The design of CO_2-based working fluids for high-temperature heat source power cycles

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Introduction

Context

- Power plants exploiting heat source at 500-800°C

Objective

- **Determination of a suitable working fluid**
- **Determination of the performances of the selected working fluid** and comparison with a state of art plant

Methodology

- **Development of in-house code** for calculation of the thermodynamic property, also at the critical point
- **Definition of the working fluid**
- **Definition of a scheme of plant**

Hi-performance cycles

An option is the Brayton-cycle, it can be applied with real-gas.

General considerations for **Real-Fluid-Brayton-Cycle** for increasing the performances:

- Working with higher maximum temperature
- Reaching maximum pressure pumping a liquid phase

These imply:

- Thermal stability of the working fluid
- Minimum temperature of the cycle higher than the critical temperature of the working fluid

State of art for high temperature heat source

Possible high-temperature (500-800 °C) heat sources are:

- nuclear
- solar technologies
- high-temperature waste thermal sources (from industrial processes).

The amount of thermal energy made available by these sources could be not enough to enable the application of efficient steam power cycles.

Mainly due to the thermal decomposition of organic working fluids, the high-grade of these heat sources does not allow the application of ORC especially above 400 °C.

CO_2 cycles represent potential reliable candidates for these applications

Plants with CO_2

Critical temperature: 31 °C

Critical pressure: 73.8 bar

Efficiency of these cycles is highly affected by the temperature of the cooling source. In general it is dependent by the ambient temperature:

- at about 15 °C CO_2 may be favourably pumped in subcritical liquid conditions
- at higher temperature the CO_2 requires compression of the gas or trans-critical fluid

Subcritical condition can be obtained adding small amount of a high-critical temperature second component

Criteria for selecting of the second component

The selection of CO_2-additives should be performed so that their addition to CO_2 leads to a mixture being

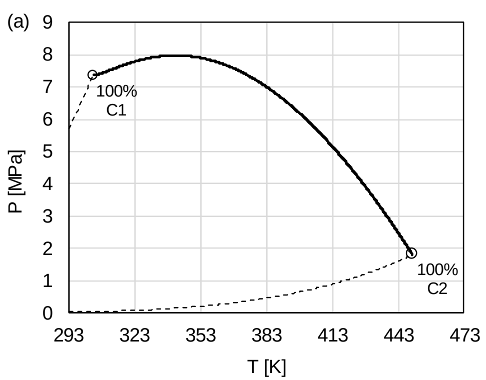
1. thermally stable;
2. characterized by a critical temperature greater than 40 °C;
3. moderate mixture critical pressure;

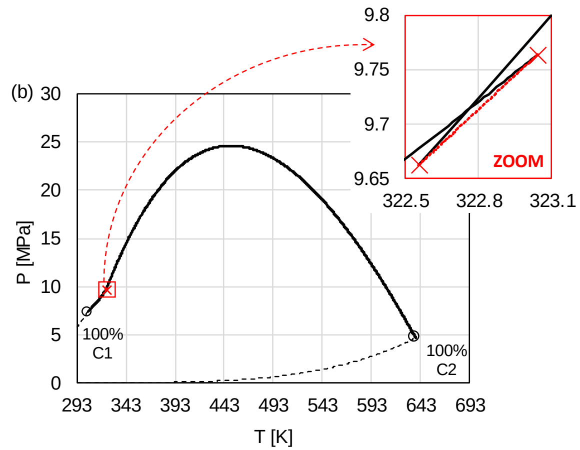
It should be preferable

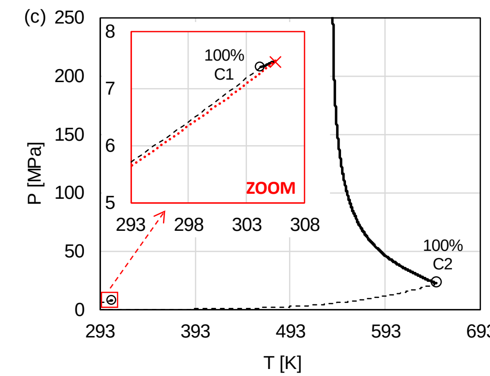
a) environmental benign (low-GWP and zero-ODP);
b) non-toxic and non-flammable.

Three type CO_2-based binary mixtures
(van Konynenburg and Scott based on locus of critical points)

OBJ: mixture with critical temperature higher then Tcr_{CO2} adding small amount of a high-critical temperature component to CO_2







CO_2 - C_6F_{14}

increase of the critical temperature of the resulting mixture, positively maintaining a moderate critical pressure

CO_2-NOA

This "jump" discontinuity derives from the emergence of a three-phase line that results in the co-existence of multiple critical points

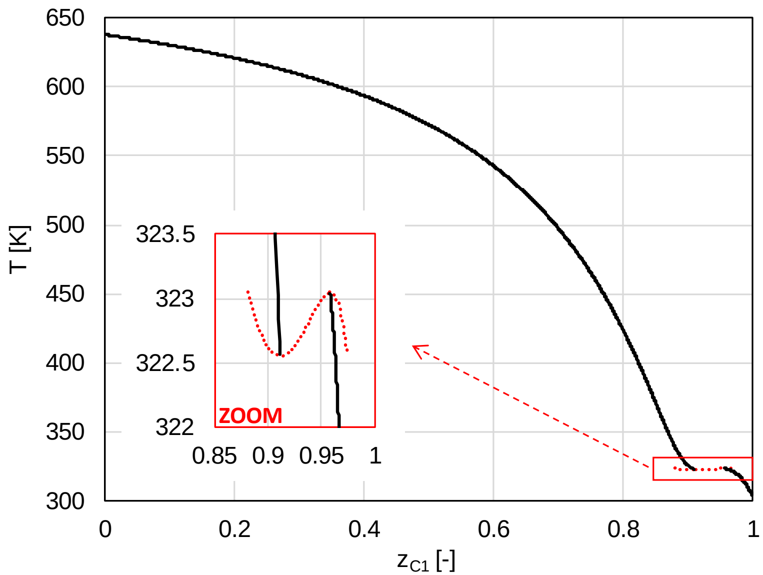
CO_2-H_2O

limited increase of critical temperature indefinitely high-value of the critical pressure infinite-discontinuities

Design of the mixture

Variation of the critical temperature of CO_2+NOA mixtures, as a function of its global composition.

Calculation with Peng-Robinson equation of state (van der Waals mixing rules) calibrated over vapour-liquid equilibrium and enthalpy change due to mixing (kij=0.07).



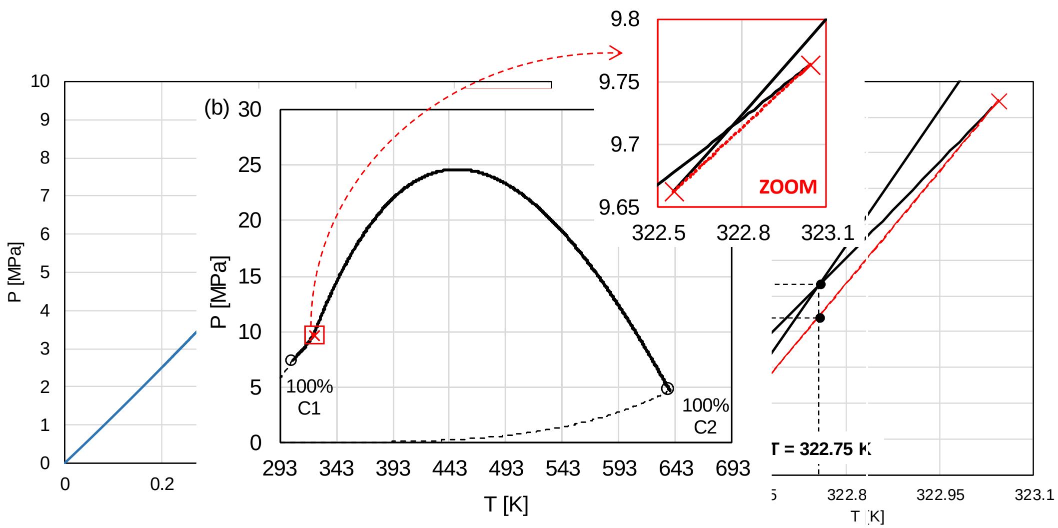
Critical temperature equal to 45°C can be obtained by mixing 97.5%$_{mol}$ of CO_2 with 2.5%$_{mol}$ of NOA.

Effect on thermodynamic properties (and on the functioning of the power cycle components) is negligible

Effect on properties

Evaluation of the isothermal change of volume and enthalpy resulting from pressure variations on the CO_2-NOA mixture, at one of the temperatures where there is the presence of multiple isothermal critical points (i.e., in the range 322.55 K - 323.04 K).

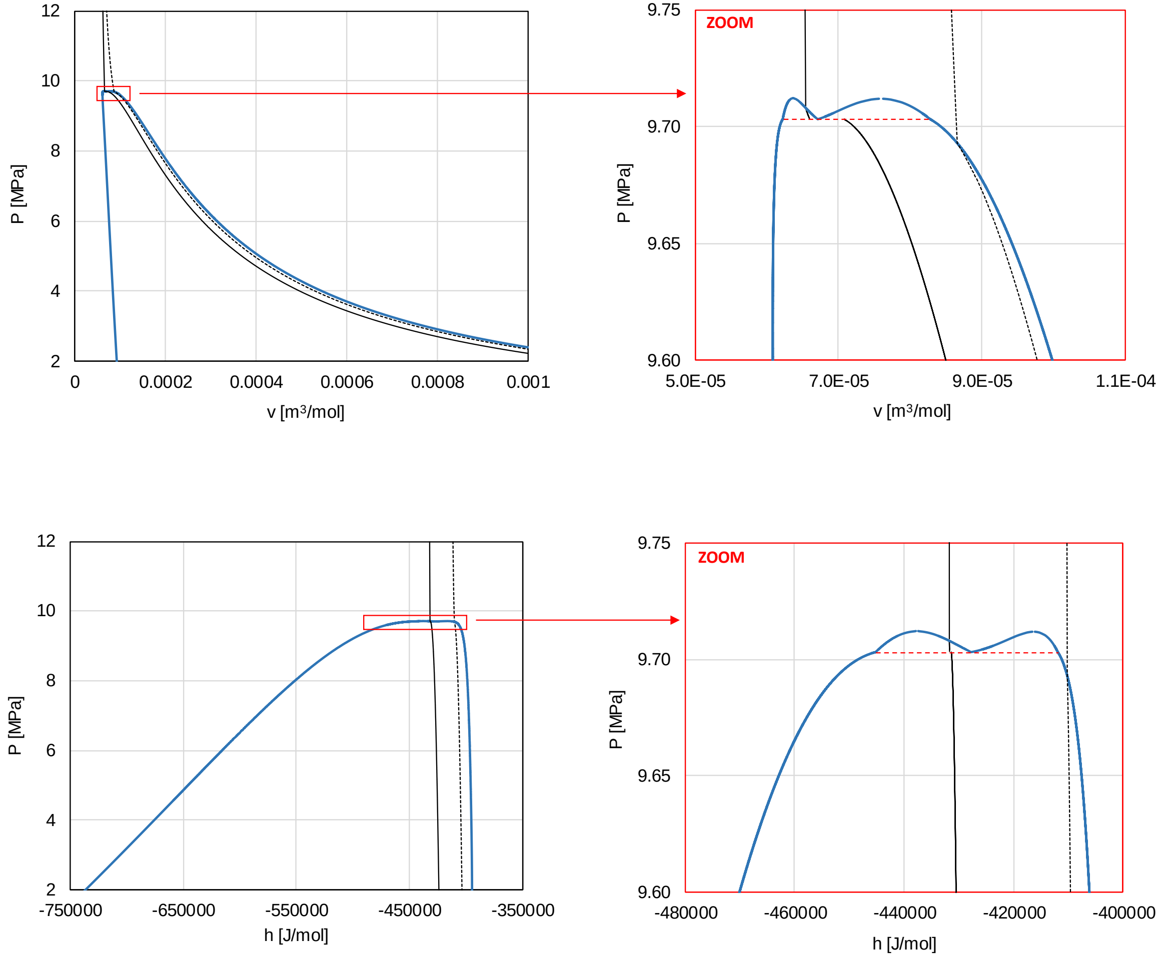
The resulting mixture is characterized by two equal-pressure vapour-liquid and liquid-liquid critical points.



Isothermal *v* and *h* function of pressure variations

Isothermal volume and enthalpy change across a critical region characterized by multiple critical points.

The presence of NOA enhance the increase of density around the critical region, which is characterized by high-density liquid-liquid critical points: reduction of power consumption.



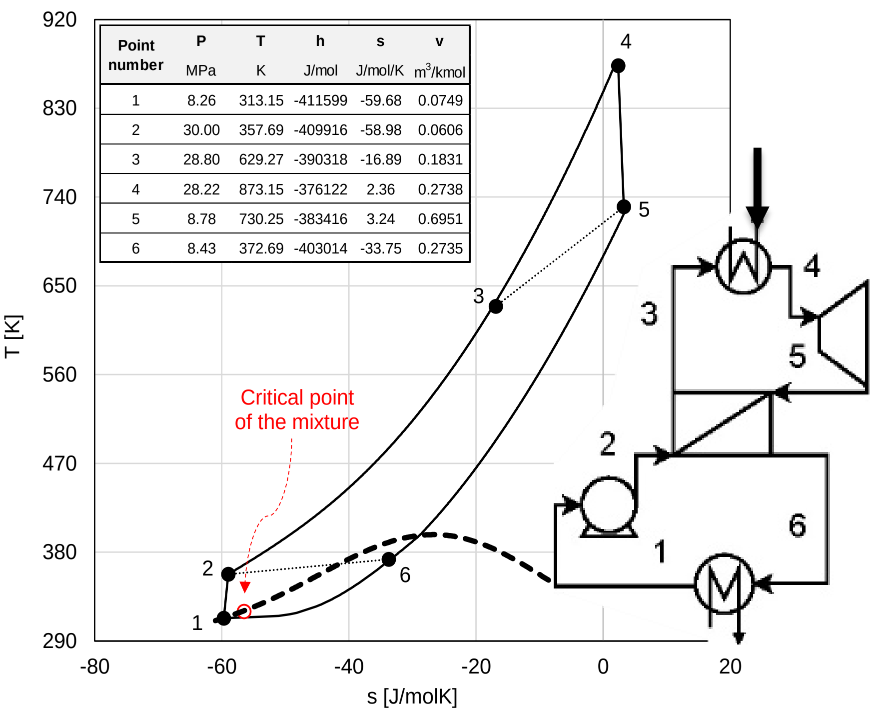
Basic assumptions for comparisons

	CO_2	CO_2-NOA (2.5%$_{mol}$)
Maximum T of the cycle (T_{max}) [°C]	400-600	
Minimum T of the cycle (T_{min}) [°C]	40	
Maximum P of the cycle (P_{max}) [bar]	300	
Minimum P of the cycle (P_{min}) [MPa]	To max power efficiency	Saturation pressure at T_{min}
Isentropic turbine efficiency [-]	0.92	
Isentropic compressor efficiency [-]	0.85	
Pressure drops ($\Delta P/P_{in}$)	Recuperator: 0.04 / Primary HX: 0.02 / Condenser: 0.02	
Min ΔT hot-cold streams in recuperator [°C]	15	
Electro-mechanical efficiency [-]	0.95	

Scheme of plants

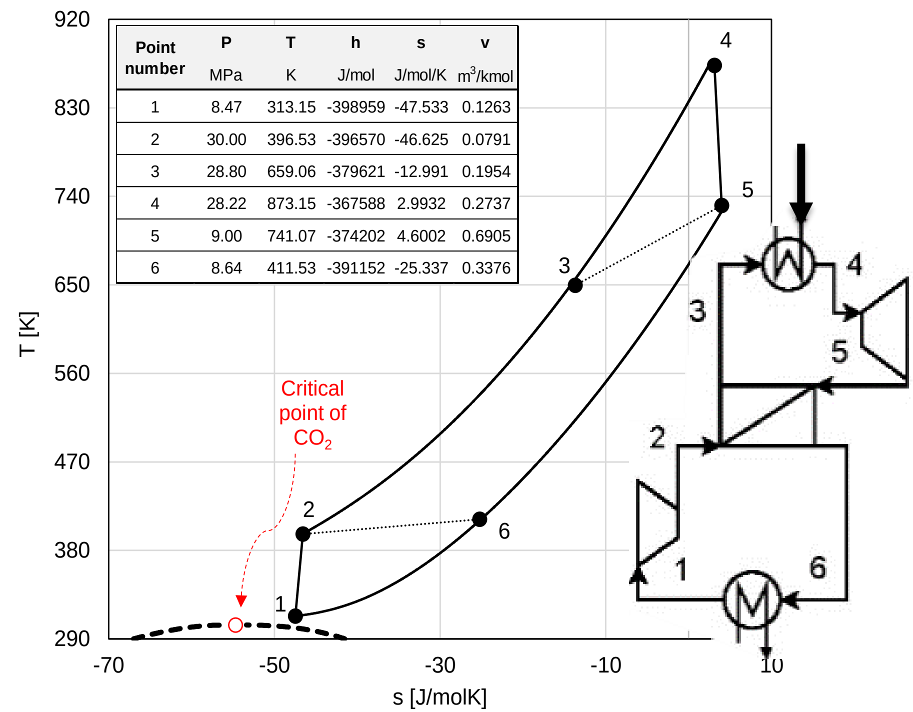
Recuperative plants

MIX



Point number	P MPa	T K	h J/mol	s J/mol/K	v m^3/kmol
1	8.26	313.15	-411599	-59.68	0.0749
2	30.00	357.69	-409916	-58.98	0.0606
3	28.80	629.27	-390318	-16.89	0.1831
4	28.22	873.15	-376122	2.36	0.2738
5	8.78	730.25	-383416	3.24	0.6951
6	8.43	372.69	-403014	-33.75	0.2735

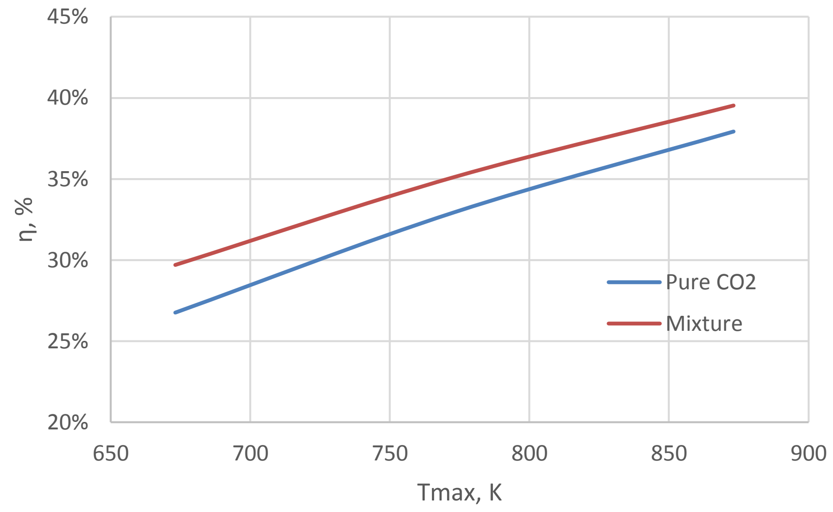
Pure CO_2



Point number	P MPa	T K	h J/mol	s J/mol/K	v m^3/kmol
1	8.47	313.15	-398959	-47.533	0.1263
2	30.00	396.53	-396570	-46.625	0.0791
3	28.80	659.06	-379621	-12.991	0.1954
4	28.22	873.15	-367588	2.9932	0.2737
5	9.00	741.07	-374202	4.6002	0.6905
6	8.64	411.53	-391152	-25.337	0.3376

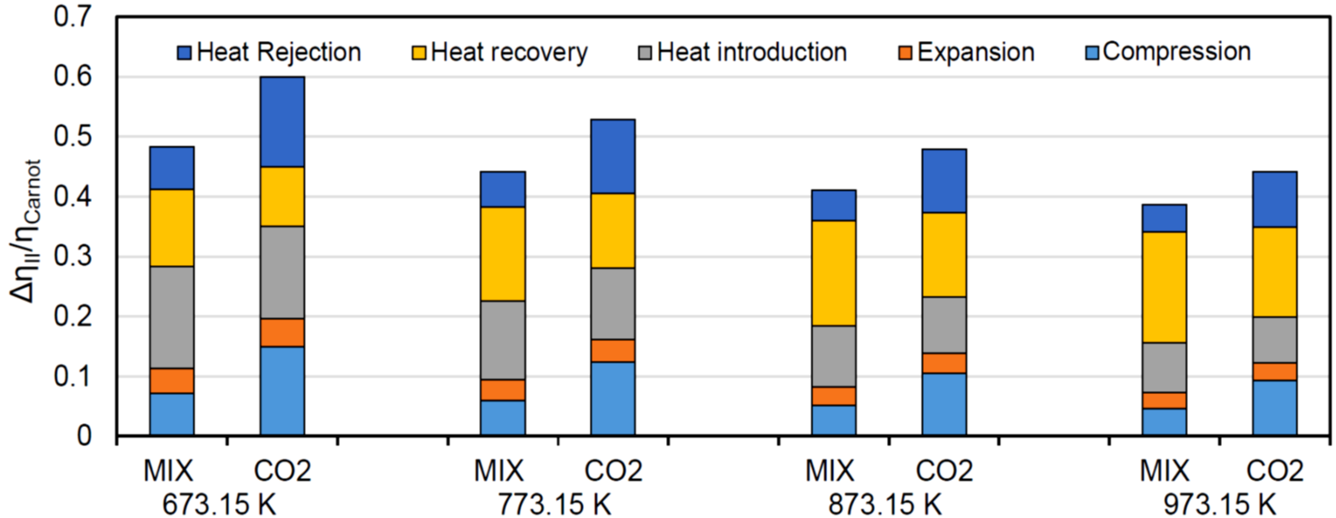
Performances

Comparison of efficiency for maximum pressure of 300 bar



Greater benefit of the mixture at lower temperature: about 3 %point at 400 °C and almost 2 %point at 600 °C

Efficiency penalty by Second-law analysis



$\Delta\eta_{II}$ heat rejection and compression decrease significantly by adopting the condensing mixture.

$\Delta\eta_{II}$ heat exchanges in the recuperator and in heat introduction increase, but their effect is much lower than the former advantages.

Higher log-mean-temp difference within the recuperator.

Lower T value of the fluid entering the primary HX, allows a major cooling of the heat source – whether available at variable temperature.

Conclusions

- Small amount of the NOA increase the critical temperature of the working fluid from the one of CO_2
- Efficient application of CO_2-based power cycles for high-temperature heat sources even when the heat sink temperature is above 25°C
- The in-house software is able to calculate the properties also at the critical point

Further investigation related to the mixture composition, alternative layouts of the power plant and the evaluation of the design of their components.

Acknowledgements

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