Chapter

Thermal Energy Storage for Solar Energy Utilization: Fundamentals and Applications

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Abstract

Solar energy increases its popularity in many fields, from buildings, food productions to power plants and other industries, due to the clean and renewable properties. To eliminate its intermittence feature, thermal energy storage is vital for efficient and stable operation of solar energy utilization systems. It is an effective way of decoupling the energy demand and generation, while plays an important role on smoothing their fluctuations. In this chapter, various types of thermal energy storage technologies are summarized and compared, including the latest studies on the thermal energy storage materials and heat transfer enhancements. Then, the most up-to-date developments and applications of various thermal energy storage options in solar energy systems are summarized, with an emphasis on the material selections, system integrations, operational characteristics, performance assessments and technological comparisons. The emerging and future trends are finally outlined. This chapter will be a useful resource for relevant researchers, engineers, policy-makers, technology users, and engineering students in the field.

Keywords: thermal energy storage, solar energy utilization, sensible heat storage, latent heat storage, thermochemical heat storage, heat transfer

1. Introduction

Currently, energy, environment and sustainable development are the major concerns to the countries all over the world. The long term usage of fossil fuels (e.g., coal, oil and natural gas) has caused environment pollutions and greenhouse effects. The resulting global climate change and resource exhaustion can seriously threaten human survival and development. Renewable energy sources, including solar, wind, hydro, geothermal, etc. [1], have been increasingly attractive to many countries for their natural advantages on sustainability and cleanliness. Solar energy is considered as one of the most promising renewable energy sources, because of its abundance and easy-access to the most parts of the world. However, due to the intermittency in availability and constant variation of solar radiation, the output of a solar energy system is highly fluctuating if no or small inertia (thermal or electrical) is included. This poses strong needs for energy storage in solar energy systems to store energy at high solar irradiances for later uses whenever there is a demand while solar irradiance is not enough. With the energy storage systems associated to reduce the discrepancy between the demand and supply, solar energy systems can be more reliable and efficient in operation.

In order to develop efficient and economical energy storage systems, various energy storage technologies have been proposed [2], such as compressed air energy storage, pumped storage hydro-power, flywheel energy storage, thermal energy storage, electrochemical energy storage, hydrogen storage and so on. They are employed in different application fields depending on their specific characteristics on energy storage. Among all the storage methods, thermal energy storage (TES) is one of the most economical systems in practical applications, and it allows the storage of thermal energy by heating or cooling a storage medium to be used at a later time [3]. TES has been applied in a broad range of fields: district heating, domestic hot water, thermal comfort, concentrated solar plants (CSP), chemical industry, food industry, etc. [4–7]. It has also been proven that the usage of TES can improve the performance of whole system operation, save the fuel consumption, lower the investment and operation costs, increase the energy supply security and mitigate the pollution to the environment if it is appropriately designed. To obtain the above benefits for an energy system, it is critical to choose a suitable thermal energy storage approach. The selection of thermal energy storage depends on the type of energy source, required storage duration, operating condition, economic viability, etc. The most mature and widely used approach is sensible heat storage. Latent heat storage and thermochemical energy storage have also attracted extensive research and development efforts in the last two decades, as they can offer higher heat storage capacities and lower heat losses during the energy storage processes.

The aim of this chapter is to provide a state-of-the-art review of TES technologies and their applications in solar utilization systems. The principles of several energy storage methods and evaluation approaches of storage capacities are firstly described. Sensible heat storage technologies, including the solid and liquid storage methods, are briefly reviewed. Latent heat storage systems associated with phase change materials (PCMs) as well as thermochemical storage are also introduced and summarized. Further discussions on important criteria of energy storage technologies suitable for solar energy applications are also presented. Later, TES technologies applied in solar energy systems like solar power systems, solar heating/cooling systems are reviewed with the detailed analyses about the material selections and system integrations of TES and solar energy systems.

2. Thermal energy storage technologies

TES is one of the most practiced technologies to store energy in the form of heat to eliminate the gap between the energy supply and demand. As shown in **Figure 1**, there are three main thermal energy storage technologies [9]: sensible heat storage through a temperature change (sensible heat) of a material, latent heat storage through phase change (latent heat) of a material and thermochemical heat (chemical energy) by thermally inducing changes in materials' chemical states. As compared in **Table 1**, the choice of TES method depends on a variety of factors such as the storage capacity, cost, temperature range, duration requirement as well as the specific application.

2.1 Sensible heat storage

Solid sensible heat storage is an attractive option for thermal energy storage regarding the investment and maintenance costs. Sensible heat storage stores the thermal energy by varying the temperature of storage materials, without

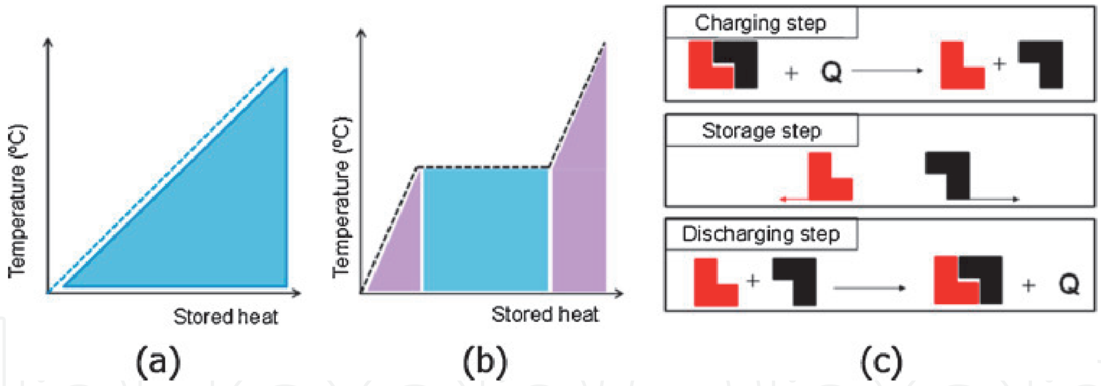

Figure 1.
Main approaches of thermal energy storage: (a) sensible heat, (b) latent heat, (c) thermo-chemical reactions [8].

TES technology	Capacity (kWh/t)	Cost (/kWh)	Storage period
Sensible	10–50	0.1–10	Days/months
Phase change materials	50–150	10–50	Hours/months
Chemical reactions	120–150	8–100	Months/seasons

Table 1.
Comparison of typical parameters of three TES technologies [10].

undergoing any form of phase change within the working temperature range. The amount of thermal energy stored or released is proportional to the density ρ, volume V, specific heat c_p, and temperature variation of the storage materials:

$$Q_{sen} = \int_{T_i}^{T_f} m c_p dT = \rho V c_p \left(T_f - T_i\right), \tag{1}$$

where Q_{sen} is the amount of sensible heat stored, dT is the temperature interval, T_i is the initial temperature and T_f the final temperature of storage medium during

Material	Type	Density (kg/m^3)	Thermal conductivity (W/m·K)	Heat capacity (kJ/kg·K)	Cost (€/m^3)
Rock	Solid	1500–2800	0.85–3.5	1	64–742
Concrete	Solid	2000	1.35	1	76
Sand and gravel	Solid	1700–2200	2	0.910–1.180	6–8
Ceramic tile	Solid	2000	1	0.8	1600–3500
Gypsum (coating)	Solid	1000	0.4	1	78
Ceramic brick	Solid	1800	0.73	0.92	36–64
Wood	Solid	450	0.12	1.6	404
Water	Liquid	990	0.63	4.19	1.6
Oil	Liquid	888	0.14	1.88	6560
Nitrite salts	Liquid	1825	0.57	1.5	2200
Carbonate salts	Liquid	2100	2	1.8	6050
Liquid sodium	Liquid	850	71	1.3	2000

Table 2.
Available sensible heat storage materials used in the thermal energy storage systems [11].

the storage process. Basically, specific heat c_p, density ρ and thermal conductivity k are the key thermal properties of sensible heat storage materials. According to the materials' phase state, sensible heat storage materials can be divided into two main categories: solid and liquid heat storage. **Table 2** lists the most common solid and liquid heat storage materials with their thermal properties.

2.1.1 Solid heat storage

Solid storage materials have been applied in many TES systems for their reliability, low cost, easy implementation and applicability in extensive practical cases [12, 13]. Different from liquid heat storage, there are no vapor pressure or leakage issues in solid heat storage. However, a fluid, usually air or oil, is needed to work as the heat transfer fluid (HTF) to transport the thermal energy that is to be stored into or released from the solid heat storage system. As listed in **Table 2**, the most frequently used solid heat storage materials include rock, concrete, brick, sand and so on [14–16].

- **Rock** is always loosely piled in a packed bed through which the HTF like air or oil can flow. Thermal energy is stored in the packed bed by forcing heated HTF flowing through the rocks and utilized again by recirculating the HTF through the heated rocks. Typically, the characteristic size of rock pieces varies from 1 to 5 cm. There is a large contact surface area available for heat transfer between HTF and rocks which is beneficial for the heat transfer. The amount and temperature level of energy stored in a packed bed storage system with rocks depend on the rock size and shape, packing density, HTF, etc. As a sensible energy storage option, rock has advantages like being non-toxic, non-flammable, cheap and easily available. This type of storage is operated very often for temperatures up to 100°C in conjunction with solar air heaters and thus convenient to be implemented in buildings. The heat storage with rocks can also be used for higher temperature applications, up to 1000°C. When rock is employed as thermal storage material, there are several drawbacks, including the poor thermal conductivity, high pressure drop under large flow rates of HTF.

- **Concrete** is a promising candidate as it has a low cost and is easy to obtain and process directly on site. Concrete is a construction material comprised of cementitious materials and/or calcium aluminate cement, coarse and fine aggregates, water and possibly chemical admixtures. Besides, it has relatively high specific heat and good mechanical properties. The heat exchanger between concrete and HTF is usually designed as the pipes embedded into the concrete block where HTF flows internally. As cracks may form after repeated cycles due to thermal expansion and contraction at high temperatures, research efforts have been devoted to developing appropriate concrete compositions, optimizing chemical–physical and durability performances at high temperatures. Long-term stability of concrete has been proven in oven experiments and through strength measurements up to 500°C. The main challenges to use the concrete as TES materials include: potential cracks, relatively low thermal conductivity, durability after long-term thermal cycling and high costs for heat exchangers to charge/discharge thermal energy.

- **Sand** grains are shown to be a promising low-cost candidate material that is suitable for concentrated solar power (CSP) applications with high-temperature thermal storage. The average size of sand grains is around 0.2–0.5 mm and they are commonly used in the form of packed beds for heat storage with air as HTF. It is possible to use desert sands directly as collected from the field of CSP, removing the need for third-party suppliers. Moreover, they can be used directly in solar receivers to collect solar thermal energy. After absorbing the heat of concentrated solar rays, due to the gravity forces, the sands can fall from the top of solar receiver tower and then they can be collected in an insulated storage tank below. Temperature of hot sands can go up to 700–1000°C which is appropriate for producing steam to drive a Rankine cycle [17].

2.1.2 Liquid heat storage

- **Water** is the most common liquid material for TES due to its high specific heat, none-toxicity, low-cost and easy-availability [18]. However, due to its high vapor pressure, water requires costly insulation and pressure withstanding containment for high temperature applications from 100 to 700°C (in the form of steam). Water in liquid phase is widely used for low temperature heat storage below 100°C in solar based applications, such as space heating and hot water supply [19]. Water in liquid state can also form thermal stratification or thermocline. Due to density difference caused by heating of liquid, the buoyancy force causes stratification of the water, forming a thermal gradient across the storage. Under such a condition, the hot fluid can be supplied to the upper part of a storage tank during charging, and the cold fluid can be extracted from the bottom part during discharging [20]. Thus, the efficiency of thermal energy store and release process can be improved. In some high temperature applications like CSP plants, water is stored in steam phase in high pressure tanks (steam accumulator) to work as TES systems. In additional, water can be also used in chilled water form or in ice form for cold energy storage, which is useful in refrigeration systems. The main drawbacks for using water as the TES material are its high vapor pressure and corrosiveness to the container above its boiling point.

- **Molten salt** is currently one of the most popular TES materials used in CSP plants. Compared to other liquid heat storage materials, molten salts have relative low costs, high energy storage densities, excellent thermal stabilities, low viscosities and non-flammabilities. Molten salts in liquid state can be operated at high temperatures of several hundred degree centigrade while its vapor pressure is much lower than that of water, so it is very suitable for high temperature CSP plants. The pure molten salt usually has a melting point above 200°C which hampers its further application at low temperatures. It is desirable to have a molten salt with a lower melting point so that it can remain the liquid state when storing the thermal energy. A new series of ternary salt mixtures have been proposed with ultra-low melting temperatures at 76°C, 78°C or 80°C, and they can prevent the solidification at low temperatures to enable the TES systems suitable for a wider applications. Molten salt also has several drawbacks that limit its application: low thermal conductivity, volume change during the melting and corrosivity to the container.

- **Thermal oil** is usually a kind of organic fluid and works as a HTF in many power and energy systems. When using as a thermal storage medium, thermal oil can remain in liquid phase at temperatures of 350–400°C with stable thermal properties, which is much higher than the liquid water. It means that thermal oil can store more thermal energy based on the wider temperature operation range. Compared to water, thermal oil also has a lower vapor pressure, which is beneficial for mechanical designs of relevant pipes and containers. Unlike molten salts, thermal oil does not freeze during the night in pipes so that it doesn't need any antifreeze system. However, the cost of thermal oil is usually higher than water and molten salts.

2.1.3 Pros and cons of sensible heat storage

Sensible heat storage materials are typically based on relatively low cost materials and thus extensively used, except the liquid metals. Due to the relatively good thermal stability, heat transfer performance and transport properties, sensible heat storage materials are the most used TES materials for high temperature applications. Compared to the latent heat storage, specific heat of sensible heat storage materials is 50–100 times smaller, leading to the requirement of large volumes or quantities in order to deliver the amount of energy storage necessary for high temperature thermal energy storage applications. The other main issue of sensible heat storage is that the temperature of the storage medium decreases during discharging process, so the HTF temperature also decreases with time.

2.2 Latent heat storage

Latent heat storage utilizing PCMs is an alternative TES technique compared to the sensible heat storage [11]. PCMs are substances which can absorb or release large amount of energy, i.e., so-called latent heat, when they experience phase transitions among solid, liquid and gas states. Although the highest latent heat of phase change is the liquid-gas phase change, it is hard to utilize this due to the enormous volume change associated with material evaporation. While another kind, 'solid-solid' latent heat storage material has its latent heat of transition one order of magnitude smaller than the solid-liquid PCMs [21], which is commonly applied for latent heat thermal energy storage. Solid-liquid PCMs should have a melting point near the required operation temperature range of the TES system, melt congruently with minimum subcooling [22], and also is desired to be chemically stable, cost competitive, non-toxic and non-corrosive. The amount of energy storage of the latent heat system with PCMs is calculated as:

$$Q_{lat} = m\left(c_{p,s}(T_m - T_i) + \alpha L_h + c_{p,l}\left(T_f - T_m\right)\right), \tag{2}$$

where Q_{lat} is the amount of heat stored, $c_{p,s}$ and $c_{p,l}$ are the specific heat of PCMs in solid and liquid state, L_h is the latent heat of fusion, α is the melting fraction, T_i and T_f are the initial and final temperatures of the storage materials, and T_m is the melting temperature. This section briefly introduces the classification of PCMs and the related heat transfer enhancement techniques.

2.2.1 Phase change materials

Solid-liquid PCMs are competitive alternatives to the sensible TES materials. Compared to sensible heat storage materials, PCMs can operate at the phase change temperature with small temperature variations between heat storage (charging) and heat releasing (discharging) as illustrated in **Figure 1(b)**, and **Figure 2** shows the classification of PCMs family for TES [23]. Different kinds of PCMs are introduced in the following subsections. **Table 3** presents the characteristics of several common PCMs.

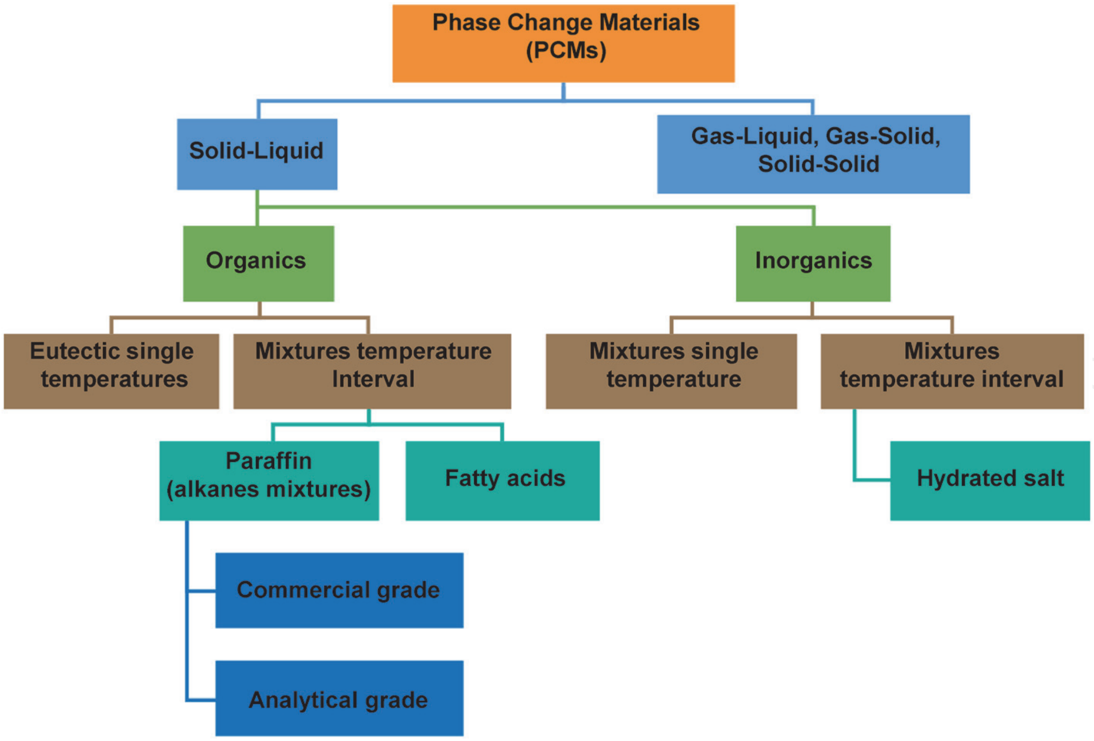

Figure 2.
Classification of latent heat materials with solid–liquid phase change behavior.

- **Organic PCMs** and their eutectic mixtures have been successfully implemented in many commercial applications, such as space heating in buildings, electronic devices, refrigeration and air-conditioning, solar air/water heating, textiles, automobiles, food and space industries [23]. Organic PCMs featured of congruent melting without phase separation usually have relative

Name	Melting point (°C)	Latent heat (kJ/kg)	Density (kg/m^3)	Thermal conductivity (W/m·K)	Heat capacity (kJ/kg·K)
(Organic)					
n-Octadecane	27.7	243.5	865/785	0.19/0.148	2.14/2.66
Paraffin wax	32	251	830	0.514/0.244	1.96/3.26
RT 55	55	172	880/770	0.2	2
RT 70 HC	69–71	260	880/770	0.2	2
(Inorganic)					
$CaCl_2{\cdot}6H_2O$	29.6	190.8	1562	N/A	N/A
$Ba(OH)_2{\cdot}8H_2O$	78	265–280	2070/1937	1.225/0.653	N/A
E117	117	169	1450	0.7	2.61
$LiNO_3$-$NaNO_3$	195	252	N/A	N/A	N/A
$NaNO_3$	306	172	2261	388.9	N/A
KNO_3	333	266	2110	N/A	0.5
KOH	380	150	2044	N/A	0.5

Table 3.
The thermal properties of organic and inorganic phase change thermal storage materials [24, 25].

low melting points. Commonly used organic PCMs are paraffin, fatty acids, esters, alcohols and glycols. Among them, paraffin wax is an excellent heat storage material and has been widely applied for low temperature heat storage applications [26]. It consists of straight n-alkanes chain (CH_3-(CH_2)-CH_3), featuring a high specific heat capacity (2.14–2.9 J/g·K), a low price (~1 USD/kg) with a moderate heat storage density (200 kJ/kg) and a narrow range of melting temperatures from −10 to 67°C [27], a small degree of subcooling, chemically stable and non-toxic properties. Due to the purity and specific composition, the organic PCMs show up a remarkable latent heat capacity in narrow temperature ranges. In addition, they are chemically inert and have an unlimited lifetime. However, their low thermal conductivities (0.1–0.35 W/m·K) limit their practical applications.

- **Inorganic PCMs** can be classified into two groups: salt/salt hydrates, and metals and their alloys. In general, inorganic PCMs not only have nearly doubled heat storage densities but also higher thermal conductivities, higher operating temperatures compared to the organic ones [28]. However, inorganic PCMs are corrosive to metals leading to a short service life of the system and a higher maintenance cost. The inorganic PCMs (salt/salt hydrates) can also suffer from phase segregation and supercooling, which would reversibly affect the energy storage capacity. For high temperature applications, however, metal and metallic alloys are potential PCM candidates as they don't suffer from these disadvantages. The inorganic salt means salt or its hydrates, which can be expressed as A_xB and $A_xB_y \cdot n(H_2O)$ respectively, where A_xB represents metal carbonate, sulfite, phosphate, nitrite, acetate or chloride and n represents number of water molecules. Although the inorganic PCMs show very promising and advantageous characteristics, these materials still face many problems to be commercial products for practical applications: (1) volume change at phase transition, (2) low thermal conductivity (nearly 1 W/m·K), (3) supercooling of salt hydrates, (4) corrosion with metal containers, (5) different melting temperatures of salt hydrates and (6) high cost of some specific salts.

- **Eutectic PCMs** are composites of two or more components, which usually do not interact with each other to form a new chemical compound but at certain ratios, inhabit the crystallization process of one another resulting in a system having a lower melting point than either of the components. The eutectic mixtures can be further classified into organic-organic, organic-inorganic and inorganic-inorganic PCMs. Eutectic PCMs generally melt and freeze congruently and leave no chances of separation of components. Molten salt is one of the best candidates for middle to high temperature applications in the range of 120–1000°C [28]. For solar energy utilization, normally middle-high temperature PCMs are applied and the "middle-high" temperature means the range of 100–300°C. The molten salts offer a favorable density around 1880 kg/m^3, a high specific heat around 1.5 kJ/kg·K, a very low chemical reactivity, a low vapor pressure and a low cost about 0.4–0.9 USD/kg [29]. A popular commercial molten salt used in the solar power generation as PCM is called "solar salt", which is a mixture of $NaNO_3$ and KNO_3 mixing at a weight ratio of 6:4 with a freezing point of 221°C. Despite its relatively high melting point, the low cost makes it widely utilized in CSP applications. Another similar molten salt product is named "HTEC", which is a ternary salt mixture system of $NaNO_3$, KNO_3 and $NaNO_2$, and has a freezing point of 141°C. Different salt combination brings the melting point down but the lack of combination of optimum thermal properties limits its further applications.

- **Composite PCMs** are the mixtures prepared by dispersing the high thermal conductive particles like carbon, graphite or metals into PCMs. One should note that the embedded thermal conductive materials should be compatible with the base PCMs. Although the nano-composite has less ability to store heat, it has higher ability to conduct heat. For example, the graphite based nano-composite has 12 times higher thermal conductivity than that of pure stearic acid [30]. Graphite can be applied as thermal promoters in various forms like graphite flakes (natural graphite), expanded natural graphite or the expanded graphite powder (50–500 nm). Expanded graphene is one of the most suitable PCM support materials due to its extraordinary thermal conductivity. The dispersion of expanded graphene to binary nitrate salts consisting of $NaNO_3$ and KNO_3 (6:4) by aqueous solution method adopting ultrasonic and the 2% integration enhanced the thermal conductivity to 4.9 W/m·K but reduced the latent heat by 11% [27]. It is also reported that the use of expanded graphene in molten salts can prevent the liquid leakage after the melting [31]. Different from expanded graphene, a highly conductive additive expanded natural graphite treated with sulfuric acid was introduced into the binary salt, $KNO_3/NaNO_3$ nitrate mixture and the additive establishes effective heat transfer matrix for more efficient heat transfer. The results showed that the thermal conductivity has been improved and the highest effective thermal conductivity is about 50.8 W/m·K, almost 110 times larger than the thermal conductivity of the salt powder. A slight decrease of latent heat was observed from the measurements with no obvious variation in the phase change temperature [32]. Another way to enhance the thermal conductivity is to add chloride as addictive into the nitrate salt composite by statical mixing method. It was found that an addition of 5% chlorides into KNO_3-$NaNO_3$-$NaNO_2$ composite increased the thermal conductivity, thermal stability with an higher operating temperature from 500 to 550°C. Lower freezing point was obtained and the loss of nitrite content was observed [33]. Those enhanced composite PCMs with enhanced thermal performance and stability can be used to create compact thermal energy storage systems when the space is limited. Not only different nanostructures but also different types of nanoparticles can be applied as the thermal conductivity promoters, such as, the carbon-based nanostructures, metals, metal oxides and silver nanowires. A review of the current experimental studies on variations in thermo-physical properties of PCMs due to the dispersion of nanoparticles is performed in the reference [30].

- **Microencapsulated PCMs (MEPCMs)** can be described as particles that contain core PCMs surrounded by a coating or a shell and have diameters in the scale of micrometers. The microencapsulated PCMs usually have required morphologies, uniform diameters, shell mechanical strengths, penetration abilities and thermal stabilities. Pouches, tubes, spheres, panels or other receptacles containing MEPCM can directly act as heat exchangers. They can be incorporated into the building materials for thermal energy storage. The shell can hold the liquid PCM inside and prevent changes in its composition. The encapsulation not only increases the contact surface area for heat transfer but also adds the mechanical stability with the rigid shell. Common encapsulation shell materials include urea-formaldehyde (UF) resin, melamine-formaldehyde (MF) resin and polyurethanes (PU). Specialized techniques to prepare the encapsulation with a polymer cover and a PCM core include coacervation, suspension polymerization, emulsion polymerization, polycondensation and polyaddition. The MEPCMs are widely applied into the building materials and are able to retain or improve the building structural performance, as well as the energy performance (**Figure 3**).

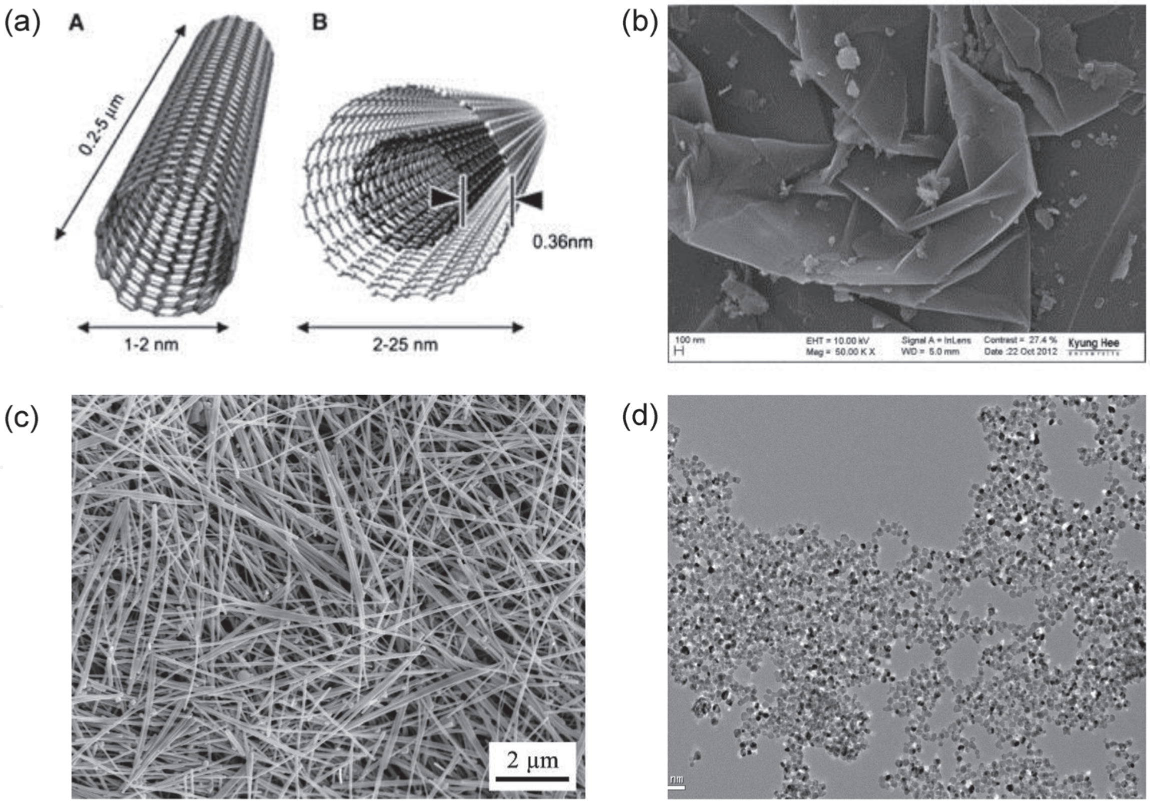

Figure 3.
Common applied thermal enhancement promoters: (a) carbon nanotubes/nanofibers [30], (b) graphite/graphene flakes [34], (c) metal nanoparticles (silver nanowires) [35], (d) metal oxide nanoparticles (γ-Al_2O_3) *[36].*

2.2.2 Heat transfer enhancement of PCMs

Although the usage of PCMs is attracting because of its high energy storage density, most PCMs have a low thermal conductivity (~0.5 W/m·K), which restrains the heat transfer rate during charging and discharging processes. Except the enhancement approaches by dispersing thermal enhancement promoters to form composite PCMs as introduced above, there are also other methods developed for heat transfer enhancement, such as adding metal fins to increase the heat transfer area or embedding metal fins (foam), using multiple PCMs, heat pipes, or manipulating the designs of the latent heat storage system to increase the natural convection heat transfer intensity, as shown in **Figure 4**.

- **Metal fins and extended surfaces** can effectively increase the contact area and enhance the heat conduction between the heat source and the PCMs. Commonly applied fin materials are steel (50.2 W/m·K), aluminum (205 W/m·K), copper (385 W/m·K) or graphite foil (140 W/m·K in x-y direction) [24]. Graphite foil is suitable for high temperature applications and has many advantages like high thermal conductivity, low density, good corrosion resistance against nitrate salts and nitrite at high temperatures. It occupies less volume for the same performance compared with steel fins. Aluminum is suitable for low temperature applications below 400°C and does not show corrosion effect when contacted with galvanized steel pipes. The introduction of fins into the PCM changes the PCM interior structure and hence affects the natural convection in the liquid phase of PCM during melting [37, 38].

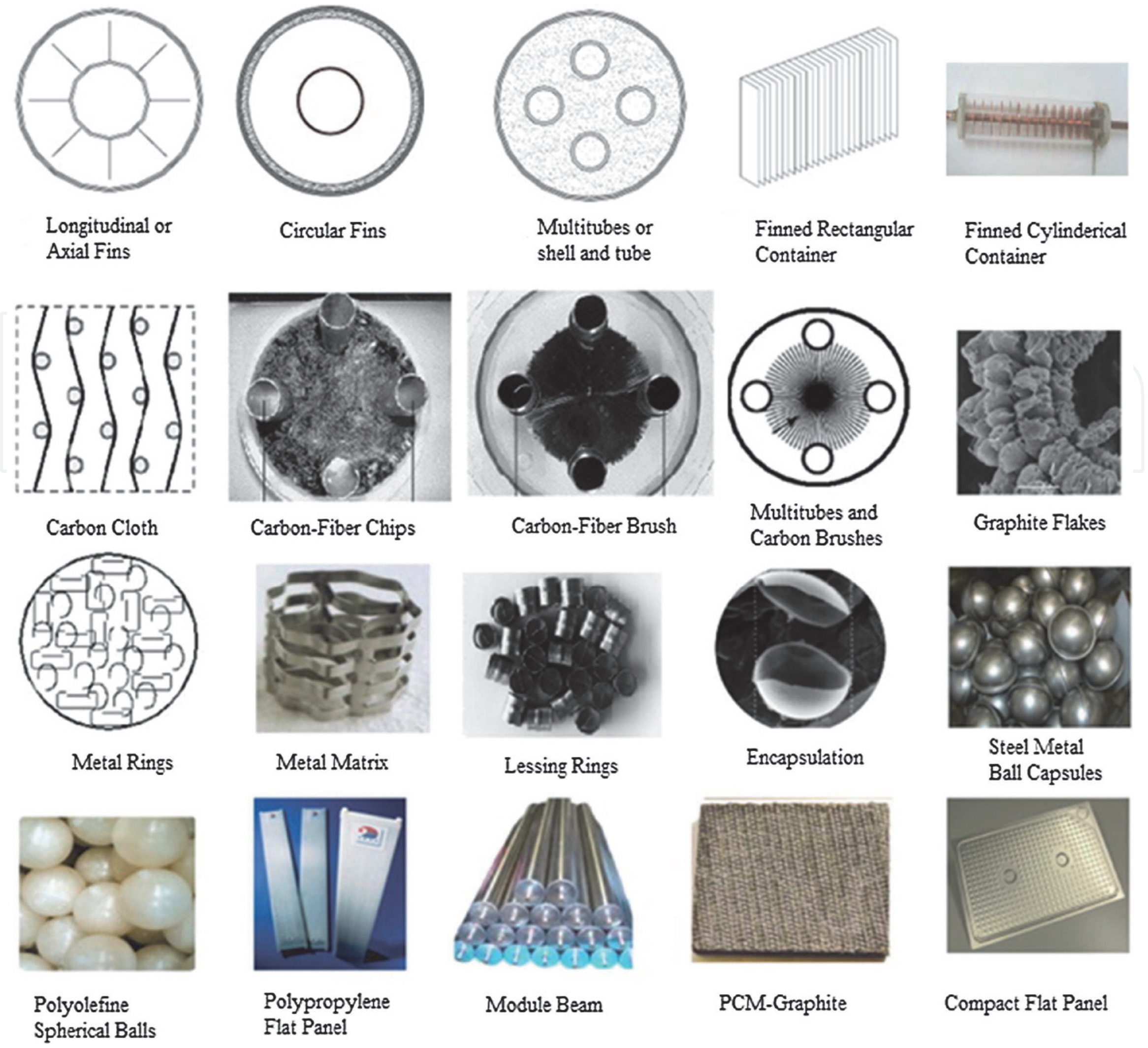

Figure 4.
Heat transfer enhancement techniques used in LHS systems [25].

- **Embedded porous matrices** made of copper, aluminum or a naturally porous material like graphite, metal foam can be embedded into interior PCM to enhance the heat transfer. The integration of metal foam helps the distribution of heat evenly into the PCM and is able to greatly enhance the PCM melting rate [24], even achieving as high as 41.2% enhancement on the melting process in a comparison with a pure PCM system [39]. One should note that the performance improvement with metal foam depends on the structure porosity and thermal conductivity.

- **Heat pipe** has a high thermal conductivity and it can be added to PCMs to increase the performance of the latent heat storage system. It serves as a thermal channel between the HTF and the PCMs. Within a heat pipe, there exist two regions, i.e., evaporation and condensation, and the working fluid like mercury evaporates and condensates for heat exchange. Metal fins can also be integrated with a heat pipe to further reduce the thermal resistance and a corresponding simulation showed that the addition of fins on a heat pipe leads to a threefold increase in the heat storage during the first 3 h of charging and a 79% increase in energy discharged within the first 3 h of releasing [40].

2.2.3 Pros and cons of latent heat storage

Latent heat storage with PCMs has a large latent heat of fusion so that it can store more amount of heat than sensible heat storage. This large difference gives PCMs the advantage of a high energy storage density, which reduces the volume of TES vessel and the outer wall surface area, and minimizes the heat loss. Compared to the sensible heat storage, the discharging process of the latent heat storage can maintain the temperature constant and make the contacting medium like HTF or the adjacent space temperature stable. However, the main drawback of the latent heat storage is the low thermal conductivity of PCMs. Moreover, the heat transfer design and media selection are more difficult, and the experience with low temperature PCMs like inorganic salts has shown that the performance of the materials can degrade after moderate number of freezing-melting cycles.

2.3 Thermochemical heat storage

Different from sensible heat storage systems and latent heat storage systems, a thermochemical heat storage system uses reversible endothermic/exothermic reactions to absorb, store and release energy between solar heat and chemical reactants. As depicted in **Figure 5**, during the charging process, heat is absorbed to dissociate material A, resulting in the products B and C. This reaction is endothermic and the amount of thermochemical heat stored is determined by the reaction enthalpy. It can be calculated by:

$$Q_{chem} = n_A \Delta H_r \tag{3}$$

where n_A is the mol number of A and H_r is the enthalpy of the endothermic reaction. During the discharging process, the products from the endothermic reaction, i.e., B and C, are mixed together at certain temperature and pressure conditions to reform the initial material A. This reaction is exothermic and the regenerated heat can be converted into electricity or used for other thermal powered systems.

To develop a thermochemical heat storage system, the first consideration is the selection of the reversible reaction and to characterize its operating temperature and pressure, the reaction rate, the reversibility and the kinetic properties, etc. For a high temperature energy storage, for instance, the endothermic reaction for the heat charging process should occur at temperatures below 1000°C to reduce the material restriction. The exothermic reaction, on the other hand, should be able to release heat at temperatures higher than 500°C [41]. Two parameters are usually used to assess the reactions from the thermodynamic perspective [42]. The first parameter is the turning temperature T^*. For a reversible reaction at a given

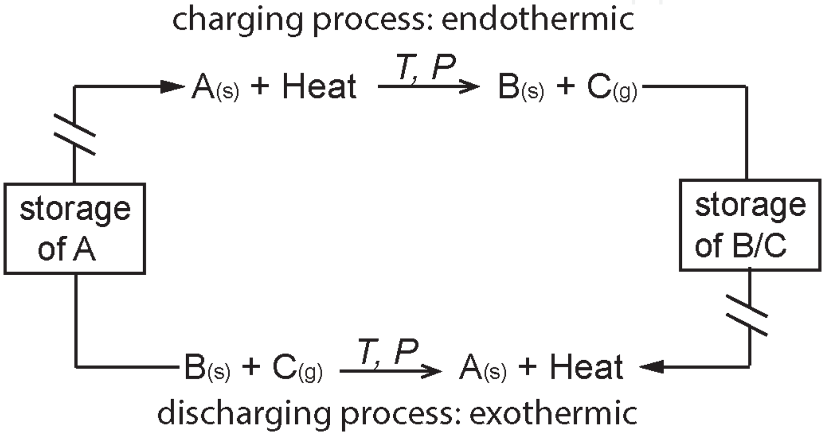

Figure 5.
Schematic of a thermochemical heat storage system.

pressure p, T^* is the temperature at which forward and reverse reactions are thermodynamically equilibrium. It can be approximated as

$$T^* = \frac{\Delta H_r(T^*, p)}{\Delta S_r(T^*, p)}, \tag{4}$$

where ΔH_r and ΔS_r are the reaction enthalpy and entropy at pressure p and temperature T^*. The other parameter is the ratio of the maximum recovery work to the actual recovery work, namely the maximum work recovery efficiency η_{max}. The value of η_{max} equals to 1 when the process is completely reversible. In the presence of irreversibility of a process, η_{max} is less than 1 due to the entropy generation and cannot be used for work. In order to achieve the maximum work, it is hence required that both endothermic and exothermic reactions should be completely reversible.

2.3.1 Reactions for thermochemical heat storage

A large number of reactions have been tested under the laboratory scale to determine their feasibility as thermochemical storage materials. These reactions can be classified according to their reaction family, namely carbonate system, hydroxide system, redox system, metallic hydride system, ammonia system and perovskite oxide system [43, 44].

- **Carbonate system** is operated by the decarbonation reaction of carbonate. The reaction can be expressed as

$$MCO_{3(s)} + \Delta H_r \rightleftharpoons MO_{(s)} + CO_{2(g)}. \tag{5}$$

In carbonate systems, chemical reactions are usually from inorganic oxide/carbon dioxide because of their high chemical reaction heat. These reactions generally occur at a temperature higher than 450°C. Many inorganic oxides can be used as thermal energy storage materials in carbonate systems [45]. Most attention is drawn on the calcium oxide (CaO)/carbon dioxide (CO_2) reaction for chemical reaction heat storage, especially for solar thermal energy storage [46]. Kyaw et al. [47, 48] carried out a series of investigations on the process of CaO/CO_2 reaction for chemical reaction heat storage. They listed the characteristics of this system such as high energy storage density, high working temperature, high reversibility, nontoxic process and low cost. More recently, Ortiz et al. [49] reported a study based on the CaO/CO_2 reaction for concentrated solar power plants. It is found that high overall efficiencies can be achieved by integrating the CaO/CO_2 reaction into concentrating solar power plants.

- **Hydroxide system** relies on the heat consumption and release when the reactant contacts with water. The universal reaction can be described as

$$M(OH)_{2(s)} + \Delta H_r \rightleftharpoons MO_{(s)} + H_2O_{(g)}. \tag{6}$$

This reaction usually occurs at moderate temperatures ranging from 250 to 450°C [43]. Using this reaction for thermal energy storage was first proposed by Ervin [50]. He successfully completed 290 reaction cycles with an average conversion rate of 95%. Criado et al. [51] analyzed the CaO/$Ca(OH)_2$ system on its reversibility and cyclicity. The author claimed that it is one of the best candidates for thermal energy storage. Brown et al. [52] discussed the feasibility of a thermochemical heat storage system using CaO/$Ca(OH)_2$ reaction from a technic-economic perspective.

Schaube et al. [53] experimentally explored this system on a fixed bed reactor and completed 25 cycles without reversibility loss.

- **Redox system** makes use of oxidation and decomposition reactions of oxide/peroxide for heat converting. The general reaction is

$$M_xO_{y(\mathrm{s})} + \Delta H_r \rightleftharpoons xM_{(\mathrm{s})} + y/2O_2. \tag{7}$$

These reactions occur at temperatures within 400–1000°C [43]. A couple of oxide/peroxide pairs include Co_3O_4/CoO, MnO_2/Mn_2O_3, CuO/Cu_2O, Fe_2O_3/FeO, Mn_3O_4/MnO and V_2O_5/VO_2 have been studies by Wong et al. [54]. Among the reactions suitable for thermochemical heat storage system, the Co_3O_4/CoO pair is considered as the most promising candidate due to its high reaction enthalpy, high reaction temperature and reversibility [43].

- **Metallic hydride system** is based on the reversible reaction between metals and hydrogen under certain conditions. For thermal energy storage process, the metallic hydride is thermally dehydrogenated and expressed as

$$MH_{y(\mathrm{s})} + \Delta H_r \rightleftharpoons M + n/2H_2. \tag{8}$$

The reversible metallic hydride reactions can be used in many industrial applications such as hydrogen storage [55], heat pumps [56], thermal energy storage [55], etc. The two metallic hydrides which have been intensively investigated for the solar thermal energy storage are magnesium hydride (MgH_2) and calcium hydride (CaH_2). Magnesium hydride reaction occurs at temperatures from 250 to 500°C and has a high energy storage density [47]. Attempts have also been extended by doping a third metal powder into Mg powder to form a Mg-based ternary hydride for thermal energy storage. It has been proved that the chemical reaction rate and cyclicity can be improved by mixing the metals such as Ni, Fe, Co, Na, etc. [57, 58].

- **Ammonia system** here refers to the dissociation and synthesis cycle of ammonia (NH_3) and the process has been known for hundred years. The reaction is

$$2NH_{3(g)} + \Delta H_r \rightleftharpoons N_{2(g)} + 3H_{2(g)}. \tag{9}$$

The reaction occurs at temperatures of 400–700°C. It was first considered for thermochemical heat storage by Carden [59] and Williams [42]. It is worth to note that catalysts should be applied for both forward and reverse reactions which increase the complexity of the system.

- **Perovskite oxide system** is a class of materials with similar crystal structure which can be generically expressed as ABO_3. The structure of perovskite is reviewed by Borowski [60]. Owing to the nature of its structure, perovskite oxides allow reversible accumulation and release of oxygen at high temperature with limited phase transition between different crystal structures [44, 61]. A general form of the reaction is given as

$$ABO_3 + \Delta H_r \rightleftharpoons ABO_{3-\delta} + \delta/2O_2. \tag{10}$$

The crystal structure facilitates the flexibility in replacement of the cations, i.e., A and B in the oxide. A variety of compounds have been synthesized and analyzed for thermochemical heat storage. Babiniec et al. [62] synthesized $La_xSr_{1-x}Co_yM_{1-y}O_{3-\delta}$ (M = Mn, Fe) materials for high temperature thermochemical energy storage owing to its good reaction reversibility. Albrecht et al. [63] evaluated the thermochemical energy storage system with the perovskite strontium-doped calcium manganite ($Ca_{0.9}Sr_{0.1}MnO_{3-\delta}$) in terms of specific storage and overall solar-to-electric efficiency. More recently, Gokon et al. [61] examined $La_xSr_{1-x}(Mn, Fe, Co)O_{3-\delta}$ and $Ba_ySr_{1-y}CoO_{3-\delta}$ redox powers in terms of reactivity and repeatability. They found that $Ba_{0.3}Sr_{0.7}CoO_{3-\delta}$ and $Ba_{0.7}Sr_{0.3}CoO_{3-\delta}$ powders were suitable thermochemical storage materials operating at above 600°C.

2.3.2 Pros and cons of thermochemical heat storage

Thermochemical heat storage system is unique and suitable for solar energy storage owing to its advantages: high volumetric storage density, low volume requirement, long energy preservation duration periods with limited heat loss, low storage temperature (ambient temperature) and unlimited transport distance. However, it also has some issues to be tackled, such as poor reactivity and reversibility of reactions, harsh reaction conditions, toxic and corrosive products from reactions, etc. Currently, most studies are conducted at laboratory scales. Large-scale tests are needed to verify the feasibility and the durability for long-term thermal energy storage. Furthermore, the criteria of material selections for thermochemical heat storage should be established.

3. Thermal energy storage for solar energy systems

Solar energy systems are found in many applications with a wide range of scales for different sectors, such as CSP, space heating for buildings, and hot water supply for houses. One major drawback of solar energy is its intermittence. To overcome this issue, one solution is to use backup energy sources or hybridisation of different energy sources, such as using gas as the backup solution for heating and electric grid for electricity. Another solution is to use a thermal energy storage system to store heat during sunshine periods and release it whenever demand is needed while solar irradiance is insufficient to cover the demand.

Thermal energy storage in solar energy systems usually has the following functions [5]:

- Mitigating short fluctuation of solar energy. Variations in solar irradiance can cause rapid fluctuations in energy generation (i.e., heat or power). These strong fluctuations influence not only the availability of energy, but also the stability of the power grid, heating network or gas-supplying systems. Integrating thermal energy storage units into the solar energy system can increase the thermal inertia, smooth the fluctuations and help the system continue supplying energy during short cloudy periods, thus increasing the system stability.

- Matching the energy generation and demand. Peak energy demand may not coincide with the peak solar insolation. Thermal energy storage can improve dispatchability of a solar energy system by storing heat during off-peak hours and discharging it during peak hours of demand. This helps match the energy generation and demand, and also increases the profitability as peak-hour electricity tariffs are higher. The duration of this energy-shifting mechanism can be within a day, a week, or seasons.

- Extending the energy delivery period. Solar energy is only available during some hours of the day and thermal energy storage can extend the energy delivery period to hours when no sun is available. If the thermal energy storage unit is large enough, the whole solar energy system, for either power generation or heating/cooling, can operate for 24 h.

In practical applications, solar energy is mainly used for delivering either electricity or heating/cooling [64]. Depending on applications, there are a wide range of technologies used for thermal energy storage. In CSP plants, thermal energy storage systems operate at relatively high temperatures as the thermal efficiency of power plants is proportional to the temperature. In solar heating/cooling systems, such as space heating in buildings, solar hot water supply, and solar absorption refrigeration systems, low-temperature thermal energy storage is often involved.

3.1 Thermal energy storage for solar power systems

One of the most important applications of solar energy is to generate electricity, which can be realized by either solar photovoltaic (PV) panels or solar-thermal driven power cycles [65]. To mitigate the intermittence of solar energy, PV systems usually use batteries to store energy in terms of electricity, while solar-thermal driven power cycles often store energy in terms of heat via thermal energy storage technologies. Comparisons between different energy storage technologies have shown that the thermal storage option is more cost-competitive than the battery option for large-scale energy storage [24, 66].

The most commonly known solar-thermal driven power technologies are CSP systems, in which high-temperature thermal energy storage is often involved [67, 68]. Another type is small-scale solar power systems driven by low-temperature solar heat [69], which is typically categorized as distributed solar power systems and where low-temperature thermal energy storage technologies are needed. Whatever the solar-thermal driven power cycle technologies are, the main processes in such systems include three steps: collection, storage and conversion, as shown in **Figure 6**. Solar energy is first collected via concentrated or non-concentrated solar collectors in terms of thermal energy, then transferred to and stored in thermal energy storage units through a heat transfer loop connecting the collectors and the storage units, and the thermal energy, either stored in the thermal energy storage units or collected directly from the solar collectors, is finally converted into electricity through heat-to-power conversion technologies, e.g., Rankine cycles.

3.1.1 Material selections

About half of the CSP plants in operation are integrated with a thermal energy storage system. There is an increase in the use of thermal energy storage for CSP

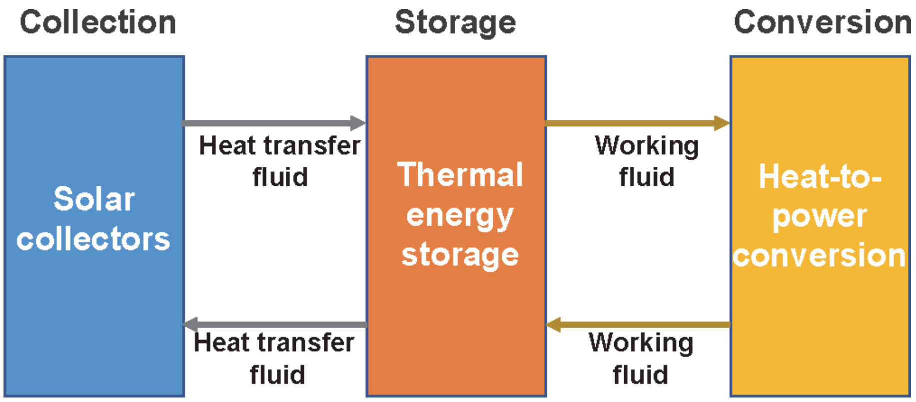

Figure 6.
The main processes of solar-thermal driven power technologies.

plants under construction and planned (>70%) [70]. The trends indicate the maturity and economic competitiveness of installing a thermal energy storage system in CSP plants. The most commonly used thermal energy storage materials in CSP applications include molten salt, water/steam, liquid sodium, thermal oil, concrete and rocks. Molten salt is the most widespread storage material in CSP commercial applications, due to its features of excellent thermal stability at high temperatures, low vapor pressure, low viscosity, non-flammability and non-toxicity [70]. **Table 4** lists the summaries of the world's operational CSP plants integrated with thermal energy storage. The molten salt fluids commonly used are nitrate mixtures with a weight composition of 60 wt% $NaNO_3$ and 40 wt% KNO_3, also called Solar Salt. The storage temperature of the molten salts in these commercial CSP plants are typically around 400°C and can go up to around 550°C. Steam is also used as the storage material for several CSP plants, such as Khi Solar One, Puerto Errado 2 and eLLO. The steam storage temperatures in these plants are normally around 270°C - 285°C. In Jemalong Solar Thermal Station in Australia, liquid sodium at 560°C is used as the storage material. Thermal oils have also been used in Dahan Power Plant in China and in many researches [67]. Apart from these fluid-type thermal energy storage materials, solid materials (concrete and rocks) are another option for thermal energy storage [71, 72]. Solid materials generally have a wide range of working temperatures (200–1200°C), with high thermal conductivities (from 1 W/m·K to 40 W/m·K) and relatively low costs (0.05–5 $/kg) [70]. Examples of such CSP plants using solid storage materials include Airlight Energy Ait-Baha Pilot Plant in Morocco (packed-bed rocks for parabolic trough CSP) and Jüich Solar Tower in Germany (ceramics for power tower CSP). In small-scale distributed solar power systems, such as solar-driven ORC systems [69, 73], low-temperature thermal energy storage materials can be used. For example, water, organic aliphatic compounds, inorganic hydrated-salt PCMs and thermal oils have been investigated for solar combined heat and power applications [74].

3.1.2 System integrations

Thermal energy storage materials are usually stored in tanks to form plant-scale storage subsystems for the CSP systems. Based on the motion state of storage materials during charging and discharging, thermal energy storage system can be categorized into active and passive systems. In active storage systems, the storage medium itself flows through a heat exchanger to absorb (charge) or release (discharge) heat by forced convection, while in passive storage systems, the storage medium stays stationary and is heated (charged) or cooled (discharged) by a HTF.

Active storage systems can be classified into direct and indirect systems. In active direct storage system, storage medium also has the function of transferring heat as a HTF. The use of molten salts or steam as a HTF or storage materials at the same time eliminates the need for an expensive heat exchanger. The cost of thermal energy storage system can be reduced and the system performance can be improved. One of the active direct systems is the two-tank direct storage system, which consists of a hot and a cold storage tank, as shown in **Figure 7(a)**. In such systems, molten salt or thermal oil collects heat from the solar field and the high-temperature fluid is directly stored in the hot storage tank for later uses, i.e., steam generation, in cloudy periods or nights. The cooled HTF (also the storage medium) after the steam generator is pumped into the cold storage tank. The two-tank direct storage concept is often used in tower CSP plants where molten salt is used as the storage medium and HTF [75], as solar tower can achieve higher temperatures, as shown in **Table 4**.

Another type of active direct storage system uses water/steam as the HTF and storage medium, as shown in **Figure 7(b)**. This system is also named as direct steam

CSP plant	**Technology**	**Turbine capacity**	**Heat transfer fluid**	**Storage material**	**Storage capacity**	**Storage type**	**Inlet–outlet temperature**
Xina Solar One (South Africa)	Parabolic Trough	100 MW	Thermal oil	Molten salt	5 h	Two-tank indirect	N/A–395°C
Termosol 2 (Spain)	Parabolic Trough	50 MW	Thermal oil	Molten salt	9 h	Two-tank indirect	293–393°C
Solana Generating Station	Parabolic Trough	250 MW	Therminol VP-1	Molten salt	6 h	Two-tank indirect	293–393°C
NOOR II (Morocco)	Parabolic Trough	200 MW	Thermal oil	Molten salt	7 h	Two-tank indirect	293–393°C
Manchasol-2 (Spain)	Parabolic Trough	50 MW	Diphenyl/diphenyl oxide	Molten salt	7.5 h	Two-tank indirect	293–393°C
Aste 1B (Spain)	Parabolic Trough	50 MW	Dowtherm A	Molten salt	8 h	Two-tank indirect	293–393°C
Bokpoort (South Africa)	Parabolic Trough	55 MW	Dowtherm A	Molten salt	9.3 h	Two-tank indirect	293–393°C
Kathu Solar Park (South Africa)	Parabolic Trough	100 MW	Thermal oil	Molten salt	4.5 h	Two-tank indirect	293–393°C
Ashalim (Israel)	Parabolic Trough	110 MW	N/A	Molten salt	4.5 h	Two-tank indirect	N/A
Archimede (Italy)	Parabolic Trough	5 MW	Molten salt	Molten salt	8 h	Two-tank direct	290–550°C
SUPCON Delingha 50 MW Tower (China)	Power Tower	50 MW	Molten salt	Molten salt	7 h	Two-tank direct	N/A
Shouhang Dunhuang 100 MW Phase II (China)	Power Tower	100 MW	Molten salt	Molten salt	11 h	Two-tank direct	N/A
Qinghai Gonghe 50 MW CSP Plant (China)	Power Tower	50 MW	Molten salt	Molten salt	6 h	Two-tank direct	N/A
Gemasolar Thermosolar Plant (Spain)	Power Tower	19.9 MW	Molten salt	Molten salt	15 h	Two-tank direct	290–565°C
Greenway CSP Mersin Tower Plant (Turkey)	Power Tower	1.4 MW	Water	Molten salt	4 MWh	Single 3-pase tank	N/A
Airlight Energy Ait-Baha	Parabolic Trough	3 MW	Air at ambient pressure	Rocks	5 h	Packed-bed	270–570°C

CSP plant	Technology	Turbine capacity	Heat transfer fluid	Storage material	Storage capacity	Storage type	Inlet–outlet temperature
Pilot Plant (Morocco)							
Dahan Power Plant (China)	Power Tower	1 MW	Water	Saturated steam and oil	1 h	N/A	104–400°C
Khi Solar One (South Africa)	Power Tower	50 MW	Water/steam	Steam	2 h	Steam accumulators	N/A
Puerto Errado 2 Thermosolar Power Plant (Spain)	Linear Fresnel Reflector	30 MW	Water	Steam	0.5 h	Single-tank thermocline	140–270°C
eLLO Solar Thermal Project (France)	Linear Fresnel Reflector	9 MW	Water	Steam	4 h	Steam drum	190–285°C
Jülich Solar Tower (Germany)	Power Tower	1.5 MW	Air	Ceramic	1.5 h	N/A	N/A
Jemalong Solar Thermal Station (Australia)	Power Tower	1.1 MW	Liquid sodium	Liquid sodium	3 h	Two-tank direct	293–560°C

Table 4.
In-operation CSP plants with thermal energy storage [https://solarpaces.nrel.gov/by-status/operational].

generation (DSG) plant. The only commercial thermal energy storage technology for DSG plants is using steam accumulators, where steam is stored at a high pressure in accumulator tanks [75, 76].

The dominant thermal energy storage technologies in parabolic trough CSP plants are the active two-tank indirect storage systems, as shown in **Figure** 7(**c**). The list of commercial parabolic trough CSP plants and their thermal storage types are given in **Table 4**. The two-tank indirect system uses different mediums for heat transfer and storage [77]. During charging phase, the storage medium in the cold storage tank is pumped through a heat exchanger, heated by the hot HTF flowing from the solar field, and then stored in the hot storage tank. During discharging phase, the flow direction of the storage material is reversed to release heat to the HTF to generate steam for power generation. In two-tank indirect systems, the storage medium is typically molten salt, and the HTF is often thermal oil.

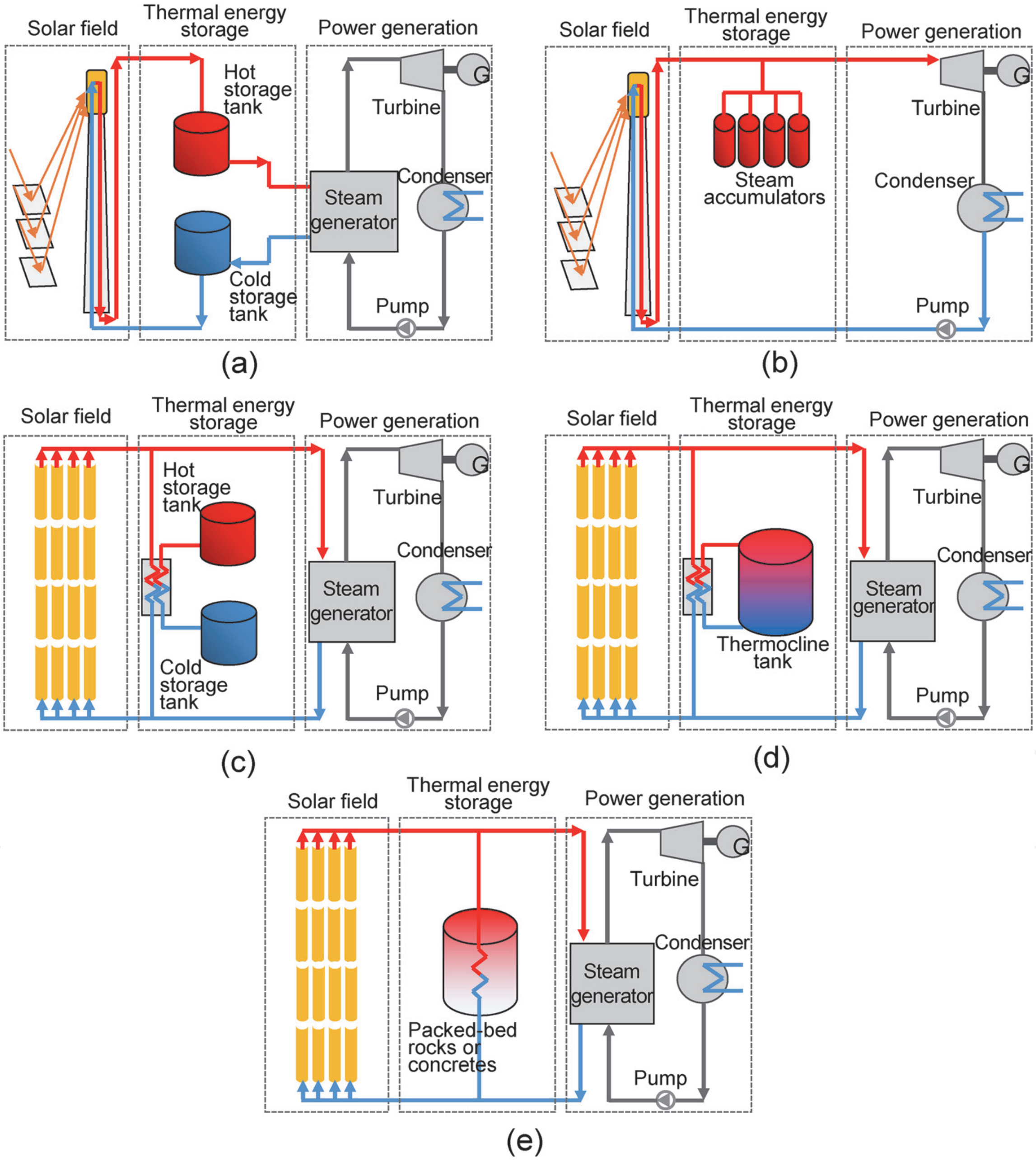

Figure 7.
Schematics of CSP systems integrated with different thermal energy storage technologies: (a) active two-tank direct storage system, (b) active direct steam storage system, (c) active two-tank indirect storage system, (d) active single-tank indirect storage system, (e) passive pack-bed rocks (or concrete, or castable ceramics) storage system. Note that although solar tower and parabolic trough collectors are illustrated here, other types of concentrated solar collectors (Linear Fresnel, dish) may also be used.

An alternative to two-tank indirect storage system is using a single tank (see **Figure 7(d)**) where hot fluid is stored at the top and the cold fluid is stored at the bottom by stratification. The zone between the hot and cold fluids is called the thermocline. A single tank system is about 35% cheaper than a two-tank system [11].

In passive storage system, solid materials are typically used as the thermal storage medium while a HTF passes through the storage medium to charge or discharge heat. Possible storage materials include concrete, castable ceramics, rocks, etc., while the HTF can be thermal oil or air. In the case of concrete, tubular heat exchangers are integrated with the concrete to enhance heat transfer rate. Rocks can be used in a packed bed after crushing to rough sizes of around 5 cm [70]. The hot fluid flows through the gaps of the packed rocks and heats the rocks during charging process, and the cold fluid flows through the gaps and absorbs heat from the hot rocks during discharging process. The typical system schematic is shown in **Figure 7(e)**.

3.2 Thermal energy storage for solar heating/cooling systems

Heating and cooling take a significant share of the total energy consumption in the world. For example, half of EU's primary energy is consumed for heating and cooling purposes. Currently, most of the heating and cooling demands are still met by fossil fuels, mainly natural gas. However, solar energy is starting to play an important role. In solar heating/cooling systems, solar energy is typically collected as low-temperature heat, for provisions of space heating, hot water, grain drying, etc. In hot seasons or hot regions, solar heat can be used to create cooling via thermally driven refrigerators, e.g., absorption chillers. Thermal energy storage is frequently involved in these solar heating/cooling systems, as it provides much more stable energy delivery capability and closes the gap between energy generation and demand.

3.2.1 Material selections

Water is regarded as a favorable storage medium for solar heating/cooling applications, due to its advantages of high specific heat, non-toxicity, low cost and easy availability. Therefore, water is the dominant material for space heating and hot water provisions. The capacity of the storage depends on the size of the water storage tanks, which could range from a few hundred liters to a few thousand cubic meters. In water tanks, thermal stratification can be formed due to the buoyancy effect, i.e., hotter water is lighter and gathered at the top while colder water drops at the bottom. Thermocline is then formed between the hot and cold water layers, which in-turn minimizes water mixing and heat losses. Apart from using water tanks, water is also used for large-scale seasonal thermal energy storage in underground aquifers where sand mixed with water is the storage medium [78]. This is a low-cost thermal storage option as it only uses natural materials and no tanks are involved. The problem of this aquifer thermal energy storage is the high heat losses, as the system cannot be insulated. It is also possible to use water tanks for seasonal thermal energy storage, although the tank size has to be large and it is often fully or partially buried in the ground. Borehole thermal energy storage is another competitive option for seasonal storage of heat or cold. It uses ground (soil) as the storage medium [78]. Multiple boreholes are drilled in the ground to a certain depth and U-shape pipes are inserted in those boreholes to charge or discharge thermal energy. PCMs have attractive extensive attentions in recent years as an effective thermal energy storage medium and have been integrated in various devices and applications. In some work, PCMs are directly integrated with the solar collectors for space heating or drying purposes [79, 80]. In other work, they can be embedded in concretes of walls for buildings [81], to store heat from daytime for night use. Rock is a low-cost thermal energy storage material which usually uses air as the HTF. Packed-bed rock thermal energy storage has been widely used for greenhouse heating [79].

3.2.2 System integrations

Water tanks are widely installed in solar heating system, including those for distributed and centralized heating for residential, industrial and commercial applications. **Figure 8** shows a typical solar heating system for the provisions of domestic space heating and hot water. Solar radiation is absorbed in terms of heat by the solar collectors, e.g. evacuated tube collectors, flat-plate collectors, or hybrid photovoltaic-thermal collectors [65]. A circulating HTF loop is used to collect heat from the solar collectors and store it in the water tank when the fluid temperature from the collectors is higher than the water temperature in the tank. The demands of the space heating and hot water are met by circulating or drawing hot water from the tank. Unlike the two-tank thermal energy storage systems, only one tank is typically involved in these applications and the water temperature thus fluctuates depending on the balance between energy storage and usage. Sizing of the water tank as well as the solar collectors is important and depends on various factors, including local weather conditions (solar irradiance, wind speed, air temperature, etc.) and demands (types, quantities and shapes). Annual simulations are often needed to fully assess the potential of a solar heating system [82]. Although water is the most popular storage material in such systems, PCM-based thermal energy storage has also been explored more recently [83]. The system integration is similar to water-based systems, but the storage temperature can be more stable, and its energy capacity can be larger for the same volume.

Solar energy has not only a daily period but also a seasonal period. For some period of a year, solar thermal production exceeds the demand for heating or cooling, while in other periods the production is less than the demand. Seasonal thermal energy storage would be a solution to store heat at the time that is not needed and use is for the time that is required. The concept of seasonal thermal energy storage is illustrated in **Figure 9(a)**. The implementation of seasonal thermal energy storage is shown in **Figure 9(b)**, with borehole thermal energy storage as an example. In summer period, excess heat from the solar thermal collectors, process heat, or other heat sources are transferred to the ground via borehole heat exchangers, while in winter the stored heat is released from the ground by a heat transfer loop for heating purposes. There are other types of seasonal storage systems, mainly including aquifer storages, cavern storages, pit storages, seasonal water storages, water-gravel storages,

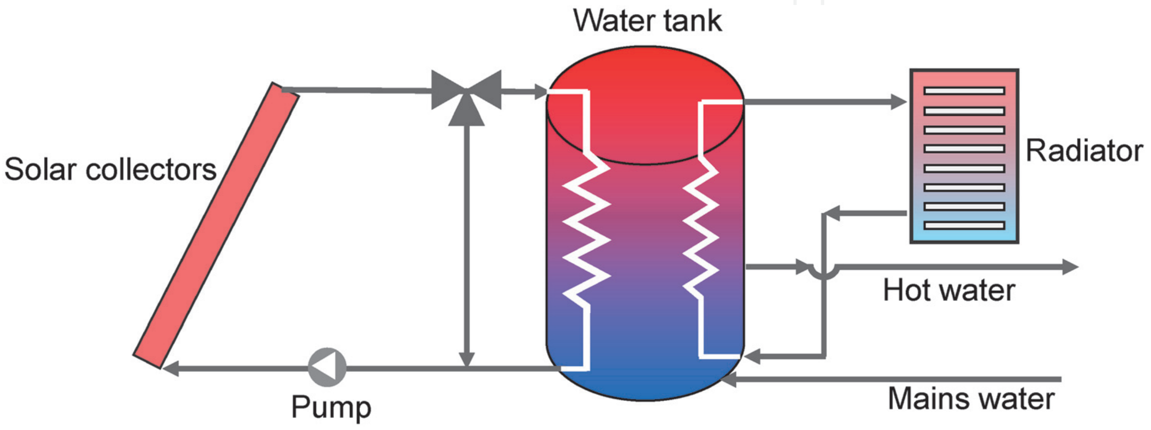

Figure 8.
Typical layout of a solar heating system for domestic space heating and hot water.

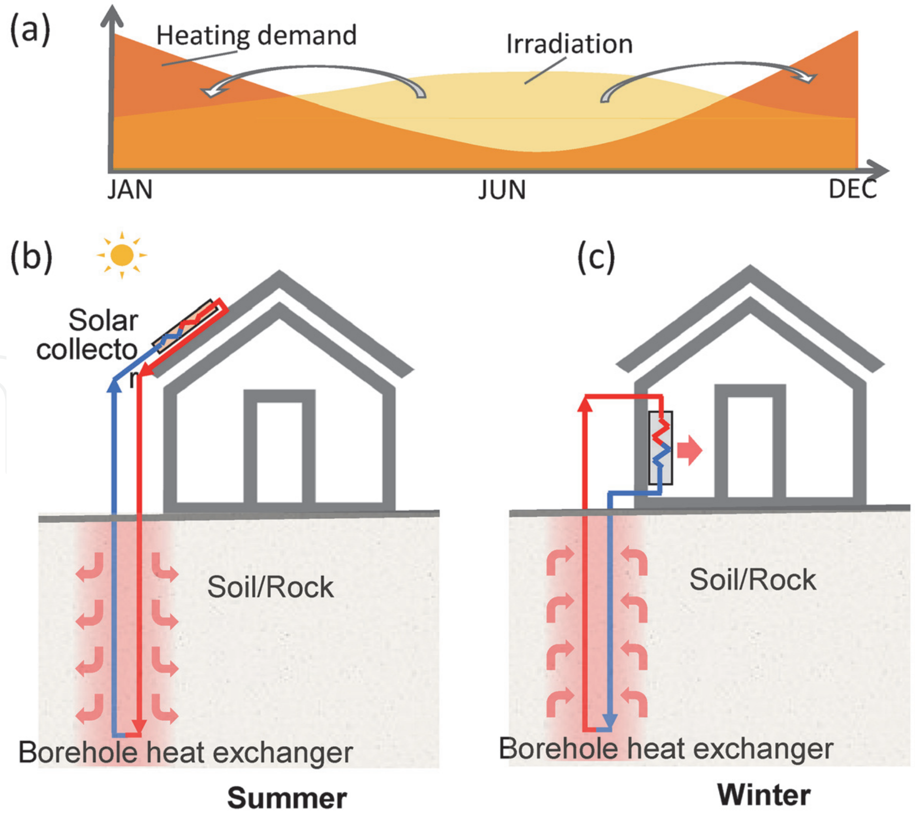

Figure 9.
Seasonal thermal energy storage based on borehole heat exchangers: (a) concept of seasonal thermal energy storage and (b) borehole thermal energy storage.

thermochemical storages, etc. [84]. The development of seasonal thermal energy storage is mainly motivated by the growing popularity of district heating [20]. Low energy and net-zero energy buildings are attracting increasing attention, through the incorporation of solar energy systems and thermal energy storage among others. Incorporating thermal energy storage into the building design, structure and facades have been explored to reach the above goals. These systems can be categorized into active and passive systems. In active systems, external mechanical driving systems are involved to transfer and distribute solar heat [85], such as an evacuated tube collector based space heating system, or a space cooling system based on solar-absorption refrigerators. In passive solar building systems, windows, walls and floors are designed to collect, store, reflect and distribute solar energy in the form of heat in the winter and reject heat in the summer. Thermal energy storage can be incorporated with these structures to enhance the energy efficiency. An example structure is given in **Figure 10(a)**, which is named as solar wall or Trombe wall [86]. The wall

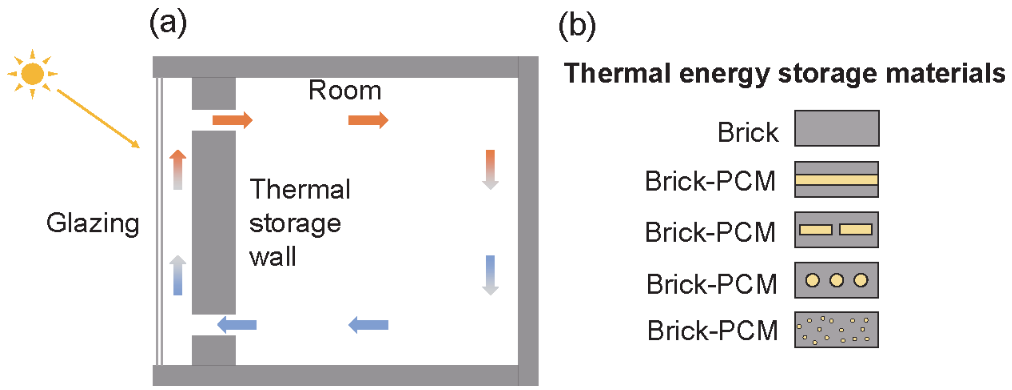

Figure 10.
Schematic of (a) a solar wall (Trombe wall), and (b) different thermal energy storage materials for solar wall.

with a high heat capacity is built on the winter sun side with a glass external layer and an air layer for thermal insulation. Sunlight passing through the glass is absorbed by the wall and stored for later uses at night. The stored heat then re-radiates in the far-infrared spectrum and trapped by the glass, and thus heats the inner side of the room. The materials used for storage could be bricks, stones, or bricks integrated with PCMs, as shown in **Figure 10(b)**.

4. Conclusions

This work reviewed some recent developments on the thermal energy storage technologies, where sensible, latent and thermochemical heat each offers a contribution to eliminate the mismatch between the energy supply and demand by different working principles. The thermal energy storage material categorization, long-term stability and compatibility with container materials, thermal performance analysis and thermal performance enhancement techniques were reviewed in detail. The sensible heat storage in solid or liquid is widely applied for thermal storage. Rock, sand and water are the typical storage mediums used in the solar energy systems from low to high temperatures due to their high specific heat, none-toxicity, low cost and easy availability. Molten salt in liquid is the most popular thermal energy storage material used in the medium and high temperature concentrated power plants for its excellent thermal stability, low cost and low viscosity. The main drawback of sensible heat storage is the temperature decrease during the discharging process. Latent heat storage with phase change materials is a popular energy storage technology today, as it brings higher storage density and nearly constant temperature. Several materials in organic, inorganic, eutectic and composite have been analyzed and identified. To overcome their low thermal conductivities, metal fins, embedded porous matrices, heat pipes and other heat transfer enhancement technologies have also been developed. The chemical storage technology is also a potential technology in terms of its high storage density and long energy preservation duration periods. Several reaction systems have been reviewed and discussed. However, it is much less developed than the sensible and latent heat ones for solar energy storage. Thermal energy storage provides a reliable technology for energy storage and security, but it also faces some barriers and needs to be further developed, such as material costs, thermal properties and stabilities, system integration and process parameters, especially for the latent and thermochemical storage systems.

Thermal energy storage for solar energy systems is then reviewed, focusing on the most common storage materials, components and their integrations with wider systems. In solar power systems, high-temperature thermal energy storage materials are widely used for concentrated solar power (CSP), including molten salt, water/steam, liquid sodium, thermal oil, concrete and rocks, etc. Molten salt remains as the dominant commercial storage option for CSP, while steam and concrete are also being demonstrated. Two-tank storage system is the main solution in CSP applications. In low-temperature solar power systems, water and low-temperature phase change materials (PCMs) are normally used and stored in tanks, which are integrated with low-temperature power cycles, such as organic Rankine cycles. These could be of interest to waste heat recovery and domestic applications. Compared to CSP systems, thermal energy storage in solar heating/cooling systems is mainly based on low-temperature materials, with water as the dominant storage material. Water tanks are widely used as a short-term storage option and typically coupled with solar thermal collectors for solar heating/cooling purposes. Long-term storage, i.e., seasonal storage, can be achieved by large water tanks or borehole thermal energy storage. The demand for seasonal thermal storage is mainly driven by district heating. Thermal energy storage can also be directly integrated into the building structures, e.g., walls, windows, and floors. In these systems, the storage medium is either the construction material itself or appropriately embedded/integrated with the construction materials. Although the development of thermal energy storage materials is very critical, further development of applications of more stable and efficient solar energy systems, system designs and integrations are equally important. Innovative technologies for thermal energy storage materials and solar energy systems are highly desirable.

Nomenclature

c_p	heat capacity of thermal storage material
H_r	enthalpy of the endothermic reaction
k	thermal conductivity of thermal storage material
L_h	latent heat of thermal storage material
m	mass of thermal storage material
Q_{chem}	amount of thermochemical heat stored
Q_{lat}	amount of latent heat stored
Q_{sen}	amount of sensible heat stored
S_r	entropy of the endothermic reaction
T_f	final temperature of thermal storage process
T_i	initial temperature of thermal storage process
T^*	temperature at thermodynamically equilibrium
V	volume of thermal storage material
α	melting fraction of PCM
ρ	density of thermal storage material

Abbreviations

CSP	concentrated solar plant
HTF	heat transfer fluid
MEPCM	microencapsulated PCM
PCM	phase change material
PU	polyurethanes
PV	photovoltaic
TES	thermal energy storage
UF	urea-formaldehyde

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