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TITLE OF PAPER

ADVANCED THERMODYNAMIC POWER CYCLES UTILIZING CARBON DIOXIDE BASED MIXTURES AS WORKING FLUIDS FOR HIGH TEMPERATURE WASTE HEAT RECOVERY

Authors:
Abubakr Ayub, Gioele Di Marcoberardino, Costante Mario Invernizzi, Paolo Iora*
Affiliations:
Department of Mechanical and Industrial Engineering,
Universita Degli Studi Di Brescia, Brescia, Italy.

Abubakr Ayub

a.ayub@unibs.it; abubakrayub@gmail.com
PhD student (2019-now)
Department of Mechanical and Industrial Engineering (DRIMI)
Holder of PhD scholarship offered by Universita Degli Studi Di Brescia, Brescia, Italy.

PhD research topic.
Advanced carbon dioxide thermodynamic cycles for power production

Professor:
Costante Mario Invernizzi
Full Professor, Department of Mechanical and Industrial Engineering
Universita Degli Studi Di Brescia, Italy.

Academic background:
Masters in Mechanical Engineering from Capital University of Science and Technology, Islamabad, Pakistan (2016-2018).
MS Thesis: Supercritical carbon dioxide power cycles for waste heat recovery of gas turbine

Background and main challenges

High temperature waste heat sources:

- Fluid catalyst cracking in Refineries ($T \approx 700$℃)
- Cement industry ($T \approx 300$℃ $- 500$℃)
- Steel and glass manufacturing industries

Effective ways to exploit waste heat for power production:

- Steam Rankine cycles
- Organic Rankine cycles
- Supercritical/Transcritical carbon dioxide cycles

Organic Rankine cycles

Many engines are developed and currently installed.

Main challenge is thermal stability of working fluid at high temperatures.

Supercritical carbon dioxide power cycles

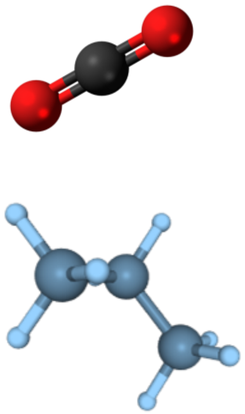
Suitable for high temperature waste heat recovery.

Main challenges are:

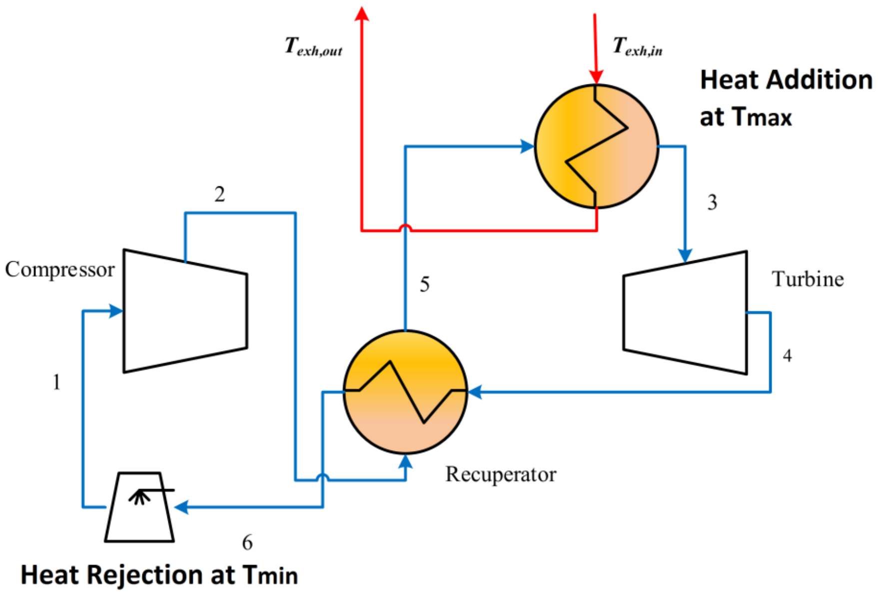
- Higher maximum operating pressures.
- Complex plant layouts (including cascade heating and dual expansion processes).

Potential of carbon dioxide mixtures as working fluids

- To achieve higher total efficiency ***(heat recovery effectiveness x cycle efficiency)***
- Employing simpler power plant scheme
- To lower power cycle operating pressures.
- And, to reduce plant specific cost and levelized cost of electricity.



CO_2 binary mixtures working fluid



Potential of carbon dioxide mixtures as working fluids

1. Choice of additives for CO_2 mixtures
2. Thermodynamic properties of CO_2 mixtures
3. Thermodynamic modeling of power cycles
4. Thermodynamic performance comparison

Potential of carbon dioxide mixtures as working fluids

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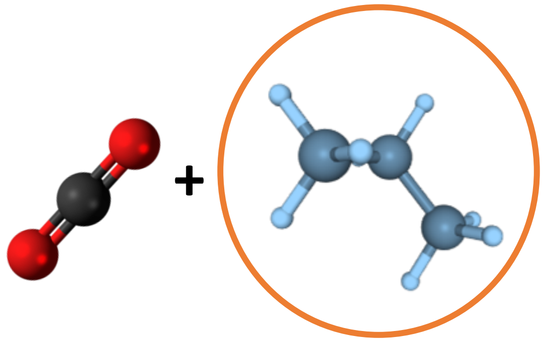
3. Thermodynamic modeling of power cycles

4. Thermodynamic performance analysis and comparison

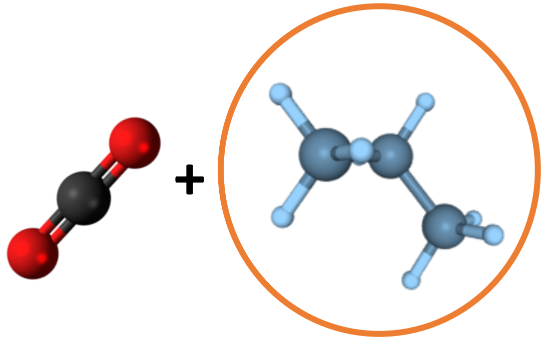


Selection criteria

- $T_{cr} > T_{cr}$ of CO_2
- Moderate P_{cr}
- Thermally stable up to 400°C
- Lower molecular complexity
- Low GWP and ODP
- Non-flammable, nontoxic

Potential of carbon dioxide mixtures as working fluids

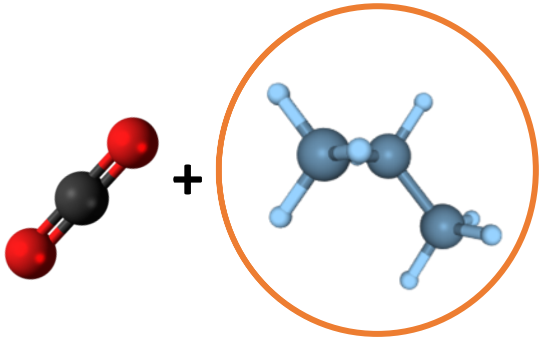
1. Choice of additives for CO_2 mixtures



Working fluid	T_{cr} (C)	P_{cr} (bars)	Molecular weight	Parameter of Molecular Complexity	Acentric factor ω	Thermal stability
CO_2	31.06	73.83	44.01	-9.340	0.22362	>700 °C
R134a	101.03	40.56	102.03	-2.429	0.32687	350 to 370 °C
NOVEC5110	146	21.44	266.04	17.145	0.42919	200-300°C
NOVEC649	168.66	18.69	316.04	28.165	0.471	
HFO1234yf	94.7	33.82	114.04	-1.017	0.28203	
HFO1234ze(E)	109.36	36.62	114.04	0.046	0.32376	

Potential of carbon dioxide mixtures as working fluids

1. Choice of additives for CO_2 mixtures



Working fluid	ODP	GWP in 100 years	Flammability	Health	Instability	ASHRAE 34 safety group
CO_2	0	1	0	2	0	A1
R134a	0	1370	0	1	1	A1
NOVEC 5110	0	1	1	3	0	
NOVEC649	0	1	0	3	1	
HFO1234yf	0	< 4.4	4	2	0	A2L
HFO1234ze(E)	0	6	n.a.	n.a.	n.a.	A2L

Potential of carbon dioxide mixtures as working fluids

1. Choice of additives for CO_2 mixtures
2. Thermodynamic properties of CO_2 mixtures
3. Thermodynamic modeling of power cycles
4. Thermodynamic performance analysis and comparison

- Identification of Equation of state (EoS)
- Calibrate EoS parameters using experimental data.
- Use EoS to determine thermodynamic properties of CO_2 mixtures at different composition:
  - P-T phase diagrams
  - Critical points
  - Densities, enthalpies and entropies

Potential of carbon dioxide mixtures as working fluids

2. Thermodynamic properties of CO_2 mixtures

Peng Robinson EoS with van der Waals mixing rules

$$P = \frac{RT}{v-b} - \frac{\alpha a}{v(v+b)+b(v-b)}$$

$$\alpha = \left[1 + k(1-\sqrt{T_r})\right]^2$$

$$k = 0.37464 + 1.54226\omega - 0.26992\omega^2$$

$$a = 0.45724\frac{R^2T_c^2}{P_c} \qquad b = 0.0778\frac{RT_c}{P_c}$$

Mixing rules

$$a_m = \sum_j \sum_j z_i z_j a_{i,j}$$

$$b_m = \sum_j \sum_j z_i z_j b_{i,j}$$

$$a_{i,j} = \sqrt{a_i a_j}\left(1 - k_{ij}\right)$$

$$b_{i,j} = \frac{b_i + b_j}{2}$$

EoS requires:

- Pure fluid properties.
- Binary interaction parameter (k_{ij})

Potential of carbon dioxide mixtures as working fluids

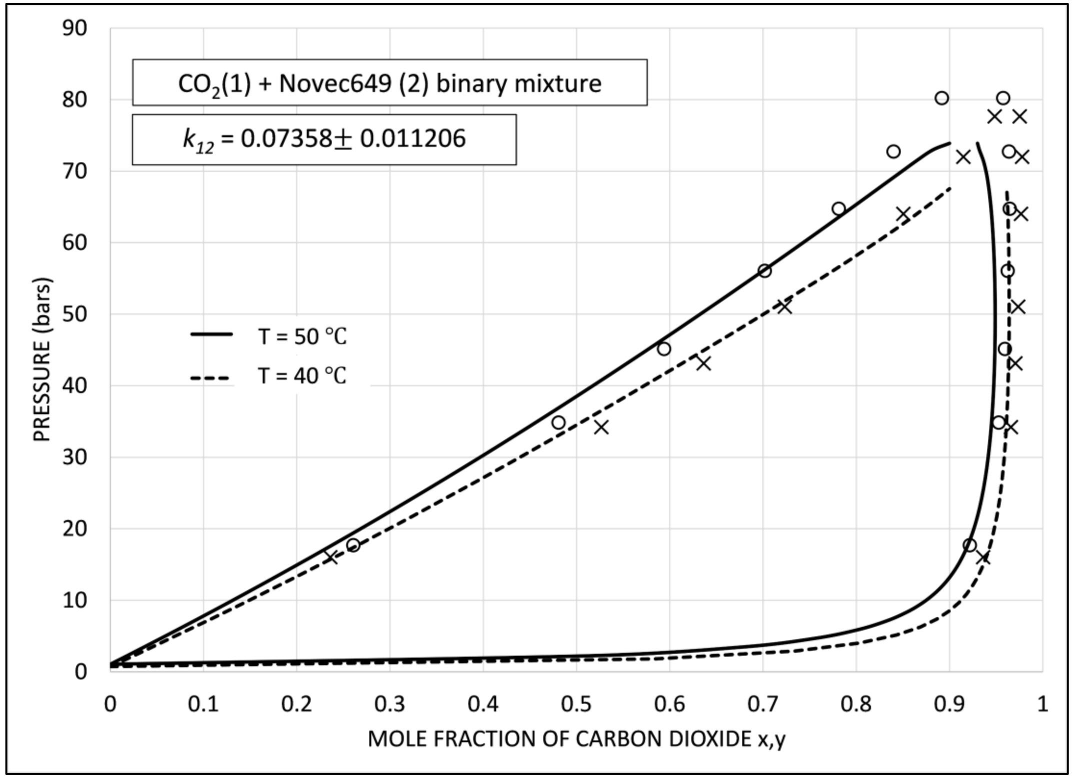
2. Thermodynamic properties of CO_2 mixtures

Fitting Equation of state on experimental vapor-liquid equilibrium (VLE) data

Value of binary interaction parameter (k_{ij}) is determined by fitting EoS on experimental data.

CO_2-Novec649 mixture

- Experimental VLE (scatter points)
- Solid line shows VLE computed by EoS
- $k_{1,2} = 0.07358 \pm 0.011206$

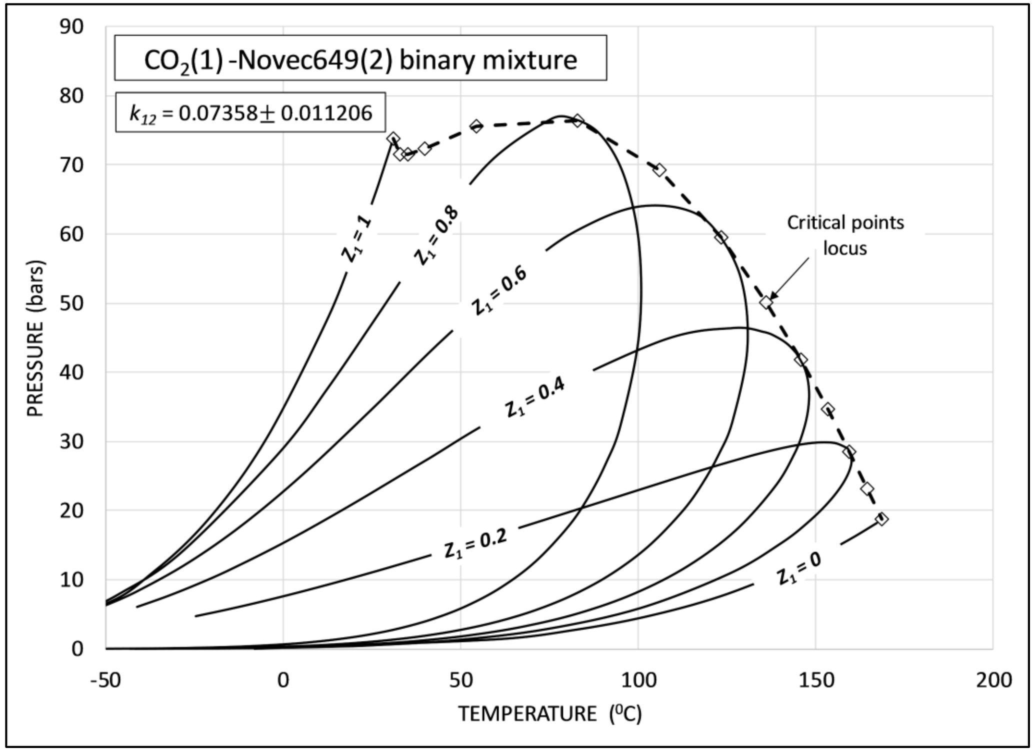


Potential of carbon dioxide mixtures as working fluids

2. Thermodynamic properties of CO_2 mixtures

CO_2-Novec649 mixture

- $k_{1,2} = 0.07358 \pm 0.011206$
- P-T envelop and critical points of CO_2-Novec649 mixture are calculated.



- Information about bubble and dew points, critical locus and temperature glide *(temperature difference between bubble and dew point at constant pressure).*

Potential of carbon dioxide mixtures as working fluids

2. Thermodynamic properties of CO_2 mixtures

- In case, No experimental VLE data are available
- The correlation between $\mathbf{a_{1,2}}$ and $\mathbf{a_2}$ is developed using data of some known CO_2 mixtures.

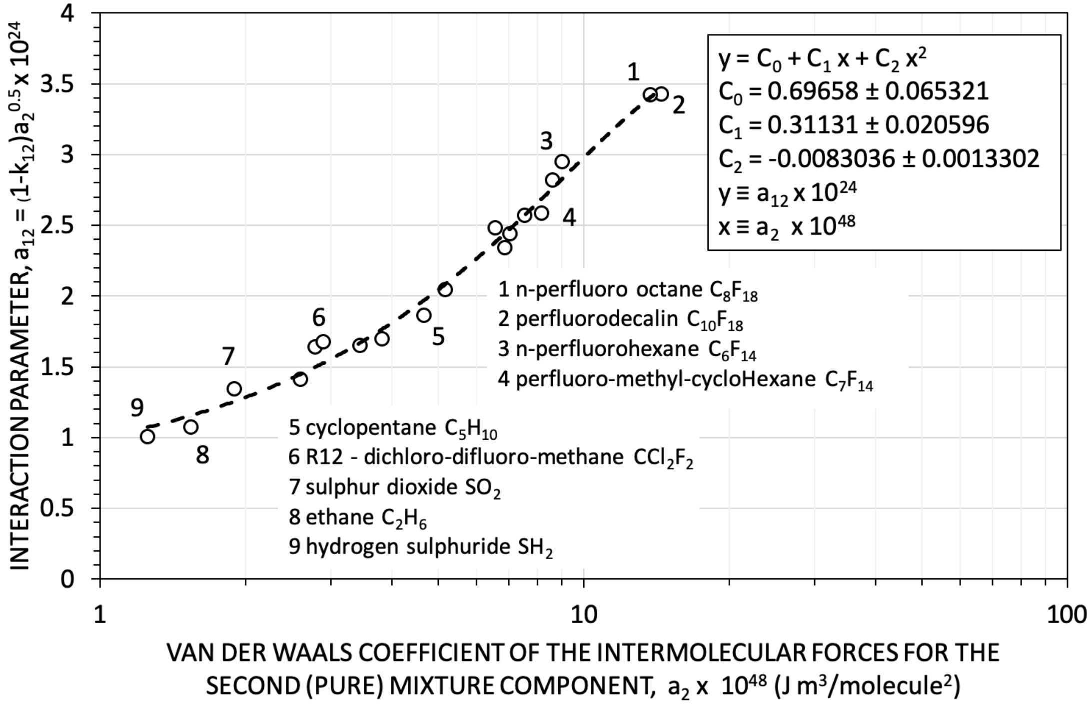
$$a_{1,2} = \sqrt{a_1 a_2}\left(1 - k_{1,2}\right)$$

$$y = C_0 + C_1 X + C_2 X^2$$

$\boldsymbol{y} \equiv a_{12} * 10^{24}$, Interaction parameter of a CO_2 mixture

$\boldsymbol{X} \equiv a_2 * 10^{48}\ \frac{Jm^3}{molecule^2},$

van der Waals coefficient of intermolecular forces for the additive (or dopant).



Potential of carbon dioxide mixtures as working fluids

2. Thermodynamic properties of CO_2 mixtures

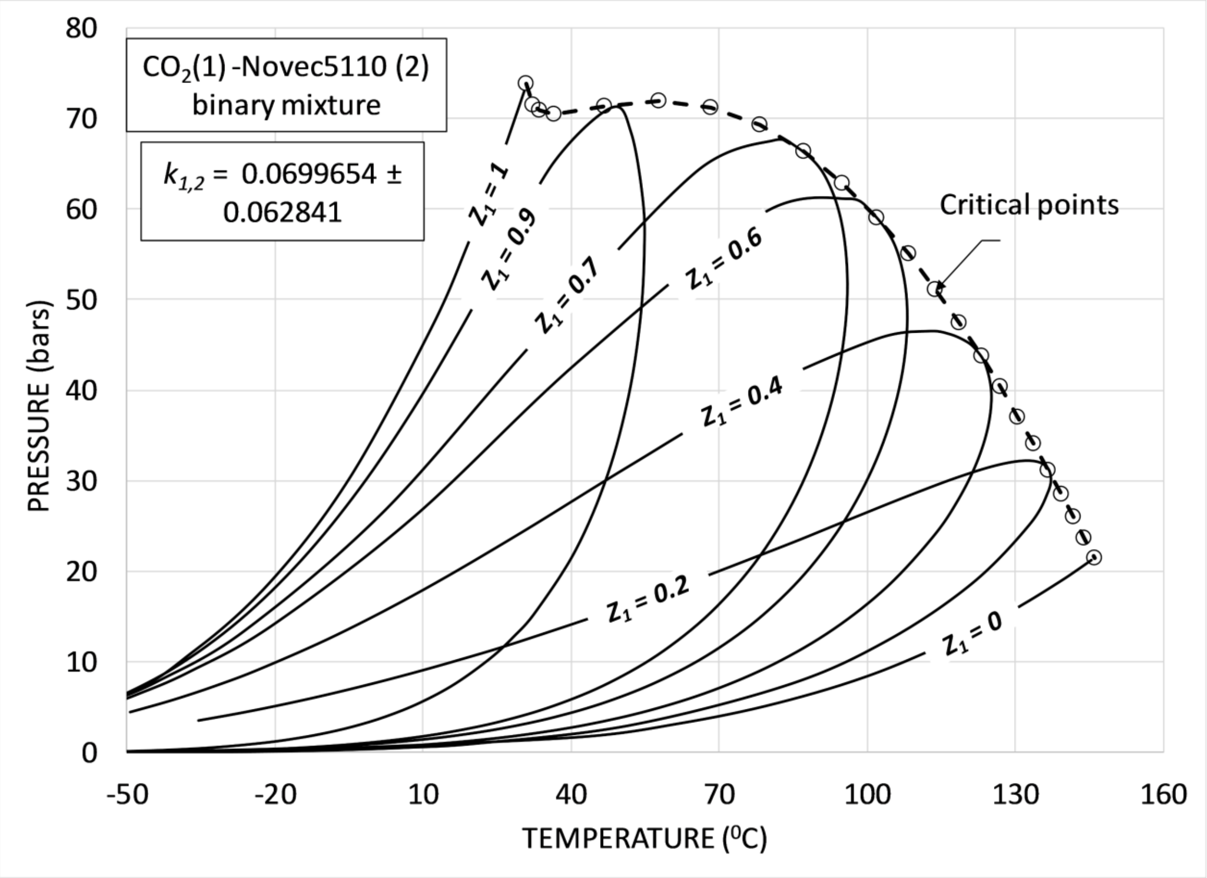
CO_2-NOVEC 5110 mixture

$$a_{1,2} = \sqrt{a_1 a_2}\left(1 - k_{1,2}\right)$$

$k_{1,2} = 0.06996 \pm 0.062841$

computed using uncertainty propagation

P-T envelop and critical points



Potential of carbon dioxide mixtures as working fluids

2. Thermodynamic properties of CO_2 mixtures

Values of $k_{1,2}$ for CO_2 mixtures computed by either:

- Fitting EoS on experimental VLE data.
- Estimated using correlation in case of No experimental data*

CO_2 mixtures	Experimental VLE data	$k_{1,2}$	Standard deviation
CO_2-Novec649	VLE at T= 40 °C, 50°C, 60°C and 70°C	0.07358	0.01120
CO_2-R134a	VLE at T= -21 °C T= -1 °C, 19°C, 50°C, 55°C 56°C, 60°C,65°C, 66°C ,70°C and 81°C	0.0166	0.00824
CO_2-Novec5110	Not available	0.06996*	

Potential of carbon dioxide mixtures as working fluids

1. Choice of additives for CO_2 mixtures
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4. Thermodynamic performance analysis and comparison

Thermodynamic power cycles with supercritical CO_2 working fluid.

Thermodynamic power cycles with CO_2 mixtures working fluid

- ***Working fluid:***
  CO_2
- ***Power cycle layouts:***
  Three different cycle configurations are selected from best practice in literature

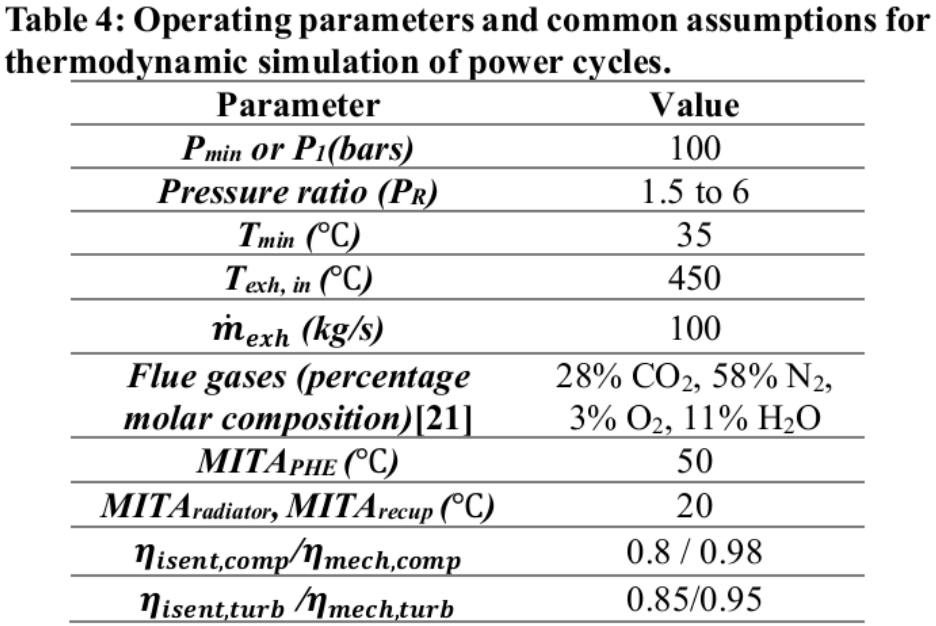
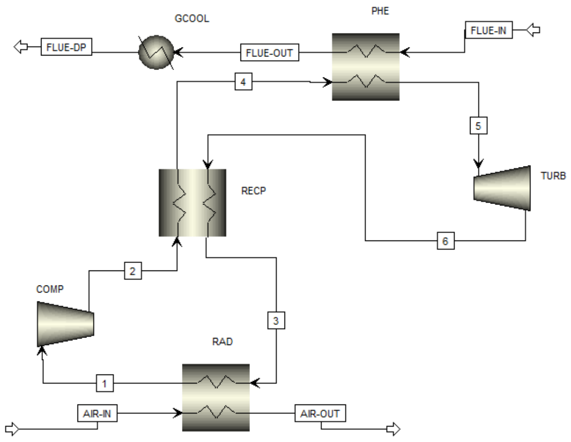


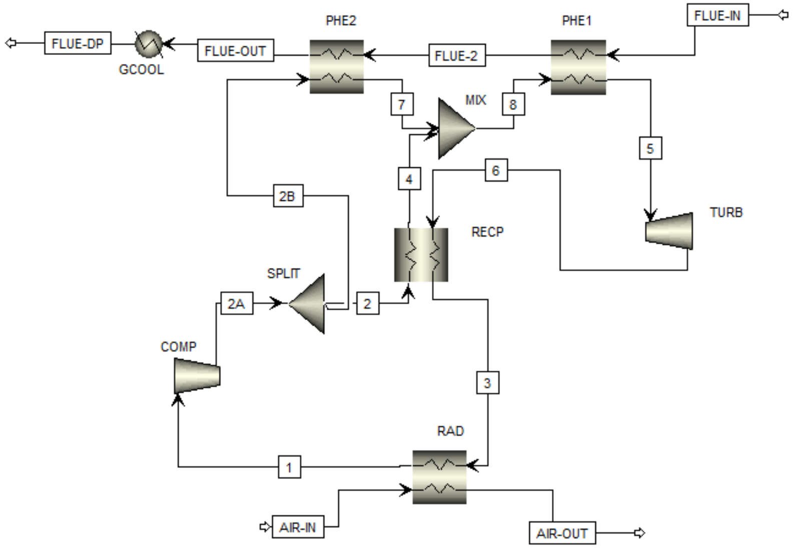
Table 4: Operating parameters and common assumptions for thermodynamic simulation of power cycles.

Parameter	Value
P_{min} or P_1(bars)	100
Pressure ratio (P_R)	1.5 to 6
T_{min} (°C)	35
$T_{exh,\ in}$ (°C)	450
$\dot{m}_{exh}$ (kg/s)	100
Flue gases (percentage molar composition)[21]	28% CO_2, 58% N_2, 3% O_2, 11% H_2O
$MITA_{PHE}$ (°C)	50
$MITA_{radiator}$, $MITA_{recup}$ (°C)	20
$\eta_{isent,comp}/\eta_{mech,comp}$	0.8 / 0.98
$\eta_{isent,turb}/\eta_{mech,turb}$	0.85/0.95

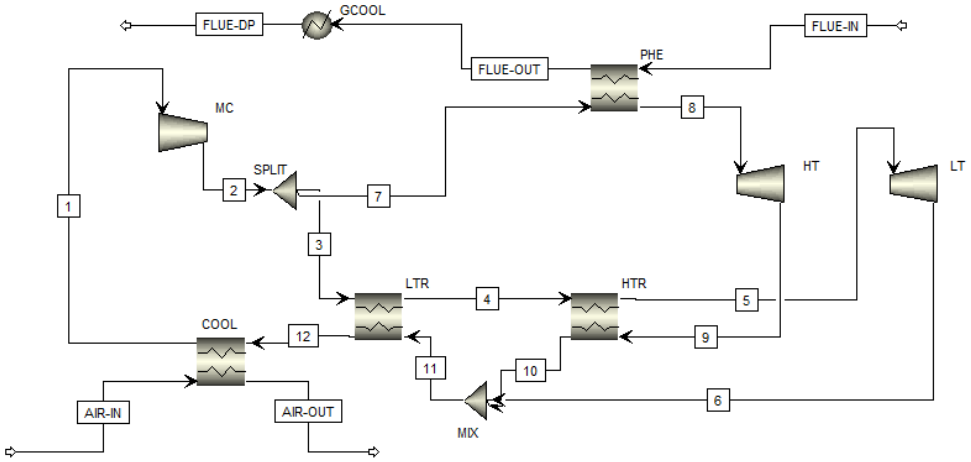
1. Simple Recuperative cycle



2. Recuperative cycle with split



3. Single flow split dual expansion cycle



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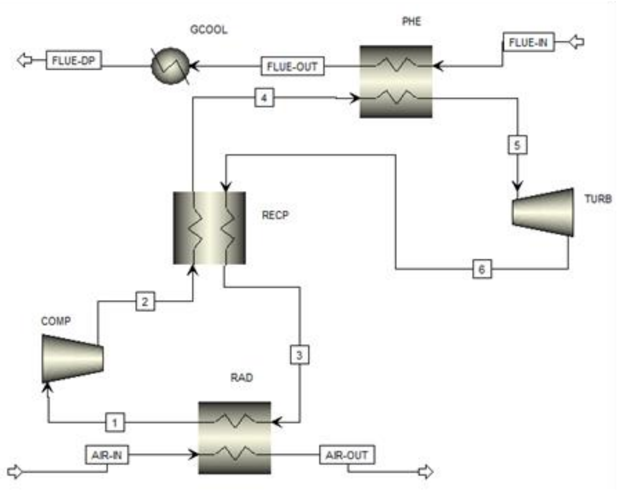
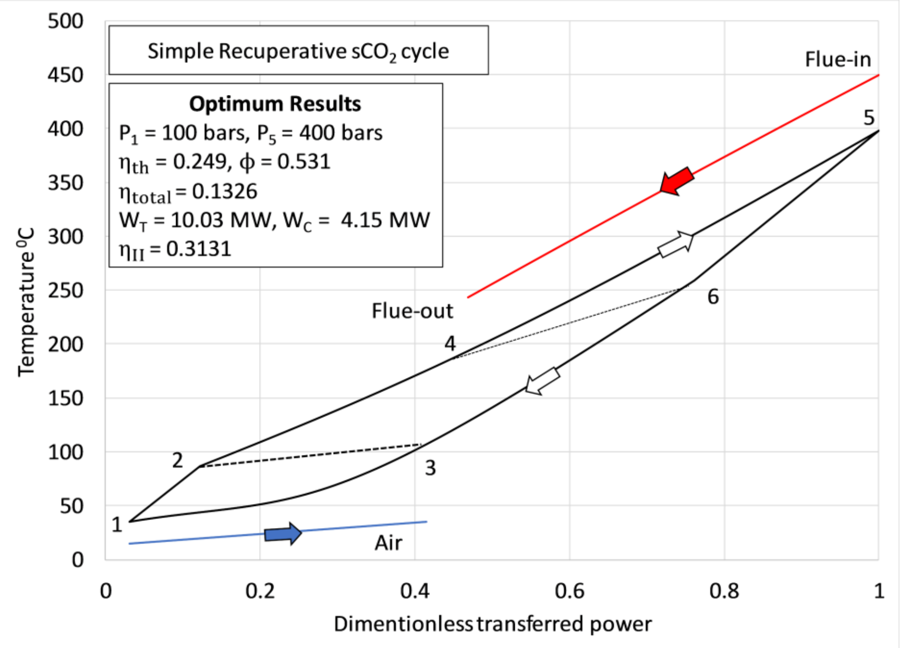




Optimum Results

P_1 = 100 bars, P_5 = 400 bars

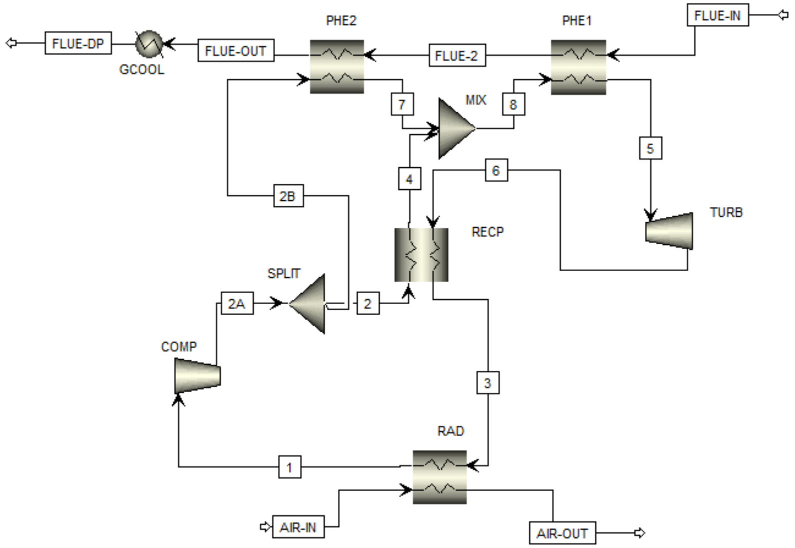
η_{th} = 0.249, ϕ = 0.531

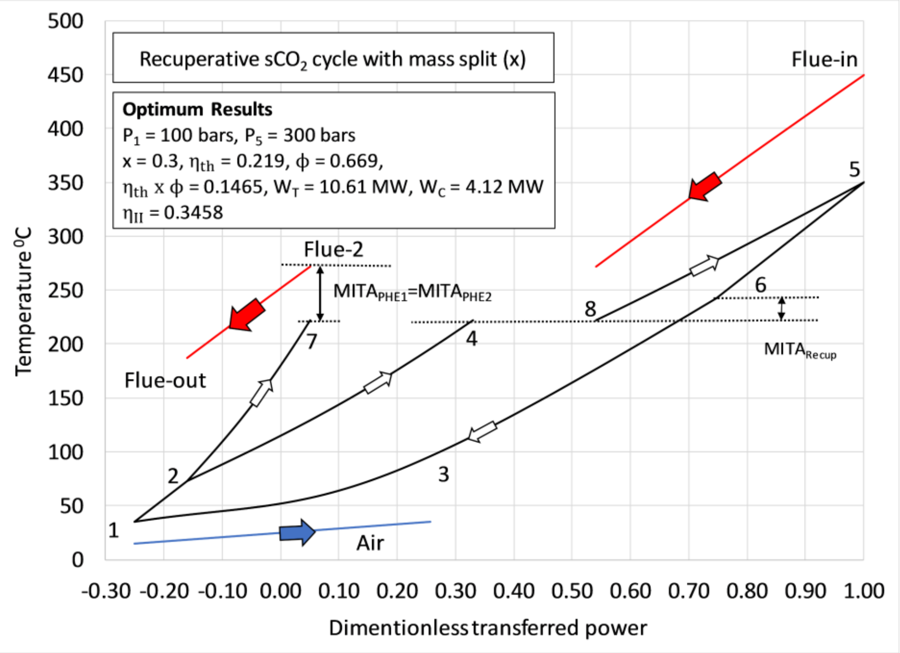
η_{total} = 0.1326

W_T = 10.03 MW, W_C = 4.15 MW

η_{II} = 0.3131

2. Recuperative cycle with split





Optimum Results

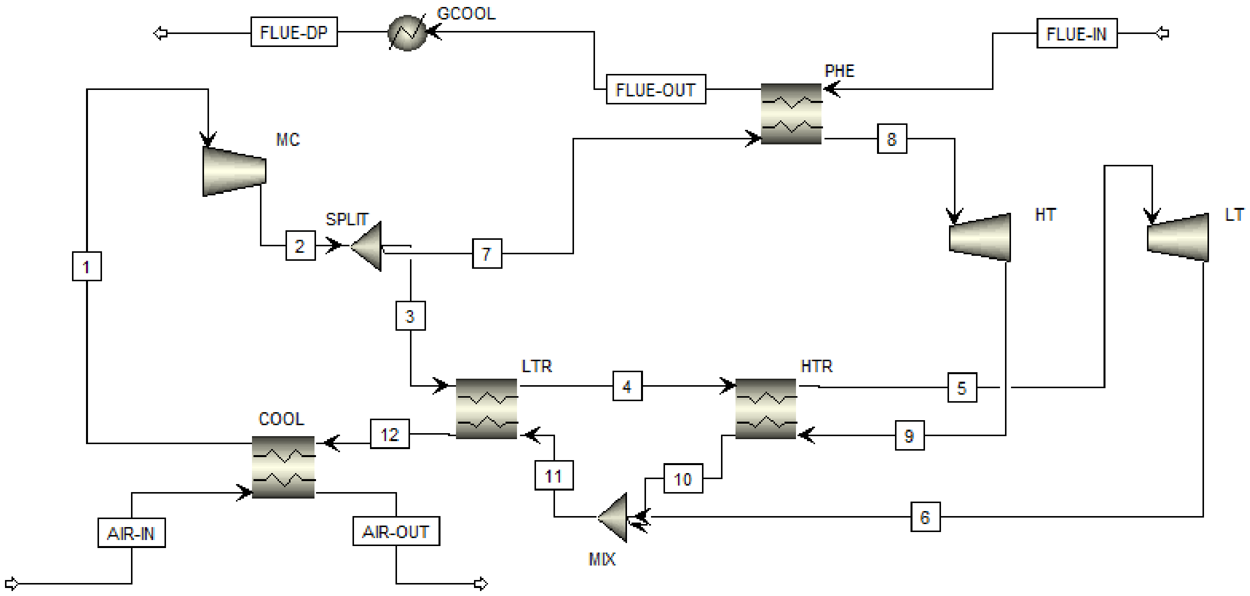
P_1 = 100 bars, P_5 = 300 bars

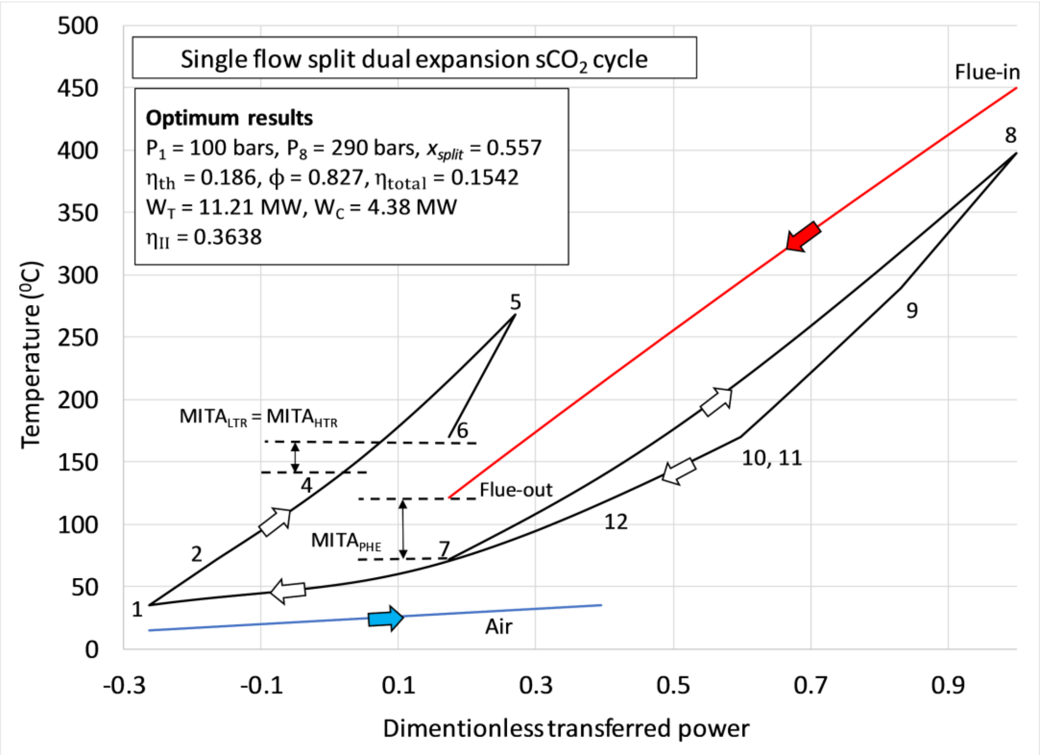
x = 0.3, η_{th} = 0.219, ϕ = 0.669,

η_{th} x ϕ = 0.1465, W_T = 10.61 MW, W_C = 4.12 MW

η_{II} = 0.3458

3. Single flow split dual expansion cycle




Single flow split dual expansion sCO$_2$ cycle

Optimum results
P_1 = 100 bars, P_8 = 290 bars, x_{split} = 0.557
η_{th} = 0.186, ϕ = 0.827, η_{total} = 0.1542
W_T = 11.21 MW, W_C = 4.38 MW
η_{II} = 0.3638

- Dual expansion processes.
- Different mass flow through recuperators (LTR and HTR) to balance heat capacities and improve thermal match.

Thermodynamic performance comparison of three CO$_2$ power cycles

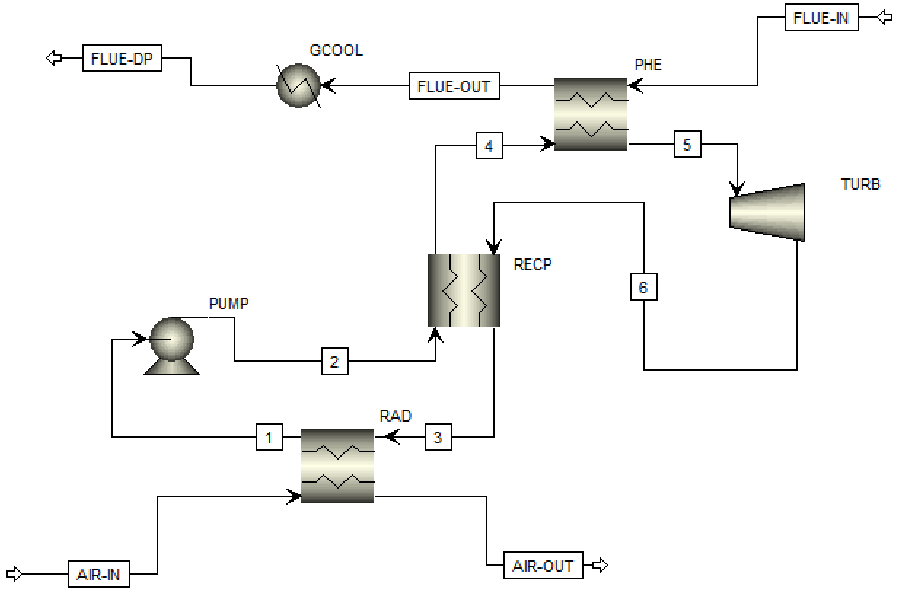
- SRC is not proven to be effective in heat extraction from flue gases.
- There is **10.56%** and **16.29%** gain in total efficiency for RCS and SFDE cycles, respectively relative to SRC.

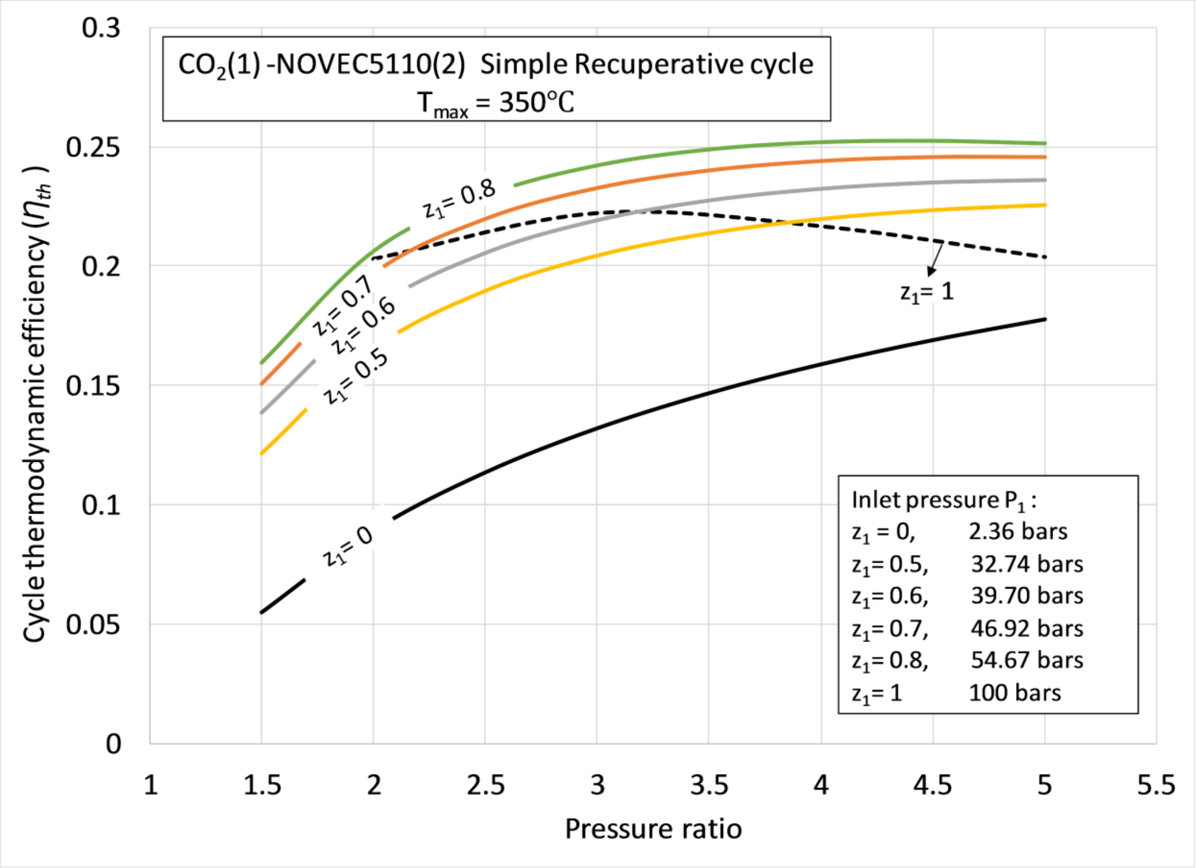
CO$_2$ Power cycles	**T_{max} (°C)**	**P_R**	**$\dot{W}_{net}$ (kW)**	η_{th}	ϕ	$\eta_{total} = \eta_{th} \times \phi$	**Exergy efficiency**
SRC	400	4	5873	0.249	0.532	0.132	0.313
RCS	350	3	6487	0.219	0.669 ⬆	0.146 ⬆	0.345
SFDE	400	2.9	6826	0.186	0.827 ⬆	0.154 ⬆	0.363

Thermodynamic power cycles with CO_2 mixtures working fluid

- ***Working fluid:***
  CO_2-Novec5110
- ***Heat source***:
  Flue gases at T = 450°C and $\dot{m}_{flue}$= 100 kg/s

Simple Recuperative transcritical cycle





Inlet pressure P_1 :

z_1 = 0,	2.36 bars
z_1= 0.5,	32.74 bars
z_1= 0.6,	39.70 bars
z_1= 0.7,	46.92 bars
z_1= 0.8,	54.67 bars
z_1= 1	100 bars

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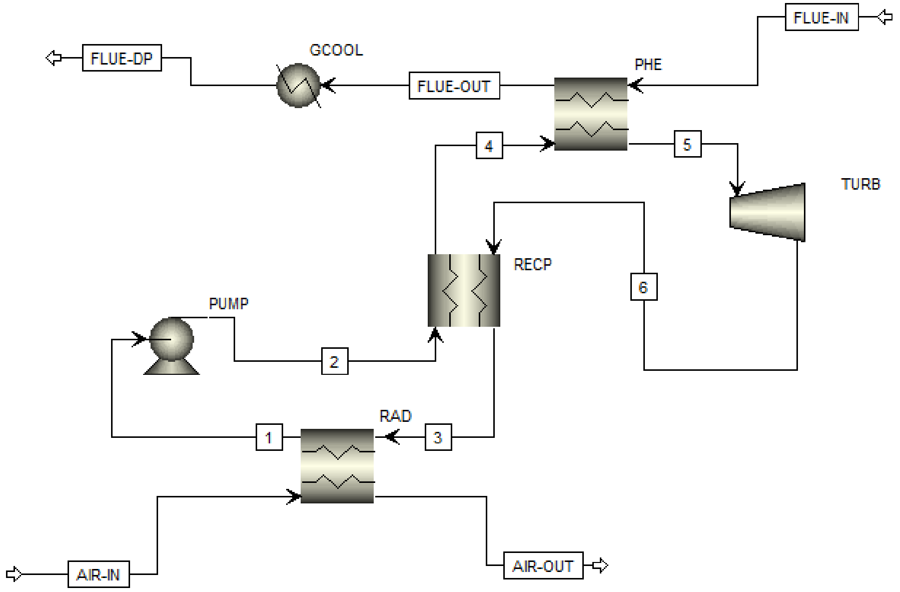
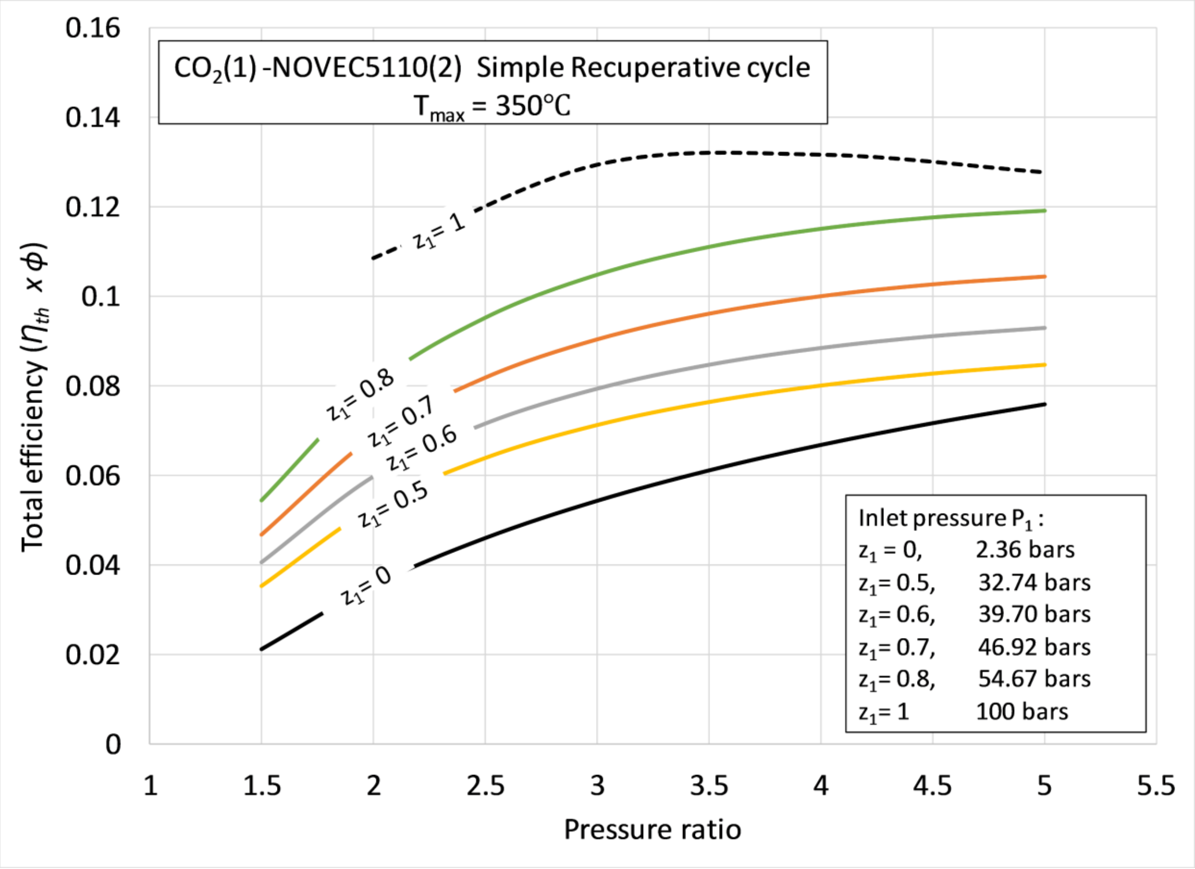
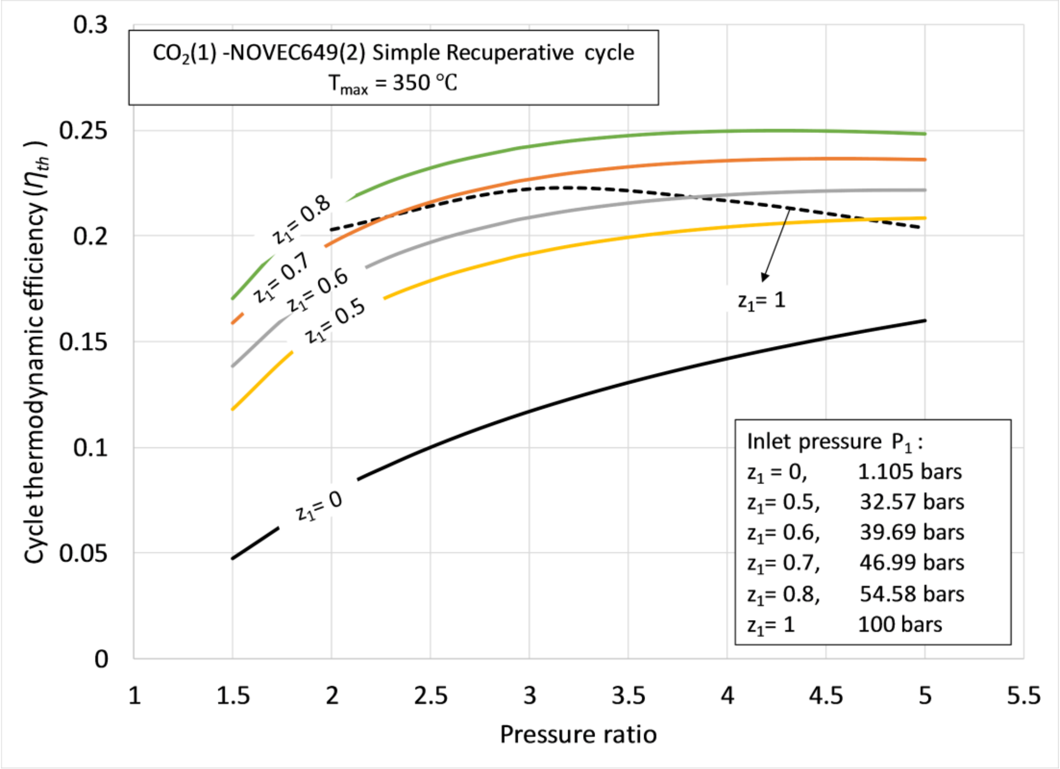
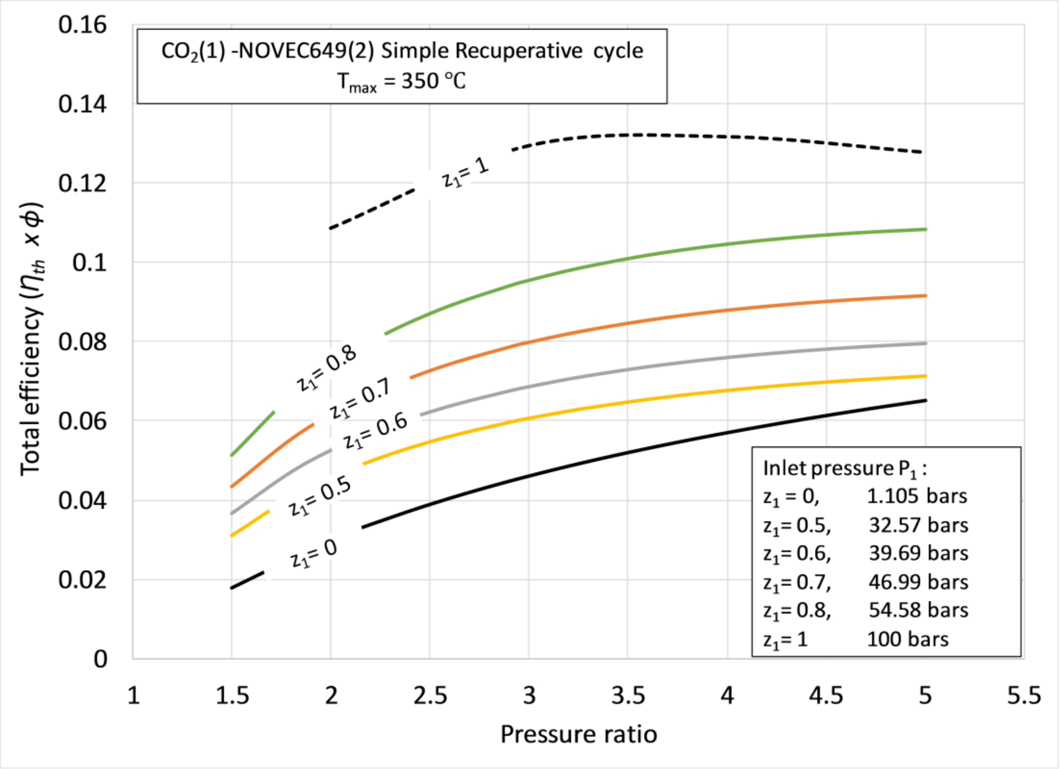




Thermodynamic power cycles with CO_2 mixtures working fluid

- ***Working fluid:***
  CO_2–*Novec649*
- ***Heat source***:
  Flue gases at T = 450°C and $\dot{m}_{flue}$= 100 kg/s





Conclusion

- CO_2-Novec mixtures show comparable η_{th} compared to sCO_2 simple recuperative cycle
- 3 percentage points higher η_{th} compared to recuperative with mass split cycle.
- Lower expansion in turbine compared to CO_2 power cycles owing to higher molecular complexity of Novec fluids.

Comparison of promising thermodynamic cycle results for supercritical CO_2 and transcritical CO_2 mixtures power cycles.

Working fluid	η_{total}	η_{th}	$\dot{W}_{net}$ **(kW)**	P_{max} ***(bars)***	P_{min} ***(bars)***
sCO_2 (Simple recuperative cycle)	0.132	0.249	5873	400	100
sCO_2 (Recuperative cycle with mass split)	0.146	0.219	6464	300	100
CO_2 (0.8)-Novec649 (0.2)	0.108	**0.248**	4782	273	54.58
CO_2(0.8)-Novec5110 (0.2)	0.117	**0.252**	5180	246	54.67
CO_2 (0.7)-R134a (0.3)	**0.147**	**0.248**	6509	200	24.54

Conclusion

With **CO_2-R134a mixture** working fluid:

- Comparable total efficiency is achieved.
- 3 percentage points rise in η_{th} is obtained compared to recuperative with mass split sCO_2 cycle.

Lower maximum operating pressures for power cycles operating with CO_2 mixtures.

Beneficial in component design point of view since lower pressures are proportional to lower mechanical stresses in cycle components.

Comparison of promising thermodynamic cycle results for supercritical CO_2 and transcritical CO_2 mixtures power cycles.

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THANK YOU FOR YOUR ATTENTION.