

4E evaluations of salt hydrate-based solar thermochemical heat transformer system used for domestic hot water production

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ABSTRACT

A critical step toward the widespread use of renewables is the development of effective energy storage technology. An impressive solution for energy storage and heat upgrade is the salt hydrate-based solar thermochemical heat transformer (THT). The article aims at the temperature lift effects of pressurization-assisted THT systems employing different salts to fulfill the heat requirements of domestic hot water (DHW) generation. To grasp the sustainability of the GJ-level THT systems, energy, exergy, economic, and environmental (4E) assessments are performed under various working conditions. Results manifest that the majority of THT systems enable discharging temperatures (T_{dis}) to surpass 65°C, matching regular DHW production. T_{dis} can be further boosted by the two-stage pressurization whereas at the expense of lowering thermodynamic properties. The SrBr_2 -based system almost exhibits the best 4E performances with a T_{dis} of 74.3°C, although its levelized energy cost (LEC) of 0.1162 \$/kWh is slightly higher than that of the LiOH-based system (0.1147 \$/kWh). Both systems yield great usable heat, up to 11,667 MJ and 11,140 MJ, respectively, with maximum exergy efficiency of 89.16% and 63.41%. Albeit capable of generating higher temperature DHW ($\geq 90^\circ\text{C}$), the usable heat and thermodynamic performances of the FeCl_2 and CaCl_2 based systems are unsatisfactory. By contrast, the K_2CO_3 and LiOH based systems render higher temperature DHW while ensuring acceptable thermodynamic properties and usable heat. Targeting the regular and higher temperature DHW productions, the lowest CO_2 emission are separately achieved

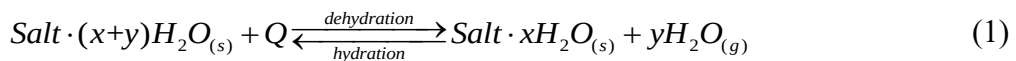
by the SrBr_2 and LiCl based systems, i.e., 15 kg/MWh and 56.2 kg/MWh; and the former shows the slowest growth rate in carbon emission with increased T_{dis} . Augmenting solar irradiation and duration contributes to reducing LEC , and the ideal operating condition in thermo-economic performances may differ from system to system.

Keywords: Salt hydrate; Thermochemical heat transformer; DHW production; Discharging temperature; 4E assessments

1. Introduction

In 2021 global energy-related CO_2 emissions reached 33 Gt with a growth of 4.8%, returning to pre-pandemic levels as demand for coal, oil, and gas rebounded with the economy [1,2]. The growing population and increasing energy expenditure, particularly in the field of building where energy usage accounts for over 40%, exert a substantial impetus on energy demand [3,4]. Of which the largest portion can be attributed to thermal energy for residential purposes, mainly including space heating (SH) and domestic hot water (DHW) generation [5]. Efforts have been underway in recent years to foster an energy revolution, shifting from carbon-based sources to inexhaustible renewables [6].

Solar energy is acknowledged as a highly promising renewable source, capable of being integrated with buildings to provide both SH and DHW [7–9]. Considering the intermittence and spatial-temporal dependence [10], scholars are devoting significant endeavors towards the advancement of thermal energy storage (TES) technology. Diverging from sensible and latent heat storage technologies, chemisorption heat storage, which falls within the realm of thermochemical energy storage (TCES), has garnered significant interest recently. This attention is primarily attributed to its theoretically exceptional energy storage density (ESD) and low heat losses. Salt hydrate-based chemisorption emerges as a more auspicious and viable option among the TCES systems [11–13]. The reversible gas-solid reaction encompassing dehydration (heat charging) and hydration (heat discharging) processes is elucidated below:



For finding prospective hydrated salts for long-term TCES utilizations, N'Tsoukpoe et al. [14] exhaustively evaluated 45 potential hydrated salts by focusing on application-oriented criteria. The findings indicated that $\text{SrBr}_2 \cdot 6\text{H}_2\text{O}$ and $\text{LaCl}_3 \cdot 7\text{H}_2\text{O}$ exhibited the

most promise as thermochemical materials (TCMs) with volumetric-ESDs of ~ 630 kWh/m³ and 590 kWh/m³, respectively. They additionally introduced the idea of cascaded TCES employing a multi-material system to facilitate efficient production of SH and DHW [15,16]. Sögütoglu et al. [17] performed a comparative analysis of the hydrates of K₂CO₃, MgCl₂ and Na₂S in terms of ESD, chemical stability, and thermal power. Despite K₂CO₃ exhibiting lower ESD (0.95-1.28 GJ/m³) and output power compared to the other two hydrates, it was deemed a favorable candidate for DWH due to its favorable cyclability and overall performance. Moreover, they also used a series of theories including thermodynamic, classical nucleation, and transition state to reveal the de/re-hydration reaction behaviors of some salts [18–20]. Zhang et al. [21] numerically studied a solar photovoltaic/thermal-powered TCES system integrating a heat exchanger using CaCl₂·6H₂O as TCM, and the results show that the overall thermal efficiency of the TCES system is 56%. A lab-scale honeycomb heat exchanger filled with SrBr₂·6H₂O was developed as a reactive bed by Fopah-Lele, the test results suggested the closed TCES system with an ESD of 213 kWh/m³ yielded the output temperature of 20–40°C, which is suitable for building heating [22]. By experimental screening, Clark et al. [23] recommended SrCl₂·6H₂O be adopted as TCM for building heating. Using a visualization experiment, Xu et al. [24] unveiled the intricate multistep phase changes of MgCl₂·6H₂O and concluded that the dehydration behavior and reaction pathways were influenced by water vapor pressure, gaseous atmosphere, heating rate, and so on.

To enhance the stability and reaction kinetics of pure salts, constructing composite TCM by impregnating salt in porous matrices is the most universal technique. Rehman et al. [25] synthesized and characterized the MgSO₄/MXene composite; it was found nanohybrid has stronger adsorption capacity than pure MgSO₄ due to MXene nanosheets' larger interlayer gaps, with an ESD above 1800 kJ/kg. Nguyen et al. [26] dispersed MgSO₄ into bead activated carbon as composite TCM, under the test condition (dehydration at 150°C, and hydration at 30°C with 60 % RH), the composite achieved the ESD of 920 kJ/kg and exhibited good cyclability. Luo et al. [27] used MOF as the matrix to develop the UiO-66/CaCl₂ composite, by regulating the salt content, the maximum ESD of ~ 1400 kJ/kg was obtained, accompanied with superior stability. To simultaneously maintain high ESD and power output, Aarts et al. [28] employed a highly porous mm-sized polymer matrix to encapsulate K₂CO₃, CaCl₂, and LiCl, the peak powers output achieved during discharging up to 300 W/kg, and the delivery temperatures were

respectively 60°C, 61°C, and 45°C when the vapor pressure is 12 mbar. Likewise, several studies on the property regulation and characterization of new TCMs, including K₂CO₃/expanded vermiculite [29], CaCl₂/alumina-supported MOF [30], LiCl/graphene aerogel fibers [31], LiOH-LiCl/EG [32], MgCl₂-CaCl₂/zeolite [33], SrCl₂/bentonite clay [34], were also carried out.

In addition to studying the reaction mechanisms and performance enhancements of reactive salts, research efforts have also been devoted to the gas-solid reaction unit. For instance, based on topology optimization, the enhancement effect of heat and mass transfer of the tree-like fins-embedded reactor used for hydrate-based TCES were numerically analyzed [35–38].

It is clear from the review above that published papers primarily focused on two orientations: 1) The development of salt-based TCMs, including preparation, characterization, elucidation of reaction mechanisms, and performance adjustment. 2) Improving heat and mass transport by designing and optimizing gas-solid reactors. However, there exists a significant scarcity of investigations analyzing the overall performance of TCES systems. Additionally, the discharging temperature (T_{dis}) was usually performed within the range of 25–40°C. While this scope notionally matches SH in buildings, it is deficient for producing DHW, which normally necessitates temperatures exceeding 45°C. Considering the temperature difference during the heat transfer process, a higher discharging temperature of around 65°C becomes imperative [10,28]. Furthermore, a limited number of works have sought to evaluate the integrated economy for sorption TCES systems.

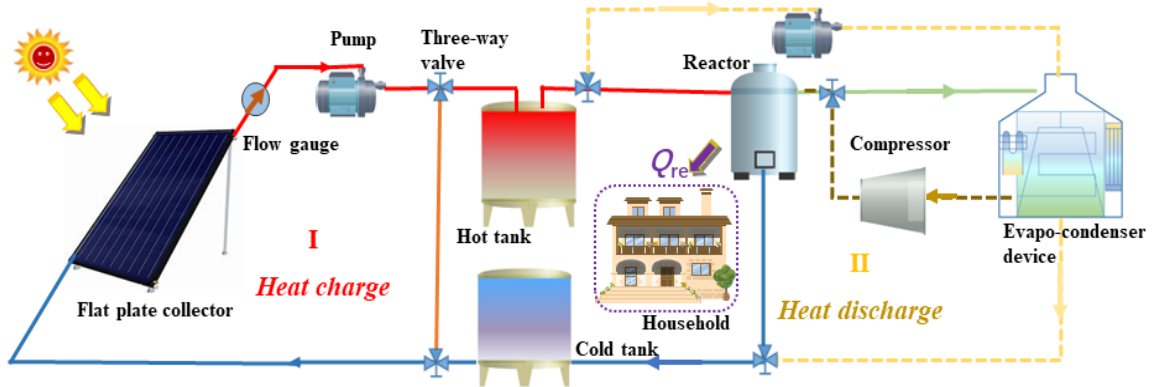
Given the above situations, a thermochemical heat transformer (THT) system, which can achieve heat storage and output temperature upgrade is proposed. The existing challenge of low hydration temperature in salt-based TCES systems can be addressed by pressurizing the reaction vapor and thus elevating the output temperature. And the conception has been experimentally validated [39,40]. The energy, exergy, economic, and environmental (4E) analysis of the GJ-scale THT system using different potential salts is performed, which is the primary novelty of this article. The results can serve as references and offer a strategic framework for the construction and optimization of large-scale salt hydrate-based TCES systems specifically tailored for DHW production in household applications.

2. THT System description

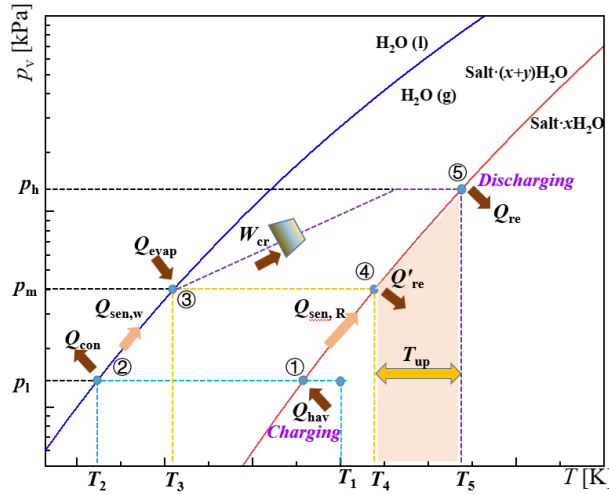
Fig. 1(a) illustrates the schematic of a salt hydrate-based solar THT system aiming at DHW production, and the related p - T diagram of the pressurization-assisted THT cycle is presented in Fig. 1(b). The equilibrium curve corresponding to the gas-solid reactions exhibits monovariant behavior, aligning with the Clausius-Clapeyron relationship:

$$\ln\left(\frac{p_{eq}}{p_{ref}}\right) = -\frac{\Delta H_r}{RT_{eq}} + \frac{\Delta S_r}{R} \quad (2)$$

where p_{ref} is the reference pressure, ΔH_r and ΔS_r are the reaction enthalpy and entropy.



(a)



(b)

Fig. 1. Schematic of (a) the pressurization-assisted THT system and (b) the p - T diagram for heat upgradation.

The heat transfer fluid (HTF) supplied from the cold tank is heated to a predetermined level during sunlit periods thanks to solar energy captured by the flat plate collector. Given the heat transfer temperature difference and reaction hysteresis, a

temperature of 15°C above the equilibrium temperature is used for charging (T_1). Subsequently, HTF is directed into a hot tank, while a fraction of it is utilized to heat the salt hydrate within the reactor. The desorbed vapor is directed towards the evaporator and condensed at an ambient temperature of 15°C (T_2). The cooled HTF is then recirculated back to the cold tank for reheating until the charging stage is finished. During chilly times, the condensate water is heated by the warm HTF supplied from the hot reservoir to the given evaporation temperature T_3 . The produced vapor is pressurized using a compressor and subsequently directed into the reactor for TCM hydration. The generated heat will be recovered for producing DHW.

For the conventional THT system, the evaporated water vapor flows straightway into the reactor at pressure p_m , and the hydration reaction's associated equilibrium temperature is T_4 , which might not satisfy the needed temperature for DHW generation. The pressurization-assisted THT system involves further pressurizing the vapor to a higher pressure, p_h , enabling the exothermic reaction to happen at T_5 . By adjusting the compression ratio of the compressor at the cost of electricity consumption, this will be easily customized to meet the end-user's requirements. Notably, the pressurization-assisted THT system achieves a temperature lift (T_{up}), surpassing that of the classical salt-based THT system.

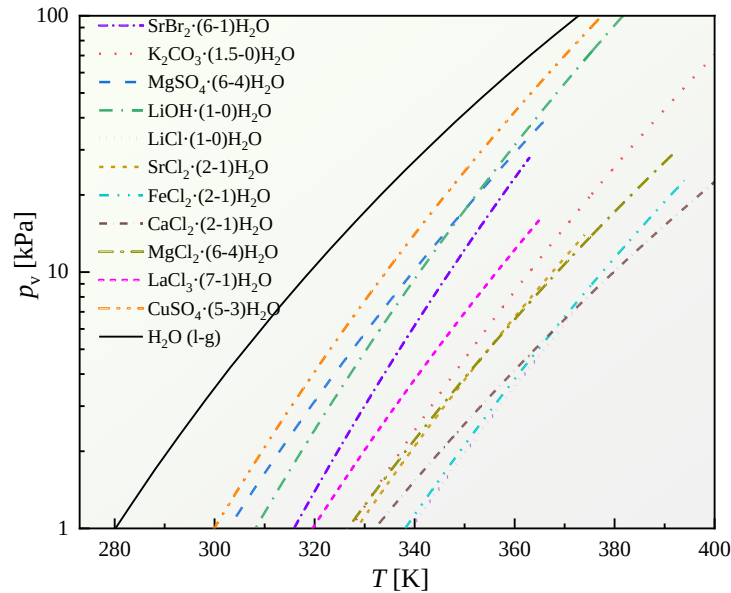
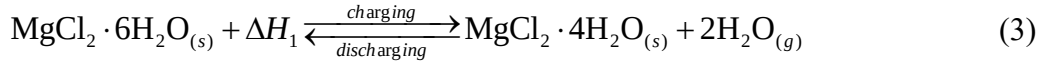


Fig. 2. Thermodynamic equilibrium curve for the employed reactive salts.

Some prospective salt candidates mentioned in the literature are chosen to analyze the salt-based THT system from the 4E standpoint. The relevant thermophysical parameters are gathered from the Refs [14,16,41–44], and the equilibrium curves depicting the dehydrated

and hydrated states were illustrated in Fig. 2. Taking $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ as an instance, the reversible reaction of heat (dis)charging is:



3. Methodology

3.1. Conditions and premises

The preheating process is supposed to raise the evaporating temperature of the water in discharge by 10°C . For the convenience of research, the average irradiation intensity and time for the basic case are assumed as 400 W/m^2 and 6 h. In order to achieve the TES with Gigajoule level, the volume of the TCM is set to 10 m^3 with a porosity of 0.4 [37] in this study. Assuming the reactor used here is the amplified module devised by Stengler et al. in Ref [36] that has excellent heat-mass transport capability via optimizing the structure, its volume ratio of aluminum fins is approximately 17%. Hence, we assume the heat and mass in the reactor are ideally transferred. The system functions in steady-state, also, the following hypotheses are made:

- (1) The thermophysical properties of the reactive salt remain unchanged during reactions. Considering the slow reaction rate at the end of hydration, the discharging process is viewed as completed when the hydration conversion reaches 0.9.
- (2) The temperature field within the components is homogeneous; the heat loss and pressure drop through the devices, the pipelines, and the reactor are negligible.
- (3) There is no liquid entrainment and the compressor's isentropic efficiency is set to 0.8.
- (4) The heat and mass in the reactor and other components are ideally transferred, and the agglomeration and deliquescence of salts are not considered.
- (5) The power consumption of the HTF pumps is ignored.

3.2. Calculation of model

3.2.1. Energy and exergy modeling

The following formula is used to derive the heat input needed by the reactor during charging, which is equal to the thermal energy collected by the HTF from solar collector:

$$Q_{\text{coll}} = m_{s1} \cdot \alpha \cdot \Delta H_{r,m} + c_{p,s1} \cdot m_{s1} \cdot (T_1 - T_2) + c_{p,\text{met}} \cdot m_{\text{met}} \cdot (T_1 - T_2) \quad (4)$$

where the three terms represent the reaction heat, sensible heat of salt hydrate and metal

within the reactor during charging. m and α denote mass and reaction degree, $\Delta H_{r,m}$ the reaction heat, kJ/kg; c_p the specific heat capacity, kJ/kg/K; the subscripts s1 signifies hydrated state.

The sensible heat needed to elevate the condensate water in the preheating process from the ambient temperature T_2 to the evaporation temperature T_3 is:

$$Q_{\text{sen, w}} = c_{p, w} \cdot \alpha \cdot m_w \cdot (T_3 - T_2) \quad (5)$$

The desorbed water vapor m_w during the heat charging stage is equivalent to the mass content of crystal water in salt hydrates:

$$m_w = m_{s1} \cdot \frac{M_{\text{H}_2\text{O}}}{M_{s1}} \quad (6)$$

where $M_{\text{H}_2\text{O}}$ and M_{s1} are the molar mass of water and hydrated salt.

The latent heat required to evaporate the water is determined as follows:

$$Q_{\text{evap, w}} = \alpha \cdot m_w \cdot L \quad (7)$$

where L denotes the latent heat of water at the evaporation temperature, kJ/kg.

The usable heat extracted from the reactor is the energy released by the reaction salt minus the sensible heat:

$$Q_{\text{usa}} = m_{s1} \cdot \alpha \cdot \Delta H_{r,m} - c_{p,s0} \cdot m_{s0} \cdot (T_5 - T_2) - c_{p,\text{met}} \cdot m_{\text{met}} \cdot (T_5 - T_2) - c_{p,v} \cdot m_v \cdot \alpha \cdot (T_5 - T_0) \quad (8)$$

where the total hydration reaction heat is signified by the first term on the right. The second and third terms represent the sensible heat supplied to raise the temperature of the dehydrated salt and metal reactor from the environment temperature to the discharging temperature T_5 . The fourth one is the sensible heat needed to raise the vapor's temperature to T_5 after it has left the compressor outlet (T_0). Noted that the last term will favorably contribute to the rise of released heat if T_0 is higher than T_5 .

Eq. (9) is used to determine the amount of work consumed by the compressor during vapor pressurization:

$$W_{\text{cr}} = \alpha \cdot m_v \cdot \frac{R}{M_v} \cdot T_3 \cdot \frac{n}{n-1} \left(\kappa^{\frac{n-1}{n}} - 1 \right) / \eta_{\text{cr}} \quad (9)$$

where m_v and M_v denote mass and molar mass of water vapor, n the adiabatic index of vapor (1.33), η_{cr} is the isentropic efficiency of the compressor, the compression ratio κ , is

1 defined as the ratio of discharge pressure (p_h) to suction pressure (p_m):

$$2 \quad \kappa = \frac{p_h}{p_m} \quad (10)$$

3 Thus, the exhaust temperature of the compressor is calculated as follows:

$$4 \quad T_o = T_3 + \frac{T_3 \cdot \kappa^{\frac{n-1}{n}} - T_3}{\eta_{cr}} \quad (11)$$

5 The thermal efficiency (η_{th}) and the coefficient of performance (COP_{tw}) representing
6 the thermal-work ratio, are defined to analyze this THT system from the first law of
7 thermodynamics view:

$$8 \quad \eta_{th} = Q_{usa} / (Q_{coll} + Q_{sen, w} + Q_{evap} + Q_{cr}) \quad (12)$$

$$9 \quad COP_{tw} = Q_{usa} / W_{cr} \quad (13)$$

10 Q_{cr} is the consumed heat to maintain the work generation of the compressor. Assuming
11 the thermal-electricity conversion rate of the power plant is 40% and the efficiency of
12 converting electricity into effective work is 80%, hence the relationship between the two
13 is:

$$14 \quad Q_{cr} = W_{cr} / 0.32 \quad (14)$$

15 The sensible heat needed by the reactor during discharging, which contains the metal
16 and reactive salt, is calculated as follows:

$$17 \quad Q_{sen, dis} = c_{p, s0} \cdot m_{s0} \cdot (T_5 - T_2) + c_{p, met} \cdot m_{met} \cdot (T_5 - T_2) + c_{p, v} \cdot m_v \cdot \alpha \cdot (T_5 - T_o) \quad (15a)$$

18 Therefore, the total sensible heat in the discharging stage is:

$$19 \quad Q_{sen} = Q_{sen, dis} + Q_{sen, w} \quad (15b)$$

20 Furthermore, the exergy efficiency of the THT system denoting the ratio of the
21 maximum useful energy output from the system under discharging condition to the
22 maximum useful energy input into the system under charging condition, is defined below
23 from the second law of thermodynamics standpoint:

$$24 \quad \eta_{ex} = \frac{Q_{usa} \cdot (1 - T_2/T_5)}{Q_{coll} \cdot (1 - T_2/T_1) + (Q_{sen, w} + Q_{evap}) \cdot (1 - T_2/T_3) + Q_{sen, r} \cdot (1 - T_2/T_5) + W_{cr}} \quad (16)$$

3.2.2. Economic modeling

The prices (\$) of the flat-plate solar collector [45], HTF (thermal storage water) [46], storage tanks [46], valve [47], and reactor [36,40] are given below:

$$Cost_{sc} = 163 \cdot A_{sc} \quad (17)$$

$$Cost_{HTF} = 0.0016 \cdot m_{HTF} \quad (18)$$

$$Cost_{tank} = 167.19 \cdot V_{tank} \quad (19)$$

$$Cost_{val} = 114.5 \cdot q_{HTF} \quad (20)$$

$$Cost_r = 1780 \cdot V_r \quad (21)$$

where A_{sc} , m_{HTF} , q_{HTF} , V_{tank} , and V_r are the area of solar collector, HTF mass, HTF mass flow rate, and volumes of tank and reactor. Additionally, the module costing technique is employed to determine the bare module cost of each component, and the present capital cost is obtained using the chemical engineering plant cost index (*CEPCI*) [48]. The evapo-condenser device is considered a combination of an evapo-condenser and a water storage tank. Based on Eqs.(22)-(25), the costs of all components in the system are calculated.

$$C_{BM} = C_p^0 F_{BM} = C_p^0 (B_1 + B_2 F_M F_p) \quad (22)$$

$$\log(C_p^0) = K_1 + K_2 \log(X_j) + K_3 \log[\log(X_j)]^2 \quad (23)$$

$$\log(F_p) = C_1 + C_2 \log(p_j) + C_3 \log[\log(p_j)]^2 \quad (24)$$

$$Cost_{cyc, total} = \sum_j C_{BM} \frac{CEPCI_{2020}}{CEPCI_{2001}} \quad (25)$$

These constants and their significance were explained in Ref. [49]. The dimensionless numbers of $CEPCI_{2001}=397$ and $CEPCI_{2020}=596.2$ are used to renovate the capital investment [50].

Moreover, the levelized energy cost (*LEC*), a synthetic indicator taking into account the thermodynamic and economic performance of the system, is utilized as the economy index [50–52]. It is given by:

$$LEC = (CRF \cdot Cost_{total} + C_{OM}) / (N \cdot Q_{usa}) \quad (26)$$

where N is the annual cycle for energy discharge. Given the occurrence of cloudy or rainy days intermittently, the system is assumed to run for 240 yearly. The capital recovery factor CRF , as well as the operational and maintenance cost (C_{om}) for this system are determined as follows:

$$CRF = i(1+i)^{LT} / \left[(1+i)^{LT} - 1 \right] \quad (27)$$

$$C_{OM} = 1.5\% Cost_{total} \quad (28)$$

where interest rate i and the equipment lifetime LT are 5% and 25 years, respectively.

3.2.3. Environmental modeling

The evaluation indicator used to determine how the system affects the environment is the CO₂ emissions per unit of usable heat output:

$$\phi_{CO_2} = \frac{m_{CO_2}}{Q_{usa}} \quad (29)$$

In this work, the work produced by the compressor essentially comes from electricity generated by the plant, the CO₂ emissions thus can be calculated. Since 1 kg of standard coal generates ~3 kWh of electricity while producing ~2.5 kg of CO₂ [53], the amount of CO₂ produced by releasing 1 MWh of required heat ($T_{dis} \geq 65^\circ\text{C}$) in this study is:

$$m_{CO_2} = \frac{2.5}{3} Q_{cr} \times 1000 \quad (30)$$

4. Results and discussion

4.1. Capability for temperature lift

In this study, some potential salt candidates mentioned in the literature are used as TCMs and combined with the THT system for heat upgradation capability analyses. The melting points of hydrates and reaction heat are provided in Table 1. A constraint condition is that the maximum T_{dis} of salt and the exhaust temperature of the compressor cannot exceed the melting point and 160°C, respectively.

Table 1. Melting temperatures and reaction heats of salt hydrates [14,16,41–44].

Salt hydrates	SrBr ₂ · (6-1) H ₂ O	K ₂ CO ₃ · (1.5-0) H ₂ O	MgSO ₄ · (6-4) H ₂ O	LiOH · (1-0) H ₂ O	CuSO ₄ · (5-3) H ₂ O	SrCl ₂ · (2-1) H ₂ O	FeCl ₂ · (2-1) H ₂ O	CaCl ₂ · (2-1) H ₂ O	MgCl ₂ · (4-2) H ₂ O	LaCl ₃ · (7-1) H ₂ O	LiCl · (1-0) H ₂ O
Melting points	89	>180	93	>250	110	100	120	175	118	91	99

(°C)											
Reaction	947.9	577.5	241.6	1400	450.5	303.3	373.9	384.3	352.8	159.6	1029.
heat ΔH					7						6
(kJ/kg)											

The compressor pressurizes evaporated vapor, which interacts with dehydrated salt and produces a larger T_{dis} than the reaction with salt directly. The change of T_{dis} with the vapor compression ratio κ is presented in Fig. 3(a). The reaction equilibrium relation explains why T_{dis} rises with κ . The T_{dis} of LiOH, for instance, rises from 50.63°C to 67.05°C when boosting κ from 1 to 3 (increase with a step of 0.25), implying T_{dis} can be upgraded in answer to the heating need via adjusting κ . It can be found among these salts, FeCl₂ theoretically has the potential to achieve the highest output temperatures, whereas CuSO₄ has the lowest. The discharge temperatures of the two are 115.06°C and 61.61°C when κ is 3.25 (Further compression will cause the compressor's exhaust temperature to exceed the upper limit). Except for CuSO₄, all other salts are possible to be used for DHW supply (65°C) if only from the output temperature perspective.

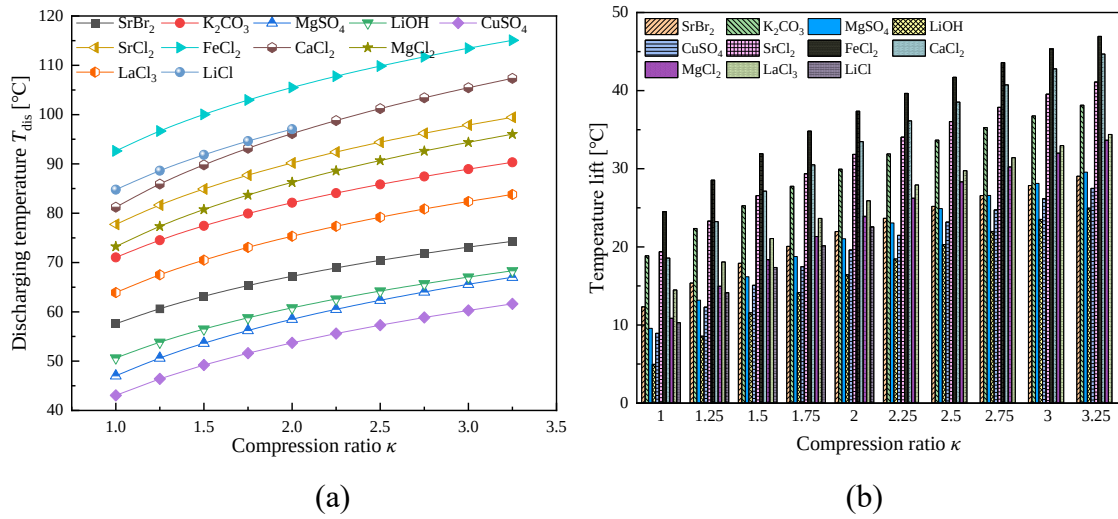


Fig. 3. Variations of (a) T_{dis} and (b) temperature lift with κ for different salts.

Fig. 3(b) shows when compared with the traditional TCES mode, a significant temperature lift can be reached for various salts when the vapor is pressurized ($\kappa=1$ signifying the vapor evaporates at the preheating temperature without compression). With κ increases, the temperature rises are enlarged. The THT system using FeCl₂ as TCM has the largest temperature lift, while the one based on LiOH is the lowest. For example, when $\kappa=2$, the temperature lifts for hydrates of SrBr₂, K₂CO₃, MgSO₄, LiOH, CuSO₄, SrCl₂, FeCl₂, CaCl₂, MgCl₂, LaCl₃, and LiCl are 21.96°C, 29.95°C, 21.04°C, 16.43°C, 19.59°C, 31.84°C, 37.37°C, 33.47°C, 23.91°C, 25.91°C, and 22.56°C, respectively. The above

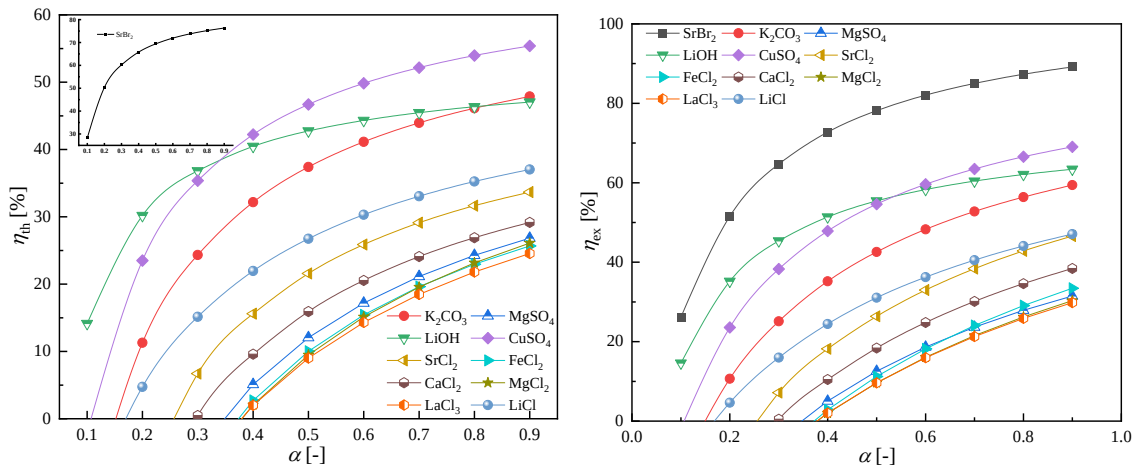
results preliminarily confirm the great potential for utilizing the salt-based THT system in producing DHW.

4.2. Thermodynamic analyses of the THT cycle

4.2.1. Influence of reaction conversion extent

The variations in η_{th} , η_{ex} , and COP_{tw} with hydration conversion extent at the maximum compression ratio ($\kappa = 3.25$) are exhibited in Fig. 4(a-c). As can be seen, the system efficiency is positively correlated with reaction conversion degree, the reason is that more thermal energy is released as the α of TCM continues to advance. E.g., as α ascends from 0.2 to 0.9, the K_2CO_3 -based system exhibits a rise in η_{th} , η_{ex} , and COP_{tw} from 11.29%, 35.19%, and 6.14 to 47.88%, 59.41%, and 19.24, respectively. The maximum η_{th} , η_{ex} , and COP_{tw} are found in the $SrBr_2$ -based THT system, while the $LaCl_3$ -based one has the lowest performance due to its relatively low ESD. Although these indicators increase as the reaction progresses, the growth rate gradually diminishes because the energy consumed for generating water vapor during discharging stage continually rises.

It can be observed that for most salts there exists a reaction conversion threshold after which η_{th} , η_{ex} , and COP_{tw} are greater than 0, meaning the THT system operates profitably. The reason behind this is the heat released is smaller than the Q_{sen} required to maintain the reactor system at T_{dis} if the hydration conversion is too small. Fig. 4(a-c) indicates the threshold values for $SrBr_2$ - and $LiOH$ -based systems (< 0.1) are smaller when compared to other THT systems; while for the $FeCl_2$ -, $MgCl_2$ -, and $LaCl_3$ -based systems, the indicators are positive only when α is close to 0.4. The above results emphasize the importance of the reactor's heat-mass transfer capability. Excellent heat and mass transfer can promote the conversion of reactants and therefore improve the overall performance of the system.



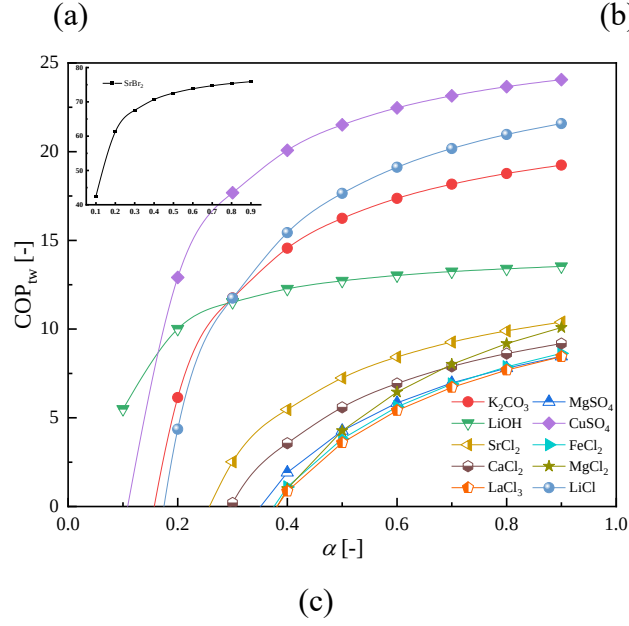


Fig. 4. Effect of α on (a) η_{th} , (b) η_{ex} , and (c) COP_{tw} .

4.2.2. Effect of compression ratio

Fig. 5(a-c) revealed how κ affects η_{th} , η_{ex} , and COP_{tw} of the THT system. Fig. 5(a) suggests that η_{th} gradually decreases with the increasing κ . This is because as κ increases, the T_{dis} of the system rises, and more sensible heat would be consumed by the reactants and reactor. $SrBr_2$ -based THT system possesses the greatest η_{th} when compared with systems using other salts, η_{th} declines from 79.09% to 76.32% as κ rises from 1 to 3.25. Followed by the $CuSO_4$ -based system despite its output temperature being lower than 65°C. Although $LiOH$ has the greatest ESD, η_{th} of the $LiOH$ -based system is only moderate (47.14%-50.66%). The reason is the high water content of $LiOH \cdot H_2O$ causes a huge heat consumption for water generation during hydration. η_{th} of the $LaCl_3$ -based system is the lowest (< 30%) because of its low ESD.

Furthermore, the $SrBr_2$ -based system has the highest η_{ex} . It exhibits an ascent trend from 73.54% to 89.16% (Fig. 5(b)). While for the THT systems using $LiOH$, K_2CO_3 , and $LiCl$ as TCMs the amplification of η_{ex} is relatively small. E.g., the η_{ex} increases from 56.72% to 59.41% as κ rise from 1 to 3.25. As for other salt-based systems, η_{ex} presents a reduction trend. The different variation trends can be ascribed to the comprehensive effect of usable heat Q_{usa} and T_{dis} . COP_{tw} dramatically descends with κ (Fig. 5(c)). The $SrBr_2$ -based THT system also realizes the largest COP_{tw} , followed by the $CuSO_4$ - and K_2CO_3 -based ones. Since COP_{tw} is essentially impacted by the released heat and work consumed to pressurize vapor, while large amounts of vapor are needed to hydrate $LiOH$, the $LiOH$ -based system

does not excel in terms of COP_{tw} , dropping from 78 to 13.5, far less than that of $SrBr_2$ -based system (454.2 to 75.9) though $LiOH$ has the highest gravimetric-ESD. Similar to η_{th} and η_{ex} , the lowest COP_{tw} is still found in the $LaCl_3$ -based system.

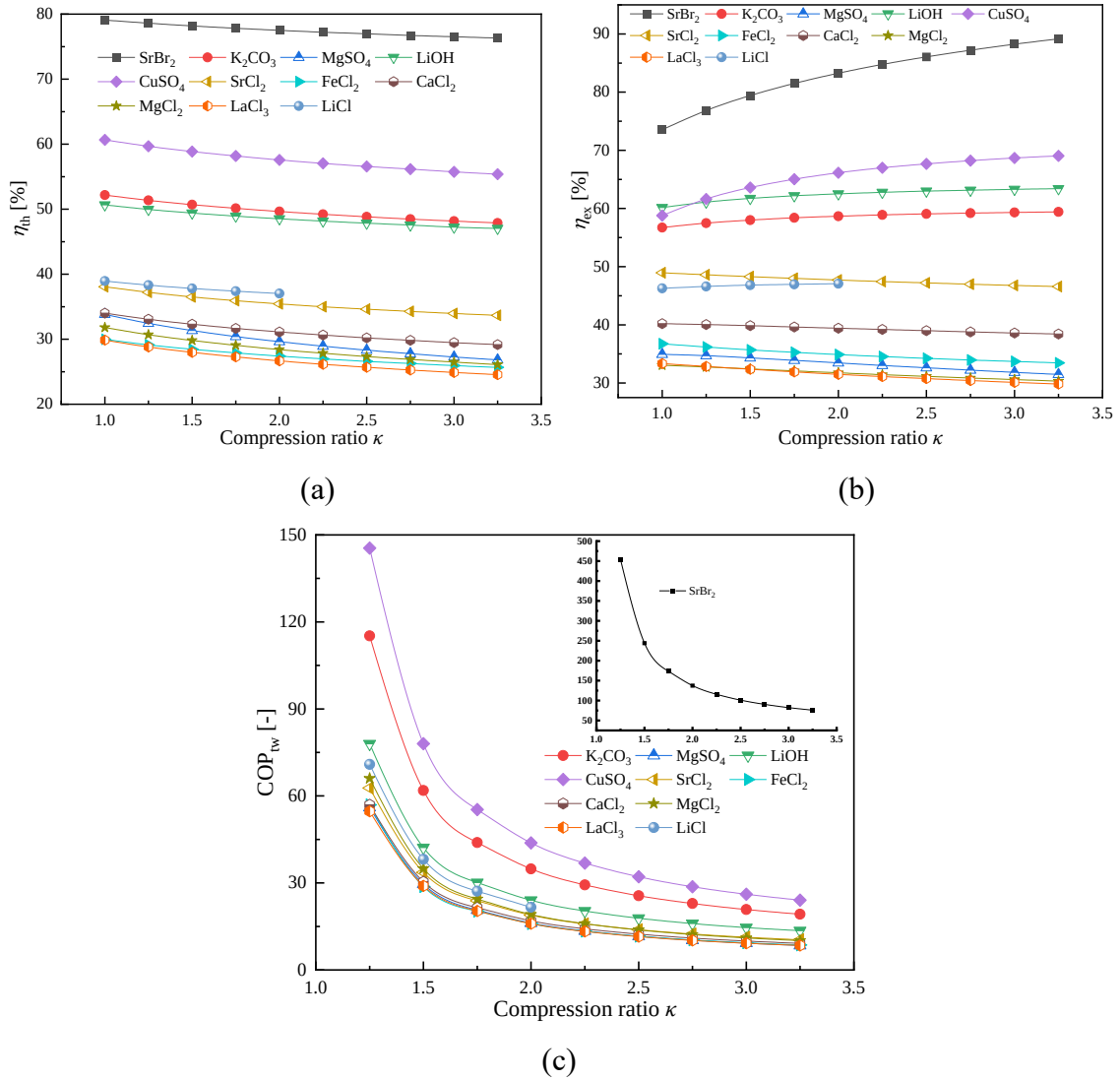


Fig. 5. Effect of κ on (a) η_{th} , (b) η_{ex} , and (c) COP_{tw} .

4.2.3. Comparison in heat and discharge temperature

The objective of the THT system is to elevate the release temperature for residential purposes. To achieve this, it is recommended to set the systems to attain the highest T_{dis} possible while ensuring that the T_{dis} remains below the melting points of the hydrates and that the compressor's exhaust temperature does not surpass the permissible temperature.

The portions of the solar collector captured heat, sensible heat for water preheating, evaporation heat for vapor generation, the usable heat in discharging, and the work produced by the compressor, as well as the maximum T_{dis} of the THT system using different

TCMs, are portrayed in Fig. 6. One can observe that the FeCl_2 -based system provides the highest T_{dis} , which is 115.06°C . Followed by the CaCl_2 - and SrCl_2 -based ones (107.35°C and 99.45°C). Also, the LiCl -, MgCl_2 -, and K_2CO_3 -based systems yield discharging temperatures over 90°C , specifically, 97.04°C , 96.02°C , and 90.31°C , respectively. The maximum T_{dis} of 61.61°C occurred on the CuSO_4 -based system, which is inadequate to produce DHW (65°C). Despite the high output temperatures achieved by the FeCl_2 - and CaCl_2 -based systems, their corresponding Q_{usa} are just 2,901.1 MJ and 2,646.4 MJ due to the relatively small reaction heat. The values for SrBr_2 - and LiOH -based systems are 11,667 MJ and 11,140 MJ, respectively. Because of the high ESDs of SrBr_2 , LiOH , and LiCl , the heat used for charging Q_{ch} is greater than that of other systems. The value of W_{cr} is insignificant compared with other types of energy. In comparison to the consumption of Q_{sen} , the heat required for vaporizing the liquid water is more remarkable, particularly in systems with a high content of vapor, such as the $\text{LiOH}/\text{H}_2\text{O}$ pair, in which Q_{sen} and Q_{evap} are 421.83 MJ and 8,509.3 MJ, respectively.

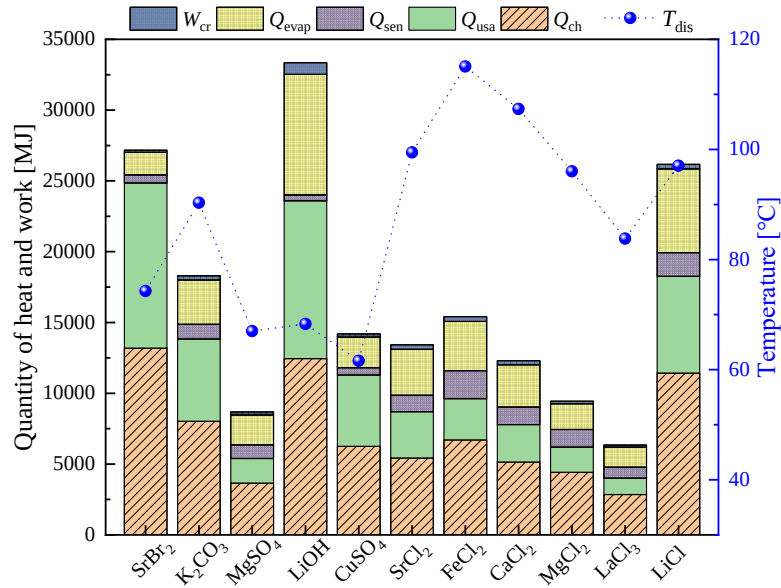


Fig. 6. Different types of energy shares and discharging temperatures for systems based on various salts.

4.2.4. Two-stage pressurization THT system

The above findings manifest that κ cannot be excessively large owing to the permissible temperature of the compressor, which in turn restricts the temperature rise of the THT system during discharging. Although the output temperature of 65°C (considering a transfer temperature difference of $10\text{--}15^\circ\text{C}$) can meet most residential applications like shower, a higher output temperature is also needed for hospital buildings applications such

as cleaning, laboratories, sterilization of operating room instruments [54], as illustrated in Fig. 7. To overcome this challenge, a two-stage pressurization-assisted THT system with an intermediate cooler is implemented (Fig. 8(a)). As depicted in Fig. 8(b), this system cools the vapor after the first pressurization (p_m to p_{h1}) and then sends it into the second compressor to undergo additional pressurization (p_{h1} to p_{h2}).

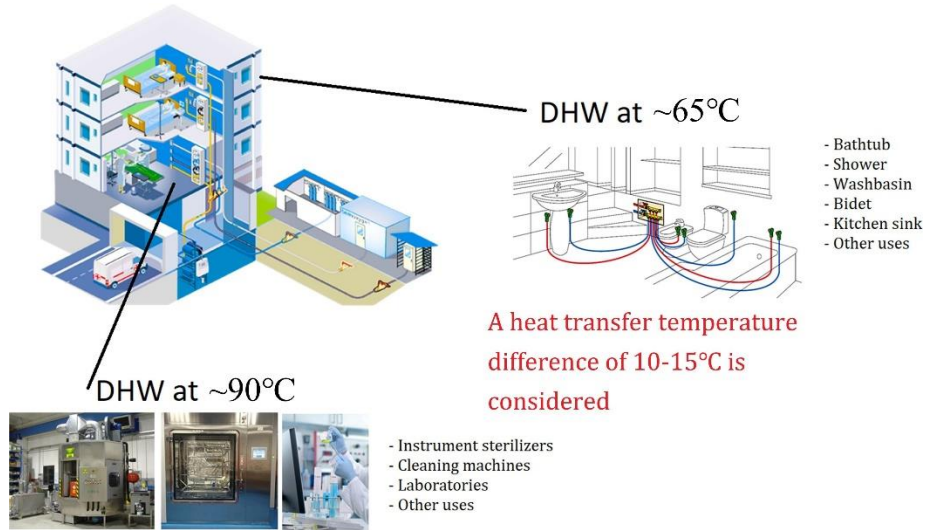
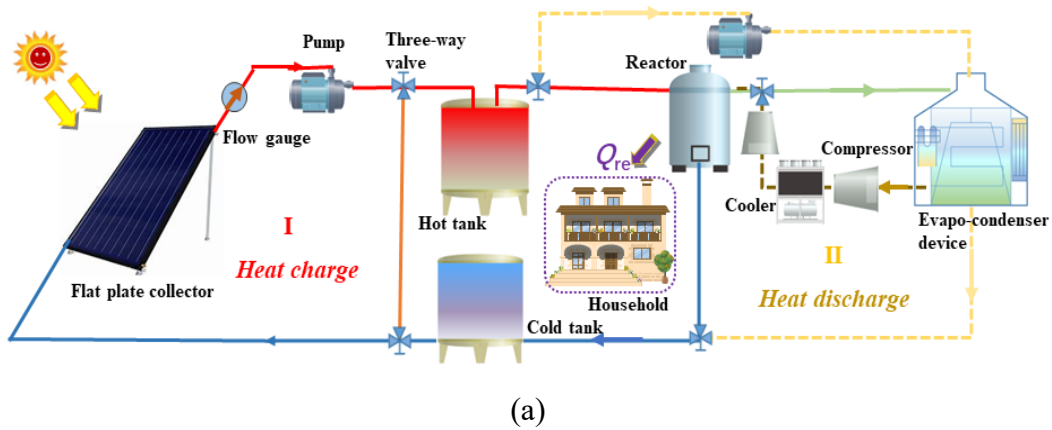
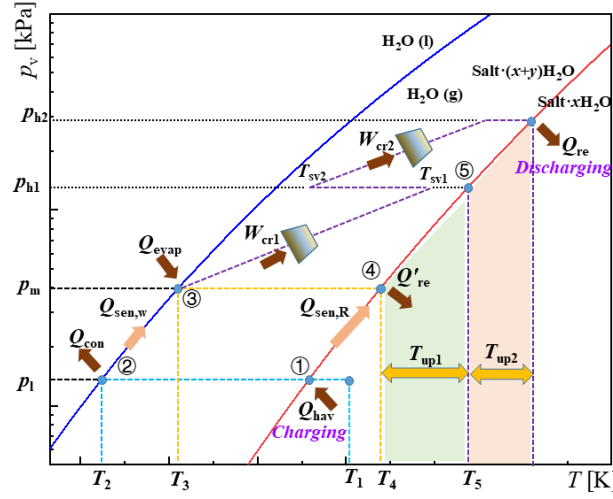


Fig. 7. Two types of DHW production temperatures for hospital users.





(b)

Fig. 8. (a) Schematic and (b) p - T diagrams of the two-stage pressurization THT system.

Following entry into the intercooler, the superheated vapor at T_{sv1} is cooled to an unsaturated vapor state (T_{sv2}) at constant pressure. This allows for controlling the vapor temperature below the permissible temperature of the compressor, while still maintaining a relatively high pressure. As a result of the increased pressure difference, there is a further temperature rise (T_{up2}) compared with the single-stage pressurization technique. The intercooler-generated temperature decrease of superheated vapor, $T_{sv1}-T_{sv2}$, can be calculated as $0.8(T_{sv1}-T_{sat1})$ [55]. Hence, the suction temperature of the second compressor is determined by:

$$T_{sv2} = 0.2 \cdot T_{sv1} + 0.8 \cdot T_{sat1} \quad (31)$$

where T_{sat1} represents the saturation temperature corresponding to p_{h1} .

The total κ_{total} for the two-stage pressurization is given by:

$$\kappa_{total} = \kappa_1 \cdot \kappa_2 = p_{h2}/p_1 \quad (32)$$

In this section, κ_1 and κ_2 are set as 3.0 and 2.25, respectively. The comparisons of η_{th} , η_{ex} , COP_{tw} , and temperature lift T_{up} of several salts-based THT systems using one-stage and two-stage pressurization are displayed in Fig. 9(a-d). The $SrBr_2$ -based system exhibits the highest η_{th} , η_{ex} , and COP_{tw} regardless of the pressurization mode, and the values are 73.94%, 95.56%, and 45.09 when using two-stage pressurization. Following are the systems based on $CuSO_4$, $LiOH$, and K_2CO_3 . On the other hand, the two-stage pressurization systems slightly underperform compared to the one-stage systems in terms of thermodynamic performance, primarily owing to the higher share of sensible heat

consumption. For instance, the η_{th} , η_{ex} , and COP_{tw} of the K_2CO_3 -based system utilizing one-stage and two-stage modes are around 47.88%, 59.41%, 19.24 and 43.86%, 57.04%, 11.14, respectively. A special case is that the two-stage $SrBr_2$ -based system possesses a higher η_{ex} than that of the one-stage, the reason is that the role of temperature rise dominates compared to the $\dot{W}_{cr}$ consumption and the $\dot{Q}_{sen}$ consumption. A greater temperature lift can be seen for the two-stage systems when compared to the one-stage systems. E.g., the T_{up} elevates from 29.04°C to 40.28°C for the $SrBr_2$ -based system. This is because, as per the salt hydrate reaction equilibrium principle, a higher vapor pressure corresponds to a higher equilibrium temperature for the reaction. Although the greatest T_{up} of 62.9°C is yielded by the $CaCl_2$ -based system, it is still subpar in thermodynamic performance because of the low reaction enthalpy. Similarly, the systems based on $MgSO_4$ and $MgCl_2$ are inferior to the ones based on $SrBr_2$ and K_2CO_3 in η_{th} , η_{ex} , and COP_{tw} . Overall, through further pressurization, a larger temperature rise can be achieved but usually comes at the cost of decreased thermodynamic performances.

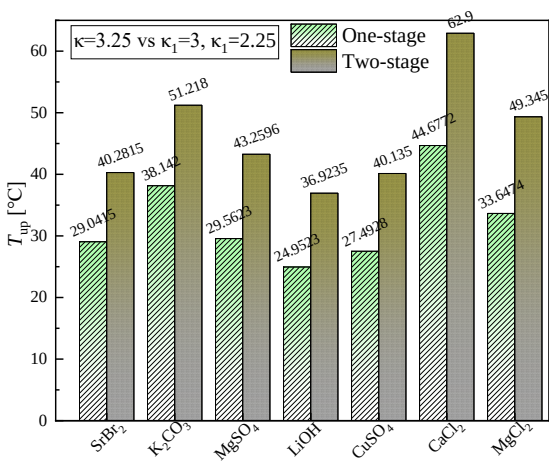
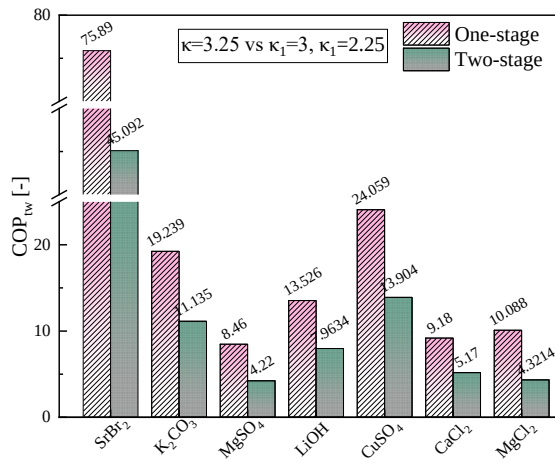
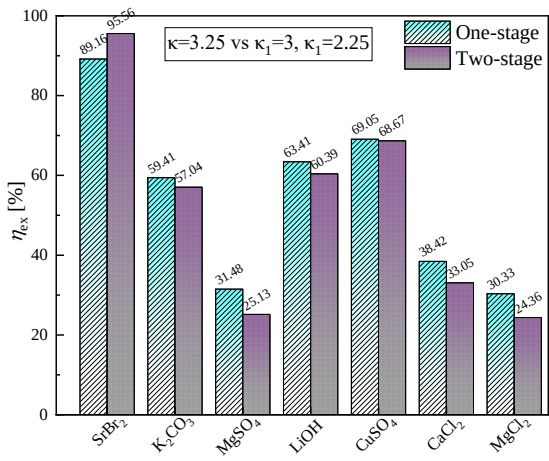
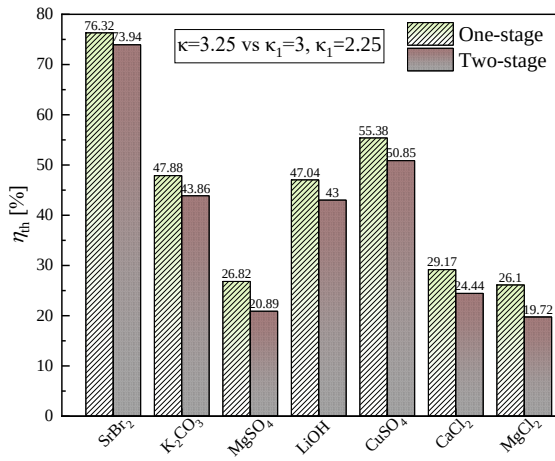


Fig. 9. Comparison of one-stage and two-stage pressurization THT systems in (a) η_{th} ,
(b) η_{ex} , (c) COP_{tw} , and (d) T_{up} .

Table 2 further compares the two kinds of THT systems in Q_{usa} and T_{dis} . One can see that higher output temperatures are obtained due to the greater total κ . Even in the case of the smallest T_{dis} observed in the $CuSO_4$ -based system, it is boosted from 61.61°C to 74.26°C, which meets the criterion for DHW production. On the other hand, the Q_{usa} is reduced when rising total κ , e.g., the Q_{usa} is decreased from 11,667 MJ and 11,140 MJ to 11,540 MJ and 10,904 MJ for the $SrBr_2$ -based and $LiOH$ -based systems. This can be attributed to the fact that the proportion of the system's sensible heat consumption is enlarged as the T_{dis} is elevated.

Table 2. Comparison in Q_{usa} and T_{dis} for the one-/two-stage systems ($\kappa=3.25$ vs. $\kappa_1=3$, $\kappa_2=2.25$).

Salt hydrates	Usable heat (MJ)	Discharge temperature (°C)
$SrBr_2$	11667/ 11540	74.3/ 85.54
K_2CO_3	5815.8/ 5603.3	90.31/ 103.39
$MgSO_4$	1730.5/ 1436.7	67.01/ 80.71
$LiOH$	11140/ 10904	68.31/ 80.29
$CuSO_4$	5045.6/ 4854	61.61/ 74.26
$CaCl_2$	2646.4/ 2363.7	107.35/ 125.57
$MgCl_2$	1783.5/ 1521.5	96.02/ 111.72

4.3. Economic estimation of the THT system

4.3.1. Solar collector system

Based on the hypotheses and conditions described in section 3.1, the total mass of HTF m_{HTF} , the solar collector area A_{sc} , and the tank volume V_{tank} required by the THT systems employing various reactive salts are shown in Fig. 10. It is evident that the $LiOH$ -based system requires the largest solar collector area due to its high ESD, with a requirement of 2581.3 m². This is followed by the systems using $LiCl$ and $SrBr_2$, which require areas of 2485.3 m² and 1778.5 m², respectively. Contrarily, the $LaCl_3$ -based system has the minimum collector area requirement, with only 431.8 m² needed. The m_{HTF} and V_{tank} of the $LiOH$ -based system are also the greatest, i.e., 127.83 t and 128.47 m³, which is attributed to the highest water content of $LiOH \cdot H_2O$. For another promising hydrate, $SrBr_2 \cdot 6H_2O$, the needed m_{HTF} and V_{tank} are notably lower, i.e., 23.86 t and 23.98 m³, this is advantageous for the THT system's economy.

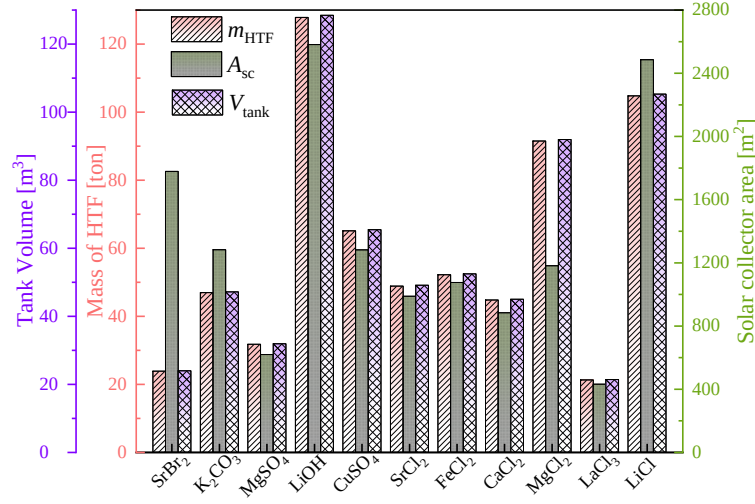


Fig. 10. Total m_{HTF} , the A_{sc} , and the V_{tank} required by the THT systems employing various salts.

4.3.2. Cost and LEC analysis

In this section, the T_{dis} exceeding 65°C is set as the aim and meanwhile ensures the maximum η_{ex} . Taking into account the two criteria concurrently, the total cost and levelized energy cost (LEC) of the solar THT systems utilizing different TCMs are depicted in Fig. 11. Please noted that for some reactive salts such as FeCl_2 , the discharging temperatures are higher than 65°C even when the vapor is not compressed, and the η_{ex} decreases with κ , the compressor is thus not included. Fig. 11 suggests that the SrBr_2 -based system needs the highest capital investment with \$1,051,611.81. Followed by the LiOH and LiCl -based systems, which are \$991,375.43 and \$917,893.59, respectively. The total cost of the system is basically proportional to the energy storage capacity. Despite the high total costs, the LEC of the above systems is merely 0.1147 \$/kWh, 0.1162 \$/kWh, and 0.1271 \$/kWh thanks to their high ESDs, less than that of other salt-based systems. Conversely, the largest LEC of 0.3662 \$/kWh is formed for the LaCl_3 -based system though its total cost is only \$357,027.17. A similar situation is observed for the MgSO_4 -based and MgCl_2 -based systems. In short, the THT systems using LiOH , SrBr_2 , and K_2CO_3 exhibit low LEC of less than 0.15 \$/kWh. These systems offer favorable economic performance in terms of heat release for DHW production.

The breakdown of the cost distribution within the systems based on SrBr_2 , LiOH , and CaCl_2 is displayed in Fig. 12(a-c). The results manifest that the cost of the solar collector constitutes the highest proportion in THT systems regardless of the salt used, which are 41.4%, 63.73%, and 54.22%, respectively. For the SrBr_2 -based system, the cost of TCM occupies 35.98%, ranking second in cost share, which can be attributed to the

high price of $\text{SrBr}_2 \cdot 6\text{H}_2\text{O}$. The evapo-condenser device possesses the second highest capital investment for the LiOH and CaCl_2 -based systems, 8.87% and 21.85%; and the TCM cost shares are 5.56% and 1.21%, respectively. The capital ratios of compressors for SrBr_2 and LiOH -based systems take up around 7% whereas the corresponding value is 0 for the CaCl_2 -based system due to the absence of a compressor. Also, the proportions of pumps, tanks, reactor, and valves are all less than 5% for the SrBr_2 -based system, while the capital investment of tanks for the other systems are 7.65% and 6.66% due to the great water content of the LiOH -based system and the relatively low total cost of the CaCl_2 -based system. For all three systems, the cost share of the HTF is essentially negligible ($<0.05\%$).

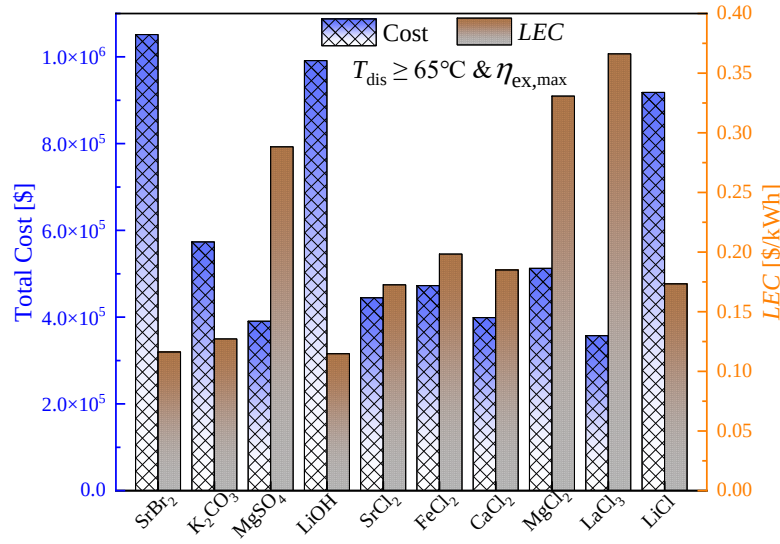
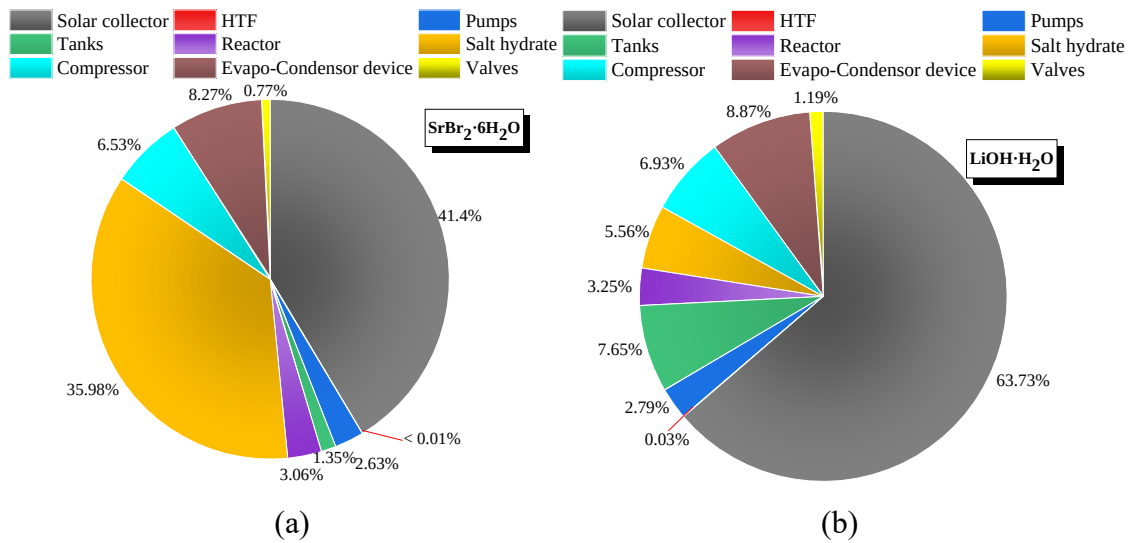


Fig. 11. Total capital investment and LEC of the THT systems using various salts.



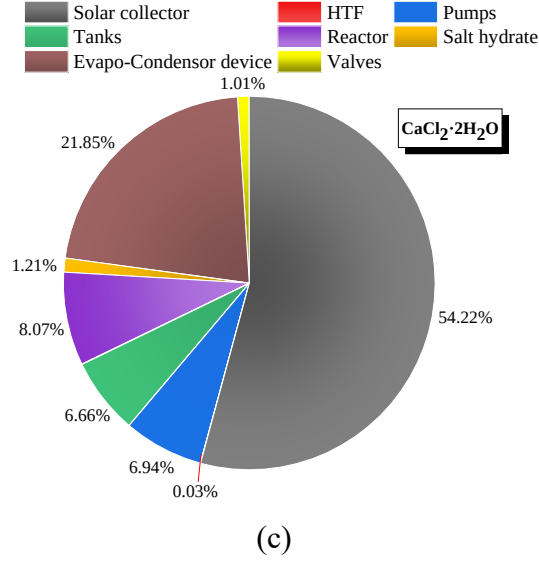


Fig. 12. Capital investment proportion of main components in the THT systems based on (a) SrBr₂, (b) LiOH, and (c) CaCl₂.

4.4. Carbon footprint assessment

In this part, the two types of DHW production demands (regular temperature of 65°C and higher temperature of 90°C) using different reactive salts are considered, and the reactive salts that fit hydration reactions near the corresponding temperatures are chosen separately. Fig. 13(a) indicates for regular DHW production, φ_{CO_2} is 15 kg/MWh, 281.4 kg/MWh, 162.8 kg/MWh, and 47.6 kg/MWh for the THT systems using SrBr₂, MgSO₄, LiOH, and LaCl₃ as TCM, far less than the current electricity-driven DHW level of 833 kg/MWh [53]. As φ_{CO_2} is directly affected by W_{cr} and Q_{usa} , and the SrBr₂-based system has a great Q_{usa} and a small W_{cr} , it exhibits exceptional environmental friendliness. In contrast, the LiOH-based system has a relatively high CO₂ emission. This is because, despite the high ESD of LiOH·H₂O, the power consumption of the compressor in this system is also large. As presented in Fig. 13(b), when generating DHW with about 90°C, φ_{CO_2} is 135.4 kg/MWh, 137.8 kg/MWh, 100.4 kg/MWh, 189 kg/MWh, and 56.2 kg/MWh for the systems based on K₂CO₃, SrCl₂, CaCl₂, MgCl₂, and LiCl. Noticeably, the theoretical φ_{CO_2} for the FeCl₂-based system is zero because this salt can achieve T_{dis} above 90°C without using a pressurization process. Similarly, the systems mentioned in Fig. 13(b) can theoretically achieve net-zero emission of CO₂ under the condition of discharging at 65°C.

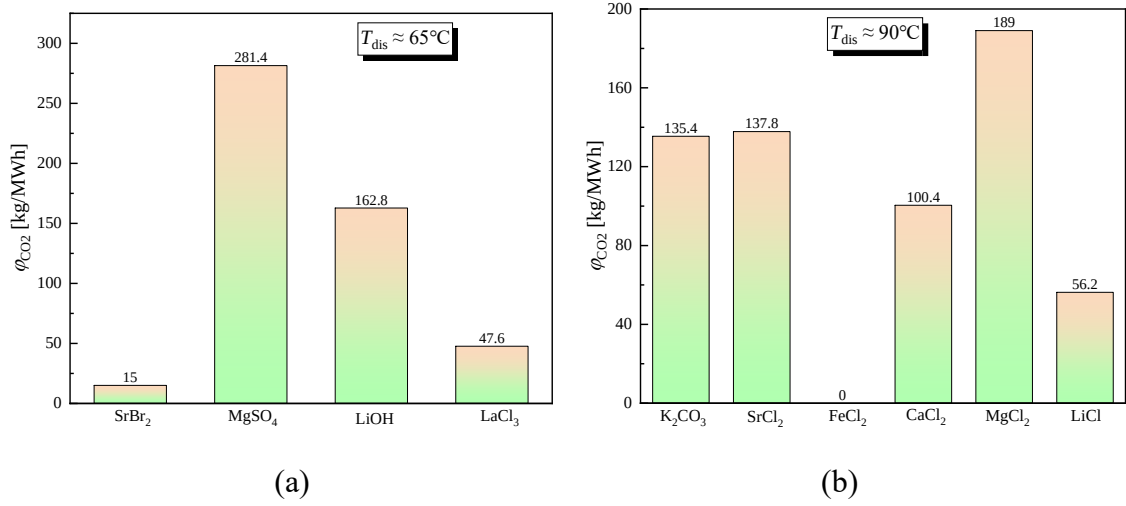


Fig. 13. ϕ_{CO_2} for the two kinds of DHW production: (a) $65^\circ C$, (b) $90^\circ C$.

Fig. 14 further reveals the variations of ϕ_{CO_2} with T_{dis} for different salt-based systems. Evidently, ϕ_{CO_2} presents an upward trend when T_{dis} rises, which can be ascribed to the increased W_{cr} and the drop in Q_{usa} . Nevertheless, the growth rate of ϕ_{CO_2} is not exactly the same. E.g., ϕ_{CO_2} ascends from 5.7 kg/MWh to 34.3 kg/MWh when T_{dis} increases from $60.6^\circ C$ to $74.3^\circ C$ for the SrBr₂-based system; while ϕ_{CO_2} of LiOH-based system sharply soars from 86.4 kg/MWh to 192.5 kg/MWh as T_{dis} rises from $58.8^\circ C$ to $68.3^\circ C$. Although the CaCl₂-based system is capable of releasing heat at high temperatures, the dramatic growth of ϕ_{CO_2} may be not favorable to environmental friendliness. The LaCl₃, MgCl₂, SrCl₂, and LiCl-based systems also show a quick rise in ϕ_{CO_2} with increasing T_{dis} . The case for the K₂CO₃-based systems performs slightly better but the rise in ϕ_{CO_2} with T_{dis} is still remarkable, escalating from 22.6 kg/MWh to 135.7 kg/MWh when T_{dis} elevates from $74.5^\circ C$ to $90.3^\circ C$.

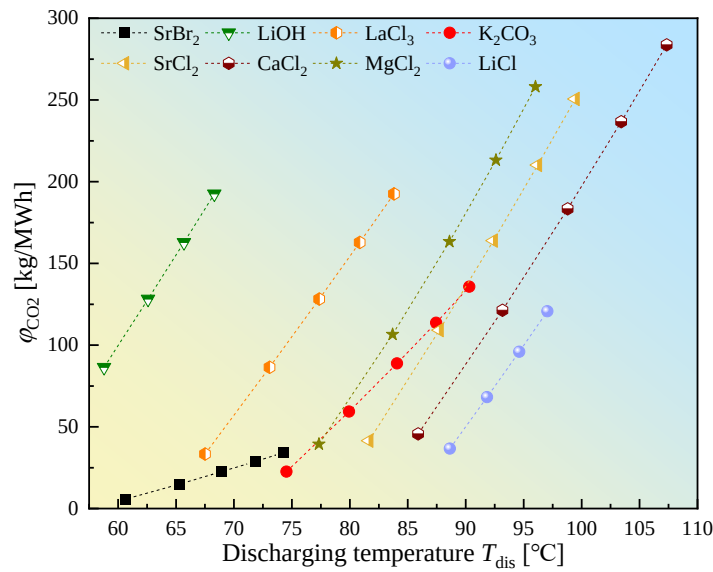


Fig. 14. Variations of ϕ_{CO_2} with T_{dis} for different salt-based systems.

4.5. Sensitivity analysis

4.5.1. Effect of solar irradiation and sunshine duration

It is necessary to study the impact of the intensity and duration of irradiation on a solar-driven system. E.g., due to the different natural environments, the system performance may differ when applied to Xinjiang and Shanghai in China.

As specified in section 4.3.2, T_{dis} above 65°C and meanwhile ensuring the maximum η_{ex} are used as the criterion. Fig. 15(a) discloses the downward trend of LEC when average solar irradiation I_{sol} is intensified. For example, the LEC of LiOH-based system declines from 0.1391 $\$/\text{kWh}$ to 0.0948 $\$/\text{kWh}$ as I_{sol} boosts from 300 W/m^2 to 550 W/m^2 . The reason is that the solar collector area needed in the system is reduced and the capital investment is saved. Compared to other systems, the LEC s of the systems based on K_2CO_3 , LiOH, and SrBr_2 are lower regardless of I_{sol} . Moreover, the LEC of the LiOH-based system eventually becomes smaller than that of the SrBr_2 -based one as I_{sol} increases. This is because the cost share of solar collector for the former is more significant, as proved in Fig. 12. Similarly, the LEC of the SrCl_2 -based system is more sensitive to I_{sol} than that of other systems, and it descends from 0.393 $\$/\text{kWh}$ to 0.2799 $\$/\text{kWh}$ when I_{sol} rises from 300 W/m^2 to 550 W/m^2 .

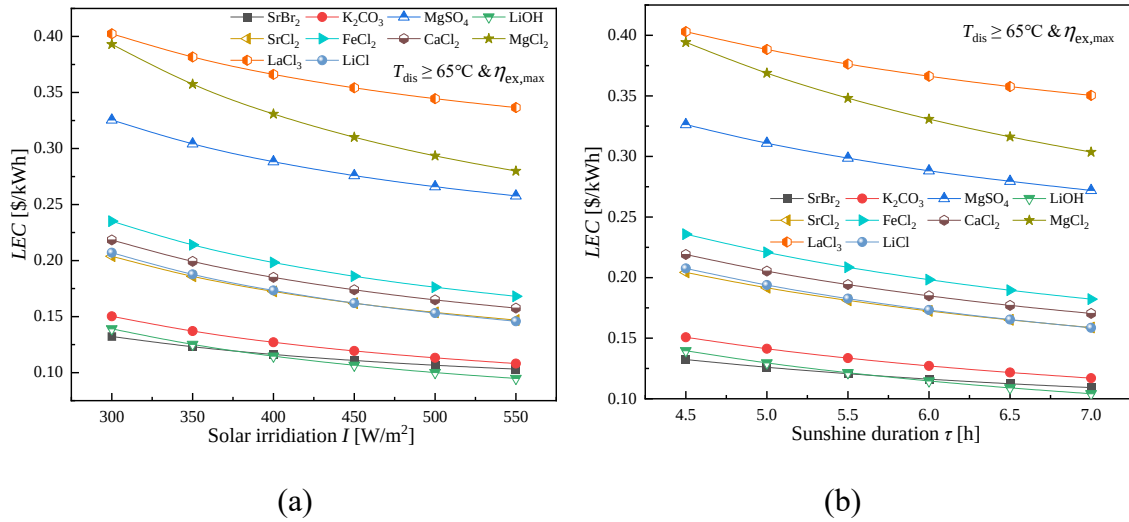


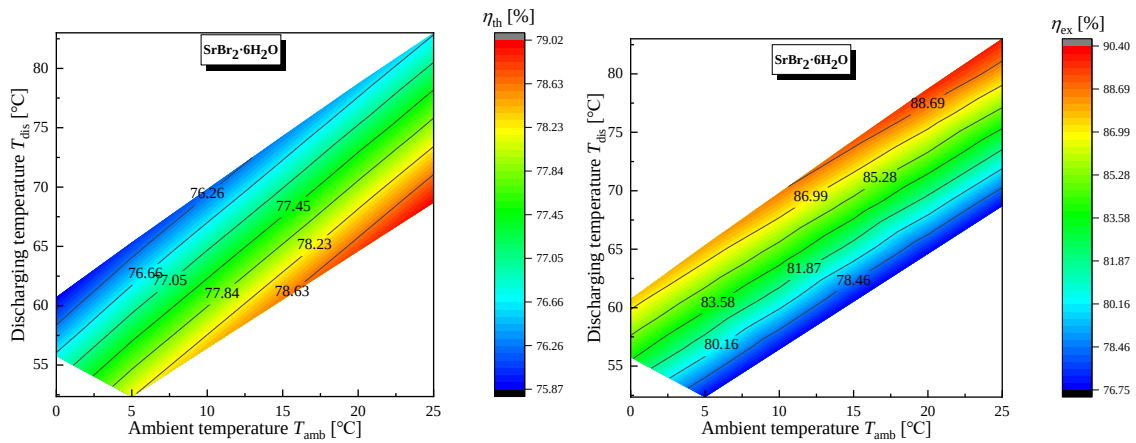
Fig. 15. Variation of LEC with (a) solar irradiation and (b) sunshine duration.

Similar to I_{sol} , the extension in radiation duration τ_{sol} contributes to LEC reduction (Fig. 15(b)). E.g., the LEC of the LiOH-based system drops from 0.1396 $\$/\text{kWh}$ to 0.1041 $\$/\text{kWh}$ when τ_{sol} increases from 4.5 h to 7 h. The reason is for a fixed heat storage capacity in the system, longer τ_{sol} means lower storage power or heat transfer rate, and therefore

lower flow rates of the HTF through the solar collector, which ultimately results in a corresponding reduction in the required collector area. Prolonging τ_{sol} and improving I_{sol} are essentially reducing the required collector area, thus reducing the cost. Therefore, the change trend of LEC under the two working conditions is similar.

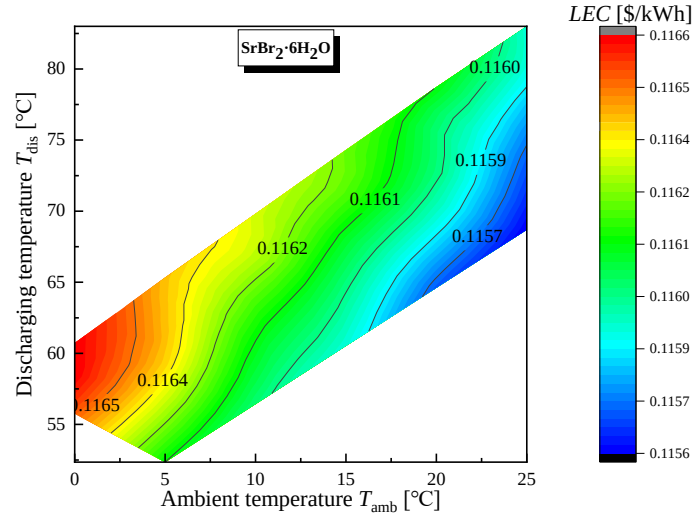
4.5.2. Effect of ambient and discharging temperatures

Given the results in the above sections, the systems using the most promising salts of SrBr_2 , K_2CO_3 , and LiOH are selected as the research objects, and the CaCl_2 -based system is also studied for comparison thanks to its high output temperature. Fig. 16(a) uncovers the impacts of T_{amb} and T_{dis} on the SrBr_2 -based system's η_{th} . Higher T_{amb} contributes to the greater η_{th} but higher T_{dis} is detrimental to η_{th} . This is because the increase helps to reduce the consumption of the system's sensible heat and increases Q_{usa} during discharging. On the other hand, since the enhanced T_{dis} is the result of boosting κ , the work consumption is enlarged, and it is not conducive to η_{th} gains. The maximum η_{th} of 79.02% can be achieved when T_{amb} and T_{dis} are 25°C and 68.7°C, respectively. Fig. 16(b) unveils that the maximum η_{ex} occurs in the region with the highest T_{amb} and T_{dis} , which is 90.38% when T_{amb} and T_{dis} are 25°C and 83.1°C. The reason is, according to Eq. (16), heightening T_{dis} means the upgradation of exergy in discharging. Besides, as explained above, high T_{amb} facilitates the improvement of Q_{usa} . Although higher T_{amb} leads to larger W_{cr} , which is detrimental to η_{ex} , this effect is relatively small. Fig. 16(c) elucidates that high T_{amb} and low T_{dis} are beneficial for LEC reduction, and the minimum LEC of 0.1156 \$/kWh is found at the same condition as the maximum η_{th} , i.e., T_{amb} and T_{dis} are 25°C and 68.7°C. Contrarily, the largest LEC of 0.1165 \$/kWh is yielded when T_{amb} and T_{dis} are 0°C and 58.5°C. Even so, the LEC fluctuation with T_{amb} and T_{dis} is small.



(a)

(b)



(c)

Fig. 16. Effect of T_{amb} and T_{dis} on (a) η_{th} , (b) η_{ex} , and (c) LEC in the SrBr_2 -based system.

The influences of T_{amb} and T_{dis} on η_{th} , η_{ex} , and LEC of the K_2CO_3 -based system are similar to that of the SrBr_2 -based system, as portrayed in Fig. 17(a-c). The maximum η_{th} and the lowest LEC are observed in the region characterized by the highest T_{amb} . Specifically, when T_{amb} and T_{dis} are 25°C and 83.8°C, the system achieves a peak η_{th} of 51.61% and the smallest LEC of 0.1262 \$/kWh. The maximum η_{ex} of 59.62% is obtained at the highest T_{dis} of 100.5°C as T_{amb} is 25°C. Once T_{dis} is fixed, η_{ex} would drop with T_{amb} increases, which can be attributed to the decrease of exergy.

Fig. 18(a) suggests the influences of T_{amb} and T_{dis} on η_{th} of the LiOH -based system are similar to that of the SrBr_2 and K_2CO_3 based systems, i.e., the point of highest η_{th} of 51.65% corresponds to the combination of the highest T_{amb} and a relatively lower T_{dis} . While for η_{ex} and LEC , they are not the case. As shown in Fig. 18(b), the maximum η_{ex} (63.66%) happens at $T_{\text{amb}} = 0^\circ\text{C}$ with $T_{\text{dis}} = 54^\circ\text{C}$ rather than $T_{\text{amb}} = 25^\circ\text{C}$ with $T_{\text{dis}} = 77.6^\circ\text{C}$. This is because, though high T_{dis} contributes to enhancing exergy, the consumed work of the compressor for temperature lift is significantly risen due to the high water content of $\text{LiOH} \cdot \text{H}_2\text{O}$. As a result, the maximum η_{ex} does not appear at the operating condition with the highest T_{dis} . Different from the above systems, Fig. 18(c) displays that the lowest LEC of 0.1139 \$/kWh occurs at the location with the largest T_{amb} (25°C) and T_{dis} (77.6°C). The reason for this counterintuitive phenomenon is that in the process of elevating T_{dis} by vapor pressurization, the temperature of exhaust vapor from the compressor is very high, which in turn can improve T_{dis} . Compared with other systems, the vapor content of this system is higher, hence Q_{usa} increases with the increasing T_{dis} , which is beneficial to reduce the LEC .

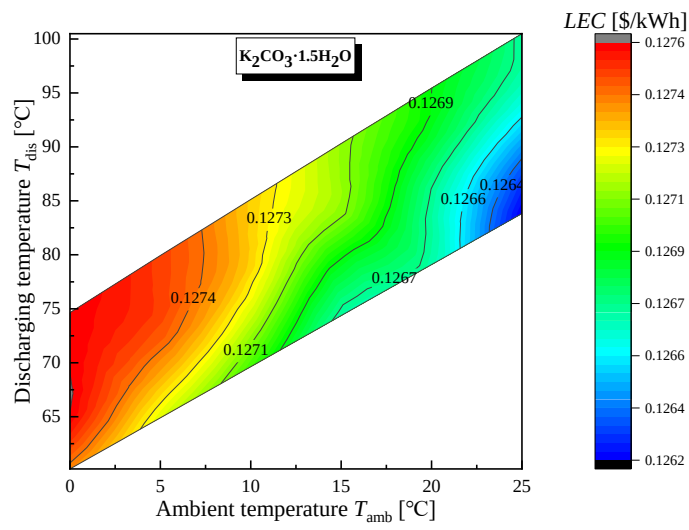
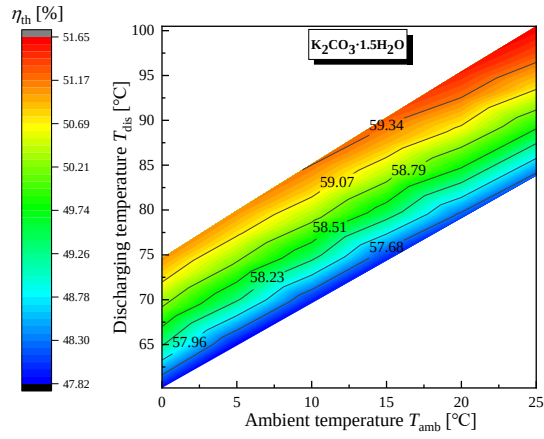
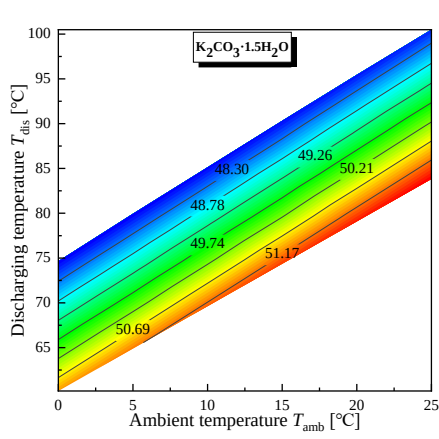
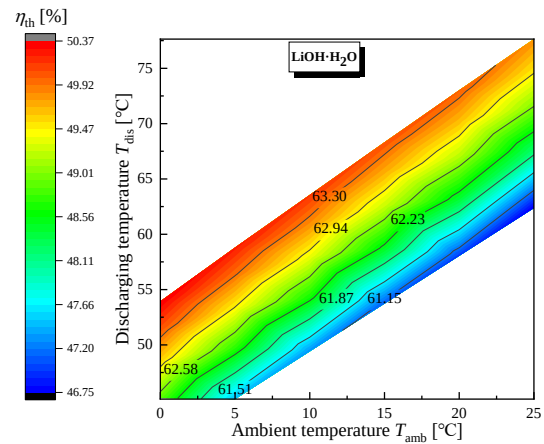
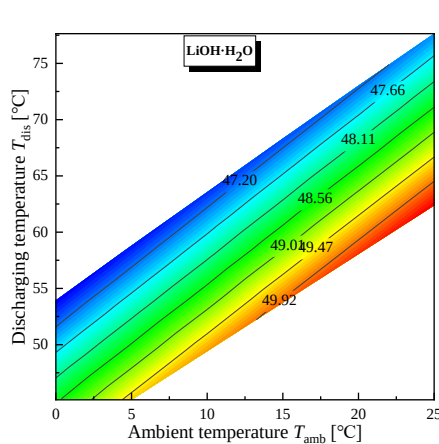
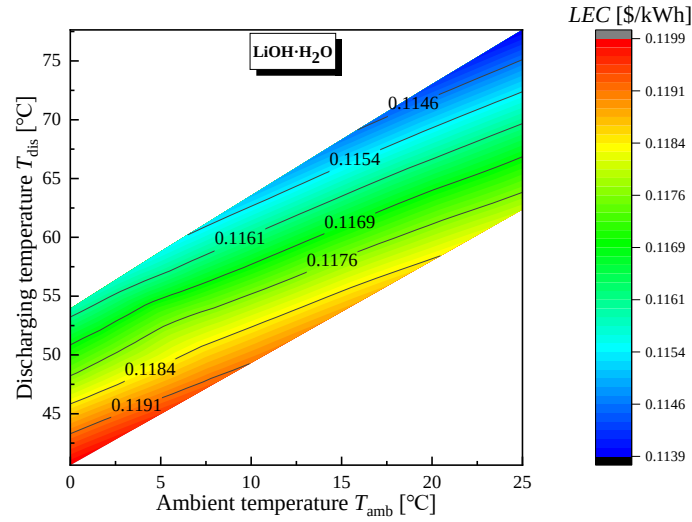


Fig. 17. Effect of T_{amb} and T_{dis} on (a) η_{th} , (b) η_{ex} , and (c) LEC in the K_2CO_3 -based system.

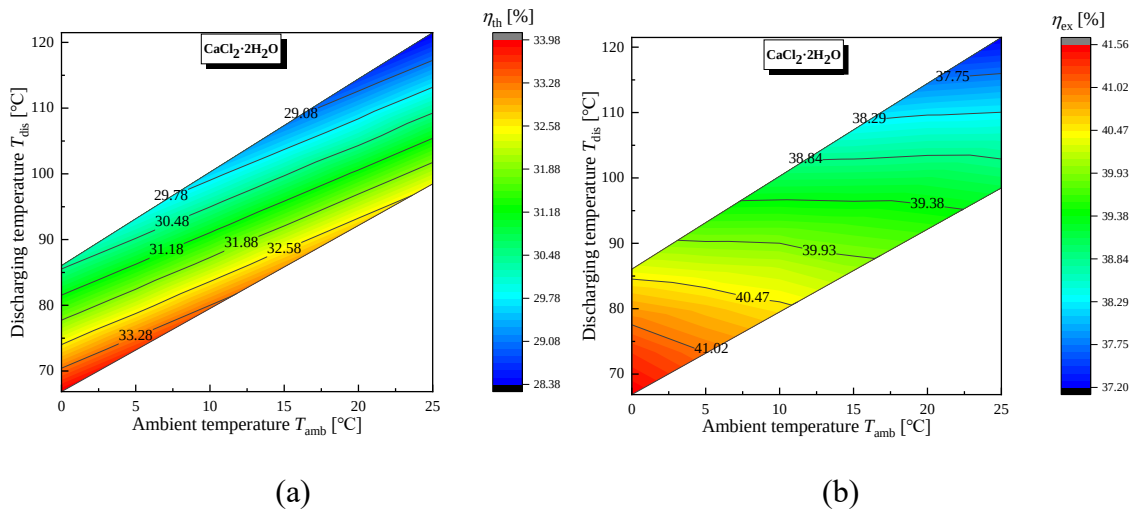




(c)

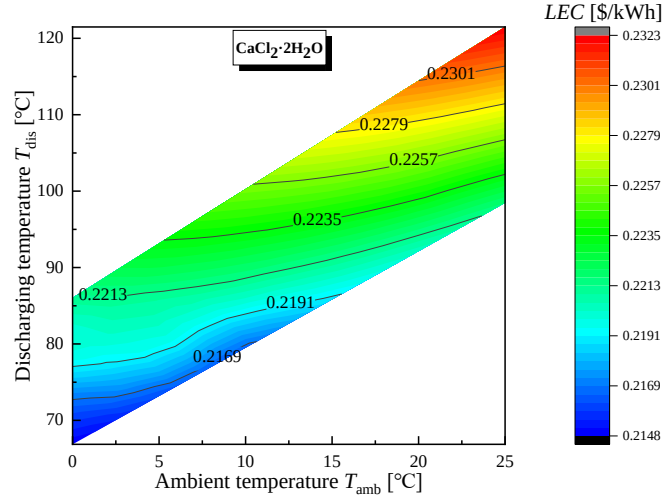
Fig. 18. Effect of T_{amb} and T_{dis} on (a) η_{th} , (b) η_{ex} , and (c) LEC in the LiOH-based system.

As presented in Fig. 19(a-c), for the CaCl_2 -based system, the maximum η_{th} (33.98%) and η_{ex} (41.56%), as well as the lowest LEC (0.2148 \$/kWh), all occur in the lower left corner of the graphs, i.e., 0°C of T_{amb} and 66.9°C of T_{dis} . This is because, though increasing T_{amb} is beneficial to improve η_{th} , when raising T_{dis} , W_{cr} will also increase; as the heat storage capacity of this system is relatively small, the effect of increased W_{cr} becomes more pronounced, ultimately leading to a decrease in η_{th} and η_{ex} . Also, like other systems, high T_{amb} is not conducive to η_{ex} . Since the consumption of sensible heat is evident when lifting T_{dis} , the smallest LEC appears at the lowest T_{amb} and T_{dis} due to the significant effect of Q_{usa} reduction. Contrarily, the maximum LEC of 0.2323 \$/kWh is located at the position with the highest T_{amb} (25°C) and T_{dis} (121.5°C).



(a)

(b)



(c)

Fig. 19. Effect of T_{amb} and T_{dis} on (a) η_{th} , (b) η_{ex} , and (c) LEC in the CaCl_2 -based system.

4.6. Comprehensive assessment

Some salt hydrates like LiOH , SrBr_2 , K_2CO_3 , LiCl , and CaCl_2 , appear to be hopeful TCMs thanks to their theoretically favorable performance or high T_{dis} . These typical candidates are thus selected for comparative study from the thermo-economic views, as portrayed in Fig. 20. SrBr_2 -based system demonstrates exceptional overall performance, with the highest Q_{usa} (11,667 MJ), η_{ex} (89.16%), η_{th} (76.32%), and COP_{tw} (75.89), although its LEC (0.1162 \$/kWh) is slightly higher than that of LiOH -based system (0.1147 \$/kWh). For the latter, it also yields a comparable Q_{usa} (11,139.84 MJ) and the second highest η_{ex} of 63.41% but with the lowest T_{dis} and COP_{tw} . Although the CaCl_2 -based system is capable of achieving a very high T_{dis} (Fig.3), under the present constraint, the LiCl -based system obtains the highest T_{dis} of 97.04°C, followed by the K_2CO_3 -based system, 90.31°C. Except for the relatively high LEC of the LiCl -based system (0.1733 \$/kWh), this system and the K_2CO_3 -based one also present an acceptable thermodynamic performance. In contrast, the CaCl_2 -based system exhibits the worst performances in Q_{usa} , η_{ex} , η_{th} , and LEC .

Combined with the findings discussed in previous sections, one can see that for these selected hydrates that can be used to realize SH, all candidates are capable of realizing regular DHW production, except $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ because of its low T_{dis} (Fig. 3). Among these salt candidates, SrBr_2 , K_2CO_3 , LiOH , and LiCl based systems exhibit superior (e.g., SrBr_2 system) or barely satisfactory (e.g., LiCl) 4E performances (Figs. 5, 6, 14, and 20). Additionally, some systems such as FeCl_2 -based systems can achieve a higher T_{dis} ($\geq 90^\circ\text{C}$) for several special DHW production demands. Consequently, they are also probable

options if the output temperature is the primary target. However, the 4E performances and ESD usually are particularly considered in practice. The screening process of the potential salts for DHW production is illustrated in Fig. 21. Briefly, the SrBr_2 , K_2CO_3 , and LiOH based THT systems are promising for DHW production because of their good overall performances, and the LiCl -based one also shows acceptable results.

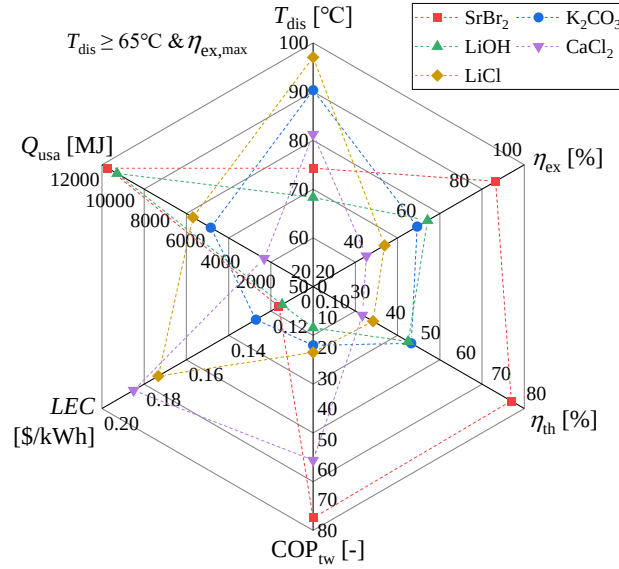


Fig. 20. Comparisons in thermo-economic performances for several typical salts.

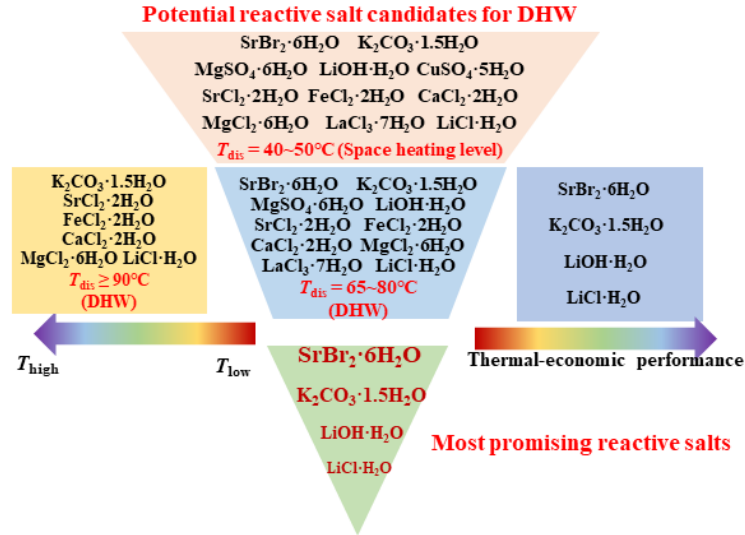


Fig. 21. Screening for promising salt hydrates.

5. Conclusions

Based on the specified conditions, the following key conclusions can be drawn:

- 1) The pressurization-assisted THT systems with GJ-level heat storage capacity demonstrate efficient heat upgrading capability and flexibility in discharging stage,

allowing for adjustment of κ to meet user demands. T_{dis} above 65°C for regular DHW generation can be realized by the THT systems based on different salts except for CuSO_4 , and the FeCl_2 and CaCl_2 based systems can easily achieve higher DHW production (>90°C), but the ESD and thermodynamic performances are low.

- 2) The SrBr_2 -based system realizes the largest η_{th} , η_{ex} , and COP_{tw} , and the systems based on CuSO_4 , K_2CO_3 , and LiOH also show good performances. Both η_{th} and COP_{tw} descend with the increasing κ , while η_{ex} exhibits an upward trend. The maximum η_{ex} for the abovementioned systems are 89.16%, 69.05%, 59.41%, and 63.41%, respectively. Furthermore, the Q_{usa} of the SrBr_2 and LiOH based systems are the greatest, which are 11,667 MJ and 11,140 MJ. Followed by the LiCl and K_2CO_3 based systems, which are 6,828.7 MJ and 5,815.8 MJ, and the corresponding T_{dis} are 97.04°C and 90.31°C, respectively. T_{dis} can be further heightened by the two-stage pressurization, but this comes at the expense of lowering thermodynamic performance.
- 3) Aiming for maximum η_{ex} and T_{dis} above 65°C, SrBr_2 and LiOH based systems achieve the lowest LEC of 0.1162 \$/kWh and 0.1147 \$/kWh, though their capital investments are the highest. Moreover, the solar collector constitutes the largest proportion of the total cost, which are 41.4% and 63.73% for the two systems; also, the cost share of TCM in the SrBr_2 -based system is considerable because of the high price of $\text{SrBr}_2 \cdot 6\text{H}_2\text{O}$, while the share of HTF in all systems is ignorable.
- 4) Among the THT systems matching for regular DHW production, the SrBr_2 -based system yields the least ϕ_{CO_2} of 15 kg/MWh whereas ϕ_{CO_2} for the LiOH -based system is 162.8 kg/MWh. For cases of high temperature DHW production (90°C), the LiCl -based system exhibits the lowest ϕ_{CO_2} of 56.2 kg/MWh. Although ϕ_{CO_2} linearly surges with T_{dis} for the THT systems, the growth rate of SrBr_2 -based system is the slowest.
- 5) Sensitive analysis results manifest that the LEC declines with the increasing solar irradiation intensity and sunshine duration. Under the combinations of T_{amb} and T_{dis} , the optimal operating conditions of the salt-based system in thermo-economic performances may vary from system to system.

Overall, $\text{SrBr}_2 \cdot 6\text{H}_2\text{O}$ emerges as the most promising TCM for the pressurization-assisted THT system thanks to the excellent 4E performances, making it a highly attractive option for DHW production. The K_2CO_3 and LiOH based systems also offer competitive overall performances, and the LiCl -based system achieves marginally satisfactory results,

although the three systems may exhibit mediocre performance in one or two aspects. The findings of this study prove a great possibility for the exploitation of this salt hydrate-based THT system for DHW production.

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Author contributions

Wei Li: Conceptualization, Methodology, Investigation, Modelling, Software, Data curation, Formal analysis, Validation, Writing- Original draft, Writing - Review & Editing; **Christos N. Markides:** Conceptualization, Writing -Review & Editing; **Min Zeng:** Project administration, Funding acquisition; **Xiang Ling:** Writing -Review & Editing.

References

- [1] Li W, Zhang L, Ling X. Thermo-economic assessment of salt hydrate-based thermochemical heat transformer system: Heat upgrade for matching domestic hot water production. *Energy Conversion and Management* 2023;277:116644.
- [2] Gul E, Baldinelli G, Bartocci P, Shamim T, Domenighini P, Cotana F et al. Transition toward net zero emissions - Integration and optimization of renewable energy sources: Solar, hydro, and biomass with the local grid station in central Italy. *Renewable Energy* 2023;207:672–86.
- [3] Houben J, Sögütöglü L, Donkers P, Huinink H, Adan O. K₂CO₃ in closed heat storage systems. *Renewable Energy* 2020;166:35–44.
- [4] Mikos-Nuszkiewicz N, Furmański P, Łapka P. A mathematical model of charging and discharging processes in a thermochemical energy storage reactor using the hydrated potassium carbonate as a thermochemical material. *Energy* 2023;263:125642.
- [5] Yue W, Wang S, Xu M, Rong Q, Xu C, Su M. The potential of mitigating greenhouse gas emissions from urban domestic water systems in highly urbanized areas. *Journal of Cleaner Production* 2023;382:135206.
- [6] Zheng N, Zhang H, Duan L, Wang X, Wang Q, Liu L. Multi-criteria performance analysis and optimization of a solar-driven CCHP system based on PEMWE, SOFC, TES, and novel PVT for hotel and office buildings. *Renewable Energy* 2023;206:1249–64.
- [7] Lapertot A, Segond G, Fasquelle T, Kadoch B, Le Métayer O. Multi-criteria optimization of an experimental system for the production of domestic hot water. *Energy Conversion and Management* 2022;267:115875.
- [8] Zhang H, Liu S, Shukla A, Zou Y, Han X, Shen Y et al. Thermal performance study of

- thermochemical reactor using net-packed method. *Renewable Energy* 2022;182:483–93.
- [9] Li W, Luo X, Yang P, Wang Q, Zeng M, Markides CN. Solar-thermal energy conversion prediction of building envelope using thermochemical sorbent based on established reaction kinetics. *Energy Conversion and Management* 2022;252:115117.
- [10] Crespo A, Fernández C, Vérez D, Tarragona J, Borri E, Frazzica A et al. Thermal performance assessment and control optimization of a solar-driven seasonal sorption storage system for residential application. *Energy* 2023;263:125382.
- [11] Fan YB, Jiang L, Zhang XJ, Xu XG, Frazzica A. Heat pump assisted open three-phase sorption thermal battery for efficient heat storage. *Energy Conversion and Management* 2023;277:116630.
- [12] Li W, Klemeš JJ, Wang Q, Zeng M. Salt hydrate-based gas-solid thermochemical energy storage: Current progress, challenges, and perspectives. *Renewable and Sustainable Energy Reviews* 2022;154:111846.
- [13] Mukherjee A, Pujari AS, Shinde SN, Kashyap U, Kumar L, Subramaniam C et al. Performance assessment of open thermochemical energy storage system for seasonal space heating in highly humid environment. *Renewable Energy* 2022;201:204–23.
- [14] N'Tsoukpoe KE, Schmidt T, Rammelberg HU, Watts BA, Ruck WK. A systematic multi-step screening of numerous salt hydrates for low temperature thermochemical energy storage. *Applied Energy* 2014;124:1–16.
- [15] N'Tsoukpoe KE, Osterland T, Opel O, Ruck WK. Cascade thermochemical storage with internal condensation heat recovery for better energy and exergy efficiencies. *Applied Energy* 2016;181:562–74.
- [16] N'Tsoukpoe KE, Mazet N, Neveu P. The concept of cascade thermochemical storage based on multimaterial system for household applications. *Energy and Buildings* 2016;129:138–49.
- [17] Söğütöglu LC, Donkers P, Fischer HR, Huinink HP, Adan O. In-depth investigation of thermochemical performance in a heat battery: Cyclic analysis of K_2CO_3 , $MgCl_2$ and Na_2S . *Applied Energy* 2018;215:159–73.
- [18] Mazur N, Huinink H, Borm B, Sansota S, Fischer H, Adan O. Thermodynamic analysis of dehydration of $K_2CO_3 \cdot 1.5H_2O$. *Thermochimica Acta* 2022;715:179286.
- [19] Houben J, Langelaan D, Brinkman L, Huinink H, Fischer HR, Adan OC. Understanding the Hydration Process of Salts: The Relation between Surface Mobility and Metastability. *Crystal Growth & Design* 2022;22(8):4906–16.
- [20] Blijlevens MA, Mazur N, Kooijman W, Fischer HR, Huinink HP, Meekes H et al. A study of the hydration and dehydration transitions of $SrCl_2$ hydrates for use in heat storage. *Solar Energy Materials and Solar Cells* 2022;242:111770.
- [21] Zhang Y, Hu M, Chen Z, Su Y, Riffat S. Modelling analysis of a solar-driven thermochemical energy storage unit combined with heat recovery. *Renewable Energy* 2023;206:722–37.
- [22] Fopah-Lele A, Rohde C, Neumann K, Tietjen T, Rönnebeck T, N'Tsoukpoe KE et al. Lab-scale experiment of a closed thermochemical heat storage system including honeycomb heat exchanger. *Energy* 2016;114:225–38.
- [23] Clark R-J, Gholamibozanjani G, Woods J, Kaur S, Odukomaiya A, Al-Hallaj S et al. Experimental screening of salt hydrates for thermochemical energy storage for building heating application. *Journal of Energy Storage* 2022;51:104415.
- [24] Xu J, Li T, Yan T, Chao J, Wang R. Dehydration kinetics and thermodynamics of magnesium

- chloride hexahydrate for thermal energy storage. *Solar Energy Materials and Solar Cells* 2021;219:110819.
- [25] Ur Rehman A, Zhao T, Shah MZ, Khan Y, Hayat A, Dang C et al. Nanoengineering of MgSO_4 nanohybrid on MXene substrate for efficient thermochemical heat storage material. *Applied Energy* 2023;332:120549.
- [26] Nguyen MH, Zbair M, Dutournié P, Bennici S. Thermochemical sorption heat storage: Investigate the heat released from activated carbon beads used as porous host matrix for MgSO_4 salt. *Journal of Energy Storage* 2023;59:106452.
- [27] Xu W, Wang Y, Xing H, Peng J, Luo Y. Optimization of UiO-66/CaCl_2 composite material for thermal energy storage. *Microporous and Mesoporous Materials* 2023;355:112574.
- [28] Aarts J, van Ravensteijn B, Fischer H, Adan O, Huinink H. Polymeric stabilization of salt hydrates for thermochemical energy storage. *Applied Energy* 2023;341:121068.
- [29] Shkatulov AI, Houben J, Fischer H, Huinink HP. Stabilization of K_2CO_3 in vermiculite for thermochemical energy storage. *Renewable Energy* 2020;150:990–1000.
- [30] Touloumet Q, Postole G, Silvester L, Bois L, Auroux A. Hierarchical aluminum fumarate metal-organic framework - alumina host matrix: Design and application to CaCl_2 composites for thermochemical heat storage. *Journal of Energy Storage* 2022;50:104702.
- [31] Hou Y, Sheng Z, Fu C, Kong J, Zhang X. Hygroscopic holey graphene aerogel fibers enable highly efficient moisture capture, heat allocation and microwave absorption. *Nature communications* 2022;13(1):1227.
- [32] Li W, Klemeš JJ, Wang Q, Zeng M. Characterisation and sorption behaviour of LiOH-LiCl@EG composite sorbents for thermochemical energy storage with controllable thermal upgradeability. *Chemical Engineering Journal* 2021;421:129586.
- [33] Ji W, Zhang H, Liu S, Wang Z, Deng S. An experimental study on the binary hydrated salt composite zeolite for improving thermochemical energy storage performance. *Renewable Energy* 2022;194:1163–73.
- [34] Ait Ousaleh H, Sair S, Mansouri S, Abboud Y, Zahouily M, Faik A et al. Enhanced inorganic salts stability using bentonite clay for high-performance and low-cost thermochemical energy storage. *Journal of Energy Storage* 2022;49:104140.
- [35] Humbert G, Sciacovelli A. Topology optimization for mass transfer enhancement in open thermochemical energy storage reactors. *Journal of Energy Storage* 2023;64:107132.
- [36] Stengler J, Bürger I, Linder M. Performance analysis of a gas-solid thermochemical energy storage using numerical and experimental methods. *International Journal of Heat and Mass Transfer* 2021;167:120797.
- [37] Kant K, Pitchumani R. Analysis of a novel constructal fin tree embedded thermochemical energy storage for buildings applications. *Energy Conversion and Management* 2022;258:115542.
- [38] Ye H, Tao YB, Chang H, He Y. Structure optimization of a novel porous tree-shaped fin for improving thermochemical heat storage performance. *Applied Thermal Engineering* 2023;225:120190.
- [39] Michel B, Dufour N, Börtlein C, Zoude C, Prud'homme E, Gremillard L et al. First experimental characterization of CaCl_2 coated heat exchanger for thermochemical heat transformer applications in industrial waste heat recovery. *Applied Thermal Engineering* 2023;227:120400.

- [40] Stengler J, Linder M. Thermal energy storage combined with a temperature boost: An underestimated feature of thermochemical systems. *Applied Energy* 2020;262:114530.
- [41] Donkers P, Söğütöglu LC, Huinink HP, Fischer HR, Adan O. A review of salt hydrates for seasonal heat storage in domestic applications. *Applied Energy* 2017;199:45–68.
- [42] Trausel F, Jong A-J de, Cuypers R. A Review on the Properties of Salt Hydrates for Thermochemical Storage. *Energy Procedia* 2014;48:447–52.
- [43] Richter M, Habermann E-M, Siebecke E, Linder M. A systematic screening of salt hydrates as materials for a thermochemical heat transformer. *Thermochimica Acta* 2018;659:136–50.
- [44] Lide DR. *CRC handbook of chemistry and physics*, 87th ed. CRC Press: Boca Raton 2007.
- [45] Fathabadi H. Novel low-cost parabolic trough solar collector with TPCT heat pipe and solar tracker: Performance and comparing with commercial flat-plate and evacuated tube solar collectors. *Solar Energy* 2020;195:210–22.
- [46] Iqbal Q, Fang S, Zhao Y, Yao Y, Xu Z, Gan H et al. Thermo-economic assessment of sub-ambient temperature pumped-thermal electricity storage integrated with external heat sources. *Energy Conversion and Management* 2023;285:116987.
- [47] Fan R. Energy, exergy, economic (3E) analysis, optimization and comparison of different Carnot battery systems for energy storage. *Energy Conversion and Management* 2022;252:115037.
- [48] Turton R, Bailie RC, Whiting WB, Shaeiwitz JA. *Analysis, synthesis and design of chemical processes*: Pearson Education; 2008.
- [49] Song J, Wang Y, Wang K, Wang J, Markides CN. Combined supercritical CO₂ (SCO₂) cycle and organic Rankine cycle (ORC) system for hybrid solar and geothermal power generation: Thermoeconomic assessment of various configurations. *Renewable Energy* 2021;174:1020–35.
- [50] Algieri A, Morrone P. Thermo-economic investigation of solar-biomass hybrid cogeneration systems based on small-scale transcritical organic Rankine cycles. *Applied Thermal Engineering* 2022;210:118312.
- [51] Zhang F, Feng Y, He Z, Xu J, Zhang Q, Xu K. Thermo-economic optimization of biomass-fired organic Rankine cycles combined heat and power system coupled CO₂ capture with a rated power of 30 kW. *Energy* 2022;254:124433.
- [52] Yu X, Qiao H, Yang B, Zhang H. Thermal-economic and sensitivity analysis of different Rankine-based Carnot battery configurations for energy storage. *Energy Conversion and Management* 2023;283:116959.
- [53] Kim S, Ko Y, Lee GJ, Lee JW, Xu R, Ahn H et al. Sustainable energy harvesting from post-combustion CO₂ capture using amine-functionalized solvents. *Energy* 2023;267:126532.
- [54] Matera N, Mazzeo D, Congedo PM. Energy-sustainable hospitals: Integration of a novel compound parabolic concentrator system with two storage tanks for domestic hot water production at high and low temperatures. *Applied Thermal Engineering* 2023;221:119773.
- [55] Zeng T, Li J, Deng L, He Z, Kobayashi N, Wu R et al. Mechanical Booster Pump-Assisted Thermochemical Mode for Low-Grade Heat Storage and Upgrading: A Thermodynamic Study. *Front. Energy Res.* 2022;10.