The 5th European sCO₂ Conference for Energy Systems
March 14-16, 2023, Prague, Czech Republic

2023-sCO2.eu-109

EXERGETIC AND ENTROPY ANALYSIS OF THE PCRC AND RCMCI BRAYTON CYCLES USING S-CO_2 MIXTURES. CASE STUDY: MARINE APPLICATIONS

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ABSTRACT

Brayton cycle using supercritical carbon dioxide (s-CO_2) as a working fluid is a high-efficiency trend technology that has been an understudy for improvement. The performance of the cycles explains with a thermodynamic analysis that accounts for two aspects: on one side a general trend in their behavior and on the other the effect of the irreversibilities, especially the irreversibilities taking place in the regenerator.

This study focuses on the impact of binary mixtures based on pure CO_2 on the thermal efficiency of the configurations: Recompression with Main Compressor Intercooling (RCMCI) and Partial Cooling with Recompression (PCRC) cycles at the design point, considering the irreversibilities caused by each component of the cycle. In the PCRC cycle, small-size heat recuperators and low-temperature high-heat recuperators are achieved. The efficiency in the RCMCI cycle is better due to the low recompressor work. The methodology used in the calculation of the plant performance is to establish heat recuperator total conductance values of between 5 and 20 MW/K. Based on the exergetic and entropy analysis of the cycles studied, a comparison between pure supercritical carbon dioxide and s-CO_2 mixtures (CO_2/CH_4, C_3H_8, and CO_2/H_2S) is carried out. Acquired results have revealed that the blends increase thermal efficiency compared to the standard fluid in the cycles studied. In PCRC configurations, the mixture that obtains the highest efficiency is the one that contains Methane, while in RCMCI configurations it is the one that contains Hydrogen Sulfide. Meanwhile, in the RCC cycle, the mixture with Propane is the one with the highest efficiency.

INTRODUCTION

The interest of the scientific community in recent years has focused on the study of s-CO_2 Brayton cycles because it achieves high efficiencies and the components are small. Several authors agree that CO_2 Brayton cycles are promising for applications in concentrated solar power plants (CSP) [1-3], however, they have also been evaluated in nuclear [4-5], geothermal [6-7], waste heat recovery [8], heat pump [9-10], marine applications [11,12 and 27], among others.

In the study by [11], they model a waste heat recovery system coupled to a regenerative recompression s-CO_2 Brayton cycle in shipboard applications. In the analysis of some parameters, it is concluded that the increase in the minimum temperature of the cycle (32-50°C) produces a decrease in the efficiency of the cycle of almost 11%. On the contrary, if the maximum temperature of the cycle is increased by 100 °C, the efficiency increases by around 10%. In his recent research [12] he developed a thermodynamic model of the recompression cycle for marine applications, the optimized cycle reaches a maximum efficiency of 43.98% and if the efficiency of the recuperators increases up to a value of 0.95, then the size total Decreases turbomachinery. The studies analyzed for this research have shown that s-CO_2 technology has great potential if combined with marine applications that have waste heat recuperator systems, helping to improve the energy efficiency of ships, and leading to a significant reduction in CO_2 emissions into the environment [27].

All these applications have different ambient temperature conditions, so it is necessary to optimize the compressor inlet temperature (in addition to other parameters such as compressor

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DOI: 10.17185/duepublico/77263

inlet pressure, mass fraction going to the recompressor, etc.) to achieve better performance [13]. One way of unleashing the great thermodynamic potential of the s-CO_2 Brayton cycles is by performing the compression around the critical point of CO_2, a little above it, to avoid the sudden change in the thermophysical properties of the fluid. However, applications such as cryogenics and nuclear that are at low ambient temperatures or in CSP with high ambient temperatures imply that the compressor inlet temperature decreases or increases as the case may be, causing the thermal efficiency of the cycle to drop.

To correct this drawback, numerous authors have investigated the addition of certain dopants, generally chemical compounds to carbon dioxide, producing a mixture that has a lower or higher critical temperature than the pure base fluid (pure CO_2). Valencia et al. [14] evaluated different dopants and classified them into compounds that help lower the critical temperature (C_2H_6, CH_4, Kr, He) and compounds that help raise the critical temperature (C_3H_8, C_5H_{10}, C_5H_{12}, H_2S, SO_2) compared to the pure CO_2. Manzolini et al. [15] evaluate two additives (Ni_2O_4 and $TiCl_4$), their study considers typical ambient temperatures of solar thermal plants and turbine inlet temperatures of 550°C and 700°C, obtaining efficiencies between 43% and 50%, respectively. The efficiencies obtained are 2% higher than those obtained with pure CO_2. Siddiqui, M [15], in his research, analyzes the binary mixture CO_2/C_7H_8 to improve performance in a recompression cycle. Assuming a minimum temperature of 50°C and turbine inlet temperatures of 350°C and 400°C, the results show an increase in efficiency of 14.5% and 8%, respectively. Along the same lines, Tafur et al. [17] present four chemical compounds as dopants for CO_2 in recompression CO_2 Brayton cycles coupled to CSP. The authors perform an economic and performance evaluation. Concluding that the CO_2/COS mixture with a molar fraction of 0.70/0.30 obtains an efficiency of around 45%, surpassing that of pure CO_2, which obtained around 41.25%. In a recent investigation [18], two additives (C_6F_6 and $TiCl_4$) are proposed as working fluids in Rankine and Pre-compression cycles with maximum cycle temperatures and pressures of 550°C and 700°C, 200 bar, and 300 bar. The results obtained show efficiencies above 50%.

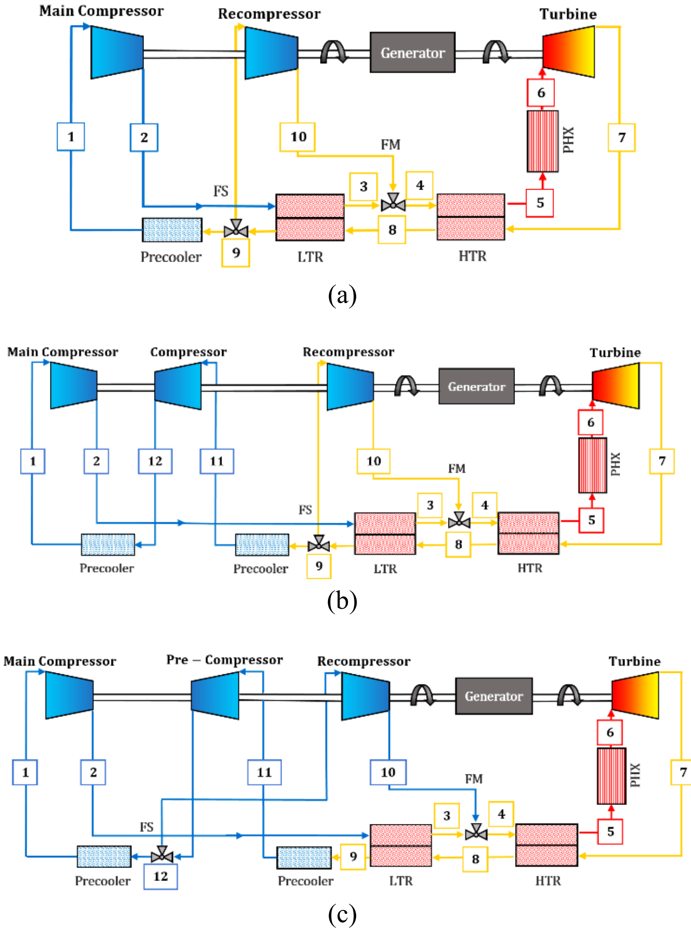
Finally, Niu et al. [19] studied six dopants divided into three groups. In the first group: mixtures increase the temperature of the critical point of CO_2 but reduce the specific work of the system. In the second group: the same previous condition but with results of increased specific work. Finally, the third group: are the mixtures with a lower critical pressure and a higher critical temperature than pure CO_2. The results showed that the CO_2/C_3H_8 mixture (third group) has potential for application in solar power tower systems due to the increase in thermal efficiency of 2.34% and exergetic efficiency of 1.51% compared to pure CO_2.

The cited bibliography indicates that the addition of dopants is applied to working fluids in cycles that are coupled to solar energy concentration systems. However, the literature also shows that there are dopants that relocate the critical point, thus obtaining critical temperatures around 20 and 30 °C even lower, therefore, they can be of relevant analysis and study as working fluids in s-CO_2 Brayton cycles for marine applications.

The main objective of this work is to carry out a thermodynamic analysis of three additives (CH_4, C_3H_8, and H_2S) that improve the thermal efficiency of s-CO_2 Brayton cycles under typical temperature conditions of marine applications.

MATERIALS AND METHODS

In this work, three configurations [28] are considered to analyze the three mixtures under study: Recompression with Main Compressor Intercooling (RCMCI, Figure 1b) and Partial Cooling with Recompression (PCRC, Figure 1c), which are derived from the main cycle that is the Recompression cycle (RCC, Figure 1a).



(a)

(b)

(c)

Figure 1. Relevant s-CO_2 Brayton cycles layout, (a) Recompression, (b) Recompression with Main Compressor Intercooling, and (c) Partial Cooling with Recompression.

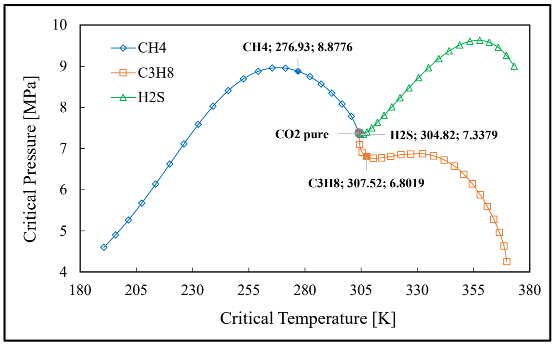
Table 1 lists the main assumptions for the present investigation. On the one hand, the compressor inlet temperature is evaluated in a range between 32°C and 40°C, the turbine inlet temperature is 550°C and the maximum pressure of the cycle is

20 MPa, to contrast the results with other investigations with the same parameters [11]. The efficiencies of the compressors and turbine are 0.89 and 0.93, respectively. On the other hand, this takes into account the pressure drops in the components of the cycle, the values considered, as well as the methodology applied to calculate the maximum efficiency that has been obtained from previous research [14, 17, 20-22].

TABLE I. MAIN IMPUT PARÁMETERS

	Nomenclature	*Value*	*Units*
Compressor inlet temperature	T_1	32 – 40	°C
Maximum cycle pressure [11 – 12]	P	20	MPa
Maximum cycle temperature [11 – 12]	T_6	550	°C
Compressor and turbine efficiency [14, 17, 20-22]	η_{mc}, η_t	0.89/0.93	-
UA (Heat Total Recuperator Conductance) for the LTR and HTR [14, 17, 20-22]	UA_{LT}, UA_{HT}	2500 to 10000	kW/K

The software SCSP (Supercritical Concentrated Solar Power Plant) [23] is used for the evaluation of the s-CO_2 Brayton cycle. This software has been developed for the Grupo de Investigaciones Termoenergéticas of Universidad Politécnica de Madrid. The fluid's properties, shown in Figure 2, were obtained from the REFPROP v10.0 database developed by NIST [24].



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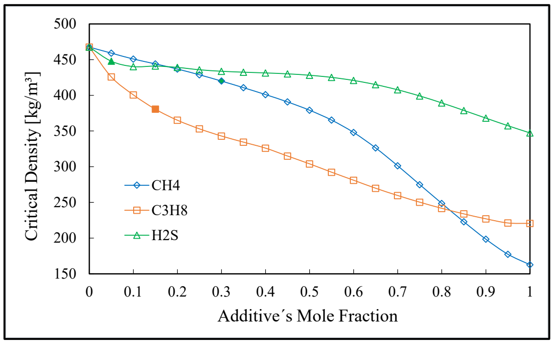


(b)

Figure 2. Fluid's Properties. (a) Critical pressure vs. Critical temperature, (b) Critical density vs Additive's mole fraction.

Figure 2a shows the evolution of the critical pressure and critical temperature as a function of the molar fraction of the added compound. In the case of the CO_2/CH_4 mixture, the critical temperature decreases, while the critical pressure increases to a maximum point and then drastically decreases, compared to the values of pure CO_2. In the mixtures CO_2/ C_3H_8 and CO_2/H_2S the critical temperature increases, in the one containing C_3H_8 the critical pressure also decreases; in the one containing H_2S, the critical pressure increases to a maximum point and then decreases, always maintaining its values above pure CO_2.

Figure 2b shows the evolution of the critical density against the molar fraction of the additive. In this case, all the mixtures decrease their critical density as the molar fraction of the added compound increases.

Energetic Analysis

Based on the first law of thermodynamics, the energy balance equations in the heat recuperators (LTR and HTR) of the RCMCI configuration are presented:

$$(1-\gamma)\,(h_3-h_2) = h_9-h_8 \tag{1}$$

$$h_5-h_4 = h_8-h_7 \tag{2}$$

The heat transfer rates ($\dot{Q}_{PHX}, \dot{Q}_{Pre}$) to and from the cycle:

$$\dot{Q}_{PHX} = \dot{m}_{mix}(h_5-h_6) \tag{3}$$

$$\dot{Q}_{Pre\_1} = (1-\gamma)\dot{m}_{mix}(h_{11}-h_9) \tag{4}$$

$$\dot{Q}_{Pre\_2} = (1-\gamma)\dot{m}_{mix}(h_1-h_{12}) \tag{5}$$

The expressions for the work in the turbine ($\dot{W}_T$), compressors ($\dot{W}_C, \dot{W}_{RC}, \dot{W}_{MC}, \dot{W}_{Pre-C}$), net output ($\dot{W}_{net}$), and thermal efficiency (η_{th}) are as follows:

$$\dot{W}_T = \dot{m}_{mix}(h_6-h_7) \tag{6}$$

$$\dot{W}_{MC} = (1-\gamma)\dot{m}_{mix}(h_2-h_1) \tag{7}$$

$$\dot{W}_C = (1-\gamma)\dot{m}_{mix}(h_{12}-h_{11}) \tag{8}$$

$$\dot{W}_{Pre-C} = \dot{m}_{mix}(h_{12}-h_{11}) \tag{9}$$

DOI: 10.17185/duepublico/77263

$$\dot{W}_{RC} = \gamma * \dot{m}_{mix}(h_{10} - h_9) \quad (10)$$

$$\dot{W}_{net,RCC} = \dot{W}_T - \left(\dot{W}_{MC} + \dot{W}_{RC}\right) \quad (11)$$

$$\dot{W}_{net,RCMCI} = \dot{W}_T - \left(\dot{W}_{MC} + \dot{W}_C + \dot{W}_{RC}\right) \quad (12)$$

$$\dot{W}_{net,PCRC} = \dot{W}_T - \left(\dot{W}_{MC} + \dot{W}_{Pre-C} + \dot{W}_{RC}\right) \quad (13)$$

$$\eta_{th} = \frac{\dot{W}_{net}}{\dot{Q}_{PHX}} \quad (14)$$

Exergetic Analysis

Based on the second law of thermodynamics, the expressions for entropic generation and exergy flow are proposed:

$$\sigma_T = \dot{m}_{mix}(s_7 - s_6) \quad (15)$$

$$\sigma_{MC} = (1-\gamma)\dot{m}_{mix}(s_2 - s_1) \quad (16)$$

$$\sigma_C = (1-\gamma)\dot{m}_{mix}(s_{12} - s_{11}) \quad (17)$$

$$\sigma_{RC} = \gamma * \dot{m}_{mix}(s_{10} - s_9) \quad (18)$$

$$\sigma_{LTR} = \dot{m}_{mix}(s_9 - s_8) + (1-\gamma)\dot{m}_{mix}(s_3 - s_2) \quad (19)$$

$$\sigma_{HTR} = \dot{m}_{mix}(s_8 - s_7) + \dot{m}_{mix}(s_5 - s_4) \quad (20)$$

The total heat input exergy and the exergetic efficiency are expressed as [25]:

$$\dot{E}_{in} = \dot{Q}_{PHX}\left(1 - \frac{T_o}{T_{hs}}\right) \quad (21)$$

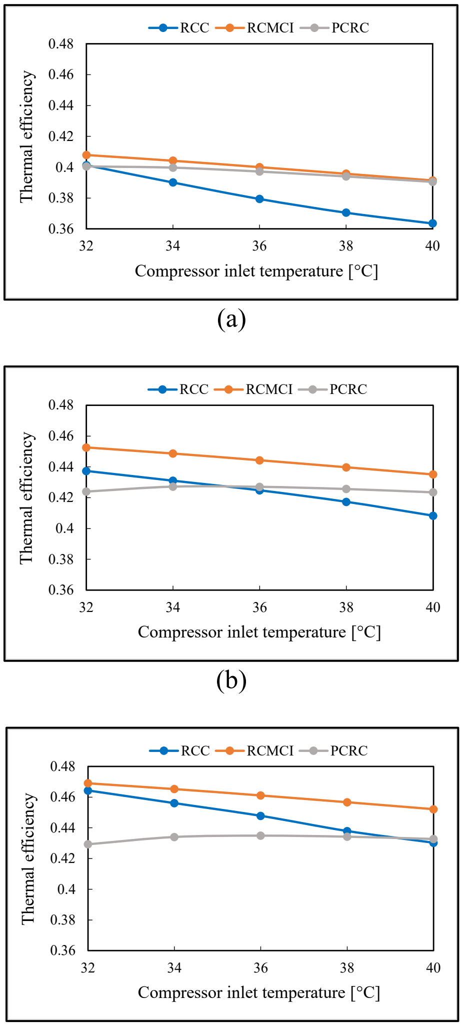
$$\eta_{ex} = \frac{\dot{W}_{net}}{\dot{E}_{in}} \quad (22)$$

$$\eta_{ex,} = \frac{\eta_{th}}{\eta_{carnot}} \quad (23)$$

Where T_o is the ambient temperature and T_{hs} is the temperature of the heat source [11].

RESULTS AND DISCUSSION

Figure 3 shows the efficiencies obtained when using pure CO₂ as the working fluid. In addition, it is observed that the thermal size (UA) in heat recuperators has an important influence on the increase in thermal efficiency. In addition, the results of thermal efficiencies of this study consider a very important design parameter in heat exchangers ("pinch point"), it has been considered as eligible values of efficiency those that are above a pinch point of 5°C.



(a)

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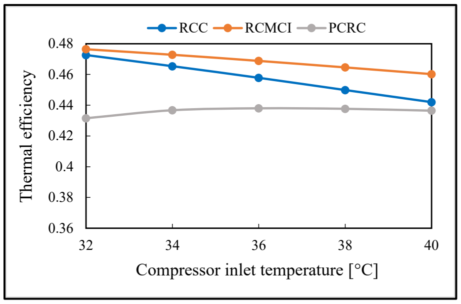


(d)

Figure 3. Thermal Efficiency vs Compressor inlet temperature. Using CO_2 pure. (a) 5000 kW/K, (b) 10000 kW/K, (c) 15000 kW/K and (d) 20000 kW/K.

In the RCC and RCMCI cycles, the efficiencies decrease as the compressor inlet temperature increases. While in the PCRC cycle, the efficiency drops a little when the UA is 5000 kW/K (Figure 3a), however, when the UA values increase (Figure 3b, c, d) the thermal efficiency in this cycle starts to increase as the compressor inlet temperature increases.

Table 2 summarizes the results obtained and compares them with previous investigations. The efficiencies values show a slight deviation, this is due to the pressure drops in the components considered by the authors, [26] in the heat exchangers with 130 kPa with a conservative design and another with the best design, [11] without taking pressure drops into account and with the best design. And finally, the results of the presented model for an RCC cycle with a UA value of 15000 kW/K that consider pressure drop values of 2% in the heat recuperators (LTR and HTR), a primary heat exchanger (PHX) and precoolers (PC). The efficiency values obtained are in agreement with the literature studied. Their values differ due to the pressure drop values used by each author.

TABLE II. COMPARISON OF RESULTS WITH THE PUBLISHED LITERATURE. CONSERVATIVE DESIGN (C.D.) AND BEST DESIGN (B.D.)

Design parameters	**Literature [26]**		**Literature [11] B.D.**	**Present model results**
	C.D.	**B.D.**		
Maximum cycle temperature	550 °C	550 °C	550 °C	550 °C
Minimum cycle temperature	32 °C	32 °C	32 °C	32 °C
Maximum cycle pressure	20 MPa	20 MPa	20 MPa	20 MPa
Cycle pressure ratio	2.6	2.6	2.6	2.7
Compressor efficiency	89 %	95.5 %	95.5 %	89 %
Turbine efficiency	90 %	92.9 %	92.9 %	93 %
Pressure drop	130 kPa in HX	130 kPa in HX	-	2 % in HX´s and Precooler
Thermal efficiency	45.27 %	47.36 %	48.45 %	46.43 %

CO_2/CH_4 mixture

Figure 4 compares the efficiencies obtained with pure CO_2 (segmented line) versus those obtained by the mixture containing methane (solid line). The study shows that in the RCC and RCMCI cycle, better efficiencies are achieved with pure CO_2, however, in the PCRC cycle the mixture obtains better efficiencies between 32 °C and 35 °C of compressor inlet temperature.

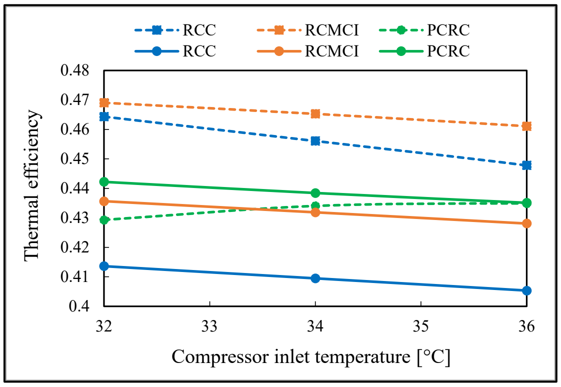


Figure 4. Thermal Efficiency vs Compressor inlet temperature. Using CO_2/CH_4 mixture (solid line), with mole fraction 0.70/0.30 and 15000 kW/K.

Figure 5 shows the values of the irreversibilities (entropic generation) in percentages produced in the different components of the cycle and the thermal efficiency of the cycle. The values obtained with pure CO_2 are compared to the mixture for a compressor inlet temperature of 32 °C. It is shown that the irreversibilities in LTR and HTR are relevant since the sum of them represents around 79% and 57% when pure CO_2 and the mixture are used as working fluid, respectively.

From the analysis, it is obtained that this mixture increases the heat transfer rates in the HTR, LTR, and precooler between streams 12 and 1. And it is only less in the precooler between streams 9 and 11. Furthermore, the mass fraction flowing to the recompressor also decreases when using the mix with a value of 0.38. Whereas, when pure CO_2 is used it is 0.52.

Finally, the mass flow rate of each working fluid are 502.77 kg/s for standard fluid and 488.85 kg/s for the mixture with methane.

In the exergetic analysis, the efficiency of the second law is obtained, and the results show values of 76.51% and 79% for pure CO_2 and the mixture, respectively.

DOI: 10.17185/duepublico/77263

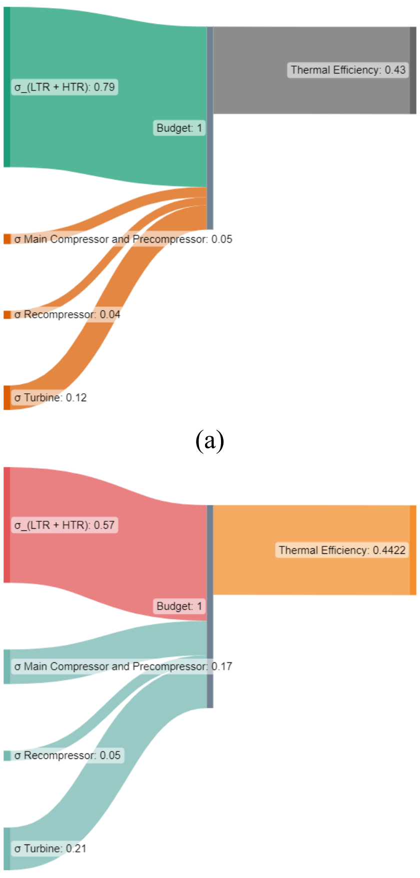


Figure 5. Entropic generation in the components of the PCRC cycle. (a) CO_2 pure and (b) CO_2/CH_4 mixture.

CO_2/H_2S mixture

Figure 6 compares the efficiencies obtained with pure CO_2 (segmented line) versus those obtained by the mixture containing hydrogen sulfide (solid line). The study shows that in the RCC and RCMCI cycle, better efficiencies are achieved with the mixture, however, in the PCRC cycle the mixture obtains slightly lower efficiencies between 32 °C and 34 °C of compressor inlet temperature, while similar values are obtained at 34 °C and 40 °C.

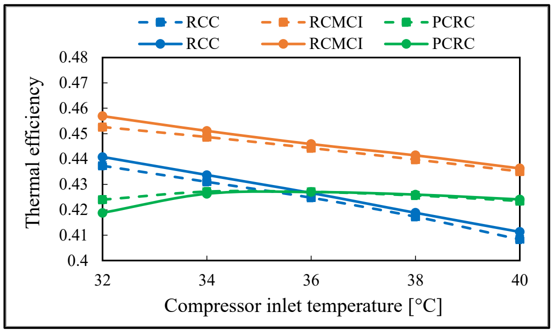


Figure 6. Thermal Efficiency vs Compressor inlet temperature. Using CO_2/H_2S mixture (solid line), with mole fraction 0.95/0.05 and UA 10000 kW/K.

Figure 7 shows the values of the irreversibilities (entropic generation) in percentages produced in the different components of the cycle and the thermal efficiency of the cycle. The sum of the irreversibility values of the HTR and LTR are around 67% and 69% when using pure CO_2 and the mixture, respectively.

When the analysis of the cycle parameters is carried out, it is obtained that with the mixture the work of the main compressor and the other compressor is reduced. The values of the work of the recompressor and turbine are similar. The heat transfer rate in the precooler between lines 9 and 11 increases, between streams 12 and 1, and the LTR decreases. The mass fractions and the mass flow in the mixture and the pure fluid are similar with values of 0.41; 563.1 kg/s and 552.8 kg/s respectively.

In the exergetic analysis, the efficiency of the second law is obtained, and the results show values of 79.45% and 80.29% for pure CO_2 and the mixture, respectively.

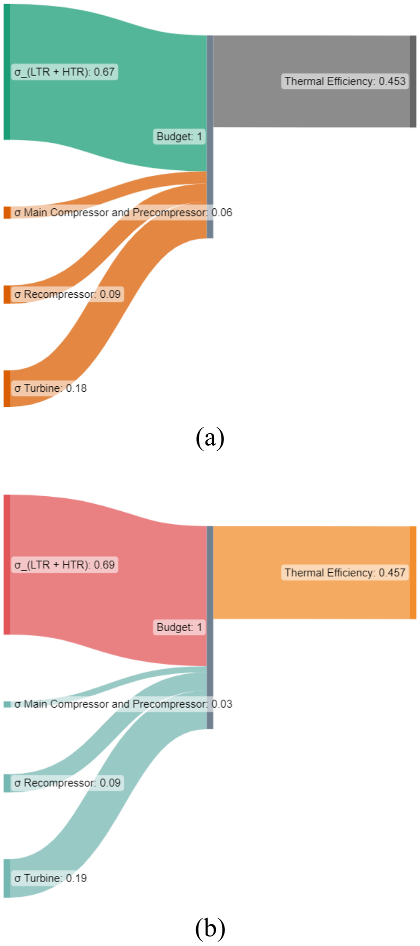


Figure 7. Entropic generation in the components of the RCMCI cycle. (a) CO_2 pure and (b) CO_2/ H_2S mixture.

DOI: 10.17185/duepublico/77263

CO_2/C_3H_8 mixture

Figure 8 compares the efficiencies obtained with pure CO_2 (segmented line) versus those obtained by the mixture containing propane (solid line). The study shows that in the PCRC and RCMCI cycles, slightly lower efficiencies are achieved with the mixture, however, in the RCC cycle the mixture obtains a better efficiency for values of 36 °C and 40 °C of compressor inlet temperature.

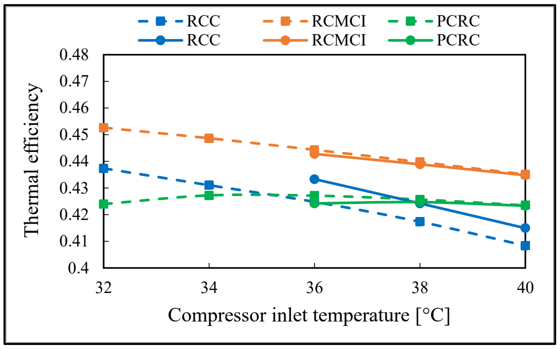
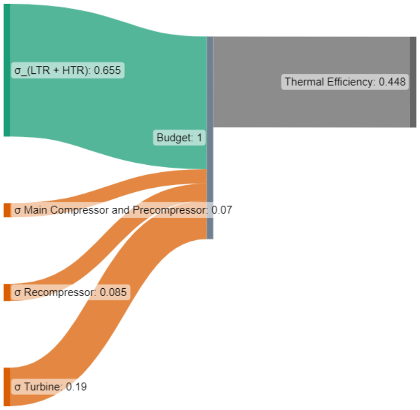


Figure 8. Thermal Efficiency vs Compressor inlet temperature. Using CO_2/C_3H_8 mixture (solid line), with mole fraction 0.85/0.15 and UA 10000 kW/K.

Figure 9 shows the values of the irreversibilities (entropic generation) in percentages produced in the different components of the cycle and the thermal efficiency of the cycle. The values obtained with pure CO_2 are compared with the mixture for a compressor inlet temperature of 36 °C (Critical temperature of the mixture). It is shown that the sum of the irreversibilities in LTR and HTR represent similar values of the order of 65.5% and 65% when using pure CO_2 and the mixture, respectively.

When this mixture is used, the main compressor work increases, but the recompressor and turbine work decreases. Heat transfer rates in the HTR and Precooler increase, however in the LTR they decrease. The mass fraction flowing to the recompressor is 0.36 for the mixture and 0.38 for pure CO_2. In addition, the mass flow also decreases when using the mixture with a value of 538.84 kg/s; while, in the standard fluid it is 645 kg/s.

In the exergetic analysis, the efficiency of the second law is obtained, and the results show values of 79.5% and 80.05% for pure CO_2 and the mixture, respectively.



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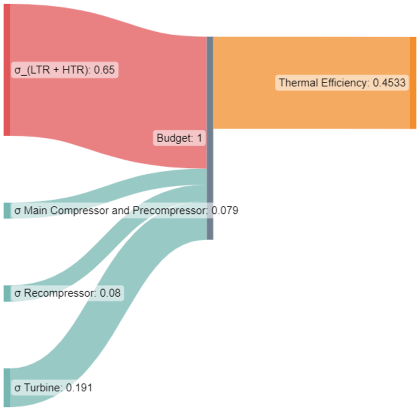

(b)

Figure 9. Entropic generation in the components of the RCC cycle. (a) CO_2 pure and (b) CO_2/C_3H_8 mixture.

CONCLUSIONS

An energy and exergy analysis of s-CO_2 Brayton cycle configurations using binary mixtures as working fluid for shipboard power applications has been presented. This work takes into account the influence of the main operating parameters such as the temperature at the compressor and turbine inlet, the pressure ratio, the irreversibilities generated, and the pressure drop in the system components, etc. Within the thermal efficiency analysis, it is obtained that the CO_2-based mixtures produce a better efficiency than the pure fluid. The entropic generation in the heat recuperators (LTR and HTR) is significantly higher compared to the other components. The sum of their values represents more than 55% of the irreversibilities of the entire system. Temperature variation at the compressor inlet will result in drastic changes in thermal and exergetic efficiency. In addition, the value of the exergetic efficiency given by the mixtures is always higher than with pure CO_2.

DOI: 10.17185/duepublico/77263

The study of the three Brayton s-CO_2 cycle configurations has determined that the configuration that obtains the best thermal efficiency values is the RCMCI followed by the RCC and finally the PCRC when the compressor inlet temperature is 32°C. Each configuration has a particular mixture that gives better efficiency than the standard fluid.

- For the RCMCI configuration, the CO_2/H_2S mixture in mole fraction (0.95/0.05):

  A slight increase in the irreversibilities of the components is shown, however, the works of the main compressor and the other compressor are reduced as well as the rates of heat transfer in the LTR and precooler between streams 12 and 1.

- For the PCRC configuration the CO_2/CH_4 mixture with a molar fraction of 0.70/0.30:

  This mixture provides a higher rate of heat transfer in the HTR, LTR, and precooler between streams 12 and 1. In addition, the work of the main compressor, precompressor, and turbine is also greater. In this case, the irreversibilities generated in the heat recuperators (HTR and LTR) decrease by 20%.

- For the RCC configuration the CO_2/C_3H_8 mixture with a molar fraction of 0.85/0.15:

  When using this mixture, the irreversibility values in the components are similar. However, it shows an increase in the heat transfer rate in the HTR and precooler and the work of the recompressor and turbine decreases in comparison with the values obtained when pure CO_2 is used.

Finally, the thermal efficiency values obtained by the mixtures are higher than the values obtained by pure CO_2 in each studied architecture. This improvement in efficiency will be of great help to reduce the levels of CO_2 emissions on shipboard systems, contributing to a great extent to the objectives of sustainable development, specifically with Climate Action.

NOMENCLATURE

COS	Carbonyl sulfide
CSP	Concentrated solar power
CH_4	Methane
C_3H_8	Propane
C_6F_6	Hexafluorobenzene
C_7H_8	Toluene
CO_2	Carbon dioxide
h	Enthalpy [kJ/kg]
H_2S	Hydrogen sulfide
HTR	High temperature recuperator
$\dot{m}_{mix}$	Mass flow of the mixture [kg/s]
NIST	National Institute of Standards and Technology
Ni_2O_4	Dinitrogen tetroxide
RCC	Recompression cycle
LTR	Low temperature recuperator
PCRC	Partial Cooling with recompression
$\dot{Q}_{Pre\_1}$	The heat transfer rates in the precooler 1 [kW]
$\dot{Q}_{Pre\_2}$	The heat transfer rates in the precooler 2 [kW]
$\dot{Q}_{PHX}$	The heat transfer rates in the primary heat exchanger [kW]
REFPROP	Reference Fluid Thermodynamic and Transport Properties
RCMCI	Recompression with main compressor intercooling cycle
s	Entropy [kJ/kg-K]
s-CO_2	Supercritical carbon dioxide
SCSP	Supercritical Concentrated Solar Power Plant
$TiCl_4$	Titanium chloride
T_{hs}	Temperature of the heat source [K]
T_o	Ambient temperature [K]
UA	Heat total recuperator conductance [kW/K]
$\dot{W}_{net}$	Net work output [kW]

Greek Symbols

$\dot{E}_{in}$	Total heat input exergy [kW]
η_{carnot}	Carnot Efficiency
η_{th}	Thermal Efficiency
η_{ex}	Exergetic Efficiency
σ_C	Entropy generated in the compressor [kW/K]
σ_{HTR}	Entropy generated in the high-temperature recuperator [kW/K]
σ_{LTR}	Entropy generated in the low-temperature recuperator [kW/K]
σ_{MC}	Entropy generated in the main compressor [kW/K]
σ_{RC}	Entropy generated in the recompressor [kW/K]
σ_T	Entropy generated in the turbine [kW/K]
γ	Split Fraction

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Published in: 5th European sCO2 Conference for Energy Systems, 2023

DOI: 10.17185/duepublico/77263

URN: urn:nbn:de:hbz:465-20230427-101857-6