



New Knowledge on the Performance of Supercritical Brayton Cycle with CO₂-Based Mixtures

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Abstract: As one of the promising technologies to meet the increasing demand for electricity, supercritical CO₂ (S-CO₂) Brayton cycle has the characteristics of high efficiency, economic structure, and compact turbomachinery. These characteristics are closely related to the thermodynamic properties of working fluid. When CO_2 is mixed with other gas, cycle parameters are determined by the constituent and the mass fraction of CO₂. Therefore, in this contribution, a thermodynamic model is developed and validated for the recompression cycle. Seven types of CO₂-based mixtures, namely CO₂-Xe, CO₂-Kr, CO₂-O₂, CO₂-Ar, CO₂-Ne, CO₂-Ne, and CO₂-He, are employed. At different CO₂ mass fractions, cycle parameters are determined under a fixed compressor inlet temperature, based on the maximization of cycle efficiency. Cycle performance and recuperators' parameters are comprehensively compared for different CO₂-based mixtures. Furthermore, in order to investigate the effect of compressor inlet temperature, cycle parameters of CO₂-N₂ are obtained under four different temperatures. From the obtained results, it can be concluded that, as the mass fraction of CO₂ increases, different mixtures show different variations of cycle performance and recuperators' parameters. In generally, the performance order of mixtures coincides with the descending or ascending order of corresponding critical temperatures. Performance curves of these considered mixtures locate between the curves of CO₂-Xe and CO₂-He. Meanwhile, the curves of CO₂-O₂ and CO_2 -N₂ are always closed to each other at high CO_2 mass fractions. In addition, with the increase of compressor inlet temperature, cycle performance decreases, and more heat transfer occurs in the recuperators.

Keywords: supercritical Brayton cycle; CO₂-based mixture; thermodynamic performance; compressor inlet temperature

1. Introduction

1.1. Background

According to the BP (British Petroleum) Statistical Review of World Energy 2019, global energy demand grew by 2.9% and carbon emissions grew by 2.0% in 2018. With energy demand and carbon emissions growing at their fastest rate for years, there is a growing mismatch between societal demands for action on climate change and the actual pace of progress [1]. Therefore, the need to develop renewable energy and improve the energy conversion efficiency is urgent. As one of the most promising candidates that can potentially replace the steam Rankine cycle, the supercritical

 CO_2 (S- CO_2) power cycle has the advantage of high efficiency, economic structure, and compact turbomachinery. This is because CO_2 has the low critical temperature (T_{c0} = 304.13 K) and moderate pressure (P_{c0} = 7.38 MPa), so that the compressor work can be greatly reduced when operating around the critical point. Furthermore, due to the fact that the inert gas S- CO_2 is compatible with structural materials, the S- CO_2 cycle has the potential to achieve a higher turbine inlet temperature [2]. Today, the S- CO_2 cycle has been widely applied in various energy sources, such as nuclear energy, solar energy, geothermal energy, and waste heat utilization [3–7]. Much effort has been paid to conduct the theoretical modeling on the thermodynamic processes and the performance comparison of different cycle layouts based on the property characteristics of S- CO_2 [8,9].

1.2. Cycle Layouts and Performance Comparison

In order to improve the cycle efficiency and alleviate the temperature mismatch in the heat exchanger, many advanced S-CO₂ cycle layouts such as simple recuperation cycle, recompression cycle and partial cooling cycle have been proposed, based on the original configuration of Brayton cycle [10]. For the recuperation cycle, a recuperator is introduced to recover the exhaust heat of S-CO₂ at the low-pressure side. Although the recuperation cycle can improve the efficiency greatly, it still suffers the temperature pinch-point problem in the recuperator, which is caused by the huge difference in the heat capacity between the hot and cold sides of the recuperator. Thus, the recompression cycle divides the recuperator into the high-temperature recuperator (HTR) and the low-temperature recuperator (LTR) and reduces the difference of heat capacity in LTR by splitting the flow stream of S-CO₂ at the inlet of gas-cooler [11]. For the partial cooling cycle, it is generally derived from the recompression cycle. The flow stream is usually split after the pre-cooler [12]. In addition, thermodynamic processes such as the reheating and the intermediate cooling can also be used to improve the efficiency of existing cycles further [10]. For these cycle layouts, a detailed description has been given in the literature [13].

Performance of different cycle layouts has been comprehensively compared by researchers. For instance, Turchi et al. [14] explored the thermodynamic performance of different S-CO₂ cycle layouts from the perspective of a concentrating solar power application. The results indicated that under dry cooling, cycle efficiency 50% could be obtained by partial-cooling S-CO₂ Brayton cycle with reheating and intercooling S-CO₂ Brayton cycle with reheating. Zhu et al. [15] developed a mathematical model to conduct the thermodynamic analysis and comparison for different direct-heated S-CO₂ Brayton cycles integrated into a solar power tower system. It was found that the intercooling S-CO₂ cycle achieved the highest overall efficiency, followed by the recompression, the partial-cooling, the pre-compression, and the simple cycles at different turbine inlet temperatures. Thereafter, Wang et al. [9] simultaneously compared the efficiency and specific work for different S-CO₂ cycle layouts by obtaining the Pareto optimal fronts of multi-objective optimizations. The results suggested that the inter-cooling cycle layout and the partial-cooling cycle layout can generally yield the most excellent performances, followed by the recompression cycle layout and the precompression cycle layout. As for the application in nuclear energy, Moisseytsev and Sienicki [16] studied the performance of alternative S-CO₂ cycle layouts for a sodium-cooled fast reactor (SFR). It has been confirmed that slight gains in efficiency (0.3%) of recompression cycle could be achieved by increasing the pressure to 22 MPa. Kulhanek and Dostal [17] compared thermal efficiency of precompression cycle, simple Brayton cycle and partial cooling cycle in nuclear reactors. It was found that the precompression cycle could achieve equivalent efficiency as the recompression cycle when turbine inlet temperature was above 700 °C.

1.3. Current Status of CO²-Based Mixtures

Besides the structures of S-CO₂ power cycle, another way to improve the cycle performance is to use the CO₂-based mixture as working fluid. This is because mixing with other gases can adjust the critical point of CO₂, so as to change the lowest operation condition of the Brayton cycle. The direction and range of the critical point variation of CO₂ depend on the mixed component and its amount. So far, a few studies have been conducted to discuss the feasibility and performance of the supercritical CO₂-based mixture power cycle. For example, Sandia National Laboratories performed experimental tests on the compatibility of CO_2 mixtures with the turbomachinery and the compressor operation in the supercritical region of mixtures [18]. Jeong et al. [19,20] developed a supercritical cycle model, based on the mixture properties. They investigated the performance of a supercritical CO₂-based mixture cycle, which was applied to the power conversion of sodium cold fast reactor. It was found that the mixtures of CO_2 -He, CO_2 -Xe, and CO_2 -Kr had an increase in the total cycle efficiency, when the inlet temperature of main compressor is 1 K above the critical temperature of mixtures. Thereafter, Hu et al. [21] analyzed the performance of a nuclear reactor integrated with the CO₂-based mixture cycle. The obtained results indicated that the adoption of CO₂-He and CO₂-Kr could increase the cycle efficiency and decrease the amounts of heat transfer in the HTR and LTR. In order to reduce the air-cooled waste heat removal difficulty, Baik and Lee [22] compared the simple cycle performance of CO₂-SF₆, CO₂-R123, CO₂-R134a, CO₂-R32, and CO₂- toluene under the minimum temperature 304.15–313.15 K and the maximum temperature 573.15 K. It was concluded that CO₂-R32 and CO₂-Toluene could potentially reduce the efficiency degradation of pure S-CO₂ power cycles at higher heat sink temperatures. Recently, Guo et al. [23] also analyzed the thermodynamic performance of four different Brayton cycles using CO₂ mixtures in the molten salt solar power tower systems. The used mixtures were CO_2 -Xe (0.7/0.3) and CO_2 -butane (0.95/0.05). The results indicated that adding xenon into S-CO₂ cycle could obviously improve the overall thermal efficiency and exergy efficiency, while the effects of butane as an additive were converse. On the other hand, in engineering application of Brayton cycle, S-CO₂ will be inevitably mixed with the gas impurities. Therefore, Vesely et al. [24] investigated the effect of gaseous admixtures on the cycle efficiency at a fixed inlet temperature of main compressor. They found that all researched mixtures except CO₂-H₂S had negative effects on the cycle efficiency and net power output. Thereafter, they examined the effect of different impurity compositions on the performance of various cycle components at different inlet temperatures of main compressor [25]. The above studies on the Brayton cycle with CO₂-based mixtures are summarized in Table 1.

Authors	Year	Mixtures	<i>T_c</i> /Mole Fraction	Inlet Temperature of Compressor	Performance Parameters
Jeong et al. [20]	2011	CO ₂ -N ₂ CO ₂ -O ₂ CO ₂ -He CO ₂ -Ar	292 K-304 K	$T_c + 1$	cycle efficiency
Conboy et al. [18]	2012	CO ₂ -He CO ₂ -Ne CO ₂ -methane CO ₂ -butane	0.9/0.1 0.81/0.19; 0.92/0.08	—	Compatibility; compressor flow
Jeong et al. [19]	2013	CO ₂ -Xe CO ₂ -Kr CO ₂ -N ₂ CO ₂ -O ₂ CO ₂ -Ar	292 K-304 K	$T_c + 1$	cycle efficiency
Hu et al. [21]	2015	CO ₂ -O ₂ CO ₂ -He CO ₂ -Ar CO ₂ -Kr	284.15 K-304.15 K	$T_c + 1$	heat transfer; mass flow rate;
		CO ₂ -cyclohexane CO ₂ -He CO ₂ -H ₂	304.15 K-324.15 K		cycle power; cycle efficiency
Vesely et al. [24]	2016	$\begin{array}{c} \text{CO}_2\text{-}\text{O}_2\text{ CO}_2\text{-}\text{H}_2\text{S}\\ \text{CO}_2\text{-}\text{N}_2\text{ CO}_2\text{-}\text{Ar}\\ \text{CO}_2\text{-}\text{SF}_6\\ \text{CO}_2\text{-}\text{SF}_6\end{array}$	impurity: 0–0.05	307.15 K	cycle efficiency
Baik and Lee [22]	2018	CO_2 -R123 CO_2 -R134a CO_2 -R32 CO_2 -toluene	CO ₂ : 0–1	304.15 K-313.15 K	cycle efficiency
Ma et al. [26]	2018	CO ₂ -Kr	Kr: 0–0.48	—	cycle efficiency; cooling capacity
Vesely et al. [25]	2019	CO ₂ -He CO ₂ -CO CO ₂ -O ₂ CO ₂ -N ₂ CO ₂ -Ar CO ₂ -Xe	impurity: 0–0.10	307.15 K-313.15 K	cycle power; heat transfer
Guo et al. [23]	2019	CO ₂ -butane CO ₂ -Xe	0.95/0.05 0.7/0.3	313.15 K–333.15 K 303.15 K–333.15 K	cycle efficiency; exery efficiency

Table 1. Research summary on the Brayton cycle with CO₂-based mixtures.

From Table 1, it can be observed that the existing studies have the following limits:

(1) For the studies of Jeong et al. [19,20] and Hu et al. [21], the inlet temperature of main compressor is always assumed to be 1 K above the critical temperature of corresponding mixture, namely

 T_c + 1. However, due to the fact that T_c is different for various mixtures, this assumption will cause the performance comparison of mixtures under different compressor inlet temperatures.

- (2) For the work of Vesely et al. [24,25] and Guo et al. [23], the range of employed gas fraction is too less. Although Baik and Lee [22] considered the whole fraction range 0–1, most of the employed additives belong to organic fluids, which may decompose in the high temperature. Furthermore, Baik and Lee [22] only analyzed the performance of simple Brayton cycle.
- (3) Cycle efficiency is mainly employed to evaluate the cycle performance of different CO₂-based mixtures. Thus, more detailed performance comparisons are required.

1.4. Contribution of the Study

Considering the limits of the existing studies on the CO_2 -based mixtures, this work will comprehensively conduct the investigation of recompression cycle performance and the recuperator analysis under the same inlet temperature of main compressor. The studied range of CO_2 mass fraction is 0–1. Parameters such as cycle efficiency, specific work, mass flow rate, heat input and heat conductance, are compared for different CO_2 -based mixtures. Furthermore, considering that the inlet temperature of main compressor is closely related with ambient temperature, this work will also reveal the effect of compressor inlet temperature on the performance of CO_2 -based mixtures and recuperators in the recompression cycle.

2. Cycle Layout and CO₂-Based Mixtures

2.1. Cycle Layout

For different configurations of the S-CO₂ power cycle, the recompression cycle is the most representative, because of its relative simplicity and higher efficiency [20,23]. Furthermore, introducing a reheating process into the cycle can further improve the performance. Thus, in this work, the recompression cycle with reheater is employed to analyze and compare the performances of different CO₂-based mixtures. As shown in Figure 1, the considered cycle consists of a primary heater, reheater, HPT (high pressure turbine), LPT (low pressure turbine), HTR, LTR, compressor, recompressor and gas cooler. The working fluid firstly receives the thermal energy in the primary heater. After generating work in the HPT, the working fluid is reheated at the medium pressure and then produces work in the LPT. Thereafter, the low-pressure fluid flows through the HTR and LTR in turn. Before entering the gas cooler, the flow is split into two streams. One stream flows through the cooler and then is compressor. The high-pressure in the main compressor flows into the LTR and absorbs heat from the low pressure working fluid. Then, the preheated stream merges with the working fluid from the recompressor. After that, the combined flow is further preheated by the low-pressure working fluid in the HTR, and finally returns to the primary heater.



Figure 1. Schematic of recompression cycle with reheater.

For the above recompression cycle with a reheater, when employing CO_2 as working fluid, the corresponding T-s (Temperature-entropy) diagram is presented in Figure 2. As the lowest cycle operation parameters, the inlet temperature and pressure of main compressor should be located just above the critical point of CO_2 to reduce the required compressor work. Furthermore, when two divided streams merge at the inlet of HTR, the corresponding temperature difference should be small enough to avoid thermal fatigue cracking of the channel wall. Thus, a suitable flow split ratio must be determined for the recompression cycle.



Figure 2. Temperature-entropy diagram of S-CO₂ recompression cycle with reheater.

2.2. CO₂-Based Mixtures

Table 1 lists the considered CO₂-based mixtures in the existing studies. Thermodynamic properties of these mixtures are always obtained by REFPROP [19–26]. According to the shift direction of critical temperature, these mixtures can be classified into two groups: the ascending critical temperature group and the descending critical temperature group. In general, the ascending critical temperature group contains organic fluids such as butane, R134a, and R123. These constituents may decompose at high temperatures. However, for the descending critical temperature group, the additives usually include O_2 , N_2 , and Ar, which have the characteristics of safety, thermostability, and compatibility. Under the high temperature and pressure conditions, these gases would not be reacted with CO₂. Furthermore, in engineering applications of the S-CO₂ cycle, the gases usually appear as the impurities. Therefore, in this work, seven additive gases are employed, as presented in Table 2.

Table 2. Pure fluids involved in the considered CO₂-based mixtures.

						C_p [KJ/(kg·K)]	
Pure Fluid	<i>M</i> [g/mol]	<i>T_b</i> [K]	<i>T_c</i> [K]	P _c [MPa]	$D_c [\mathrm{kg/m^3}]$	<i>T_{c0}</i> + 150, 7.5 Mpa	T_{c0} + 150, 25 Mpa
CO ₂	44.01	194.69	304.13	7.38	467.60	1.14	1.55
Xe	131.29	165.05	289.73	5.84	1102.90	0.21	0.32
Kr	83.80	119.73	209.48	5.53	909.21	0.28	0.34
O2	32.00	90.19	154.58	5.04	436.14	1.00	1.08
Ar	39.95	87.30	150.69	4.86	535.60	0.55	0.61
N ₂	28.01	77.36	126.19	3.40	313.30	1.09	1.16
Ne	20.18	27.10	44.49	2.68	481.91	1.04	1.05
He	4.00	4.22	5.20	0.23	69.58	5.19	5.18

Table 2 lists the pure gases involved in the considered CO_2 -based mixtures, according to the decrease sequence of critical temperature: $CO_2 > Xe > Kr > O_2 > Ar > N_2 > Ne > He$. For every gas,

Table 2 provides molecular weight, boiling temperature and critical properties. Furthermore, under the temperature T_{c0} + 150 K (454.13 K), heat capacities at pressures 7.5 MPa and 25 MPa are given, based on the calculation of REFPROP. From the table, it can be seen that CO₂ has the highest critical temperature 304.13 K, while He has the lowest critical temperature 5.1953 K. For the seven additive gases, Xe has closest critical temperature (289.73 K) to that of CO₂. Furthermore, the boiling temperature and the critical pressure decrease with the decrease of critical temperature. For the critical density, Xe has the highest value (1102.9 kg/m³), while He has the lowest density (69.58 kg/m³). As for the heat capacity, He has much higher value than other fluids under the same condition. In addition, the heat capacity at high pressure is always larger than that at low pressure. However, for different fluids, with the decrease of critical temperature is small, if the difference is multiplied by the mass flow rate, the difference of total heat capacity will be considerable to affect the heat exchange in the recuperator. That is why the split flow process is widely employed in the configurations of the S-CO₂ power cycle. The mismatch of heat capacity in the LTR can be greatly alleviated by adjusting the mass flow rate at the high-pressure side of heat exchanger.

For the considered CO_2 -based mixtures, the corresponding thermodynamic properties are evaluated by the newest version REFPROP 10 [27]. The variations of critical temperature and pressure with the mass fraction of CO_2 are respectively presented in Figures 3 and 4. Figure 3 indicates that the critical temperature of mixture increases monotonously with the increase of CO_2 mass fraction. The curves of these mixtures are distributed according to the order of critical temperature of pure gases. However, it should be noted that although critical temperature satisfies $O_2 > Ar$, CO_2 -Ar has an obviously higher critical temperature than that of CO_2 - O_2 at mass fractions larger than 0.2. Critical temperature of mixtures usually satisfies the following order: CO_2 -Xe > CO_2 -Kr > CO_2 -Ar > CO_2 -O₂ > $CO_2-N_2 > CO_2-N_e > CO_2$ -He. Furthermore, when CO_2 mass fraction is larger than 0.5, the curves of CO_2 - O_2 and CO_2 - N_2 are close to each other. As for the critical pressure of mixture in Figure 4, there exist very different variation trends among the mixtures. From Figure 4, it can be seen that with the increase of CO₂ mass fraction, critical pressures of mixtures CO₂-Ar, CO₂-N₂, and CO₂-O₂ first increase and then decrease. It means that there exists a high peak value of critical pressure, especially for CO₂-Ar. For the mixtures CO₂-Xe, CO₂-Kr, and CO₂-Ne, as the mass fraction of CO₂ increases, the critical pressure shows slowly increase monotonously. As for CO₂-He, it should be noted that when CO_2 mass fraction approaches to 1.0, the critical pressure of CO_2 -He is a little higher than that of CO_2 in a small range of mass fraction.



Figure 3. Critical temperature of mixtures at different mass fractions of CO₂.



Figure 4. Critical pressure of mixtures at different mass fractions of CO₂.

3. Thermodynamic Model and Validation

3.1. Model Establishment

In order to analyze the cycle performance of CO_2 -based mixtures, a simulation model is developed for the recompression cycle with reference to Figures 1 and 2. For the simplicity of modeling, the following assumptions are applied in the establishment of simulation model.

- The recompression cycle is reached in steady state operating condition.
- Pressure drops and heat losses in the pipes and heat exchangers are ignored.
- Recuperators are considered as counter-flow heat exchangers.

The power generated by the HPT and LPT can be determined as follows:

$$W_{\rm HPT} = m_c (h_1 - h_2) = m_c (h_1 - h_{2s}) \eta_{\rm HPT}$$
(1)

$$W_{\rm LPT} = m_c (h_3 - h_4) = m_c (h_3 - h_{4s}) \eta_{\rm LPT}$$
⁽²⁾

For the consumed work in the main compressor and recompressor, it can be expressed from Equations (3) and (4).

$$W_{MC} = SR \times m_c \times (h_8 - h_7) = SR \times m_c \times (h_{8s} - h_7) / \eta_{MC}$$
(3)

$$W_{RC} = (1 - SR) \times m_c \times (h_{9'} - h_7) = (1 - SR) \times m_c \times (h_{9's} - h_7) / \eta_{RC}$$
(4)

where split ratio (SR) denotes the ratio of the main compressor mass flow to the cycle mass flow and is defined as

$$SR = m_{MC}/m_c \tag{5}$$

Thus, the net power output is

$$W_{net} = W_{\rm HPT} + W_{\rm LPT} - W_{MC} - W_{RC} \tag{6}$$

The input heat through the primary heater and reheater is expressed as

$$Q_{ph} = m_c (h_1 - h_{10}) \tag{7}$$

$$Q_{rh} = m_c (h_3 - h_2)$$
 (8)

For the primary heater, the temperature increase of working fluid is defined as

$$\Delta t = T_1 - T_{10} \tag{9}$$

Furthermore, for the reheater, according to the reference [28], the intermediate pressure of working fluid is set as the average of the high and low pressures.

Based on the above parameters, the thermal efficiency can be described using Equation (10)

$$\eta_c = W_{net} / (Q_{ph} + Q_{rh}) \tag{10}$$

As for the heat exchange in the LTR and HTR, energy balance is satisfied.

$$h_4 - h_5 = h_{10} - h_9 \tag{11}$$

$$h_5 - h_6 = SR \times (h_{9''} - h_8) \tag{12}$$

In the modeling of recuperators, the effectiveness approach is employed. For LTR and HTR, the effectiveness is respectively defined as [5]

$$\varepsilon_{LTR} = (h_5 - h_6) / (h_5 - h(T_8, P_L))$$
(13)

$$\varepsilon_{HTR} = (h_4 - h_5) / (h_4 - h(T_9, P_L))$$
(14)

Furthermore, for the mixing process of two divided flows, it is governed by

$$SR \times h_{9'} + (1 - SR) \times h_{9''} = h_9 \tag{15}$$

For the recuperators, since heat transfer coefficients of mixtures are different with each other, heat conduction (UA), as a product of heat transfer coefficient and area, is employed to represent the required size and transfer performance of the heat exchangers. In general, a larger UA results into a higher cost of heat exchanger. UA can be calculated by knowing the inlet and outlet temperatures of recuperator. Considering that the thermodynamic properties of CO_2 -based mixture vary greatly with the temperature, the recuperator is discretized into N sub-heat exchangers. Due to the slight variation of properties, they can be assumed as constants in each sub-heat exchanger. Accordingly, the total heat transfer rate of recuperator is divided into N sections. For each sub-heat exchanger, the transferred heat is expressed by

$$Q_j = m_{hot}(h_{hot,in,j} - h_{hot,out,j}) = m_{cold}(h_{cold,out,j} - h_{cold,in,j})$$
(16)

The corresponding logarithmic mean temperature difference is expressed as

$$\Delta t_{j,m} = \left[(t_{hot,in,j} - t_{cold,out,j}) - (t_{hot,out,j} - t_{cold,in,j}) \right] / \ln \frac{(t_{hot,in,j} - t_{cold,out,j})}{(t_{hot,out,j} - t_{cold,in,j})}$$
(17)

Then, the heat conductance of sub-heat exchanger can be obtained, and the overall conductance is calculated as

$$UA = \sum_{j=1}^{N} Q_j / \Delta t_{j,m}$$
(18)

In order to compare the cycle performance of different mixtures, main parameters of the recompression cycle are specified in Table 3. These parameters are designed by National Renewable Energy Laboratory for the application of S-CO₂ Brayton cycle in concentrating solar power. The corresponding reference values have been employed in the performance comparison among the simple cycle, recompression cycle and partial-cooling cycle [28]. In the table, the efficiencies of

turbomachinery are provided, and the effectiveness of heat exchanger is given. In order to guarantee the heat transfer in HTR and LTR, the temperature difference in heat exchanger is set to be above 5 °C. In addition, the highest cycle temperature and maximum pressure are set to be 650 °C and 25 MPa, respectively. As for the lowest cycle temperature, the reference value of compressor inlet temperature is set to be just 1K above the critical temperature of CO_2 (T_{c0} + 1). However, in order to investigate the effect of compressor inlet temperature on the cycle performance, the inlet temperature also varies from T_{c0} + 1 to T_{c0} + 30. Furthermore, it is assumed that the recompression system has a net power output of 35 MW.

Design Parameters	Value Range	Reference Value
Turbine efficiency	0.93	0.93
Compressor efficiency	0.89	0.89
Heat exchanger effectiveness	0.97	0.97
Temperature difference in heat exchanger	≥5 °C	≥5 °C
Turbine inlet temperature	650 °C	650 °C
Compressor inlet temperature	$T_{c0} + 1 - T_{c0} + 30$	$T_{c0} + 1$
Upper pressure	25 MPa	25 MPa
Net power output	35 MW	35 MW

 Table 3. Main parameters for the recompression power cycle with reheater.

Under the design parameters in Table 3, pressure ratio and split ratio are optimized for each fluid based on the criteria of maximum cycle efficiency. The optimization procedure is shown in Figure 5. For the calculation of LTR and HTR, the temperature distributions are obtained, and the minimum temperature differences are checked at the pinch point. If the pinch point temperature difference (PPTD) is lower than 5 °C, parameters of LTR and HTR are recalculated by setting PPTD = 5 °C. Computer programs for this calculation procedure are developed on the platform of MATLAB 2015. REFPROP 10 is embedded into the program to determine the thermodynamic properties of CO_2 -based mixtures at different state points.



Figure 5. Calculation flow chart of the cycle with CO₂-based mixtures.

3.2. Model Validation

The established model is validated by comparing the results with the data of Neises and Turchi's study [28]. In the validation, the working fluid is supercritical CO₂ and the adopted parameters are consistent with the reference values in Table 3, except that the compressor inlet temperature is assumed to be 50 °C. Based on the above parameters, Neises and Turchi got results using Engineering Equation Solver (University of Wisconsin-Madison, Madison, WI, US), while results of the present model are obtained by running MATLAB. Table 4 gives the comparison results of these two models. It can be seen that there exists a good agreement between the present model and the reference.

Cycle Parameters	REF [28]	Present Study
Pressure ratio	2.50	2.50
Split ratio	0.71	0.71
UA _{LTR} [MW/K]	3.21	3.21
UA _{HTR} [MW/K]	5.33	5.31
UA _{total} [MW/K]	8.54	8.52
Cycle efficiency	0.49	0.49

Table 4. Comparison results between the present study and reference [28].

4. Results and Discussions

Under the design conditions in Table 3, optimized results of recompression cycle are obtained for CO₂-based mixtures. The employed CO₂ mass fraction varies from 0 to 1 at an interval of 0.1. The corresponding calculated data are listed in Supplementary Materials. On this basis, thermodynamic analysis on cycle performance and recuperator is conducted for mixtures under a fixed compressor inlet temperature (T_{c0} + 1). Thereafter, cycle parameters are optimized at different compressor inlet temperatures, so that the effect can be revealed for mixtures.

4.1. Cycle Performance Analysis

Figure 6 presents the calculated cycle efficiency of mixtures at different mass fractions of CO₂. It can be seen that every mixture has a unique variation curve of cycle efficiency with the increase of CO_2 mass fraction. For CO_2 -Xe, as the CO_2 mass fraction increases from 0 to 1, the cycle efficiency firstly increases from the value of Xe (0.538) and then decreases slowly to the value of CO_2 (0.539). It means that there exists a peak value of cycle efficiency around the CO_2 mass fraction 0.2. Due to the little difference of critical temperatures between CO_2 and Xe, the range of efficiency variation is small for CO_2 -Xe. Unlike the mixture CO_2 -Xe, the efficiency of the rest mixtures always increases with the increase of CO_2 mass fraction. Since the critical temperature of CO_2 is much higher than temperatures of pure gases, cycle efficiencies of these gases are far lower than that of CO₂ under the fixed compressor inlet temperature. Furthermore, for mixtures CO₂-O₂, CO₂-Ar, CO₂-N₂, CO₂-Ne, and CO₂-He, the cycle efficiency increases slowly at the fraction range 0-0.9. However, when CO₂ mass fraction approaches to 1.0, a sharp increase of efficiency is observed. On the other hand, for the considered mixtures, the legend is illustrated according to the descending order of the critical temperatures of pure gases. Figure 6 indicates that with the critical temperature decrease of pure gases, the corresponding mixtures usually have lower cycle efficiency. However, for the gases O₂ and Ar, efficiency of CO₂-Ar is always higher than that of CO_2 - O_2 . This is because, although the critical temperature of O_2 is higher than that of Ar, the critical temperature of CO_2 - O_2 is lower than that of CO_2 -Ar. Thus, the considered mixtures satisfy the following order of cycle efficiency: CO_2 -Xe > CO_2 -Kr > CO_2 -Ar > CO_2 -O₂ > CO_2 -N₂ > CO_2 -Ne > CO_2 -He. In addition, when the critical temperature of mixture is far from the compressor inlet temperature, the efficiency difference of different mixtures such as CO₂-N₂, CO₂-Ne, or CO₂-He becomes smaller.



Figure 6. Cycle efficiency of mixtures at different mass fractions of CO₂.

For the mixtures, Figure 7 presents the variation of specific work (output work per mass flow rate) with the mass fraction of CO₂. It can be seen that specific work of He (396.14 kW) is much higher than that of CO₂ (139.61 kW). Thus, the mixture CO₂-He shows a continue decrease of specific work in the CO₂ mass fraction range 0–0.9. When the mass fraction approaches to 1.0, the output work will increase to that of pure CO₂. For the other mixtures, as CO₂ mass fraction increases, the corresponding output work slowly increases from the value of pure gas to that of CO₂. However, the variation range is smaller than that of CO₂-He. It is interesting to note that CO₂-He has the lowest efficiency, while the output work of CO₂-He is the highest in the CO₂ mass fraction rang 0–0.8. Furthermore, due to the fact that the net power output is given in the simulation, mass flow rates of mixtures can be determined, as shown in Figure 8. Mass flow rates of Kr, Xe, and Ar reach to 1225.14 kg/s, 982.78 kg/s, and 744.22 kg/s, respectively. With the increase of CO₂ mass fraction, the flow rates gradually decrease to the value of CO₂ (250.69 kg/s). Although mass flow rates of CO₂-Ne, CO₂-O₂, and CO₂-N₂ satisfies the order CO₂-Ne > CO₂-O₂ > CO₂-N₂, the curves of these mixtures are close to each other. The lowest curve of mass flow rate is observed for CO₂ (250.69 kg/s).



Figure 7. Specific work of mixtures at different mass fractions of CO₂.



Figure 8. Mass flow rate of mixtures at different mass fractions of CO₂.

Besides cycle efficiency, output work, and mass flow rate, amounts of heat input are also compared for different mixtures, as illustrated in Figure 9. Since the total net power output is fixed, the amount of absorbed heat is inversely proportional to cycle efficiency. Thus, the absorbed heat of CO₂-Xe is the lowest. The value first decreases from Xe (64.95 MW) and then increase to CO₂ (64.90 MW). As for the other mixtures, the absorbed heat gradually decreases to that of CO₂. When mass fraction of CO₂ is beyond 0.5, the heat input has the following order: CO₂-He > CO₂-Ne > CO₂-O₂ > CO₂-O₂ > CO₂-Ar > CO₂-Kr > CO₂-Xe. At high mass fraction of CO₂, the curve of CO₂-N₂ almost coincides with that of CO₂-O₂, due to the fact that critical temperatures of CO₂-N₂ and CO₂-O₂ are close to each other.



Figure 9. Heat input of mixtures at different mass fractions of CO₂.

In the simulation, the high cycle pressure is fixed at 25 MPa and pressure ratio is optimized for every mixture. Based on the determined pressure ratio, the low cycle pressure can be calculated. The corresponding variation curves are presented in Figure 10 for the considered mixtures. It can

be observed that low cycle pressures for pure gases are higher than that of CO₂. As the CO₂ mass fraction increases, the pressure of CO₂-Xe firstly shows a decrease and then a slowly increase, while other mixtures shows continue decrease of low pressure. For the considered mixtures, the highest curve of pressure is CO₂-He, while the lowest is CO₂-Xe. When the mass fraction is higher than 0.5, the low cycle pressure satisfies the following order: CO₂-He > CO₂-Ne > CO₂-Ar > CO₂-N₂ > CO₂-O₂ > CO₂-Kr > CO₂-Xe. It should be noted that little difference exists for the pressure of CO₂-Ar, CO₂-N₂, and CO₂-O₂ at high mass fractions of CO₂.



Figure 10. Low cycle pressure of mixtures at different mass fractions of CO₂.

When the S-CO₂ power cycle is applied to solar energy, temperature increase of working fluid in the primary heater is an important index to evaluate the performance of solar power system. The larger the temperature increase, the greater the heat storage of molten salt [13]. Thus, Figure 11 presents the temperature increase of mixtures in the primary heater. It indicates that CO₂-Xe has the highest temperature difference, followed by CO₂-Kr. For the CO₂-Xe mixture, the temperature difference continues to decrease from Xe (235.24 K) to CO₂ (147.58 K), while CO₂-Kr firstly decrease from Kr (147.58 K) and then increase to CO₂ (147.58 K) slowly. For other mixtures, the temperature difference continues to increase, as the CO₂ mass fraction increases. At mass fraction larger than 0.5, the temperature difference has the order: CO₂-Xe > CO₂-Kr > CO₂-Ar > CO₂-N₂ > CO₂-O₂ > CO₂-Ne > CO₂-He. It should be noted that the curves of CO₂-Ar, CO₂-N₂, and CO₂-O₂ are close to each other.



Figure 11. Temperature increase of mixtures in the primary heater.

4.2. Recuperator Analysis

For the recompression cycle, the recuperator is a key component to improve cycle performance. Thus, the heat transfer and the required conductance of HTR and LTR are calculated for mixtures according to the conditions in Table 3. HTR heat and conductance are respectively presented in Figures 12 and 13. For the heat transfer in HTR, the heat of Xe (35.47 MW) is the lowest, then followed by CO₂ (99.82 MW). The highest heat is for He (167.16 MW). With the increase of CO₂ mass fraction, HTR heat of CO₂-Xe increases, while other mixtures show downtrend of HTR heat in a whole. The irregularly small variation of HTR heat is because of nonlinear properties of mixtures. At different mass fractions of CO_2 , CO_2 -Xe has the lowest heat transfer, while heat of CO_2 -He is the highest. Compared with the heat input in Figure 9, HTR heat of mixtures is much higher except CO_2 -Xe at low mass fraction of CO₂. As for the heat conductance of HTR. It is proportional to the transferred heat, as shown in Figure 13. It can be observed that the conductance variation of mixtures with CO_2 mass fraction is similar to that of HTR heat. The lowest conductance is 1.8 MW/K for Xe, while the highest value is 15.0 MW/K for He. CO₂ has the conductance 3.26 MW/K. In order to meet so much high heat transfer, it's thought that printed circuit heat exchanger (PCHE) has the potential to be applied, because of the great compactness and capability to withstand the high temperature and pressure. Furthermore, for the order of HTR heat and conductance in mixtures at high CO₂ mass fraction, it has the following order: CO₂-He > CO₂-Ne > CO₂-O₂ > CO₂-N₂ > CO₂-Ar > CO₂-Kr > CO₂-Xe.



Figure 12. High-temperature recuperator (HTR) heat of mixtures at different mass fractions of CO₂.



Figure 13. HTR conductance of mixtures at different mass fractions of CO₂.

In order to analyze the heat transfer difference between pure fluids and mixtures, temperature distributions in HTR are calculated for seven mixtures. The corresponding figures are presented in Supplementary Materials. Here, take CO_2 - N_2 as an example, the temperature distributions for CO_2 , CO_2 - N_2 (0.5/0.5) and N_2 are illustrated in Figure 14. It can be seen that the transferred heats of CO_2 - N_2 (0.5/0.5) and N_2 are much higher than that of CO_2 . In general, the pinch point of heat transfer locates at the cold end of HTR. The corresponding minimum temperature differences of CO_2 , CO_2 - N_2 (0.5/0.5) and N_2 are 10.88 °C, 10.79°C and 10.76 °C, respectively. Furthermore, for the considered mixtures, the calculated minimum temperature differences are provided in Supplementary Materials.



Figure 14. Temperature distributions of CO₂- N₂ in HTR.

Figure 15 illustrates the LTR heat of mixtures at different mass fractions of CO₂. It can be seen that the LTR heat is far lower than those of heater and HTR, and the heat difference of LTR between different mixtures is also less than that presented in Figures 9 and 12. For the considered mixtures, CO_2 -Xe has the lowest LTR heat. As the CO_2 mass fraction increases, LTR heat of the mixture gradually decrease from Xe (40.02 MW) to CO₂ (38.06 MW). Being similar to CO₂-Xe, CO₂-Kr also shows a slow decrease of LTR heat. However, for the other mixtures, when CO_2 mass fraction is higher than 0.9, there exists a sharp decrease of LTR heat, as shown in Figure 15. As for the curves of LTR conductance, they are given in Figure 16. It indicates that although the LTR conductance of mixtures decreases with the increase of CO₂ mass fraction, the variation range is smaller than that of HTR conductance. Special care should be given for CO_2 -Xe. When CO_2 mass fraction is less than 0.2, there is a sharp decrease of LTR conductance. Even if the heat transfer of LTR is the lowest for CO_2 -Xe, the corresponding conductance is higher than that of other mixture at low CO_2 mass fractions. This phenomenon can be explained by the matched heat capacities of the cold and hot sides. When the temperature match is improved, the logarithmic mean temperature difference will be reduced. On the other hand, at high mass fractions of CO₂, mixtures have the following order of LTR heat and conductance: CO₂-He > $CO_2-Ne > CO_2-O_2 > CO_2-N_2 > CO_2-Ar > CO_2-Kr > CO_2-Xe$. It should be noted that the curves of CO₂-O₂ and CO₂-N₂ are close to each other.



Figure 15. Low-temperature recuperator (LTR) heat of mixtures at different mass fractions of CO2.



Figure 16. LTR conductance of mixtures at different mass fractions of CO₂.

As for the temperature distributions in LTR, all figures are provided in Supplementary Materials for the considered mixtures. Figure 17 illustrates the temperature distributions of CO₂, CO₂-N₂ (0.5/0.5), and N₂. It can be observed that although there are large differences of specific heat capacity between hot and cold streams at low temperatures, the differences of total heat capacity are greatly minimized by introducing splitting progress, so that the temperature mismatch in LTR is alleviated. For CO₂, CO₂-N₂ (0.5/0.5) and N₂, the minimum temperature differences are 10.89 °C, 10.80 °C, and 10.76 °C, respectively. Similarly, the minimum temperature differences of all mixtures are given in the Supplementary Materials.



Figure 17. Temperature distributions of CO₂- N₂ in LTR.

In order to reduce the difference of specific heat capacity between the cold and hot sides in LTR, split ratio is optimized. The corresponding values are presented in Figure 18. It can be observed that split ratio of pure gas is higher than that of CO₂ (0.63). The reason is that heat capacity difference decreases with the decrease of critical temperature, as illustrated in Table 2. The larger the heat capacity difference, the lower the split ratio. Therefore, As CO₂ mass fraction increases, split ratio decreases. Except CO₂-Xe and CO₂-Kr, all mixtures show slow decrease firstly and then rapid decrease, especially for CO₂-He. For these mixtures, the lowest curve is for CO₂-Xe, while CO₂-He has the highest curve. The values of CO₂-He are close to 1.0. Similarly, at high mass fractions of CO₂, split ratio has the order: CO₂-He > CO₂-Ne > CO₂-N₂ > CO₂-O₂ > CO₂-Ar > CO₂-Kr > CO₂-Xe.



Figure 18. Split ratio of mixtures at different mass fractions of CO₂.

4.3. Effect of Compressor Inlet Temperature

In order to investigate the effect of compressor inlet temperature, temperatures $T_{c0} + 1$, $T_{c0} + 10$, $T_{c0} + 20$, and $T_{c0} + 30$ are considered. Cycle performance and recuperator parameters of the considered mixtures are analyzed under the provided conditions in Table 3. Since the effect of compressor inlet temperature on the cycle parameters keeps the same for different mixtures, results of a typical mixture are presented in the following study. Considering that N₂ is the most abundant gas in the air, it is highly possible to mix with CO₂ so as to affect the performance of supercritical power cycle. Thus, CO₂-N₂ is selected.

Figure 19 gives the cycle efficiency of CO_2 -N₂ for the four temperatures. As the inlet temperature increases, cycle efficiency naturally decreases. For instance, at T_{c0} + 1 and T_{c0} + 30, CO_2 has cycle efficiency 0.54 and 0.48, respectively. Furthermore, with the increase of inlet temperature, the efficiency difference between N₂ and CO_2 decreases, so as to make the curve rise more smoothly, especially at the CO_2 mass fraction beyond 0.9. As for the specific work, the increased temperature results into a greater power consumed by the main compressor. This makes the reduction of specific work, as shown in Figure 20. On the other hand, due to the increase of compressor inlet temperature is fixed at 650 °C, the temperature difference in the primary heater will automatically decreases, as presented in Figure 21. Meanwhile, with the increase of compressor inlet temperature, the corresponding curve shows a slow increase from N₂ to CO_2 , especially when CO_2 mass fraction is higher than 0.9.



Figure 19. Cycle efficiency of CO₂-N₂ at different compressor inlet temperatures.



Figure 20. Specific work of CO₂-N₂ at different compressor inlet temperatures.



Figure 21. Temperature increase of CO_2 - N_2 in the primary heater at different compressor inlet temperatures.

In the simulation, the total net power output is fixed. When the cycle efficiency decreases with the increase of compressor inlet temperature, the absorbed heat from the heat source will increase. Meanwhile, considering the temperature difference of mixture in the primary heater decreases, cycle mass flow rate is certain to increase to assure the required heat. This will result into more heat transfer in the recuperators. As presented in Figures 22 and 23, heat conductance of HTR and LTR increase with the increase of compressor inlet temperature. Furthermore, compared with the LTR conductance, the HTR conductance is more easily to be influenced by the increase of inlet temperature. Take CO₂ as example, when inlet temperatures are T_{c0} + 1 and T_{c0} + 30, HTR conductance are 3.26 MW/K and 6.30 MW/K, while LTR has the conductance 2.84 MW/K and 3.54 MW/K, respectively.



Figure 22. HTR conductance of CO₂-N2 at different compressor inlet temperatures.



Figure 23. LTR conductance of CO₂-N₂ at different compressor inlet temperatures.

5. Conclusions

In the present study, a thermodynamic model is established for the recompression cycle. Seven types of CO_2 -based mixtures are employed to investigate the effect of mixtures on the supercritical power cycle from the perspective of thermodynamic analysis. Based on the optimized results, cycle performance and recuperators' heat transfer for different mixtures are comprehensively compared and analyzed at different mass factions of CO_2 .Therafter, in order to reveal the effect of compressor inlet temperature, cycle parameters of CO_2 -N₂ are obtained and compared under four different temperatures. The main conclusions can be drawn as follows:

- (1) Under the fixed compressor inlet temperature, except CO₂-Xe and CO₂-He, cycle efficiency, specific work and temperature increase in the primary heater for other mixtures are generally lower than those for pure CO₂. However, mass flow rate, heat input and low cycle pressure of these mixtures are generally higher than those of CO₂. For the analyzed parameters, the order of mixtures almost coincides with the descending or ascending order of corresponding critical temperature. Performance curves of the considered mixtures locate between the curves of CO₂-Xe and CO₂-He. Furthermore, when the mass fraction is close to 1.0, there usually exists a sharp change of cycle performance for CO₂-He, CO₂-Ne, CO₂-N₂, CO₂-Ar, and CO₂-O₂.
- (2) For the recuperators of recompression cycle, compared with the LTR heat, the HTR heat of mixtures is larger. Except CO₂-Xe, the transferred heat and the required conductance of HTR and LTR decrease with the increase of CO₂ mass fraction. At high mass fractions of CO₂, the considered mixtures satisfy the order: CO₂-He > CO₂-Ne > CO₂-O₂ > CO₂-Ar > CO₂-Kr > CO₂-Xe. As for the split ratio, the larger the heat capacity difference of mixtures between hot and cold sides in LTR, the lower the split ratio. All mixtures have higher split ratio than pure CO₂. The order of split ratio for mixtures almost coincides with the above sequence. In general, the curves of CO₂-O₂ and CO₂-N₂ are close to each other.
- (3) For the effect of compressor inlet temperature, the increase of inlet temperature will cause the decrease of cycle efficiency, specific work, and temperature difference in the primary heater. Heat conductance of recuperators will be increased. However, the obvious benefit of increasing inlet temperature is that it can increase the temperature difference between the working fluid and the cooling source, especially in hot or arid environments. This will greatly reduce the mass flow of cooling source and the required heat exchange area of gas cooler. Thus, how to determine the optimal inlet temperature of compressor is worth investigating by considering the thermodynamic and economic performances of working fluid simultaneously.

In engineering, CO_2 is inevitably mixed with impurity gases, such as N_2 or O_2 . This work is helpful to reveal the effect of these impurities on the performance of S-CO₂ Brayton cycle. Furthermore,

for the utilization of CO_2 -based mixtures to improve the cycle performance, based on the property calculation of REFPROP, this study provides preliminary comparison results for seven types of mixtures under certain conditions. Therefore, in the future research, properties of CO_2 -based mixtures have to be deeply studied to ensure the application of mixtures. More investigations about the environmental impacts, costs, and experimental limitations should be performed for supercritical Brayton cycle with CO_2 -based mixtures by considering different driven heat sources.

Supplementary Materials: The following are available online at http://www.mdpi.com/1996-1073/13/7/1741/s1. Figure S1: Temperature distributions of CO₂-Xe in a high-temperature recuperator (HTR); Figure S2: Temperature distributions of CO₂-Xe in a low-temperature recuperator (LTR); Figure S3: Temperature distributions of CO₂-C₂ in HTR; Figure S4: Temperature distributions of CO₂-C₂ in LTR; Figure S5: Temperature distributions of CO₂- O₂ in HTR; Figure S6: Temperature distributions of CO₂- O₂ in LTR; Figure S7: Temperature distributions of CO₂- Ar in HTR; Figure S8: Temperature distributions of CO₂- N₂ in LTR; Figure S9: Temperature distributions of CO₂- N₂ in HTR; Figure S10: Temperature distributions of CO₂- N₂ in LTR; Figure S11: Temperature distributions of CO₂- Ne in HTR; Figure S12: Temperature distributions of CO₂- Ne in LTR; Figure S13: Temperature distributions of CO₂- Ne in HTR; Figure S14: Temperature distributions of CO₂- Ne in LTR; Figure S15: Minimum temperature differences of considered mixtures in HTR; Figure S16: Minimum temperature differences of considered mixtures in HTR; Figure S16: Minimum temperature differences of considered mixtures in HTR; Figure S16: Minimum temperature differences of considered mixtures are completely calculated for the seven mixtures. The corresponding data are listed in Excel. Furthermore, for these mixtures, temperature distributions in the HTR and LTR are also presented in the form of figure.

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Nomenclature

Symbols	
С	Heat Capacity, KJ/(kg·K)
D	Density, kg/m ³
HTR	High temperature recuperator
HPT	High pressure turbine
h	Enthalpy, kJ/kg
LTR	Low temperature recuperator
LPT	Low pressure turbine
т	Mass flow rate, kg/s
М	Molar mass, g/mol
Р	Pressure, MPa
PPTD	Pinch point temperature difference, °C
Q	Heat, kJ
S-CO ₂	Supercritical CO ₂
SFR	Sodium-cooled fast reactor
SR	Split ratio
Т	Temperature, K
W	Work, kW
UA	Heat conductance, MW/K
Greeks	
ε	Effectiveness of recuperator
η	Efficiency
Δ	Difference
Subscripts	
1, 2, 10	State points of recompression cycle
b	Boiling temperature
С	Cycle/critical temperature
<i>c</i> ₀	Critical temperature of CO ₂
HPT	High pressure turbine
HTR	High temperature recuperator
LPT	Low pressure turbine
LTR	Low temperature recuperator
MC	Main Compressor
net	Net work
р	Heat capacity
ph	Primary heater
RC	Recompressor
rh	Reheater
S	Equal entropy

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