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Review article

## Review of Recent Developments in Thermochemical Energy Storage Materials and Systems

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### ABSTRACT

Thermochemical energy storage (TES) is emerging as a transformative solution for enhancing thermal energy management in buildings and industrial applications. Unlike conventional sensible and latent heat storage, TES systems store energy through reversible chemical reactions, offering significantly higher energy densities and minimal standby losses. This review provides a comprehensive overview of recent developments in TES materials and system configurations, including both closed-cycle systems (e.g., chemical heat pumps, adsorption/absorption cycles) and open-cycle systems integrated with solar thermal collectors. Advances in material engineering—particularly in salt hydrates, composite sorbents, and nanostructured materials—have led to improvements in cyclic stability, regeneration temperature, and thermal efficiency. The paper also highlights innovative reactor designs such as fixed-bed, fluidized-bed, and plate-fin heat exchangers, alongside smart control and additive manufacturing approaches. Key technical challenges, including reaction kinetics, long-term stability, and heat/mass transfer complexity, are discussed to identify future research needs. This review aims to support the development of high-performance, scalable TES systems for sustainable and flexible energy infrastructure.

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## 1. INTRODUCTION

En Space heating accounts for over 68% of energy use in the European Union, highlighting the need for efficient technologies to reduce demand and CO<sub>2</sub> emissions (Liu et al., 2018). Thermochemical energy storage (TES) has emerged as a promising solution, offering higher energy densities and minimal standby losses compared to sensible and latent heat storage (Elkhatat and Al-Muhtaseb, 2023). TES enables long-term energy storage through reversible chemical reactions. Studies suggest its application across the EU could save up to 1215 TWh of thermal energy (Connolly et al., 2014), significantly improving energy efficiency and

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sustainability (Sadeghi, 2022). Recent advances in materials science have enhanced TES performance, especially in low- and medium-temperature ranges, through improved kinetics, durability, and reduced regeneration temperatures (Daniarta et al., 2023). These innovations support integration with solar thermal and waste heat systems.

This review outlines TES fundamentals, material developments, system design strategies, and integration methods. It also discusses key challenges and future directions, offering insights into how TES can contribute to a more sustainable energy future.

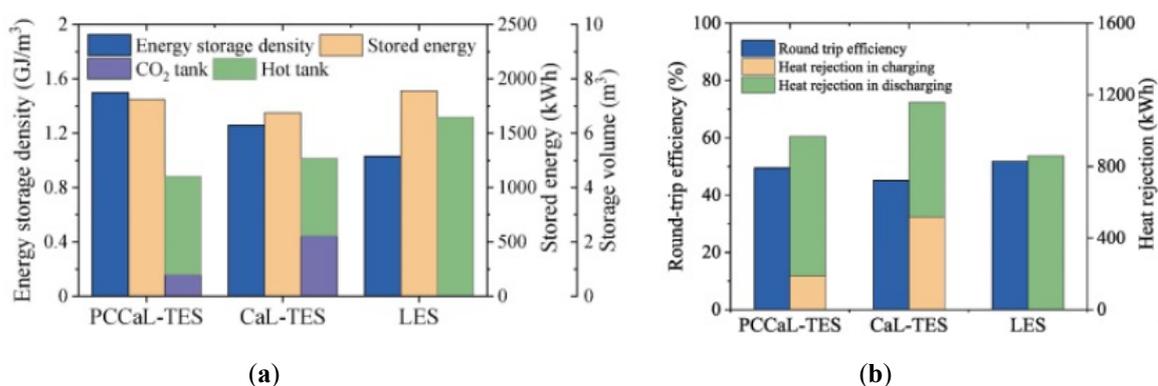
## 2. FUNDAMENTALS AND CLASSIFICATION OF THERMOCHEMICAL ENERGY STORAGE (TES)

Thermochemical energy storage (TES) harnesses reversible chemical reactions to convert and store thermal energy as chemical energy, enabling high energy densities and minimal standby losses (James et al., 2021). Unlike sensible storage, which depends on temperature changes, or latent storage, which relies on phase transitions, TES employs processes such as dehydration or dehydrogenation to absorb energy during endothermic reactions and release it during the corresponding exothermic reactions (Shi et al., 2022). TES systems are commonly organized into closed and open cycle configurations. Closed cycle systems, incorporating technologies like chemical heat pumps, adsorption, and absorption cycles, enable precise control over energy transfer (Riaz et al., 2022), while open cycle systems capitalize on the direct interaction between the working fluid and ambient air to achieve cost-effective energy storage and release (Amir et al., 2023). The performance and reliability of TES depend critically on the thermodynamic and kinetic characteristics of these reactions, as well as on material properties such as stability, cyclic durability, and appropriate regeneration temperatures (Ding et al., 2021).

### 2.1. BASIC PRINCIPLES OF TES

Thermochemical energy storage (TES) systems utilize reversible chemical reactions, such as salt hydration and dehydration to convert thermal energy into chemical potential (James et al., 2021, Shi et al., 2022). During charging, heat drives an endothermic reaction, while discharging releases energy via an exothermic reverse process. Compared to sensible or latent storage, TES enables much higher energy densities by storing energy within chemical bonds.

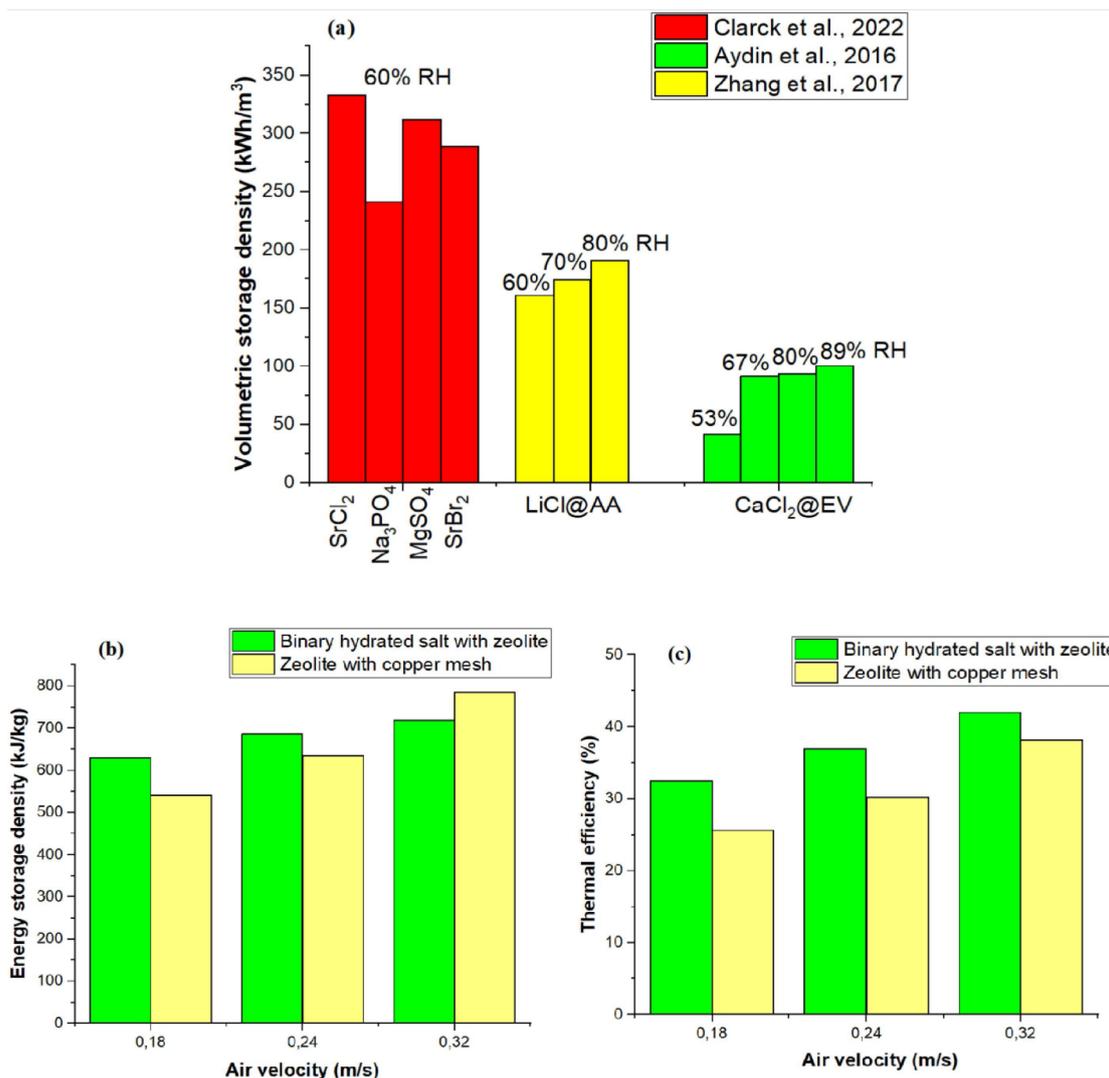
Studies have shown that TES materials, including advanced salt hydrates, can achieve energy storage densities significantly above traditional water tanks while maintaining performance across multiple cycles. For instance, PCCaL-TES systems employing  $\text{CaCO}_3/\text{CaO}-\text{CaCl}_2$  composites have demonstrated energy densities approaching  $1.5 \text{ GJ/m}^3$  with improved round-trip efficiency (Wu et al., 2021). These developments underline the promise of TES in delivering compact, long-term thermal energy storage.



**Figure 1.** (a) Energy storage density, stored energy, and storage volume of PCCaL-TES, conventional CaL-TES, and LES. (b) Round-trip efficiency and heat rejections in the charging and discharging processes (Wu et al., 2021).

Salt hydrate-based TES also offers long-duration storage with minimal losses, an advantage for building heating. Optimal material formulations, such as salt-loaded porous composites, have been shown to deliver energy densities over  $2 \text{ MJ/kg}$  under moderate ambient humidity (Moulakhnif et al., 2024). This suggests

potential for decentralized heating solutions with efficient thermal retention.



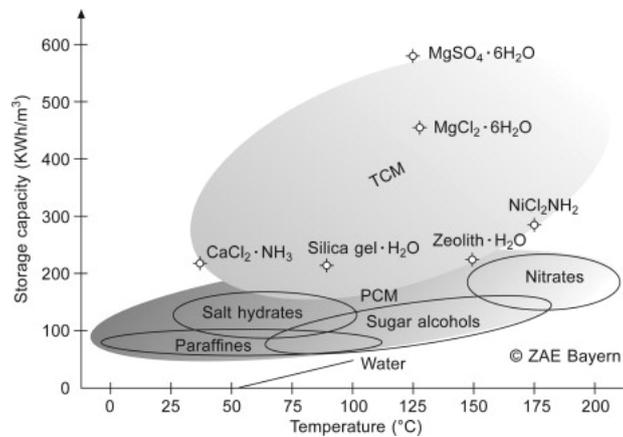
**Figure 2.** Effect of (a) humidity on TCES performance, (b,c) energy storage density and thermal efficiency at different air velocities (Moulakhnif et al., 2024, Ji et al., 2022, Zhang, H., 2022).

Flexibility in operating temperatures is a crucial advantage of TES, as it allows materials to be engineered for optimal performance under diverse thermal conditions. Recent studies have shown that through precise tailoring of salt hydrate compositions and controlled processing techniques, the operational temperature window of TES systems can be significantly expanded. According to Daniarta et al.'s research, modifications in the crystalline structure and composite formulation enable TES materials to perform efficiently across both low and medium temperature regimes, thereby ensuring effective energy storage and release even when integrated with low-grade heat sources such as solar thermal collectors or industrial waste heat recovery systems (Daniarta et al., 2023). This enhanced adaptability not only improves overall system efficiency but also broadens the practical applications of TES technologies in sustainable energy infrastructures.

## 2.2. COMPARISON WITH SENSIBLE AND LATENT HEAT STORAGE

Sensible heat storage (SHS) relies on raising the temperature of a medium, such as water or solid blocks, to store energy (Li, 2016). While cost-effective and technically simple, its energy density is limited by material properties and the achievable temperature range (Dicaire and Tezel, 2013). Latent heat storage (LHS), on the other hand, stores thermal energy through phase transitions in materials like paraffin or salt hydrates (Boldoo et al., 2024). These systems often achieve higher energy densities than SHS but suffer from challenges such as phase-change hysteresis and subcooling, which can reduce performance over repeated cycles (Hekimoğlu

et al., 2023). In contrast, TES systems store energy chemically, allowing significantly higher energy densities and better retention over time. Salt hydrate-based TES systems, such as those using  $\text{CaCl}_2$ , can surpass  $250 \text{ kWh/m}^3$  and retain energy effectively without significant thermal loss (Nejhad, 2019, Barbatelli, 2023).



**Figure 3.** Storage capacities of PCM and TCM compared to water (Cabeza et al., 2015).

### 2.2.1. SENSIBLE HEAT STORAGE

Sensible heat storage (SHS) is one of the most established and straightforward approaches to thermal energy storage. In SHS, energy is stored by raising the temperature of a storage medium, such as water, concrete, or specialized ceramics, resulting in an increase in its internal energy (Li, 2016). Despite its simplicity and relatively low cost, the energy density of sensible heat storage is intrinsically limited by the specific heat capacity of the material and the maximum temperature difference that can be safely achieved. For instance, even when advanced materials are employed, practical energy densities typically remain within the range of tens of kilowatt-hours per cubic meter. Dicaire et al. provided a comprehensive analysis of various storage media and concluded that under optimal conditions, sensible heat storage systems rarely exceed energy densities of about  $60 \text{ kWh/m}^3$  (Dicaire and Tezel, 2013). Moreover, SHS systems are prone to continuous heat losses due to conduction, convection, and radiation, which can become significant over long durations. These losses limit the feasibility of SHS for applications requiring long-term or seasonal energy storage, despite its technical simplicity and widespread use.

### 2.2.2. LATENT HEAT STORAGE

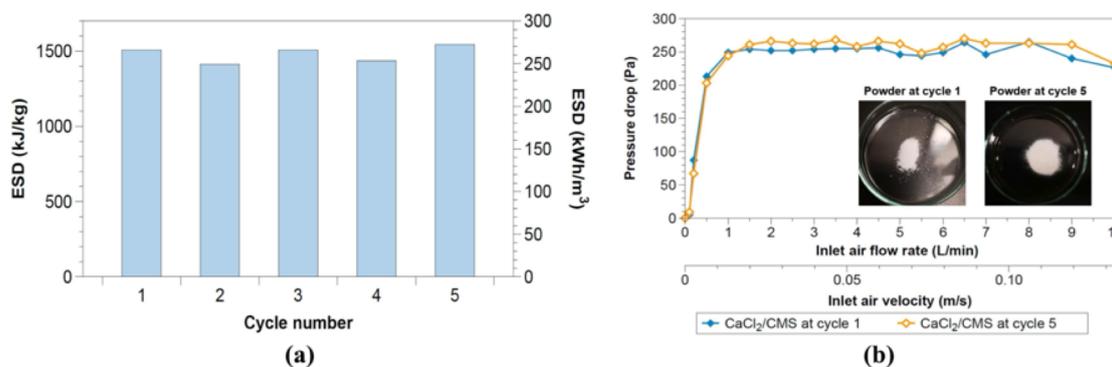
Latent heat storage capitalizes on the energy exchanged during phase transitions, such as the melting and solidification of phase change materials (PCMs). This approach often achieves higher energy densities than sensible heat storage, as the latent heat of fusion can be substantial even over narrow temperature ranges. For example, many organic and inorganic PCMs can store energy in the range of  $150\text{-}250 \text{ kJ/kg}$  during phase changes (Boldoo et al., 2024). However, latent heat storage systems encounter their own challenges. One major issue is phase change hysteresis, where the melting and solidification temperatures differ, leading to incomplete energy recovery. Sub-cooling, a phenomenon in which the material remains in a supercooled liquid state below its expected freezing point, further complicates the energy retrieval process. In a study by Hekimoğlu et al., researchers explored innovative encapsulation methods and composite material formulations aimed at mitigating these issues, yet they emphasized that ensuring stable, repeatable performance over numerous cycles remains a critical challenge (Hekimoğlu et al., 2023). Additionally, the need for reliable containment systems to manage the volume changes during phase transitions can add complexity and cost, further restricting the large-scale implementation of latent heat storage solutions.

### 2.2.3. ADVANTAGES OF TES SYSTEMS OVER CONVENTIONAL METHODS

Thermochemical energy storage (TES) differs fundamentally from conventional thermal storage methods

by using reversible chemical reactions to retain thermal energy in the form of chemical potential. This mechanism allows for significantly higher energy densities, often in the range of 250–350 kWh/m<sup>3</sup> when using salt hydrates such as CaCl<sub>2</sub>, which exceeds the storage capacity typically achieved by sensible or latent heat systems (Nejhad, 2019, Barbatelli, 2023). Moreover, because TES stores energy at the molecular level rather than as elevated temperature, it experiences minimal heat loss during long-term storage, even under suboptimal insulation conditions (Ding et al., 2021).

Another advantage of TES lies in its configurational flexibility. By selecting appropriate reaction pairs and tuning reaction kinetics, TES systems can be adapted to operate efficiently within specific temperature ranges. This enables effective integration with low-grade heat sources, including solar thermal and industrial waste heat systems (Miró et al., 2016, Liu, G., 2024). For instance, Liu et al. (Liu, X., 2024) examined salt–silica composites in fluidised-bed TES setups and reported that CaCl<sub>2</sub>-loaded mesoporous silica achieved energy densities around 1500 kJ/kg under humid ambient conditions, highlighting its potential for stable and compact thermal energy storage. Taken together, the high energy density, low standby losses, and adaptability of TES position it as a compelling alternative to traditional thermal storage technologies.



**Figure 4.** (a) ESDs of the CaCl<sub>2</sub>/CMS composite over 5 consecutive heat charging-discharging cycles; (b) pressure drops at different flow rates for the dehydrated CaCl<sub>2</sub>/CMS composite sample at cycle 1 and cycle 5 (Liu, X., 2024).

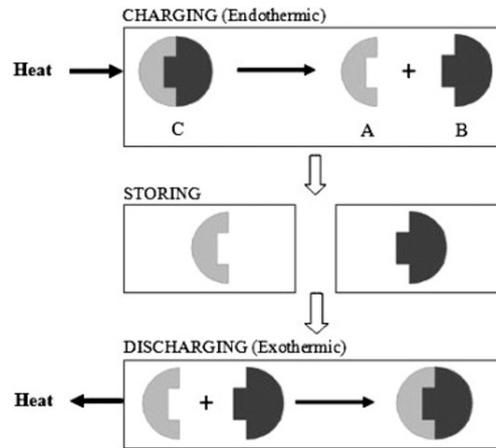
### 3. TES SYSTEM DESIGN AND APPLICATIONS

TES system designs have evolved to meet diverse operational requirements, and recent advances have enabled these systems to be optimized for both heating and cooling applications (Kant and Pitchumani, 2022). Recent work has focused on improving system efficiency, integration with renewable energy, and enhancing the overall reliability of these systems. In this section, we review both closed cycle and open cycle configurations and present representative examples from recent studies.

#### 3.1. CLOSED CYCLE SYSTEMS

Closed cycle TES systems isolate the working fluid from the ambient environment, allowing precise control over the energy storage and release processes. Such designs typically incorporate either chemical heat pumps or adsorption/absorption cycles, which can be fine-tuned to serve both heating and cooling applications.

The main processes of closed thermochemical heat system include three parts: Charging, storing and discharging part (Figure 5). The closed system includes working fluids and thermochemical materials. The internal substances should be separated from heat transport fluid. Thermal energy in the system from heat resource can be transferred to working fluid (Abedin and Rosen, 2012).



**Figure 5.** Processes of closed thermochemical energy storage system. (Abedin and Rosen, 2012).

An energy balance for the closed system (Abedin and Rosen, 2012) can be written as shown in Equation (1), while the efficiency of the charging process is expressed in Equation (2).

$$m_c C_p (T_1 - T_2) - Q_1 = \Delta H_c \quad (1)$$

$$\eta_{c,cl} = \frac{\Delta H_c}{m_c C_p (T_1 - T_2)} = \frac{\Delta H_c}{Q_{in}} \quad (2)$$

Where:

$m_c$  : mass of working fluid (kg).

$C_p$  : specific heat capacity of the working fluid at constant pressure (J/kg/K).

$T_1$  : working fluid initial temperature (K).

$T_2$  : working fluid final temperature (K).

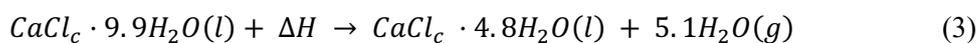
$Q_1$  : initial energy (Wt).

$\Delta H_c$  : the enthalpy change in reaction process.

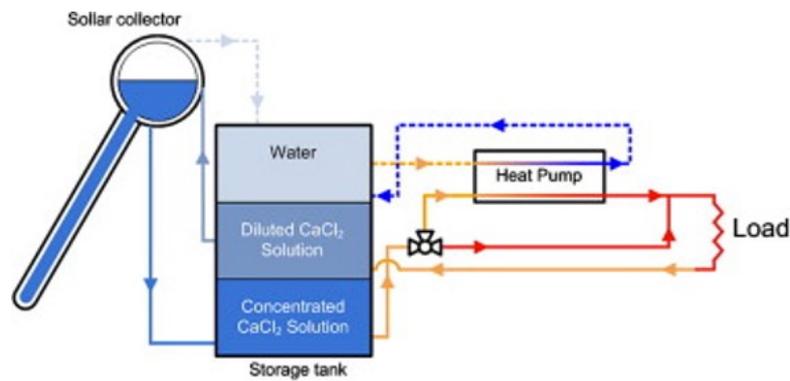
$Q_{in}$  : is the energy input during charging part.

### 3.1.1. CHEMICAL HEAT PUMPS

Chemical heat pumps (CHPs) employ reversible thermochemical reactions to upgrade low-grade heat, enabling efficient thermal energy storage and temperature lifting. Early experimental systems, such as those using  $\text{NH}_3\text{-H}_2\text{O}$  or  $\text{NaOH-H}_2\text{O}$  reaction pairs, demonstrated the theoretical potential for high efficiency and heat storage densities ranging from approximately 119 to 250 kWh/m<sup>3</sup> (P, 1987, Hadorn J C, 2006). More recent designs have integrated calcium chloride ( $\text{CaCl}_2$ ) as a working medium, benefitting from its affordability and favourable thermochemical properties. In solar-assisted CHP systems,  $\text{CaCl}_2$  can undergo hydration and dehydration cycles to store and release heat with significantly reduced standby losses. When combined with external energy inputs such as solar thermal or industrial waste heat, the effective energy density of these systems can exceed 380 kWh/m<sup>3</sup> (Figure 6) (Yang B, 2014, Quinnell and Davidson, 2014). And also, desiccant  $\text{CaCl}_2$  is cheaper than  $\text{LiCl}_2$  and  $\text{LiBr}$ , which are always selected for cooling applications. The solar charging and discharging processes can be described by the following reactions (J.A. Quinnell, 2011; Woods J., 2011; Woods J., 2013), where the charging process is represented in Equation (3) and the discharging process is represented in Equation (4).



Thermal heat energy density depends on the density of  $\text{CaCl}_2$  solution. The energy density of  $\text{CaCl}_2$  is 106 kWh/m<sup>3</sup>, however, the material energy density can rise to 381 kWh/m<sup>3</sup> when system combined with extra heat source, such as solar thermal collector or waste heat recovery (J.A. Quinnell, 2011).



**Figure 6.** A closed cycle of  $\text{CaCl}_2$  solar heating system. (J.A. Quinnell, 2011).

Recent advances in reactor architecture have further improved CHP performance. For instance, high-performance reactors integrating plate-tube heat exchangers with enhanced surface area, porous metal media, and packed beds of  $\text{CaCl}_2$  have demonstrated temperature upgrading from  $100^\circ\text{C}$  to  $155^\circ\text{C}$  with volumetric heat output exceeding  $380 \text{ kW}\cdot\text{m}^{-3}$ . System optimisation in terms of timing and flow conditions has achieved coefficients of performance (COP) near 0.5 and stable hourly outputs around  $72 \text{ kWh}\cdot\text{m}^{-3}$  (Qin et al., 2024). This system integrates parabolic trough solar collectors, a thermochemical reactor, and an internal combustion engine with both thermal and chemical energy storage, effectively upgrading mid-to-low temperature solar and exhaust heat via methanol thermochemical decomposition. Under the design conditions, the overall energy efficiency reached 72.09%, exergy efficiency 37.65%, and net solar-to-electric efficiency 24.63%, while fuel consumption and  $\text{CO}_2$  emissions were reduced by 32.97% and 25.33%, respectively. These results highlight the promising potential for efficient and flexible utilization of solar energy and fuels in CHP systems.

### 3.1.2. ADSORPTION AND ABSORPTION SYSTEMS FOR COOLING AND HEATING

Closed-cycle sorption systems utilise physical or chemical interactions between a sorbent and a working fluid, commonly water vapour, to facilitate thermal energy storage and conversion. In adsorption-based systems, porous solid materials such as silica gel or metal-organic frameworks (MOFs) play a critical role in reversible vapour uptake and release. Material innovation has been central to improving performance in recent years. For example, Zhu et al. (Zhu et al., 2006) tested a  $\text{CaCl}_2$ -impregnated silica gel composite that stored low-grade heat with high efficiency. It achieved a water uptake of  $0.73 \text{ g/g}$  and a thermal capacity near  $1 \text{ kJ/g}$ , with stable performance over 500 cycles due to the combined effects of salt loading and porous structure. The improvement was attributed to a synergistic effect between salt loading and porous structure optimisation, which accelerated mass transfer. Similarly, Chen et al. (Chen et al., 2022) assessed a solar-assisted absorption-compression system designed for residential heating and cooling. Their results showed that low-grade solar heat at  $60^\circ\text{C}$  significantly enhanced system performance, raising COP by up to 56% and reducing electricity use by over 40%, demonstrating strong potential for efficient, low-carbon building applications.

Further studies demonstrate the versatility of sorption systems for both heating and cooling. For instance, Liu et al. (Liu et al., 2005) developed a compact adsorption chiller using silica gel–water, achieving a COP of 0.5 and  $9 \text{ kW}$  cooling capacity at  $13^\circ\text{C}$  evaporation. System improvements such as heat and mass recovery further enhanced efficiency under low-grade heat input between  $70\text{--}95^\circ\text{C}$ . Another study by Aman et al. (Aman et al., 2014) evaluated a  $10 \text{ kW}$  solar-assisted ammonia/water absorption chiller for residential air conditioning. Their analysis showed that while the system's COP is modest, substantial exergy losses occur in the absorber and generator, revealing key optimisation targets for improving solar-driven cooling efficiency.

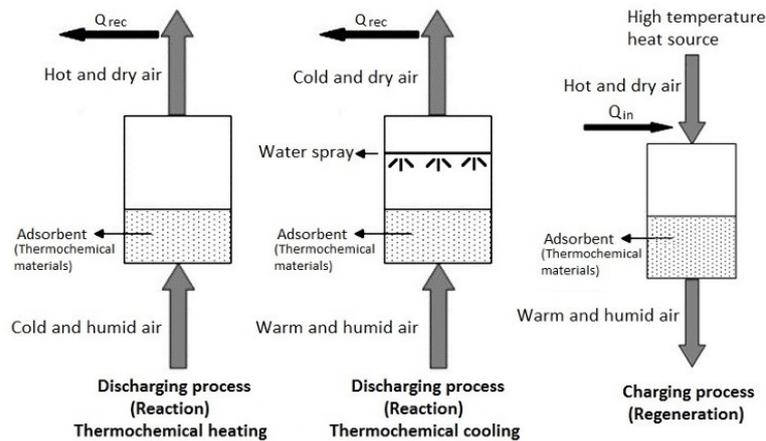
These findings collectively highlight how adsorption and absorption technologies can be tailored for dual-mode operation with improved efficiency, particularly when integrated with low-grade or renewable heat sources.

### 3.2. OPEN CYCLE SYSTEMS

In the closed cycle vapour absorption system, it has a very low thermal COP range of 0.5 in single-effect cycle and up to 1.2 in double-effect cycle that leads to the intensive use of thermal energy (Theo Elmer, 2016).

Open systems are working at atmospheric pressure. Water vapour is used as working fluid, which will be exhausted to the ambient environment. Moreover, because of its relative high operation pressure, high operating temperature, expensive and large corrosive chemical solutions, its development has been limited and not a valuable option for small scale heating, e.g. Domestic heating (Z. Duan, 2012, Theo Elmer, 2016). Therefore, open cycle vapour absorption system is an alternative to closed cycle vapour absorption. It is also known as desiccant air conditioning and evaporative cooling system (Theo Elmer, 2016).

The open system includes working fluid and thermochemical materials. In the charging process, thermal energy is transferred by medium for thermochemical materials. After a storing period, energy release from thermochemical material is absorbed by the working fluid for heating (Figure 7).



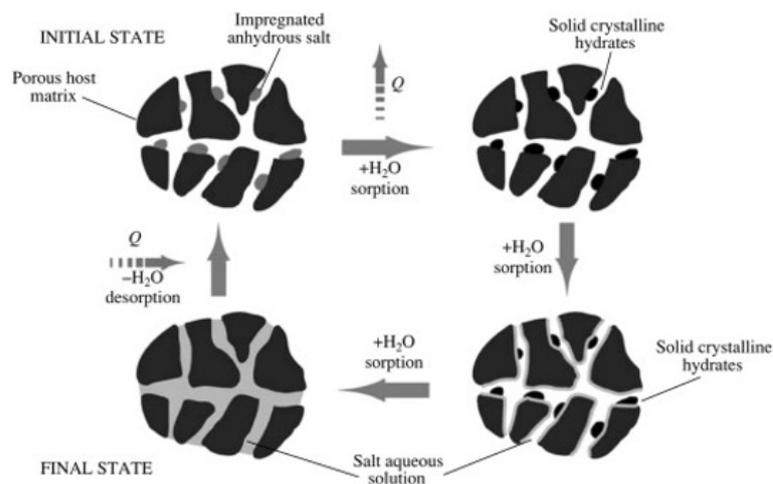
**Figure 7.** Charging and discharging process in open thermochemical energy storage system. (Hauer, 2002, Abedin and Rosen, 2012).

In thermochemical heating, moist and cool air enters the reactor, where it reacts with active materials, releasing heat and supplying warm, dry air indoors. For cooling, warm humid air interacts with water-sprayed thermochemical media, producing cool, dehumidified air. Regeneration involves drying the material with hot air, ideally from solar thermal sources. Using materials that regenerate at lower temperatures can further reduce energy demand.

Solar-driven open-cycle systems deliver cooling and dehumidification by directly exposing water to ambient air. These systems, often used for indoor comfort, are classified into evaporative and desiccant types, the latter further divided into solid and liquid sorbent technologies (J, 1985). Open-cycle setups suit both residential and industrial ventilation applications.

### 3.2.1. SORPTION HEAT SYSTEM

Thermochemical sorption heat storage system is an advanced technology to address the balance between energy consumption and energy demand in building service system. In sorption process (Figure 8) heat is stored by breaking the binding force between the sorbent and the sorbate by chemical potential.

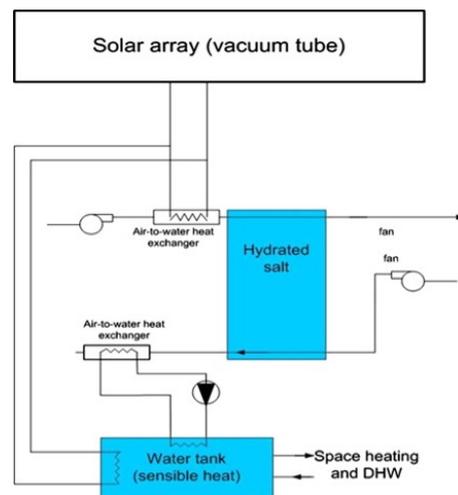


**Figure 8.** Sorption process on silica gel with CaCl<sub>2</sub> (Yu et al., 2013) (Aristov, 2007).

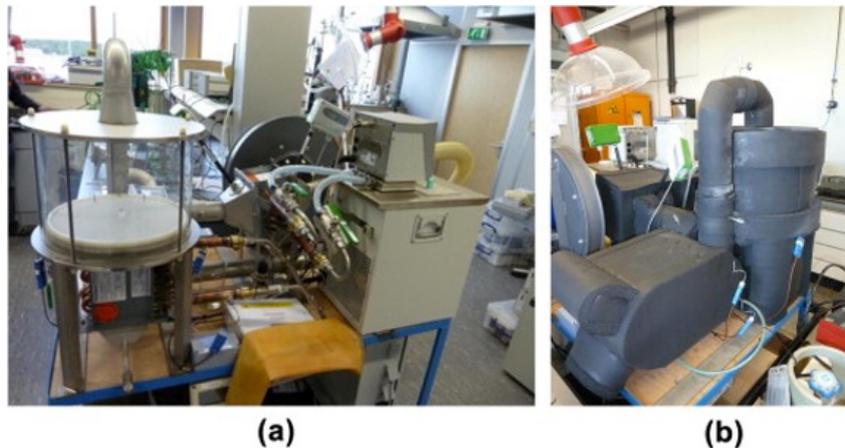
Thermochemical materials have a much higher energy density than common sensible and latent heat storage materials, and also, thermochemical heat storage system has a much lower heat loss (Aydin et al., 2015, Bales, 2006, H Abedin and A Rosen, 2011). Thermochemical heat storage system includes different types: based on physisorption in adsorbing materials (e.g. zeolites), based on absorption in hygroscopic solutions (e.g. NaOH solution) and based on absorption in salts (e.g. salt hydrates) (Zondag et al., 2013).

Recent researches in THS focus on composite material, which combines salts and matrix, or salt in matrix (Sahlot and Riffat, 2016). Because of the porosity of the adsorption materials, thermochemical materials such as vermiculite, pillar layered silica, silica gel, zeolite and carbon fibre are also used as host materials. A variety of porous materials have been investigated as hosts for thermochemical energy storage due to their sorption properties, structural characteristics, and cost-effectiveness. Traditional materials like vermiculite and silica gel offer moderate water uptake (0.03–0.35 g/g) with low regeneration temperatures (<150°C) and relatively low cost (Aydin et al., 2015, Zhang et al., 2016). Zeolites, including 13X, exhibit higher thermal stability and moderate uptake, though regeneration typically requires temperatures above 200 °C (Aydin et al., 2015, Bahrami, 2012, Li et al., 1999, Kyotani et al., 1997, Tatsidjodoung et al., 2016, Rao et al., 2006). Activated carbon materials, both powder and fibre, provide high specific surface areas (up to 1850 m<sup>2</sup>/g) and variable porosity, making them promising for sorption applications (Hamamoto et al., 2006b, Tso and Chao, 2012, Aydin et al., 2015, Hamamoto et al., 2006a, Wang et al., 2005). Expanded graphite (Aydin et al., 2015, Wu and Wang, 2015, Zhang and Fang, 2006, Du and Jana, 2007) and mesoporous silica (e.g., SBA-15) (Glaznev et al., 2011, Chen et al., 2009, Carrero et al., 2017) have also demonstrated good performance, particularly under vacuum or moderate heating conditions. Some novel natural materials, such as Wakkanai Siliceous Shale (WSS) (Liu et al., 2015), combine moderate porosity (60%) with low regeneration temperatures (~80°C), offering additional potential for low-grade heat recovery systems.

In the simple solar driven thermochemical energy storage system (Figure 9), energy was stored in the hydrated salt in hot summer and released in cold winter. In summer, solar array provides heat to charge the system (dry materials) and water vapour will be released to the ambient environment. In winter, cold and humid air goes into the fan and adsorbed by hydrated salt, then released to the ambient as warm and dry air (Zondag et al., 2013).

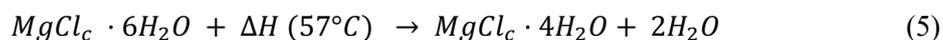


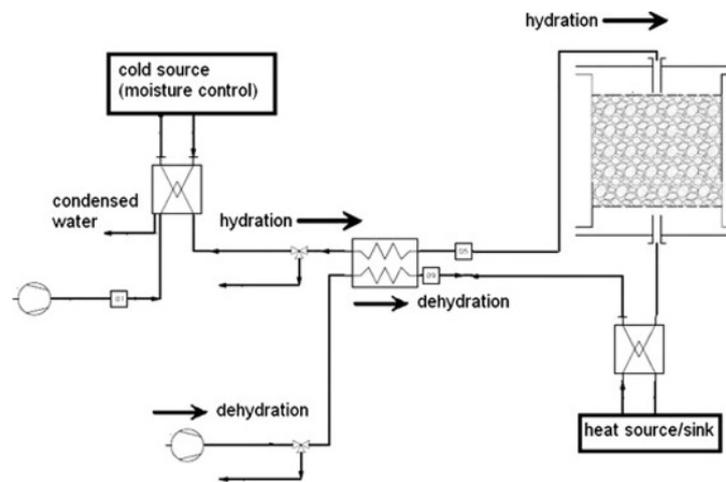
**Figure 9.** Solar driven open sorption thermochemical heat storage system (Zondag et al., 2013).



**Figure 10.** Photographs of prototype thermochemical storage system, (a) before and (b) after insulation (Zondag et al., 2013).

In Zondag et al. research, a prototype was built with a capacity of 17 L  $MgCl_2 \cdot 6H_2O$  as sorption materials includes a solar PV heat source, heat exchangers and fan (Figure 2-8) (Figure 2-9) (Zondag et al., 2013). An air flow was about 500 l/min with the pressure of 12 mbar. Results showed that  $MgCl_2 \cdot 6H_2O$  has a very high energy density of  $0.5 \text{ GJ/m}^3$  and the system can supply about 150 W of thermal energy with only 50 W heat loss for over 40 hours with a COP of 12. The reaction formula (Zondag et al., 2013) is shown below:





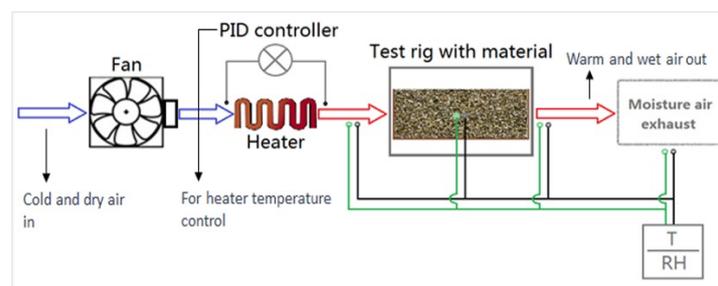
**Figure 11.** Schematic representation of thermochemical reactor storage system setup (Zondag et al., 2013).

Jong et al. stated that thermochemical materials provide a promising solution to achieve a long-term 100% renewable energy economy (de Jong et al., 2016). In their simulation within the MERITS project,  $\text{Na}_2\text{S}$  had a heat storage density of  $0.14 \text{ GJ/m}^3$  in the experiment. Development has been done to improve the heat storage density by enhancing vapour and heat transport level (de Jong et al., 2016). However,  $\text{Na}_2\text{S}$  has the risk of corrosion and reaction and a hazard of  $\text{H}_2\text{S}$  emissions (Craig, 1995, Warnqvist, 1980, Roelands et al., 2015, Jiang et al., 2016, Donkers et al., 2017). The Australia Group claimed that  $\text{Na}_2\text{S}$  is a dual use material (Isbell, 2016).

$\text{NaS/H}_2\text{O}$  was used on the SWEAT prototype by Boer et al. (Boer R, 2004) and the energy storage density was measured as  $1.1 \text{ kWh/kg}$  ( $1980 \text{ kWh/m}^3$ ) for heating ( $\text{COP}=0.84$ ) and  $0.7 \text{ kWh/kg}$  for cooling ( $\text{COP}=0.57$ ).

During reaction process, thermochemical materials (sorbate) adsorb moisture from the ambient air directly or a humidifier. In the charging process, heat from solar or other heat source can dry the materials to store energy for later use. The thermochemical heat sorption system is an easy process design operation system; however, the long-term storage performance of the reactor is the most important part as the moisture adsorption and heat generation act at same time which may cause some heat loss.

In open-cycle systems, water vapour from ambient air directly contacts the TES material, streamlining the setup by removing the need for separate fluid circuits. Zhang et al. (Zhang, Y., 2022) tested a prototype using a hygroscopic salt that absorbed moisture and stored heat during charging, then released both during discharging to supply warm, dry air indoors. While effective for combined heating and dehumidification, the system still faced issues such as humidity regulation and thermal losses. Nonetheless, the results suggest open-cycle configurations hold promise for low-cost, decentralised heating in moderately humid climates.



**Figure 12.** Charging cycle in open loop thermochemical energy storage system. (Zhang, Y., 2022).

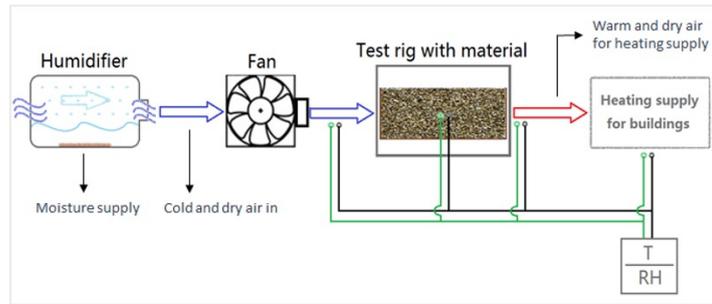


Figure 13. Discharging cycle in open loop thermochemical energy storage system. (Zhang, Y., 2022).

3.2.2. INTEGRATION WITH RENEWABLE HEAT SOURCES (E.G., SOLAR THERMAL)

Integrating TES with renewable heat sources—especially solar thermal—plays a key role in enhancing the reliability and sustainability of energy systems. Recent developments have shown that such integration can efficiently convert fluctuating low-grade heat into a stable energy supply. For example, a solar-assisted open-loop cooling system was proposed that combines a desiccant wheel and indirect evaporative coolers with a transcritical CO<sub>2</sub> heat pump powered largely by PV panels (Basso et al., 2023). Simulations over a year revealed renewable shares exceeding 50%, with potential to reach 77% (electric) and full thermal self-sufficiency, while the CO<sub>2</sub> heat pump’s COP could be optimised from 2.3 to 6.5. In another study, a solar-driven sorption cooling unit incorporating a dehumidifier and desiccant cold storage achieved 800–900 W cooling output and reduced ventilation air temperature by up to 19 K (Nielsen et al., 2022). Silica gel performed best among tested materials, and airflow tests showed acceptable pressure drops, supporting the system’s applicability in eight out of fourteen Sunbelt climate zones.

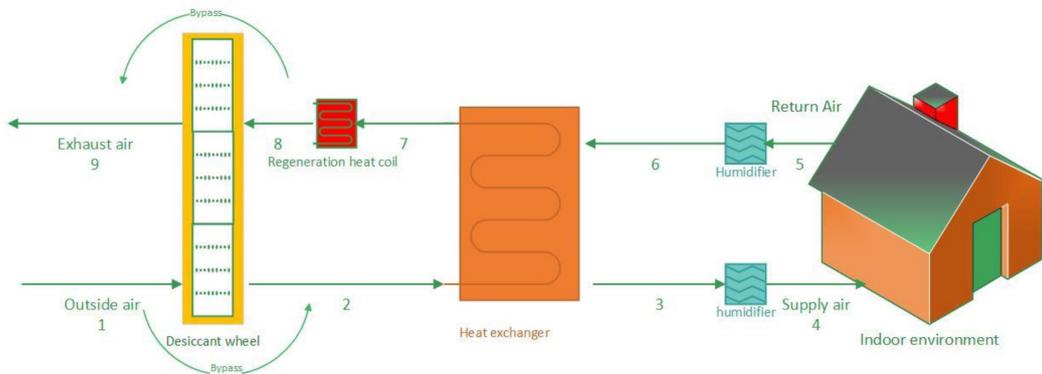
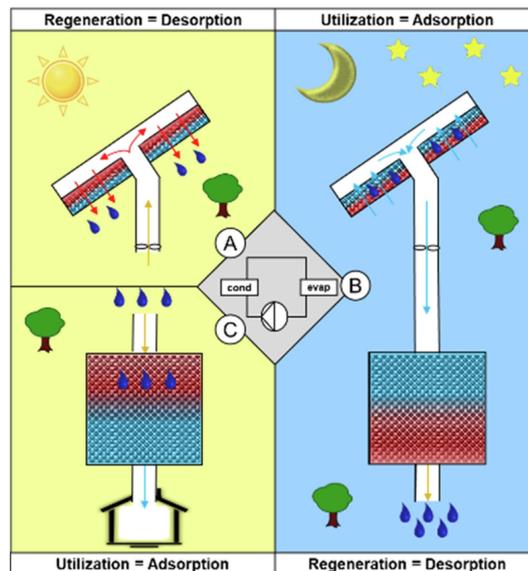


Figure 14. Schematic of desiccant wheel system. (Basso et al., 2023).



**Figure 15.** Principle diagram of cooling system. (Nielsen et al., 2022).

Linking TES systems with renewable sources like solar thermal not only helps stabilise the supply of low-grade heat but also enhances energy reliability and efficiency. By smoothing out fluctuations in heat availability, such integration supports continuous storage operation and more consistent thermal output—key to resilient energy infrastructure.

Recent innovations across both closed and open TES configurations have strengthened this potential. From chemical heat pumps to sorption-based and open-cycle designs, these systems are increasingly tailored for renewable integration. As a result, TES is emerging as a flexible and low-emission solution for reducing primary energy demand and reinforcing the sustainability of future energy systems.

#### 4. REACTOR DESIGN FOR THERMOCHEMICAL ENERGY STORAGE SYSTEMS

Reactor design plays a pivotal role in the performance, reliability, and scalability of thermochemical energy storage (TES) systems. An effective reactor not only ensures optimal contact between the heat transfer fluid and the active TES materials but also minimizes thermal losses, facilitates efficient reaction kinetics, and supports long-term cycling durability. This section outlines key reactor configurations, design considerations, and example illustrations to provide a comprehensive overview of recent progress in this area.

##### 4.1. DESIGN CONSIDERATIONS

The design of TES reactors must address several key criteria:

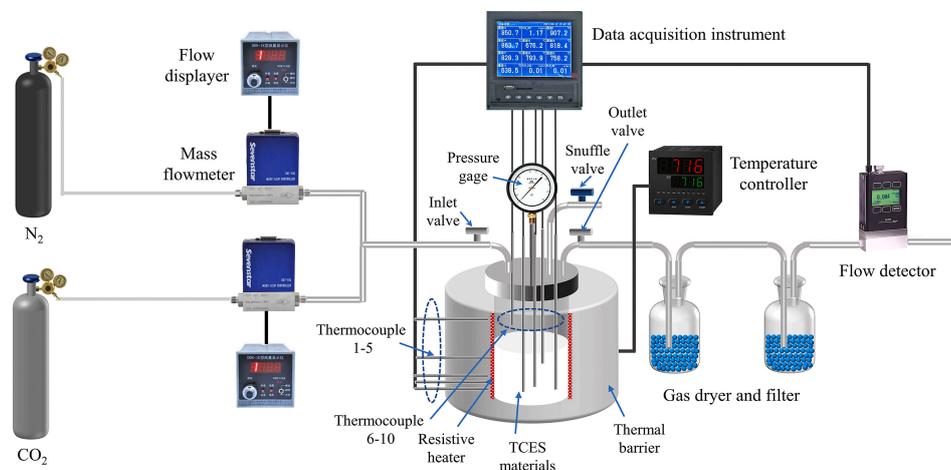
- **Heat and Mass Transfer Efficiency:** To facilitate rapid charging and discharging, the reactor must support efficient heat exchange and vapor diffusion. Composite materials with tailored porosity and enhanced thermal conductivity are often used to accelerate energy transfer.
- **Thermal Management:** Temperature gradients within the reactor must be minimized to prevent localized overheating or underutilization of storage media.
- **Mechanical Stability:** Reactors must maintain structural integrity through numerous thermal cycles and accommodate any volume changes in active materials.
- **Scalability and Modularity:** Modern reactor designs aim to be modular to ease system integration, especially for building-scale or industrial applications.

## 4.2. TYPICAL REACTOR CONFIGURATIONS

### 4.2.1. FIXED-BED REACTOR

Fixed-bed reactors are widely adopted in TES systems, where the storage medium remains stationary while heat-carrying air or steam flows through. Their low cost and straightforward design make them attractive, though they can face issues like flow non-uniformity and limited heat transfer in larger applications.

Recent work on CaL-based TES systems has shown promising results using this configuration. For example,  $\text{CaCO}_3$  decomposition in nitrogen at  $850^\circ\text{C}$  achieved nearly 64% conversion, while subsequent carbonation at  $750^\circ\text{C}$  reached 67.2% (Tian et al., 2024). Reducing the material filling improved heat efficiency but lowered total output. Simulations further revealed that higher calcination temperatures and porosity levels (0.6–0.7) significantly influence performance, whereas carbonation temperature and material conductivity were less critical. These insights support improved reactor design and material optimisation for thermochemical applications.



**Figure 16.** Schematic of a fixed-bed TES reactor.(Tian et al., 2024).

### 4.2.2. FLUIDIZED-BED REACTOR

Fluidized-bed reactors improve thermal performance by suspending TES particles in a gas stream or using mechanical mixing, which enhances contact between the heat transfer medium and reactive materials. This configuration is particularly effective for low-temperature applications with porous salt composites.

One study proposed a mechanically stirred plow-share fluidized bed to overcome the poor flowability and low conductivity of  $\text{CaO}/\text{Ca}(\text{OH})_2$  powders (Risthaus et al., 2022). By replacing gas flow with mechanical agitation, the system achieved hydration and dehydration with heat transfer coefficients significantly higher than those of fixed beds, confirming its compact and efficient potential. Another fluidized-bed design, powered by solar energy, used doped  $\text{CaCO}_3$  pellets and sustained over 85% energy capacity after 100 cycles (Zheng et al., 2023). Improved absorptance and kinetics raised solar-thermal efficiency from 9% to 19%, while fluidization reduced thermal gradients and mass transfer limitations.

A third study presented an autothermal, directly irradiated fluidized-bed reactor tailored for concentrated solar power TES systems (Padula et al., 2021). Using limestone-based reactions and a built-in counterflow heat exchanger, the design recovered sensible heat and achieved simulated charging efficiencies up to 90% at  $\sim 900^\circ\text{C}$ , with discharge efficiencies around 80%. These examples underscore the scalability and efficiency of fluidized-bed technologies in solar TES.

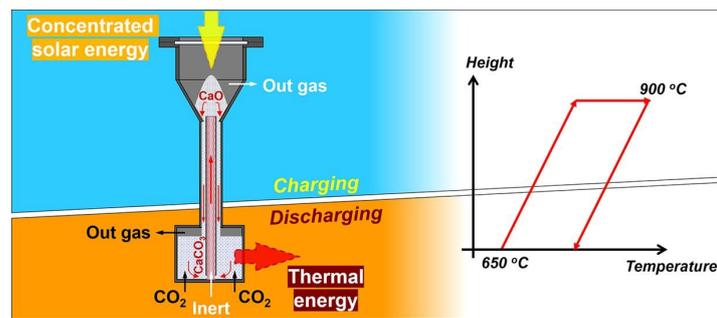


Figure 17. Outline of the thermochemical battery.

#### 4.2.3. PLATE-FIN AND TUBE-IN-TUBE HEAT EXCHANGER REACTORS

To enhance heat transfer in TES systems, finned plates and tube structures are often used to embed thermochemical materials and increase effective surface area. For example, aluminum plate–tube exchangers combined with porous elements like nickel foam have shown high heat output in CaCl<sub>2</sub>-based reactors. A notable case is the hybrid solar–methanol energy system developed by Qin et al. (Qin et al., 2024), which combines parabolic trough solar collectors, a thermochemical reactor with plate-tube geometry, and an internal combustion engine. This setup delivered 72.09% total energy efficiency and 24.63% solar-to-electric conversion, alongside significant reductions in both fuel use (32.97%) and CO<sub>2</sub> emissions (25.33%). The compact heat exchanger design played a key role in maintaining efficient and flexible performance under varying solar conditions.

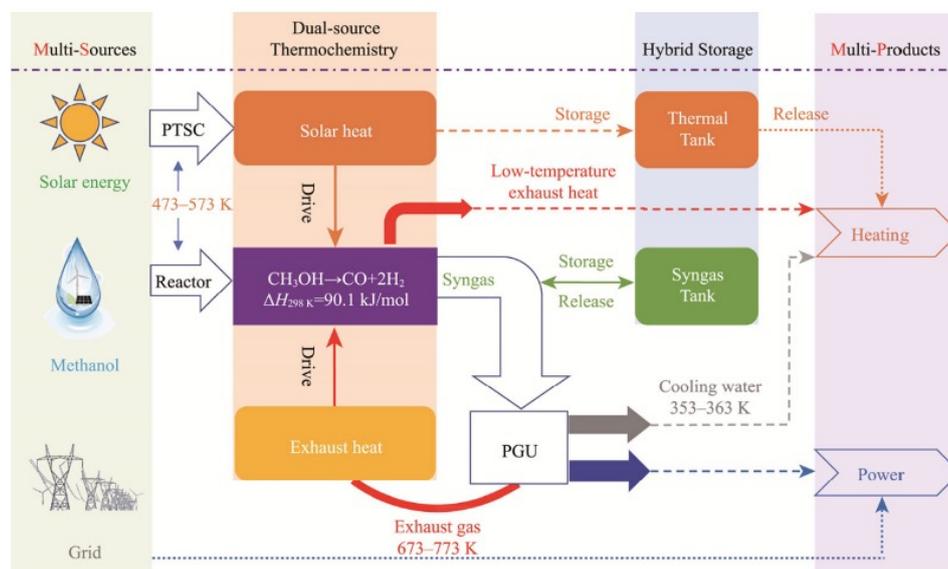
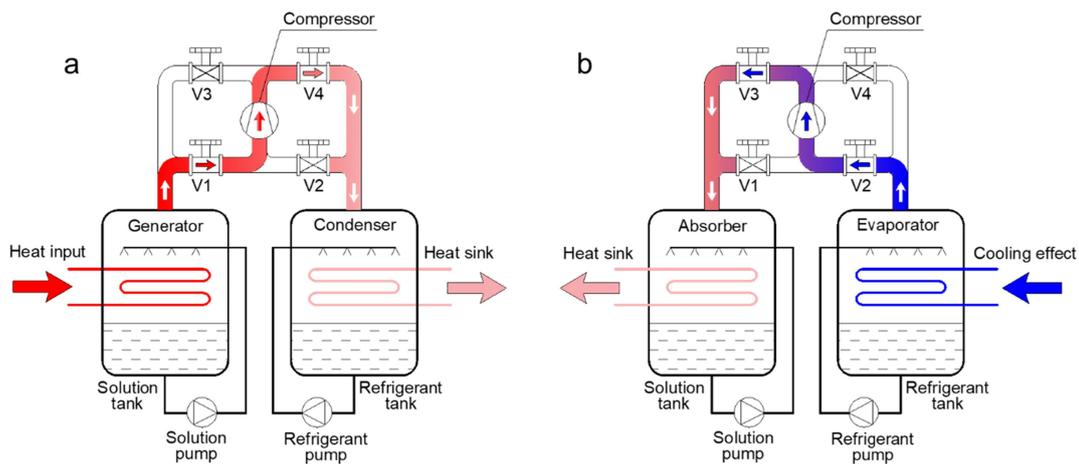


Figure 18. Hybrid CHP with solar/exhaust thermochemical and thermal energy storage.(Qin et al., 2024).

Building on this, Ding and Wu (Ding and Wu, 2021) introduced a compression-assisted absorption TES cycle that improves performance by applying auxiliary compression during both charging and discharging phases. This design boosted energy efficiency from 0.58 to 0.67 and more than doubled the energy density to 282.8 kWh/m<sup>3</sup>, even at a relatively low charging temperature of 80°C. Enhanced reactor configuration also enabled quicker thermal response, making the system a strong candidate for efficient low-temperature heat storage.



**Figure 19.** Schematic diagrams of the CATES cycle. (a) Charging process. (b) Discharging process (Ding and Wu, 2021).

#### 4.3. FUTURE DIRECTIONS IN REACTOR DESIGN

As thermochemical energy storage (TES) moves toward large-scale use, innovative reactor designs are essential to address current challenges in heat transfer, material efficiency, and operational flexibility. Future reactors must balance thermal performance, manufacturing cost, and integration with renewable systems. Several emerging strategies offer promising directions:

1. **Additive Manufacturing:** 3D printing enables precise control over reactor geometry and porosity, enhancing heat transfer and allowing for complex, customized components. It also supports rapid prototyping and scalable production.
2. **Smart Reactors:** Integrating sensors and control systems allows real-time monitoring and adaptive operation based on temperature, humidity, and system demand, improving efficiency, safety, and system responsiveness.
3. **Hybrid Designs:** Combining reactor types can maximize energy density and adaptability, supporting diverse heat sources like solar or waste heat.

#### 4.4. POTENTIAL CHALLENGES AND RESEARCH NEEDS

Despite the significant advancements in thermochemical energy storage (TES) reactor designs and materials, several technical challenges remain that must be addressed to enable large-scale deployment and long-term reliability. Recognizing these limitations is essential for guiding future research and development efforts.

1. **High Regeneration Temperatures:** Many thermochemical systems, particularly those using metal oxides or salt hydrates, require high temperatures (often exceeding 600°C) for regeneration. This limits their compatibility with low-grade heat sources and increases system complexity and cost. Research into novel materials with lower regeneration thresholds and higher reaction reversibility is therefore critical.
2. **Complex Heat and Mass Transfer Coupling:** TES reactors inherently involve simultaneous heat and mass transfer, especially during hydration/dehydration or adsorption/desorption processes. Managing this coupling efficiently—while avoiding local hotspots, incomplete reactions, or uneven flow distribution—remains a core engineering challenge. Advanced simulation tools and reactor architectures are needed to address these issues.
3. **Unsteady and Degraded Performance Over Cycles:** TES materials often suffer from reduced reactivity due to sintering, phase separation, or loss of surface area over repeated thermal cycles. This can lead to declining storage efficiency and unstable reactor output. Long-term cycling studies and material stabilization strategies, such as doping or composite structuring, are key research priorities.
4. **Corrosion and Material Compatibility:** High temperatures, humid environments, and reactive species can lead to corrosion of reactor components, especially metal-based heat exchangers and structural materials. Ensuring chemical compatibility between TES materials and reactor surfaces is essential for

durability. Protective coatings and corrosion-resistant alloys are areas of ongoing research.

5. System Integration and Control Complexity: Integrating TES reactors with solar thermal collectors, industrial waste heat systems, or district energy networks introduces control challenges due to fluctuating energy input and variable demand. Advanced control algorithms, real-time sensing, and predictive system models will be essential for stable operation and energy dispatch optimization.

Addressing these challenges requires coordinated efforts across multiple disciplines, including materials science, reactor engineering, system modeling, and experimental validation under realistic operating conditions. Collaborative research that bridges these fields is essential to develop robust materials, optimize reactor designs, and ensure reliable, scalable system performance. Progress in these areas will be crucial for transitioning thermochemical heat storage from promising laboratory-scale prototypes to commercially viable, widely deployable energy solutions.

## 5. CONCLUSION AND FUTURE WORK

Thermochemical energy storage (TES) systems offer a compelling solution to the challenges of efficient thermal management and renewable energy utilisation. This review has systematically examined recent progress in TES materials, system architectures, and reactor designs. Closed-cycle configurations, including chemical heat pumps and sorption-based systems, demonstrate significant potential for compact, long-duration storage, particularly when integrated with low-grade or intermittent heat sources. Meanwhile, open-cycle systems leveraging direct air contact provide simpler, decentralised solutions, particularly advantageous for building applications in moderate climatic conditions.

Advances in TES materials such as salt-impregnated porous matrices, mesoporous composites, and engineered sorbents, which have substantially improved energy densities, reduced regeneration temperatures, and enhanced cyclic stability. Reactor design innovations, including fluidised-bed, plate-fin, and modular configurations, have addressed critical barriers related to heat and mass transfer, enabling higher storage efficiencies and operational flexibility. Furthermore, the integration of TES with renewable energy technologies, particularly solar thermal systems, has demonstrated significant gains in overall system efficiency, resilience, and carbon footprint reduction.

Despite these achievements, several critical challenges remain. Material degradation during cycling, non-uniform heat and mass transfer within reactors, and the relatively high regeneration energy requirements of certain systems limit the widespread deployment of TES technologies. Moreover, real-world system integration, control strategies for dynamic operation, and scalability under variable renewable input conditions require further investigation.

Future research priorities should include the development of low-temperature, high-capacity TES materials with improved long-term stability; the design of advanced reactor architectures capable of minimising thermal gradients and enhancing dynamic response; and the integration of smart control algorithms to optimise TES performance within hybrid renewable energy networks. Cross-disciplinary approaches combining materials science, thermal engineering, and energy systems modelling will be essential to overcome existing limitations and realise the full potential of TES as a cornerstone technology for sustainable energy infrastructure.

## AUTHOR CONTRIBUTIONS

**Yanan Zhang:** Led the study, Conducted the main literature review and synthesis, Drafted the original manuscript. **Aydin Devrim:** Contributed to parts of the literature review, Critically revised, Edited the manuscript. **Hasila Jarimi:** Contributed to the review of specific sections, Provided technical input on thermochemical energy storage systems. **Cagri Kutlu:** Contributed to selected parts of the review, Provided technical feedback on system design and applications.

## COMPETING INTERESTS

The authors declare no competing interests.

## DATA ACCESSIBILITY

The data used in this study will be made available upon request.

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