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1	Thermodynamic Analysis of a Novel Fossil-
2	Fuel-Free Energy Storage System with a
3	Trans-Critical Carbon Dioxide Cycle and
4	Heat Pump
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11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26	Abstract: This paper presents and analyzes a novel fossil-fuel-free trans-critical energy storage system that uses CO_2 as the working fluid in a closed loop shuttled between two saline aquifers or caverns at different depths, one a low-pressure reservoir, and the other a high-pressure reservoir. Thermal energy storage and a heat pump are adopted to eliminate the need for external natural gas for heating the CO_2 entering the energy recovery turbines. We carefully analyze the energy storage and recovery processes to reveal the actual efficiency of the system. We also highlight thermodynamic and sensitivity analyses of the performance of this fossil-fuel-free trans-critical energy storage system based on a steady-state mathematical method. It is found that the fossil-fuel-free trans-critical CO_2 energy storage system has good comprehensive thermodynamic performance. The exergy efficiency, round-trip efficiency, and energy storage volume is 2.12 kW·h/m ³ , and the main contribution to exergy destruction is the turbine re-heater, from which we can quantify how performance can be improved. Moreover, with a relatively higher energy storage and recovery pressure and lower pressure in the low-pressure reservoir, this novel system shows promising performance.
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32 33 34 35	the final published paper. Please read and cite the final published paper:Hao, Y., He, Q., Liu, W., Pan, L. and Oldenburg, C.M., Thermodynamic analysis of a novel fossil-fuel–free energy storage system with a trans-critical carbon dioxide cycle

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38 **1. Introduction**

Increasing energy demand and rising concern about greenhouse gas emissions 39 from fossil-fuel power generation have led to worldwide interest in renewable energy 40 sources [1]. Rapid development and worldwide utilization of renewable energy sources 41 bring not only diversification of the global energy industry, but also challenges in 42 43 integrating renewable energy such as wind and solar energy into the electricity grid due to intermittency and instability over a wide range of time scales from short (minute) to 44 long (seasonal) [2-5]. In order to optimize integration of wind and solar power into the 45 electricity grid, practical large-scale (bulk) energy storage systems (ESS) are urgently 46 needed. The technologies currently are available to provide bulk energy storage include 47 pumped hydro storage (PHS) and compressed air energy storage (CAES) [6-8]. The 48 development of batteries for bulk energy storage is ongoing, but there are only a few 49 utility-scale stationary battery storage projects in place for long-term (daily) storage 50 51 and these systems are expensive and provide only a small fraction of energy stored by pumped hydro storage [9,10]. 52

It is well known that the only two current operating conventional CAES plants rely 53 54 on natural gas for energy recovery resulting in greenhouse gas emissions. The fact that renewable energy stored by CAES may result in greenhouse gas emissions upon energy 55 recovery has motivated thinking about novel CAES systems, some of which can avoid 56 the need for natural gas. Among the many novel CAES systems that have been proposed 57 are the super-critical CAES (SC-CAES) [11], porous media CAES (PM-CAES) [12], 58 and small scale CAES [13]. In addition, several new approaches to adiabatic CAES 59 have recently been introduced. For example, advanced adiabatic CAES (AA-CAES) 60 [14-16] and high-temperature adiabatic CAES [17] have been analyzed and show 61 potential to solve the economic and environmental challenges related to the use of fossil 62 fuel combustion during energy recovery. Thermodynamic analyses have become 63 standard for these systems for design and efficiency analyses [18-20]. Several of new 64 CAES systems [21, 22] have been proposed to improve thermal efficiency of CAES, 65

and liquefied air energy storage (LAES) [23, 24] has been studied to improve energystorage density.

68 Recently, growing interest has been focused on the use of carbon dioxide (CO₂) in compressed gas storage because of its unique properties and characteristics. Utilizing 69 CO₂ instead of air in compressed gas energy storage will not only improve the system 70 performance but also offer a possibility for utilization of CO₂ with corresponding 71 reductions in carbon emission [25]. Wu et al. [26] proposed a novel trans-critical 72 73 compressed CO₂ energy storage system that showed good performance, energy storage density, and high efficiency. Liu et al. [27] proposed a system that combined 74 compressed gas energy storage in deep subsurface reservoirs (porous media or caverns) 75 and utilization of CO₂ which gets much higher energy density and good energy storage 76 efficiency. Buscheck et al. [28] were investigating ways to exploit deep reservoirs for 77 both their ability to store CO₂ beneficially in both the geologic carbon sequestration 78 context and for energy storage, including exploitation of natural geothermal heating of 79 the CO₂. Ahmadi et al [29-32] explored a few of novel CO₂ power cycles and 80 81 thermodynamic optimizations on these systems have been performed. Mehmet et al. [33] posed novel electro-thermal energy storage with trans-critical CO₂ cycles, aiming 82 to make improvement on the CO₂ machines and the system performance. An 83 optimization on thermodynamic performance of the turbine turbomachinery in an 84 energy storage system with CO₂ as working fluid has been performed [34]. Based on 85 CO_2 in a Brayton cycle, a compressed CO_2 energy storage cycle has been proposed and 86 87 thermodynamic optimization showed much better thermal performance compared with other CAES systems [35]. 88

Based on the above research, the development of compressed gas energy storage utilizing CO₂ as working fluid has become a focus of research and development. In this paper, we present and analyze a novel closed-loop energy storage system that uses CO₂ as the working fluid that is cycled between high-pressure and low-pressure reservoirs. The innovation highlight in this system is that we analyze the use of a heat pump instead of fossil fuel to recover and reheat stored heat of compression during the energy recovery process. We present mathematical thermodynamic models of the proposed

96 compressed trans-critical CO₂ energy storage system, and carry out parametric analyses
97 to examine the effects on system performance of key thermodynamic parameters.

98 2. System description

We propose a closed-loop energy storage system that takes advantage of the large 99 100 volumes and remote subsurface locations of saline aquifers or large storage caverns for hosting two CO₂ storage reservoirs. One reservoir is low-pressure, and the other is high-101 pressure, which serve to store, respectively, CO2 entering the electricity-producing 102 turbines, and CO₂ following compression in the storage cycle. In this novel energy 103 storage system, the CO₂ transitions from supercritical state to gaseous state in the 104 turbines, which is denoted as a trans-critical compressed CO₂ energy storage (TC-105 CCES). The schematic of this novel TC-CCES is depicted in Fig. 1, and its T-S graph 106 is illustrated in Fig. 2. The schematic of the heat pump sub-system of the TC-CCES 107 system is shown in Fig. 3. 108

109 **2.1 Energy storage process**

As shown in Fig. 1, the green background represents the energy storage process (compression phase), and the orange background represents the energy recovery process (generation phase). The overlapping region in the middle includes the heat storage unit, cold storage unit, and low- and high-pressure reservoirs (LR and HR), all of which are involved in both energy storage and energy recovery process.

115 The working principle of the storage process is as follows:

(a) 14-1: The working fluid (trans-critical CO₂) stored in LR is cooled through a
pre-cooler (PC) and injected into the compressor, with the heat of compression (19-20)
stored in the heat storage unit.

- (b) 1-2, 3-4, 5-6: During hours when excess renewable electricity is available, the
 CO₂ is pressurized in the compressor to temperatures and pressures above the critical
 point (304.15K, 7.4 MPa).
- 122 (c) 2-3, 4-5: The compressed CO_2 heats up in the process, and is then cooled by 123 the inter-cooler heat exchangers (IC1 and IC2), and the heat generated during the

- 124 compression process (15-16, 17-18) is stored in the heat storage unit.
- (d) 6-7: The compressed CO₂ with high temperature and pressure then is directlyinjected into HR for storage.
- 127 2.2 Energy recovery process

128 The working principle of the recovery process is as follows:

(a) 7-8: CO₂ at high temperature and high pressure, potentially with additional
geothermal heat absorbed from the deep reservoir, is adjusted to a fixed pressure
through the high-pressure valve, and is fed into the energy recovery turbine.

(b) 8-9, 10-11, 12-13: The high-pressure CO₂ powers the turbines resulting in
strong cooling of the CO₂, which is then fed into LR.

- (c) 9-10, 11-12: The CO₂ exhausted from the turbines in front (8-9 or 10-11) is too
 cold to feed the next turbines (10-11 or 12-13). This exhausted CO₂ is reheated in TR1
 or TR2 to prevent liquid CO₂ from forming and to provide enough volume throughput
 to drive each turbine. This reheating is accomplished using the heat provided by the hot
 water from the heat storage unit added by the heat pump system.
- (d) 22-23: The temperature of the hot water stored in the heat storage unit (21-22) after absorbing the CO_2 compression heat is not high enough to reheat the exhausted CO_2 in the generation turbine train. Therefore, the hot water withdrawn from the heat storage unit is further heated by means of the heat pump (27-23) to raise its temperature to a required level. This heat pump is the key new feature of the system included to obviate the need for natural gas in the energy recovery process.
- 145 2.3 Heat pump system

The term high-temperature heat pump (HTHP) is frequently used in connection with industrial heat pumps, mainly for waste heat recovery in process heat supply [36]. In the compression system proposed here, the temperature of the heat storage unit would not be sufficient to maintain CO₂ pressure after exiting from Turbine 1 to drive Turbine 2, and similarly for exiting from Turbine 2 to drive Turbine 3 to generate electricity. What is needed is a way to transfer the waste heat stored in the heat storage unit which is at approximately 383K into the exhaust streams of the turbines which are at a temperature of approximately 363K. Due to the relatively high inlet temperature
(approximately 423K) of Turbine 2, a heat pump is needed to make full use of the stored
waste heat.

In selecting a working fluid for the heat pump, we prioritized efficient and steady performance along with low environmental impact factor and high safety. We found that R245fa is a low-pressure, high-temperature, and environmentally safe fluid with a high enough critical temperature (427K) for use as the heat pump working fluid [36, 37]. We evaluated the thermodynamic properties of R245fa using PEFPROP [38]. The physical properties of R245fa are given in Table 1. The schematic of the heat pump is illustrated in Fig. 3. The working principle of the heat pump can be described as:

163

(a) 29-30: R245fa is compressed during a non-isentropic process.

(b) 30-31: Gaseous high-pressure R245fa is cooled by hot water from the heat
storage unit (22) resulting in condensation that provides latent heat to the water exiting
(23) to the turbine exhaust heating loop at a specified temperature (433.15K).

167 (c) 31-32: Liquid R245fa expands through the expansion valve in a non-isentropic168 process.

(d) 32-29: Liquid R245fa is heated through the evaporator by water from the
turbine exhaust cooling loop (27) causing R245fa to vaporize and causing cooling of
the water that exits to the 'cold' water storage tank.

3. Theoretical model

173 For simplicity, we make the following assumptions about the proposed TC-CCES: (a) The TC-CCES system uses the thermodynamic model based on the 174 175 thermodynamic law and operates at steady-state conditions, and we ignore pressure drops and heat losses in the pipes, heat exchangers, heat storage tank, and heat pump. 176 The water stored in the cold storage unit will be cooled down to room temperature 177 (298.15K) before it is used to cool the CO₂ from LS being fed to the compressor train. 178 (b) Equal CO₂ mass flow rates are assumed during the energy storage process 179 (withdrawing CO₂ from the LR and injecting CO₂ at high-pressure into the HR) and the 180 energy recovery process (withdrawing high-pressure CO₂ from the HR and injecting 181

182 low-pressure CO_2 into the LR).

(c) The system is closed (there are no losses of CO₂ within the storage reservoirs or
in the above-ground facility) and the stored energy of compression is large enough that
we can neglect kinetic and potential energy changes as CO₂ flows through the closedloop system. In addition, the details of wellbore flow are ignored in the analysis and we
assume constant wellhead P-T conditions during withdrawal and injection periods.

188 **3.1 Compressor train**

The compressors used for storing energy have isentropic efficiencies given by

190

189

$$\eta_c = \frac{h_{i,s}'' - h_i'}{h_i'' - h_i'} \tag{1}$$

where, h'_i is the enthalpy of inlet compressor; $h''_{i,s}$ is the isentropic enthalpy of outlet compressor; h''_i is the real entropy of outlet compressor; and *i* is the stage of compressor train, *i* = 1, 2, 3.

194 The power consumed by compression $W_{c,i}$ is 195 $W_{c,i} = h''_i - h'_i$ (2)

196 **3.2 Turbine train**

¹⁹⁷ The turbines used for recovering energy have efficiencies and power needs ¹⁹⁸ analogous to those of the compressors. The isentropic efficiency of expansion in the ¹⁹⁹ turbine η_T is

200

205

$$\eta_T = \frac{h'_j - h''_{j,s}}{h'_j - h''_j} \tag{3}$$

where, h'_j is the enthalpy of inlet turbine; $h''_{j,s}$ is the isentropic enthalpy of the outlet turbine; h''_j is the real enthalpy of the outlet turbine; and j is the stage of the turbine train, j=1, 2, 3.

The power output during expansion by the turbine $W_{T,j}$ is

$$W_{T,j} = h'_j - h''_j$$
 (4)

206 **3.3 Storage model**

For a saline aquifer storage reservoir, the groundwater in the aquifer has a pressure

 P_{hs} given by

209

$$P_{hs} = \rho_w gZ \tag{5}$$

The LR is envisioned to be located at a shallower depth than the HR because the CO₂ well bottom pressure must exceed the reservoir pressure for injection to occur. Cavern pressures are more flexible, and there are no a priori restrictions on the depths of the low- and high-pressure reservoirs for caverns.

Similar to pressure, temperature increases with depth as given by the geothermalgradient, *G*, making *T* at any depth given by

$$T = T_s + GZ \tag{6}$$

²¹⁷ where, T_s is the temperature at the ground surface.

To estimate saline aquifer reservoir volume, V_s is calculated from the following equations,

220

$$V_{s} = \frac{M_{co_{2}}}{(\rho_{co_{2}}^{\prime} - \rho_{co_{2}}^{\prime\prime})}$$
(7)

221 **3.4 Heat exchanger model**

222 Both inter coolers and heaters of this system are applicable to the following model. 223 The model for the heat-exchange processes involving CO_2 must be divided up into 224 small steps to accommodate the large changes in CO₂ properties that occur as the 225 temperature changes around the CO₂ critical point [39]. In the inter cooler between two 226 compressors, the working fluid on the hot-stream side and cold-stream side are CO₂ and 227 water, respectively. We suppose that the temperature difference ΔT on the hot-stream 228 side is fixed and separated into N equal parts. Therefore, the heat transfer rate for the k-229 th part and mass flow rate of water can be illustrated below,

230
$$\dot{Q}_{he,k} = \dot{m}_{CO_2} C_{P,CO_2,k} \left(T_{CO_2,k} - T_{CO_2,k+1} \right)$$
(8)

231
$$\dot{Q}_{he,k} = \dot{m}_w C_{p,w,k} \left(T_{w,k+1} - T_{w,k} \right)$$
(9)

245

$$\dot{m}_{w} = \frac{\sum_{k}^{N} \dot{Q}_{he,k}}{(h_{w,out} - h_{w,in})} \tag{10}$$

3.5 Heat pump system

The high-temperature heat pump system is composed of a compressor, a condenser, an expansion valve, and an evaporator.

236 **3.5.1** Compressor

Similar to the energy storage compressor, but with R245fa as working fluid instead
of CO₂, the principal calculation is the same as that of energy storage compressor.

239 **3.5.2** Condenser

In the heat pump condenser, the working fluids on both the hot-stream side and cold-stream side are R245fa and water, respectively. The mass flow rate of water is modeled by the equations

$$\dot{Q}_{he} = \dot{m}_{R245fa} C_{p,R245fa} \left(T'_{R245fa} - T''_{R245fa} \right)$$
(11)

244
$$\dot{Q}_{he} = \dot{m}_w C_{p,w} (T_w'' - T_w')$$
(12)

$$\dot{m}_w = \frac{\dot{Q}_{he}}{(h_w' - h_w')} \tag{13}$$

246 **3.5.3 Evaporator**

In the evaporator of heat pump, R245fa is on the cold-stream side and water is on the hot-stream side. The principal calculation is the same as that of the condenser of the heat pump, except that the hot and cold streams are swapped.

250 **3.5.4 Expansion valve**

The expansion valve expands and depresses in the heat pump system and the entropies in the front and rear valves are equal, so the power is zero.

253 4. Performance criteria

To evaluate and compare the performance of the proposed TC-CCES system, we calculate the energy round-trip efficiency, energy storage efficiency, exergy efficiency, and energy generated per unit volume as quantities indicative of performance [40, 41].

257 4.1 Energy analysis

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258 4.1.1 Round-trip efficiency

In general, for an energy cycle, the round-trip efficiency is often used to measure the performance of power unit that has an energy storage component. Round-trip efficiency is defined as the ratio of the electricity output during the recovery phase over the sum of the electricity consumed during the storage phase and the electricity (or equivalent energy) consumed during recovery phase [41], specifically,

$$\eta_{RT} = \frac{E_T}{E_C + \sum E_i} \tag{14}$$

where, E_T is the electricity output in the energy recovery process; E_C represents the total energy consumed during the energy storage process, and $\sum E_i$ is the electricity (or equivalent energy, e.g., natural gas converted into electricity in a conventional CAES power plant) consumed in the recovery process.

In the TC-CCES presented here, the latter term in Eq. (14) is the electricity used to power the heat pump.

271 **4.1.2 Energy storage efficiency**

While round-trip efficiency is a useful measure of the efficiency of a power plant 272 with storage component, it is not a direct measurement of storage efficiency, i.e., how 273 274 much stored energy can be recovered, because the large portion of electricity output may come from added natural gas during recovery in a conventional CAES system. As 275 a result, it may be misleading to compare the efficiency of a CAES system against a 276 battery-based electricity storage system using round-trip efficiency because the natural 277 gas added during recovery in a conventional CAES system is really not a part of storage. 278 To facilitate the comparison of storage efficiency across different type storage systems, 279 we introduce a new performance criterion, named energy storage efficiency, which is 280

defined as the ratio of the net energy that can be recovered from the system over theenergy that consumed during storage:

$$\eta_{ES} = \frac{E_T - \sum E_i}{E_C} \tag{15}$$

where, $E_T - \sum E_i$ is the net energy recovered from storage process.

285 4.1.3 Energy generated per unit volume

The energy generated per unit volume of storage (EGV) for a TC-CCES system with two saline reservoirs is

$$EGV = \frac{E_{GEN}}{V_S} = \frac{W_T \cdot t_{recovery}}{V_S}$$
(16)

289 4.2 Exergy analysis

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Approaches for improving the performance of the system can be found by energy flow analysis. Therefore, we have carried out an exergy analysis to calculate exergy destruction in the TC-CCES system and its components.

The n^{th} component of the system can be described by its exergy balance equation [42, 43]

 $\dot{E}_{d,n} = \dot{E}_{F,n} - \dot{E}_{P,n}$ (17)

where, $\dot{E}_{d,n}$, $\dot{E}_{F,n}$ and $\dot{E}_{P,n}$ are the exergy destruction rate, fuel exergy rate, and the product exergy rate, respectively.

- We define exergy efficiency as
 - $\eta_{EX} = \frac{E_P}{E_F} \tag{18}$

The equations we use to calculate the component-by-component exergy destruction are listed in Table 2. Each component (*n*) of the system has an exergy destruction ratio defined as

303
$$X_{d,n}^* = \frac{\dot{E}_{d,n}}{\dot{E}_{F,n}}$$
(19)

5. Results and discussion

The properties of the system as summarized in Table 3 were used for the simulations and parametric analysis.

307 5.1 Thermodynamic analysis

Due to the use of an underground gas storage environment in the TC-CCES system, 308 the temperature of CO₂ stored in HR may change in three different ways depending on 309 the local geothermal gradient. (1) CO_2 could gain geothermal energy from the rock and 310 become hotter; (2) heat stored in the CO_2 could be absorbed by rock in the HR region 311 and cool; or (3) the CO_2 may neither gain nor lose heat and instead stay at approximately 312 the same temperature. The thermodynamic analysis presented here assumes the first 313 case because HR is likely to be deep whether it is an aquifer or a cavern. The analysis 314 results of the TC-CCES system with heat pump are presented in Table 4, and the results 315 of the power of compressors, turbines and heat pump are shown in Table 5. The results 316 of the system efficiency and EGV are shown in Table 6. A summary of the results of 317 performance criteria of the TC-CCES system and the results in [27] are shown in Table 318 7. The value of η_{RT} and η_{EX} of the TC-CCES system are 66.00% and 67.89%, 319 respectively, which are better than the corresponding 63.35% and 53.02% in [27]. In 320 particular, we find the value of η_{ES} is 58.41%, which is almost three times that in [27]. 321 We also find that the energy generated per unit storage volume (EGV) of this novel TC-322 CCES system is 2.12 kW·h/m³, lower than that in [27], which is 3.07 kW·h/m³. The 323 324 reason can be explained from Table 7. From the data on power distribution in energy recovery process in [27], the power output of the turbine train is derived from two 325

sources: (1) the energy stored by the compression process, and (2) the energy supplied 326 by extra fuel to heat the cold turbine output gas. The total power output of the turbine 327 train is 254.82 kW, and the extra fuel input is 217.86 kW, which accounts for 85.5% of 328 the whole power output, so the net electricity power supplied by the storage process is 329 very low, only 36.96 kW, which accounts for 14.5% of the total power output. 330 Meanwhile, the utilization rate of fuel exergy is as high as 89%. In the novel TC-CCES 331 system with heat pump, no extra fuel energy is input during energy recovery process, 332 but the heat pump requires electricity power equal to 44.24 kW, which accounts for 333 334 28.1% of total output. During the turbine train work in the energy recovery process, and the energy stored by the compression process is supplied to the turbine train making the 335 energy storage efficiency higher than in [27]. The utilization of heat exergy in TR is 336 337 55.1% because of the large use of fuel, the exergy utilization is higher than thermal for the part of using turbine re-heater instead of fuel on the reheating the turbines process, 338 but energy storage efficiency, exergy efficiency and round-trip efficiency of the TC-339 CCES system are larger than that in [27]. According to Eq. (7) and Eq. (16), the value 340 of EGV mainly depends on two parts: (1) the net electricity power output and (2) the 341 density difference between the inlet, and outlet CO₂ in the storage reservoir. In the prior 342 TC-CCES, the value of the density difference is much smaller than that in the TC-CCES 343 system. Hence, the value of EGV in [27] is larger than that in the TC-CCES system. In 344 order to use the TC-CCES, a large underground storage reservoir volume is needed, 345 346 consistent with use of an aquifers or solution-mined caverns.

The exergy destruction percentages for the various system components are depicted in Fig. 4. From Fig. 4, one sees for the TC-CCES system that 44.91% of the irreversibility occurs in TR, 20.46% in HP, 16.63% in IC, 4.95% in C, 4.41% in T, 4.13%
in HR, 3.17% in PC, and 1.32% in LR.

5.2 Sensitivity analysis

From the thermodynamic performance analysis, we find the novel TC-CCES system has high exergy efficiency, energy storage efficiency and round-trip efficiency. The main properties controlling the efficiency and EGV of the system are, the energy storage pressure (inlet pressure of HR), energy recovery pressure (inlet pressure of the T1), and pressure of the LR (outlet pressure of the T3) [44]. We conducted a sensitivity analysis with parameter ranges listed in Table 8 to quantify how performance can be improved.

359 5.2.1 Effect of energy storage pressure

It is noted that the pressure drop across the high-pressure throttle valve maintains 360 2 MPa and stays almost constant. When the energy storage pressure varies from 15 MPa 361 to 25 MPa, the energy recovery pressure will also change, varying from 13 MPa to 23 362 MPa with a 1 MPa increment, while the pressure of LR is set as 1 MPa, and other 363 parameters remain unchanged. As shown in Fig. 5, the overall pressure of the storage 364 system plays a large role in the TC-CCES efficiency. Specifically, the value of η_{RT} , 365 η_{ES} , and η_{EX} increase as energy storage pressure increases. Note that there is a 366 crossover of η_{RT} and η_{EX} at a pressure of 20 MPa. This occurs because an increase 367 in the energy storage pressure leads to an increase of net energy output during the 368 energy recovery process, which can increase the value of EGV. The required volume of 369 the HR is reduced by high energy storage pressure, whereas variation of the power 370 371 output is contrary to that of the required volume. Hence, EGV will rise along with increase of the energy storage pressure. 372

Fig. 6 depicts the changes in the power of the compressor train, turbine train, and heat pump with the changes in energy storage pressure. As the energy storage pressure increases, the output of the heat pump gently increases, whereas the net output of compressor and turbine have stronger growth trends that level off at high pressures. The reason why growth is gradually slowing down is that for the compressor train, as the

storage pressure increases, the CO₂ working fluid changes from a trans-critical state to 378 a supercritical state. Due to the physical properties of the supercritical CO₂ itself, the 379 power consumed by the compressor will reduce and the power output by the turbine 380 will reduce, so both growth rate of the power consumption of the compressor train and 381 output power of the turbine train gradually decreases. Energy storage pressure also 382 383 controls the exergy destruction percentage in the main components. In Fig. 7, it is seen that exergy destruction occurs mainly in TR, HP, and IC, with the largest exergy 384 destruction coming from TR. The inlet pressure of the turbine will grow with the rise 385 of the energy storage pressure, and all other setting parameters held constant. Hence, 386 the temperature difference of the heat exchangers will grow, therefore, the exergy 387 destruction percentage increases from 62.42 kW to 83.89 kW in IC, and decreases from 388 184.6 kW to 176.3 kW in TR. The exergy destruction rate occurring in C, T, and HR 389 have a similar increasing trend with rise in energy storage pressure, which is caused by 390 the pressure difference between the inlet and outlet of each component; the higher the 391 pressure drop is, the larger the exergy destruction will become. 392

393

5.2.2 Effect of energy recovery pressure

394 It is noted that when the pressure of energy recovery changes from 8 MPa to 15 395 MPa with 1 MPa increment, the energy storage pressure and the pressure of LR are set 396 to 17 MPa and 1 MPa while the other setting parameters listed in Table 3 remain 397 unchanged . In Fig. 8 it is illustrated the dependence of η_{RT} , η_{ES} , and EGV with the 398 energy recovery pressure. The value of η_{ES} increases from 41.63% to 58.41%, the 399 value of η_{RT} rises from 52.54% to 62.16%, the value of η_{EX} has a gentle change from 400 66.9% to 68.87%. What's more, the growth in energy recovery pressure will result in a 401 rise in the output power of the turbine train, the pressure drop will decline which causes 402 a smaller volume required for HR. Therefore, the EGV will increase with higher energy 403 recovery pressure.

The effects of energy recovery pressure on the power in the compressor train, turbine train and heat pump are shown in Fig. 9. The power of the compressor train is constant and the power of the turbine train increases rapidly from 124.82 to 157.06 kW with growth of the energy recovery pressure. In addition, the power of the heat pump
mainly depends on the amount of heat exchange required for the reheating of the turbine
during the energy recovery process, whereas it is independent of the energy recovery
pressure. Therefore, the heat pump power requirement is almost constant in the energy
recovery process.

412 Fig. 10 illustrates the influence of energy recovery pressure on the exergy destruction rate of the system components. The exergy destruction rate of TR and PC 413 414 decline with larger energy recovery pressure in the TC-CCES system, which varies from 186.1 kW to 183.6 kW in TR and 21.17 kW to 12.96 kW in PC. The reason is that 415 the exergy destruction of TR and PC are mainly controlled by their temperature 416 differences. In fact, the temperature differences across TR and PC will be smaller with 417 larger energy recovery pressure. Therefore, the exergy destruction in TR and PC will 418 be smaller for greater energy storage pressure in the case that all other parameters 419 remain unchanged. And it can be also found that the exergy destruction of other 420 components change only slightly with energy recovery pressure. 421

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- 423

5.2.3 Effects of pressure in LR

When the pressure in the low-pressure reservoir has a change from 1 MPa to 2 424 425 MPa, with a 0.2 MPa increment, the energy storage pressure and energy recovery pressure are set as 17 MPa and 15 MPa, respectively, and other setting parameters are 426 kept constant. In Fig. 11 it can be observed that as with higher pressure of LR, the values 427 of η_{RT} , η_{ES} , η_{EX} , and EGV of the TC-CCES system are reduced. The maximum 428 429 change is in η_{ES} which decreases from 58.41% to 37.6%, the second largest change is 430 in η_{RT} which reduces from 66.16% to 49.3%, the value of η_{EX} has a gentle decline of 3.54%. When CO₂ in the LR is in a trans-critical state, the pressure change of LR has 431 a greater effect on the change of the CO₂ density, so the volume change of the gas 432 433 storage reservoir becomes larger, the EGV decreases larger. Fig. 12 shows the influence 434 of the pressure of LR on the power of the compressor train, turbine train, and heat pump. With increase of pressure of the LR, the power of the turbine train decreases sharply 435 from 157.06 to 117.16 kW. The reason is that in the case of other design parameters 436

unchanged, the increase of pressure of LR causes the power of each stage of the turbine
to be reduced and the net output of the system to be reduced, while the consumption of
the system compressor remains constant.

The effects of the various components on exergy destruction rate as a function of 440 the pressure of LR are shown in Fig. 13. The analysis shows that the exergy destruction 441 442 rates of TR and PC rise with growing pressure of LR, which increases from 184.5 to 192 kW in TR and from 1.3 to 14 kW in PC. The reason for this increase is that the 443 444 outlet temperature of each turbine increases and the power of the turbine decreases with higher LR pressure and therefore the exergy destruction of TR and PC increases. In 445 addition, the pressure difference becomes larger in LR, which varies from 5.4 to 46.1 446 kW, as pressure in LR increases, making the exergy destruction rate of LR increase. 447

448 **6.** Conclusions

This study contained a thermodynamic analysis of a novel, fossil-fuel-free, TC-CCES system that uses two saline aquifers or caverns for storing compressed CO₂ and that includes two thermal storage tanks and a heat pump system as thermal storage and recovery systems, respectively and an investigation of its operational behavior and efficiency. The main conclusions are:

(1) Under a typical trans-critical operation condition, the round-trip efficiency is
66%, energy storage efficiency is 58.41%, exergy efficiency is 67.89% and EGV is 2.12
kW·h/m³, which indicates a good thermodynamic performance of the novel TC-CCES
system.

458 (2) Sensitivity analysis shows that higher energy storage pressure, energy recovery 459 pressure and lower the pressure of LR will improve the four performance indicators 460 including η_{RT} , η_{ES} , η_{EX} and EGV.

461 (3) By comparing the exergy destruction rate of the main components in the system, 462 we find the exergy destruction rate of the heat exchangers accounts for a large 463 proportion of exergy destruction with 49.3% in TR and 16.46% in IC, respectively. It 464 indicates that significant potential improvement in system performance can be made by 465 optimizing the turbine re-heater exchanger to reduce the exergy destruction rate.

We note finally that the operating efficiency of the system is good, the working parameters are not extreme during operation, and the requirements of the components in the system are reasonable suggesting it may be practical to build and operate this novel fossil-fuel-free trans-critical CO₂ energy storage system.

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Fig. 2 T-S graph of the TC-CCES system



Fig. 3 Schematic of heat pump sub-system





Fig. 4. The exergy destruction in the main components of the TC-CCES system. C = compressor; T = turbine; HR = high-pressure reservoir; LR = low-pressure reservoir; IC =598 inter cooler of compressor; PC = pre-cooler; TR = turbine re-heater; HP = heat pump. 599 600



601 602

Fig. 5 Energy storage pressure control on system efficiency and EGV.



Fig. 6. Energy storage pressure control on power of compressor train, turbine train and heat pump





Fig. 7. Energy storage pressure control on exergy destruction rate.



Fig. 8. Energy recovery pressure control on system efficiency and EGV.



Fig. 9. Energy recovery pressure control on power of compressor train, turbine train and heatpump.



Fig. 10. Energy recovery pressure control on exergy destruction rate.



Fig. 11 Pressure of LR control on efficiency and EGV.





Fig. 12. Pressure of LR control on power of compressor train, turbine train and heat pump.



619 620

Fig. 13 Pressure of LR control on exergy destruction rate.

	Table 1. Physical properties of R245fa.							
	Item	Valu	e	Unit				
	Molecular formula	CHF2CH	2CF3					
	Critical temperature	427.15		К				
	Critical pressure 3.65			MPa				
Boiling temperature		288.0	288.05		K			
	Table 2. Exergy calculation of components in the TC-CCES system							
	Component	$\dot{E}_{F,n}$	$\dot{E}_{P,n}$	$\dot{E}_{d,n}$				
	Compressor	W_c	$\dot{E}_c^{\prime\prime}-\dot{E}_c^\prime$	$\dot{E}_{F,c} - \dot{E}_{P,c}$				
	Turbine	$\dot{E}_T' - \dot{E}_T''$	W_T	$\dot{E}_{F,T} - \dot{E}_{P,T}$				
	Heat exchanger	$\dot{E}'_{hot,HE} - \dot{E}''_{hot,HE}$	$\dot{E}^{\prime\prime}_{cold,HE}-\dot{E}^{\prime}_{cold,HE}$	$\dot{E}_{F,HE} - \dot{E}_{P,HE}$				
	Storage reservoir	\dot{E}'_{SC}	$\dot{E}_{SC}^{\prime\prime}$	$\dot{E}_{F,SC} - \dot{E}_{P,SC}$				
	Valve	\dot{E}_V'	$\dot{E}_V^{\prime\prime}$	$\dot{E}_{F,V} - \dot{E}_{P,V}$				
-	Table 3. Properties of the TC-CCES system							
-	Item			Value	Unit			
	Ambient temperature			298.15	K			
	Inlet temperature of compressor			308.15	K			
	Depth of LR			100	m			
	Depth of HR			1700	m			
	Throttle valve pressure drop in energy recovery process			0.2	MPa			
	Throttle valve pressure drop in energy storage process			2	MPa			
	Inlet temperature of cooling water			298.15	K			
	Inlet pressure of cooling water			0.2	MPa			
	Inlet pressure of compressor			0.8	MPa			
	Outlet pressure of the third stage compressor			17	MPa			
	Outlet pressure of the third stage turbine			1	MPa			
	Isentropic efficiency of compressor			86	%			
	Isentropic efficiency of turbine			88	%			

Table 4. Material stream parameters of TC-CCES system

Stream No.	Temperature (K)	Pressure(MPa)	Mass flow rate (kg/h)
1	308.15	0.8	3600
2	395.85	2.216	3600
3	308.15	2.216	3600
4	399.95	6.138	3600
5	308.15	6.138	3600
6	396.85	17	3600
7	447.65	17	3600
8	441.75	15	3600
9	363.39	6.084	3600
10	423.15	6.084	3600
11	352.44	2.467	3600
12	423.15	2.467	3600
13	357.29	1	3600
14	361.29	1	3600
15	298.15	0.2	829.4
16	385.85	0.2	829.4
17	298.15	0.2	1110
18	389.95	0.2	1110
19	298.15	0.2	781.2
20	351.30	0.2	781.2
21	377.75	0.2	2721
22	377.75	0.1	3600
23	433.15	0.2	5164
24	406.35	0.1	5164
25	433.15	0.2	5540
26	407.45	0.1	5540
27	406.95	0.1	10700
28	363.15	0.1	3600
29	406.65	0.68	3600
30	435.85	1.7	3600
31	387.75	1.1	3600
32	377.05	0.3	3600

Table 5. Results of the main components in the TC-CCES Term Unit Value 73.77 C1 power kW C2 power kW 68.14 C3 power kW 51.23 T1 power kW 49.18 T2 power kW 52.21 T3 power kW 55.67 kW Heat pump power 44.24 631 632 Table 6. Results of the performance criteria of the TC-CCES Item Unit **TC-CCES** Ref.[27] Energy storage efficiency % 20.04 58.41 Round-trip efficiency % 63.35 66.00 Exergy efficiency % 67.89 53.02 EGV 2.12 3.07 kW·h/m³ 633 634 Table 7. The power distribution in recovery process of the TC-CCES Item Unit **TC-CCES** Ref.[27] Whole electricity output kW 157.48 254.82 Extra fuel input kW 0 217.86 44.24 0 Consume electricity kW Net electricity recovered from storage kW 113.24 36.96 635 636 Table 8. Ranges of parameters for the sensitivity analysis Parameters Unit Range Energy storage pressure MPa 16-25 8-15 Energy recovery pressure MPa Pressure of LR MPa 1.0-2.0 637 Nomenclature Т Temperature (K) Р Pressure (MPa) W Power (kW) Ε Electricity power (kW·h) Ò Heat transfer rate (kW) C_{p} Specific heat capacity at constant pressure (kJ/(kg K)) G Geothermal gradient (K/km) 'n Mass flow rate (kg/h) VVolume (m³) Ζ Reservoir depth (m)

t

Δ

Greek symbols

Time (h)

Change quantity

η	Efficiency				
ρ	Density (kg/m ³)				
Subscripts					
Т	Turbine				
С	Compressor				
i	Stage of compressor				
j	Stage of turbine				
'	Inlet stream				
"	Outlet stream				
Abbreviatio	Abbreviations				
CO ₂	Carbon dioxide				
TC-CCES	Trans-critical compressed CO ₂ energy storage				
CCES	Compressed CO ₂ energy storage				
CAES	Compressed air energy storage				
A-CAES	Adiabatic CAES				
AA-CAES	Advanced adiabatic CAES				
HP	Heat pump				
HR	High-pressure reservoir				
IC	Inner cooler exchanger				
PC	Pre-cooler exchanger				
TR	Turbine re-heater exchanger				
С	Compressor				
Т	Turbine				
LR	Low-pressure reservoir				