</sub>-based binary mixtures, respectively characterized by these three types of critical loci, containing one of the following high-critical temperature fluids: C<sub>6</sub>F<sub>14</sub>; NOA (an environmental friendly Non-Organic Additive currently under patenting process); H<sub>2</sub>O.

Figures 1(a)-(c) aim at showing the resulting locus of critical points (solid black lines) of the three systems as a function of temperature, pressure and composition of the mixtures, which extremes coincide with the critical points of the two pure components (round mark), C<sub>1</sub> and C<sub>2</sub>, end-points of their saturation curves (dotted black lines). Dotted red lines represent equilibrium lines where three vapour-liquid-liquid phases co-exist. A more detailed description is provided in the followings.

Fig. 1(a) represents the continuous locus of critical points that characterize the mixture CO<sub>2</sub>-C<sub>6</sub>F<sub>14</sub>. As it can be observed, the addition of a small amount of C<sub>6</sub>F<sub>14</sub> to CO<sub>2</sub> allows the increase of the critical temperature of the resulting mixture, positively maintaining a moderate critical pressure. The only limit of C<sub>6</sub>F<sub>14</sub> is represented by its thermal stability, which temperature limit has been experimentally attested to be around 350 °C [3].

Fig. 1(b) shows the discontinuous locus of critical point of the CO<sub>2</sub>-NOA mixture. This discontinuity derives from the emergence of a three-phase line that results in the co-existence of two critical points in VL and LL conditions (red dotted line in the zoomed area). More details about this peculiarity are given in the next section. As for the CO<sub>2</sub>-C<sub>6</sub>F<sub>14</sub> system, the critical pressure undergoes an acceptable moderate increase in the critical temperature of the system.

Fig. 1(c) shows how the addition of a very small amount of water to CO<sub>2</sub> results in an extremely limited increase of critical temperature of the system (from the critical temperature of pure CO<sub>2</sub> (304.1K) to, about, 305.5K) and in an indefinitely high-value of the critical pressure. This system and similar CO<sub>2</sub>-based mixtures characterized by infinite-discontinuities, occurring at the low-CO<sub>2</sub> concentrations of our interest, cannot evidently be applied.

Actually, our research for proper additives has led to the preliminary selection of the organic C<sub>6</sub>F<sub>14</sub> and C<sub>6</sub>F<sub>6</sub>, of NOA and of the further non-organic reacting N<sub>2</sub>O<sub>4</sub> (which decomposes into NO<sub>2</sub>, NO and O<sub>2</sub> at the considered operating conditions). The effect of adding N<sub>2</sub>O<sub>4</sub> is currently under modelling study. In the next section we focus on the thermodynamic characterization of the mixture obtained by adding NOA to CO<sub>2</sub>.

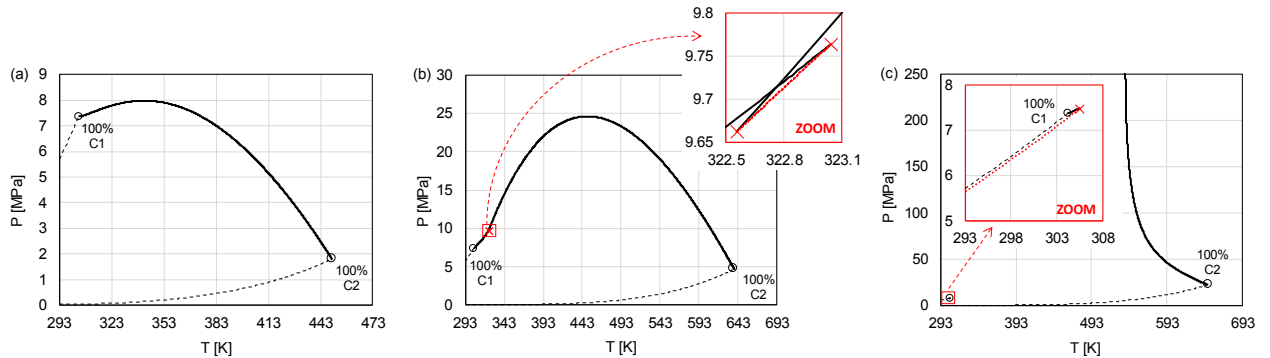


Fig. 1. Global Phase Equilibrium Diagrams of CO<sub>2</sub> (C1) + C<sub>6</sub>F<sub>14</sub> (C2) (fig. (a)) / NOA (C2) (fig. (b)) / H<sub>2</sub>O (C2) (fig. (c)). These diagrams result from the application of the Peng-Robinson [7] equation of state, with the following calibrated binary interaction parameters:  $k_{\text{CO}_2\text{-C}_6\text{F}_{14}} = 0.0151$  [8],  $k_{\text{CO}_2\text{-NOA}} = 0.07$  (references are not provided because NOA is under patenting),  $k_{\text{CO}_2\text{-H}_2\text{O}} = 0.0504$  [8]

### 3. Definition of mixture composition

As mentioned in section 2, mixtures under design must be finally characterized by a critical temperature greater than 45 °C, resulting from the addition to CO<sub>2</sub> of an additive (in this case NOA). This section thus quantifies the variation of the critical temperature of CO<sub>2</sub>+NOA mixtures, as a function of its global composition, with the aim of (1) defining the global mixture composition to be finally used as working fluid of the analyzed CO<sub>2</sub>-based transcritical power cycles and (2) describing the thermodynamic features of the designed mixture. It is further specified that all calculations performed in the following result from the application of the Peng-Robinson equation of state [7] calibrated over vapour-liquid equilibrium and enthalpy change due to mixing experimental data available in the literature. It is not possible to specify references for these data since the fluid is under patenting. The class of cubic equation of state models has been selected since it actually enables the most accurate representation of locus of critical points of mixtures, with respect to SAFT models [9] and multi-parameter models. The latter, in fact, would require to be optimized over a high-number of experimental data currently unavailable. Finally, it is specified that the applied standard Peng-Robinson equation of state is based on van der Waals mixing rules grounded on assumptions of ideal random mixing. More precise calculations of loci of critical points could be obtained by applying more accurate mixing rules based on local composition models [10] which would more realistically account for molecular interactions. All thermodynamic calculations reported in this paper have been performed with an in-house Fortran code.

Fig. 2 shows how does the critical temperature of the CO<sub>2</sub>-NOA mixture varies with mixture composition. In particular, it is possible to attest that a critical temperature equal to 45°C can be obtained by mixing 97.5%<sub>mol</sub> of CO<sub>2</sub> with 2.5%<sub>mol</sub> of NOA. As it is visible from fig. 2, such a global composition is close to a discontinuity in the locus of critical points, already observed in fig. 1(b), resulting from the occurrence of three co-existing phases (dotted red line). It is worth observing that each one of the points of the three-phase dotted red line observed in the T-P plane of fig. 1(b) corresponds to three isothermal and isobar points on the plane T-z<sub>C1</sub>, each one characterized by the composition of one of the three phases at equilibrium conditions (see fig. 2).

Furthermore, it is highlighted that this diagram results from the application of the Peng-Robinson-78 [7] equation of state, optimized over a scarce number of available experimental data. The optimized binary interaction parameter is thus highly uncertain ( $k_{ij} = 0.07 \pm 0.03$  at 95% conf. level). As a direct consequence, either the actual occurrence or the precise location of such a three-phase line is uncertain. There is thus a possibility that, in the reality, the selected global composition (CO<sub>2</sub>/NOA : 97.5%<sub>mol</sub>/2.5%<sub>mol</sub>) actually leads to the emergence of multiple critical points arising from the presence of multiple-phase equilibria. However, it is shown in the following that, also in this case, the effect on thermodynamic properties (and on the functioning of the power cycle components) is negligible.

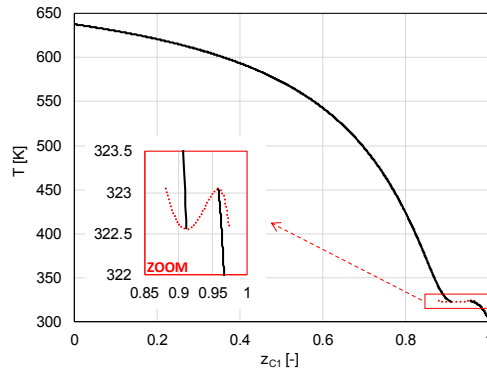


Fig. 2. Global Phase Equilibrium Diagrams of CO<sub>2</sub> (C1) + NOA (C2). Projection on T- $z_{C1}$  plane.

We thus evaluate, in the following, the isothermal change of volume and enthalpy resulting from pressure variations on the CO<sub>2</sub>-NOA mixture, at one of the temperatures where the zoomed area of fig. 1(b) reveals the presence of multiple isothermal critical points (i.e., in the range 322.55 K - 323.04 K). In particular, fig. 1(b) shows that, considering a temperature of 322.75 K, the resulting mixture is characterized by two equal-pressure vapour-liquid and liquid-liquid critical points. This is also shown in the resulting isothermal phase diagram represented in fig. 3. It is also specified that, in general, no more than two critical points could be found.

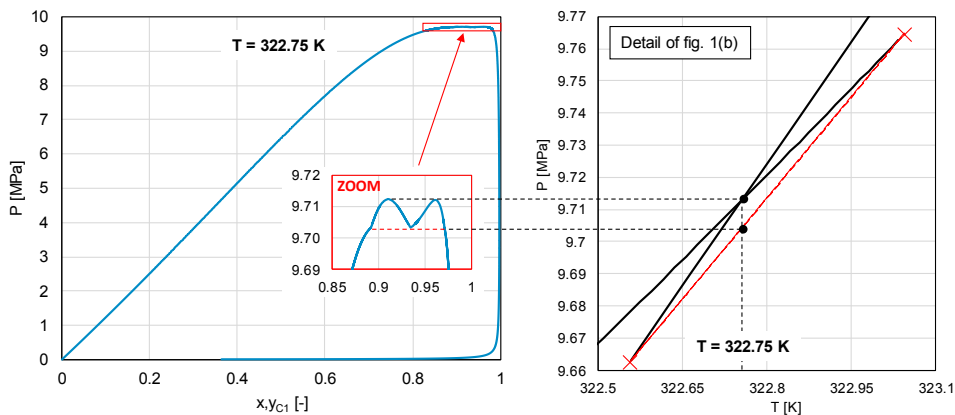


Fig. 3. Isothermal P-xy phase diagram of CO<sub>2</sub> (C1)+NOA (C2) at 322.75 K, with zoom on critical region showing two LL and VL critical points (on the left). Figure on the right shows the pressure of critical points and of the three-phase line corresponding to the considered isotherm.

Fig. 4 and Fig. 5 respectively show how do isothermal volume and enthalpy change across a critical region characterized by multiple critical points, as a consequence of pressure variations. In particular, it is highlighted that the presence of NOA in CO<sub>2</sub> enhances the increase of density around the critical region, which is characterized by high-density liquid-liquid critical points, enabling the further reduction of power consumed to compress this fluid in the vicinity of such region. These considerations, on the one hand, and the necessity of correctly calculating the thermodynamic properties of these fluids, on the other, reveal that the occurrence of such discontinuities should be carefully predicted when designing binary mixtures characterized by a specific critical point temperature, for the mentioned industrial application.

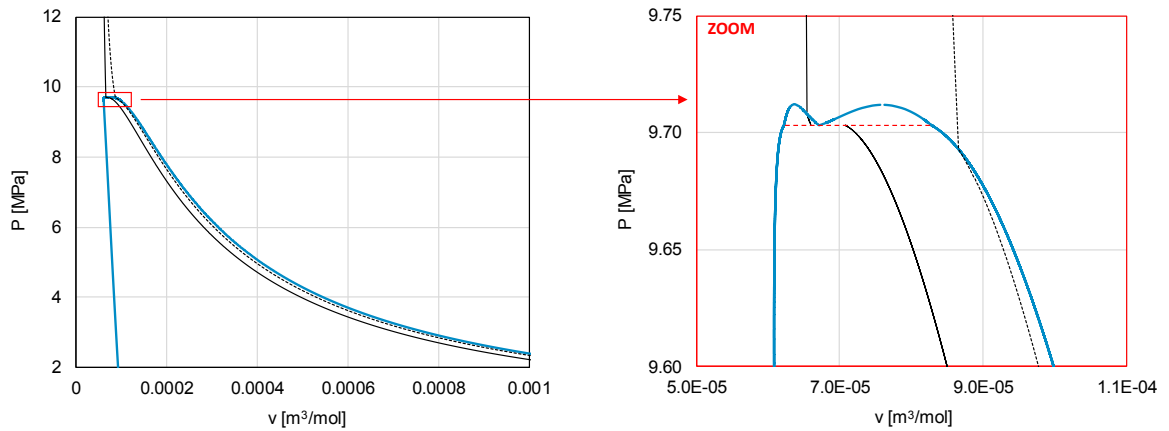


Fig. 4. Isothermal P-v phase diagram of CO<sub>2</sub> (C1) + NOA (C2) at T = 322.75 K (solid blue curve) with isothermal (T = 322.75 K) P-v curves at  $z_{C2} = 0.025$  (dotted black line) and  $z_{C2} = 0.075$  (solid black line). The zoom on the critical region shows two LL and VL critical points.

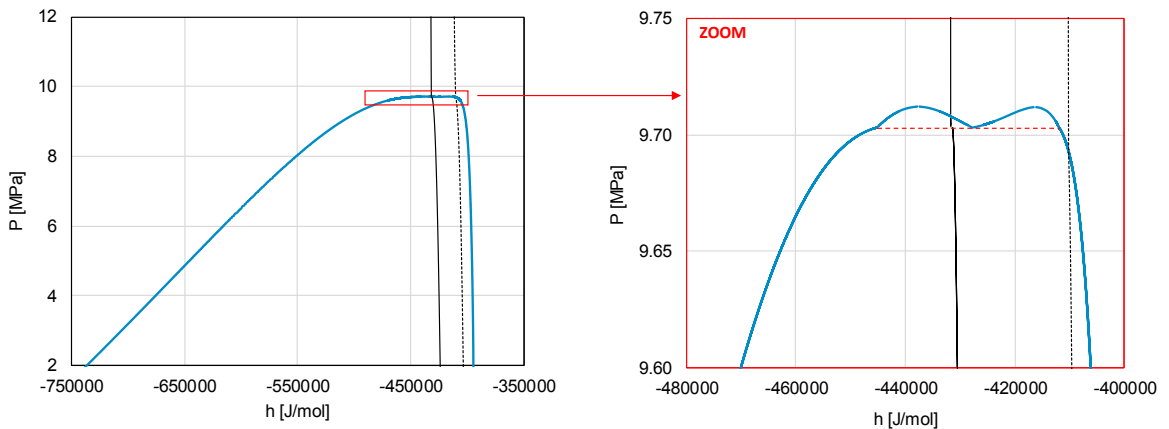


Fig. 5. Isothermal P-h phase diagram of CO<sub>2</sub> (C1) + NOA (C2) at T = 322.75 K (solid blue curve) with isothermal (T = 322.75 K) P-h curves at  $z_{C2} = 0.025$  (dotted black line) and  $z_{C2} = 0.075$  (solid black line). The zoomed area on the critical region shows two LL and VL critical points.

#### 4. Performance of CO<sub>2</sub> versus CO<sub>2</sub>+NOA power cycles

This section presents preliminary results of the performance of recuperative CO<sub>2</sub>-Brayton cycles and recuperative CO<sub>2</sub>-NOA transcritical cycles. The heat source has been considered at constant temperature. In such case the best configuration should be the one with split-flow and recompression, but for this study a simpler layout has been selected. Calculations have been performed considering assumptions reported in Table 1. The minimum pressure for the pure CO<sub>2</sub> cycle is the one that maximizes the efficiency.

Table 1. Assumptions for calculations on recuperative power cycle configurations

	CO <sub>2</sub>	CO <sub>2</sub> -NOA (2.5%mol)
Maximum T of the cycle ( $T_{max}$ ) [K]	673.15 – 873.15	
Minimum T of the cycle ( $T_{min}$ ) [K]	313.15	
Maximum P of the cycle ( $P_{max}$ ) [MPa]	30	
Minimum P of the cycle ( $P_{min}$ ) [MPa]	Value which maximizes power efficiency	Saturation pressure at $T_{min}$
Isentropic turbine efficiency [-]	Values from correlations reported in [11] for three-stages turbines (about 0.92)	
Isentropic compressor efficiency [-]	0.85	
Pressure drops ( $\Delta P/P_{in}$ )	Recuperator: 0.04 / Primary heat exchanger: 0.02 / Condenser: 0.02	
Minimum $\Delta T$ between hot and cold streams in recuperator [K]	15	
Electro-mechanical efficiency [-]	0.95	

Results obtained for the two thermodynamic cycles, in the specific case of  $T_{max} = 873.15$  K, reveal that the use of the  $CO_2$ -NOA mixture as working fluid enables the increase of cycle efficiency, from 35.1% to 39.5%.

Figure 6 shows the T-s diagrams of these two power cycles, having the same minimum temperature of 313.15 K, together with the calculated thermodynamic properties. At lower maximum temperatures, the improvement in cycle efficiency is still more pronounced, as shown in Fig. 7. To gain a better understanding of the advantages brought about by the use of the proposed mixture, a comparison of efficiency penalties obtained by a second-law analysis with reference to an ideal reversible (Carnot) cycle operating between the maximum and the minimum cycle temperature is performed for pure and mixture cycles. The real efficiency  $\eta$  of a closed cycle is computed by:

$$\eta_{II} = \eta_{rev} - T_{min} \sum_{i=1}^N \Delta S_i / Q_{in} = \eta_{rev} - \sum_{i=1}^N \Delta \eta_{II,i}$$

where  $\eta_{rev}$  is the efficiency of a reversible cycle operating with constant temperature  $T_{max}$  heat source and constant temperature  $T_{min}$  heat sink and  $\Delta \eta_{II,i}$  are 2<sup>nd</sup>-law efficiency penalties related to the N-cycle irreversible processes [1].

As shown in Fig. 8, the performances of both power cycles improve with maximum temperature for both working fluids. The merits of mixture are more evident at lower maximum temperatures, where real gas effects are more pronounced. In particular, efficiency penalties taking place in the heat rejection and in the compression decrease significantly by adopting a condensing mixture. On the opposite, the efficiency penalties related to heat exchanges in the recuperator and in heat introduction increase, but their effect is much lower than the former advantages.

In addition to these considerations about cycle efficiencies, it is observed that higher logarithmic mean temperature difference between streams within the recuperator, resulting from the use of the  $CO_2$ -NOA mixture rather than of pure  $CO_2$ , enables the reduction of heat exchanger surface. A final remark, that also favors the use of the  $CO_2$ -NOA mixture, concerns the lower temperature value of the hot stream entering the primary heat exchanger (point numbered with “3” in Fig. 6), which allows a major cooling of the heat source – whether available at variable temperature.

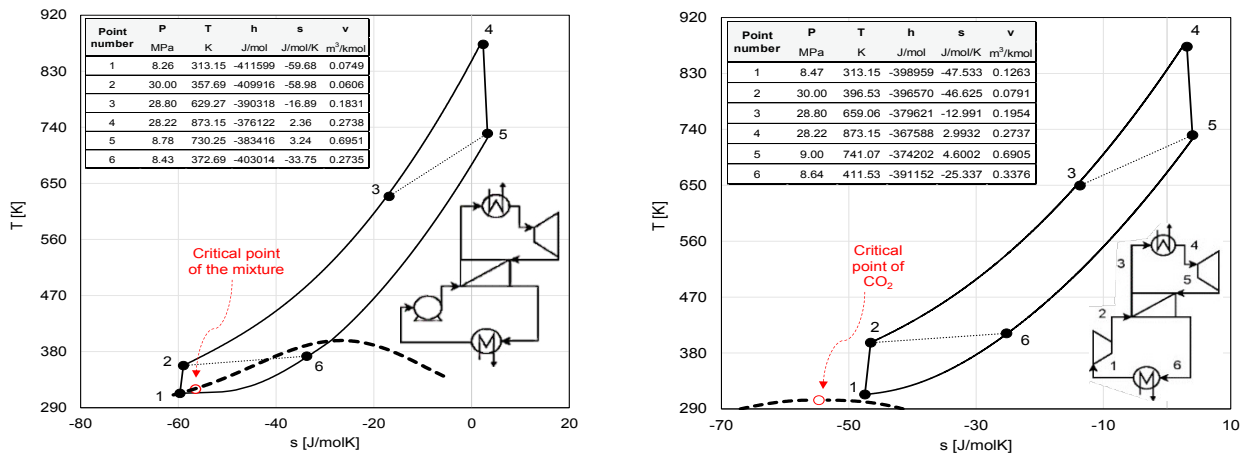


Fig. 6. T-s diagrams of  $CO_2$ +NOA cycle (on the left) and of pure  $CO_2$  cycle (on the right), both at  $T_{max} = 873.15$  K and under assumptions reported in Table 1.

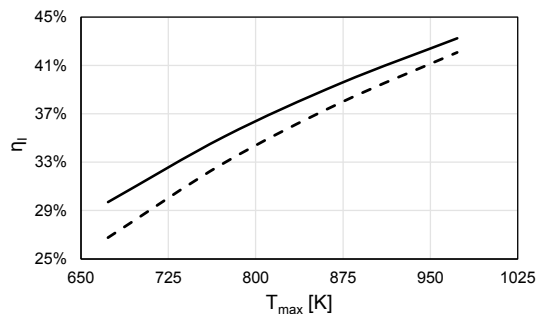


Fig. 7. Trend of cycle efficiency (solid line: mixture  $CO_2$ -NOA, dashed line: pure  $CO_2$ ) as a function of the cycle maximum temperature, at maximum pressure of 30 MPa

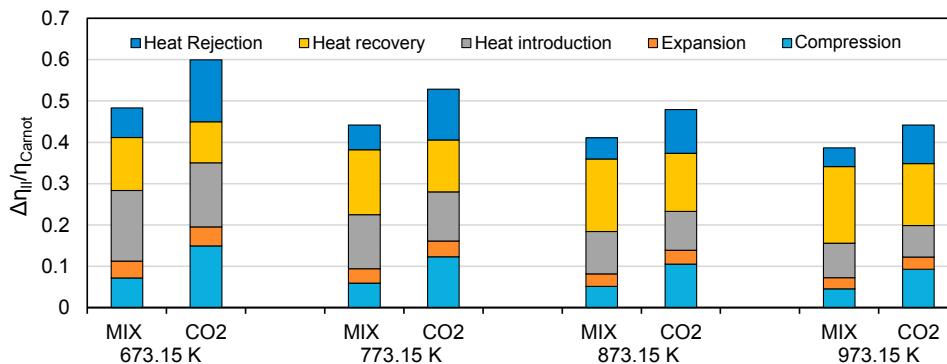


Fig. 8. Second-law efficiency losses, relative to Carnot efficiency  $\eta_{Carnot} = 1 - T_{min}/T_{max}$  ( $T_{min} = 313.15$  K). The lowest the sum of the efficiency penalties, the highest is the thermodynamic quality of the power cycle.

## 5. Conclusions and future works

This paper shows that the increase the critical temperature of the working fluid from the one of CO<sub>2</sub>, by adding to CO<sub>2</sub> a properly selected additive, enables the efficient application of CO<sub>2</sub>-based power cycles for high-temperature heat sources even when the heat sink temperature is above 25°C. Performance calculations are shown considering results obtained from the use of a specific CO<sub>2</sub>-based mixture under patenting, being stable up to - at least - 600°C, environmentally friendly, non-toxic, non-flammable and characterized by a moderate critical pressure (lower than 100 bar). According to results here presented, the novel mixture enables the increase of cycle efficiency up to 2.9 percentage points compared with the pure CO<sub>2</sub> cycle.

The promising results of the mixture are worthy of further investigation related to the mixture composition, alternative layouts of the power plant and the evaluation of the design of their components.

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