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

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ABSTRACT

This paper proposed CO_2 mixtures as working fluids in closed Brayton power cycles using flue gases at relatively high temperature (400-450 °C) as waste heat source. Firstly, a comprehensive selection criterion is defined for choice of working fluids to be employed as additives in CO_2 mixtures. Secondly, the thermodynamic properties of the mixtures are calculated at different molar compositions using an appropriate equation of state. The binary interaction parameters involved in the equation of state are obtained with the help of available experimental VLE data or by estimation method in case of non-availability of the VLE data. As a benchmark, the study also investigates the thermodynamic performance of advanced sCO_2 cycle layouts to compare with the performance of cycles operating with CO_2 mixtures. Sensitivity analysis reveals that the power cycles operating with CO_2-Novec5110 mixture (with 0.2 mole fraction of Novec fluids) show 3 percentage points rise in cycle thermodynamic efficiency (0.219 versus 0.252) with lower cycle operating pressures as compared to recuperative with mass split sCO_2 cycle. In case of CO_2-R134a mixture working fluid (with 0.3 mole fraction of R134a), total efficiency of about 0.15 is obtained at cycle maximum pressure of 200 bars compared to simple recuperative sCO_2 cycle with total efficiency of 0.13 at rather higher maximum pressure of 400 bars.

INTRODUCTION

One of the possible ways of energy recovery from industrial waste heat is to use highly efficient thermal power thermodynamic engines. Organic Rankine Cycles (ORCs) and Steam Cycles are two prominent power cycles commercialized in last years for waste heat recovery[1]. In recent years, supercritical carbon dioxide (sCO_2) cycles are also investigated for vast range of waste heat sources from medium to high temperatures. sCO_2 cycles offer lower compression work due to higher density near critical point and compact turbomachinery.

Numerous studies analyzed thermodynamic performance of different sCO_2 cycle layouts namely partial heating cycle, dual recuperated cycle, precompression cycle, single-recuperated with dual expansion cycle and some novel cycle layouts [2], [3]. The main intend of these studies are: (i) to gain knowledge about contribution of different processes (intercooling, reheating, recompression and/or mass split) on total efficiency of the power cycle, and (ii) to select the best possible cycle layout in terms of power output, heat recovery and size footprint. In essence, the studies found that higher heat recovery effectiveness of sCO_2 power cycle comes with lower cycle thermodynamic efficiency. Moreover, sCO_2 cycle layouts which presented higher heat recovery effectiveness have higher maximum operating pressures and they are comprised of larger cycle components with complex operational scheme, for example Dual flow split with dual expansion cycle.

To mitigate this drawback, this study proposed novel carbon dioxide mixtures as working fluid in waste heat recovery power cycles. The use of CO_2 mixtures to alter the properties of CO_2 and to achieve higher cycle efficiency is recently explored by some research works [4], [5]. Here in this paper, we explored possibility of CO_2 based mixtures as working fluid in waste heat recovery power cycles to address following main challenges:

(i) to improve the heat recovery effectiveness of CO_2 power cycle, (ii) to reduce cycle maximum operating pressures in order to avoid mechanical stresses in cycle components and, (iii) to keep power cycle layout simpler.

SELECTION AND CHARACTERIZATION

The choice of appropriate additive (or dopant) for CO_2 mixtures is challenging since it depends on the heat source application, required thermodynamic properties, health and safety characteristics of working fluids. Particularly for heat recovery application, the required additive should possess following characteristics:

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Table 1: Main physical properties of new refrigerants selected for CO_2 mixtures. Physical properties for Novec fluids are taken from [6].

Working fluid	T_{cr} (℃)	P_{cr} (bars)	Boiling point (℃)	Molecular weight	Molecular Complexity [7]	Acentric factor ω	Thermal stability
CO_2	31.06	73.83	-78.45	44.0098	-9.340	0.223621	>700 ℃
R134a	101.03	40.56	-25.92	102.031	-2.429	0.326878	350 to 370 ℃
Novec 5110	146	21.44	26.5	266.04	17.145	0.429196	
Novec 649	168.66	18.69	49.05	316.046	28.165	0.471	200-300℃
HFO1234yf	94.7	33.82	-28.85	114.042	-1.017	0.282037	
HFO1234ze(E)	109.36	36.62	-18.17	114.042	0.046	0.32376	

Table 2: Safety and environmental impact characteristics of new refrigerants selected for CO_2 mixtures [8], [9].

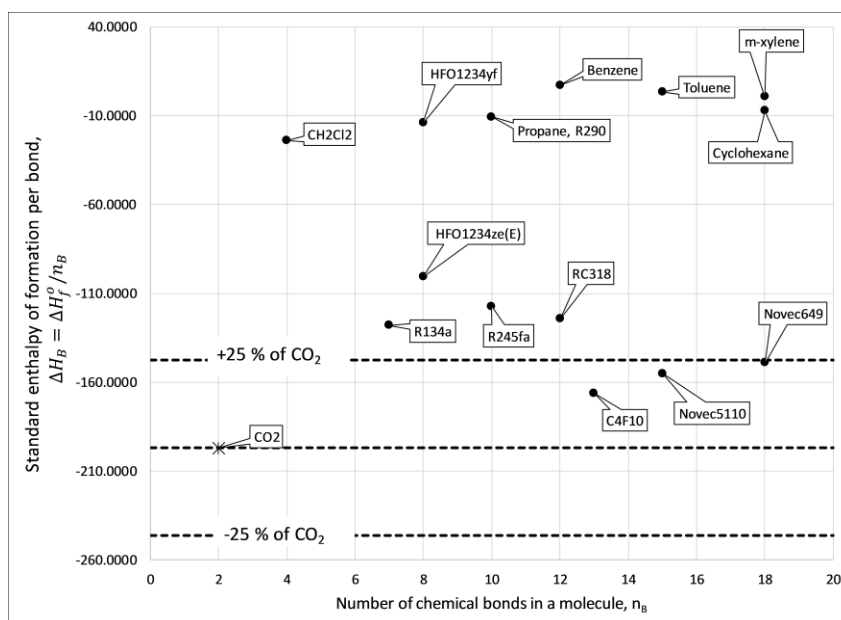| Working fluid	ODP [10]	GWP in 100 years [10], [11]	Flammability [12]	Health [12]	Instability [12]
CO_2	0	1	0	2	0
R134a	0	1370	0	1	1
Novec 5110	0	1	1	3	0
Novec 649	0	1	0	3	1
HFO1234yf	0	< 4.4	4	2	0
HFO1234ze(E)	0	6	n.a.	n.a.	n.a.

Figure 1: Standard enthalpy of formation per bond of some working fluids with respect to number of bonds in a molecule. Value of Novec5110 is taken from 3M™ producers. For Novec649, value is estimated using JOBACK group contribution method. Values of remaining fluids are taken from NIST and ASPEN databank. CO_2 is considered as reference fluid for comparison owing to its well established higher chemical stability.

1. Critical temperature (T_{cr}) higher than T_{cr} of CO_2 to enable condensation which possibly reduces the compression work in the power cycle
2. Moderate value of critical pressure (P_{cr}) to maintain operating pressures in the power cycle within allowable range suggested by mechanical design of cycle components.
3. Thermally stable at higher temperature i.e. thermal stability < 400℃ is adequate for heat recovery from flue gases at 450℃.
4. Lower value of parameter of molecular complexity (value close to 0) is preferable to obtain larger expansion in turbine or to obtain more cooling of working fluid at turbine outlet while also avoiding the subcritical conditions.

5. Higher molecular weight which is beneficial in terms of lower turbine stages.
6. Lower ozone depletion potential (ODP) and global warming potential (GWP), nontoxic and non-flammable.

Practically, it is quite difficult to find a dopant which meet all the above mentioned criteria. However, criteria numbers 1 and 2 regarding P_{cr} and T_{cr} and criteria number 6 regarding environmental aspect of working fluid are considered foremost priority during screening of different chemical compounds available in literature. **Table 1** shows the main thermodynamic properties of potential candidate compounds which are selected as additive for CO_2 mixtures. The environmental and safety parameters of these compounds are shown in **Table 2**.

Novec 5110 (1,1,1,3,4,4,4-Heptafluoro-3-(trifluoromethyl)-2-butanone) and Novec 649 (1,1,1,2,2,4,5,5,5-nonafluoro-4-(trifluoromethyl-yl)-3-pentanone) belongs to chemical family of fluorinated ketones. Empirical formulas of Novec 649 and Novec 5110 are $C_6F_{12}O$ and $C_5F_{12}O$ respectively. They are engineered fluid with environmentally friendly properties (ODP=0, GWP =1), especially produced by 3M^{TM} to substitute high GWP working fluids like SF_6 and hydrofluorocarbons (HFCs). Novec fluids are stable till 300℃ in the absence of water according to 3M^{TM} producers [8]. However, further investigations on thermal stability at temperatures greater than 300 ℃ are necessary to enable their use in high temperature power cycle applications. In recent studies, Novec 649 is also used as working fluid in Organic Rankine Cycles.

HFO1234yf and HFO1234ze(E) are also environmentally friendly refrigerants belongs to chemical family of hydrofluoroethers. The maximum allowable operating temperature for these refrigerants suggested by thermal stability tests are 200 to 250 ℃ [13], [14]. R134a is also a good candidate fluid as an additive owing to its large use as working fluid in ORCs despite having larger GWP. The maximum allowable operating temperature of R134a is 350-370℃ as per the experimental thermal stability tests [15].

For preliminary evaluation of thermochemical stability of some new additive fluids, the standard enthalpy of formation per bond (ΔH_B) is determined. The more negative value of standard enthalpy of formation (ΔH_f^o) implies more stable compound. However, it is not wise to generalize all compounds with negative value of enthalpy of formation as stable compounds. For example, Benzene with positive value of enthalpy of formation (+48.7 KJ/mol) is well known as stable liquid. Therefore, a more in depth information about thermodynamic and chemical stability of a compound can be acquired using the knowledge of path of reaction followed and activation energy of a reaction. Anyways, ΔH_f^o can be a useful parameter for first indication about thermochemical stability of any compound and can also be useful in classification of additives.

Figure 1 shows the parameter ($\Delta H_B = \Delta H_f^o / n_B$) with respect to number of chemical bonds in the molecule of additive fluid. CO_2 is considered as reference fluid for comparison owing to its well established higher chemical stability.

After selection of appropriate additive with desirable thermodynamic and environmental properties for CO_2 binary mixtures, the subsequent step is to analyze the fluid behavior of CO_2 mixture at different molar composition. This requires an accurate thermodynamic method: activity coefficient method or equation of state method depending on the range of temperatures and pressure in which the properties are needed. In this study, cubic Peng Robinson equation of state (PR-EoS) with van der Waals mixing rules is selected because of its applicability both at low pressures and higher pressures greater than critical point. Different modifications to PR-EoS and mixing rules are applied in recent research works to enhance the accuracy and applicability of EoS for polar and non-polar compounds.

Firstly, the calculation method requires pure fluid physical properties i.e. T_c, P_c, acentric factor (ω) and gas constant (R). These fluid properties for both CO_2 and the additive compound are available as reported in **Table 1**. Secondly, considering van der Waals mixing rule formulation for a binary mixture, one binary interaction parameter ($k_{i,j}$) is also needed to determine interaction coefficient $a_{i,j}$ as shown,

$$a_{i,j} = \sqrt{a_i a_j}(1 - k_{i,j}) \qquad \textbf{Eq. 1}$$

Where, a_i and a_j are pure component parameters.

The accurate value of $k_{i,j}$ can be computed using regression analysis with available experimental or pseudo-experimental vapor-Liquid equilibrium (VLE) data. Once $k_{i,j}$ is determined, the PR-EoS is used to calculate pressure-temperature envelop at different mixture composition, densities, enthalpies and entropies at different isobars from subcritical to supercritical phases. All the thermodynamic properties calculations for pure fluids and CO_2 mixtures are carried out in Aspen Plus V10 simulation software [16].

It is also important to compute critical points CO_2 mixtures at different molar compositions and validate the results with available experimental critical point data (which mostly is not available for all CO_2 mixtures). In general, for a binary mixture, the critical temperature and pressure do not correspond to the maximum values on the saturation curve. Therefore, a numerical code is developed to calculate the actual critical point of binary mixtures. The algorithm of critical point code is based on the equations developed in ref [17], is programmed and executed in MATLAB version R2019a with the help of INTLAB toolbox [18]. The efficient root finding capability of INTLAB is exploited to solve the non-linear system of equations of critical point. The code requires pure component critical points, molar composition of each component, acentric factors and binary interaction parameter ($k_{i,j}$) corresponding to considered equation of state as input information to compute the critical points of a binary mixture. In addition, the initial interval which contains the minimum and maximum range in which the root can occur is also required. The code is capable to compute both stable and metastable critical points at given composition of any binary mixture without the need of initial guesses. More description on characterization of pure and mixture working fluids used in power plant application are given in ref [19].

For CO_2-Novec649 mixture, **Figure 2** shows the VLE at 40 °C and 50 °C calculated using PR-EoS with regressed $k_{1,2}$, the scatter points represents experimental VLE data. The pressure-temperature envelop and critical points locus at different mixture composition for CO_2-Novec649 mixture are shown in **Figure 3**. Same procedure is followed to compute VLE and P-T envelop for CO_2-134a, CO_2-R1234yf and CO_2-R1234ze(E) mixtures. The regressed values of $k_{1,2}$ for CO_2 mixtures considered in this study are reported in **Table 3**.
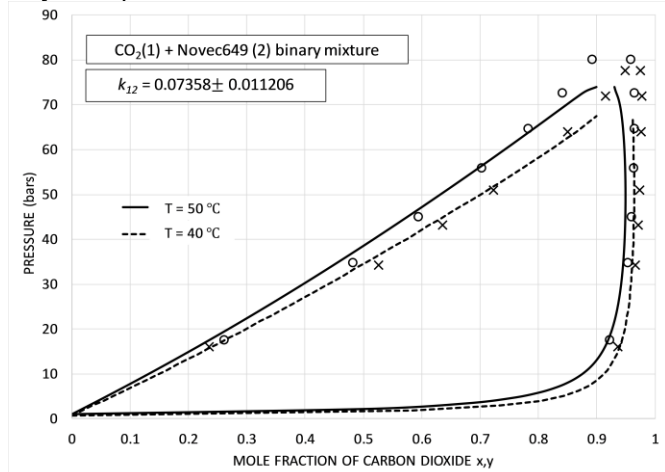
Figure 2: Vapor-Liquid equilibrium at two temperatures for CO_2-Novec649 mixture. Scatter points show experimental data [20]. Solid lines show computation using PR-EoS with regressed $k_{1,2}$.
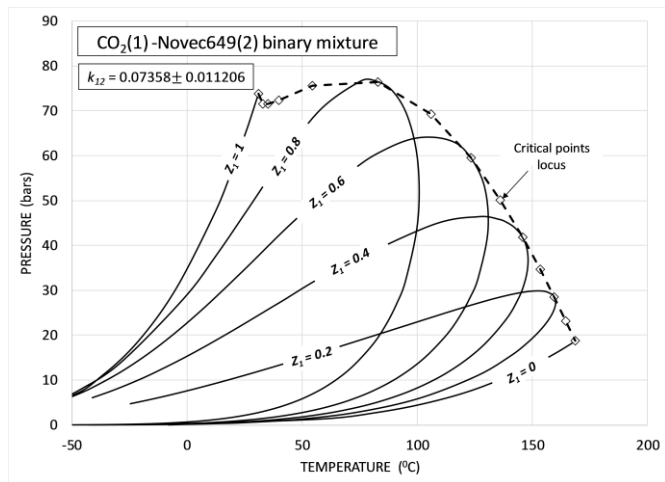
Figure 3: P-T envelop and vapor-liquid critical points of CO_2-Novec649 mixture at different molar composition.

In calculation of thermodynamic properties of CO_2 mixtures, there are instances when the experimental VLE data for a particular CO_2 binary mixture are not available for computation of interaction parameter $k_{1,2}$. For such cases, a correlation between $a_{1,2}$ and a_2 is developed by regressing the available data of 19 CO_2 mixtures (for example, CO_2-ethane, CO_2-H_2S, CO_2-propane etc.). Consequently, the correlation provide the

estimated value of $a_{1,2}$ to insert into Eq.1 and determine value of $k_{1,2}$. More details on this approach and regression model are given in ref [21]. Meanwhile, in this study, we used this developed correlation to compute $k_{1,2}$ of CO_2-Novec5110 mixture since the experimental VLE data is not present in literature for this mixture. The estimated value is,

$$k_{1,2} = 0.0699654 \pm 0.062841$$

Thus, with estimated $k_{1,2}$, PT envelop and critical points at different molar composition are calculated as shown in **Figure 4** for CO_2-Novec5110 mixture.

Table 3: Binary interaction parameters ($k_{1,2}$) required in van der Waals mixing rules for considered CO_2 mixtures.

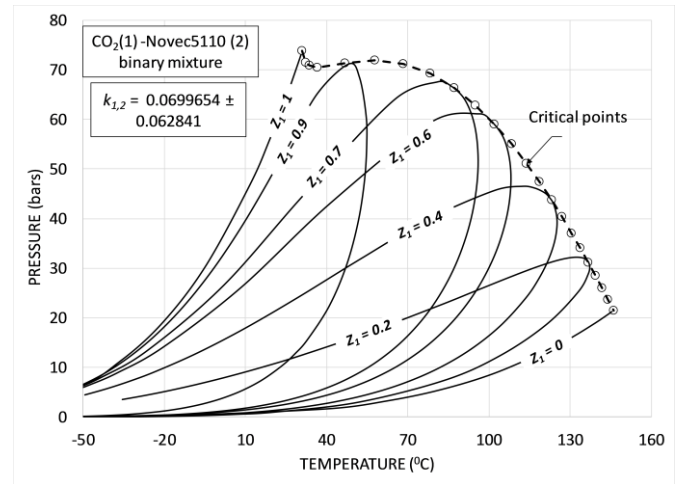| CO_2 mixture	$k_{1,2}$	Standard deviation	Source of experimental VLE data
CO_2-R134a	0.0166	0.00824	[22], [23]
CO_2-Novec649	0.07358	0.01120	[20]
CO_2-R1234yf	0.03943	0.00444	[24]
CO_2-R1234ze(E)	0.015631	0.00522	[25]

Figure 4: P-T envelop and vapor-liquid critical points of CO_2-Novec5110 mixture at different molar composition.

PURE CO_2 THERMODYNAMIC POWER CYCLES

This section discusses the thermodynamic analysis of supercritical carbon dioxide (sCO_2) power cycles exploiting flue gases at T=450°C as heat source. The characteristics of heat source and main operating parameters for cycle design point analysis are shown in **Table 4**. Different cycle layouts are studied in literature to enhance the heat recovery effectiveness of sCO_2 cycles [26]. However, in this paper, three cycle layouts are selected which are representative of both traditional and novel cycle layouts practiced in literature. Thermodynamic performance of the power cycles is evaluated using thermodynamic cycle efficiency ($\eta_{th} = \dot{W}_{net}/\dot{Q}_{in}$) and total efficiency ($\eta_{tt} = \dot{W}_{net}/\dot{Q}_{available}$) parameters.

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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

Simple recuperative power cycle (SRC)
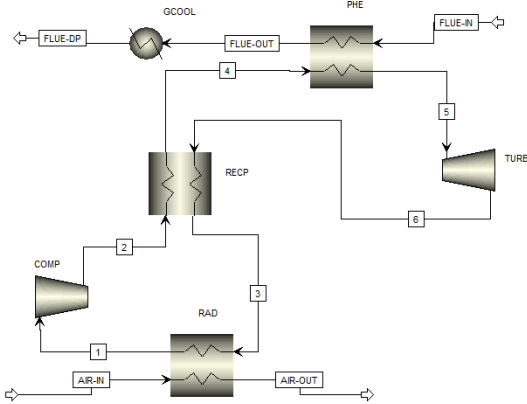
Figure 5: Schematic diagram of simple recuperative sCO₂ cycle layout for heat recovery (SRC).
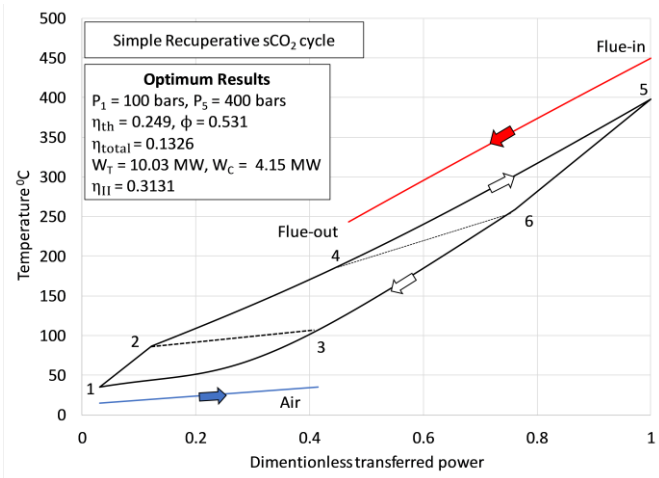
Figure 6: Thermodynamic process diagram and optimum results of simple recuperative sCO₂ cycle on temperature-dimensionless heat transferred plane.

The first reference CO_2 power cycle considered for heat recovery is simple recuperative sCO₂ power cycle as shown in **Figure 5**. The cycle thermodynamic performance is investigated at different minimum pressures (P_{min}), pressure ratio (P_R) and maximum temperature (T_{max}). Based on sensitivity analysis, optimum total efficiency is obtained at P_{min} = 100 bars, T_{max} = 400 ℃ and pressure ratio of 4. **Figure 6** demonstrates optimum cycle results in T-Q plane.

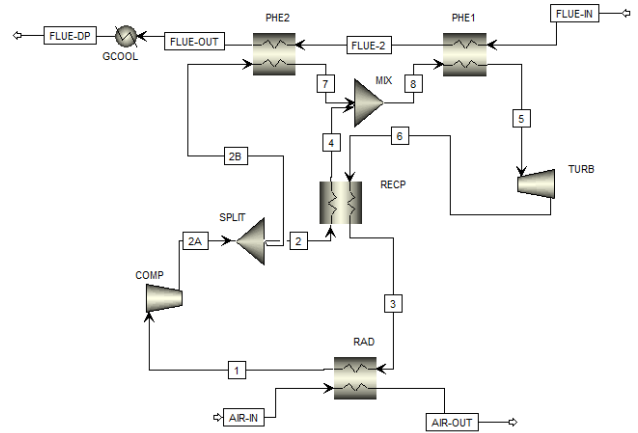**Recuperative cycle with mass split (RCS)**

Figure 7: Schematic diagram of recuperative sCO₂ cycle with mass split (RCS).

This cycle scheme consists of mass split (*x*) and added heat recovery heat exchanger in addition to simple recuperative cycle layout as shown in **Figure 7**.
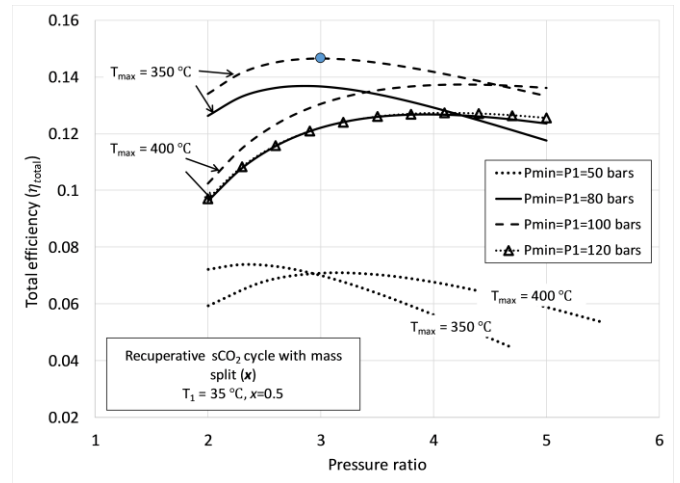

Figure 8: Total efficiency at different minimum cycle pressures and maximum cycle temperatures versus pressure ratio for recuperative cycle with mass split. Blue mark shows the optimum performance point.

Due to split of mass flow rate after compression process; certain CO_2 mass flow towards heat exchanger for heat recovery, remaining go towards recuperator depending on the specified

value of mass split. Two CO_2 streams after heating from heat exchanger and recuperator mix together and then heated in primary heat exchanger to achieve required turbine inlet temperature. The expansion in turbine occurs to minimum cycle pressure, followed by cooling of CO_2 stream in recuperator and through radiator to obtain minimum cycle temperature. The main aim of mass split (x) is to enhance heat recovery potential of the power cycle and to achieve more cooling of the flue gases as discussed previously in literature [26]. Sensitivity analysis is carried out to evaluate the effect of mass split on total efficiency and exergy efficiency of the cycle. The thermodynamic analysis at different cycle minimum pressures, pressure ratios and maximum temperatures is performed to study the effect of these variables and to obtain optimum performance conditions. The underlying idea is to assess the impact of mass split on cycle performance relative to simple recuperative cycle layout.

Keeping $x = 0.5$, **Figure 8** shows the influence of cycle minimum pressure and maximum temperature (or T_5) on total efficiency. The optimum performance is achieved at $P_R = 3$, $P_{min} = 100$ bars and $T_{max} = 350$ °C. At constant P_{min}, the total efficiency at $T_{max} = 350$°C is better than at $T_{max} = 400$°C. This is because, at lower value of T_{max}, the temperature at entry of primary heat exchanger reduces, which results in more utilization of heat from flue gases and more cooling of flue gases. Thus, larger cooling of flue gases improves the heat recovery effectiveness, hence total efficiency of the cycle.

At lower value of P_{min} i.e. $P_{min} = 50$ bars, the compression work increases significantly since the compression inlet conditions are far from critical point, this implies reduction in thermal efficiency, as a consequence reduction in the total efficiency of the cycle. At $P_{min} > 100$ bars for example 120 bars, the total efficiency is lower owing to reduction in thermal efficiency of the cycle.

$x=0.3$ is decided as optimum mass split since it results in both higher cycle thermal efficiency and total efficiency. Finally, the cycle optimum results are shown in **Figure 9** on T-Q plane.
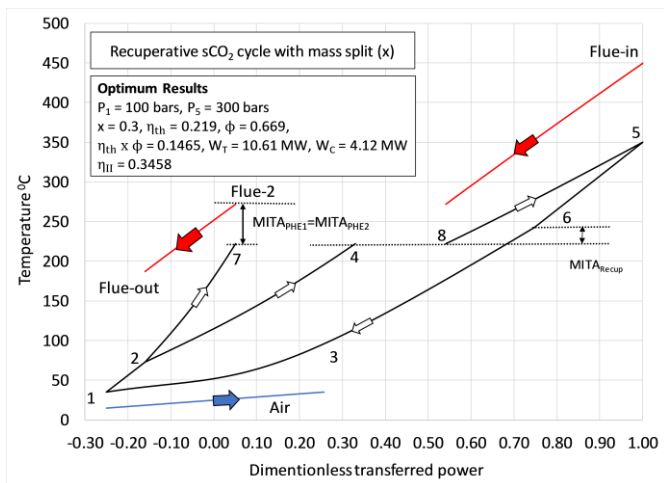

Figure 9: Thermodynamic process diagram and optimum results of recuperative with mass split sCO₂ cycle on temperature-dimensionless heat transferred plane.

Single Flow split dual expansion cycle (SFDE)

The schematic diagram of single flow split dual expansion cycle is shown in **Figure 10**. Cycle components in this configuration are greater due to addition of one low temperature (LT) turbine compared to RCS configuration. CO_2 is compressed in the main compressor and then flow is divided into two streams. One stream is heated in PHE and expanded in high temperature (HT) turbine. While, the other stream is heated in LTR and HTR followed by expansion in the LT turbine. The different mass flow in recuperators balances the heat capacities between hot and cold streams inside the recuperators in order to achieve better thermal match.
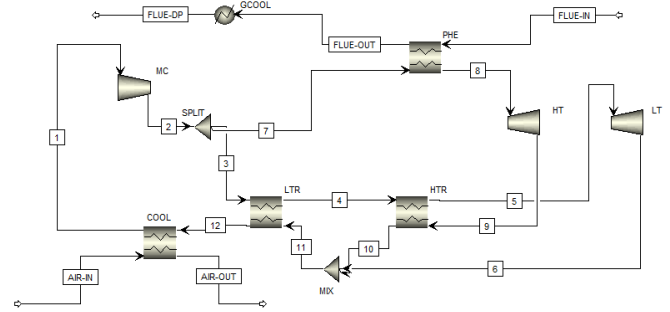

Figure 10: Schematic diagram of single flow split dual expansion cycle

As in the analysis of previous cycle configurations, the performance study of SFDE cycle also involves the sensitivity of cycle efficiency, heat recovery effectiveness and total efficiency at different T_{max}, P_R and P_{min}. However, the role of mass split in SFDE configuration is to enhance the turbine inlet temperature in LT turbine to improve the cycle efficiency. Besides, it is also essential to achieve same temperatures at mixer inlet (i.e. $T_6 \approx T_{10}$) to reduce mixing losses and in turn maintain higher cycle efficiency. On the other side, the temperature at the inlet of PHE (T_7) depends on the compressor outlet temperature, in other words, the pressure ratio (P_R).

In cycle thermodynamic calculations, optimum mass split x is calculated at which the cycle efficiency and total efficiency are higher. In addition, optimum point is also decided considering the sensitivity of total efficiency at different compressor inlet pressure (P_{min}). To ensure the accuracy of cycle thermodynamic model, cycle calculations are carried out at same conditions as given by Manente *et* al [27] and the results are compared. Validation of results shows that optimum mass split, cycle efficiency and total efficiency calculated using present approach are the same as computed by Manente *et* al.

The influence of different compressor inlet pressure (P_{min}) and T_{max} on total efficiency are presented in **Figure 11**. Maximum total efficiency is obtained at $T_{max} = 400$ °C, $P_{min} = 100$ bars and P_R of 2.9. Total efficiency is smaller at both P_{min} of 120 bars and 80 bars. At $P_{min} = 80$ bars, the temperature at entry of PHE (i.e.T_7) enhances which bring about reduction in heat recovery effectiveness. Whereas in case of $P_{min} = 120$ bars, there is very slight improvement in heat recovery effectiveness due to T_7 as

compared to P_{min} = 100 bars, so the decrease in total efficiency in this situation is more attributed to lower cycle efficiency. **Figure 12** illustrates the optimum results on T-Q plane.

The efficiency losses in total efficiency ($\Delta\eta_{total}$) and resulting exergy efficiency at optimum conditions for SRC, RCS and SFDE cycles are recorded in **Table 5**. SRC shows higher η_{th}, however, it is not proven to be effective in heat extraction from flue gases. The total efficiency and exergy efficiency of RCS are higher with lower pressure ratio compared to SRC.

Thus, the introduction of mass split and addition of another heat exchanger (i.e. PHE2) results in higher thermodynamic quality of the RCS compared to SRC. Relative to SRC, there is 10.56 % and 16.29% improvement in total efficiency for RCS and SFDE cycles respectively. SFDE cycle tends to enhance heat recovery effectiveness and shows better exergy efficiency, however, the improvement is not justifiable in comparison to layout complexity of the power cycle.
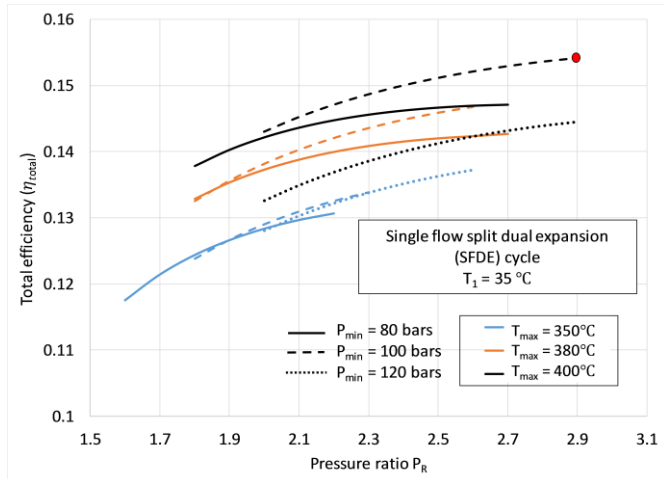

Figure 11: Simultaneous effect of cycle minimum pressure and maximum temperature on total efficiency of SFDE cycle. Red mark shows the optimum performance point.
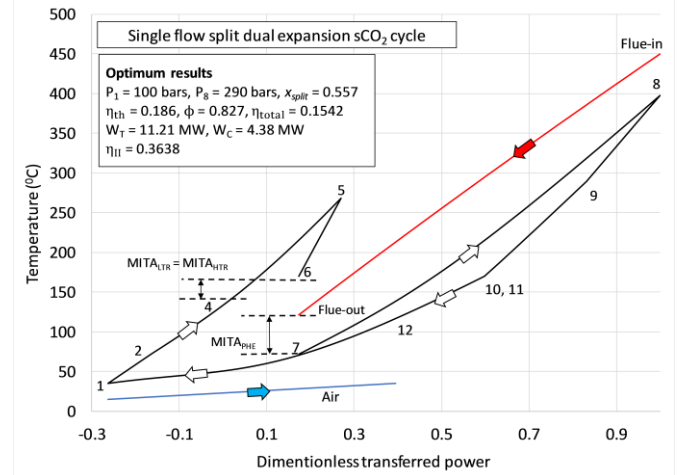

Figure 12: Thermodynamic process diagram and optimum results of single flow split dual expansion sCO₂ cycle on temperature-dimensionless heat transferred plane.

CO₂ MIXTURES WORKING FLUIDS IN THERMODYNAMIC POWER CYCLES

It clearly appears from thermodynamic analysis of pure CO_2 cycles that the gain in total efficiency can only be achieved by introducing mass split to obtain cascade heating and by dual expansion to enhance power output. Both cascading and dual expansion processes increase the components of power cycle and make operational scheme difficult in terms of size and cost of the power cycle. To cope with this problem, this study attempted to design CO_2-based binary mixtures as working fluids in simple recuperative cycle layout.

This section deals with thermodynamic performance of cycles operating with CO_2-Novec649 and CO_2-Novec5110 mixture as working fluids. The thermodynamic properties are calculated using PR-EoS as explained in the section 2. The cycles in case of CO_2 mixtures are transcritical cycles with pump inlet pressure (P_1) at bubble point corresponding to inlet temperature. As the molar composition of mixture changes, the pump inlet pressure also changes. Moreover, other design conditions and common assumptions are the same as given in **Table 4**.

Table 5: Summary of efficiency losses, total efficiency and exergy efficiency of three supercritical pure CO₂ heat recovery power cycles at optimum conditions.

Power cycles	T_{max} (°C)	P_R	$\dot{Q}_{available}$ (kW)	$\dot{W}_{max}$ (kW)	η_{ideal}	$\Delta\eta_{total}$	$\dot{W}_{net}$ (kW)	η_{th}	ϕ	η_{total}	Exergy efficiency $\eta_{II} = \dfrac{\eta_{total}}{\eta_{ideal}}$
SRC	400	4	44279	18764	0.423	0.277	5873	0.249	0.532	0.132	0.313
RCS	350	3	44279	18764	0.423	0.262	6487	0.219	0.669	0.146	0.345
SFDE	400	2.9	44279	18764	0.423	0.254	6826	0.186	0.827	0.154	0.363

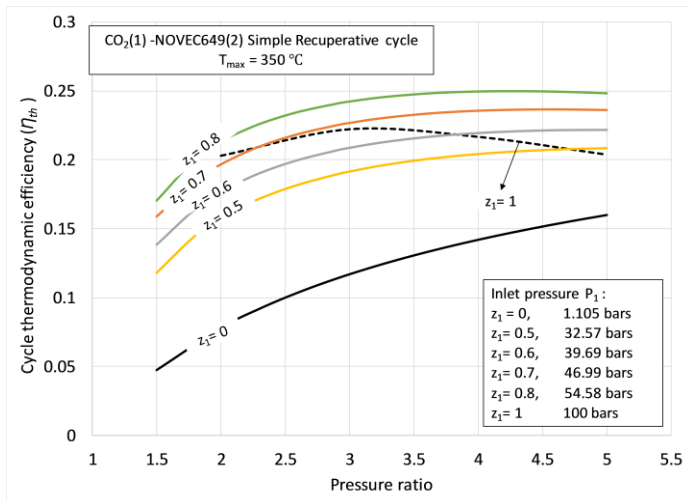**Figure 13: Influence of different mixture molar composition and cycle pressure ratio on cycle thermodynamic efficiency with CO_2-$C_6F_{12}O$ (Novec 649) mixture working fluid.**

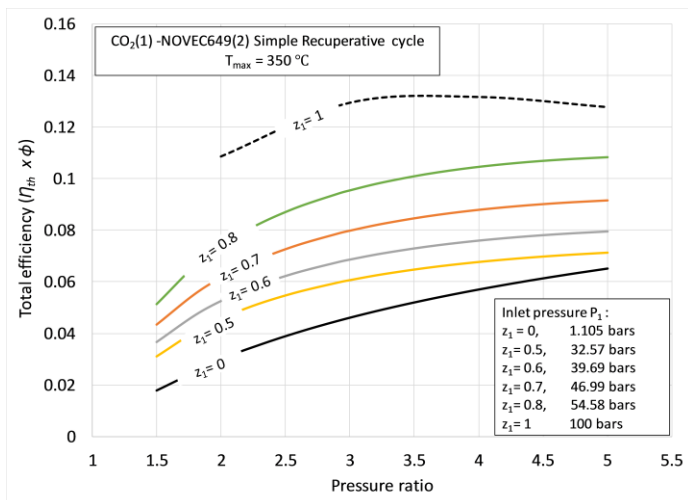**Figure 14: Influence of different mixture molar composition and cycle pressure ratio on total efficiency with CO_2-$C_6F_{12}O$ (Novec 649) mixture working fluid.**

Figure 13 and Figure 14 shows cycle efficiency and total efficiency respectively for CO_2-Novec649 mixture. Results shows that total efficiency of CO_2-Novec649 mixture remains lower than pure CO_2 cycle at all pressure ratios and mixture molar compositions. Increase in amount of CO_2 in the mixture brings about increase in total efficiency. On the other hand, thermodynamic cycle efficiency is greater than pure CO_2 at molar composition greater than 0.6 and pressure ratios higher than 3. Similar trend of cycle efficiency and total efficiency can be observed in case of CO_2-Novec5110 binary mixture as shown in Figure 15 and 16 respectively.

The main reason of lower total efficiency is higher molecular complexity of Novec fluids (see Table 1). The higher molecular complexity produces higher temperature at turbine outlet which results in larger recuperator and higher temperature at inlet of PHE. Consequently, higher temperature at inlet of PHE reduces the heat recovery capability of power cycle, results in reduction of heat recovery effectiveness and total efficiency. Instead, the cycle thermodynamic efficiency in case of CO_2-Novec mixtures is higher since heat addition is occurring at higher temperature.

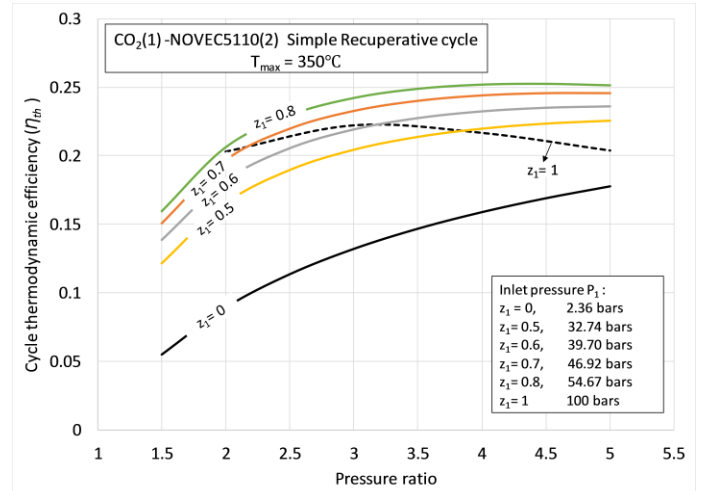**Figure 15: Influence of different mixture molar composition and cycle pressure ratio on cycle thermodynamic efficiency with CO_2-$C_5F_{10}O$ (Novec5110) mixture working fluid.**
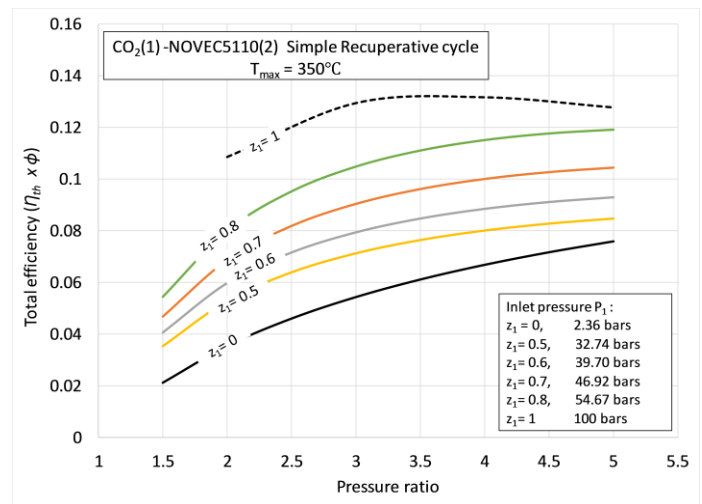

Figure 16: Influence of different mixture molar composition and cycle pressure ratio on total efficiency CO_2-$C_5F_{10}O$ (Novec 5110) mixture working fluid.

Table 6 presents the thermodynamic results of some CO_2 mixtures power cycles in comparison with supercritical CO_2 power cycles. Comparison shows that CO_2-Novec mixtures working fluids with 20% amount (molar composition) of Novec fluid show comparable cycle thermodynamic efficiency compared to sCO₂ simple recuperative cycle (i.e. 0.249 versus 0.252) and 3 percentage points higher cycle thermodynamic efficiency compared to recuperative with mass split cycle (i.e.

0.219 versus 0.252). Whereas, around 2 percentage points lower total efficiency(i.e. 0.132 versus 0.117) is achieved which is the manifestation of higher molecular complexity of Novec fluids, as a consequence, lower power is produced.

The power cycle analysis for CO_2-R134a binary mixture at different mixture composition is also carried out and results are published in a recent research article [21]. For comparison of main outcome, Table 6 also shows the results of CO_2-R134a working fluid mixture with 30% molar composition of R134a operating in simple recuperative cycle. Results indicates that comparable total efficiency and cycle thermodynamic efficiency with lower maximum operating pressures are obtained compared to sCO_2 cycles.

Table 6: 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)
sCO₂ (Simple recuperative cycle)	0.132	0.249	5873	400	100
sCO₂ (Recuperative cycle with mass split)	0.146	0.219	6464	300	100
CO₂ (0.8)-Novec649 (0.2)	0.108	0.248	4782	273	54.58
CO₂(0.8)-Novec5110 (0.2)	0.117	0.252	5180	246	54.67
CO₂ (0.7)-R134a (0.3)	0.147	0.248	6509	200	24.54

CONCLUSION

This work proposed novel CO_2 based mixtures as working fluids for high temperature waste heat recovery closed Brayton sCO_2 power cycles. The goal is enhancing heat recovery effectiveness and total efficiency of sCO_2 power cycles keeping simple cycle layout and using novel CO_2 mixtures rather than pure CO_2 as working fluid. Firstly, selection criteria for choice of adequate additive in CO_2 mixtures is defined in which both thermodynamic and environmental characteristics are taken into account. Five refrigerants with lower ODP, lower GWP and favorable thermodynamic properties are selected as additives in CO_2 mixtures.

Peng-Robinson equation of state with van der Waals mixing rules is selected for computation of thermodynamic properties and critical points of CO_2 mixtures at different mixture molar composition. The binary interaction parameter ($k_{1,2}$) is estimated using regression with available experimental VLE data or by using already developed correlation in case of non-availability of experimental VLE data. Thermodynamic analysis of three promising sCO_2 cycle layouts are carried out in order to select best possible layout as benchmark to compare performance with CO_2 mixtures power cycles. An improvement of 10% and 16% in total efficiency is obtained for recuperative cycle with mass split (RCS) and single flow spit dual expansion cycle (SFDE)

respectively compared to simple recuperative cycle (RCS). However, recuperative sCO_2 cycle with mass split is selected as compromise solution owing to its higher total efficiency, nominal plant complexity and comparatively lower cycle maximum pressure.

CO_2-Novec mixtures (with 20% molar composition of Novec fluid in the mixture) as working fluids in power cycles showed 3 percentage points higher cycle thermodynamic efficiency compared to recuperative with mass split sCO_2 power cycle.

For CO_2-Novec mixtures working fluids, heat addition is occurring at higher temperature which brings about higher cycle thermodynamic efficiency. On the other hand, the expansion in turbine is lower compared to pure CO_2 power cycles owing to higher molecular complexity of Novec fluids. In this point of view, CO_2-Novec fluids cannot be considered as promising mixtures for applications in which improvement in power output is the prime objective.

With CO_2-R134a mixture (with 30% molar composition of R134a in the mixture) as working fluid in simple cycle, comparable total efficiency and 3 percentage points rise in thermodynamic cycle efficiency is obtained compared to recuperative with mass split sCO_2 cycle.

The minimum and maximum operating pressures for power cycles operating with CO_2 mixtures are lower which is beneficial in component design point of view since lower pressures are proportional to lower mechanical stresses in cycle components.

Results suggests that, employing CO_2 mixtures as working fluid is a much more convincing option for high temperature heat recovery owing to higher cycle efficiencies achievable with rather simple cycle layout and lower cycle maximum operating pressures compared to sCO_2 cycles. Nevertheless, the cycle analysis using novel working fluids helps in selection of promising fluids and optimum parameters for improvement in thermodynamic performance of sCO_2 power cycles. Besides cycle analysis, a great deal of research work is needed to calculate accurate thermodynamic and transport properties of novel CO_2 mixtures and decide thermal stability temperature experimentally.

NOMENCLATURE

GWP	Global warming potential
ODP	Ozone depletion potential
PHE	Primary or Heat recovery heat exchanger
PR-EoS	Peng Robinson equation of state
P_R	Pressure ratio
RCS	Recuperative cycle with mass split
SRC	Simple recuperative cycle
SFDE	Single flow split dual expansion cycle
ΔH_f^o	Standard enthalpy of formation of a compound
ϕ	Heat recovery effectiveness
η_{total}	Total efficiency
η_{th}	Cycle thermodynamic efficiency
z_1	Molar composition of CO_2

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