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Abstract:	The use of a binary cycle coupled to the complete reinjection of non-condensable gases could provide a valid answer to the improvement of the sustainability of geothermal plants. In recent years, the interest in the use of CO 2 as a working fluid in transcritical cycles has increased. However, the low critical temperature of carbon dioxide (≈ 30°C) requires the cooling cycle, temperatures below 15°C, which are not always available. In this work, to overcome this limitation and obtain a higher critical temperature and a lower maximum pressure for more flexible applications of transcritical binary cycles, the possibility of using a second component, mixed with CO 2 , has been evaluated. For this purpose, the following fluids have been proposed: R1234yf, R1234ze(E), n-butane, n-hexane, n-pentane and propane, with a minimum considered carbon dioxide molar content of 60%. To carry out a cycle analysis, the knowledge of the thermodynamic properties of CO 2 -mixtures is fundamental; however, suitable equations of state under the appropriate conditions for these blends have not been clearly defined yet. Therefore, in the first part of this paper, different EoS for predicting thermodynamic properties of pure CO 2 and CO 2 -based mixtures are analysed and compared with reference data obtained from works published in the literature. However, because of the lack of experimental data of the selected blends, the values of density, enthalpy and entropy, obtained with the selected EoS are compared with NIST REFPROP results. The EoS involved in the evaluation are cubic-type (PR, PR-Twu, PRSV, RK, SRK, GCEOS), Virial-type (LKP, BWRS), Helmholtz-type (SW) and SAFT-type (PC-SAFT). In a power cycle, the fluid works under different conditions, involving several possible states across the components. So the influence of the different EoS on each power cycle's key component for pure CO 2 and two selected CO 2 -based mixtures has been assessed. The thermodynamic results show that the CO 2 -based mixtures, in a transcritical configuration, can achieve efficiencies higher than the sCO 2 power cycle.

Evaluation of the property methods for pure and mixture of CO_2 for power cycles analysis

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1. Abstract

The use of a binary cycle coupled to the complete reinjection of non-condensable gases could provide a valid answer to the improvement of the sustainability of geothermal plants. In recent years, the interest in the use of CO_2 as a working fluid in transcritical cycles has increased. However, the low critical temperature of carbon dioxide (≈ 30°C) requires the cooling cycle, temperatures below 15°C, which are not always available. In this work, to overcome this limitation and obtain a higher critical temperature and a lower maximum pressure for more flexible applications of transcritical binary cycles, the possibility of using a second component, mixed with CO_2, has been evaluated. For this purpose, the following fluids have been proposed: R1234yf, R1234ze(E), n-butane, n-hexane, n-pentane, and propane, with a minimum considered carbon dioxide molar content of 60%. To carry out a cycle analysis, the knowledge of the thermodynamic properties of CO_2-mixtures is fundamental; however, suitable equations of state under the appropriate conditions for these blends have not been clearly defined yet. Therefore, in the first part of this paper, different EoS for predicting thermodynamic properties of pure CO_2 and CO_2-based mixtures are analyzed and compared with reference data obtained from works published in the literature. However, because of the lack of experimental data of the selected blends, the values of density, enthalpy and entropy, obtained with the selected EoS, are compared with NIST REFPROP results. The EoS involved in the evaluation are cubic-type (PR, PR-Twu, PRSV, RK, SRK, GCEOS), Virial-type (LKP, BWRS), Helmholtz-type (SW), and SAFT-type (PC-SAFT). In a power cycle, the fluid works under different conditions, involving several possible states across the components. So the influence of the different EoS on each power cycle's key component for pure CO_2 and two selected CO_2-based mixtures has been investigated. Finally, a qualitative study of the flammability of the new blends is carried out. The thermodynamic results show that the CO_2-based mixtures, in a transcritical configuration, can achieve efficiencies higher than the sCO_2 power cycle.

Keywords: CO_2, CO_2-based mixtures, equation of state, low-temperature application, power cycle analysis.

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2. Introduction

Improving sCO_2 cycle performance always remains an interesting topic for researchers, even further revamped in recent years. In these cycles, maintaining the compressor inlet condition near the CO_2 critical condition is essential to benefit from the low compression efficiency. Several studies discussed the cycle configurations and proposed new schemes, while others attempted to evaluate the cycle performance by alternative working fluids. Utilizing sCO_2-based mixtures as a working fluid increases the degree of freedom and makes the possibility of adjusting the critical point of CO_2 by adding various fluids. The magnitude of decrease or increase of the critical point depends on the mixture composition and properties of the added components. The desired mixture, with a modified critical point, manipulates the restriction of low heat rejection temperatures and the power cycle can be extended to higher heat rejection temperatures, which contributes to higher efficiency [1], while allowing transcritical cycles with condensation in the medium and high-temperature climatic areas. Moreover, the new working fluid mixtures could bring new flammability and toxicity level with different environmental impacts, costs, and operational safety concerns, which should be considered in the overall evaluation [2]. Also, the prediction of the solubility and thermal stability of fluids are factors largely discussed in the literature [3] [4] and it is worth mentioning them, anyway, they are not detailed in this paper.

The studies related to CO_2-based mixtures are listed in Table 1, where researchers adopted several gas mixtures as working fluids candidates in the sCO_2 cycles, in which CO_2 is mixed with other gases. The majority of the studies are referred to the binary mixture of CO_2 and noble gases. Several studies investigated the binary mixtures of CO_2 with hydrocarbons, and some are related to performing analysis on zeotropic and azeotropic mixtures.

Due to the crucial role of the intermolecular forces under supercritical conditions, a real gas model is required to estimate the properties of either the pure fluids or the mixture. Therefore, according to the conditions and the components of the fluid mixture, the most appropriate EoS should be chosen. As listed in Table 1, several EoS and database types are investigated in the literature for the fluid property estimation to be used for the design and performance analysis of CO_2-based supercritical cycles and mixtures. The EoS can be classified into four categories: Cubic-based equations, Virial-based equations, Helmholtz function, and the Statistical Associating Fluid Theory (SAFT). Based on the literature, other types of EoS are out of discussion for the sCO_2-related case studies.

Table 1 – Literature review of working fluids and thermodynamic references used for CO_2 power cycle analysis

Author and Year	Fluid and Mixture type	Reference Models /software
Maczek et al., 1997 [5]	CO_2-R32, R134a	REFPROP V5.0
Kim et al., 2002 [6]	CO_2-R134a CO_2-R290	REFPROP V6.0
Sarkar et al. 2009 [7]	CO_2-R600 CO_2-R600a	REFPROP CO2PROP [8]
Wright et al., 2011 [9]	CO_2-SF_6, CO_2-Butane	REFPROP V9.0
Wright, et al., 2011 [1]	Pure CO_2, Two-phase CO_2	REFPROP V8.0
Lewis et al., 2011 [10]	SF_6- CO_2, C4- CO_2	REFPROP, PR
Jeong et al., 2011 [11]	CO_2+ (H_2, N_2, O_2, He, Ar, Kr,)	REFPROP V8.0
Conboy et al., 2012 [12]	CO_2-He, CO_2-Ne, CO_2-CH_4 CO_2-nC4, CO_2-SF_6	REFPROP V9.0
Jeong et al., 2013 [13]	CO_2–H_2S, CO_2-cyclohexane	REFPROP V8.0

Yin et al., 2013 [14]	CO2-SF_6	REFPROP V8.0
NETL guideline 2014 [15]	-	LK-PLOCK
Hakkaki-Fard et al., 2014 & 2015 [16] [17]	zeotropic mixture R32-CO_2	REFPROP V9.0
Hu et al., 2015 [18]	CO_2-Ar, CO_2-O_2, CO_2-He, CO_2-Xe, CO_2-Kr, CO_2-Butane, CO_2-cyclohexane	REFPROP V9.0
Mecheri et al. 2016 [19]	CO_2	REFPROP, PENG-ROB PR-BM (PR- Boston Mathias), RK-SOAVE, SRK (Redlich-Kwong-Soave) BWRS (Benedict-Webb-Rubin-Starling) LK-PLOCK (Lee-Kesler-Plocker)
Weiland et al., 2016 [20]	CO_2-HCL-NH_3	Peng-Robinson-Boston-Mathias (PR-BM) in Aspen Plus
Vesely et al., 2016 [21]	CO_2-He, CO_2-CO, CO_2-O_2 CO_2-N_2, CO_2-Ar, CO_2-Xe	REFPROP V9.1
Manikantachari et al. 2017 [22]	CO_2	RK, SRK, PRS, REFPROP V7.0
Ma et al., 2018 [23]	CO_2-Kr	REFPROP V9.0
Manikantachari et al., 2018 [22]	CH_4-O2-CO_2, H2-O2-CO_2	SRK in CHEMKIN-RG Exp. (Ignition Delay Times)
Baik et al., 2018 [24]	SF_6-CO_2, CO_2-R123, CO_2-R134a CO_2-R32, CO_2-R22	REFPROP Exp.
White et al., 2018 [25]	CO_2-H_2O	REFPROP (2007), PR-BM, LK-PLOCK PC-SAFT, BWRS, BWRS-LS SRK, SR-POLAR, GRAYSON
Guo et al., 2019 [26]	CO_2-Xenon, CO_2-Butane	REFPROP
Vesely et al., 2019 [27]	CO_2-He, CO_2-CO, CO_2-O_2, CO2-N2, CO_2-Ar, CO_2-C1, CO_2-H_2S	REFPROP V9.1 & COOLPROP in PYTHON TREND 2.0 [28]
Liu et al., 2019 [29]	CO_2-cyclohexane, CO_2-butane, CO_2-isobutane, CO_2-propane, CO_2-H_2S	LK-PLOCK property Aspen Plus (2010)
Manzolini, Invernizzi et al., 2019 [30]	CO_2-N_2O_4, CO_2-$TiCl_4$	REFPROP, Peng-Robinson EOS
Yu et al., 2020 [31]	CO_2-Xe, CO_2-Kr, CO_2-O_2, CO_2-Ar, CO_2-N_2, CO_2-Ne, CO_2-He	REFPROP V10.0, MATLAB
Barak et al., 2020 [32]	CH_4-O_2-CO2-N_2	Exp. (Ignition Delay Times)
Saengsikhiao et al., 2020 [33]	Azeotropic Mixtures: R463A (R32-R125-R134a-R1234yf-CO_2) R445A (R1234z3-R134-CO_2) R455A (R1234yf-R32-CO_2)	REFPROP CYLCE_D-HX [34]
Bonalumi, Lasala, Macchi, 2020 [35]	CO_2-$TiCl_4$	Peng-Robinson EOS

On the other hand, one of the most common databases used by the NIST database [36] is REFPROP, which provides the fluid's properties based on either the related experimental data or the proven models from the literature. Most of these experimental data belong to pure fluids, like the one for pure CO_2 derived from the research of Span Wagner [37]. As listed in Table 1, several studies on the sCO_2 power cycles are carried out basing on this database, with different versions during the

years. In the prediction of mixtures property, the REFPROP performance depends on the availability of specific models and experimental data for the required binary or multi-component mixtures, which are incorporated within the database. In some cases, due to the temperature limits, computations fail for property predictions by the database [25]. Other databases are COOLPROP [38], an open-source program able to determine the property of pure and pseudo-pure fluids; CO2PROP, which is a subroutine, developed based on Helmholtz free energy function and AIChE's "DIPPR 801", which is a source of critically evaluated thermophysical properties by American Institute of Chemical Engineers (AIChE) [39]. There is also a generated data developed by Aspen Technology based on the most well-known EoS widely used in the literature. National Energy Technology Laboratory (NETL) already evaluated the data available on the Aspen properties database, including NIST REFPROP, Peng-Robinson (PR) variants [40], PR-Twu [41], PR-BM (PR-Boston Mathias) [42], RK (Redlich-Kwong) [43], SRK (Redlich-Kwong-Soave) [44], BWRS (Benedict-Webb-Rubin-Starling) [45], and LKP (Lee-Kesler-Plocker) [46]. Both PR variants and LKP have the best prediction near the critical point compared to REFPROP, while the LKP has superior performance at high pressure and temperature. The LKP is also recommended by the NETL, due to higher consistency in the critical region [15].

The software packages are Honeywell UniSim Design [47] [48], DWSIM [49], Aspen HYSYS [50], and similar solvers that, in some cases, introduce some improvements and modifications of the basic EoS when treating mixtures. These modifications are mainly related to the mixing rules, binary interactions, and solubility. The various numerical solvers provide only marginally different results even for pure fluids [19].

Most of the case studies discussed in the literature are related to specific thermodynamic applications rather than analytic thermodynamic property evaluation. Their focus is on power cycles, alternative configurations, and various applications. In most of those, the new mixtures are limited to the extraction of data from the common database. As shown in Figure 1, the present study fills in the thermodynamic evaluation gap and provides a cross-check between the available models and experimental data for the pure CO_2 and CO_2-based mixtures (blank box).

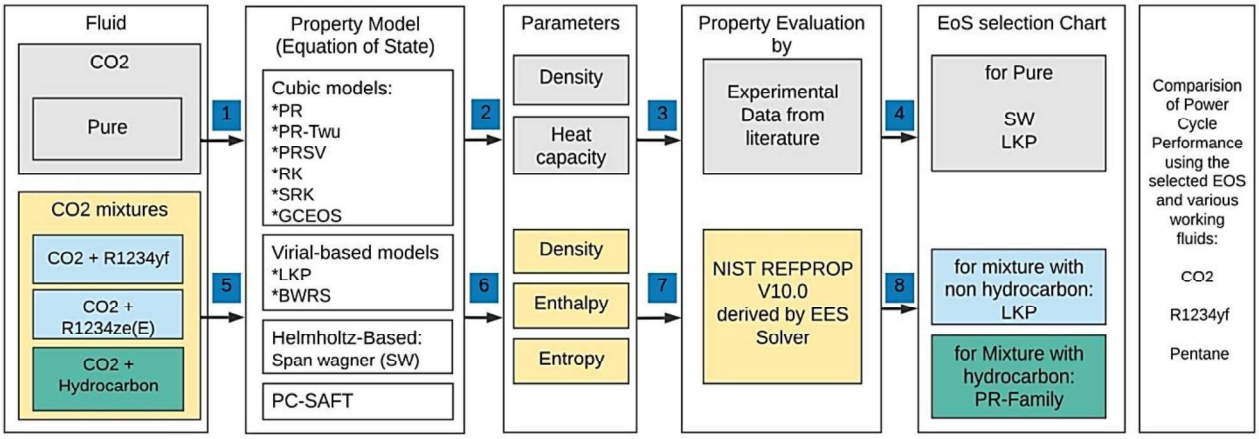

Figure 1 – Research outline for property model evaluation

3. Methods and implementation

3.1. Pure CO_2

Available experimental data and Gaps regarding pure CO_2

In order to provide a reliable power cycle simulation, using accurate working fluid's thermodynamics properties is fundamental. Since the 1950s, increasingly accurate experiments have been conducted for pure CO_2 properties. In this work, to verify the reliability of calculation models and equations of state, more than 880 experimental measurements of density and specific heat capacity of pure CO_2 are collected from the literature. Among all the available publications, only the experimental data included in a temperature and pressure range of 303-615 K and 7-35.5 MPa, respectively, were selected because typical of sCO_2 geothermal power plants. The references used for pure CO_2 are shown in Table 2 and Table 3.

Table 2 – Literature references on experimental measurements of the density of pure CO_2

Reference for CO_2	Year	T range (K)	P range (MPa)	N°points
Kennedy [51]	1954	313.15 - 615	7.50 - 35.00	176
Langenfeld et al. [52]	1992	313.15 - 423.15	8.21 - 29.90	17
Knetz [53]	1995	333.15 - 373.15	10.00 - 30.00	28
Fenghour et al. [54]	1995	330 - 613	7.2 - 34	29
Seitz [55]	1996	323.15 - 573.15	9.94 - 29.93	17
Pohler and Kiran [56]	1996	323.00 - 423.00	15.46 - 30.78	27
Van der Gulik [57]	1997	303.05	7.23 - 35.31	33
Tomoya Tsuji et al [58]	1998	304, 310, 320	7 - 10	67
Ferri et al. [59]	2004	353.20 - 393.20	16.00 - 30.00	17
Garmroodi et al. [60]	2004	308.00 - 348.00	12.20 - 35.50	40
Skerget et al. [61]	2005	313.20 - 353.20	7.83 - 30.37	55
Pečar and Doleček [62]	2007	308.15 - 333.15	10.00 - 35.00	10
Liu et al. [63]	2007	320, 355, 369	13 - 34	8
Pensado et al. [64]	2008	303 - 353	10 - 35	57
Mantilla et al. [65]	2010	310 - 450	10 - 35	26
Laura Gil [66]	2010	304.21 - 308.15	7.01 - 20	103
Kodama et al. [67]	2013	313.15	7 - 10	4

Table 3 – Literature references on experimental measurements of the specific heat of pure CO_2

Reference for CO_2	Year	T range (K)	P range (Mpa)	N° points
Lowell [68]	1960	304 - 322	7.2 - 8.7	38
Dordain And Coxam [69]	1995	327 - 416	7.3 - 25.8	100
Ishmael [70]	2016	333 - 423	10 - 30	28

3.2. CO_2-based mixtures

Correlation of thermodynamic models with VLE data

Typically, to define the Binary Interaction Parameters (BIP) of a mixture, the VLE points are used as data regression. The Nishiumi et al. [71] binary interaction coefficients are used in the present study (Table 4), which are also of the UniSim library. The PR-mod is a modified Peng-Robinson version, with the coefficients suggested by UniSim, available only for CO_2+HC. The coefficients of Helmholtz type equations are those implemented in REFPROP 10.0 version. The charts below show the equilibrium points obtained from experimental campaigns on the VLE, already existing in literature for the selected mixtures, compared to those estimated with the most promising EoS, chosen from the ones previously tested for pure CO_2. For this study, the potential of UniSim and DWSIM is exploited. Similarly, by using REFPROP 10.0 libraries [36] through EES (Engineering Equation Solver) [72] the accuracy of the models implemented in the program was estimated. In Table 5, the publications of the VLE experimental measurements used in the present study are reported.

Table 4 – Binary Interaction Parameters of the selected mixtures for each EoS [71]

	PR	PR mod	PR-Twu	LKP	GCEOS
CO_2 + R1234yf	0.1113	-	0.101	0	-
CO_2 + R1234ze(E)	0.11129	-	0.101	0	-
CO_2 + n-butane	0.1298	0.06374	0.1298	0.9456	0.13
CO_2 + n-hexane	0.125	0.04971	0.125	1.0196	0.125
CO_2 + n-pentane	0.125	0.05672	0.125	0.9833	0.125
CO_2 + propane	0.135	0.07075	0.135	0.9211	0.135

Table 5 – CO_2-based mixtures and VLE references

Fluids	VLE reference
CO_2 + R1234yf	Juntarachat et al. [73] G. Di Nicola et al. [74]
CO_2 + R1234ze(E)	Juntarachat et al. [73]
CO_2 + n-butane	Shlbata et al. [75]
CO_2 + n-hexane	Ying-Hsiao Li et al. [76]
CO_2 + n-pentane	Huazhe Cheng et al. [77]
CO_2 + propane	Ju Hyok-Kim et al. [78] J. C. Acosta [79]

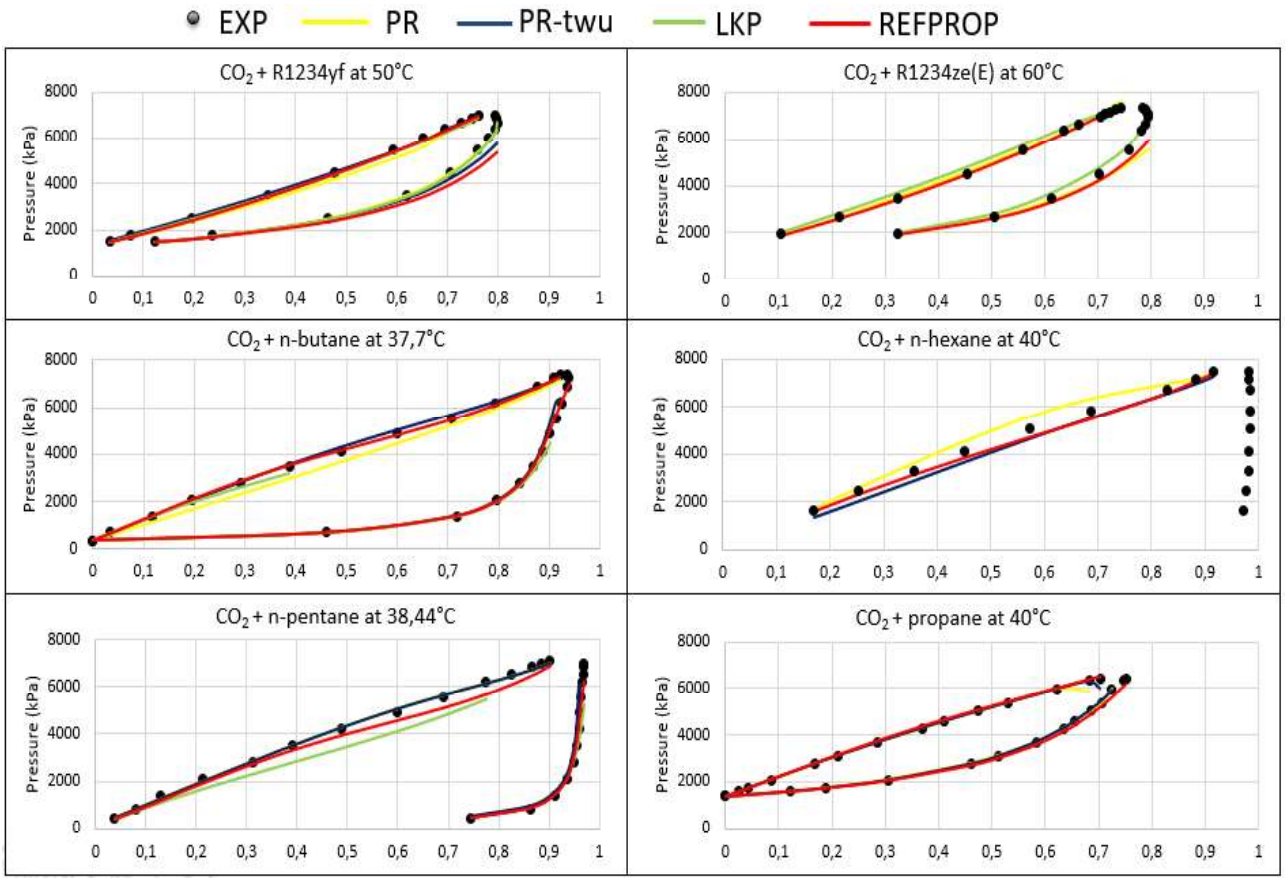

Figure 2 – VLE isotherms for carbon dioxide-based mixtures from the models, compared with the experimental data shown in Table 5

The comparison, shown in Figure 2, clarifies the models' prediction level compared to the reference of NIST REFPROP. The LKP, imported by DWSIM for the VLE analysis, seems the best for the simulation of the binary equilibrium of CO_2 - refrigerants mixtures. On the other hand, the Peng-Robison EoS demonstrates an acceptable regression of the experimental points for mixtures with hydrocarbons.

4. Results and discussion

4.1. Pure CO_2

The experimental data, reported in Figure 3, were compared with the values of density and specific heat calculated by different EoS, included in the UniSim database. Two dimensionless parameters were adopted to compare the various models: the absolute average deviation (AAD), and the root mean square error (RMSE).

$$AAD = \frac{1}{n}\sum_{i=1}^{n}\left|\frac{\rho_{exp,i}-\rho_{calc,i}}{\rho_{exp,i}}\right| \qquad RMSE = \sqrt{\frac{\sum_{i=1}^{n}(\rho_{exp,i}-\rho_{calc,i})^2}{n}}$$

Where ρ_{calc} is the calculated density by EOS, ρ_{exp} is the experimental density and n is the number of experimental data.

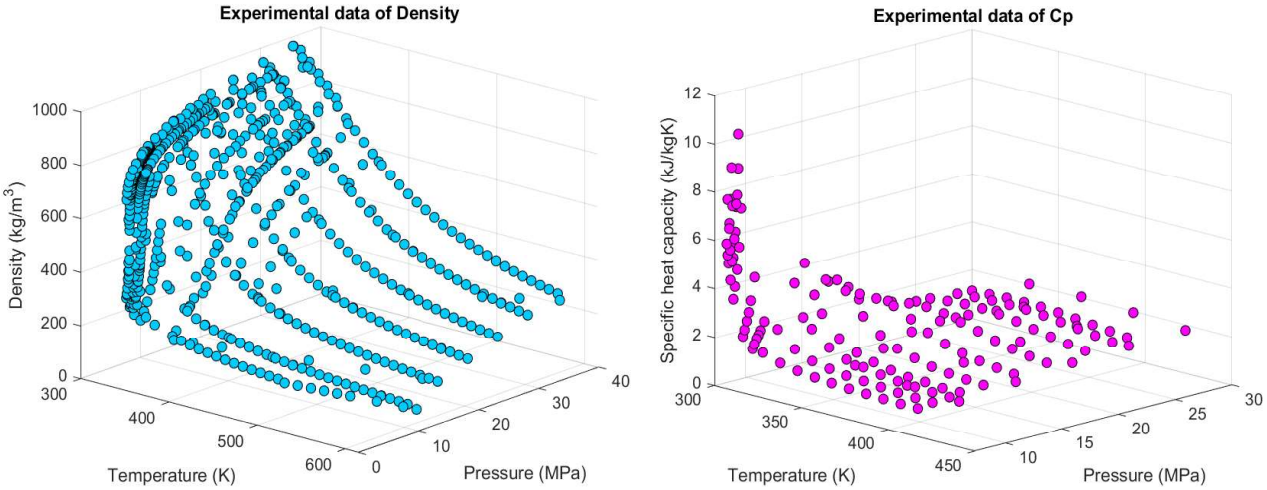

Figure 3 - Reference experimental data for density (left) and heat capacity, C_p (right)

The results of the comparison are shown in Table 6. It is evident that the use of the Helmholtz-type Span-Wagner equation [37], implemented in the REFPROP software, provides the best matching with the experimental data in the whole range. The related AAD and RMSE of density and Cp are the lowest compared to the other EoS. In particular, the calculated ρ-RMSE is more than three times lower than the second-best equation. The SW model implemented in the open-source COOLPROP software was also tested, with very similar results to the REFPROP version. Looking at the equations of state implemented in UniSim software, the LKP seems to provide reasonable accuracy. Alternatively, the DWSIM version of the Lee-Kesler-Plocker (LKP) EoS was also employed with significant improvements. The GCEOS and PR-family equations are acceptable at a moderate extent, with ρ-AAD and Cp-AAD about 3.3% and 7%, respectively. On the contrary, the worst prediction of density in the analyzed region is achieved by the SRK, BWRS, and PC-SAFT equations, with an average deviation of around 10%. According to the present work, the temperature increase contributes to a decrease in the deviation for a fixed pressure. The here achieved results agree with those of other studies [80].

Table 6 - Comparison of property estimation by EoS compared with REFPROP as the reference

EOS	Density (AAD)	Density (RMSE)	Cp (AAD)	Cp (RMSE)
PR	3.949%	33.98	6.724%	0.536
PR-Twu	3.348%	30.54	6.916%	0.479
PRSV	3.481%	35.54	7.571%	0.483
LKP	2.544%	24.55	3.584%	0.388
LKP (DWSIM)	1.478%	10.39	2.925%	0.342
SRK	9.878%	74.72	5.789%	0.492
SRK-Twu	11.034%	82.03	5.587%	0.474
BWRS	5.612%	69.43	11.208%	1.069
GCEOS	3.272%	31.06	7.570%	0.483
PC-SAFT	4.810%	49.62	10.513%	1.174
SW (REFPROP)	0.479%	7.11	2.471%	0.227

SW (COOLPROP)	0.471%	7.32	2.472%	0.227

Analysis of the viscosity model

The viscosity describes a fluid's resistance to flow, and it is one of the most critical transport properties. For this reason, an accurate model for its representation in thermo-fluid dynamic problems is often necessary. The results of available viscosity models are evaluated with related experimental data (Table 7). REFPROP solver comprises Fenghour model [54] and Quinones-Cisneros model [81]; the UniSim solver includes the Chung Lee Starling viscosity model and a dedicated database which is based on external property dataset of DIPPR® 801 [39]. Also, an additional model of Laesecke and Muzny [82] out of those solvers is taken into account for the viscosity evaluation. These models are independent of the EoS.

Table 7 – Available references for the viscosity of pure CO_2

Reference for CO_2	Year	T range (K)	P range (MPa)	N°points
Van Der Gulik [57]	1997	308.15	8.61 - 35.50	16
Liu et al. [83]	2007	320 - 355 - 369	13 - 34	8
Pensado [64]	2008	303 - 353	10 - 60	32

The results of the comparison are shown in Figure 4. Among the selected models, Laesecke and Muzny Model [82] gives the best result. Also, both the Fenghour and Quinones models give accurate predictions with AAD of about 1%, and both are available as REFPROP sub-model for the viscosity. The Chung Lee Starling model is the next-ranked model, which is also available in the UniSim solver. The internal database of UniSim design gives the worst performance compared to experimental data, with an absolute error higher than 24%.

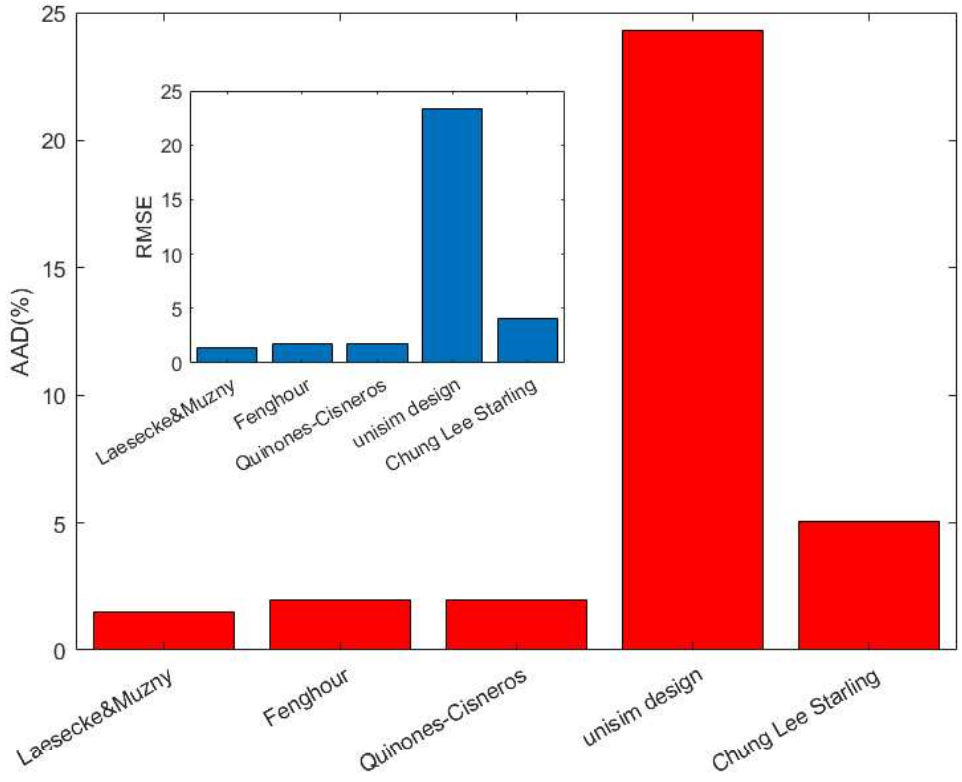

Figure 4 – Comparison of viscosity achieved by the EoS implemented on different models and software packages

4.2. CO_2-based mixture

EoS comparison with REFPROP

There are no available experimental data of density, nor other thermodynamic properties, of the selected CO_2-based mixtures from the literature. A comparison with REFPROP data was determined to validate the results of the different EoS for each blend. Considering that the present study aims to evaluate CO_2-based binary fluids, the upper concentration of the second component was limited at 40%. Table 8 shows the pressure and temperature ranges for which the analysis of the mixtures was carried out. The equations inside the open-source software COOLPROP were also included in comparison with REFPROP. The Fluids R1234yf and R1234ze(E) are not included in the UniSim library; therefore, it was necessary to import the properties of the fluid from the external module of DWSIM and to set up manually the critical properties (Table 9).

Table 8 – Temperature and Pressure ranges selected for thermodynamic analysis of mixtures of CO_2 and the following fluids

	R1234yf	R1234ze(E)	n-butane	n-pentane	n-hexane	propane
T range (°C)	30 - 240	30 - 240	30 - 240	30 - 240	30 - 240	30 - 240
P range (MPa)	3 - 30	3 - 30	1 - 20	0.6 - 20	0.6 - 20	1 - 20

Table 9 – Basic and critical properties of fluids that are necessary to set up in UniSim [36], [38]

Fluid	Tc (°C)	Pc (kPa)	Ideal Liq. Density (kg/m^3)	Critical Volume ($m^3/kmol$)	MM (kg/kmol)	NBP (°C)	Acentricity (-)
R1234yf	94.7	3382	1100	0.2398	114.04	-30	0.2760
R1234ze(E)	109	3636	1293	0.2331	114.04	-19	0.3131

The thermodynamic properties tested for this comparison were the density, enthalpy, and entropy difference. Figures 6, 7, and 8 report the calculated average absolute error of each EoS tested for the y-axis and the variation of the molar concentration of CO_2 for the x-axis. Generally, the AAD referred to the REFPROP database is about 5-6% for the three selected properties, with some peaks over 10%. The behaviour of the curves for enthalpy and entropy is very similar, while there are more significant differences with the density.

For refrigerants, the Lee-Kesler-Plocker equation allows for density errors of less than 2% for R1234yf and less than 4% for R1234ze (E). The error for ΔH and ΔS is higher but never exceeds 6% compared to Peng-Robinson and PR-Twu. Although there are limited references for the evaluation of the results, the experimental data of the mixture of CO_2-R1234ze(E) in supercritical conditions at 333K and 353K [84] are considered, and the accuracy of LKP and REFPROP has been verified in Figure 7. The Twu modification of PR is recommended by the UniSim software manual [85] because its α-function has an exponential term that provides smooth transition through the critical conditions; therefore, they are more practical for process simulation.

For hydrocarbons, the PR family proves to be the most effective and reliable one. The PR is the equation that is widely used to predict the thermodynamic properties of pure hydrocarbons. In principle, PR-Twu gives similar results compared to simple PR except for the mixture with n-butane. The best performance of PR is for the mixture of n-butane and propane with the lowest errors. Therefore, ρ-AAD, ΔH-AAD, and ΔS-AAD are consistently under 3% in the molar content range. The worst performance of PR is for n-hexane with a ρ-AAD of around 4%, ΔH-AAD, and ΔS-AAD around 5%. The corrective coefficients proposed by UniSim show an improvement in the results of ΔH-AAD and ΔS-AAD, especially for n-pentane and propane, but also an increase of the density deviation with the decrease of the CO_2 concentration in the mixture. Therefore, it may be interesting to consider a compromise between the two versions of PR depending on the molar concentration of carbon dioxide for each blend. The molecular weights of propane and carbon dioxide are 44.09 g/mol and 44.01 g/mol, respectively. Therefore, the performance of LKP, as a virial-type EoS, for the case study of propane-blend is because of the similarity of mixture components molecules. Finally, the results obtained with COOLPROP deserve consideration, showing the reliability of this open-source database.

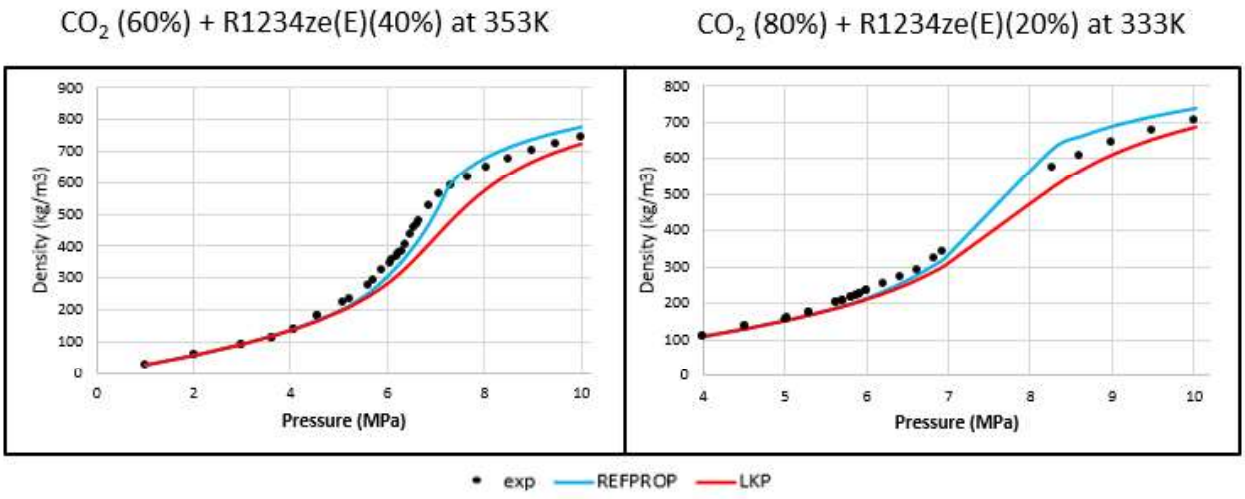

Figure 5 – The LKP and REFPROP accuracy to fit the supercritical experimental data [84] of CO_2 and R1234ze(E) mixture

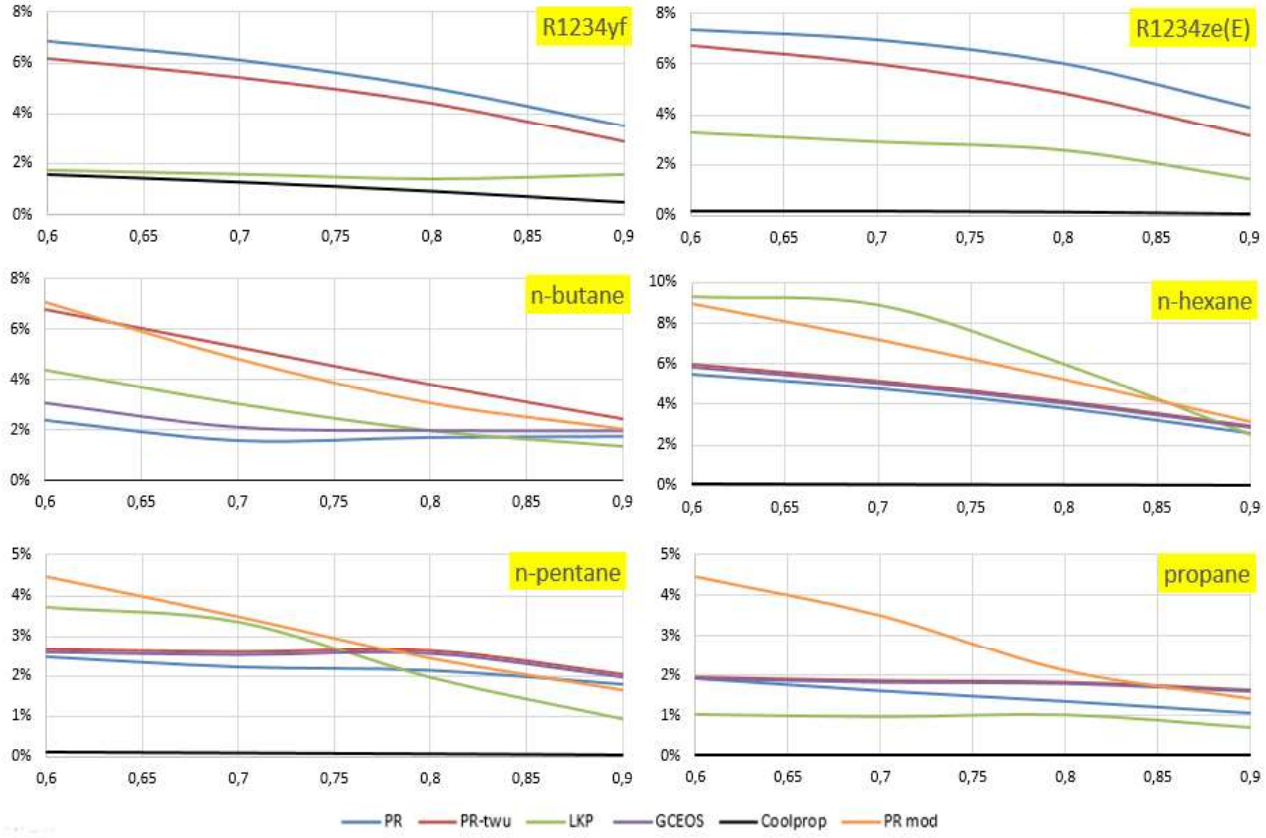

Figure 6 – AAD of density comparing EoS and REFPROP model with the variation of the molar concentration of CO_2 in the mixture

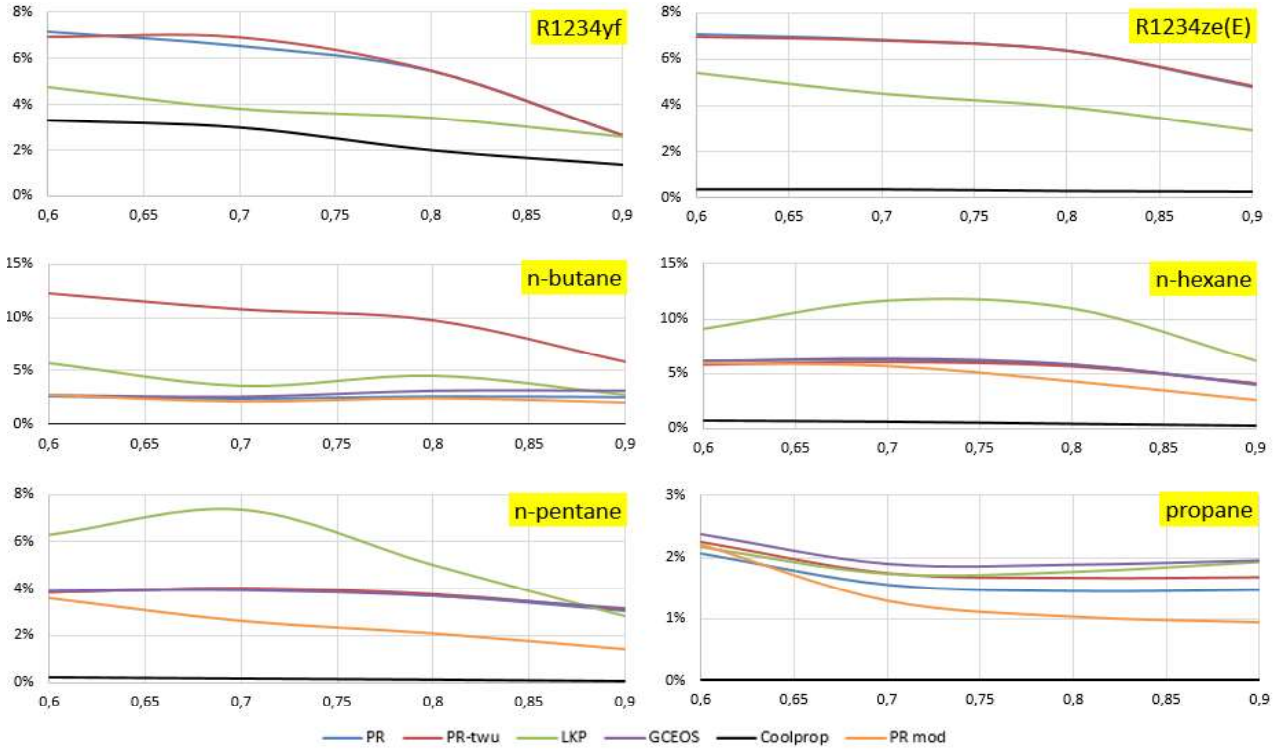

Figure 7 – AAD of the enthalpy difference comparing EoS and REFPROP model with the variation of the molar concentration of CO_2 in the mixture

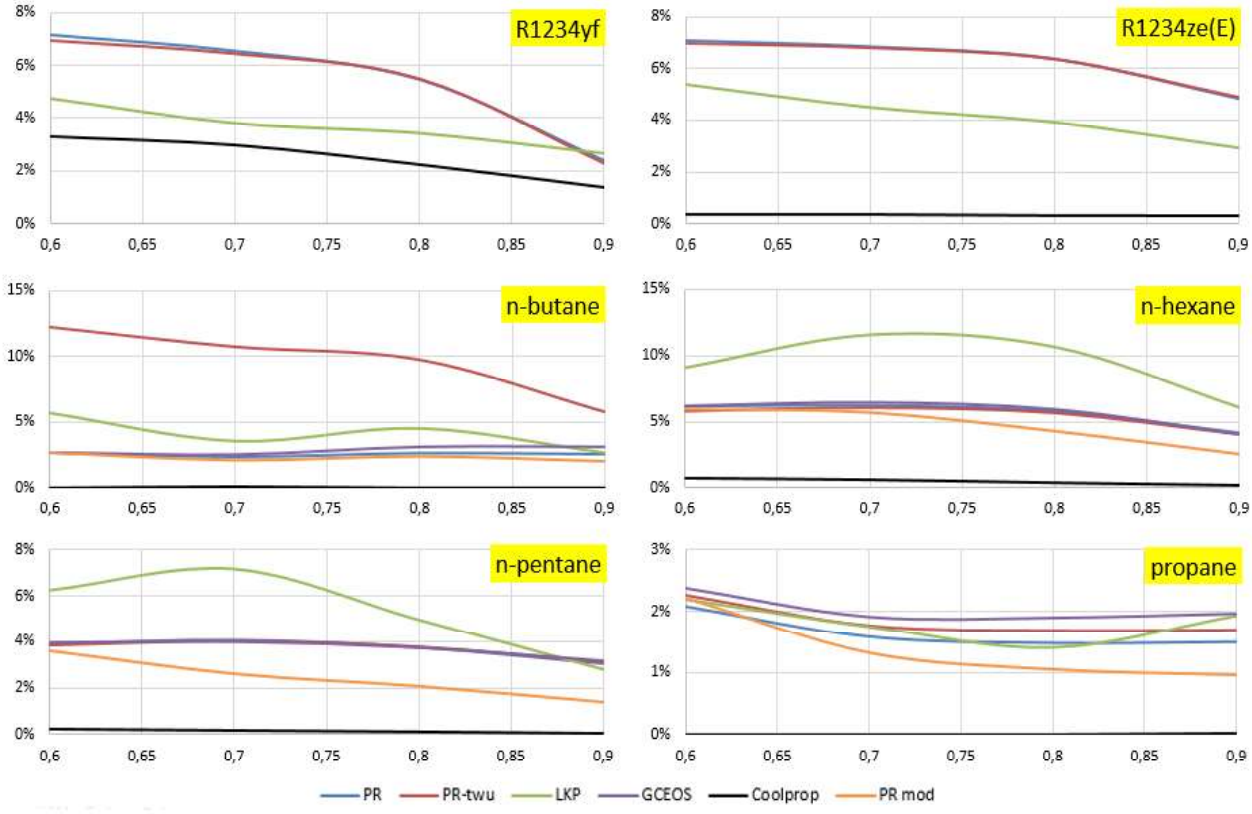

Figure 8 – AAD of the entropy difference comparing EoS and REFPROP model with the variation of the molar concentration of CO_2 in the mixture

5. The power cycle

As previously discussed, using sCO_2-based mixtures as a working fluid increases the degrees of freedom and makes possible the modification of the critical point of CO_2 by adding various fluids and manipulating the constraint of low heat rejection temperatures. So, the power cycle can be extended to higher heat rejection temperatures with the possibility of realizing a transcritical cycle configuration, which contributes to higher efficiency. Moreover, the new working fluid mixtures could lead to reducing the maximum pressure of the cycle with different equipment costs and operational safety concerns. The main objective of this chapter is to investigate the influence on the accuracy of the results of the different discussed EoS when applied to the analysis of power cycles working with CO_2 based mixtures. Such a comprehensive analysis is very useful to the designers and researchers of energy systems to address the uncertainty of thermodynamic cycles results when working with novel mixtures, not currently available in literature so far.

The layouts of the power cycle simulated with pure CO_2 and with the selected blends are shown in Figures 9 and 10, respectively. The first is a supercritical Brayton power cycle with recuperation; the second is a recuperative closed-loop Rankine cycle. The working fluid is indirectly heated by a low–medium temperature hot source (e.g. solar, geothermal, waste heat, biomass, etc.) through a heat exchanger up to 230°C. The fluid at the output of the cold side of the recuperator is then cooled down to 30°C, corresponding to the value at the compressor inlet or pump inlet. For a mixture, differently from a pure fluid, in the case of the transcritical cycle, it is not possible to set a defined pinch point because of the non-isothermobaric condensation line. Therefore, to avoid a large heat transfer area, a control function of the minimum temperature difference of each heat exchanger was implemented. The temperature limit at the condenser and recuperator pinch point was assumed within the range of 5°C to 10°C. Also, the approach point at the evaporator was assumed as 10°C. Finally, the adiabatic efficiency of the pump and the turbine was taken equal to 90%. The simulations have been carried out in an EES environment using the procedure to access the REFPROP database, furthermore, the energy and mass balances are reported in Appendix A.

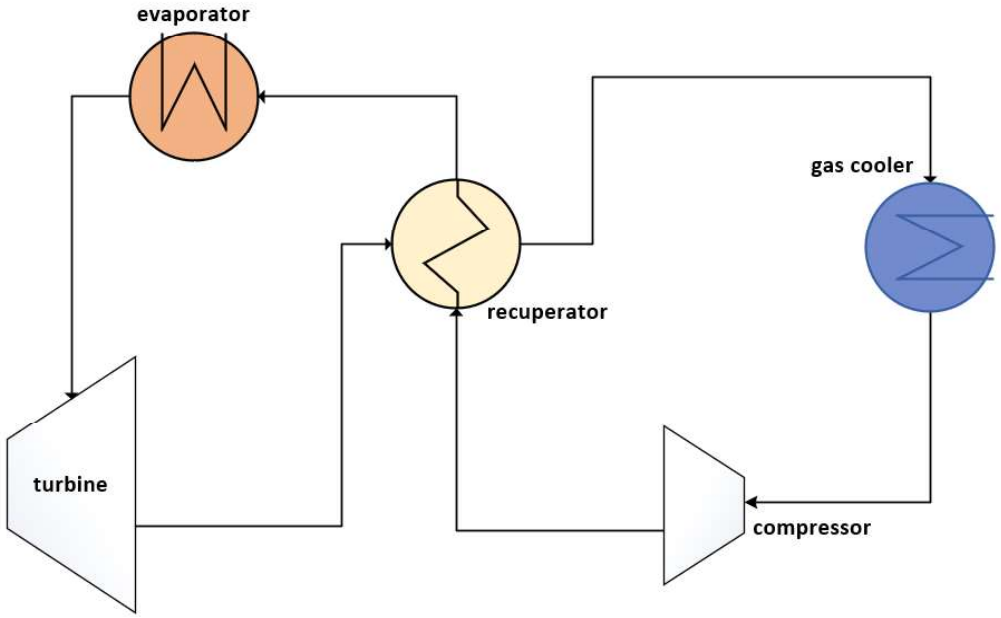

Figure 9 – Supercritical recuperative closed-loop Brayton cycle

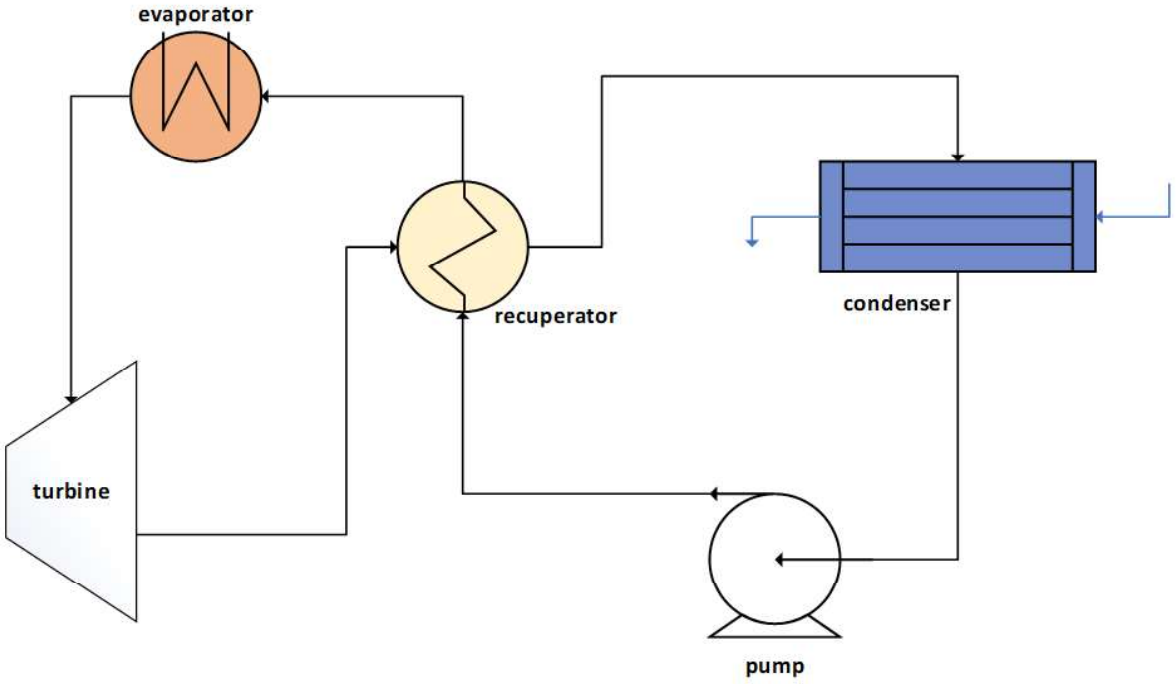

Figure 10 – Recuperative closed-loop Rankine cycle

To make a comparison with pure sCO_2, in terms of thermodynamic performance and energy efficiency of the cycle, the influence of the selected mixture composition and the maximum pressure of the cycle has been investigated.

$$\eta = \frac{W_t - W_p}{Q_{in}}$$

With W_t the work produced by the turbine, W_p the work absorbed by the pump or the compressor and Q_{in} the total heat energy input entering the system by the evaporative heat exchanger.

Where possible and respecting the previously defined pinch point of the heat exchangers, the molar fraction of CO_2 has been ranged from 90% to 60%, and the maximum pressure range was set between 200 and 100 bar. The results presented in Figure 11 to Figure 16 highlight the benefits of the new mixtures compared to pure CO_2, enhancing thermodynamic efficiency up to more than 23%. The efficiency of the power cycle decreases with the reduction of the maximum pressure for most of the fluids, except for the mixture with pentane and hexane, however remaining higher than the sCO_2 cycle efficiency. Moreover, the lower the maximum pressure, the higher the efficiency improvement. In the case of mixing carbon dioxide with R1234yf, R1234ze(E), or propane, the reduction of CO_2 molar concentration allows better performance. On the other hand, the highest efficiency of the cycle mixing carbon dioxide with butane, hexane, and pentane is achieved with a CO_2 molar content of 70%, 80%, and 80%, respectively.

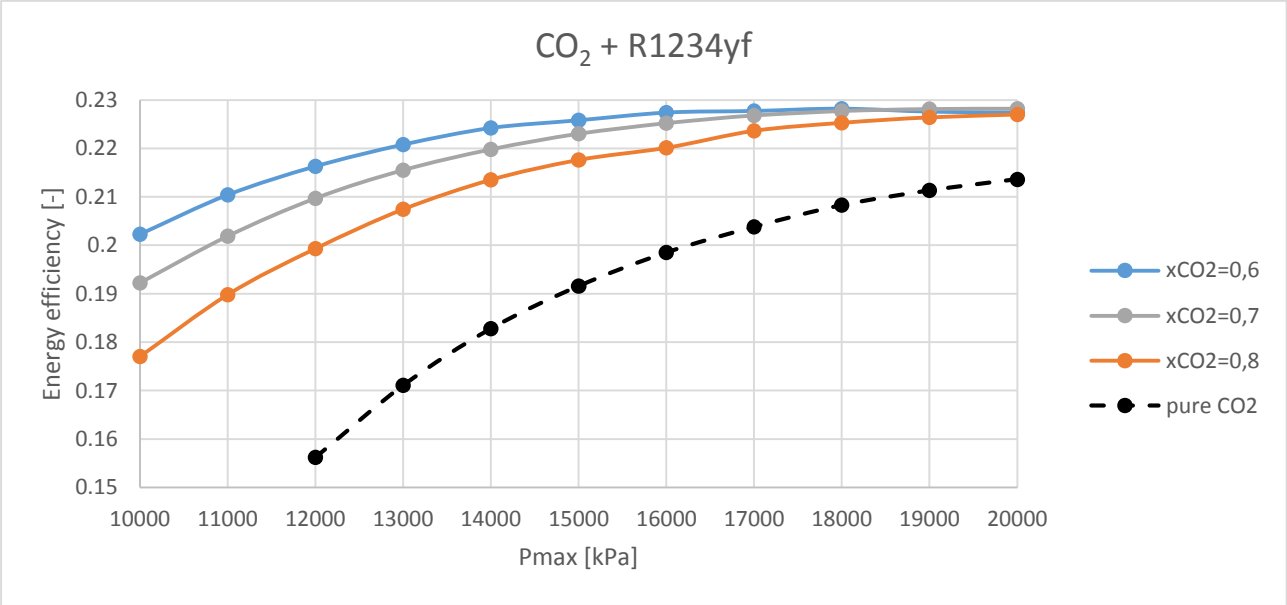

Figure 11 – Energy efficiency of the power cycle vs. maximum pressure of the cycle, at a variable molar concentration of CO_2 in the mixture, comparing pure sCO_2 and CO_2+R1234yf

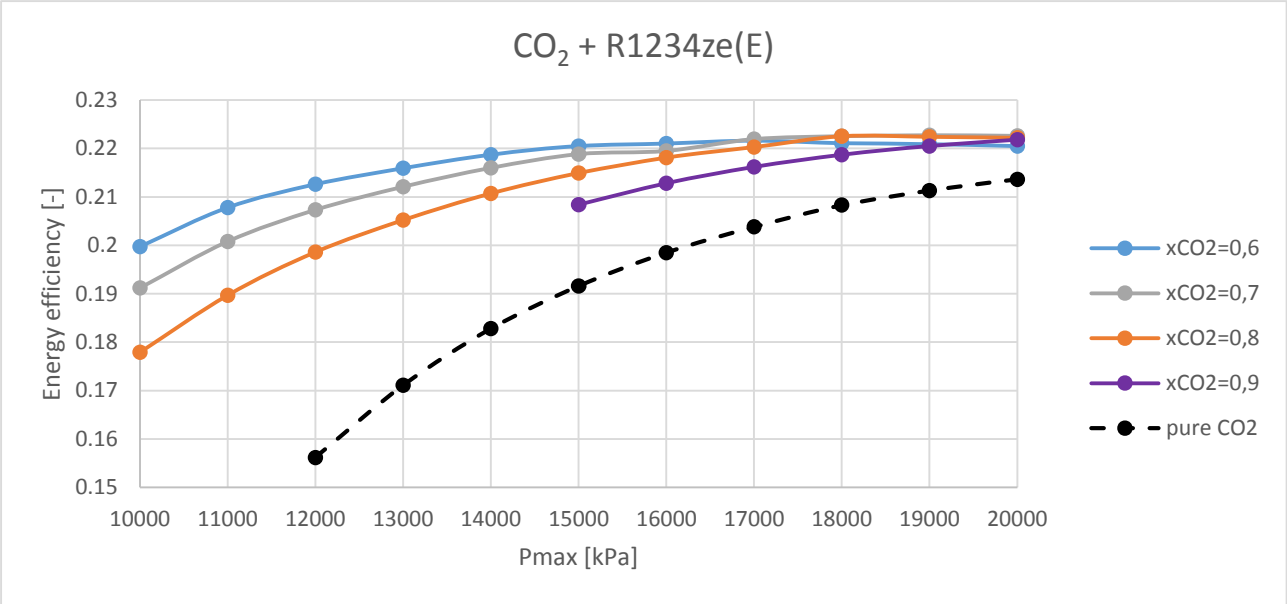

Figure 12 – Energy efficiency of the power cycle vs. maximum pressure of the cycle, at a variable CO_2 in the mixture, comparing pure sCO_2 and CO_2+R1234ze(E)

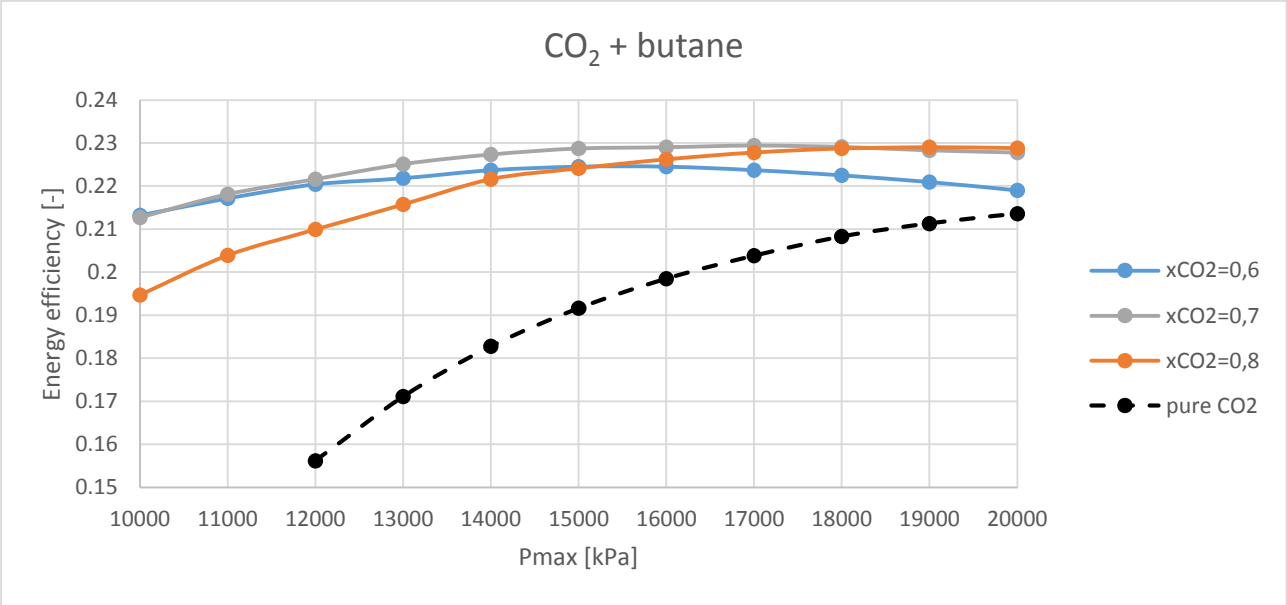

Figure 13 – Energy efficiency of the power cycle vs. maximum pressure of the cycle, at a variable molar concentration of CO_2, comparing pure sCO_2 and CO_2+butane

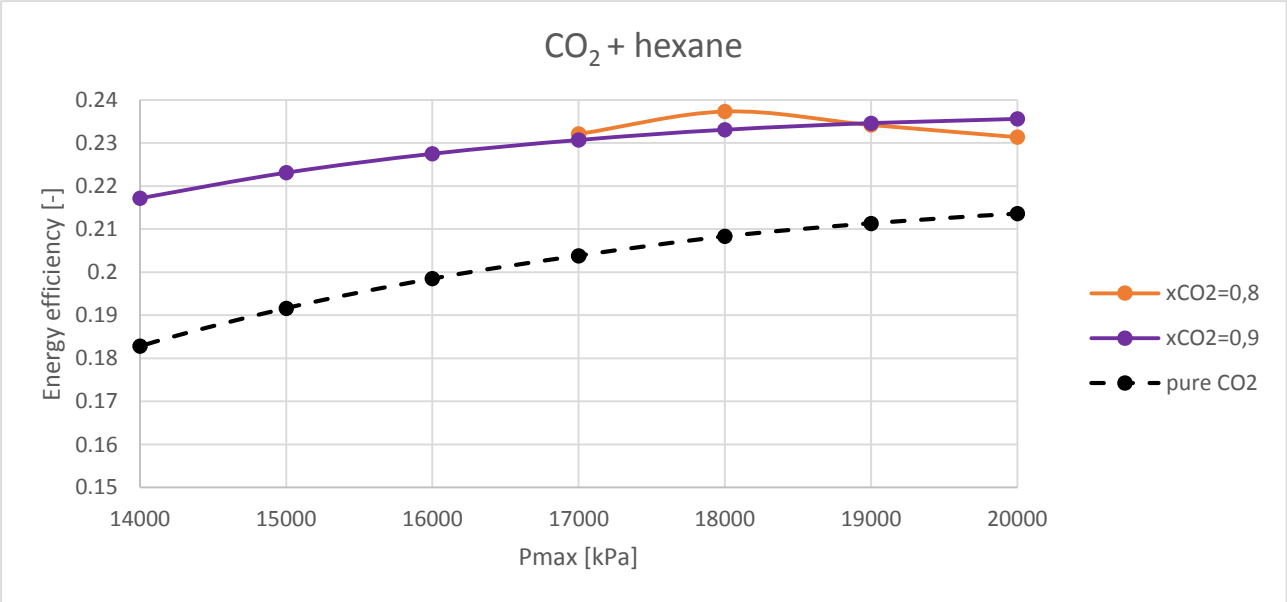

Figure 14 – Energy efficiency of the power cycle vs. maximum pressure of the cycle, at a variable molar concentration of CO_2 in the mixture, comparing pure sCO_2 and CO_2+hexane

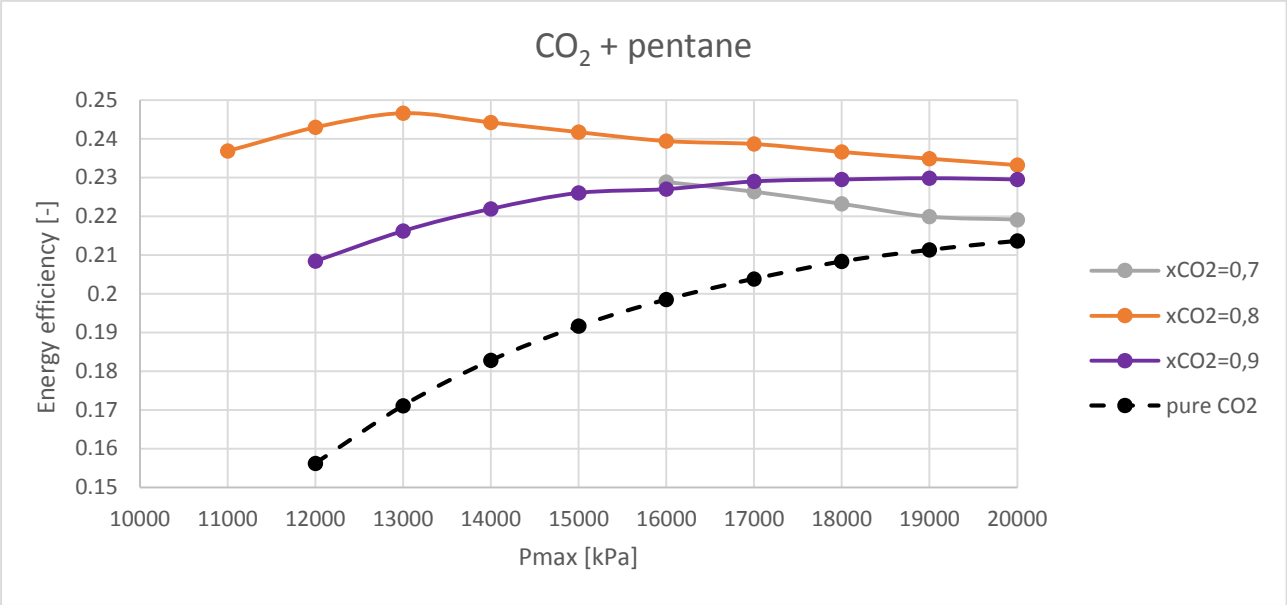

Figure 15 – Energy efficiency of the power cycle vs. maximum pressure of the cycle, at a variable molar concentration of CO_2 in the mixture, comparing pure sCO_2 and CO_2+pentane

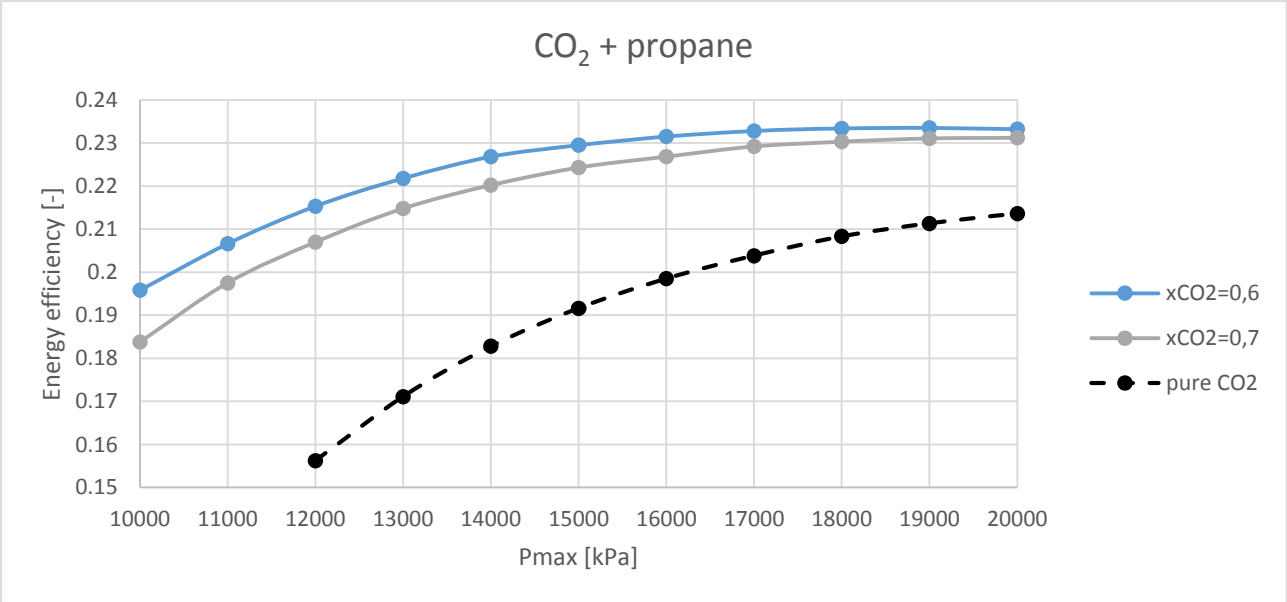

Figure 16 – Energy efficiency of the power cycle vs maximum pressure of the cycle, at a variable molar concentration of CO_2 in the mixture, comparing pure sCO_2 and CO_2+propane

As above discussed, the deviation of the EoS from the actual fluid physical properties also depends on the fluid state. In a power cycle, the fluid works under different conditions, involving several possible states across the components. The influence of the different EoS in pure CO_2 and CO_2-based mixtures when working in power cycles has been investigated. For this purpose, among the studied refrigerants and the hydrocarbons, two of the most promising and potential blends were

selected: CO_2(60%)-R1234yf(40%) and CO_2(80%)-pentane(20%), for which the relative main thermodynamic properties of the power cycle are collected in Table 10. The T-s diagrams of the related power cycles are shown in Figures 17 and 18: it is worth noting that the prediction of the dew and bubble curves, through the REFPROP saturation functions, is not complete near the critical point; however, it is sufficiently accurate to have effective, reliable representation of the power cycle. The outputs of some selected cycle parameters, obtained with REFPROP, were compared with those from UniSim simulations of the same power cycle. It allowed assessing the influence of the EoS on the results of each cycle key component and the overall performance (Figures 19-20-21).

Table 10 – Main parameters of CO_2-based mixtures power cycle.

		CO_2(60%)-R1234yf(40%)			CO_2(80%)-pentane(20%)		
Power cycle state points		T [°C]	P [kPa]	h [kJ/kg]	T [°C]	P [kPa]	h [kJ/kg]
3	Turbine inlet	230	14000	594,2	230	13000	659,2
4	Turbine Outlet	154,7	3863	540,6	168,4	5089	601,6
5	Condenser inlet	55,57	3863	399,6	50,44	5089	335,4
6	Condenser Outlet	30	3863	254,3	30	5089	195
7	Pump Outlet	40,17	14000	266	37,84	13000	206,8
8	Evaporator Inlet	116,6	14000	407	135,8	13000	473
Energy Efficiency			**22,4%**			**24,6%**	

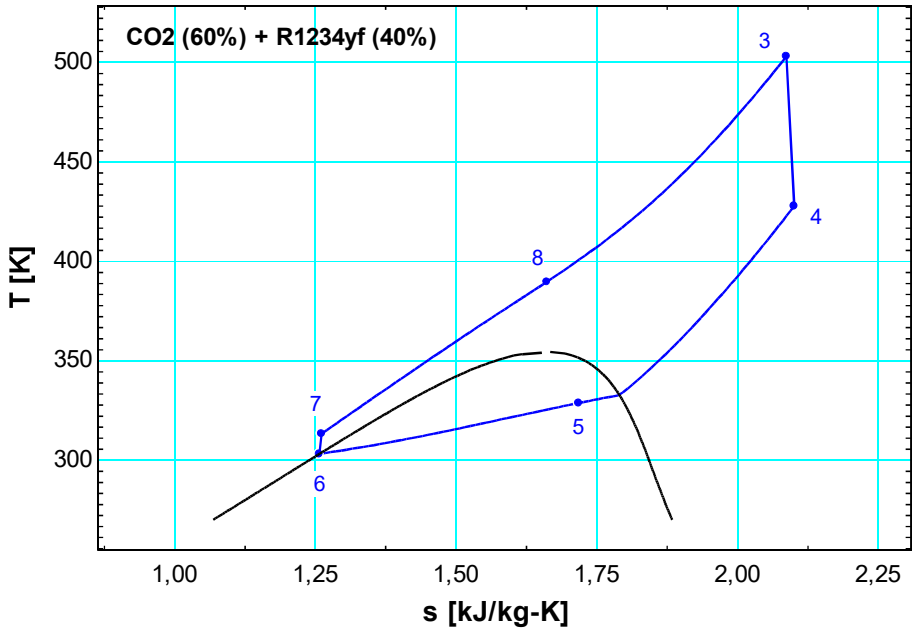

Figure 17 – T-s diagram of the recuperative Rankine power cycle simulated with CO_2(60%)-R1234yf(40%) as working fluid in EES environmental

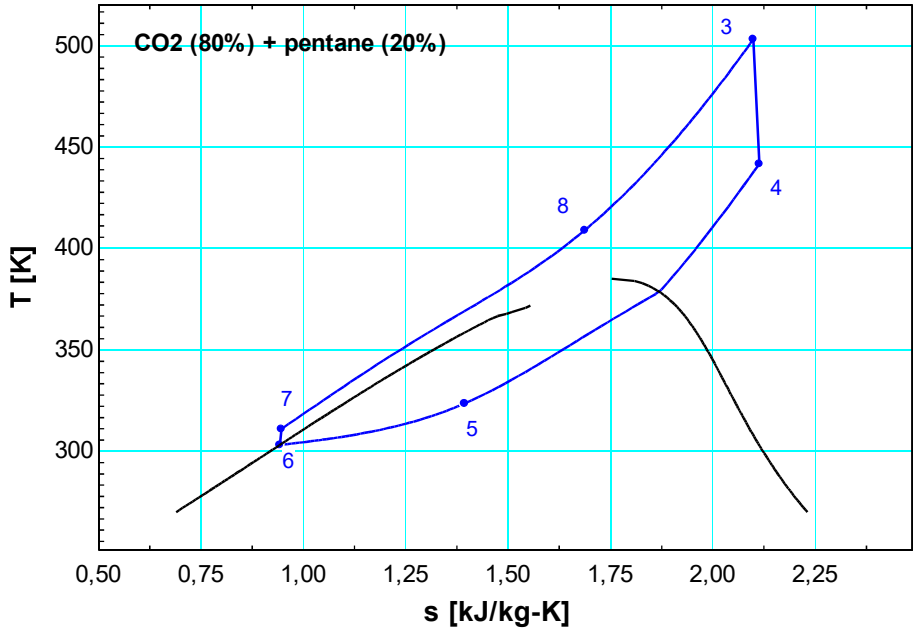

Figure 18 – T-s diagram of the recuperative Rankine power cycle simulated with CO_2(80%)-pentane(20%) as working fluid in EES environmental

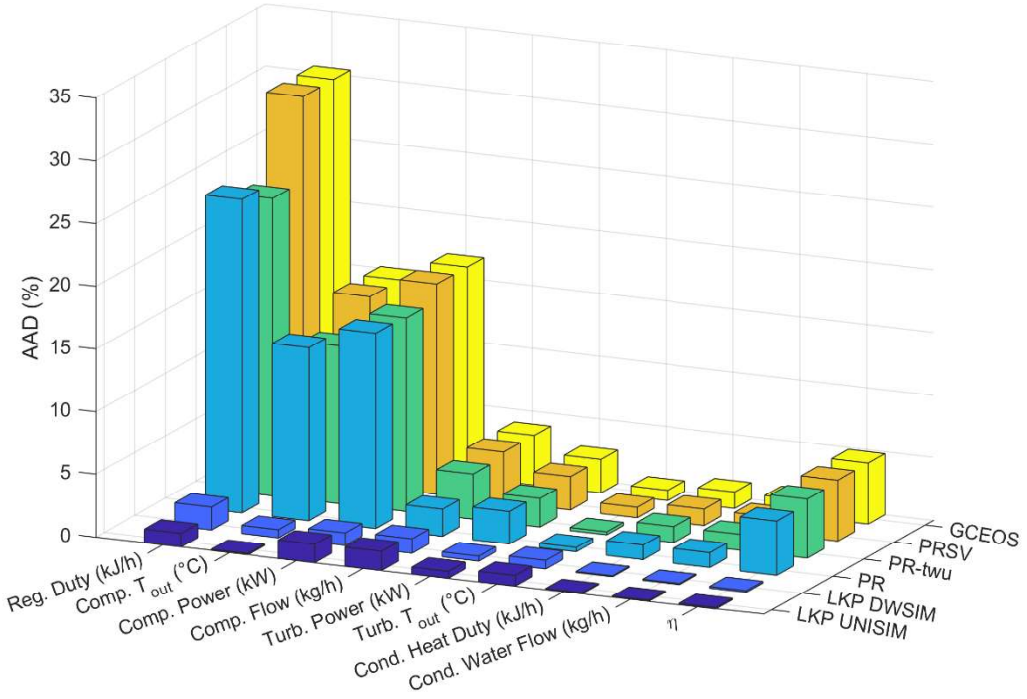

Figure 19 – Influence of the EoS on the AAD of each sCO_2 cycle key component

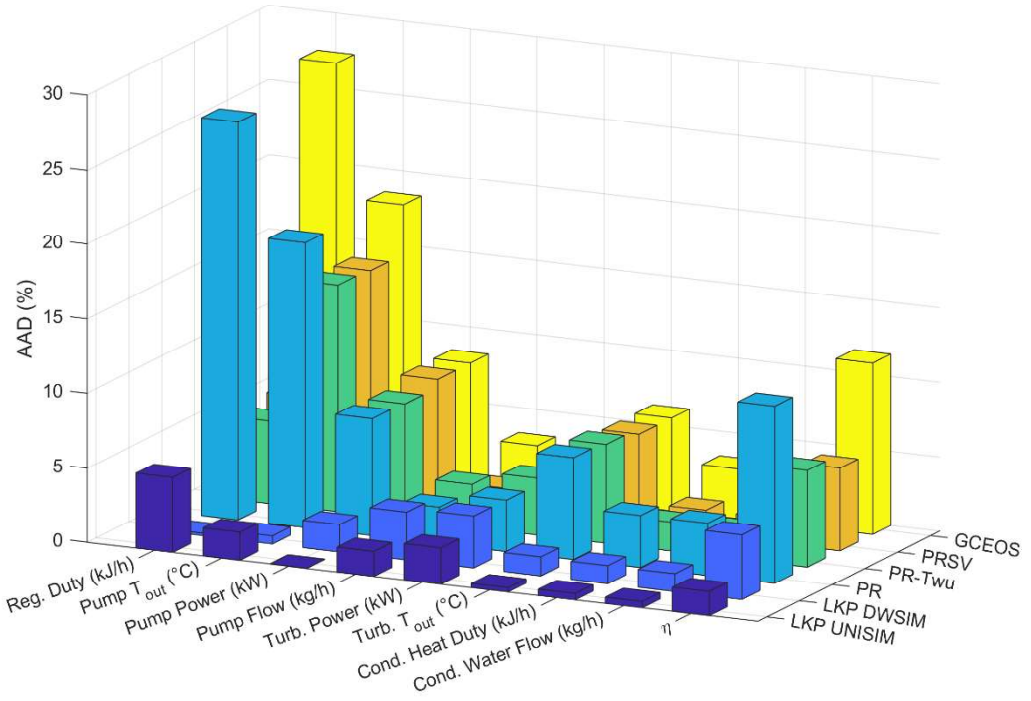

Figure 20 – Influence of the EoS on the AAD of each cycle key component with CO_2(60%)-R1234yf(40%) mixture as working fluid

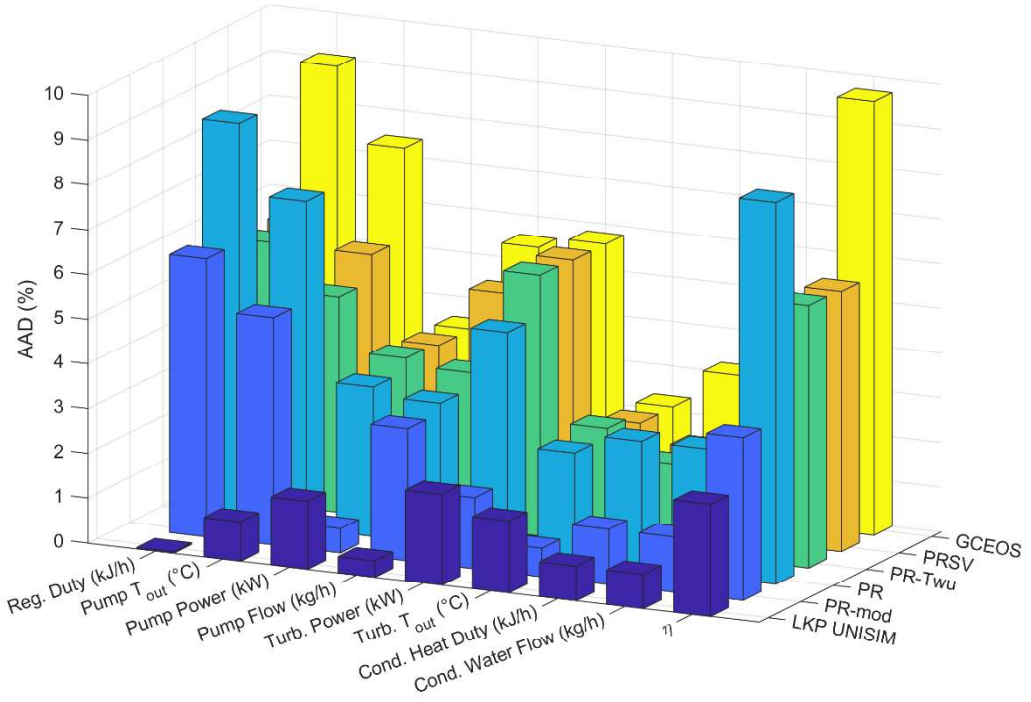

Figure 21 – Influence of the EoS on the AAD of each cycle key component with CO_2(80%)-pentane(20%) mixture as working fluid

The results summarized in Figures 19, 20, and 21 confirm the relevance of the current investigation, revealing the significant influence of the selected EoS in the analysis of power cycles working with sCO_2 and CO_2 based novel mixtures. Specifically, the higher reliability of LKP is confirmed, as well as the larger deviation achieved when using other EoS (particularly cubic PR and GCEOS), especially when working with mixtures. It effectively points out, in a quantitative manner, the importance of the selected EoS when dealing with these problems.

6. Conclusions

In the present study, most of the EoS available in the literature for calculating the properties of pure-CO_2 and CO_2-based mixtures under different thermodynamic conditions when working into sCO_2 cycles are discussed and compared, also with the support of available experimental data. Such a comparison is essential to assess the reliability of the EoS adopted for the simulation of the sCO_2 power cycle. It is even more important when dealing with power cycles working with CO_2-based mixtures, designed to better adapt the CO_2 properties to different possible heat source behaviour and/or to raise the critical temperature at suitable environmental levels to allow transcritical configurations. This kind of critical review and validation, especially for mixtures, is currently not retrievable in the literature of energy systems, where often the EoS available into the specifically used thermodynamic tools are adopted without a critical approach, sometimes resulting in questionable comparisons of different cycles configurations and working conditions.

The first significant outcome of the present research is that it is practically impossible addressing a specific EoS or an EoS-based database as the most reliable one. Moreover, based on the type of the fluid and the thermodynamic zone on the fluid phase envelope, the most suitable EoS family may be selected to improve the reliability of the results. On the whole, the following relevant conclusions may be outlined from this research:

I. REFPROP is a stand-alone program, generally based on the most advanced EoS often validated against available experimental literature data. It is accurate for single-component fluids, mentioned by several studies, and, in most cases, it is considered a benchmark for several, even new, approaches and EoS. However, it evidenced some limits on the temperature/pressure range and/or against experimental data of new CO_2-based mixtures. The accuracy may vary from the released version.
II. Other alternative EoS, built with specific mixing rules, may be adopted for common and novel CO_2-based mixtures (e.g. CO_2+R1234yf and CO_2+R1234ze(E)) under a wider range of conditions. Among the discussed EoS, the LKP showed to be the most reliable one for the property estimation of pure CO_2. If possible, the use of EoS available in DWSIM is recommended.
III. When dealing with CO_2-based mixtures, the results showed that the Lee-Kesler-Plocker equation, with BIP set at zero, is also reliable for mixtures of CO_2 and HFOs (e.g. R1234yf and R1234ze(E)). The suggested model for CO_2-hydrocarbons mixtures is not a single one, but it is determined as a table covering various fluids and mixture compositions [84]. Hence, as a relevant part of the conclusions, a summary table with our recommendations is reported hereafter:

Table 11 – EoS recommended for the analysed mixtures

Mixtures	LKP	PR	PR mod
CO_2 + R1234yf	$0.6 < xCO_2 < 1$		
CO_2 + R1234ze(E)	$0.6 < xCO_2 < 1$		
CO_2 + n-butane		$0.6 < xCO_2 < 1$	
CO_2 + n-hexane		$xCO_2 < 0.7$	$xCO_2 > 0.7$
CO_2 + n-pentane			$0.6 < xCO_2 < 1$
CO_2 + propane		$0.6 < xCO_2 < 1$	

IV. For both blends of refrigerants and hydrocarbons, a general increase of the mean absolute error with the increasing molar concentration of the second component was found. Therefore, the EoS-based approaches are generally more accurate at lower concentrations of the non-CO_2 component.

V. The thermodynamic results show that the CO_2-based mixtures, in a transcritical configuration, can achieve efficiencies higher than the sCO_2 power cycle. Generally, the lower the maximum pressure, the higher the efficiency improvement. In the case of mixing carbon dioxide with R1234yf, R1234ze(E), or propane, the reduction of CO_2 molar concentration drives better performance. On the other hand, the highest efficiency of the cycle mixing carbon dioxide with butane, hexane, and pentane is achieved with an intermediate CO_2 molar content. These considerations are summarized in Table 12.

Table 12 – CO_2 molar content for each mixture which leads to the best thermodynamic efficiencies

Mixture	Best CO_2 molar content
CO_2 + R1234yf	60%
CO_2 + R1234ze(E)	60%
CO_2 + n-butane	70%
CO_2 + n-hexane	80%
CO_2 + n-pentane	80%
CO_2 + propane	60%

VI. The reliability performance indicators, applied to various CO_2 mixtures and pure sCO_2 cycle processes, were estimated for several property methods (EoS) and compared to REFPROP. For example, when dealing with the recuperative sCO_2 cycle, the Recuperator Heat Duty was the most significantly affected parameter, and the results showed that LK-PLOCK performs most similarly to REFPROP under the analysed cycle conditions. Looking at the analyzed mixtures, for CO_2(60%)-R1234yf(40%), as widely expected, LKP confirms to be the most reliable EoS to predict the several states of the working fluid across the cycle components. For CO_2(80%)-pentane(20%) PR-mod demonstrates more suitability than PR and the other Cubic-equations of state. However, the Lee-Kesler-Plocker model seems to be the most accurate, especially close to the pump operating points thanks to the good prediction of mixtures' density (Figure 6); but, according to Figure 7 and Figure 8, it is reasonable to expect a worsening of the thermodynamic prediction with reducing the CO_2 molar content in the fluid.

Overall, the most relevant outcome of the present study is helping and addressing the property methods selection in the design and analysis of CO_2 and CO_2-based mixture power cycles, which is

a fundamental step to realize reliable simulation procedures of power cycles working with novel CO_2 mixtures. The here proposed accurate investigation is a valuable contribution to a current lack in the literature dealing with power cycles working with sCO_2 and CO_2 mixtures.

7. Appendix A

Based on the first law of thermodynamic, the main thermodynamic relations and the energy balance equations of the regenerated Rankine cycle, used for the simulations in EES environmental, are shown in the following section.

- **Turbine (3-4)**

Turbine inlet temperature: $T_3 = T_1 - \Delta T_{approach}$ **(Eq.A1)**

Turbine work: $W_t = m_{wf}(h_3 - h_4)$ **(Eq.A2)**

Isentropic turbine efficiency: $\eta_{t;is} = \frac{h_3 - h_4}{h_3 - h_{4;is}}$ **(Eq.A3)**

- **Recuperator (4-5 / 7-8)**

Recuperator energy balance: $Q_{REC} = m_{wf}(h_4 - h_5) = m_{wf}(h_8 - h_7)$ **(Eq.A4)**

- **Condenser (5-6 / 9-10)**

Condenser outlet temperature: $T_6 = T_{10} - \Delta T_{pinch\,point}$ **(Eq.A5)**

Condenser energy balance: $Q_{COND} = m_{water}(h_{10} - h_9) = m_{wf}(h_5 - h_6)$ **(Eq.A6)**

- **Pump (6-7)**

Pump work: $W_p = m_{wf}(h_7 - h_6)$ **(Eq.A7)**

Isentropic pump efficiency: $\eta_{p;is} = \frac{h_7 - h_6}{h_{7;is} - h_6}$ **(Eq.A8)**

- **Evaporator (8-3 / 1-2)**

Evaporator energy balance: $Q_{EVA} = m_{hot\,source}(h_1 - h_2) = m_{wf}(h_3 - h_8)$ **(Eq.A9)**

- **Cycle parameters**

Net power output: $W_{net} = W_t - W_p$ **(Eq.A10)**

Power cycle energy efficiency: $\eta_{cycle} = \frac{W_{net}}{Q_{EVA}}$ **(Eq.A11)**

8. Nomenclature

μ	Viscosity
AAD	Average Absolute Deviation
AlChE	American Institute of Chemical Engineers
BWRS	Benedict Webb Rubin Starling equation
COMP	Compressor
COND	Condenser
Cp	Specific heat capacity

EES	Engineering Equation Solver
EOS	Equation of State
GCEOS	Generalized Cubic Equation of State
h	Enthalpy
HC	Hydrocarbon
LFL	Low Flammability Level
LKP	Lee-Kesler-Plocker equation
LK-PLOCK	Lee-Kesler-Plocker property method
$m_{hot\ source}$	Hot source flow rate
m_{water}	Cooling water flow rate
m_{wf}	Working fluid flow rate
PR	Peng-Robinson equation
PR-BM	Peng-Robinson-Boston-Matias equation
PR-mod	Peng-Robinson modified
PRSV	Peng–Robinson–Stryjek–Vera equation
PR-twu	Peng-Robinson Twu alpha function equation
Q_{COND}	Condenser heat duty
Q_{EVA}	Evaporator heat duty
Q_{in}	Heat energy input entering the system
Q_{REC}	Recuperator heat duty
REFPROP	Reference Fluid thermodynamic and transport Properties
REG	Regenerator
RK-SOAVE	Redlich-Kwong equation
RMSE	Root Mean Square Error
S	Entropy
sCO_2	Supercritical CO_2
SRK	Redlich–Kwong–Soave equation
SRK-twu	Redlich–Kwong–Soave Twu alpha function equation
SW	Span-Wagner equation
T	Temperature
TURB	Turbine
W_{net}	Net power output
W_p	Work absorbed by the pump
W_t	Work produced by the turbine
xCO_2	Molar content of carbon dioxide
η	Energy Efficiency
ρ	Density

9. References

[1] S. A. Wright, R. F. Radel, T. M. Conboy and G. E. Rochau, Modeling and experimental results for condensing supercritical CO2 power cycles, Sandia Report, Jan., 2011.

[2] Zhang, H. Yamaguchi and D. Uneno, "Thermodynamic analysis of the CO2- based Rankine cycle powered by solar energy," *Int J Energy Res,* vol. 31 (14), p. 1414–24, 2007.

[3] M. Rezakazemi, M. Sadrzadeh and T. Matsuura, “Thermally stable polymers for advanced high-performance gas separation membranes,” *Progress in Energy and Combustion Science,* vol. 66, pp. 1-41, 2018.

[4] E. Sorousha, M. Mesbah, N. Hajilary and M. Rezakazemi, “ANFIS modeling for prediction of CO2 solubility in potassium and sodium based amino acid Salt solutions,” *Journal of Environmental Chemical Engineering,* vol. 7, p. 102925, 2019.

[5] K. Maczek, J. Muller, K. Wojtas and P. Domanski, “Ternary zeotropic mixture with CO2 component for R22 heat pump application,” *CLIMA 2000 Conference, Proceedings,* pp. 1-9, August 1997.

[6] S. Kim and M. Kim, “Experiment and simulation on the performance of an autocascade refrigeration system using carbon dioxide as a refrigerant,” *International Journal of Refrigeration,* vol. 25, p. 1093–1101, 2002.

[7] J. Sarkar and S. Bhattacharyya, “Assessment of blends of CO2 with butane and isobutane as working fluids for heat pump applications,” *International Journal of Thermal Sciences,* vol. 48, p. 1460–1465, 2009.

[8] J. Sarkar, S. Bhattacharyya and M. Ramgopal, “Optimization of a transcritical CO2 heat pump cycle for simultaneous cooling and heating applications,” *Int. J. Refrigeration,* vol. 27(8), pp. 830-838, 2004.

[9] S. Wright, T. Conboy, E. Parma, T. Lewis and A. Suo-Anttila, Summary of the Sandia Supercritical CO2 Development Program (No. SAND2011-3375C), Albuquerque, NM (United States): Sandia National Lab.(SNL-NM), 2011.

[10] T. Lewis, T. Conboy and S. Wright, “Supercritical CO2 mixture behavior for advanced power cycles and applications (No. SAND2011-2691C),” *Sandia National Lab.(SNL-NM), Albuquerque, NM (United States),* 24-25 May 2011.

[11] W. Jeong, J. Lee and Y. Jeong, “Potential improvements of supercritical recompression CO2 Brayton cycle by mixing other gases for power conversion system of a SFR,” *Nuclear Engineering and Design,* vol. 241(6), pp. 2128-2137, 2011.

[12] T. Conboy, S. Wright, D. Ames and T. Lewis, CO2-Based Mixtures as Working Fluids for Geothermal Turbines, Albuquerque, New Mexico, 2012, p. 87185.

[13] W. Jeong and Y. Jeong, “Performance of supercritical Brayton cycle using CO2-based binary mixture at varying critical points for SFR applications,” *Nuclear Engineering and Design,* vol. 262, pp. 12-20, 2013.

[14] H. Yin, A. Sabau, J. Conklin, J. McFarlane and A. Qualls, “Mixtures of SF6–CO2 as working fluids for geothermal power plants,” *Applied energy,* vol. 106, pp. 243-253, 2013.

[15] V. Chou, D. Keairns, M. Turner, M. Woods and A. Zoelle, Quality guidelines for energy system studies: process modeling design parameters, (National Energy Technology Laboratory) NETL. DOE-341/051314, 2014, p. 13–21..

[16] A. Hakkaki-Fard, Z. Aidoun and M. Ouzzane, “Applying refrigerant mixtures with thermal glide in cold climate air-source heat pumps,” *Applied thermal engineering,* vol. 62(2), pp. 714-722, 2014.

[17] A. Hakkaki-Fard, Z. Aidoun and M. Ouzzane, “Improving cold climate air-source heat pump performance with refrigerant mixtures,” *Applied Thermal Engineering,* vol. 78, pp. 695-703, 2015.

[18] L. Hu, D. Chen, Y. Huang, L. Li, Y. Cao, D. Yuan, J. Wang and L. Pan, “Investigation on the performance of the supercritical Brayton cycle with CO2-based binary mixture as working fluid for an energy transportation system of a nuclear reactor,” *Energy,* vol. 89, pp. 874-886, 2015.

[19] M. Mecheri and Y. Le Moullec, “Supercritical CO2 Brayton cycles for coal-fired power plants,” *Energy,* vol. 103, pp. 758-771, 2016.

[20] N. Weiland, W. Shelton, C. White and D. Gray, “Performance baseline for direct-fired sCO2 cycles,” *Fifth International Supercritical CO2 Power Cycles Symposium, San Antonio, TX, Mar,* pp. 29-31, March 2016.

[21] L. Vesely, V. Dostal and J. Stepanek, “Effect of gaseous admixtures on cycles with supercritical carbon dioxide. In Turbo Expo: Power for Land, Sea, and Air,” *American Society of Mechanical Engineers,* vol. 49873, p. V009T36A016, June 2016.

[22] K. Manikantachari, S. Martin, J. Bobren-Diaz and S. Vasu, “Thermal and transport Properties for the simulation of Direct-Fired sCO2 Combustor,” *Journal of Engineering for Gas Turbines and Power,* vol. 139(12), 2017.

[23] Y. Ma, M. Liu, J. Yan and J. Liu, “Performance investigation of a novel closed Brayton cycle using supercritical CO2-based mixture as working fluid integrated with a LiBr absorption chiller,” *Applied Thermal Engineering,* vol. 141, pp. 531-547, 2018.

[24] S. Baik and J. Lee, “Preliminary study of supercritical CO2 mixed with gases for power cycle in warm environments,” *American Society of Mechanical Engineers., Turbo Expo: Power for Land, Sea, and Air,* vol. 51180, p. V009T38A017, June 2018.

[25] C. White and N. Weiland, “Evaluation of property methods for modeling direct-supercritical CO2 power cycles.,” *Journal of Engineering for Gas Turbines and Power,* vol. 140(1), 2018.

[26] J. Guo, M. Li, J. Xu, J. Yan and K. Wang, “Thermodynamic performance analysis of different supercritical Brayton cycles using CO2-based binary mixtures in the molten salt solar power tower systems,” *Energy,* vol. 173, pp. 785-798, 2019.

[27] L. Vesely, K. Manikantachari, S. Vasu, J. Kapat, V. Dostal and S. Martin, “Effect of impurities on compressor and cooler in supercritical CO2 cycles,” *Journal of Energy Resources Technology,* vol. 141(1)., 2019.

[28] R. Span, T. Eckermann, S. Herrig, S. Hielscher, A. Jager and M. Thol, TREND: Thermodynamic Reference and Engineering Data 2.0, Bochum, Germany: RuhrUniversitaet Bochum, 2015.

[29] X. Liu, Z. Xu, Y. Xie and H. Yang, “CO2-based mixture working fluids used for the dry-cooling supercritical Brayton cycle: Thermodynamic evaluation,” *Applied Thermal Engineering,* vol. 162, p. 114226, 2019.

[30] G. Manzolini, C. Invernizzi, P. Iora and D. Bonalumi, “CO2 mixtures as innovative working fluid in power cycles applied to solar plants. Techno-economic assessment,” *Solar Energy,* vol. 181(15), pp. 530-544, 2019.

[31] A. Yu, W. Su, L. Zhao, X. Lin and N. Zhou, “New Knowledge on the Performance of Supercritical Brayton Cycle with CO2-Based Mixtures,” *Energies,* vol. 13(7), p. 1741, 2020.

[32] S. Barak, O. Pryor, E. Ninnemann, S. Neupane, S. Vasu, X. Lu and B. Forrest, “Ignition Delay Times of Oxy-Syngas and Oxy-Methane in Supercritical CO2 Mixtures for Direct-Fired Cycles,” *Journal of Engineering for Gas Turbines and Power,* vol. 142(2), 2020.

[33] P. Saengsikhiao, J. Taweekun, K. Maliwan, S. Sae-ung and T. Theppaya, “Investigation and Analysis of R463A as an Alternative Refrigerant to R404A with Lower Global Warming Potential,” *Energies,* vol. 13(6), p. 1514, 2020.

[34] R. Brignoli, J. S. Brown, H. M. Skye and P. A. Domanski, “Refrigerant performance evaluation including effects of transport properties and optimized heat exchangers,” *International Journal of Refrigeration,* vol. 80, pp. 52-65, 2017.

[35] D. Bonalumi, S. Lasala and E. Macchi, “CO2-TiCl4 working fluid for high-temperature heat source power cycles and solar application,” *Renewable Energy,* vol. 147(3), pp. 2842-2854, 2020.

[36] E. Lemmon, I. Bell, M. Huber and M. McLinden, NIST Standard Reference Database 23: Reference Fluid Thermodynamic and Transport Properties-REFPROP, Version 10.0, Gaithersburg: National Institute of Standards and Technology, Standard Reference Data Program, 2018.

[37] R. Span and W. Wagner, “A New Equation of State for Carbon Dioxide Covering the Fluid Region from the Triple-Point Temperature to 1100 K at Pressures up to 800 MPa,” *Journal of Physical and Chemical Reference Data,* 1996.

[38] I. Bell, J. Wroski and S. Quolin, “Pure and Pseudo-pure Fluid Thermophysical Property Evaluation and the Open-Source Thermophysical Property Library CoolProp,” *Ind. Eng. Chem. Res.,* vol. 53, p. 2498–2508, 2014.

[39] S. b. A. Design Institute for Physical Properties, DIPPR Project 801 - Full Version, Design Institute for Physical Property Research/AIChE, 2015.

[40] D. Peng and D. Robinson, “A New Two-Constant Equation of State,” *Ind. Eng. Chem. Fundamen,* vol. 15(1), pp. 59-64, 1976.

[41] C. Twu, E. Coon, R. Cunningham and D. Bluck, “A cubic equation of state with a new alpha function and a new mixing rule,” *Fluid Phase Equilibria,* vol. 69, pp. 33-50, 1991.

[42] P. Boston and P. Mathias, *Proceedings of the 2nd International Conference on Phase Equilibria and Fluid Properties in the Chemical Process Industries,* pp. 823-849, 1980.

[43] O. Redlich and J. Kwong, “On the Thermodynamics of Solutions. V. An Equation of State. Fugacities of Gaseous Solutions,” *Chemical Reviews,* vol. 44, pp. 233-244, 1949.

[44] G. Soave, “Equilibrium constants from a modified Redlich-Kwong equation of state,” *Chemical Engineering Science,* vol. 27, p. 1197–1203, 1972.

[45] M. Benedict, G. B. Webb and L. C. Rubin, “An Empirical Equation for Thermodynamic Properties of Light Hydrocarbons and Their Mixtures: I. Methane, Ethane, Propane, and n-Butane,” *Journal of Chemical Physics,* vol. 8(4), pp. 334-345, 1940.

[46] B. Lee and G. Kesler, “A generalized thermodynamic correlation based on three-parameter corresponding states,” *AlChe Journal,* vol. 21, pp. 510-527, 1975.

[47] H. I. Inc., “UniSim® design, operations guide, R460 release,” Switzerland, 2017.

[48] P. H Niknam, L. Talluri, D. Fiaschi and G. Manfrida, “Improved Solubility Model for Pure Gas and Binary Mixture of CO2-H2S in Water: A Geothermal Case Study with Total Reinjection,” *Energies,* vol. 13(11), p. 2883, 2020.

[49] D. Medeiros, “DWSIM V6.0– Open Source Process Simulator,” [Online]. Available: http://sourceforge.net/projects/dwsim. [Accessed April 2020].

[50] A. T. Inc, “Aspen HYSYS®,” April 2020. [Online]. Available: https://www.aspentech.com/en/products/engineering/aspen-hysys.

[51] Kennedy, “Pressure-volume-temperature relations in CO2 at ELEVATED temperature and pressure,” *American Journal of Science,* vol. 252, pp. 225-2411, 1954.

[52] J. J. Langenfeld, S. B. Hawthorne and D. Miller, “Method for Determining the Density of Pure and Modified Supercritical Fluids,” *Anal. Chem.,* vol. 64, pp. 2263-2266, 1992.

[53] Z. Knez, M. Skerget, P. Senéar-Boáié and A. Riiner, “Solubility of Nifedipine and Nitrendipine in Supercritical CO2,” *J. Chem. Eng.,* vol. 40, p. 216—220, 1995.

[54] A. Fenghour, “Amount-of-substance density of CO2 at temperatures from 329 K to 698 K and pressures up to 34 MPa,” *The Journal of Chemical Thermodynamics,* vol. 27, pp. 219-223, 1995.

[55] J. C. Seitz, “Volumetric properties for {(1 –x)CO2+xCH4},{(1 −x)CO2+xN2}, and {(1 −x)CH4+xN2} at the preessures (19.94, 29.94, 39.94, 59.93, 79.93, and 99.93) MPa and the temperature 673.15 K,” *The Journal of Chemical Thermodynamics,* vol. 28, pp. 1207-1213, 1996.

[56] H. Pöhler and E. Kiran, “Volumetric Properties of Carbon Dioxide + Toluene at High Pressures,” *J. Chem. Eng. ,* vol. 41, p. 482–486, 1996.

[57] P. v. d. Gulik, “Viscosity of carbon dioxide in the liquid phase,” *Physica A: Statistical Mechanics and its Applications,* vol. 238, pp. 81-112, 1997.

[58] T. Tsuji, S. Honda, T. Hiaki and M. Hongo, “Measurement of the P–V–T relationship for carbon dioxide+n-butane and carbon dioxide+i-butane in the vicinity of the critical point,” *The Journal of Supercritical Fluids,* vol. 13, pp. 15-21, 1998.

[59] A. Ferri, “An experimental technique for measuring high solubilities of dyes in supercritical carbon dioxide,” *The Journal of Supercritical Fluids,* vol. 30, pp. 41-49, 2004.

[60] A. Garmroodi, J. Hassan and Y. Yamini, “Solubilities of the Drugs Benzocaine, Metronidazole Benzoate, and Naproxen in Supercritical Carbon Dioxide,” *J. Chem. Eng. ,* vol. 49, p. 709–712, 2004.

[61] M. Škerget, “Influence of the aromatic ring substituents on phase equilibria of vanillins in binary systems with CO2,” *Fluid Phase Equilibria,* vol. 231, pp. 11-19, 2005.

[62] Doleček, D. Pečar and Valter, “Densities of β-Carotene−Supercritical Carbon Dioxide Mixtures,” *J. Chem. Eng.,* vol. 52, p. 2442–2445, 2007.

[63] K. L. Kiran and Erdogan, “Viscosity, Density and Excess Volume of Acetone + Carbon Dioxide Mixtures at High Pressures,” *Ind. Eng. Chem.,* vol. 46, p. 5453–5462, 2007.

[64] A. Pensado, “Viscosity and density measurements for carbon dioxide + pentaerythritol ester lubricant mixtures at low lubricant concentration,” *The Journal of Supercritical Fluids,* vol. 44, pp. 172-185, 2008.

[65] I. D. Mantilla and D. E. Cristancho, “P-ρ-T Data for Carbon Dioxide from (310 to 450) K up to 160 MPa,” *J. Chem. Eng. ,* vol. 55, p. 4611–4613, 2010.

[66] L. Gil, J. Martínez-López and M. Artal, “Volumetric Behavior of the {CO2 (1) + C2H6 (2)} System in the Subcritical (T = 293.15 K), Critical, and Supercritical (T = 308.15 K) Regions,” *J. Phys. Chem.,* vol. 114, p. 5447–5469, 2010.

[67] D. Kodama, “Volumetric behavior of carbon dioxide + 2-methyl-1-propanol and carbon dioxide + 2-methyl-2-propanol mixtures at 313.15 K,” *Fluid Phase Equilibria,* vol. 357, pp. 57-63, 2013.

[68] Lowell, “Thermal Properties of Carbon Dioxide in the Critical Region,” *JOURNAL OF CHEMICAL AND ENGINEERING DATA,* 1960.

[69] L. Dordain and E. Lemmon, “Isobaric heat capacities of carbon dioxide and argon between 323 and 423 K and at pressures up to 25 MPa,” *The Journal of Supercritical Fluids,* vol. 8, pp. 228-235, 1995.

[70] M. P. Ishmael, “Isobaric heat capacity (Cp) measurements of supercritical fluids using flow calorimetry: equipment design and experimental validation with carbon dioxide, methanol, and carbon dioxide-methanol mixtures,” *The Journal of Supercritical Fluids,* vol. 117, pp. 72-79, 2016.

[71] H. A. T. &. T. K. Nishiumi, “Generalization of the binary interaction parameter of the Peng-Robinson equation of state by component family,” *Fluid Phase Equilibria,* vol. 42, pp. 43-62, 1988.

[72] F-Chart Software, [Online]. Available: http://www.fchart.com/ees/pro-comm-versions.php.

[73] N. Juntarachat, “Experimental measurements and correlation of vapor–liquid equilibrium and critical data for the CO2 + R1234yf and CO2 + R1234ze(E) binary mixtures,” *International Journal of Refrigeration,* vol. 47, pp. 141-152, 2014.

[74] G. Di Nicola, “PVTx Measurements of the Carbon Dioxide + 2,3,3,3-Tetrafluoroprop-1-ene Binary System,” *J. Chem. Eng. Data,* vol. 57, p. 450–455, 2012.

[75] S. K. Shlbata, “High-Pressure Vapor-Liquid Equilibria Involving Mixtures of Nitrogen, Carbon Dioxide, and -Butane,” *J. Chem. Eng. Data,* vol. 24, pp. 291-298, 1989.

[76] Y.-H. Li, “Vapor-Liquid Phase Equilibrium for Carbon Dioxide-n-Hexane at 40,80, and 120 °C,” *J. Chem. Eng. Data,* vol. 26, pp. 53-55, 1981.

[77] H. Cheng, “Vapor-Liquid Equilibrium in the System Carbon Dioxide + n-Pentane from 252 to 458 K at Pressures to 10 MPa,” *J. Chem. Eng. Data,* vol. 34, pp. 319-323, 1989.

[78] J. H. Kim, “Vapor–liquid equilibria for the carbon dioxide + propane system over a temperature range from 253.15 to 323.15 K,” *Fluid Phase Equilibria,* vol. 238, pp. 13-19, 2005.

[79] J. C. Acosta, “Dew and Bubble Point Measurements for Carbon Dioxide-Propane Mixtures,” *J. Chem. Eng. Data,* vol. 29, pp. 304-309, 1984.

[80] M. Mazzoccoli, B. Bosio and E. Arato, “Analysis and comparison of Equations-of-State with p-ρ-T experimental data for CO2 and CO2-mixture pipeline transport,” *Energy Procedia,* vol. 23, pp. 274-283, 2012.

[81] S. Quiñones-Cisneros, C. Zéberg-Mikkelsen and E. H. Stenby, “The friction theory (f-theory) for viscosity modeling,” *Fluid Phase Equilibria,* vol. 169(2), pp. 249-276, 2000.

[82] A. Laesecke and C. D. Muzny, “Reference Correlation for the Viscosity of Carbon Dioxide,” *J Phys Chem Ref Data,* 2018.

[83] K. Liu and E. Kiran, “Viscosity, Density and Excess Volume of Acetone + Carbon Dioxide Mixtures at High Pressures,” *Ind. Eng. Chem.,* vol. 47, 2007.

[84] Y. FU, “Density data for carbon dioxide (CO2) +trans-1,3,3,3-tetrafluoroprop-1-ene (R-1234ze(E)) mixture at temperatures from 283.32 to 353.02K and pressures up to 10 MPa,” *International Journal of Refrigeration,* 2020.

[85] H. I. Inc., “UniSim® design, Simulation Basis, R480 release,” Switzerland, 2020.

[86] K. Shigeo, T. Kenji, T. Akifumi and T. Kazuaki, “Extended Le Chatelier's formula for carbon dioxide dilution effect on flammability limits,” *Journal of Hazardous Materials,* vol. 138, pp. 1-8, 2006.

[87] *AS/NZS ISO 817:2016.*