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1	Thermodynamic analysis of a compressed carbon dioxide energy storage system
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32	Abstract: Compressed air energy storage (CAES) is one of the leading large-scale
33	energy storage technologies. However, low thermal efficiency and low energy storage
34	density restrict its application. To improve the energy storage density, we propose a
35	two-reservoir compressed CO2 energy storage system. We present here
36	thermodynamic and parametric analyses of the performance of an idealized
37	two-reservoir CO ₂ energy storage system under supercritical and transcritical
38	conditions using a steady-state mathematical model. Results show that the
39	transcritical compressed CO ₂ energy storage system has higher round-trip efficiency
40	and exergy efficiency, and larger energy storage density than the supercritical
41	compressed CO ₂ energy storage. However, the configuration of supercritical
42	compressed CO ₂ energy storage is simpler, and the energy storage densities of the two
43	systems are both higher than that of CAES, which is advantageous in terms of storage
44	volume for a given power rating.

45 Key words: Subsurface energy storage; Compressed CO₂ energy storage system;
46 Utilization of CO₂; Two saline aquifers reservoirs; Thermodynamic analysis;
47 Parametric analysis.

Н	enthalpy, kJ/kg		
S	entropy, kJ/(kg·K)		
Р	pressure, MPa		
Ė	exergy, kW		
Т	temperature, K		
T_s	surface temperature, K		
W	shaft work, kW		
$C_{ m p}$	specific heat capacity at constant pressure, $kJ/(kg\cdot K)$		
Ggeothermal gradient, K/kmVvolume, m³			
		'n	mass flow rate, kg/s
Ż	heat transfer, W		
Ζ	depth of saline reservoir, m		
Abbreviations			
A-CAES	adiabatic CAES		
AA-CAES	advanced adiabatic CAES		
С	compressor		
CAES	compressed air energy storage		
CCES	compressed CO ₂ energy storage		
HE	heater		
HS	high pressure reservoir		

LS	low pressure reservoir		
PM-CAES	porous media CAES		
RE	recuperator		
SC-CCES	supercritical compressed CO ₂ energy storage		
SC-CO ₂	supercritical CO ₂		
Т	turbine		
TC-CCES	transcritical compressed CO ₂ energy storage		
TC-CO ₂	transcritical CO ₂		

Greek symbols

$eta_{ m p}$	pore compressibility, Pa ⁻¹
$\beta_{ m w}$	change in brine density
η	efficiency
τ	temperature difference, K
ρ	density, kg/m ³

Subscripts

S	isentropic process
Comp	compressor
1	inlet stream
2	outlet stream
Т	turbine
NG	nature gas
F	fuel

tot	total
D	destruction
L	loss

49 **1. Introduction**

50 In recent years, renewable energy, particularly wind power and solar photovoltaic (PV) generation has demonstrated robust growth-worldwide motivated by concerns about 51 energy security and climate change due to CO₂ emission levels^[1-2]. But Renewable 52 53 energy sources (e.g., solar and wind energy) exhibit significant and uncontrollable 54 intermittency during power production. When these renewable energy sources are 55 connected to an electrical grid, they can cause serious safety problems for the grid; 56 hence, it is difficult to deliver power from renewable energy sources that instantly matches electricity demand^[3]. 57

58

59 To solve this dilemma and develop renewable energy sources further, viable energy 60 storage systems (ESS) are required. For example, an efficient ESS can increase the 61 penetration of wind power generation by controlling wind power plant output and 62 storage, in addition to providing ancillary services to the power system^[4-5].

63

On a utility scale, compressed air energy storage (CAES) is one of the technologies with the highest economic feasibility with potential to contribute to a flexible energy system with an improved utilization of intermittent renewable energy sources^[1]. The feasibility of using CAES to integrate fluctuating renewable power into the electricity grid has been proven by many researchers^[6-9]. Bosio and Verda^[6] analyzed the thermo-economics of a CAES system integrated into a wind power plant in the framework of the Italian Power Exchange market, which showed that a hydroelectric power plant (HPP)-CAES system was cost-effective in terms of solving local imbalances of the grid. Clearly et al.^[7] evaluated the economic benefits of CAES in mitigating wind curtailment. They showed that both wind curtailment levels and wind-farm total annual generation costs could be decreased. Arabkoohsar et al.^[8-9] simulated and analyzed CAES equipped with a solar heating system. The results showed that CAES could increase the efficiency and reliability of a PV plant.

77

However, the main drawbacks of a CAES system include its low thermal efficiency 78 79 (e.g., Huntorf CAES plant efficiency is 42% and AA-CAES efficiency is about $70\%^{[10]}$), CO₂ emissions from combustion of natural gas in the recovery system for 80 81 conventional CAES, the need for high temperature thermal storage and temperature 82 resistant materials for adiabatic CAES (A-CAES). These factors limit further development of CAES. Although large-scale caverns are also required for CAES as it 83 84 is carried out today, porous media systems such as aquifers and depleted natural gas 85 reservoirs, so-called porous media CAES (PM-CAES) systems, offer much more storage capacity^[11]. 86

87

Thermodynamic analyses of CAES systems have been performed to optimize these systems and improve their thermal efficiency. For example, Buffa et al.^[12] conducted an exergy analysis of A-CAES and found that exergy destruction mostly occurred in the compressors and coolers. Proczka et al.^[13] analyzed the effects of pressure and the

efficient sizing of pressure vessels on CAES. Zhang et al.^[14-15] analyzed the 92 93 thermodynamic effects of thermal energy storage (TES) and the air storage chamber model on a CAES system. Jubeh and Najjar et al.^[16] explored the effects of operating 94 95 variables on A-CAES performance. Najjar and Zamout analyzed the effects of dry regions on the performance of a CAES plant^[17]. The operation, experience, and 96 characteristics of Huntorf CAES were also investigated^[18]. Thermodynamic analyses 97 98 have shown that, both, decreasing the exhaust temperature and using heat of 99 compression during expansion can significantly improve CAES efficiency.

100

101 Several novel CAES systems have been proposed that reduce waste heat. A 102 recuperator was utilized to capture heat from the turbine exhaust, which could reduce the fuel consumption of the McIntosh plant by 25%^[19-20]. Safaei and Keith^[17] 103 proposed a distributed CAES (D-CAES) system that placed compressors near heat 104 demand loads to recover the heat generated during the compression stage. Liu^[2] 105 106 proposed a modified A-CAES system that used a pneumatic motor instead of a low 107 pressure turbine (LT) to reduce the exhaust temperature caused by LT, and the exergy efficiency can be improved by nearly 3% compared with that of the conventional 108 A-CAES system. Guo et al.^[21] proposed a novel A-CAES system in which an ejector 109 110 was integrated into an A- CAES system to recover pressure reduction losses; energy 111 conversion efficiency could reach 65.36%. Several demonstration A-CAES plants 112 have been built, such as a 1.5 MW A-CAES in China, where initial experimental tests 113 are on-going. An A-CAES technology that uses reversible reciprocating piston

machines is being developed by LightSail Energy Ltd. in the U.S. Other new systems include a tri-generation system based on compressed air and thermal energy storage^[22], biomass-fueled CAES, isobaric adiabatic CAES with combined cycle^[23], combined cooling, heating and power system based on small-scale CAES^[24], CAES using a cascade of phase change materials^[25], CAES combined with solar thermal capture^[26], integrating CAES with diesel engine^[27], and compressed carbon dioxide energy storage^[28].

121

Although thermal efficiency can be improved by various methods, CAES has low 122 energy density and requires large-scale storage reservoirs^[29]. To overcome these 123 124 restrictions, several studies have been conducted on novel energy storage technologies. For instance, Kim^[30] proposed a constant-pressure CAES system combined with 125 pumped hydro-storage to reduce the cavern volume. Guo et al.^[31] presented a 126 supercritical compressed air energy storage (SC-CAES). Oldenburg and Pan^[11] 127 128 modeled a porous media CAES (PM-CAES) system that uses aquifers or depleted 129 natural gas reservoirs for storage. Underwater compressed air energy storage (UWCAES) stores the compressed air under water by using a large elastic bladder^[32]. 130 Small scale CAES (SS-CAES) that stores high-pressure air in a tank or an 131 underground pipeline was also proposed^[33]. Each of these novel approaches brings 132 with it additional requirements and limitations. 133

134

135 As popularly known, CAES is derived from the Brayton cycles, and gases like CO₂

136 that are non-ideal at operating conditions are more efficient in a Brayton cycle^[34].

137

Using CO_2 as the working fluid in a compressed gas energy storage system can also achieve better performance than AA-CAES^[35]. At the same time geological CO_2 sequestration in deep formations (e.g., saline aquifers, gas and oil reservoirs, and coal beds) is a promising measure for reducing greenhouse gas emissions^[36]. Therefore, the combination of compressed gas energy storage in the deep subsurface and large-scale utilization of CO_2 is both possible and beneficial.

144

145 Although, some research has been conducted on energy power cycle and energy storage systems based on CO_2 and liquid $CO_2^{[28,35]}$, we are not aware of published 146 analyses of energy storage systems based on transcritical CO₂ (transition from 147 148 supercritical to gas) or based on supercritical CO₂ throughout the cycle. Therefore, the 149 innovation of this paper resides in the exergy analysis of a closed-loop gas storage system, conceived by two of us (Borgia and Oldenburg in January of 2012), which 150 151 comprises two reservoirs, in this case in saline aquifers but which could also be in 152 caverns, located at different depths and uses transcritical and supercritical CO₂ as the 153 working fluid. This novel energy storage system can be used in two different energy 154 cycles (e.g., transcritical CO₂ energy storage cycle, and supercritical CO₂ energy 155 storage cycle) according to the physical state of CO_2 in the process. We conducted 156 energy and exergy analyses to understand the thermal properties of the compressed 157 CO₂ energy storage system. In addition, parametric analysis was performed to investigate the effects of the physical conditions of two saline aquifer reservoir (e.g.,
energy storage pressure, energy releasing pressure, and pressure of low-pressure
reservoir) on system performance.

161

162 **2. System description**

The proposed compressed CO_2 energy storage system using two saline aquifers as 163 storage reservoirs is a closed energy-storage cycle. The first reservoir is a 164 165 low-pressure reservoir used to store CO₂ exhausted from the turbine, whereas the second reservoir is at higher pressure to store CO_2 from the compressor. This energy 166 167 storage system, although based on the same principles, can be operated in two 168 different ways according to the state of CO_2 , (1) by allowing the CO_2 to transition 169 from supercritical to gaseous conditions in the turbine, which we refer to as the 170 transcritical compressed CO₂ energy storage (TC-CCES) system, and (2) by keeping 171 the CO_2 above the critical pressure throughout the cycle, which we refer to as the 172 supercritical compressed CO₂ energy storage (SC-CCES) system. The schematic and 173 T-S diagram of compressed CO_2 energy storage (CCES) is shown in Figs. 1 and 2.

174

175 1: During off-peak hours, the working fluid (low-pressure CO₂) stored in a shallow
176 low-pressure reservoir is removed, pressurized, and injected into a deeper
177 high-pressure reservoir using surplus renewable power, such as that from wind or
178 solar.

179 2: For multi-stage compressor, the heat of compression of the CO_2 is absorbed by a 180 cooling fluid which is stored in a TES system, while the CO_2 from the last stage 181 compressor is directly injected into the high-pressure storage reservoir.

- 182 3: During peak hours, the high-pressure CO_2 is regulated to a certain pressure through
- 183 the throttle valve, and is transported to the recuperator system to absorb the heat
- 184 exhausted from the turbine in the TES.
- 185 4: The heated high-pressure CO_2 is fed into the turbine.

186 5: The high pressure CO_2 expands through the turbine generating shaft work.

- 187 6: The exhaust CO₂ is stored in the low-pressure reservoir.
- 188

189 Considering that because of the geothermal gradient the temperature of the saline-aquifer reservoirs increases with depth, the output CO₂ from the compressor 190 191 stage can be directly injected into the high-pressure reservoir storing, both heat and CO₂ directly into the rock formation. Therefore, the proposed SC-CCES does not 192 193 need a TES to store the compressed heat generated during compression, implying that 194 the aftercooler is theoretically unnecessary. In our analysis, though, to allow a direct 195 comparison with CAES and highlight the benefits of the two-reservoir CCES system, 196 we retain the heater.





Fig.1. Schematic illustration of CCES using two saline-aquifer reservoirs.



Fig.2. CCES using two saline aquifers reservoirs. a. The schematic of TC-CCES. b. The schematic of SC-CCES. c. *T-S* diagram of TC-CCES. d. *T-S* diagram of SC-CCES. C = compressor; RE = recuperator; T = turbine; HE = heater; LS = low pressure reservoir; and HS = high pressure reservoir.

205 **3. Theoretical model**

- 206 The following assumptions are made to simplify the theoretical model of the
- 207 compressed CO₂ energy storage cycle:
- 208 1. The pressure drop and heat loss in the pipes, heat exchanger, TES, and recuperator
- are ignored.
- 210 2. The compressor and the turbine have a given isentropic efficiency.
- 3. Changes in kinetic energy and potential energy are negligible relative to the stored
- energy.
- 4. The storage in the two saline aquifers is considered a closed system at hydrostatic
- 214 pressure.
- 215 5. The mass flow rate of CO_2 is the same in the storage and recovery modes of
- 216 operation, and for TC-CCES and SC-CCES.

217 **3.1. Compressor model**

218 The isentropic efficiency of compressor η_{comp} is,

219
$$\eta_{\rm comp} = \frac{h_{2s} - h_1}{h_2 - h_1}, \tag{1}$$

220

where h_1 is inlet enthalpy and h_{2s} is outlet enthalpy during isentropic compression, h_2 is the real enthalpy during compression.

222

221

During isentropic compression, the entropies of the initial and final states are the same, 223 i.e.,

$$s_{2s} = s_1,$$
 (2)

The corresponding enthalpy of the outlet stream at the end of isentropic compression can be calculated from the property relationship, f, which is derived from the equation of state,

228

225

$$h_{2s} = f\left(s_{2s}, p_2\right),\tag{3}$$

The actual enthalpy of the pressurized CO_2 at the outlet of the compressor can be calculated using the definition of compression efficiency. Hence, the power consumed, w_{comp} , is,

232
$$w_{\rm comp} = h_2 - h_1$$
, (4)

233 **3.2. Heat exchanger model**

The properties, such as density, specific heat, and viscosity are observed to undergo drastic variations within a very narrow range of temperature if the CO₂ is under supercritical pressure, which will have a great effect on system performance. Therefore, it is essential to divide the heat exchanging process into adequately small sections, such that property variations in each section are so small that constant properties can be assumed ^[37].

240

The inner cooler, pre-cooler, and recuperator function together as the heat exchanger. For the inner and pre-cooler, we assumed that the upper terminal temperature difference $\Delta \tau_{upper}$, and inner and pre-cooler temperatures are both constant. To obtain the amount of compressed heat, the overall temperature change for CO₂ is divided into *N* equal differences $\Delta \tau$. The specific heat at constant pressure at each intermediate state is determined from the known pressure and temperature. The heat
transfer for each step *i* and mass flow rate of water are calculated from the following
equations:

249
$$\dot{Q}_{i} = \dot{m}_{CO_{2}}C_{P,CO_{2},i}\left(\tau_{CO_{2},i+1} - \tau_{CO_{2},i}\right), \tag{5}$$

250
$$\dot{Q}_i = \dot{m}_{\text{water}} C_{P,\text{water},i} \left(\tau_{\text{water},i+1} - \tau_{\text{water},i} \right), \tag{6}$$

251
$$\dot{m}_{water} = \frac{\sum_{i}^{N} \dot{Q}_{i}}{(h_{water,out} - h_{water,in})} , \qquad (7)$$

For the recuperator, we assumed that lower terminal temperature difference, $\Delta \tau_{\text{lower}}$, is constant. Also the enthalpy change for hot streams is divided into *N* equal differences Δh . The cooling working fluid temperatures of preheater and recuperator at each intermediate state can be determined using the CoolProp database from the known enthalpy and pressure.

257 **3.3. Aquifer CO₂ storage model**

To inject CO_2 into a saline aquifer reservoir, the CO_2 pressure has to be at least as high as the initial groundwater pressure in the reservoir. In the present study, the CO_2 pressures in the low-pressure reservoir and high-pressure reservoir are assumed to exhibit hydrostatic variation with depth at a constant pressure gradient.

262

The geothermal gradient (underground temperature increases with depth) will control the temperature of the reservoir. Using values for the surface temperature and geothermal gradient, the underground temperature as a function of depth can be determined by,

269

 $267 T=T_s+Gz, (8)$

268 where T_s is the surface temperature; G is the geothermal gradient; z is the depth.

270 We assume the saline aquifer is a closed-storage formations^[36]. To estimate aquifer

271 storage reservoir volume, $V_{\rm S}$, the following equation is used,

272
$$V_{\rm s} = \frac{M_{\rm co_2}}{(\beta_{\rm P} + \beta_{\rm W})\rho_{\rm co_2}\Delta P},$$
 (9)

where M_{CO2} and ρ_{CO_2} are respectively the mass and density of CO₂ at reservoir conditions; Δp is the pressure buildup from beginning to the end of injection; β_p is the pore compressibility; β_w is the change in brine density.

276 **3.4. Turbine model**

The calculation method for the actual expansion is the same as that for compression.

278 The isentropic efficiency of the turbine can be calculated using,

279

280
281
i.e.,

 $\eta_{\rm t} = \frac{h_3 - h_{4s}}{h_3 - h_4},$

(10)

$$s_{4s} = s_3,$$
(11)
The corresponding enthalpy of the outlet stream at the end of isentropic expansion can
be calculated from the property relationship, *f*, which is derived from the equation of
state. That is,
(12)

286
$$h_{4s} = f(s_{4s}, p_4),$$
 (12)

287 The actual enthalpy of the pressurized CO_2 at the outlet of the compressor can be

calculated using the definition of expansion efficiency. Thus, expansion work can becalculated using,

290
$$w_{\rm T} = h_3 - h_4,$$
 (13)

291 **4. Performance`criteria**

To analyze the performance of compressed CO_2 energy storage using two saline aquifers as reservoirs, exergy efficiency, exergy destruction, round-trip efficiency, and energy storage density are introduced as the performance criteria of the overall system and the main components^[2,38].

296 **4.1. Energy analysis**

297 4.1.1. Round-trip efficiency

298 To facilitate comparisons of the novel energy storage system to other electrical 299 storage devices, the round-trip efficiency of energy storage is defined as^[38-39],

300
$$\eta_{RT,1} = \frac{E_{\rm T}}{E_{\rm C} + \eta_{\rm NG} E_{\rm F}},$$
 (14)

301 where $E_{\rm T}$ represents the electricity output; $E_{\rm C}$ represents the electricity input; $\eta_{\rm NG}E_{\rm F}$ 302 represents the amount of electricity that could have been made from the natural gas 303 input $E_{\rm F}$, if that fuel had been used to make electricity in a stand-alone power plant at 304 efficiency $\eta_{\rm NG}$ instead of to fire an energy storage unit, $\eta_{\rm NG} = 47.6\%^{[38]}$. 306 Determining the amount of electrical energy that can be produced per unit volume of 307 storage capacity (E_{GEN}/V_S) is essential to evaluate the geological requirements for 308 compressed gas energy storage. The energy produced per unit volume for compressed 309 CO₂ energy storage with two saline reservoirs is,

310
$$E_{\text{GEN}}/V_{\text{s}} = \frac{w_{\text{t}} \left(\beta_{\text{P}} + \beta_{\text{W}}\right) \left(\rho_{1,\text{CO}_{2}} \Delta P_{1} + \rho_{2,\text{CO}_{2}} \Delta P_{2}\right)}{2}, \quad (15)$$

311 **4.2. Exergy analysis**

312 The general exergy balance for the overall system is $^{[40-41]}$,

313
$$\dot{E}_{\rm F,tot} = \dot{E}_{\rm P} + \sum_{k} \dot{E}_{\rm D,k} + \dot{E}_{\rm L},$$
 (16)

where $\dot{E}_{\text{F,tot}}$, \dot{E}_{P} , $\sum_{k} \dot{E}_{\text{D},k}$, and \dot{E}_{L} represent the total amount rate of fuel exergy, product exergy, exergy destruction, and exergy loss associated with the overall considered system, respectively.

317

The general exergy balance of the k^{th} component of the overall system can be expressed as follow:

320 $\dot{E}_{\mathrm{D},k} = \dot{E}_{\mathrm{F},k} - \dot{E}_{\mathrm{P},k},$ (17)

where $\dot{E}_{D,k}$, $\dot{E}_{F,k}$, and $\dot{E}_{P,k}$ represent the exergy destruction rate, the fuel exergy, and the product exergy rate within the k^{th} component, respectively. Exergy efficiency is defined as,

324
$$\eta_{\rm ex} = \frac{E_{\rm F,tot} - \sum E_{\rm D,k} - E_{\rm L}}{E_{\rm F,tot}} = \frac{E_{\rm p}}{E_{\rm F,tot}}, \qquad (18)$$

325 Exergy destruction in each component of the system can be calculated using the 326 equations listed in Table 1. To compare the exergy destruction of dissimilar 327 components, the exergy destruction ratio of the k^{th} component is defined as

328
$$y_{\mathbf{D}k}^* = \frac{\dot{E}_{\mathbf{D},k}}{\dot{E}_{\mathbf{D},tot}},\tag{19}$$

Component	Schematic view	$\dot{E}_{\mathrm{F},k}$	$\hat{E}_{\mathbf{P},k}$	$\dot{E}_{\mathrm{D},k}$
Compressors		W	$\dot{E}_{2,C} - \dot{E}_{1,C}$	$\dot{E}_{\mathrm{F,C}} - \dot{E}_{\mathrm{P,C}}$
Storage		Ė	Ė	Ė į
cavern		£1,5C	£2,SC	E _{FSC} - E _{PSC}
Heater	1 Heater 2	$\dot{E}_{ m QH}$	$\dot{E}_{2,\mathrm{H}}-\dot{E}_{1,\mathrm{H}}$	$\dot{E}_{\mathrm{F,H}}-\dot{E}_{\mathrm{P,H}}$
Heat		<u> </u>	\dot{F} – \dot{F}	<u> </u>
exchanger		²² 3,не ²² 4,не	2,HE 21,HE	^{де} б,не ^{де} р,не
Turbine		$\dot{E}_{1,\mathrm{T}} - \dot{E}_{2,\mathrm{T}}$	W	$\dot{E}_{\rm F,T} - \dot{E}_{\rm P,T}$

Table 1. Exergy calculation in each component of the novel system.

330 5. Results and discussions

331 The simulations for the parametric analysis of the compressed transcritical and 332 supercritical CO_2 energy storage are carried out using a MATLABTM with the 333 thermodynamic properties of the working fluid calculated through CoolProp^[42]. The 334 design parameters and detailed conditions for the simulation and analysis of the compressed gas energy storage are summarized in Table 2.

336 **5.1. Thermodynamic analysis**

337 The detailed results of the analysis of compressed CO_2 energy storage using two 338 saline aquifers as reservoirs are presented in Tables 3 and 4, which show the 339 thermodynamic parameters at each node of the two storage systems, respectively. A 340 summary of the results of the energy and exergy analyses are provided in Table 5. The 341 round-trip efficiency and exergy efficiency of compressed transcritical CO₂ energy 342 storage is better than those of the compressed supercritical CO₂ energy storage. 343 Moreover, the compressed transcritical CO_2 energy storage has a higher energy 344 density (E_{GEN}/V_S) than the compressed supercritical CO₂ energy storage. In addition, the energy densities (E_{GEN}/V_S) of the two systems can reach 497.68 kWh/m³ 345 (transcritical CO₂) and 255.20 kWh/m³ (supercritical CO₂), which are better compared 346 with that for CAES $(E_{GEN}/V_S = 2-20 \text{ kWh/m}^3)^{[38]}$ because more energy can be stored 347 348 in a given reservoir. The reason that the energy storage density using transcritical CO_2 is much larger than that of supercritical CO₂ comes from the fact that the output work 349 350 of compressed transcritical CO₂ energy storage is more than two times larger than that 351 of compressed supercritical CO_2 energy storage. According to Eq. (15), the energy 352 storage density is mainly a function of w_t under the same reservoir conditions. The w_t 353 of transcritical compressed CO_2 energy storage and supercritical compressed CO_2 354 energy storage are 254.82 kW and 123.58 kW, respectively. Therefore, the energy 355 storage density using transcritical CO₂ is about two times as large as that of

supercritical CO₂ under a pressure of 40 MPa. 356

358	Fig. 3 shows the exergy destruction ratio of the different components of the
359	compressed CO_2 energy storage under simulation conditions. For the compressed
360	transcritical CO_2 energy storage, 54.37% of the irreversibility takes place in the heater,
361	11.98% in the low pressure reservoir, 10.93% in the compressor, 9.78% in the turbine,
362	9.52% in the recuperator, 3.42% in the high pressure reservoir. However, for the
363	compressed supercritical CO_2 energy storage, the largest exergy destruction is
364	contributed by high pressure reservoir, which exceeds 33.37% of the total exergy
365	destruction of the system. Secondly the heater brings larger exergy destruction, which
366	accounts for 20.98% of total exergy destruction.

367	Table 2 P
307	Table 2. Fa

Parameter	Value	Unit
Ambient temperature	308.00	K
Pressure drop in throttle valve in compression process	0.50	MPa
Inlet temperature	313.00	K
Outlet pressure of compressor train	25.00	MPa
Temperature of cooling water	308.00	Κ
Pressure drop in throttle valve in expansion process	5.00	MPa
Outlet temperature of heater	873.00	Κ
Outlet pressure of turbine train in supercritical cycle	8.00	MPa
Outlet pressure of turbine train in transcritical cycle	2.00	MPa
Isentropic efficiency of compressor	0.85	/
Isentropic efficiency of turbine	0.87	/
SCO ₂ Depth of low pressure reservoir	760.00	Μ
SCO ₂ Depth of high pressure reservoir	3000.00	Μ
TCO ₂ Depth of low pressure reservoir	200.00	Μ
TCO ₂ Depth of high pressure reservoir	3000.00	Μ

Parameters setting in the compressed CO₂ energy storage with two reservoirs.

Streams	Material stream	<i>T</i> (K)	<i>p</i> (MPa)	<i>h</i> (kJ/kg)	s(kJ/kg·K)	<i>e</i> (kJ/kg)
1	CO_2	308.05	1.50	501.50	2.23	153.86
2	CO_2	405.37	4.49	580.00	2.26	223.17
3	CO_2	313.00	4.49	473.80	1.96	209.00
4	CO_2	413.74	13.43	541.34	1.98	268.86
5	CO_2	313.00	13.43	289.61	1.27	237.68
6	CO_2	345.89	40.18	328.34	1.28	271.07
7	CO_2	382.16	20.00	446.52	1.69	267.18
8	CO_2	587.11	20.00	744.79	2.33	392.83
9	CO_2	540.60	12.62	704.10	2.34	279.87
10	CO_2	873.00	12.62	1101.81	2.91	505.91
11	CO_2	669.75	2.00	873.09	2.96	345.20
12	CO_2	387.16	2.00	574.82	2.39	174.06

Table 3. Thermodynamic data for the material streams of the compressed transcritical 369 CO_2 energy storage.

370 371

372

Table 4.Thermodynamic data for the material streams of the compressed supercritical CO₂ energy storage.

Streams	Material stream	<i>T</i> (K)	p(MPa)	<i>h</i> (kJ/kg)	s(kJ/kg·K)	e(kJ/kg)
1	CO_2	307.83	7.40	400.71	1.66	228.07
2	CO_2	432.61	40.18	484.96	1.69	302.86
3	CO_2	382.16	20.00	446.52	1.69	267.18
4	CO_2	699.02	20.00	882.22	2.54	437.04
5	CO_2	873.00	20.00	1097.20	2.81	568.41
6	CO_2	763.71	8.04	973.57	2.84	437.31
7	CO_2	387.16	8.04	537.87	2.05	243.42

373

374 375

Table 5. Results of the material streams of the transcritical and supercritical compressed CO_2 energy storage

1		Value of	Value of
Ierm	Unit	TC-CCES	SC-CCES
C1 power	kW/kg	78.37	83.81
C2 power	kW/kg	67.46	-
C3 power	kW/kg	38.56	-
T1 power	kW/kg	103.62	123.58
T2 power	kW/kg	151.20	-
Thermal energy input	kJ/s	457.70	240.73
Round-trip efficiency	%	63.35	62.28
Exergy efficiency	%	5302	51.56
E_{GEN}/V_S	kWh/m ³	497.68	255.20



376

Fig. 3. The exergy destruction ratio of main components. a. transcritical compressed CO₂ energy storage. b. supercritical compressed CO₂ energy storage. C = compressor; RE = recuperator; T = turbine; HE = heater; LS = low pressure reservoir; and HS = high pressure reservoir.

381 **5.2. Sensitivity analysis of key thermodynamic parameters**

382 Based on above analysis, the main advantage of CCES using two saline aquifers 383 reservoirs is the high energy-storage density. Energy storage pressure (outlet pressure 384 of last-stage compressor), release pressure (inlet pressure of first stage-turbine), and 385 pressure of the low-pressure reservoir (outlet pressure of last-stage turbine) are primary and significant parameters that influence the energy storage density. 386 387 Therefore, conducting a parametric analysis to understand the effects of these various 388 parameters on the performance of the storage system is essential, and parameters 389 range of variation are shown in Table 6.

Parameters	Range of variation
Energy storage pressure /MPa	40-56
Energy releasing pressure /MPa	10-26
Pressure of low pressure reservoir /MPa	2-10

Table 6. The parameters of the compressed CO₂ energy storage system.

391 5.2.1. Effects of the energy storage pressure

Fig. 4 illustrates the effect of the energy storage pressure on round-trip efficiency and 392 393 exergy efficiency. The round-trip efficiency and exergy efficiency of the TC-CCES 394 and SC-CCES increase along with the increase in the energy storage pressure. 395 Moreover, the round-trip efficiency and exergy efficiency of SC-CCES are higher 396 than those of TC-CCES when the energy storage pressure is higher than 44 MPa. And 397 the round-trip efficiency is even higher than the exergy efficiency. The reason is that for the round-trip efficiency, the input energy is electricity which includes the 398 399 consumption electricity of compressors and the conversion terms, as shown in Eq. 400 (14). However, for the exergy efficiency, the input exergy consists of two terms: 401 electricity exergy and thermal exergy, as shown in Eq. (18). According to the second 402 law of thermodynamics, the thermal exergy calculated by the input thermal energy 403 multiplied by the Carnot efficiency. The Carnot efficiency will be larger than the η_{NG} 404 when the other exergy destructions happened in power plant are considered. Therefore, 405 the round-trip efficiency is higher than the exergy efficiency.



Fig. 4. Effect of energy storage pressure on round-trip efficiency and exergy

efficiency.

408

409

410 The effect of energy storage pressure on energy storage density is shown in Fig. 5. An 411 increase in the energy storage pressure increases net energy output during discharge, 412 which can increase energy storage density. According to Eq. (15), energy storage 413 density is determined by the work output during expansion and the volume of the 414 two-saline aquifers reservoirs. A high energy storage pressure will reduce the required 415 volume of the high-pressure reservoir, whereas the change in the work output is 416 opposite to that of required volume. Therefore, energy storage density will increase 417 along with the increase in the energy storage pressure for TC-CCES and SC-CCES.



418

419 420

Fig. 5. Effect of the energy storage pressure on the energy storage density.

421 Fig. 6 shows the effect of the energy storage pressure on the exergy destruction rate of 422 the main components in TC-CCES and SC-CCES, respectively. The results of the 423 exergy analysis indicate that exergy destruction is mainly contributed by HE and RE 424 in TC-CCES, and the largest exergy destruction is contributed by HS, HE and RE in 425 SC-CCES. Moreover, the rate of RE exergy destruction decreases with the increase in 426 the energy storage pressure, whereas the change in the HE exergy destruction rate is 427 opposite to that of RE in the two energy storage systems. The outlet pressure of the 428 turbine is constant; hence, the outlet temperature of the turbine will decrease with the 429 increase in the energy storage pressure, which will result in a smaller temperature 430 difference in RE. A low outlet temperature of the turbine will lead to a low inlet 431 temperature of HE; hence, the temperature difference will be increased. Therefore, more heat is needed to heat the CO_2 in the heater. The exergy destruction of RE is 432

433 mainly contributed by the temperature difference between hot and cold working fluids. 434 The exergy destruction of HE is not only contributed by the temperature difference, but also by the amount of heat put into the heater. Consequently, the exergy 435 436 destruction rate of RE will decrease with the increase in the energy storage pressure, 437 whereas that of HE will exhibit the opposite trend. The exergy destruction rate of C, T, 438 LS, HS is caused by the pressure difference, the pressure difference is higher, the 439 exergy destruction is larger. Therefore, the exergy destruction rate will increase with 440 the increase in energy storage pressure when the outlet pressure of turbine is constant.



441 Fig. 6. Effect of energy storage pressure on exergy destruction rate. a. transcritical
442 compressed CO₂ energy storage. b. supercritical compressed CO₂ energy storage.
443 C = compressor; RE = recuperator; T = turbine; HE = heater; LS = low pressure
444 reservoir; and HS = high pressure reservoir.

445 5.2.2. Effects of energy releasing pressure

The effect of the energy releasing pressure on round-trip efficiency, exergy efficiency, and energy storage density is illustrated in Figs. 7 and 9. The round-trip efficiency and exergy efficiency of TC-CCES and SC-CCES both increase with the increase in energy-release pressure. However, the variation in energy release pressure has a larger effect on the round-trip efficiency and exergy efficiency of SC-CCES. Moreover, the 451 performance of SC-CCES is better than that of TC-CCES when energy releasing452 pressure is larger than 21 MPa.

453

459

Fig. 7 shows that transcritical CO_2 is better under a releasing pressure of ~20-22 MPa, but SC-CCES becomes better under a high pressure. The reason is that the CO_2 enthalpy will decrease with the increase in pressure at the same temperature. Moreover, the enthalpy difference between different pressures also gradually decreases along with the increase in pressure (cf. Fig. 8).



460 Fig. 7. Effect of energy releasing pressure on round-trip efficiency and exergy
461 efficiency.



462

Fig. 8. The *h*-*T* curves for CO₂.

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463

In Fig. 7, the outlet pressure of turbine is constant, so that the input work is constant 465 466 in the compression process, the input thermal energy and output work will change with the variations of releasing pressure. For supercritical CO₂ less thermal energy is 467 468 needed and more output work is produced with the increase in releasing pressure, and 469 the increasing rate of output work is also higher than that of transcritical CO₂. When 470 the releasing pressure is lower, the supercritical CO₂ need more heat energy and 471 produce less output work compared with transcritical CO₂. Therefore, transcritical CO_2 is better when the releasing pressure is low, but supercritical CO_2 becomes better 472 473 at high pressure.

474

475 Fig. 9 shows the effect of energy releasing pressure on energy storage density. As476 shown in the preceding analysis, energy storage density is determined by the work

477 output of the turbine train, as well as the outlet pressure of the turbine train and the 478 compressor train. The increase in energy release pressure will increase the work 479 output of the turbine train, and the pressure difference in the high-pressure reservoir 480 will be reduced which results in smaller volume requirement for the high-pressure 481 reservoir; hence the energy storage densities of TC-CCES and SC-CCES both 482 increase with increase in energy release pressure.



483 484

Fig. 9. Effect of energy releasing pressure on energy storage density.

485

The effect of energy releasing pressure on the exergy destruction rate of the main components is shown in Fig. 10. For TC-CCES and SC-CCES, a greater portion of exergy destruction occurred in He and RE, and they also have the similar trend with the variations in energy releasing pressure. The exergy destruction rate of RE in TC-CCES and SC-CCES decreases with the increase in the energy releasing pressure, whereas that of HE exhibits the opposite trend.

From Fig. 10, we can find that the significant differences between TC-CCES and SC-CCES are that (1) the transcritical exergy destruction rate is larger than that of supercritical CO_2 except in the HS component, and (2) the highest exergy destruction rate happens in different components.

497

498 The lower exergy destruction rate of supercritical CO_2 is caused by the fact that for 499 supercritical CO_2 , both the input energy and output work are lower than that of 500 transcritical CO_2 , so that the exergy destruction rate of supercritical CO_2 is lower.

501

502 The reason that the highest exergy destruction rate happened in different components 503 in transcritical versus supercritical CO_2 is that the injection temperature of the high-pressure reservoir is much different between the transcritical CO2 and 504 supercritical CO₂. As shown in Fig. 2, and in Tables 3 and 4, we can find that the 505 506 injection pressure of the high-pressure reservoir is equal for the transcritical CO₂ and 507 supercritical CO₂, but the injection temperature of supercritical CO₂ is higher than 508 that of transcritical CO₂. So there is a higher exergy destruction rate in the HS in the 509 compressed supercritical CO₂ energy storage system.



510

Fig. 10. Effect of energy release pressure on exergy destruction rate. a. Transcritical
compressed CO₂ energy storage. b. Supercritical compressed CO₂ energy storage.
C = compressor; RE = recuperator; T = turbine; HE = heater; LS = low pressure
reservoir; and HS = high pressure reservoir.

515 5.2.3. Effects of pressure of low pressure reservoir

516 Fig. 11 shows the effect of the pressure of the low-pressure reservoir on the round-trip efficiency and exergy efficiency of TC-CCES and SC-CCES. It indicates that the 517 518 pressure of the low-pressure reservoir exerts a larger influence on round-trip 519 efficiency and exergy efficiency for TC-CCES and SC-CCES. The round-trip 520 efficiency and exergy efficiency will firstly decrease, and then increase with increase 521 in pressure of the low-pressure reservoir. This phenomenon is caused by the 522 properties of CO₂. As shown in Fig. 12, both input work of the compressor and output 523 work of the turbine decrease along with increase in pressure of the low-pressure reservoir, but the reduction of output work is greater than the decrease of input work 524 525 of the compressor. Thus the system performance decreases when the storage system runs at transcritical state. Moreover, when the system runs at supercritical state, the 526 compressibility factor of supercritical CO₂ ranges from 0.2-0.5, which means that less 527

compression work can be consumed in the compression process^[43]. Therefore, the 528 529 reduction of input work will dramatically decrease compared with that at transcritical state. Fig. 13 shows the variations in energy storage density with the increase in 530 pressure of low pressure reservoir. It illustrates that the energy storage density 531 decreases with the increase in pressure of low pressure reservoir. Fig. 14 shows the 532 533 effect of pressure of low pressure reservoir on exergy destruction rate, which indicates 534 that the exergy destruction rates of HE decrease along with the increase in pressure of 535 the low-pressure reservoir. And when the pressure of the low pressure reservoir is 536 higher than 8 MPa, there is a larger decrease in exergy destruction rate of each 537 component except HS.

538

539 The phenomenon we have observed is that performance of SC-CCES can be explained by the properties of supercritical CO_2 and configurations of the energy 540 541 storage system. Because of the larger mass density and configurations of SC-CCES relative to transcritical CO₂, the input work in compression and the temperature 542 543 difference in the heater can be reduced. Moreover, the output work in expansion will 544 be increased due to the higher inlet temperature and pressure of the turbine and the 545 higher exhaust temperature caused by a lower pressure ratio will reduce the amount of 546 heat in the heater. Therefore the round-trip efficiency, exergy efficiency, and energy storage density will increase, whereas the exergy destruction rate of heater decreases. 547

548

549 For Figs. 11-14, the pressure range 6.5-8 MPa shows a different mechanism, which is

caused by the thermodynamic properties of CO_2 . For CO_2 , the critical point is 7.39 MPa and 304.25 K. the thermodynamic properties of CO_2 and supercritical CO_2 are very different. Especially around the critical point, the thermodynamic properties of CO_2 will greatly change with changes in *P* and $T^{[43]}$. Therefore, the compression work can be substantially decreased, as shown in Fig.12.



Fig. 11. Effect of pressure of low pressure reservoir on round-trip efficiency and
 exergy efficiency.

555









Fig. 13. Effect of pressure of low pressure reservoir on energy storage density.





Fig. 14. Effect of pressure of low pressure reservoir on exergy destruction rate. C = compressor; RE = recuperator; T = turbine; HE = heater; LS = low pressurereservoir; and HS = high pressure reservoir.

567 **6. Conclusions**

A thermodynamic analysis is carried out of a system consisting of transcritical and supercritical compressed CO_2 energy storage using two saline aquifers as reservoirs, including energy analysis, exergy analysis, and parametric analysis. The main conclusions are summarized as follows:

572

573 (1) According to the energy and exergy analysis, the proposed compressed CO_2 574 energy storage system with two saline aquifers as reservoirs has a larger energy 575 storage density (497.68 kWh/m³ for transcritical CO_2 and 255.20 kWh/m³ for 576 supercritical CO_2 compared to CAES (2-20kWh/m³) and an acceptable round-trip efficiency (63.35% for transcritical CO₂ and 62.28% for supercritical CO₂) and exergy

578 efficiency (53.02% for transcritical CO₂, and 51.56% for supercritical CO₂) compared

579 with conventional CAES $(81.7\%^{[38]})$.

580

581 (2) The use of compressed transcritical CO_2 for energy storage results in a higher 582 round-trip efficiency, exergy efficiency and energy storage density, but the 583 configuration of SC-CCES is simpler compared with TC-CCES.

584

(3) The energy release pressure has a positive effect on the three indicators including round-trip efficiency, exergy efficiency, and energy storage density forTC-CCES and SC-CCES. The performance of the two energy storage systems will become better with the increase in energy release pressure.

589

(4) The pressure of the low-pressure reservoir has a large effect on round-trip efficiency and exergy efficiency, especially when the pressure is below 8 MPa. Specifically, for TC-CCES, the round-trip efficiency and exergy efficiency dramatically decrease, whereas the energy storage density will decrease along with the increase in pressure of low pressure reservoir.

We note that for the TC-CCES, the low-pressure reservoir needs to be much shallower and larger than the supercritical CO_2 energy storage reservoir. Therefore it may pose larger potential environmental impacts, (for instance to potable groundwater), than the second system. Also, the hazard of induced seismicity and triggered seismicity may exist in both cyclic injection processes. These issues and others such as, how to reduce brine production to a minimum,, or the hydro-geo-mechanical limitations of the saline aquifer reservoirs, and the optimal cycling time given that transient pressure gradients will exist around the injection and production wells^[11] are key questions outside the scope of this study that should be addressed in the future.

604

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