

1 **An investigation of using CO<sub>2</sub> heat pumps to charge PCM storage**  
2 **tank for domestic use**

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12  
13 **Abstract**

14 Current investigations mainly focused on onefold phase change material (PCM) storage tank  
15 charging process, while the integration between a heat-source device and a PCM storage tank  
16 has been seldom considered. The investigation of using a carbon dioxide (CO<sub>2</sub>) heat pump to  
17 charge PCM storage tank is unique because PCM can enhance the system efficiency due to the  
18 delay of the outlet water temperature increase of the PCM storage tank. However, a systematic  
19 investigation about this charging process is still lacking. Therefore, this study conducted the  
20 performance investigation about the system using CO<sub>2</sub> heat pumps to charge the PCM storage  
21 tank. The charging process was simulated by the integration of the heat pump and PCM storage  
22 tank models. The reliabilities of these models were validated by experimental data. The effects  
23 of different expansion valve opening, PCM types, and tank arrangements on the system  
24 performance were analyzed. Both air-source and water-source CO<sub>2</sub> heat pumps were considered.  
25 The optimal parameters were identified by maximizing the overall performance considering the  
26 balance between the charging time and system coefficient of performance. For the system using  
27 water-source CO<sub>2</sub> heat pump with optimal parameters, charging time and system coefficient of  
28 performance were 0.29 h, and 3.48, respectively.

29  
30 **Keywords:** CO<sub>2</sub> heat pump; PCM storage tank; Charging process; Performance investigation

<b>Nomenclature</b>		<i>gs</i>	gas cooler
<i>E</i>	electricity energy use	<i>h</i>	enthalpy
<i>EX</i>	exergy	<i>in</i>	initial
<i>M</i>	mass	<i>it</i>	inlet
<i>ṁ</i>	mass flowrate	<i>lt</i>	least preferred situation
<i>o</i>	opening	<i>mt</i>	most preferred situation
<i>Q</i>	energy amount	<i>ot</i>	outlet
<i>Q̇</i>	heating capacity	<i>ov</i>	overall performance
<i>SR</i>	score	<i>pc</i>	PCM
<i>T</i>	temperature	<i>pm</i>	pump
<i>tt</i>	moment	<i>rs</i>	released
<i>Ẇ</i>	power	<i>sa</i>	starting
		<i>sd</i>	supplied
<i>Abbreviations</i>		<i>sm</i>	system
CO <sub>2</sub>	carbon dioxide	<i>st</i>	stored
COP	coefficient of performance	<i>t</i>	time
PCM	phase change material	<i>tl</i>	total
		<i>wt</i>	water
<i>Subscripts</i>		<i>z</i>	evaporator
<i>ab</i>	ambient		
<i>c</i>	specific heat	<i>Greek symbols</i>	
<i>cc</i>	charging	<i>β</i>	weight factor
<i>chp</i>	CO <sub>2</sub> heat pump	<i>δ<sub>0</sub></i>	a coefficient
<i>cp</i>	compressor	<i>δ<sub>1</sub></i>	a coefficient
<i>dc</i>	discharging	<i>δ<sub>2</sub></i>	a coefficient
<i>dg</i>	designed	<i>δ<sub>3</sub></i>	a coefficient
<i>en</i>	ending	<i>σ</i>	time span
<i>ex</i>	expansion valve	<i>η</i>	efficiency
<i>ey</i>	exergy		

## 32 **1. Introduction**

33 Rapid society development intensifies the population increase and urbanization, resulting in  
34 energy crisis [1] and environmental pollutions [2]. Therefore, it is needed to develop the  
35 sustainable energy technologies for dealing with these problems. Since heat pumps can  
36 effectively collect heat from ambient environments [3], they are known as one sustainable  
37 energy technology and have been utilized in many applications including residential heating  
38 [4], desalination [5], waste heat recovery [6], and air conditioning [7]. Dongellini et al. [8]  
39 performed the performance comparison between a hybrid heat pump system and a gas boiler  
40 system. They found that the former one could save up to 22% energy use in comparison with  
41 the latter one. Wang et al. [9] concluded that in comparison with traditional air-source heat  
42 pumps, the payback period of the system applying both air-source and water-source heat pumps  
43 was 3.66 years. Vivian et al. [10] proposed a new operating strategy for the heat pump systems  
44 for both space heating and domestic hot water purposes. It was reported that the maximum  
45 peak-power reduction could reach 35% when the strategy was applied. Kosmadakis et al. [11]  
46 investigated a high-temperature heat pump utilizing the waste heat, and they found that the  
47 shortest payback period of the system could be around 3 years.

48  
49 Using CO<sub>2</sub> as refrigerant in heat pumps can weaken the ozone depletion caused by  
50 chlorofluorocarbons and furnish high-temperature water [12]. Dai et al. [13] concluded that at  
51 the ambient temperature of -20°C the maximum coefficient of performance (COP) for the CO<sub>2</sub>  
52 heat pump was 2.13 when the vapor injection technique was applied. Ahsaee and Askari [14]  
53 found that the COP of the ground-source CO<sub>2</sub> heat pump could be improved by 16.5% when  
54 the injector was applied. Wang et al. [15] designed a novel CO<sub>2</sub> heat pump for satisfying both  
55 heating and cooling demands. It was concluded that the average COP of the system was 3.27.  
56 Chung et al. [16] found that the heating and cooling COP of CO<sub>2</sub> heat pump could be  
57 respectively improved by 7.1% and 6.8%, when the injector with optimal injection ratio was  
58 applied.

59  
60 Heat pumps are usually integrated with storage tanks in various applications, which can bring  
61 significant profits including the operating expense reduction [17]. Phase change material (PCM)  
62 has high storage density [18], which contributes to its extensively utilization in various fields  
63 including thermal management [19], photovoltaic systems [20], ventilation [21], domestic hot  
64 water use [22], and free cooling systems [23], etc. One important function of PCM is to improve

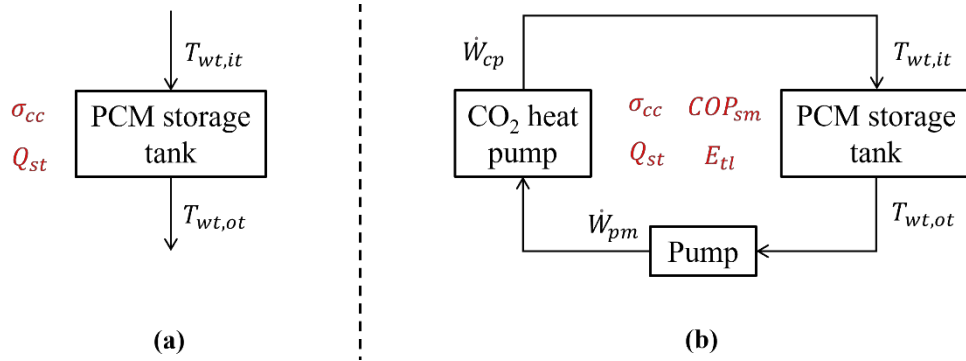
65 the thermal capacity of storage tank. Carmona et al. [24] found that the energy and exergy  
66 efficiencies could be enhanced when PCMs were applied in the tank. Pop and Balan [25]  
67 concluded that the storage tank volume could be reduced by 25% when the PCM was applied.  
68 Kozelj et al. [26] reported that the heat storage capacity could be enhanced by approximately  
69 70% when the PCM was applied in the water tank. Huang et al. [27] investigated a solar system  
70 with PCM storage tank, and they found that the solar fraction could be increased by around 30%  
71 when the PCM storage tank replaced the pure water tank in the system.

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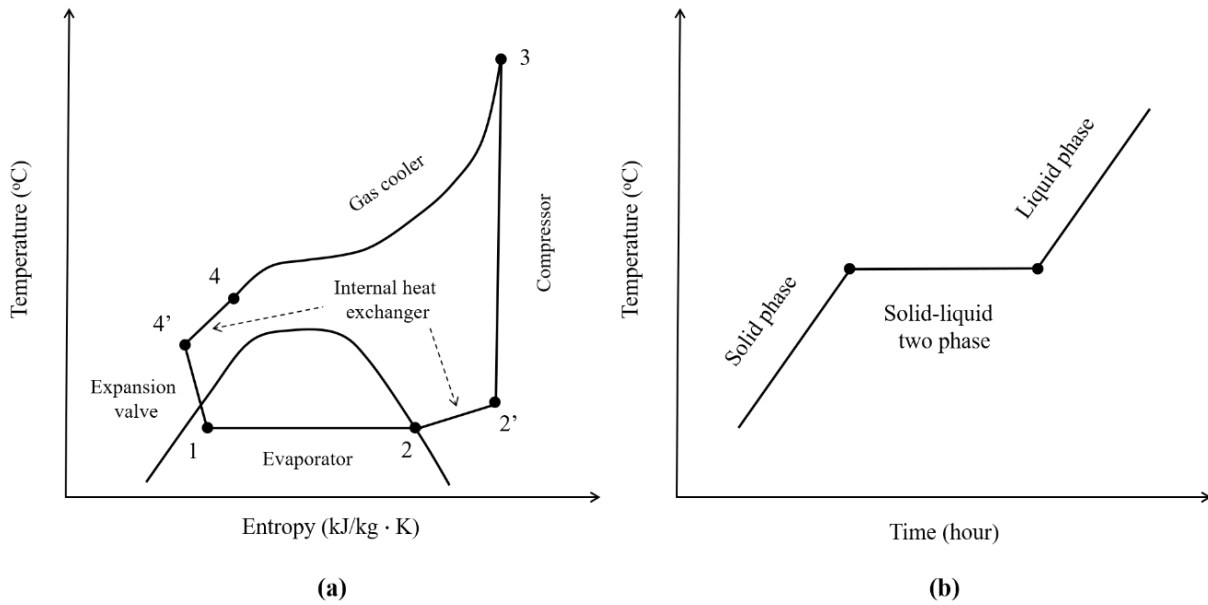
73 Many scholars have performed the studies about charging PCM storage tanks. Zhao et al. [28]  
74 found that the charging time ( $\sigma_{cc}$ ) of PCM storage tank with 90% porosity graphite foam was  
75 41.68% of that without graphite form. Li et al. [29] reported that increasing the mass flowrate  
76 of heat transfer fluid contributed to reducing  $\sigma_{cc}$  of PCM storage tank. Gorzin et al. [30]  
77 concluded that  $\sigma_{cc}$  could be reduced by 52% when the optimal PCM was applied. Alhusseny  
78 et al. [31] found that  $\sigma_{cc}$  could be effectively reduced when the metal foam was added in the  
79 PCM. Sodhi and Muthukumar [32] reported that  $\sigma_{cc}$  could be reduced by 24.5% when the  
80 non-uniform fin distribution was used in the PCM storage tank.

81

82 It could be found from the above literature summary that seldom investigations presented the  
83 behaviour about using the CO<sub>2</sub> heat pump to charge the PCM storage tank. As shown in Fig. 1,  
84 current investigations mainly aim to study the heat transfer process of charging the PCM storage  
85 tank, and seldom studies considered the issue of the integration between the heat-source device  
86 and PCM storage tank. This might cause the consideration of onefold evaluation principle for  
87 the charging process, i.e.,  $\sigma_{cc}$ . Therefore, for proper integrations, it is very meaningful to  
88 consider more evaluation principles, e.g.,  $\sigma_{cc}$  and the system coefficient of performance  
89 ( $COP_{sm}$ ). However, the systematic investigation of this issue was still lacking. As shown in Fig.  
90 2 (a), the temperature of the CO<sub>2</sub> leaving the compressor is very high. To improve the heat  
91 exchange effect between the CO<sub>2</sub> and the water from the PCM storage tank, the temperature of  
92 the water from the PCM storage tank should be low. As shown in Fig. 2 (b), during the charging  
93 process of the PCM, the PCM will go through the solid phase, solid-liquid two phase, and liquid  
94 phase. The solid-liquid two phase of the PCM will delay the temperature increase of the outlet  
95 water of the PCM storage tank, which will improve the energy efficiency of the CO<sub>2</sub> heat pump.  
96 However, the mechanisms about the effects of PCM types, tank arrangements, and expansion  
97 valve opening ( $\sigma_{ex}$ ) on the system performance are still unknown.



**Fig. 1.** Theoretical schematics of (a) current investigations and (b) this investigation



**Fig. 2.** (a) Temperature-entropy diagram of the refrigeration cycle in CO<sub>2</sub> heat pump and (b) temperature variation curve of PCM during the charging process

Hence, this study aimed to clarify the mechanisms about the effects of PCM types, tank arrangements, and  $\sigma_{ex}$  on the system performance. This study conducted the investigation about the system of using the air-source and water-source CO<sub>2</sub> heat pumps to charge the PCM storage tank. The charging process was modelling by the integration of the CO<sub>2</sub> heat pump and PCM storage tank models. The experimental data were applied to validate the reliability of the models. The effects of different PCM types, tank arrangements, and  $\sigma_{ex}$  on the system performance were analyzed.  $\sigma_{cc}$  and  $COP_{sm}$  were selected as the performance indicators. Based on the results, the multi-criterion optimization approach was performed to identify the optimal operating parameters, PCM types, and tank arrangements.

115 The novelties of this investigation are the followings: (a) This investigation considers the  
116 charging process integrating the heat-source device and PCM storage tank in the closed loop  
117 and thereby overcomes the limitations of traditional studies, which only considers the charging  
118 process of PCM storage tank in the open loop; (b) Two key performance indicators, i.e.,  
119 charging time ( $\sigma_{cc}$ ) and system coefficient of performance ( $COP_{sm}$ ), are considered in this study.  
120 This overcomes the limitations of traditional studies which only consider  $\sigma_{cc}$  as the  
121 performance indicator, realizing the consideration of energy use of pumps and CO<sub>2</sub> heat pumps  
122 in the closed loop; (c) A multi-criterion optimization approach is established to determine the  
123 optimal  $\sigma_{ex}$ , PCM types, and tank arrangements. This approach can well guide engineers to  
124 conduct the design for the charging system with the integration of heat-source device and PCM  
125 storage tank; (d) Both air-source and water-source CO<sub>2</sub> heat pumps are considered in the  
126 investigation of the charging process. These case studies play a demonstration role in the aspects  
127 of how to study the charging performance of the system integrating the advanced heat-source  
128 devices and PCM storage tank. The rest of this paper is given as the following. The  
129 methodology is introduced in Section 2. Section 3 presents the results and analysis in different  
130 expansion valve opening, PCM types, and tank arrangements. Section 4 depicts the discussion.  
131 Conclusions are given in Section 5.

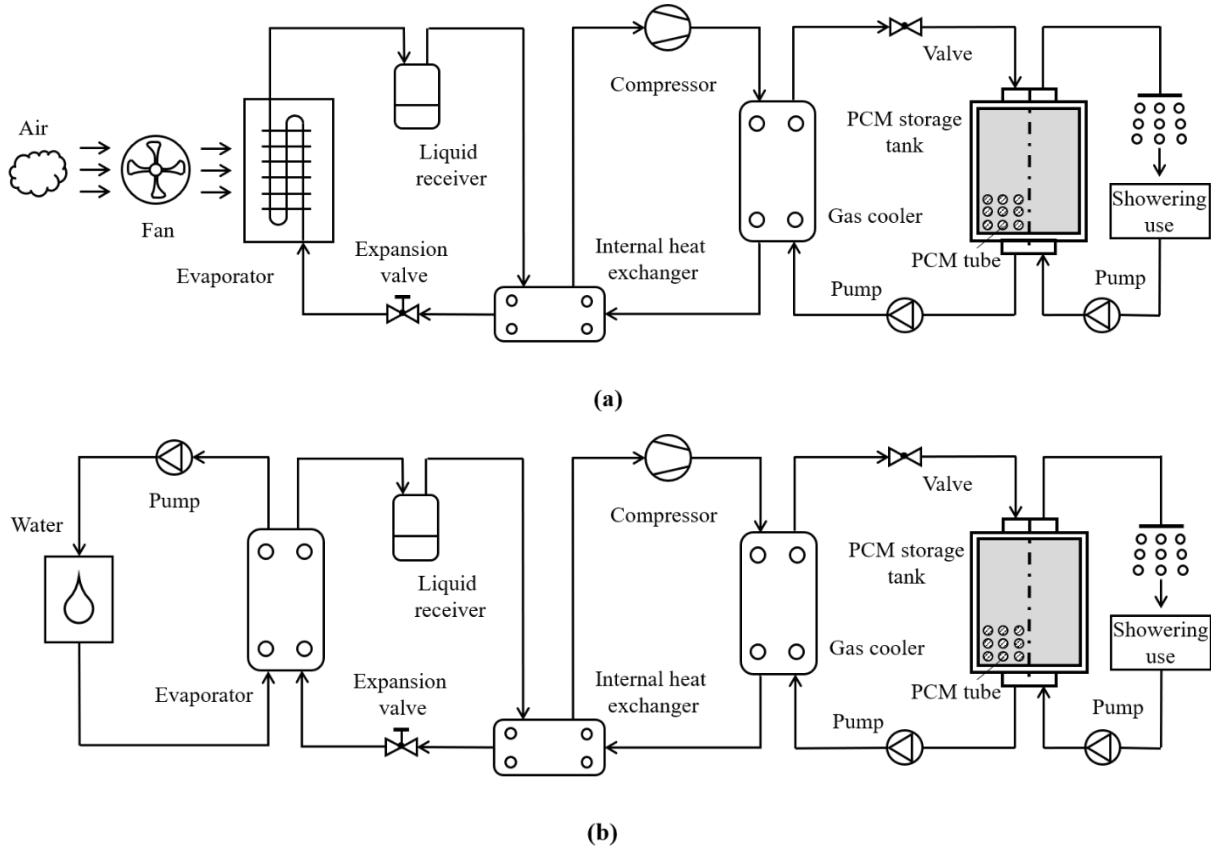
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## 133 **2. Methodology**

### 134 2.1 System description

135 Fig. 3 depicts the schematic for the systems of using (a) an air-source and (b) a water-source  
136 CO<sub>2</sub> heat pump to charge the PCM storage tank. The investigated systems were mainly  
137 comprised of the circulation pump, the expansion valve, the compressor, the liquid receiver, the  
138 evaporator, the internal heat exchanger, the gas cooler, and the PCM storage tank. The CO<sub>2</sub> in  
139 the evaporator will obtain heat from the mixture, composed of water and glycol for freezing  
140 protection. The CO<sub>2</sub> in the heat pump will go through a typical trans-critical refrigeration cycle.  
141 As shown in Fig. 2 (a), the CO<sub>2</sub> will evaporate in the evaporator. The CO<sub>2</sub> leaving the evaporator  
142 will exchange heat with that leaving the gas cooler in the internal heat exchanger. Then, CO<sub>2</sub>  
143 will be compressed and throttled in the compressor and expansion valve, respectively. Finally,  
144 the CO<sub>2</sub> will give heat to the water from the PCM storage tank in the gas cooler. The circulation  
145 pump will circulate the water between the gas cooler and the PCM storage tank. The hot water  
146 leaving the gas cooler will enter the PCM storage tank, and the cold water leaving the PCM  
147 storage tank will return the gas cooler. Normally, the charging process will be completed when

148 the outlet water temperature of the PCM storage tank reaches the set value. This set value should  
 149 be low (e.g., lower than 30°C), because the high return water temperature will reduce the COP  
 150 of the CO<sub>2</sub> heat pump, and even cause the shutdown of the CO<sub>2</sub> heat pump.  
 151



152  
 153  
 154 **Fig. 3.** Schematic for the systems of using (a) air-source and (b) water-source CO<sub>2</sub> heat pump to charge  
 155 PCM storage tank for domestic use  
 156

157 2.2 System models

158 2.2.1 CO<sub>2</sub> heat pump model

159 The integration of MATLAB and REFPROP was applied to establish the CO<sub>2</sub> heat pump models.  
 160 Mass and energy governing equations where several assumptions including one-dimension  
 161 model without pressure drop and heat loss were applied to established the gas cooler, internal  
 162 heat exchanger, and evaporator with liquid receiver models, referring to the study of Rasmussen  
 163 et al. [33]. The evaporator in the air-source CO<sub>2</sub> heat pump was fin-tube heat exchanger. The  
 164 calculations of heat transfer coefficients for the air, single-phase CO<sub>2</sub>, and two-phase CO<sub>2</sub> in  
 165 the fin-tube heat exchanger referred to the study of Deng et al. [34]. Expect the evaporator in  
 166 the air-source heat pump, other heat exchangers in the air-source and water-source CO<sub>2</sub> heat  
 167 pump were plate heat exchangers. The calculations of heat transfer coefficients for the single-

168 phase and two-phase fluids referred to the study of Mota et al. [35] and Lee et al. [36]. The  
169 compressor model referred to the study of Wang et al. [37], and it was utilized to calculate the  
170 CO<sub>2</sub> mass flowrate through the compressor and compressor power ( $\dot{W}_{cp}$ ). The relationships  
171 between the compressor efficiencies (i.e., volumetric, mechanical, and isentropic efficiencies)  
172 and pressure ratio that were applied in this model were constructed by the measured data in our  
173 previous study [38]. The expansion valve model referred to the study of Eames et al. [39], and  
174 it was used to calculate the CO<sub>2</sub> mass flowrate through the expansion valve. The relationship  
175 between the flow factor and expansion valve opening ( $o_{ex}$ ) that was applied in this model was  
176 constructed by the measured data in our previous study [38].

177

### 178 2.2.2 PCM storage tank model

179 Several assumptions were applied for establishing the PCM storage tank model. The suggested  
180 model contained unchanged PCM temperature during the melting process, no heat loss to  
181 ambient, one dimensional model, and water properties that were not influenced by temperature  
182 [40]. The PCM was encapsulated inside the tubes that were install in the tank. Governing  
183 equations of the PCM storage tank model are depicted in our previous study [41]. The water  
184 and PCM Nusselt numbers were calculated referring to Watanabe et al.'s study [42].

185

### 186 2.3 Validation

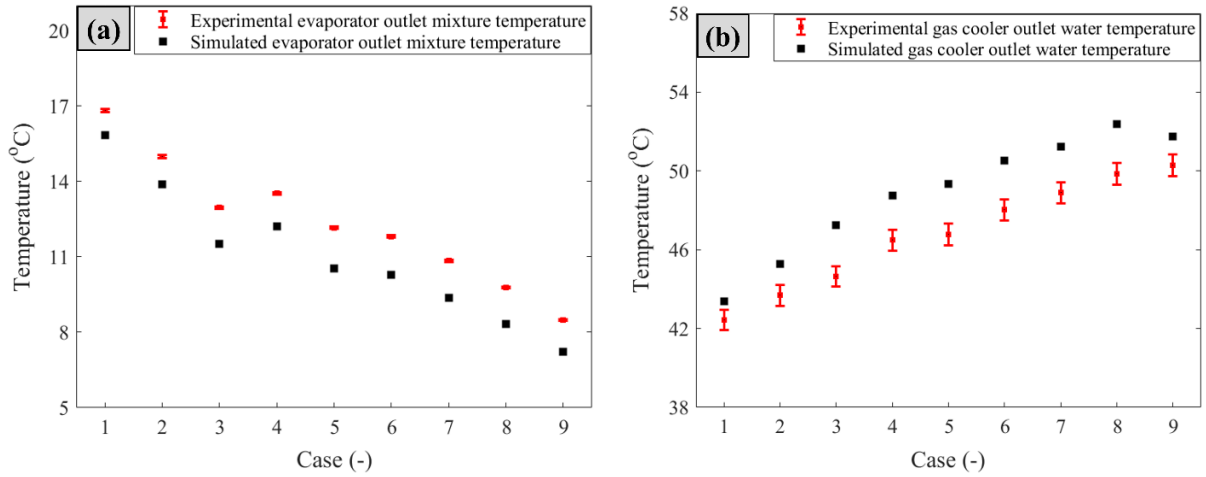
187 The experimental setup for the CO<sub>2</sub> heat pump installed in the Energy and Indoor Environment  
188 Laboratory at the Norwegian University of Science and Technology has been established to  
189 validate the reliability of the developed CO<sub>2</sub> heat pump model. The detailed information of the  
190 gas cooler, evaporator, liquid receiver, internal heat exchanger, compressor, and expansion  
191 valve were presented in our previous study [43]. The accuracy of the sensors in the experimental  
192 setup were also shown in our previous study [43]. Nine cases where the discharge pressure was  
193 maintained from 7,100 kPa to 8,700 kPa with the interval of 200 kPa were conducted. The  
194 measured outlet fluid temperature in the evaporator and the gas cooler were compared with the  
195 simulated values under the same operating conditions.

196

197 The comparisons between the experimental and simulated outlet mixture temperature in the  
198 evaporator and outlet water temperature in the gas cooler in these nine cases are presented in  
199 Fig. 4. Both the simulated outlet mixture temperature in the evaporator and outlet water  
200 temperature in the gas cooler well agreed with the experimental ones. The average temperature



201 difference between the experimental and simulated values for the outlet mixture temperature in  
 202 the evaporator and outlet water temperature in the gas cooler were 2.1 K and 1.4 K, respectively.  
 203 This indicated that the developed water-source CO<sub>2</sub> heat pump model was reliable. The reasons  
 204 resulting in these temperature difference might be the measurement error of the sensors and the  
 205 utilization of quasi-dynamic modelling approach. The experimental data from the literature has  
 206 been compared with the simulated data of the PCM storage tank in our previous study [41]. The  
 207 average relative error for the PCM storage tank model was 3.97%. The results showed that the  
 208 simulated data agreed well with the experimental data, which indicated that the PCM storage  
 209 tank model was reliable. Thus, the models applied to simulate the process of using CO<sub>2</sub> heat  
 210 pump to charge the PCM storage tank were reliable.  
 211



212  
 213 **Fig. 4.** Comparisons between experimental and simulated (a) outlet mixture temperature in evaporator and  
 214 (b) outlet water temperature in gas cooler  
 215

#### 216 2.4 Performance indicators

217 Two performance indicators including  $\sigma_{cc}$  and  $COP_{sm}$  were applied in this investigation.  $\sigma_{cc}$   
 218 was defined as Eqn. (1):

$$219 \quad \sigma_{cc} = tt_{en} - tt_{sa} \quad (1)$$

220 where  $tt_{en}$  and  $tt_{sa}$  denote the ending and starting moments for charging the PCM storage  
 221 tank, respectively.  
 222

223  $COP_{sm}$  was defined as Eqn. (2):

$$224 \quad COP_{sm} = \frac{Q_{st}}{E_{tl}} \quad (2)$$

225 where  $Q_{st}$  denotes the stored energy.  $E_{tl}$  denotes the total electricity energy use, which was  
 226 calculated by Eqn. (3):

$$227 \quad E_{tl} = E_{cp} + E_{pm,z} + E_{pm,gs} \quad (3)$$

228 where  $E_{cp}$ ,  $E_{pm,z}$ , and  $E_{pm,gs}$  denote the electricity energy use of compressor, pumps in the  
 229 evaporator and the gas cooler, respectively. They were calculated by Eqns. (4) to (6):

$$230 \quad E_{cp} = \int_{tt_{en}}^{tt_{sa}} \dot{W}_{cp} dt \quad (4)$$

$$231 \quad E_{pm,z} = \int_{tt_{en}}^{tt_{sa}} \dot{W}_{pm,z} dt \quad (5)$$

$$232 \quad E_{pm,gs} = \int_{tt_{en}}^{tt_{sa}} \dot{W}_{pm,gs} dt \quad (6)$$

233 where  $\dot{W}_{pm,z}$  denotes the pump power in the evaporator, which was assumed to be 100 W.

234  $\dot{W}_{pm,gs}$  denotes the pump power in the gas cooler, which was calculated by Eqn. (7):

$$235 \quad \frac{\dot{W}_{pm,gs}}{\dot{W}_{pm,gs,dg}} = \delta_0 + \delta_1 \frac{\dot{m}_{gs,wt}}{\dot{m}_{gs,wt,dg}} + \delta_2 \left( \frac{\dot{m}_{gs,wt}}{\dot{m}_{gs,wt,dg}} \right)^2 + \delta_3 \left( \frac{\dot{m}_{gs,wt}}{\dot{m}_{gs,wt,dg}} \right)^3 \quad (7)$$

236 where  $dg$  denotes the designed value.  $\delta_0$ ,  $\delta_1$ ,  $\delta_2$ , and  $\delta_3$  denote the coefficients, which  
 237 were 0, 0.0016, 20.0037, and 0.9671, respectively [44].  $\dot{W}_{pm,gs,dg}$  and  $\dot{m}_{gs,wt,dg}$  were 50 W  
 238 and 0.044 kg/s, respectively.

239

240 The multi-criteria approach was applied to conduct the optimization for identifying the optimal  
 241 parameters [3]. The score of the overall performance ( $SR_{ov}$ ) was defined as Eqn. (8):

$$242 \quad SR_{ov} = \beta_{\sigma_{cc}} \cdot SR_{\sigma_{cc}} + \beta_{COP_{sm}} \cdot SR_{COP_{sm}} \quad (8)$$

243 where  $SR$  denotes the score.  $\beta$  denotes the weight factor.  $SR_{\sigma_{cc}}$  and  $SR_{COP_{sm}}$  were  
 244 respectively calculated by Eqns. (9) and (10):

$$245 \quad SR_{\sigma_{cc}} = \frac{\sigma_{cc} - \sigma_{cc,lt}}{\sigma_{cc,mt} - \sigma_{cc,lt}} \quad (9)$$

$$246 \quad SR_{COP_{sm}} = \frac{COP_{sm} - COP_{sm,lt}}{COP_{sm,mt} - COP_{sm,lt}} \quad (10)$$

247 where  $lt$  and  $mt$  denote the least-preferred and most-preferred situations, respectively.

248  $\beta_{\sigma_{cc}}$  and  $\beta_{COP_{sm}}$  were user-specified, and the relationship between them should satisfy Eqn.  
 249 (11):

$$250 \quad \beta_{\sigma_{cc}} + \beta_{COP_{sm}} = 1 \quad (11)$$

251

### 252 3. Results and analysis

253 The results and analysis about the influence of different expansion valve opening ( $\theta_{ex}$ ), PCM  
 254 types, and tank arrangements on the system performance are presented in this section. Charging

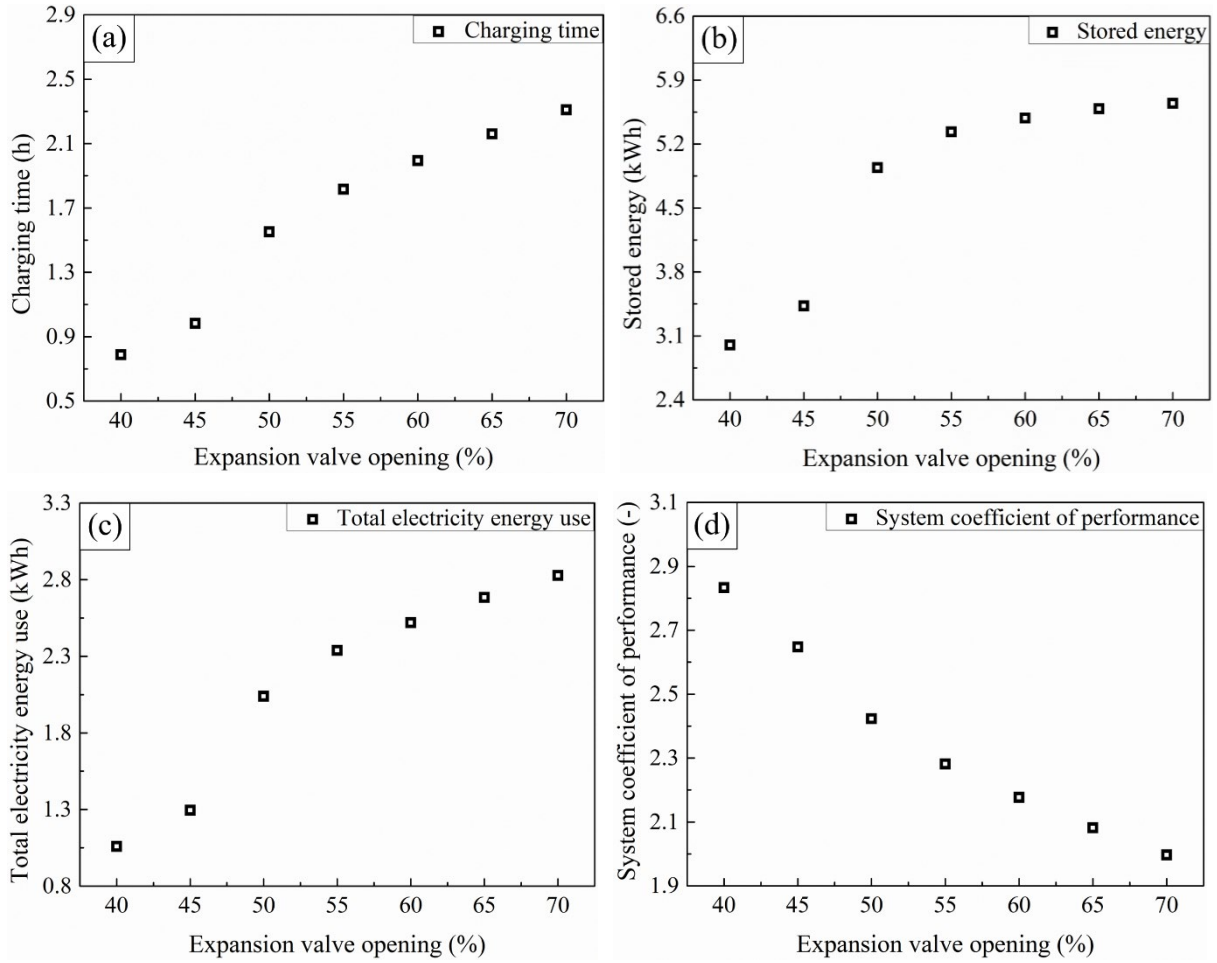
255 time ( $\sigma_{cc}$ ), stored energy ( $Q_{st}$ ), total electricity energy use ( $E_{tl}$ ), and system coefficient of  
256 performance ( $COP_{sm}$ ) are considered as performance indicators. The optimal  $o_{ex}$ , PCM type,  
257 and tank arrangement are identified according to the results of  $\sigma_{cc}$  and  $COP_{sm}$ . When the  
258 identifying optimal cases according to  $\sigma_{cc}$  and  $COP_{sm}$  are different, the score of the overall  
259 performance ( $SR_{ov}$ ) will be applied to determine the final optimal case.

260

### 261 3.1 Results and analysis in different expansion valve opening

262 This section presents the results and analyses about the effect of different expansion valve  
263 opening ( $o_{ex}$ ) on the system performance. The performance indicators included charging time  
264 ( $\sigma_{cc}$ ), stored energy ( $Q_{st}$ ), total electricity energy use ( $E_{tl}$ ), and system coefficient of  
265 performance ( $COP_{sm}$ ). Fig. 5 depicts the variations of  $\sigma_{cc}$ ,  $Q_{st}$ ,  $E_{tl}$ , and  $COP_{sm}$  with  
266 different  $o_{ex}$  using the air-source heat pump. In Fig. 5 (a),  $\sigma_{cc}$  increased as  $o_{ex}$  increased.  
267 This might be caused by that lower  $o_{ex}$  resulted in higher discharge pressure and the higher  
268 CO<sub>2</sub> temperature to the gas cooler, leading to faster completion of charging process. When  $o_{ex}$   
269 increased from 40% to 70%,  $\sigma_{cc}$  varied from 0.79 h to 2.31 h, increased by 193.1%. In Fig. 5  
270 (b),  $Q_{st}$  increased as  $o_{ex}$  increased. Increasing  $o_{ex}$  resulted in the increase of  $\sigma_{cc}$ , which led  
271 to the increase of  $Q_{st}$ . When  $o_{ex}$  increased from 40% to 70%,  $Q_{st}$  varied from 3 kWh to 5.64  
272 kWh, increased by 88.1%. In Fig. 5 (c),  $E_{tl}$  increased as  $o_{ex}$  increased. When  $o_{ex}$  increased  
273 from 40% to 70%,  $E_{tl}$  varied from 1.06 kWh to 2.83 kWh, increased by 166.9%. In Fig. 5 (d),  
274  $COP_{sm}$  reduced as  $o_{ex}$  increased. When  $o_{ex}$  increased from 40% to 70%,  $COP_{sm}$  varied  
275 from 2.83 to 2, decreased by 29.5%. According to the Eqn. (2), this phenomenon might be  
276 explained by that the increasing degree of  $Q_{st}$  varied with  $o_{ex}$  was smaller than the  
277 increasing degree that  $E_{tl}$  varied with  $o_{ex}$ . It could be concluded that 40% was the optimal  
278  $o_{ex}$ , because  $\sigma_{cc}$  in the case when  $o_{ex}$  was 40% was smaller than  $\sigma_{cc}$  in the other case and  
279  $COP_{sm}$  in the case when  $o_{ex}$  was 40% was higher than  $COP_{sm}$  in the other case.

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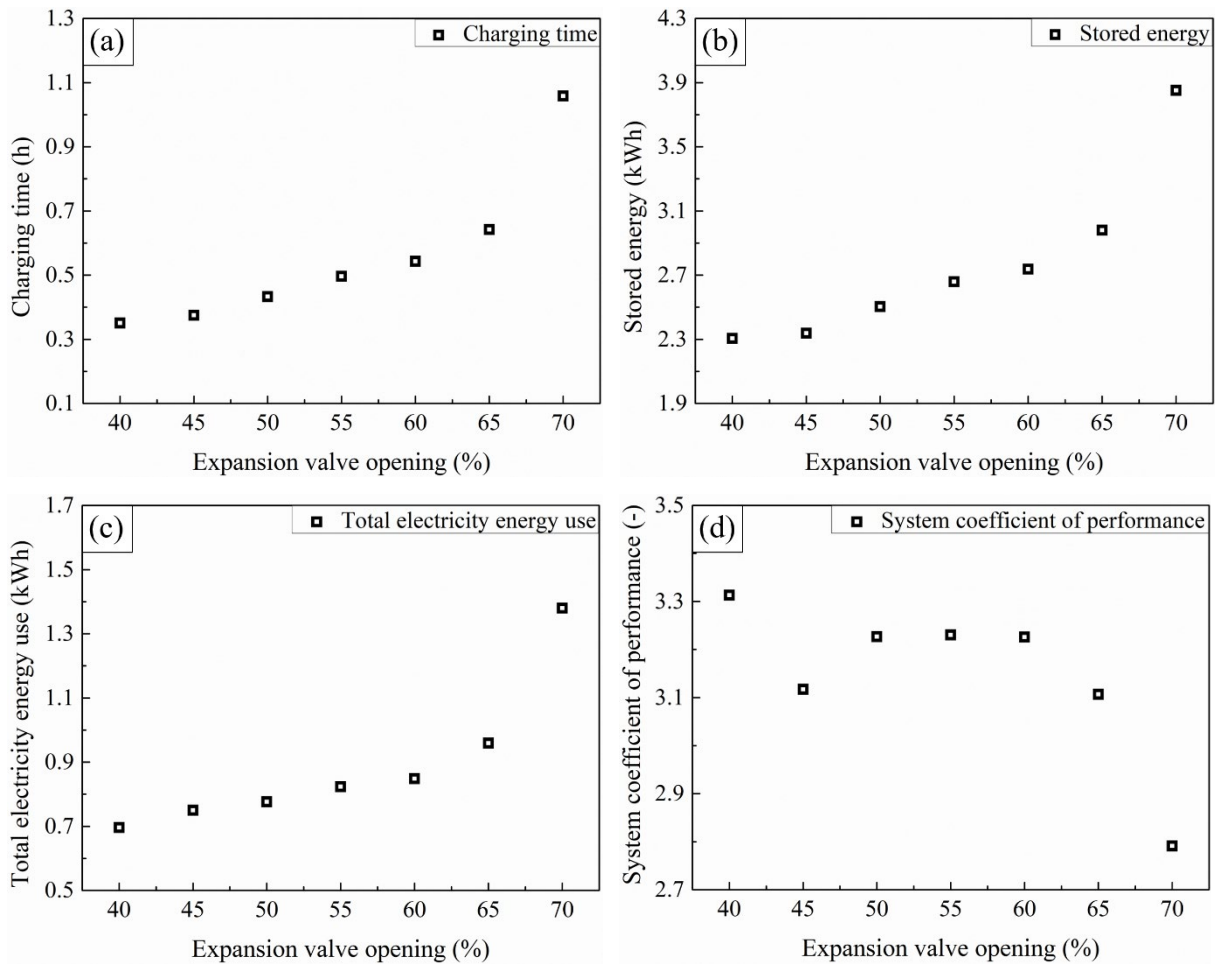


281  
 282 **Fig. 5.** Variations of (a) charging time, (b) stored energy, (c) total electricity energy use, and (d) system  
 283 coefficient of performance with different expansion valve opening using the air-source heat pump  
 284

285 Fig. 6 depicts the variations of  $\sigma_{cc}$ ,  $Q_{st}$ ,  $E_{tl}$ , and  $COP_{sm}$  with different expansion valve  
 286 opening ( $o_{ex}$ ) using the water-source heat pump. In Fig. 6 (a),  $\sigma_{cc}$  increased as  $o_{ex}$  increased.  
 287 This might be caused by that lower  $o_{ex}$  resulted in higher discharge pressure, which might  
 288 increase the CO<sub>2</sub> temperature in the gas cooler, leading to faster completion of charging process.  
 289 When  $o_{ex}$  increased from 40% to 70%,  $\sigma_{cc}$  varied from 0.35 h to 1.06 h, increased by 202.1%.  
 290 In Fig. 6 (b),  $Q_{st}$  increased as  $o_{ex}$  increased. Increasing  $o_{ex}$  resulted in the increase of  $\sigma_{cc}$ ,  
 291 which led to the increase of  $Q_{st}$ . When  $o_{ex}$  increased from 40% to 70%,  $Q_{st}$  varied from  
 292 2.31 kWh to 3.85 kWh, increased by 67.1%. Thus, the increasing degree of  $\sigma_{cc}$  was higher  
 293 than that of  $Q_{st}$ . In Fig. 6 (c),  $E_{tl}$  increased as  $o_{ex}$  increased. When  $o_{ex}$  increased from 40%  
 294 to 70%,  $E_{tl}$  varied from 0.7 kWh to 1.38 kWh, increased by 98.3%. In Fig. 6 (d), the variations  
 295 of  $COP_{sm}$  with  $o_{ex}$  was irregular. According to the Eqn. (2), this phenomenon might be  
 296 explained by that in some cases the increasing degree that  $Q_{st}$  varied with  $o_{ex}$  was smaller  
 297 than the increasing degree that  $E_{tl}$  varied with  $o_{ex}$ , while in some cases the increasing degree

298 that  $Q_{st}$  varied with  $o_{ex}$  was larger than the increasing degree that  $E_{tl}$  varied with  $o_{ex}$ . The  
 299 maximum  $COP_{sm}$  was 3.31, occurring at the case when  $o_{ex}$  was 40%. The minimum  $COP_{sm}$   
 300 was 2.79, occurring at the case when  $o_{ex}$  was 70%.  $COP_{sm}$  at the case when  $o_{ex}$  was 40%  
 301 was 1.19 times as high as  $COP_{sm}$  at the case when  $o_{ex}$  was 70%. It could be concluded that  
 302 40% was the optimal  $o_{ex}$ , since  $\sigma_{cc}$  in the case when  $o_{ex}$  was 40% was smaller than  $\sigma_{cc}$  in  
 303 the other case and  $COP_{sm}$  in the case when  $o_{ex}$  was 40% was higher than  $COP_{sm}$  in the other  
 304 case.

305



306 **Fig. 6.** Variations of (a) charging time, (b) stored energy, (c) total electricity energy use, and (d) system  
 307 coefficient of performance with different expansion valve opening using the water-source heat pump  
 308

309 It could be seen from Fig. 5 and Fig. 6 that  $COP_{sm}$  when the water-source CO<sub>2</sub> heat pump was  
 310 applied was higher than  $COP_{sm}$  when the air-source CO<sub>2</sub> heat pump was applied. The higher  
 311  $COP_{sm}$  might cause higher charging speed, which led to shorter  $\sigma_{cc}$ . The shorter  $\sigma_{cc}$  might  
 312 result in less energy stored in the PCM storage tank, which meant that  $Q_{st}$  might be less. Thus,  
 313  $\sigma_{cc}$  when the air-source CO<sub>2</sub> heat pump was applied was longer than  $\sigma_{cc}$  when the water-

314 source CO<sub>2</sub> heat pump was applied, while  $Q_{st}$  when the air-source CO<sub>2</sub> heat pump was applied  
 315 was larger than  $Q_{st}$  when the water-source CO<sub>2</sub> heat pump was applied.

316

### 317 3.2 Results and analysis in different PCM types

318 This section presents the results and analysis of the system performance for different PCM types.

319 The thermal properties of different PCM were depicted in Table 1. The PCM-1, PCM-2, PCM-

320 3, PCM-4, PCM-5, and PCM-6 have the melting temperature of 16°C, 17°C, 18°C, 19.6°C,

321 20.4°C, and 21.3°C, respectively. The latent heat of PCM-3 that is 236 kJ/kg is the maximum,

322 while the latent heat of PCM-4 that is 86 kJ/kg is the minimum. The solid thermal conductivity

323 of PCM-2 that is 1 W/(m·K) is the maximum, while the solid thermal conductivity of PCM-4

324 that is 0.05 W/(m·K) is the minimum. The liquid thermal conductivity of PCM-2 that is 0.5

325 W/(m·K) is the maximum, while the liquid thermal conductivity of PCM-4 that is 0.05 W/(m·K)

326 is the minimum. Both of the solid and liquid density of PCM-2 that are 1,800 kg/m<sup>3</sup> are the

327 maximum, while both of the solid and liquid density of PCM-4 that are 694 kg/m<sup>3</sup> are the

328 minimum. The solid specific heat of PCM-2 that is 2.5 kJ/(kg·K) is the maximum, while the

329 solid specific heat of PCM-3 that is 1.65 kJ/(kg·K) is the minimum. The liquid specific heat of

330 PCM-1 that is 2.3 kJ/(kg·K) is the maximum, while the liquid specific heat of PCM-2 that is

331 1.5 kJ/(kg·K) is the minimum.

332

333

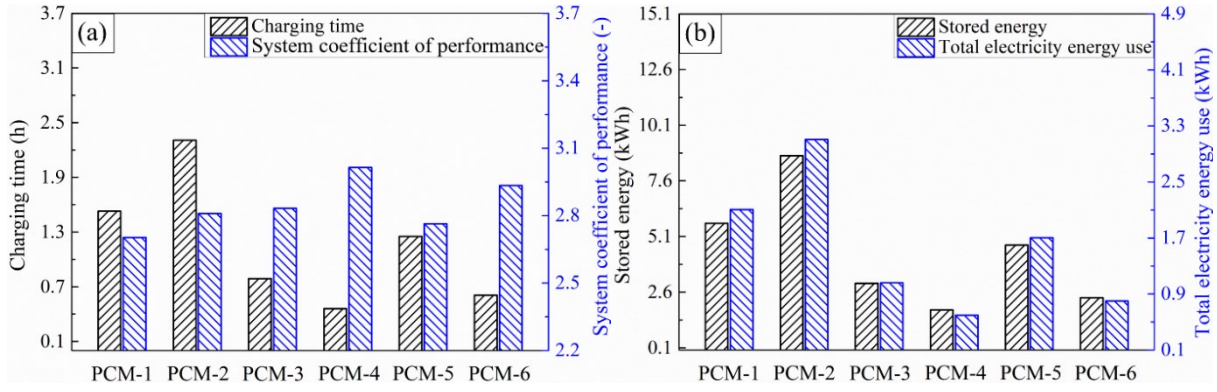
**Table 1** Thermal properties of different PCM

	PCM-1	PCM-2	PCM-3	PCM-4	PCM-5	PCM-6
	[45]	[46]	[47]	[48]	[49]	[50]
Melting temperature (°C)	16	17	18	19.6	20.4	21.3
Latent heat (kJ/kg)	213	145	236	86	138.8	152
Solid thermal conductivity (W/(m·K))	0.18	1	0.17	0.05	0.6	0.182
Liquid thermal conductivity (W/(m·K))	0.18	0.5	0.17	0.05	0.3	0.182
Solid density (kg/m <sup>3</sup> )	830	1,800	780	694	881	884
Liquid density (kg/m <sup>3</sup> )	800	1,800	780	694	881	960
Solid specific heat (kJ/(kg·K))	2.3	2.5	1.65	1.7	2	1.67
Liquid specific heat (kJ/(kg·K))	2.3	1.5	2.1	1.7	2	2.09

334 Fig. 7 (a) depicts the charging time ( $\sigma_{cc}$ ) and system coefficient of performance ( $COP_{sm}$ ) in  
335 different PCM types using the air-source heat pump. When the PCM-1, PCM-2, PCM-3, PCM-  
336 4, PCM-5, and PCM-6 were used,  $\sigma_{cc}$  were 1.56 h, 2.31 h, 0.79 h, 0.46 h, 1.25 h, and 0.61 h,  
337 respectively. Thus,  $\sigma_{cc}$  was the minimum when the PCM-4 was utilized, while  $\sigma_{cc}$  had its  
338 maximum when the PCM-2 was utilized.  $\sigma_{cc}$  when the PCM-2 was used was 5.02 times as  
339 high as  $\sigma_{cc}$  when the PCM-4 was used. These phenomena might be explained by that the  
340 density of the PCM-2 was the highest among the observed PCMs, while the density of the PCM-  
341 4 was the minimum among the PCMs. In addition, although the latent heat of the PCM-2 was  
342 lower than that of the PCM-3, the effect of the thermal capacity (i.e., multiplication of the  
343 specific heat and density) of the PCM-2 was higher than that of the PCM-3. The latent heat of  
344 the PCM-4 was evidently smaller than that of the other PCM. When the PCM-1, PCM-2, PCM-  
345 3, PCM-4, PCM-5, and PCM-6 were used,  $COP_{sm}$  were 2.7, 2.81, 2.83, 3.01, 2.76, and 2.93,  
346 respectively. Thus,  $COP_{sm}$  had its maximum when the PCM-4 was utilized, while  $COP_{sm}$  had  
347 its minimum when the PCM-1 was utilized.  $COP_{sm}$  when the PCM-4 was used was 1.11 times  
348 as high as  $COP_{sm}$  when the PCM-1 was used. It could be concluded that the PCM-4 was the  
349 optimal PCM because  $\sigma_{cc}$  in the case when the PCM-4 was applied was smaller than that when  
350 the other PCM was applied and  $COP_{sm}$  when the PCM-4 was applied was higher than that  
351 when the other PCM was applied.

352  
353 Fig. 7 (b) depicts the stored energy ( $Q_{st}$ ) and total electricity energy use ( $E_{tl}$ ) for different PCM  
354 types using the air-source heat pump. When the PCM-1, PCM-2, PCM-3, PCM-4, PCM-5, and  
355 PCM-6 were used,  $Q_{st}$  were 5.69 kWh, 8.73 kWh, 3 kWh, 1.8 kWh, 4.71 kWh, and 2.35 kWh,  
356 respectively. Thus,  $Q_{st}$  was the minimum when the PCM-4 was utilized, while  $Q_{st}$  was the  
357 maximum when the PCM-2 was utilized.  $Q_{st}$  when the PCM-2 was used was 4.85 times as  
358 high as  $Q_{st}$  when the PCM-4 was used. These phenomena might be explained by the thermal  
359 properties of the PCM-4 and PCM-2 including the latent heat, density, and specific heat. When  
360 the PCM-1, PCM-2, PCM-3, PCM-4, PCM-5, and PCM-6 were used,  $E_{tl}$  were 2.11 kWh, 3.11  
361 kWh, 1.06 kWh, 0.6 kWh, 1.7 kWh, and 0.8 kWh, respectively. Thus,  $E_{tl}$  had its minimum  
362 when the PCM-4 was utilized, while  $E_{tl}$  had its maximum when the PCM-2 was utilized.  $E_{tl}$   
363 when the PCM-2 was used was 5.18 times as high as  $E_{tl}$  when the PCM-4 was used. This  
364 might be caused by the corresponding  $\sigma_{cc}$  when the different PCM were applied.

365



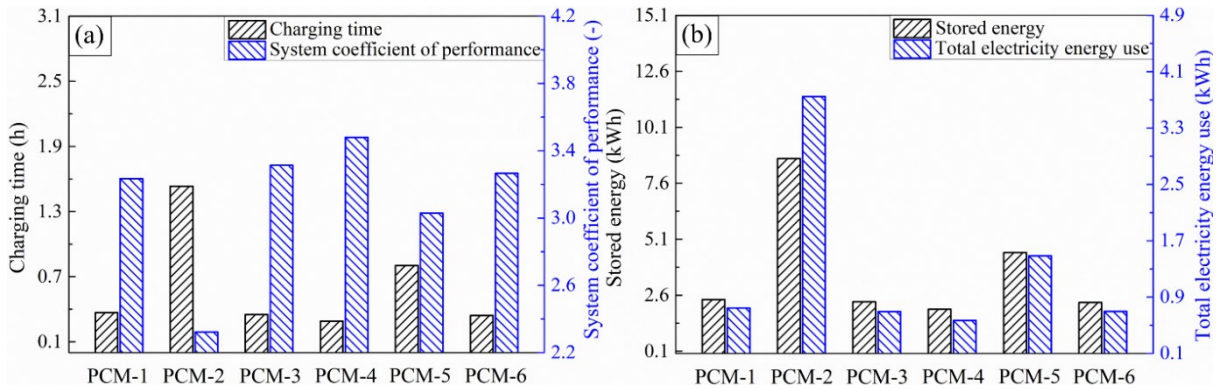
366 Fig. 7. (a) Charging time and system coefficient of performance, and (b) stored energy and total electricity  
 367 energy use in different PCM types using the air-source heat pump  
 368

369 Fig. 8 (a) depicts the charging time ( $\sigma_{cc}$ ) and system coefficient of performance ( $COP_{sm}$ ) in  
 370 different PCM types using the water-source heat pump. When the PCM-1, PCM-2, PCM-3,  
 371 PCM-4, PCM-5, and PCM-6 were used,  $\sigma_{cc}$  were 0.37 h, 1.53 h, 0.35 h, 0.29 h, 0.8 h, and  
 372 0.34 h, respectively. Thus,  $\sigma_{cc}$  was the minimum when the PCM-4 was utilized, while  $\sigma_{cc}$   
 373 was the maximum when the PCM-2 was utilized.  $\sigma_{cc}$  when the PCM-2 was used was 5.28  
 374 times as high as  $\sigma_{cc}$  when the PCM-4 was used. These phenomena might be explained by that  
 375 the density of the PCM-2 was the maximum among these PCM, while the density of the PCM-  
 376 4 was the minimum among these PCM. When the PCM-1, PCM-2, PCM-3, PCM-4, PCM-5,  
 377 and PCM-6 were used,  $COP_{sm}$  were 3.23, 2.32, 3.31, 3.48, 3.03, and 3.27, respectively. Thus,  
 378  $COP_{sm}$  was the maximum when the PCM-4 was utilized, while  $COP_{sm}$  was the minimum  
 379 when the PCM-2 was utilized.  $COP_{sm}$  when the PCM-4 was used was 1.5 times as high as  
 380  $COP_{sm}$  when the PCM-2 was used. It could be concluded that the PCM-4 was the optimal PCM  
 381 since  $\sigma_{cc}$  in the case when the PCM-4 was applied was smaller than that when the other PCM  
 382 was applied and  $COP_{sm}$  in the case when the PCM-4 was applied was larger than that when  
 383 the other PCM was applied.  
 384

385 Fig. 8 (b) depicts the stored energy ( $Q_{st}$ ) and total electricity energy use ( $E_{tl}$ ) in different PCM  
 386 types using the air-source heat pump. When the PCM-1, PCM-2, PCM-3, PCM-4, PCM-5, and  
 387 PCM-6 were used,  $Q_{st}$  were 2.41 kWh, 8.7 kWh, 2.31 kWh, 1.98 kWh, 4.5 kWh, and 2.28  
 388 kWh, respectively. Thus,  $Q_{st}$  had its minimum when the PCM-4 was utilized, while  $Q_{st}$  was  
 389 the maximum when the PCM-2 was utilized.  $Q_{st}$  when the PCM-2 was used was 4.39 times  
 390 as high as  $Q_{st}$  when the PCM-4 was used. These might be caused by the thermal properties of  
 391 the PCM-4 and PCM-2. When the PCM-1, PCM-2, PCM-3, PCM-4, PCM-5, and PCM-6 were



392 used,  $E_{tl}$  were 0.75 kWh, 3.74 kWh, 0.7 kWh, 0.57 kWh, 1.49 kWh, and 0.7 kWh, respectively.  
 393 Thus,  $E_{tl}$  had its minimum when the PCM-4 was utilized, while  $E_{tl}$  had its maximum when  
 394 the PCM-2 was utilized.  $E_{tl}$  when the PCM-2 was used was 6.56 times as high as  $E_{tl}$  when  
 395 the PCM-4 was used. This might be caused by the corresponding  $\sigma_{cc}$  when the different PCM  
 396 were applied.  
 397



398 **Fig. 8.** (a) Charging time and system coefficient of performance, and (b) stored energy and total electricity  
 399 energy use in different PCM types using the water-source heat pump  
 400

401 For the system using the air-source and water-source CO<sub>2</sub> heat pumps, the optimal PCM type  
 402 was PCM-4. When the PCM-4 was applied in the systems using air-source or water-source CO<sub>2</sub>  
 403 heat pumps,  $\sigma_{cc}$  had its minimum, and  $COP_{sm}$  had its maximum. The good thermal properties  
 404 of PCM-4 led to be that it could contribute to realizing the charging process within a shorter  
 405 period and better energy performance.  
 406

### 407 3.3 Results and analysis in different tank arrangements

408 This section presents the results and analysis of the system performance in different tank  
 409 arrangements. PCM-4 was applied in this section. The number of tubes in each column and row  
 410 in different cases were depicted in Table 2. The number of tubes in each column in Case 1, Case  
 411 2, Case 3, Case 4, Case 5, and Case 6 were 21, 20, 19, 21, 20, and 19, respectively. The number  
 412 of tubes in each row in Case 1, Case 2, Case 3, Case 4, Case 5, and Case 6 were 6, 6, 6, 5, 5,  
 413 and 5, respectively.  
 414

415 **Table 2** Number of tubes in each column and row in different cases

	Case 1	Case 2	Case 3	Case 4	Case 5	Case 6
Number of tubes in each column (-)	21	20	19	21	20	19

Number of tubes in each row (-)	6	6	6	5	5	5
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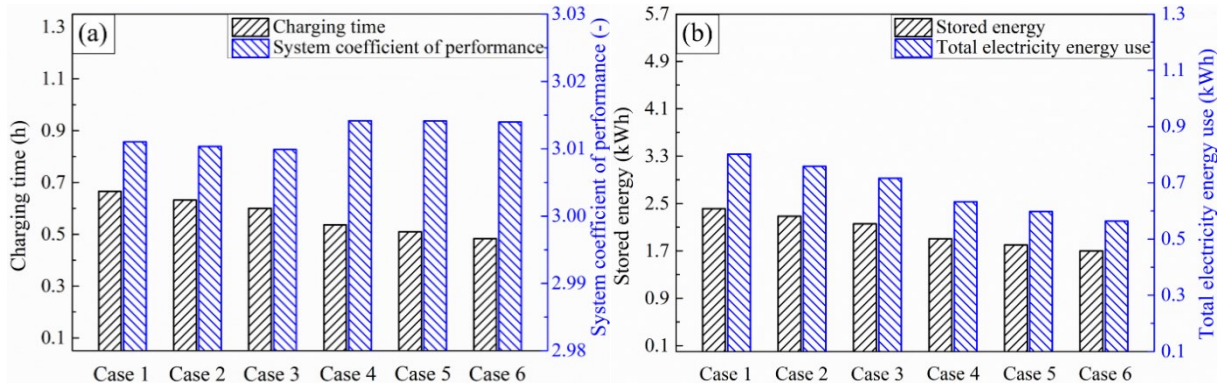
416

417 Fig. 9 (a) depicts the charging time ( $\sigma_{cc}$ ) and system coefficient of performance ( $COP_{sm}$ ) in  
418 different tank arrangements using the air-source heat pump.  $\sigma_{cc}$  in Case 1, Case 2, Case 3,  
419 Case 4, Case 5, and Case 6 were 0.62 h, 0.58 h, 0.55 h, 0.49 h, 0.46 h, and 0.43 h, respectively.  
420 Thus,  $\sigma_{cc}$  in Case 1 was the maximum, while  $\sigma_{cc}$  in Case 6 was the minimum.  $\sigma_{cc}$  in Case  
421 1 was 1.44 times as high as  $\sigma_{cc}$  in Case 6.  $COP_{sm}$  in Case 1, Case 2, Case 3, Case 4, Case 5,  
422 and Case 6 were 3.011, 3.0104, 3.0099, 3.0142, 3.0141, and 3.014, respectively. The difference  
423 of  $COP_{sm}$  between different cases was very small. According to the results of  $\sigma_{cc}$  in different  
424 cases, the tank arrangement in Case 6 was optimal because  $\sigma_{cc}$  in Case 6 was smaller than that  
425 in the other case. However, according to the results of  $COP_{sm}$  in different cases, the tank  
426 arrangement in Case 4 was optimal because  $COP_{sm}$  was slightly higher than that in the other  
427 case. Thus, it was important to identify the optimal tank arrangements based on the results in  
428 Fig. 9 (a). Further analysis for identifying the optimal tank arrangements is presented in the Fig.  
429 10.

430

431 Fig. 9 (b) depicts the stored energy ( $Q_{st}$ ) and total electricity energy use ( $E_{tl}$ ) in different tank  
432 arrangements using the air-source heat pump.  $Q_{st}$  in Case 1, Case 2, Case 3, Case 4, Case 5,  
433 and Case 6 were 2.41 kWh, 2.28 kWh, 2.15 kWh, 1.91 kWh, 1.8 kWh, and 1.7 kWh,  
434 respectively. Thus,  $Q_{st}$  in Case 1 had its maximum, while  $Q_{st}$  in Case 6 had its minimum.  
435  $Q_{st}$  in Case 1 was 1.42 times as high as  $Q_{st}$  in Case 6.  $E_{tl}$  in Case 1, Case 2, Case 3, Case 4,  
436 Case 5, and Case 6 were 0.8 kWh, 0.76 kWh, 0.72 kWh, 0.63 kWh, 0.6 kWh, and 0.56 kWh,  
437 respectively. Thus,  $E_{tl}$  in Case 6 had its minimum, while  $E_{tl}$  in the Case 1 had its maximum.  
438  $E_{tl}$  in Case 1 was 1.43 times as high as  $E_{tl}$  in Case 6. According to the structure parameters  
439 in Table 2, the volume of PCM storage tank in Case 1 and Case 6 had its maximum and  
440 minimum, respectively. Therefore, the difference of PCM storage tank volume might explain  
441 the difference of  $Q_{st}$  and  $E_{tl}$  in different tank arrangements.

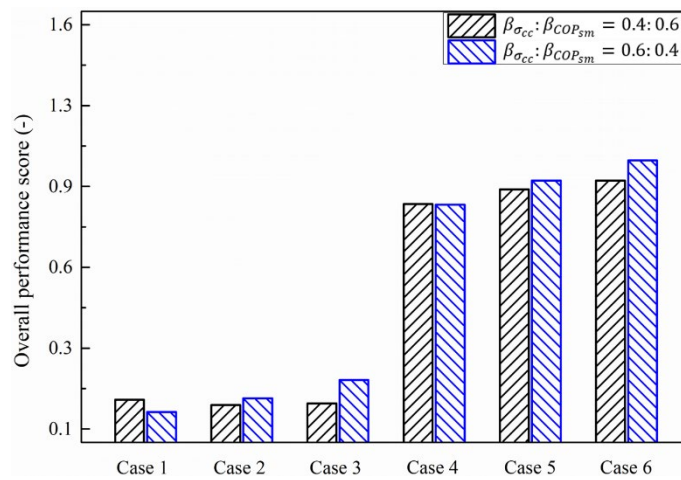
442



443 **Fig. 9.** (a) Charging time and system coefficient of performance, and (b) stored energy and total electricity  
 444 energy use in different tank arrangements using the air-source heat pump  
 445

446 Fig. 10 depicts the score of the overall performance ( $SR_{ov}$ ) in different tank arrangements using  
 447 the air-source heat pump. PCM-4 was applied in this section. When the weight factor for  $\sigma_{cc}$   
 448 ( $\beta_{\sigma_{cc}}$ ) and the weight factor for  $COP_{sm}$  ( $\beta_{COP_{sm}}$ ) were 0.4 and 0.6,  $SR_{ov}$  in Case 1, Case 2,  
 449 Case 3, Case 4, Case 5, and Case 6 were 0.16, 0.14, 0.14, 0.88, 0.94, and 0.97, respectively.  
 450 Thus, the tank arrangement in the Case 6 was optimal because  $SR_{ov}$  was the highest. When  
 451  $\beta_{\sigma_{cc}}$  and  $\beta_{COP_{sm}}$  were 0.6 and 0.4,  $SR_{ov}$  in Case 1, Case 2, Case 3, Case 4, Case 5, and Case  
 452 6 were 0.11, 0.15, 0.22, 0.83, 0.91, and 0.98, respectively. Thus, the tank arrangement in the  
 453 Case 6 was optimal because  $SR_{ov}$  was the highest. It could be seen that no matter that  $\sigma_{cc}$   
 454 had a higher weighting or  $COP_{sm}$  had a higher weighting, the tank arrangement in Case 6 was  
 455 optimal. This meant that the balance of  $\sigma_{cc}$  and  $COP_{sm}$  in Case 6 could be better established  
 456 than that in the other cases.

457



458

459

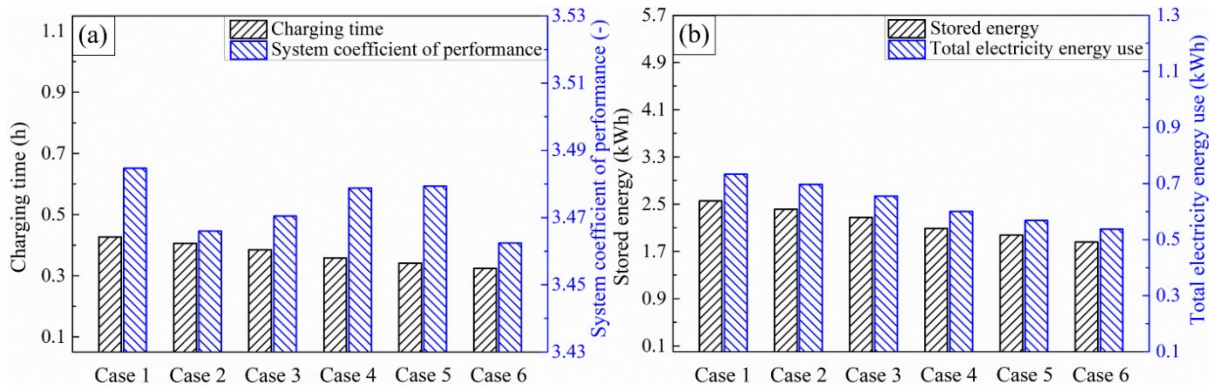
460

**Fig. 10.** Overall performance score in different tank arrangements using the air-source heat pump

461 Fig. 11 (a) depicted the charging time ( $\sigma_{cc}$ ) and system coefficient of performance ( $COP_{sm}$ ) in  
462 different tank arrangements using the water-source heat pump. PCM-4 was applied in this  
463 section.  $\sigma_{cc}$  in Case 1, Case 2, Case 3, Case 4, Case 5, and Case 6 were 0.38 h, 0.36 h, 0.33 h,  
464 0.31 h, 0.29 h, and 0.27 h, respectively. Thus,  $\sigma_{cc}$  in Case 1 had its maximum, while  $\sigma_{cc}$  in  
465 Case 6 had its minimum.  $\sigma_{cc}$  in Case 1 was 1.41 times as high as  $\sigma_{cc}$  in Case 6.  $COP_{sm}$  in  
466 Case 1, Case 2, Case 3, Case 4, Case 5, and Case 6 were 3.4847, 3.466, 3.4704, 3.4787, 3.4793,  
467 and 3.4624, respectively. The difference of  $COP_{sm}$  among different cases was small. However,  
468 it could be still found that  $COP_{sm}$  in Case 1 was the highest, while  $COP_{sm}$  in Case 6 was the  
469 lowest. According to the results of  $\sigma_{cc}$  for different cases, the tank arrangement in Case 6 was  
470 optimal because  $\sigma_{cc}$  was smaller than that in the other case. However, according to the results  
471 of  $COP_{sm}$  in different cases, the tank arrangement in Case 1 was optimal because  $COP_{sm}$  was  
472 slightly bigger than that in the other case. Thus, it was necessary to identify the optimal tank  
473 arrangement according to the results in Fig. 11 (a). Further analysis for identifying the optimal  
474 tank arrangement is presented in Fig. 12.

475  
476 Fig. 11 (b) depicts the stored energy ( $Q_{st}$ ) and total electricity energy use ( $E_{tl}$ ) in different tank  
477 arrangements using the water-source heat pump.  $Q_{st}$  in Case 1, Case 2, Case 3, Case 4, Case  
478 5, and Case 6 were 2.55 kWh, 2.41 kWh, 2.27 kWh, 2.09 kWh, 1.98 kWh, and 1.86 kWh,  
479 respectively. Thus,  $Q_{st}$  in Case 1 was the maximum, while  $Q_{st}$  in Case 6 was the minimum.  
480  $Q_{st}$  in Case 1 was 1.37 times as high as  $Q_{st}$  in Case 6.  $E_{tl}$  in Case 1, Case 2, Case 3, Case 4,  
481 Case 5, and Case 6 were 0.73 kWh, 0.7 kWh, 0.66 kWh, 0.6 kWh, 0.57 kWh, and 0.54 kWh,  
482 respectively. Thus,  $E_{tl}$  in Case 6 had its minimum, while  $E_{tl}$  in Case 1 had its maximum.  $E_{tl}$   
483 in Case 1 was 1.35 times as high as  $E_{tl}$  in Case 6. The PCM storage tank volume in Case 1  
484 and Case 6 were the maximum and minimum among these cases, respectively. This might be  
485 the reason why  $Q_{st}$  and  $E_{tl}$  had its maximum in Case 1, and  $Q_{st}$  and  $E_{tl}$  had its maximum  
486 in Case 6.

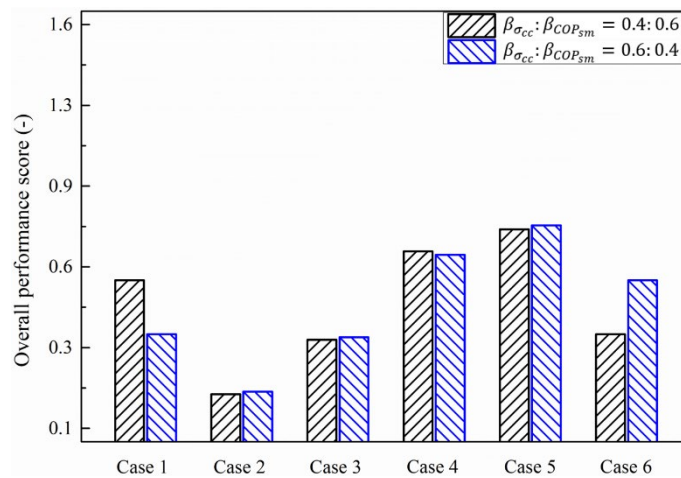
487



488 **Fig. 11.** (a) Charging time and system coefficient of performance, and (b) stored energy and total electricity  
 489 energy use in different tank arrangements using the water-source heat pump  
 490

491 Fig. 12 depicts the score of the overall performance ( $SR_{ov}$ ) in different tank arrangements using  
 492 the water-source heat pump. PCM-4 was applied in this section. When the weight factor of  $\sigma_{cc}$   
 493 ( $\beta_{\sigma_{cc}}$ ) and weight factor of  $COP_{sm}$  ( $\beta_{COP_{sm}}$ ) were 0.4 and 0.6,  $SR_{ov}$  in Case 1, Case 2, Case  
 494 3, Case 4, Case 5, and Case 6 were 0.6, 0.18, 0.38, 0.71, 0.79, and 0.4, respectively. Thus, the  
 495 tank arrangement in Case 5 was optimal because  $SR_{ov}$  was the highest. When  $\beta_{\sigma_{cc}}$  and  
 496  $\beta_{COP_{sm}}$  were 0.6 and 0.4,  $SR_{ov}$  in Case 1, Case 2, Case 3, Case 4, Case 5, and Case 6 were  
 497 0.4, 0.19, 0.39, 0.69, 0.8, and 0.6, respectively. Thus, the tank arrangement in Case 5 was  
 498 optimal because  $SR_{ov}$  was the highest. It could be seen that no matter that  $\sigma_{cc}$  had a higher  
 499 weighting or  $COP_{sm}$  had a higher weighting, the tank arrangement in Case 5 was optimal. This  
 500 meant that the balance of  $\sigma_{cc}$  and  $COP_{sm}$  in Case 5 could be better established than that in  
 501 the other case.

502



503

504

**Fig. 12.** Overall performance score in different tank arrangements using the water-source heat pump

505

506 For the system using the air-source and water-source CO<sub>2</sub> heat pumps, the optimal cases about  
507 the tank arrangements were Case 6 and Case 5, respectively. According to the Eqn. (8), the  
508 identification of optimal cases was related to  $\sigma_{cc}$ ,  $COP_{sm}$ ,  $\beta_{\sigma_{cc}}$ , and  $\beta_{COP_{sm}}$ . It might be  
509 difficult to determine the optimal tank arrangements according to the single factor. However,  
510 this section gave guidelines how to identify the optimal tank arrangements, which was  
511 significant in the engineering applications.

512

#### 513 **4. Discussion**

514 The performance of the system utilizing the CO<sub>2</sub> heat pumps to charge the PCM storage tank  
515 was studied, considering charging time ( $\sigma_{cc}$ ) and system coefficient of performance ( $COP_{sm}$ )  
516 as indicators. The effects of expansion valve opening ( $o_{ex}$ ), PCM types, and tube arrangements  
517 on  $\sigma_{cc}$ ,  $COP_{sm}$ , stored energy ( $Q_{st}$ ) and total electricity energy use ( $E_{tl}$ ) were analyzed. The  
518 multi-criteria optimization approach was applied to identify the optimal  $o_{ex}$ , PCM types, and  
519 tube arrangements. This study considered two kinds of CO<sub>2</sub> heat pumps (i.e., air-source and  
520 water-source CO<sub>2</sub> heat pumps) as case studies. This study broke the traditional research paths  
521 about the charging performance studies of PCM storage tank, which only studied the charging  
522 process in the open loop and applied  $\sigma_{cc}$  as the indicator. This study established a different  
523 research path, which considered the charging process in the closed loop, and applied both  $\sigma_{cc}$   
524 and  $COP_{sm}$  as the indicators. This study not only filled the research gap of the investigations  
525 of the system applying CO<sub>2</sub> heat pumps to charge the PCM storage tank, but also gave a  
526 guideline for engineers to well determine optimal parameters of the system. Based on our study,  
527 the future studies on the following topics may be initiated: (a) more advanced heat-source  
528 devices (e.g., ground-source and solar-assisted CO<sub>2</sub> heat pumps) should be considered in the  
529 investigations for the charging performance of the PCM storage tank in the closed loop. The  
530 effects of different parameters (e.g., borehole depth in the ground-source CO<sub>2</sub> heat pump and  
531 solar collector area in the solar-assisted CO<sub>2</sub> heat pump) on the system performance should be  
532 considered; (b) different PCM types should be considered in the investigation of the charging  
533 process. A dataset of PCM types should be established and applied in different charging systems.  
534 The optimal PCM types for different charging systems could be better to be determined; (c)  
535 optimal operating strategies (e.g., artificial neural network-based and self-adaptive optimal  
536 control methods) for different charging systems should be constructed for obtaining smaller  
537  $\sigma_{cc}$  and larger  $COP_{sm}$ . Our study gave a start point how to present and compare the results for  
538 different improvements and specific system adjustments.

## 539 **5. Conclusions**

540 The performance investigation of using the CO<sub>2</sub> heat pumps to charge the PCM storage tank  
541 was performed in this study. The modelling of the charging process was constructed by the  
542 integration of the heat pump and PCM storage tank models. Experimental data were applied for  
543 validating the reliability of these models. The influence of different expansion valve opening  
544 ( $o_{ex}$ ), PCM types, and tube arrangements on the system performance were analyzed. Both the  
545 air-source and the water-source CO<sub>2</sub> heat pumps were considered in this study. The optimal  
546 parameters were identified by maximizing the overall performance considering the balance  
547 between the charging time ( $\sigma_{cc}$ ) and system coefficient of performance ( $COP_{sm}$ ). For the  
548 systems using both air-source and water-source CO<sub>2</sub> heat pumps,  $\sigma_{cc}$  increased with the  
549 increase of  $o_{ex}$ . The optimal  $o_{ex}$  was 40% because  $\sigma_{cc}$  in was the shortest and  $COP_{sm}$  was  
550 the highest.  $COP_{sm}$  in the cases when  $o_{ex}$  was 40% using the air-source and the water-source  
551 CO<sub>2</sub> heat pumps were 2.83 and 3.31, respectively. For the systems using both the air-source and  
552 the water-source CO<sub>2</sub> heat pumps, the optimal PCM was the PCM-4 with the melting  
553 temperature of 19.6°C and the latent heat of 86 kJ/kg.  $COP_{sm}$  when the PCM-4 was applied  
554 using the air-source and the water-source CO<sub>2</sub> heat pumps were 3.01 and 3.48, respectively. For  
555 the system using the air-source CO<sub>2</sub> heat pump, the optimal tank arrangement occurred at Case  
556 6, in which the number of tubes in each column and row were 19 and 5, respectively.  $COP_{sm}$   
557 in Case 6 when the air-source CO<sub>2</sub> heat pump was applied was 3.014. For the system using the  
558 water-source CO<sub>2</sub> heating pump, the optimal tank arrangement occurred at Case 5, in which the  
559 number of tubes in each column and row were 20 and 5, respectively.  $COP_{sm}$  in Case 5 when  
560 the water-source CO<sub>2</sub> heat pump was applied was 3.4793. In sum, for the systems using both  
561 air-source and water-source CO<sub>2</sub> heat pumps, PCM-4 was the most suitable. For the system  
562 using the air-source and water-source CO<sub>2</sub> heat pumps, the optimal cases about the tank  
563 arrangements were Case 6 and Case 5, respectively. The identification of optimal cases was  
564 related to  $\sigma_{cc}$ ,  $COP_{sm}$ ,  $\beta_{\sigma_{cc}}$ , and  $\beta_{COP_{sm}}$ . It might be hard to determine the optimal tank  
565 arrangement according to the single factor. However, this study could guide engineers to  
566 identify the optimal  $o_{ex}$ , PCM types, and tank arrangements, which was significant in the  
567 engineering applications.

568

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575

### 576 **Appendix A. Performance analysis of discharging process**

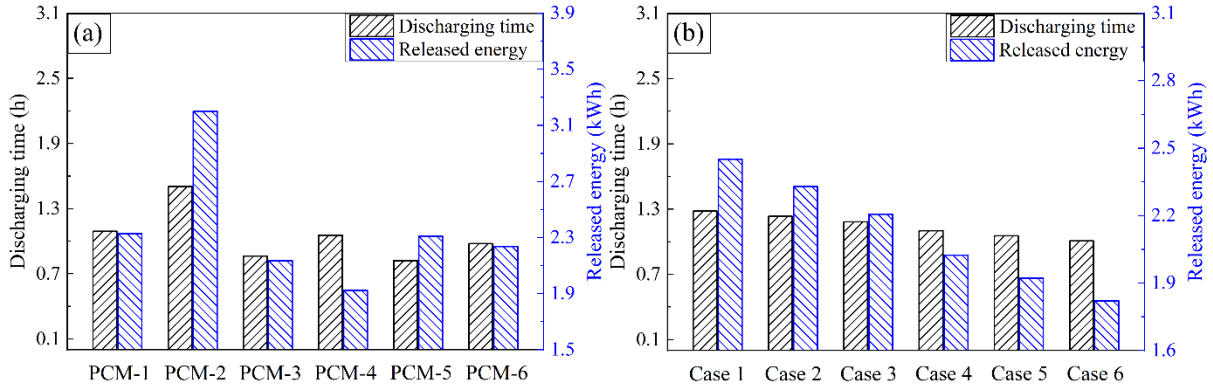
577 Fig. A1 (a) depicts the discharging time ( $\sigma_{dc}$ ) and released energy ( $Q_{rs}$ ) in different PCM types.  
578 When the PCM-1, PCM-2, PCM-3, PCM-4, PCM-5, and PCM-6 were used,  $\sigma_{dc}$  were 1.09 h,  
579 1.5 h, 0.86 h, 1.06 h, 0.82 h, and 0.98 h, respectively. Thus,  $\sigma_{dc}$  was the minimum when the  
580 PCM-5 was utilized, while  $\sigma_{dc}$  had its maximum when the PCM-2 was utilized.  $\sigma_{dc}$  when  
581 the PCM-2 was utilized was 1.83 times as high as  $\sigma_{dc}$  when the PCM-5 was utilized. When  
582 the PCM-1, PCM-2, PCM-3, PCM-4, PCM-5, and PCM-6 were used,  $Q_{rs}$  were 2.33 kWh, 3.2  
583 kWh, 2.14 kWh, 1.92 kWh, 2.31 kWh, and 2.24 kWh, respectively. Thus,  $Q_{rs}$  had its  
584 maximum when the PCM-2 was utilized, while  $Q_{rs}$  had its minimum when the PCM-4 was  
585 utilized.  $Q_{rs}$  when the PCM-4 was utilized was 1.67 times as high as  $Q_{rs}$  when the PCM-2  
586 was utilized. It could be seen that in Table 1 the density of PCM-2 was higher than that of other  
587 PCMs, and the density of PCM-4 was lower than that of other PCMs. The degree that the density  
588 of PCM-2 was higher than that of other PCMs was evident, which caused that PCM-2 has higher  
589 thermal capacity (i.e., multiplication of the specific heat and density). Meanwhile, PCM-4 has  
590 lower latent heat. Thus, thermal properties of these PCMs might explain the difference of  $\sigma_{dc}$   
591 and  $Q_{rs}$  in different PCM types.

592

593 Fig. A1 (b) depicts  $\sigma_{dc}$  and  $Q_{rs}$  in different tank arrangements.  $\sigma_{dc}$  in Case 1, Case 2, Case  
594 3, Case 4, Case 5, and Case 6 were 1.28 h, 1.23 h, 1.18 h, 1.1 h, 1.06 h, and 1.01 h, respectively.  
595 Thus,  $\sigma_{dc}$  in Case 1 was the maximum, while  $\sigma_{dc}$  in Case 6 was the minimum.  $\sigma_{dc}$  in Case  
596 1 was 1.27 times as high as  $\sigma_{dc}$  in Case 6.  $Q_{rs}$  in Case 1, Case 2, Case 3, Case 4, Case 5, and  
597 Case 6 were 2.45 kWh, 2.33 kWh, 2.21 kWh, 2.02 kWh, 1.92 kWh, and 1.82 kWh, respectively.  
598 Thus,  $Q_{rs}$  in Case 1 had its maximum, while  $Q_{rs}$  in Case 6 had its minimum.  $Q_{rs}$  in Case 1  
599 was 1.35 times as high as  $Q_{rs}$  in Case 6. According to the structure parameters in Table 2, the  
600 volume of PCM storage tank in Case 1 had its maximum, while the volume of PCM storage  
601 tank in Case 6 had its minimum. Thus, the difference of PCM storage tank volume might  
602 explain the difference of  $\sigma_{dc}$  and  $Q_{rs}$  in different tank arrangements.

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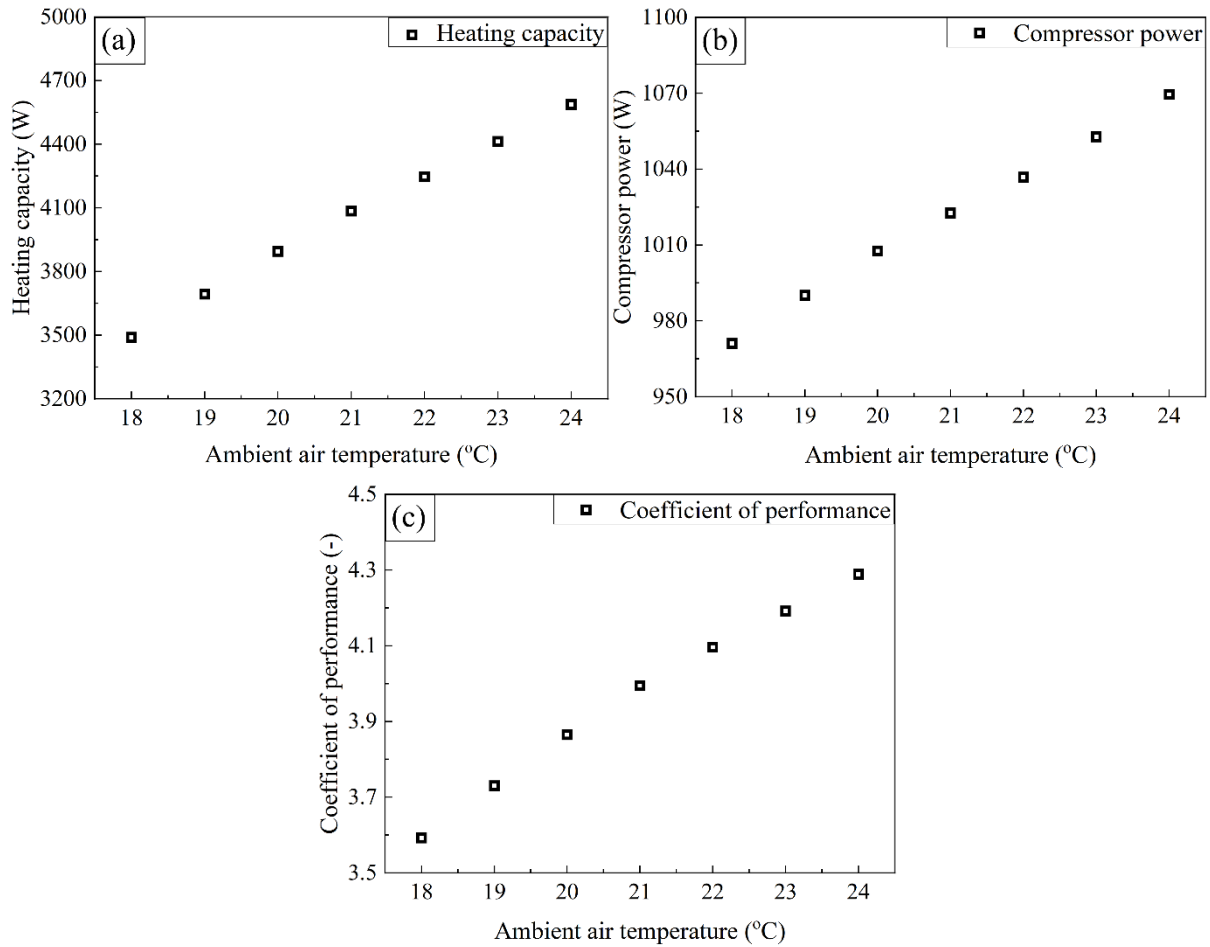


604  
605 **Fig. A1.** Discharging time and released energy in different (a) PCM types and (b) tank arrangements  
606

### 607 **Appendix B. Effect of ambient temperature on performance of CO<sub>2</sub> heat pump**

608 Fig. B1 (a) depicts the variations of heating capacity ( $\dot{Q}_{gs}$ ), compressor power ( $\dot{W}_{cp}$ ), and  
609 coefficient of performance of CO<sub>2</sub> heat pump ( $COP_{chp}$ ) with different ambient air temperature  
610 ( $T_{ab}$ ) using the air-source heat pump.  $\dot{Q}_{gs}$  increased with the increase of  $T_{ab}$ . This might be  
611 caused by that the increase of  $T_{ab}$  led to the increasing temperature difference between the  
612 ambient air and CO<sub>2</sub> in the evaporator, which improved the heat transfer effect. When  $T_{ab}$   
613 increased from 18°C to 24°C,  $\dot{Q}_{gs}$  varied from 3,488 W to 4,586.8 W, increased by 24%,  
614 respectively. The variation trend was almost linear.  $\dot{W}_{cp}$  increased with the increased of  $T_{ab}$ .  
615 When  $T_{ab}$  increased from 18°C to 24°C,  $\dot{W}_{cp}$  varied from 971 W to 1,069.5 W, increased by  
616 9.2%.  $COP_{chp}$  increased with the increased of  $T_{ab}$ . The reason of this phenomenon might be  
617 that the increasing degree of  $\dot{Q}_{gs}$  was larger than that of  $\dot{W}_{cp}$ . When  $T_{ab}$  increased from 18°C  
618 to 24°C,  $COP_{chp}$  varied from 3.59 to 4.29, increased by 16.2%.

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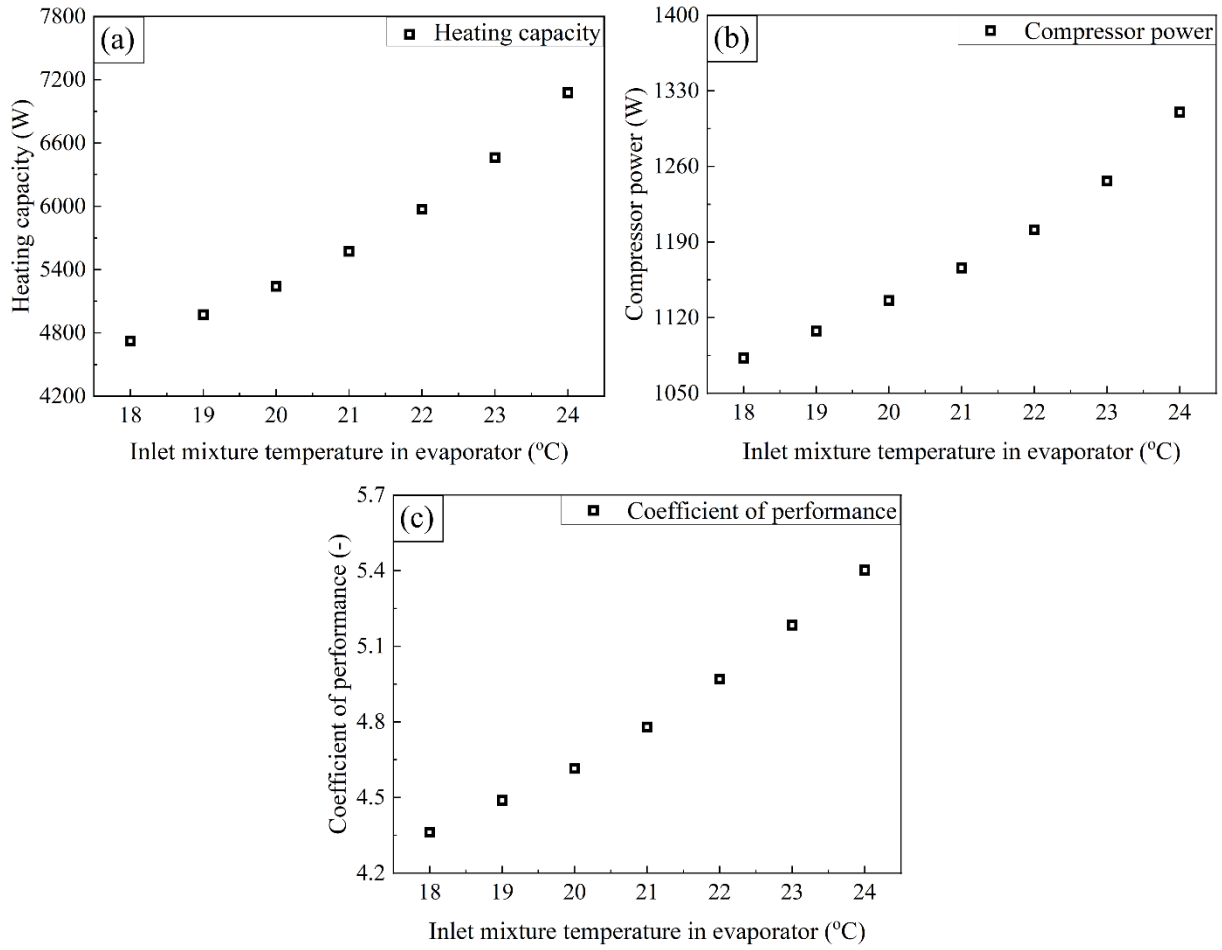
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635

**Fig. B1.** Variations of (a) heating capacity, (b) compressor power, and (c) coefficient of performance with different ambient air temperature using the air-source heat pump

Fig. B2 (b) depicts the variations of  $\dot{Q}_{gs}$ ,  $\dot{W}_{cp}$ , and  $COP_{chp}$  with different inlet mixture temperature in evaporator ( $T_{it,z}$ ) using the water-source heat pump.  $\dot{Q}_{gs}$  increased with the increase of  $T_{it,z}$ . The reason might be the enhancement of the heat transfer effect caused by the increasing temperature difference between the inlet mixture and  $CO_2$  in the evaporator. When  $T_{it,z}$  increased from 18°C to 24°C,  $\dot{Q}_{gs}$  varied from 4,721.5 W to 7,075.8 W, increased by 49.9%, respectively.  $\dot{W}_{cp}$  increased with the increased of  $T_{it,z}$ . When  $T_{it,z}$  increased from 18°C to 24°C,  $\dot{W}_{cp}$  varied from 1,082.5 W to 1,310 W, increased by 21%.  $COP_{chp}$  increased with the increased of  $T_{it,z}$ . This might be caused by that the increasing degree of  $\dot{Q}_{gs}$  was larger than that of  $\dot{W}_{cp}$ . When  $T_{it,z}$  increased from 18°C to 24°C,  $COP_{chp}$  varied from 4.36 to 5.4, increased by 23.8%.



636

637

638 **Fig. B2.** Variations of (a) heating capacity, (b) compressor power, and (c) coefficient of performance with  
 639 different inlet mixture temperature in evaporator using the water-source heat pump  
 640

641

### 641 Appendix C. Exergy analysis

642 The exergy efficiency of the PCM storage tank ( $\eta_{ey}$ ) was calculated by Eqn. (C1):

$$643 \quad \eta_{ey} = \frac{EX_{st}}{EX_{sd}} \quad (C1)$$

644 where  $EX_{st}$  and  $EX_{sd}$  denote the stored and supplied exergy by the water, respectively. The  
 645 calculation of  $EX_{st}$  and  $EX_{sd}$  referred to the study of Cheng et al. [51].  $EX_{st}$  was calculated  
 646 by Eqn. (C2):

$$647 \quad EX_{st} = EX_{wt} + EX_{pc} \quad (C2)$$

648 where  $EX_{wt}$  and  $EX_{pc}$  denote the exergy stored in the water and PCM, respectively.  $EX_{wt}$   
 649 was calculated by Eqn. (C3):

$$650 \quad EX_{wt} = \sum_i M_{wt,i} c_{wt} (T_{ab} \ln \frac{T_{in}}{T_{wt,i}} + T_{wt,i} - T_{in}) \quad (C3)$$

651 where  $M$  and  $c$  denote the mass and specific heat, respectively.  $EX_{pc}$  was calculated by Eqn.  
 652 (C4):

653 
$$EX_{pc} = \sum_i \int_{T_{in}}^T M_{pc,i} \left( \frac{T_{ab}}{T} - 1 \right) dh(T) \quad (C4)$$

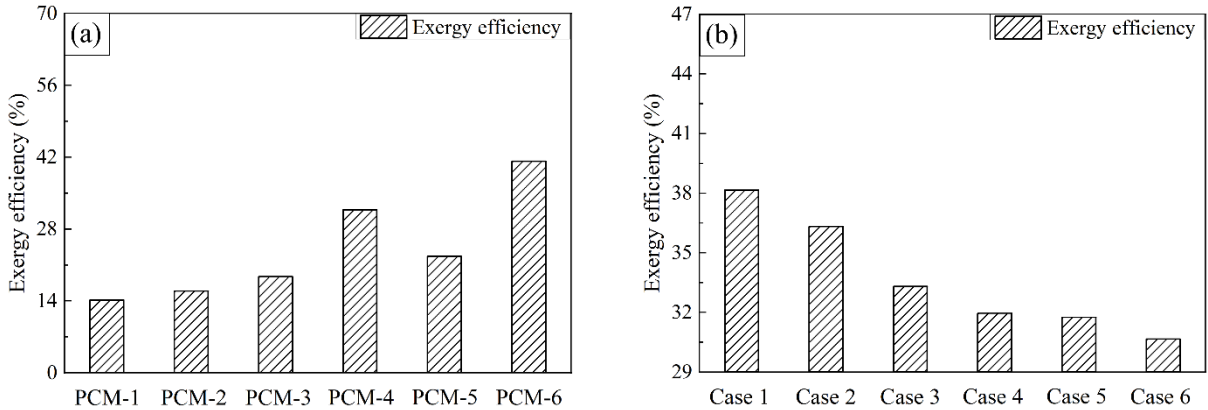
654 where  $h$  denotes the enthalpy.  $EX_{sd}$  was calculated by Eqn. (C5):

655 
$$EX_{sd} = \int_0^t \dot{m}_{wt} c_{wt} (T_{ab} \ln \frac{T_{wt,ot}}{T_{wt,it}} - T_{wt,ot} + T_{wt,it}) dt \quad (C5)$$

656

657 Fig. C1 depicts the variations of exergy efficiency ( $\eta_{ey}$ ) with different PCM types and tank  
 658 arrangements using the air-source heat pump. When the PCM-1, PCM-2, PCM-3, PCM-4,  
 659 PCM-5, and PCM-6 were used,  $\eta_{ey}$  were 14.2%, 15.9%, 18.7%, 31.8%, 22.7%, and 41.2%,  
 660 respectively. Thus,  $\eta_{ey}$  was the minimum when the PCM-1 was utilized, while  $\eta_{ey}$  was the  
 661 maximum when the PCM-6 was utilized.  $\eta_{ey}$  when the PCM-6 was utilized was 2.9 times as  
 662 high as  $\eta_{ey}$  when the PCM-1 was utilized.  $\eta_{ey}$  in Case 1, Case 2, Case 3, Case 4, Case 5, and  
 663 Case 6 were 38.2%, 36.3%, 33.3%, 32%, 31.7%, and 30.7%, respectively. Thus,  $\eta_{ey}$  in Case  
 664 6 had its minimum, while  $\eta_{ey}$  in Case 1 had its maximum.  $\eta_{ey}$  in Case 1 was 1.24 times as  
 665 high as  $\eta_{ey}$  in Case 6. According to the Eqn. (C1), the variation of  $\eta_{ey}$  was determined by  
 666 the variations of  $EX_{st}$  and  $EX_{pc}$ . When the increasing degree of  $EX_{st}$  was larger than that of  
 667  $EX_{pc}$ ,  $\eta_{ey}$  would increase, and vice versa.

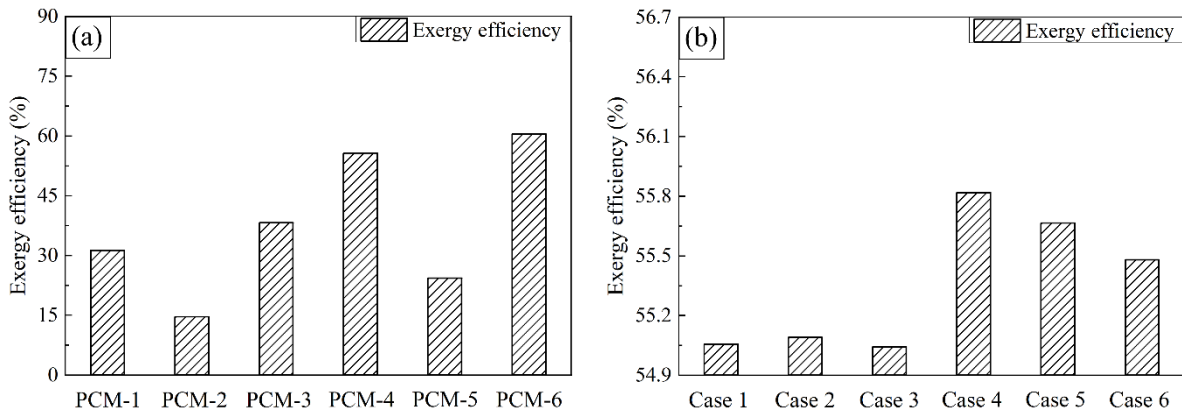
668



669 **Fig. C1.** Variations of exergy efficiency with different (a) PCM types and (b) tank arrangements using the  
 670 air-source heat pump  
 671  
 672

673 Fig. C2 depicts the variations of exergy efficiency ( $\eta_{ey}$ ) with different PCM types and tank  
 674 arrangements using the water-source heat pump. When the PCM-1, PCM-2, PCM-3, PCM-4,  
 675 PCM-5, and PCM-6 were used,  $\eta_{ey}$  were 31.3%, 14.6%, 38.2%, 55.7%, 24.3%, and 60.5%,  
 676 respectively. Thus,  $\eta_{ey}$  was the minimum when the PCM-2 was utilized, while  $\eta_{ey}$  was the  
 677 maximum when the PCM-6 was utilized.  $\eta_{ey}$  when the PCM-6 was utilized was 4.14 times as

678 high as  $\eta_{ey}$  when the PCM-2 was utilized.  $\eta_{ey}$  in Case 1, Case 2, Case 3, Case 4, Case 5, and  
 679 Case 6 were 55.1%, 55.1%, 55%, 55.8%, 55.7%, and 55.5%, respectively. Thus,  $\eta_{ey}$  in Case  
 680 3 had its minimum, while  $\eta_{ey}$  in Case 4 had its maximum.  $\eta_{ey}$  in Case 4 was 1.01 times as  
 681 high as  $\eta_{ey}$  in Case 3. According to the Eqn. (C1), the relative increasing or decreasing degree  
 682 of  $EX_{st}$  and  $EX_{pc}$  were the reason for the variations of  $\eta_{ey}$  in different PCM types and tank  
 683 arrangements.  
 684



685  
 686 **Fig. C2.** Variations of exergy efficiency with different (a) PCM types and (b) tank arrangements using the  
 687 water-source heat pump  
 688

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