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Review on thermal energy storage and eutectic nitrate salt melting point

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Abstract. In solar concentrates, thermal energy (TES) storage has a significant function (CSP). This article will discuss the forms of TES and TES content, focusing on the material for latent heat storage. Sensitive heat storage, latent heat storage and chemical reaction thermal storage classes can divide TES into three classes. Among the thermophysical properties for CSP is the latent heat storage content, which is used by more researchers. Dividing latent heat storage material into material for the organic, inorganic and eutectic phases change material (PCM). There are an advantage and downside to any form of storage material. Thermal stability at high temperature and low cost, however the specific heat capacity of the sensible heat storage material is very low compared to the latent heat storage materials..

Keywords: Thermal Energy Storage; Phase Change Material; Melting Point.

1. Introduction

Different renewable energy sources have been established since the leakage of toxic gas into the atmosphere and the death of fossil fuels have led. Unpredictable quantities of energy are required with the current population growth and global development. It has been established that solar energy is the highest abundance of renewable sources in the pursuit of alternative clean sources. Sun is providing us with 120 000 TW of energy per hour[1]. Several research studies have been performed with the aim of recognizing solar potential impacts at areas with high solar radiation such as North Africa, Southern Europe, the Middle East and South Asia; The Andosal solar energy facility, regarded as the largest CSP, provides 181.1 million kW/h of electricity up to 7.5 hours after sunset in Spain [2].



Two well-known technologies that use solar power to produce electricity are photovoltaic (PV) and CSP. A semiconductor unit turns sunlight into direct current in PV. The CSP plant consists of three main blocs that are the solar receptor, fluid transport system and power block for concentration and high temperature. The sun ray concentrates and coincides with a solar collecting field thermal fluid (HTF) which is subsequently deposited in a thermal storage tank and transported to the electricity generation block. CSP-TES plant is shown in Figure 1 [3]. HTF can also be stored as a TES unit to be used when sunlight is not available. The use of HTF as a TES substantially decreases fossil-supported fuel consumption, leading to a decrease in power costs [4]. PV is more suitable for low power demand at an affordable price. While CSP is more cost effective which is preferred to be used on a larger scale [5].

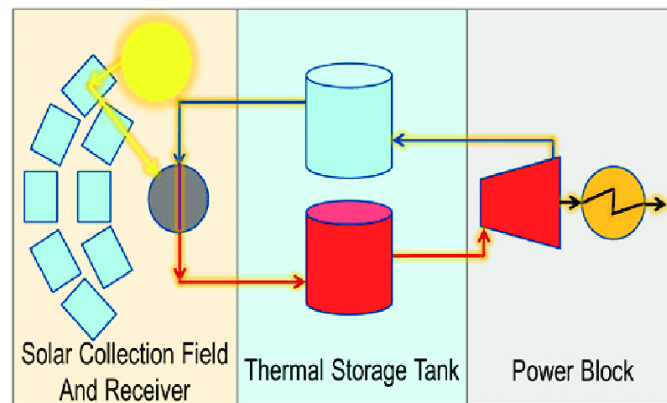


Figure 1. CSP-TES plant.

A big limitation of solar collection is that it is only available in the light of the sun. This is possible with HTF as TES. Thus, TES is an essential part of the CSP plant. For future CSP technologies, the architecture of the TES system plays a crucial role. When choosing TES such as cost efficiency, high boiling point, high chemical stability, low melting point and good thermophysical properties, few parameters should be considered. The decrease in the cost of TES decreases CSP significantly. Improved CSP quality at the boiling point. TES that is high temperature chemical stable is important as they are less corrosive. TES is important. The smaller the TES melting point is the smaller the amount of heat energy is required to keep the HTF going, thereby reducing costs [4, 6, 7].

The choice of TES material has a vital part to be played by CSP technology, and therefore in this paper, the analysis will be discussed of different types of TES material for CSP applications.

2. Thermal energy storage

Three types of sensible heat storage, latent heat storage and chemical heat storage can be categorized as a TES system. The description of TES is shown in Figure 2.

2.1 Sensible Heat Storage

In sensible heat storage (SHS) is stored by increasing the temperature of a solid or fluid thermal energy. Sensible heat can express thermal energy stored as [8]

$$Q = mC_p\Delta T \quad (1)$$

Mass (kg) is represented by m , C_p is the specific heat capacity ($\text{kJkg}^{-1}\text{K}^{-1}$) and ΔT is the temperature raised during the charging process. Table 1 shows some of the solid and liquid materials used as sensible heat storage.

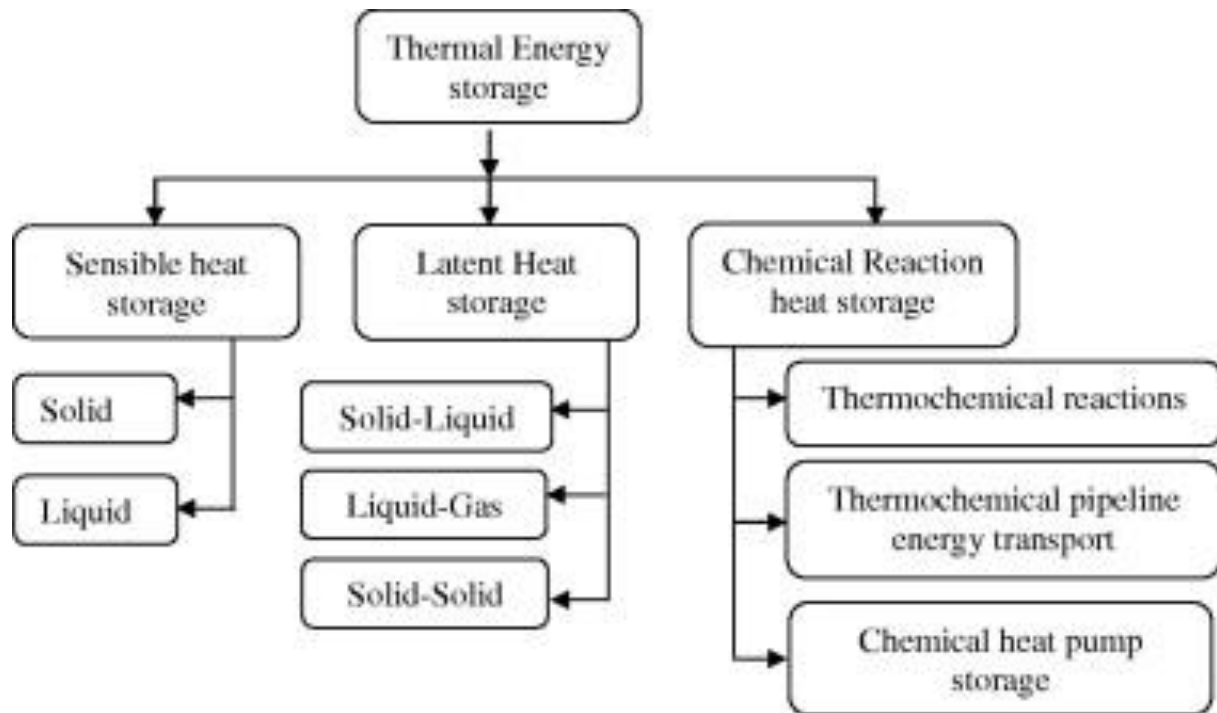


Figure 2. TES.

Table 1. List of solid and liquid materials.

| Medium | Fluid type | Temperature range (°C) | Density (kg/m ³) | Specific heat (J/kgK) |
|--------------------------|----------------|------------------------|------------------------------|-----------------------|
| Rock | - | 20 | 2560 | 879 |
| Concrete | - | 20 | 1900-2300 | 880 |
| Castable ceramic | - | - | 3500 | 866 |
| Water | - | 0-100 | 1000 | 4190 |
| Engine oil | Oil | Up to 160 | 867 | 2200 |
| Caloria HT43 | Oil | 12-260 | 888 | 1880 |
| Vegetable oil | Oil | Up to 295 | 802 | 2509 |
| Diphenyl oxide/ biphenyl | Thermal oil | 12- 257 | 897 | 1630 |
| Ethanol | Organic Liquid | Up to 78 | 790 | 2400 |
| Propanol | Organic Liquid | Up to 97 | 800 | 2500 |

The heat storage sensitive increases with a higher storage medium temperature. Thus it is advisable that the medium has long-term thermal cycling stability, compatibility with containments, high specific heat capacity and above all low costs. Sensible heat storage can be defined as the storage of liquid media or solid media by way of thermal storage media.

2.1.1 Liquid Media Storage

The liquids in heat storage are abundant and efficient economically. Below are the advantages and drawbacks of some of the media chosen.

Water is one of the best storage media at low temperatures. It has more precise heat than other materials and is available cheaply and widely. Because of its high vapor pressure, however, expensive insulation and containment resistant pressure are required for applications at high temperatures. A large variety of temperatures can use water, say 25-90°C. Water stores 250 kJ/kg or 2.5×10^5 kJ/m³ when the temperature changes 60°C. Hot water for washing, bathing, etc is required, and is often used in space

heating radiators. Water can be used as a storage device and a transport means of electricity, for example, in a solar power system. It is a widely used storage medium for warm water and solar heating applications [9, 10]. As the design requirements for water storage media have a great deal of data published [9-11], due to their simplicity. Due to the flood forces which ensure the highest temperature at the top and the lower temperature at the bottom of the tank thermal stretching or thermocline in a solar water heat storage tank may be created. Stratification is achieved by the absence of mixing during storage, obtaining a dual advantage [9, 10]: i) enhance energy efficiency by loading at a lower temperature instead of a mixed storage temperature; and ii) maximizing the energy produced if the inlet fluid of the collector is added for a charge.

A variety of materials such as steel, aluminum, reinforced concrete and fiber glass, form the water storage tanks. The tanks have glass wool, mineral wool or polyurethane insulation. The tanks used range in size between hundreds of liters and several thousand cubic metres. Underground natural aquifers were considered for large-scale storage applications. Aquifers contain groundwater and are geological formations that provide a possible way for heat storage for long periods. The medium for water storage includes gravel or sand saturated with water. There are large storage volumes as standard aquifer measurements vary from hundreds of thousands up to millions of cubic metres. For example, for every 10 K temperature difference, 105 m³ of aquifer material can store approximately 3 MJ of heat. This form of storage is suitable for seasonal storage, i.e. heat transfer from summer to heating. Due to its large nature, small loads, e.g. individual homes, cannot be stored on the water. There has been widespread recognition of the utility of aquifer thermal energy storage and many experimental and theoretical studies have been carried out [12]. However, a more thorough computer simulation analysis is required to determine the optimal system configuration, because of the many different systems and physical parameters. Due to its low cost properties, high input/output rates and large volume, the attractiveness of aquifer storages.

Solar ponds are a simple and inexpensive way to absorb and store vast volumes of solar energy in the form of low-thermal energy (50-95°C). They have potential in room heating and cooling, in the supply of heat and power for the industrial process. Four specific factors can be used to identify solar ponds as a a) conveyance, (b) a gelled and non-gelled collector or storage, (c) multilayer, or non-partitioned and (d) separate storage or storage pond. Most research activities are currently, however, focused on the non-convective solar pond salt gradient [13]. A density gradient in this form of the solar pond is formed with the use of salt water (or seawater) whose concentration increases with surface depth. The salt most frequently used in this type of pond is sodium chloride (NaCl) and magnesium chloride (MgCl₂). The black or dark bottom of the salt gradient pool absorbs solar radiation with the consequent rise in water temperature to 95°C. The absorption of thermal energy from the lower layers of the pool will effectively be accomplished without disrupting the upper layer. The biggest solar pond in the United States is a 3,354m² experimental plant in El Paso, Texas, which has been running successfully since its launch in 1986. The pond operates an organic turbine generator of 70 kWe and a 5 000 gallons a day desalination plant while supplying a neighboring food processing company with process warmth. In its heat storage zone, the pond reached and sustained temperatures above 90°C, produced over 100 kWe during peak power output and produced over 80,000 gallons of potable water over 24 hours [13].

Petroleum-based oil and molten salts are the most often suggested water substitutes. The thermal power is 25 - 40% of the weight of water. These replacements, however have lower steam pressure than water and can work at temperatures greater than 300°C. Due to stability and safety purposes, oil is limited to less than 350 °C and can be fairly costly. Therminol and Caloria-HT are some of the oil candidates considered [9]. Some molten mixtures of inorganic salts for high temperatures have been proposed (300°C and above). The first element is sodium hydroxide that can be used for temperatures of up to 800°C and has a melting point of 320°C [14]. It is highly corrosive, however and difficult at high temperatures to contain. As potential sensible heat storage media, liquid metals are also listed.

2.1.2 Solid Media Storage

Strong materials such as rocks, metals, asphalt, sand, bricks and so on can be used for low or high-temperature thermal energy storage. The energy may then be retained at low temperatures or high temperatures because these materials do not freeze or boil. Thermal energy as a sensible solid thermal heat can be retained to prevent the difficulties of the high vapor pressure of the water and the disadvantages of other liquids. In addition, their jar should not spill the solids. Cast iron is the top product in the list of solid materials that are used in critical thermal storage [14]. Therefore, it is far more costly than brick or stone, and the payback period is also longer. As the storage material due to its low cost, pebble beds or rock piles are usually favored.

The rock bed or rock battery is made up of a bed of rock material that can be packed loosely and which can be used to transport heat. The heat energy in the packaged bed is retained by pushing warm air into the bed and is recirculated to the heated bed by the ambient air. In addition to the thermophysical properties of the stone, the energy contained in a packaged bed storage system depends on many parameters, including the rock size and shape, the density of packaging, heat transfer fluid etc. Solar energy can also be contained in soil or in rocks and is useful for use in buildings. This form of storage is mostly used in combination with solar air heaters for temperatures of up to 100°C [15]. The characteristic size of the rock pieces used usually varies between 1 and 5 cm. About 300 - 500 kg of rock per square meter of solar collector area for space warming applications is an approximated thumb rule followed for sizing. The rock and the concrete are stored at around 36 kJ/kg or 105 kJ/m³ with a temperature change of 50°C. The storage of rock or steep beds can also be used up to 1000°C for much higher temperatures. To explain the geometric and thermal properties of packed litters, King and Burns [15] have several features such as particulate size, vacuum fraction, bed cross sectional surface and bed length, superficial air velocity and the Reynolds number. Fluidized beds like rock beds can be used for solar applications of medium, moderate and high temperature [16]. The exchange rate of heat between the heat transfer fluid and the storage medium in fluidized beds is much faster than in rock beds, which can be of benefit to a variety of applications. The thermal stored fluidized bed can also be used for the recovery of waste heat.

Heat storage can be found both in new and existing buildings as well as in water and air systems. Ceramic brick composed of olivine, magnesite, microthermal, and feolite is the most common storage medium. Construction and structure cement with active or passive storage designs may also be used. Manufacturers continue to make changes in isolation and storage materials. Floor warming is the most common method of construction mass used in thermal storage. The ground becomes a large radiating surface at low temperatures where concrete serves as a medium for heat storage. The floor can be heated with water, direct wiring or air ducts with heat transfer fluid. Water is the most commonly used medium of heat transfer. Many floor warm buildings don't use on peak electricity to charge the storage, but they can be modified to use on peak heating through a control system. A Swiss producer with applications in the UK, Spain, Korea and Japan has designed a state-of-the-art phase-change material for floor storage heating [14]. Inertia building and hollow core construction are two other categories of building mass storage. Controls are built to reduce heating energy costs by adding the total building mass to heat decreases over peak periods. The use of building mass inertia is a technique that does not include additional HVAC equipment but involves precise controls. In Sweden, core ventilation systems with hollow air circulated via floor slabs, connecting it to the building mass, were developed [17].

Effects for energy stockpiling are mostly either inorganic salts or metals [18, 19], as suggested for high-temperature (120-1400°C). Examples of these metals included aluminum, magnesium and zinc. When high thermal conductivity is prioritised compared to the cost, the use of a metal medium can be advantageous. The use of solid industrial waste as a store for energy storage may include copper slag, iron slag, cast iron slag, aluminum slag and copper chips.

In general, sensible heat storage materials gain from high thermal stability and inexpensive materials with exception of thermal oils and liquid metals. Although the heat-storage materials are responsive, the thermal energy storage density is 50-100 times smaller than the latent heat. The stability of the

temperature during discharge is its major downside. Over time the release phase is constant, the outlet temperature of HTF decreases steadily.

2.2 Thermochemical energy storage

In a chemical reaction, the chemical heat storage mechanism depends on the energy released and consumed by the reform and breakup of molecular bonds. The heat stored is governed by the amount of storage content, the heat reaction and the conversion scope.

$$Q = a_r m \Delta h_r \quad (2)$$

a_r is fraction reacted and Δh_r is endothermic heat of reaction,

The significant benefit of such energy storage is that the energy density is theoretically high. The chemical storage heat content is shown in table 2 [20-25]

Table 2. Chemical heat storage material.

| Compound | Reaction | Energy storage density | Reaction Temperature ($^{\circ}$ C) |
|--------------------|--|------------------------|--------------------------------------|
| Ammonia | $NH_3 + \Delta H \leftrightarrow 1/2N_2 + 3/2 H_2$ | 67 kJ/mol | 400-500 |
| Calcium Hydroxides | $Ca(OH_2) \leftrightarrow CaO + H_2O$ | 3 GJ/m ³ | 500 |
| Calcium carbonate | $CaCO_3 \leftrightarrow CaO + CO_2$ | 4.4 GJ/m ³ | 800-900 |
| Metal hydrides | $Metal xH_3 \leftrightarrow yH_2 + (x - y)H_2$ | 4 GJ/m ³ | 200-300 |
| Magnesium oxide | $MgO + H_2O \leftrightarrow Mg(OH_2)$ | 3.3 GJ/m ³ | 250-400 |

The maximum TES density and capacity to store TES with low thermal loss is the chemical thermal energy storage device. But the TES material, like Mg(OH)₂, is charged and the grain grows as decomposition takes place, leading to low porosity.

Thermochemical storage (TCS) production is undergoing a basic laboratory stage, and is far from validated design and material to be commercially transferred. However, TCS is being examined in detail because when the chemical reaction partners are separately stored and because it may provide outstanding volumetric energy density[26], it is almost uncommon to store energy. Gas-solid reversible reactions are especially ideal for heat storage due to the easy isolation of the gas emitted during heat absorption. Diverse types of reaction systems for gas-solid are being explored: metal hydrides (80–400°C), decarboxylation of metal carbonates (100–950°C), dehydration of metal hydroxides (250–800°C), thermal desoxygenation of metal oxides (600–1000°C). While reaction enthalpy (400–1100kWhm⁻³ depending on temperature) is generally extremely high, a feasible energy density is between 200 and 500 kWh. There are primarily two reasons for this: one is that the solid must be in powder or pellets; second, the reactants (solids and gas) must in most cases, be contained in different tanks (closed systems).

In the EU FP7, CaO/H₂O responses and open redox cycles are studied by the projects TCS-Power and RESTRUCTURE (2011-2014) [27]. Particularly important in steam power generation applications are the heat storage systems based on metal hydroxides, where water (steam) reacts with metal oxide (e.g. CaO). However many issues have been reported and remain unresolved for the majority of them (e.g. tendency to agglomerate solid, weak heat transport properties, low reactive kinetics, potential dehydration crystallizations, and high-temperature sintering). As it was named, thermochemical storage has a significantly large storage density that accommodates restrictions in plant space and a loss-free and long-term storing option.

Unfortunately, since the technology was in its infancy, its cyclic stabilization and its simple incorporation with solar power concentration are still doubtful. It shows promise: a large variety of temperatures, from 50°C to more than 1000°C, are used to provide a thermochemical storage environment at which sensible and latent heat will waste substantial quantities of energy in the form of

radiation. This means, thermochemical storage with solar tower receptors that can reach very high temperatures between 1300 and 1500°C can be implemented in an effective manner [27].

2.3 Latent Heat Storage

Latent heat storage (LHS) materials maintain heat in their latent temperature during a constant temperature operation, such as phase shift. Solid-liquid is the most common phase transition. While special latent thermal energy is lower for solid-solid phase transformation, it does not require leakage nor encapsulation. Phase change of liquid-gas has the highest latent phase heat, but it is not always used as a result of the large shift in storage material [28]. TES stored latent heat is expressed as

$$Q=mL \quad (3)$$

m represents mass and L is specific latent heat.

Latent heat storage materials are commonly known as phase change materials (PCM). PCM can be classified into organic, inorganic and eutectic.

2.3.1 Organic PCM

The organic PCM contains compounds paraffin and non-paraffin. The organic PCM has temperatures of phase change between 18°C and 30°C close to the normal thermal range of the human body. Although chemically stable and non-toxic, non-corrosive and easy to use, they decay at high temperatures and have very low thermal conductivity.

Paraffin is a widely used organic PCM and consists of a combination of primarily CH₃-(CH₂)-CH₃ straight n-alkanes. Upon crystallization of the chain (CH₃), a huge amount of latent heat is released. The melting point also increases as the number of atoms. Paraffin is cheaper, odorless and non-corrosive to supercool. They are chemically stable below 500°C with changes in small volumes after melting. Their vapor pressure in the melting form is low and is not separated in phase. Paraffin has a low thermal conductivity and low density, the main disadvantage. [29, 30]. The most critical group of materials for PCM storage is the non-paraffins. Research on organic material and the ester, alcohol, fatty acid and glycol that are suitable for energy storage was carried out by Sauhney and Buddhi [31] and Abhat et.al [32], Organic materials are generally heat-fused, flammable, low thermal conductivity, low flammable, different toxicity levels and not stable at high temperatures. Table 3 shows some latent heat and non-paraffin material.

The dependence of the heat potential of n-alkanes on the number of atoms C between 19 and 48 was assessed by C.M.L. Atkinson et al [33]. Detailed analyses of the available liquid heat-capacity data for the alkanes can be found in the following publications: M. In 1996 and 2001 Zábbransky'et others were focused on IUPAC-supported Projects (IUPAC) [33-35]. A number of researchers have currently been widely involved in the production of different heat storage materials on the thermal properties of paraffin waxes. All these studies have shown the high latent heat storage capacity between 200 kJ kg⁻¹ to 250 kJ kg⁻¹ and a great number of thermal temperatures with a wide range of melts with thermal stability up to 250 °C is absorbed, stored and released by waxes during phases transitions between the solid and the liquids. During repeated phase transitions, they show no segregation. They are inert chemically, odorless, durable, cheap, ecologically harmless, and not poisonous. They are not harmful. Different enthalpic fusion and melting points for the same alkanes were recorded in different studies. For instance, n-octadecane has been measured with fusion enthalpy 233.8 kJ kg⁻¹ (35.6 °C) [36], 228.2 kJ kg⁻¹ (28.1°C) [37] and 222 kJ kg⁻¹ (31.0°C). These fluctuating values can reflect changes in physical characteristics of various crystalline structures and polymorphism according to n-alkan molecular parameters and heating and cooler conditions during DSC analysis [38].

The melting point for paraffin wax increases and the inducted dipole attractions between n-alkane chains, e.g. n-dodecan melting point (12 C atoms), increase to -9.6°C for each while n-octacosane melting point (28 C atoms) increases by 62°C for each. Due to the conformational differences of specific specimens, the measured Hfusion values do not display such a frequent increase in magnitude. Research

have shown that each n-alkane crystallization temperature, which corresponds to a minute of overcooling during freezing, is slightly lower than its melting temperature. As well as supercooling, the poor thermal conductivity (k) of the paraffin waxes (approximately $0.2 \text{ W m}^{-1} \text{ K}^{-1}$, which requires improvement in order to increase their skills in thermal application [39-42], is another drawback.

Table 3. Non paraffin material.

| Material | Melting point ($^{\circ} \text{C}$) | Latent heat (kJ/kg) |
|----------------------------------|---|----------------------------|
| Isomalt | 147 | 275 |
| Pentaerythritol | 187 | 255 |
| Phenol | 41 | 120 |
| Glycerin | 17.9 | 198.7 |
| Cetyl alcohol | 49.3 | 141 |
| Diphenyl amine | 52.9 | 107 |
| Bees Wax | 61.8 | 177 |
| Hydrophosphoric acid | 55 | 213 |
| Benzoic acid | 121.7 | 142.8 |
| Quinone | 115 | 171 |
| Stearic acid | 69 | 209 |
| Polyethylene glycol 600 | 12.5 | 129.1 |
| Polyethylene glycol 35000 | 68.7 | 166.9 |

Fatty acids represent organic PCMs and have an enormous TES potential for widely used thermal storage applications [43]. Because of their reducibility from vegetable and animal oils, fatty acids have many TES benefits and are environmentally friendly [44, 45]. On the other hand, their principal nuisance is characterized as low corrosiveness, bad smell and high rates and their capacity to use these properties is restricted. The other downside is the problem of leakage during the melting process with regard to fatty acids [46]. The highest melting points and latent heat in organic PCMs are sugar alcohols. Due to temperature changes, the thermal storage systems for applications such as solar or waste heat recovery for medium temperature (90°C - 250°C) are suitable. [47]. The cost and non-toxicity of alcohols are minimal. They also exhibit polymorphism and they can occur in two or more crystalline states. The intake of alcohol in TES due to polymorphism is seriously impaired. Polymorphs of various types may have important physiochemical properties variations. The stability of alcohols is low due to oxidation of the environment by oxygen, causing changes in phase temperature and fragile material with reduced storage capabilities [47]. The change in temperature in the Polyethylene glycol (PEG) process is near to the ambient temperature, increasing with the molecular weight of the polymer. PEG is unique to other organic PCMs because it dissolves in water while the hydrophobic ones in nature. One of PEG's big issues is the highest supercooling of all organic PCMs. The difference between the smelting and freezing point can reach as high as 30°C - 40°C , which is not ideal.

2.3.2 Inrganic PCM

Metallic and salt hydrates are known as inorganic products. Usually this material is used as organic matter decomposed at high temperatures in high-temperature operations. As a PCM the advantages of metals and alloys are high heat storage capacity and maximum thermal conductivity per unit volume. Metals and alloys are expensive, but the TES criterion is the best choice. Metals and alloys have limited heat energy storage capacity per unit weight. They therefore have the issue of excess weight [48]. Cárdenas and León have identified several high-temperature potential PCM metals and metal alloys that melt temperatures above 300°C that several other researchers have proposed and investigated. As with other authors, scientists neglect the use of metal alloys as a PCM despite their beneficial properties such as high thermal conductivity, high resistance to corrosion and minor changes in volume due to changes in phases and no subcooling. Therefore in certain applications, metal and metal alloys have more

thermophysical properties and can compete with salts, particularly if weight is not a deciding factor [28]. Metal and alloys are experiencing changes in their microstructure due to precipitation, oxidation and separation. Inert atmosphere is important to prevent oxidation when using these materials. [49].

The high latent fusion heat, high thermal conductivity, high availability, low volume shift and low cost hydrates make salt hydrates one of the most attractive inorganic PCM in low temperature applications (-20-140°C). [50]. Inorganic salts with n water molecules forming a regular crystalline solid with the general formula AB*nH₂O are salt hydrates similar to [51]. The type of bond formed usually is ion-dipole or hydrogen. Although in some systems the water is more directed toward the anion and salt cation in others the molecules of the system are correctly located and oriented [52]. Salt hydrates are slightly acidic and plastic compliant, taking into account the distribution and storage. The most popular salt hydrates available are CaCl₂*6H₂O and Na₂SO₄*10H₂O. The salt hydration process may be influenced by the crystallisation/melting process. A hydrated crystal could dissociate from moles in water to a lower hydrate during melting (Eq 4) (Eq 5) [53]:



Low-specific heat, subcooling, insulation and fusion heat reduction through incongruous melting is among the disadvantages of salt hydrates. Mechanical turmoil, PCM encapsulation, incorporated thickeners and additional water use can improve the incongruous melting process. [54-57]. Mechanical turbulence, PCM encapsulation, integrated thickeners and additional water can improve the incongruous melting. Table 4 shows certain inorganic substances that may be used as PCM [58].

Table 4. Inorganic material.

| Material | Melting Point (° C) | Latent Heat (kJ/kg) |
|--|---------------------|---------------------|
| LiClO ₃ .3H ₂ O | 8 | 155-253 |
| CaCl ₂ .6H ₂ O | 29 | 190.8 |
| LiNO ₃ .2H ₂ O | 30 | 296 |
| LiNO ₃ .3H ₂ O | 20 | 189 |
| CoSO ₄ .7H ₂ O | 40.7 | 170 |
| Ni(NO ₃) ₂ .6H ₂ O | 57 | 169 |
| NaOH.H ₂ O | 64.3 | 273 |
| MgCl ₂ .6H ₂ O | 117 | 167 |
| LiNO ₃ (Lithium nitrate) | 253 | - |
| KNO ₃ (Pottasium nitrate) | 333 | 266 |
| NaNO ₃ (sodium nitrate) | 307 | 172 |
| Ca(NO ₃) ₂ (Calsium nitrate) | 561 | - |
| MgCl ₂ (Magnesium Chloride) | 714 | 452 |
| Na ₂ CO ₃ (Sodium Carbonate) | 854 | 275.7 |

2.4 Eutectics PCM

Eutectic is a minimum melting composition of two or more components that during crystallisation melts and freezes each to form a component crystal mixture. The inorganic, organic and/or organic combination may be used in this component. [59].

The use of individual composite fatty acids also has a practical constraint on achieving comfort requirements such as home heating / cooling, textiles and indoor air conditioning, because of their phase-in-transition temperature. By combining two or more fatty acid components with eutetic mixtures, the correct temperature can be mitigated until each component has a sharp, freezing peak temperature and eutectic temperatures [60]. Zhao et al. produced a phase chart and showed their transitional properties of the phase shift for a series of binary and ternary eutestic fatty acids derived from the four typical bioPCM (stearic acid, palmic acid, myric acid and lauric acid) [61]. Li et al. [62] also documented a

series of eutectic binary fatty acids, showing that the TES applications were good thermal efficiency. It is noticeable that the eutectical mixtures do not address issues like supercooling and phase separation.

Organic-organic eutectics are ideal for TES applications of low to moderate temperature thanks to their advantage of congruent melting, eco-friendly and non toxic bio-design, minute degree of supercooling, low vapor pressure during phase transformation, compatibility and durability with building material. In addition a large range of eutectic PCMs can be adapted to enhance the adaptability of PCMs for TES applications in the light of the requested thermophysical properties of LHTES. [63]. Cai et al. investigated the thermophysical properties of the prepared form of stable, acid-based Eutectic Fiber (PET). Eutectic PCMs with different quantities of PET has a working temperature range of 35-53°C [64]. Kant et al. have produced ternary eutectics of fatty acids for low-temperature applications with an experimental temperature range between 14 and 21°C. [65]. Sharma et al. [66] indicated that myrtical acid and palmitic acid were thermally reliable for long term use after the thermal analysis of these fatty acids following 1,500 melting and freezing cycles.

Huang K et al. [67] reported that the desired floor heating PCMs must have an ideal melting temperature of 26 to 32°C, given that the heating system usually has a heating surface temperature of 22 to 26°C. Furthermore, the convenient indoor temperature for the thermal storage materials in energy efficient building fields like wallboards for the phases change is usually allowed in the range of about 16-25°C. In other words, it is possible to consider and apply wallboards to decrease the temperature variance inside a room and to increase comfort inside the indoor atmosphere [68, 69] if PCMs have a melting temperature of about 16-25°C. Boulard Tet al [70] also summarized that PCMs with a melting temperature of approximately 20-28°C can by way of encapsulation in flate plastic bags or packaging into specially built polyethylene bags, considered as promising materials for the solar greenhouse heating system. Literature from Mondal S [71] and Sarier N et al [72] suggests the most productive and acceptable candidates for temperature control and isolation of cloth and textiles in PCMs with a melting temperature between 15 and 35°C. These PCMs may store or released redundant energy to adjust humans' temperature and by means of phase change processes, improve thermal comfort when the temperature of the environment is higher or lower than the temperature of human comfort.

Literature have successfully studied preparation, phase diagrams, eutetic mass ratios and thermal energy storage propagations for the binary fatty acids eutectics (e.g capric acid-lauric acid, capric acid-myristic acid, lauric acid-stearic acid and myristic acid-stearic acid, capric acid-palmitic acid, lauric acid-palmitic acid) and part of ternary fatty acid eutectics (e.g capric acid-lauric acid-palmitic acid, capric acid-myristic acid-palmitic acid, lauric acid-myristic acid-stearic acid) but also some of these have been successfully investigated in a lot works of literature. The following summarizes the cooling peak temperature ranges of binary and ternary fatty acid eutectics investigated by the researchers according to literature data and research papers [67-69, 73-79]: (1) 20-25°C: including eutectics of the capric acid-lauric acid, of the capric acid-lauric acid-palmitic acid and of the capric acid-myristic acid-palmitic acid; (2) 25-30°C: including eutectics of the capric acid-myristic acid, of capric acid-palmitic acid and of the capric acid-palmitic acid-stearic acid; (3) 30-35°C: including eutesctics of the lauric acid-myristic acid-palmitic acid, of the myristic acid-myristic acid-stearic acid and capric acid-stearic acid, of which (4) 35-40°C: including eutectics of the lauric acid-palmitic acid-stearic acid, of the lauric acid-myristic acid and of the lauric acid-palmitic acid; (5) 40-45°C: including eutectics of the lauric acid-stearic acid, (6) 45-50°C: including eutectics of stearic acid-myristic acid-palmitic acid, myristic acid-palmitic acid and stearic acid-myristic acid. (7) >50°C. Objective energy consumption criteria can obviously be considered and extended for three kinds of fatty acid eutectics namely capric acid-lauric acid, capric acid-lauric acid-palmitic acid and capric acid-myristic acid-palmitic acid eutectics. In addition, there is also very few candidates for use as PCMs in this temperature range for thermal-regulated fibers and textile applications.

Mg(NO₃)₂.6H₂O (MNH) and glutarin acid (GA) which have a melting enthalpy of 189.0 J/g higher than the raw material are produced by Suimin Li et al [80] organic-inorganic eutetic PCM. Due to the characteristics of the structure and the crystallisation behaviour, latent heat increases are associated with crystalline eutectic MNH-GA processing. Moreover, eutectic MNH-thermal GA's stability has been

improved as the melting temperature decreased by less than 66.7°C dehydration. Karthick et al. [81] developed a PCM eutectic mixture to improve copper indium diselenide PV System efficiency. The module's temperature decrease was noted up to 9°C compared to the reference module. Liu, Yang, and Na₂SO₄·10H₂O-Na₂HPO₄·12H₂O and Na₂CO₃·10H₂O Na₂HPO₄·12H₂O have been characterized as eutectics of salts hydrated to find their use in the thermal storage of various solar systems. The eutectics showed no phase separation and the supercooling level was reduced significantly[82].

Figure 4 offers a description of the storage density, operating temperature, longevity and trade status of the TES. Owing to high variations in enthalpy during the phase transition, the storage density of the LHS medium is typically higher than that of the SHS, while the thermo-chemical energy density is greater than that of all other modes. Different thermochemical energy storage materials are currently under research and no such device is available on the market. The commercial feasibility of the LHS is constrained by material characteristics and is thus mainly commercialized during the production process as opposed to SHS. Figure 4 demonstrates that in comparison to LHS materials which constitute one quarter of their lifetime and thermochemical energy storage, the life cycle of the materials is about 20 years, which is approximately 1/10 of the lives of SHS materials [83]. The LHS range of operating temperatures among those different types of TES is most versatile, with operating temperatures significantly lower for sensible and thermo-chemical energy storage [84]. The benefit of latent thermal energy over sensible thermal storage is that it has a density of approximately 10 times greater than TES, an output of 50-150 kWh/t, and an efficiency of ~75%-96% [85, 86].

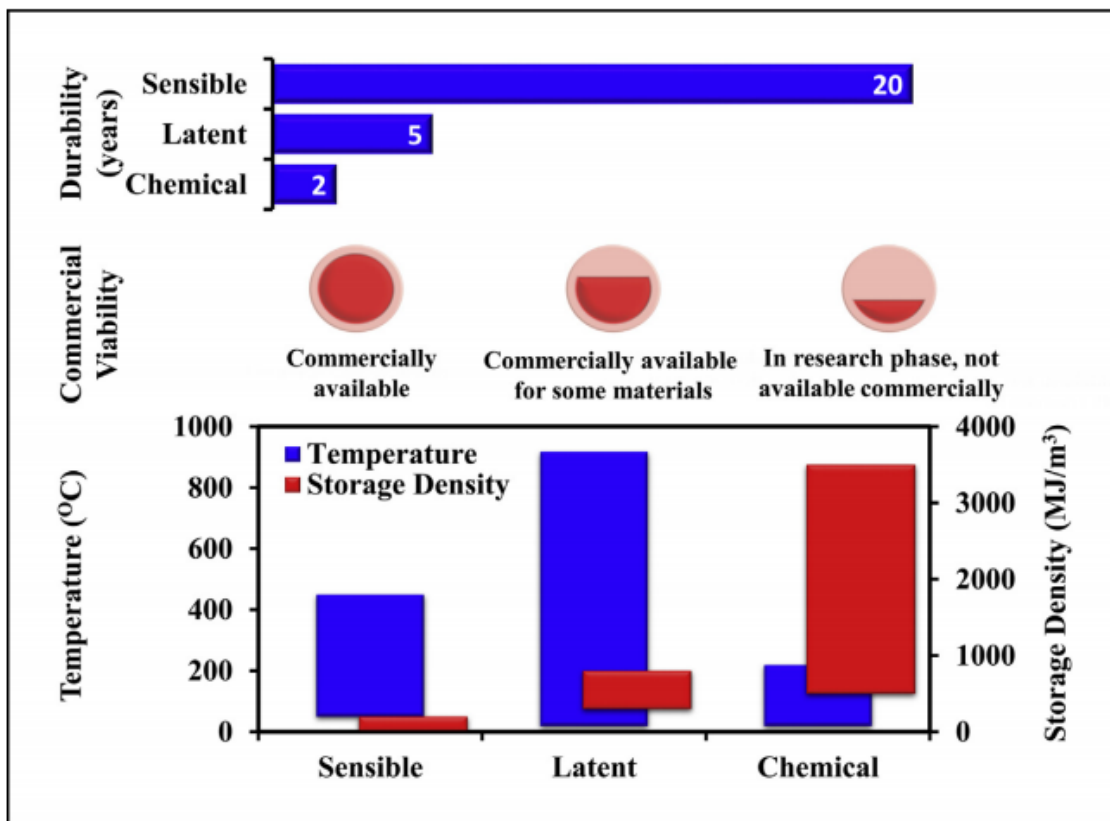


Figure 3. Overview of PCMs for TES.

3. Molten salt

The term 'molten salt' refers usually to a substance produced by the melting of inorganic salt or the mixture of salt. A number of salt mixtures have been produced to achieve unique purposes such as fluorides, carbonates, nitrates, etc. For example, molten salt fluids are needed in the CSP plant in order to get a lower freeze point in the salt tunnel. Solar salt, a combination of NaNO_3 and KNO_3 with a melting point of 236°C is used in a commercial system. Equally significant for optimum construction and cost-effective operations for use in a melting salt reactor are properties such as high temperature stability (up to 750°C), radiation stability and neutronic properties. Table 5 shows some commercially used molten salt [87].

Table 5. Molten salt and applications.

| Molten Salt | Eutectics | Applications |
|-------------|---|--|
| Fluorides | $\text{LiF}-\text{BeF}_2$ $\text{LiF}-\text{NaF}-\text{KF}$ | TES, HTF, Molten Salt Reactors (MSR), |
| Carbonates | NaBF_4-NaF $\text{Li}_2\text{CO}_3-\text{Na}_2\text{CO}_3$ | High temperature Fuel Cells, Molten Salt Oxidation |
| Chlorides | $\text{KCl}-\text{MgCl}_2-\text{NaCl}$ $\text{KCl}-\text{NaCl}$ | TES, HTF, MSR |
| Nitrates | $\text{NaNO}_3-\text{KNO}_3-\text{NaNO}_2$ $\text{KNO}_3-\text{NaNO}_3$ | HTF and TES |

Molten salts, poor thermal conductivity and liquid leakage have the two major drawbacks of reducing their use for heat storage. A very successful way of halting the leakage of the liquid was a chemically inert stable composite PCM formation, which spread through porous support. Many porous supports, including metal foams, porous carbon materials like expanded graphite (EG), graphite foams, carbon nanotubes, porous ceramics, montmorillonites, vermiculite and diatomite have been successfully used for PCMs [88]. EG is one of the best possible PCM supports due to its excellent thermal conductivity, good corrosion resistance and low density. Xiao et al [89] considered EG to help solve the issue of low thermal molten salt leakage. A cascading latent heat storage (CLHS) system has been recently recorded to serve as an efficient TES alternative that ensures the best use of the storage material. In the CLHS system, the temperatures of phase change were ordered from the lowest to the highest according to their melting temperatures.

Zhong et al [90] synthesized by means of impregnation process porous heterogeneous composite PCMs from EG and binary molten salts. The binary salts of this substance were LiNO_3-KCl , $\text{LiNO}_3-\text{NaNO}_3$ and $\text{LiNO}_3-\text{NaCl}$. The double percentage of molten salt was between 77.8 and 81.5% and the percentage of encapsulative efficiency was between 72.8 and 78.8%. Via EG impregnation, binary molten salts have increased their thermo-conductivity 4.9-6.9 times. The porous heterogeneous composite's phase change properties displayed high temperature stability that can retain their properties even after 100 cycles. Solar power plants can retain their properties at high working pressure in closed systems via the high temperature heat transfer fluid. Due to its better thermal properties than synthetic mineral oil, molten salts may be used as direct HTF in CSP plants etc. Real, due to their high freezing temperature points, the direct applications as thermal transmission fluids of molten salts are inhibited.

Sang et al [91] have researched $\text{K}_2\text{CO}_3-\text{Li}_2\text{CO}_3-\text{Na}_2\text{CO}_3$ as PCM and MgO as ceramic supporting material for ternary carbonate-based composite phase change material (CPCM) as (CSM). The composite composed of 50 wt percent salts was found to be 28 MPa highest mechanical power, 1.48 J/g·K special thermal heat capacity and 158.7 kJ/kg latent heat. These materials showed strong cycling efficiency and a wider range of operating temperatures and thus a broader prospect of application to mid and high temperatures. A NaNO_3 CPCM was manufactured by Ye et al. [92]. Using the MgO as CSM and the multicarbon nanotubes as thermal conductivity enhancement material (TCEM), the addition of

carbon nanotubes greatly improved the thermal conductivity of the composite and increased the degree of its rise, as the charge of carbon and the operating temperature increased. Qin et al. [93] investigated the use of diatomite as the same CSM process of the sodium composite, and the findings suggested that excellent chemical and physical stability was obtained at the insulation of 880°C and that a combination of mechanical strength and energy is preferred by the diatomite of 45% in the composite.

For some time, chloride salts were presented as LHTES media. The TES device accompanying the solar thermal power plant design study from Clayton suggested two ternary chloride salt pulses as PCMs: KCl-NaCl-MgCl₂ and KCl-NaCl-CaCl₂ [94]. As a promising LHTES medium, Kamimoto recommended two pure chloride salts, FeCl₃ and the double salt, KMgCl₃ [95]. However as nitrates currently are, nothing has been done to fix their possible use as critical heat-storage media in the molten state. Marcus recommended chlorides to be potential LHTES while also neglecting their use as sensible liquid storage media [96]. Tanaka's study identified the use of the eutectic system KCl-LiCl as a pcm in a TES dual-stage superheating device where pressurized water is the main stage of sensible heat storage [97]. The TES media can be called various chlorides. There are main categories of an alkaline metal chloride, alkaline earth, transition metal, p-bloc metal, and rare earth metal [98]. The general categories of content are: For the purposes of this analysis we are limited to salts that have higher melting temperatures – more than 400 degrees Celsius (Ferric Chloride, for example, is ignored since its melting temperature is 307.6 degrees Celsius [99]). In combination with eutectic mixtures, the resulting salt systems could melt in temperatures below 400°C; these materials are expected to continue to be used as fuse-sensitive storage media at elevated temperatures. Furthermore many of the pure salts assumed to be displayed cost well beyond that of other candidate salts (e.g., rare earth metals chlorides); as such, salts costing up to a minimum of kg.

3.1 Nitrates Salt

Molten alkali nitrates, especially mixtures of sodium and potassium nitrate with other additives, have been used very successfully as fluids for energy storage or heat transfer in some cases. In this section, we will study the thermophysical and thermochemical properties of binary, ternary and quaternary molten nitrates. Eutectic points occur in nitrate salt mixtures where the system solidifies with some other composition at a low temperature at a particular chemical composition. Two components of the liquid mixture are still in the balance at the eutectic point and each of the components is crystals, so if the temperature is lower than the eutectic temperature, each component will begin to crystallise out of the mixture [100].

Probably the most studied is the binary mixture method, but the detailed phase diagram is not yet accepted. In order to understand the processes for the improvement of the working of the nitrate salt mixture it is important to define thermal properties of the pure components and binary mixtures, known as binary systems and molten salt mixtures for commercial and essential applications, such as fluid for transport, which functions as a hot storage medium in the molten salt TES tank. NaNO₃ shrinks to 307°C and KNO₃ shrinks to 337°C.[101]. It is widely accepted that, the composition of 50 mol % KNO₃ and 50 mol % NaNO₃ or 54wt % KNO₃ and 46wt % NaNO₃ has always been accepted that the minimum melting point is near 220°C [102]. As for the binary mixture of 60-40 weight percentage for NaNO₃-KNO₃, commonly known as solar salt's melting point is around 221°C [103]. While this salt mixture does not have the lowest melting point, its low investment cost also emphasises it. There are some disadvantages to this binary nitrate mixture in which this molten salt can quickly freeze and obstruct the pipeline in the evening or winter. Therefore, to deal with this issue, some auxiliary costs can be added and the expenditure will increase. The molten salt mixture of binary KNO₃-NaNO₃ is stable up to temperatures of 500°C and the melt varies only slightly in weight, although some NO_x gases have formed over this temperature. Another of the most studied heat transfer fluid additives is LiNO₃, which is believed to boost the efficiency of molten salts, extend the working range of temperatures with a low melting point and greater thermal stability. Experimentally identified that at a composition of 44 mol percent NaNO₃ and 56 mol percent LiNO₃, the eutectic temperature for this binary system was 196⁰ C.

At a composition of 46 mol percent NaNO_3 , the measured eutectic point was defined. The melting point is 183°C [101].

Ternary NaNO_3 and KNO_3 mixtures have significantly smaller melting point than binary salt and alkaline earth-nitrates. For a more dynamic combination of salt, such as eutectic ternary, a more dramatic reduction of melting points can be seen. Several experiments and patents in the melt chemistry literature were conducted in order to lower KNO_3 and NaNO_3 eutectical temperature [104]. In addition, by adding the other salt or regulating the nitrate-nitrite ratio, the upper working temperature is extended [105]. Bradshaw and Siegel mentioned that the inclusion or replacement of LiNO_3 in the ternary system of KNO_3 - NaNO_2 - NaNO_3 is an acceptable function for improving the thermal stability range of salt, although its price is the crucial problem related to this additive [106]. The thermal power of the ternary mixture of LiNO_3 - NaNO_3 - KNO_3 salt, according to researcher Reddy [107]. The heat potential in the liquid state is very stable and, with little slope, increases linearly with temperature. $\text{Ca}(\text{NO}_3)_2$ shows the highest potential as an additive in solar energy. Its low cost and ability to minimise the melting point of alkaline nitrates show the tremendous potential of the additive to be integrated into new energy storage formulations of molten salts and make it a primary candidate for the substitution of binary solar salts [108].

Some molten salt has been used as heat transfer fluid, including binary mixture, ternary mixture, and more dramatically is a quaternary mixture. The potential for salt development is to enhance its physiochemical characteristics, in particular its melting point, thermal stability and heat power, to create new quaternary mixtures or to integrate new components. Quaternary salt, which contains different NaNO_3 , LiNO_3 , KNO_3 , and $\text{Ca}(\text{NO}_3)_2$ weight ratios, has stronger chemical and physical properties than the commonly used binary solar salt (60 wt % NaNO_3 -40 wt % KNO_3) [109]. Bradshaw et al. [106] are known to reveal the mixture of anhydrous compositions belonging to the quaternary system of LiNO_3 - NaNO_3 - KNO_3 - $\text{Ca}(\text{NO}_3)_2$, said that these compositions have a melting point $<95^\circ\text{C}$ and thermal stability up to 500°C . The melting point of a salt mixture based on sodium nitrate and potassium nitrate is reduced by molten salt mixtures that include calcium nitrate and lithium nitrate. The transition observed in the thermal analysis did not melt the KNO_3 content properly with the other components at temperatures above 300°C and the signal agrees with values recorded in the literature and experimental values obtained for potassium nitrate melting [110]. For this mixture, the maximum stability is 580.36°C with decomposition beginning at 469.56°C . Table 6 shows some of the binary and ternary nitrate salt compositions and their melting point.

Table 6. binary and ternary nitrate salts' melting point.

| LiNO_3 | NaNO_3 | KNO_3 | $\text{Ca}(\text{NO}_3)_2$ | Melting point | Reference |
|-----------------|-----------------|----------------|----------------------------|-------------------------|-----------|
| 56 mol% | 44 mol% | | | 196°C | [103] |
| | 60 wt% | 40 wt% | | 221°C | |
| 25.9 wt% | 20 wt% | 54.1 wt% | | 118°C | [111] |
| | 30 wt% | 18 wt% | | 120°C | [112] |
| 25.9 wt% | 54.1 wt% | 20.06 wt% | | 118°C | [109] |
| | 15 wt% | 43 wt% | 42 wt% | 175°C | [113] |
| | 10 wt% | 27 wt% | 63 wt% | 130°C | [114] |
| | 9 wt% | 30 wt% | 61 wt% | 133°C | [108] |
| | 13 wt% | 40 wt% | 47 wt% | 160°C | |
| | 12 wt% | 44 wt% | 44 wt% | 130°C | |
| | 7-34 wt% | 43-50 wt% | 16-48 wt% | $120-190^\circ\text{C}$ | [112] |

Table 7. Quaternary Nitrate salts' melting point.

| Nitrate Salt System | Melting point |
|--|---------------|
| LiNO ₃ NaNO ₃ KNO ₃ NaNO ₂ | 99 |
| LiNO ₃ NaNO ₃ KNO ₃ KNO ₂ | 96.4 |
| LiNO ₃ KNO ₂ KNO ₃ NaNO ₂ | 100.3 |
| LiNO ₃ NaNO ₃ KNO ₃ Ca(NO ₃) ₂ | 109 |

4. Conclusion

It's evident from this review that choosing a good TES material benefits the CSP process. An ideal TES material has good thermophysical properties such as high energy storage, good thermal stability, non toxic, non corrosive, non flammable, high thermal conductivity, low melting point, compatible with container and etc. Although it's difficult to identify a perfect TES many researchs have been conducted to improvise current TESs to match the requirement. Water media storage is a better SHS compared to solid media storage as the temperature range and heat storage is higher. Molten salts are more suitable PCM (especially eutectic nitrate salts) compared to other LHS as it has high thermal stability, high energy storage (compared to SHS), less corrosive and lower melting point. Among the eutectic nitrate salt quaternary salt has the lowest melting point compared to a single, binary and ternary molten salt. The addition or increased weight percentage of LiNO₃ proven to be reducing the melting point of molten salt. For future studies, a review on other thermophysical properties such as specific heat, thermal stability and thermoconductivity of the eutectic nitrate salt can be compared.

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