

# We are IntechOpen, the world's leading publisher of Open Access books Built by scientists, for scientists

6,900

Open access books available

186,000

International authors and editors

200M

Downloads

Our authors are among the

154

Countries delivered to

TOP 1%

most cited scientists

12.2%

Contributors from top 500 universities



WEB OF SCIENCE™

Selection of our books indexed in the Book Citation Index  
in Web of Science™ Core Collection (BKCI)

Interested in publishing with us?  
Contact [book.department@intechopen.com](mailto:book.department@intechopen.com)

Numbers displayed above are based on latest data collected.  
For more information visit [www.intechopen.com](http://www.intechopen.com)



---

# Thermal Stability of Phase Change Material

---

Manish K. Rathod

Additional information is available at the end of the chapter

<http://dx.doi.org/10.5772/intechopen.75923>

---

## Abstract

Along with the heat transfer mechanism for the development of a latent heat storage unit (LHSU), the choice of the phase change material (PCM) plays an important role. The enviable thermo-physical, kinetic, and chemical properties of PCM with the economy is an essential criterion for efficient thermo-economical LHSU. The most important criteria that have limited widespread use of LHSU are the useful life of phase change materials. For long term performance of LHSU, the PCM used in the system should be thermally stable and reliable. It does not deteriorate its own properties, especially latent heat and melting point after a repeated number of thermal cycles. Thus an exhaustive literature survey is carried out for different types of PCMs used. The primary objective of this chapter is to carry out a critical review of thermal stability of different group of PCM especially for low temperature applications. Further, an extensive list of different PCMs which are undergone thermal cyclic tests by different researchers is prepared. This information is towards the selection of reliable PCM for latent heat storage unit.

**Keywords:** thermal stability, thermal cycles, differential scanning calorimeter, phase change material, latent heat

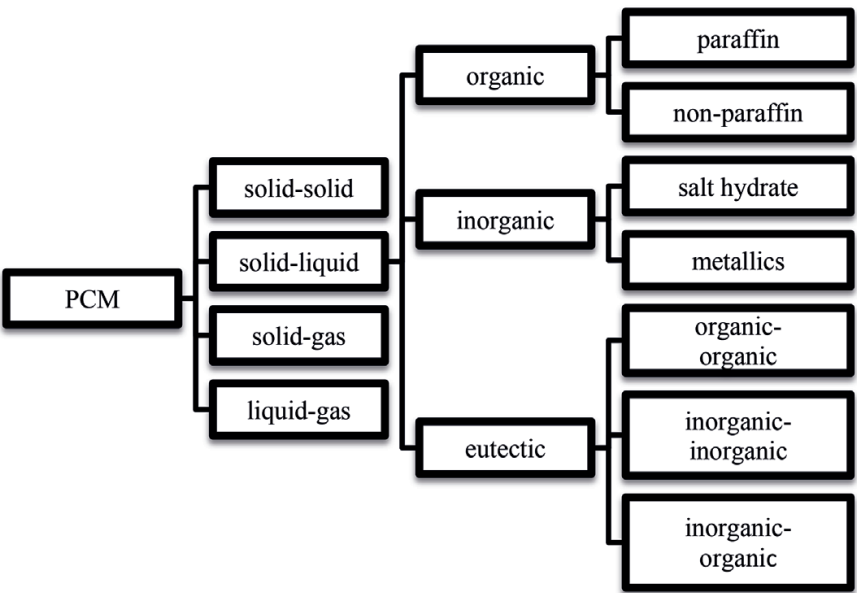
---

## 1. Introduction

Energy plays a major role in the economic prosperity and the technological competitiveness of the nation. Rapid development has led to huge demand for energy. The resource augmentation and growth in energy supply have failed to meet the ever increasing demands exerted by the multiplying population, rapid urbanization and progressing economy. In order to conserve energy and reduce dependency on fossil fuels and also to reduce the greenhouse gas emission, it is essential to develop efficient and inexpensive energy storage system [1]. Energy storage systems eliminate shortage between supply and demand and also exhilarate energy system performance and reliability. The energy storage can substantially reduce the

total energy consumption when integrated to sustainable energy sources such as solar energy, wind energy, waste heat recovery, biogas etc. And hence, conserve indigenous conventional energy sources. The thermal energy storage (TES) is also popular now and acts as a crucial aspect in engineering applications. TES may comprise sensible storage systems (energy storage by single phase heating and cooling), latent heat storage (energy storage by two phase melting and solidification) and thermochemical heat storage (energy storage by reversible chemical interactions between reactive components). The sensible heat storage (SHS) systems are widely used for low temperature solar thermal applications. However, SHS systems require a large storage volume for small temperature swing. The latent heat storage (LHS) systems stand out due to high storage density and nearly isothermal phase change [1–4].

The thermal energy storage materials used for LHS systems are also known as phase change materials (PCM). Telkes and Raymond [6] are pioneers to study PCM. A wide range of phase change materials with myriad melting points have been identified and studied exhaustively. These PCMs can be categorized as organic (paraffins and fatty acids), inorganics (salt hydrates and metallic) and eutectic combination of organic and/or inorganic materials. A detailed classification of PCM for latent heat storage applications is given in **Figure 1**.



**Figure 1.** Classification of PCMs [5].



**Figure 2.** Phase-change materials in their original states, (a) paraffin wax, (b) stearic acid, (c) sodium hydroxide.

**Figure 2** shows a sample of paraffin wax (paraffin), stearic acid (fatty acid) and sodium hydroxide (salt hydrate) in their original states, respectively.

2. Properties of PCM

Successful utilization of the latent heat storage unit (LHSU) depends considerably on the selection of the PCM, which plays an important role in development of LHSU. The feasibility of using a particular PCM for an LHSU is based on some desirable thermo-physical, kinetic, and chemical properties of the PCM. These desirable thermal, physical, kinetic, chemical and economical properties of PCM are listed below in **Table 1**.

As no single material can have all the required properties for an ideal thermal storage media, one has to use the available material and try to make up for the poor physical properties by an appropriate system design. Thus, selection of appropriate PCM is a challenge to the researchers.

<i>Thermal properties</i>	<ul style="list-style-type: none"><li>• Suitable melting point for particular application</li><li>• High latent heat of fusion per unit volume</li><li>• High thermal conductivity of solid and liquid phases for better heat transfer</li><li>• Higher specific heat for additional sensible heat storage</li></ul>
<i>Physical properties</i>	<ul style="list-style-type: none"><li>• Favorable phase equilibrium</li><li>• High density for smaller container volume</li><li>• Small volume change during phase transition</li><li>• Low vapor pressure to reduce the containment problem</li><li>• Reproducibility in the congruent during entire thermal cycle</li></ul>
<i>Kinetic properties</i>	<ul style="list-style-type: none"><li>• Little or no supercooling during freezing (Supercooling of more than a few degrees interferes with proper heat extraction)</li><li>• High rates of nucleation and high rate of crystal growth. i.e., the melt should crystallize at its thermodynamic freezing point.</li><li>• Effective heat transfer, especially at isothermal conditions</li></ul>
<i>Chemical properties</i>	<ul style="list-style-type: none"><li>• No degradation after a number of freeze/melt cycle</li><li>• Non-corrosiveness to the construction material</li><li>• No chemical decomposition</li><li>• No toxicity</li><li>• Nonpoisonous, non-flammable, non-polluting and non-explosive</li></ul>
<i>Economic criteria</i>	<ul style="list-style-type: none"><li>• Available in plenty</li><li>• Inexpensive</li><li>• Ease recycling and treatment</li></ul>

**Table 1.** Desired properties of PCM [5, 7–10].

### 3. Drawbacks of PCM

The commercialization of LHSU is found to be limited due to lack of desirable thermo-physical properties. The low thermal conductivity of PCM, variation in thermo-physical properties of PCMs under extended cycles, phase segregation, sub cooling, incongruent melting, volume change and high cost are primary factors to restrict efficient performance of LHSU. The major drawback of LHSU is the lower thermal conductivity and thermal stability of the PCM. This is typically between 0.15 and 0.3 W/mK for organic materials and between 0.4 and 0.7 W/mK for salt hydrates [11]. The effect of the lower value of conductivity is reflected during energy retrieval or withdrawal with an appreciable temperature drop during the process. As a result, the rate of phase change process (melting/solidification of PCM) has not been up to the expected level. In a nutshell, adequate amount of energy may be available, but the system may not be able to use it at the required rate.

Further, the selection of using phase change material in any latent energy storage system is based on desirable thermo-physical, kinetic, and chemical properties in addition to economic criteria. However, each class of PCM has its own characteristics, applications, advantages, and limitations. As no single material can have all the required properties for an ideal thermal storage media, one has to optimize between the desired thermal performances and the cost. The economic criterion for employing a PCM in a system depends on the life and cost of the storage material. Hence, in order to ensure long term performance and economic feasibility of latent heat storage systems a comprehensive knowledge of thermal stability of the PCMs as functions of the repeated number of thermal cycles is essential.

### 4. Thermal stability of PCM

The PCMs may degrade with repetition of storage cycles. A large degradation in terms of thermo-physical properties with time is not desirable for any PCM. If it is thermally, chemically and physically stable after a repeated number of thermal cycles of operation, then PCM is said to be reliable. It does not deteriorate its own properties, especially latent heat and melting point after a repeated number of thermal cycles. A PCM is thermally stable for latent heat storage applications if it ensures negligible change in the melting point and latent heat of fusion after a large number of thermal cycles of operation. The commercial grade PCMs are widely preferred for the latent heat storage system due to large scale availability and low cost. However, it has always been noted that the thermo-physical properties and behavior of commercial grade materials are found to be very different from those quoted in the literature for laboratory grade materials (purity more than 99%). The influence of number of thermal cycles on the melting temperature and latent heat of fusion for commercial grade PCMs is thus required to be evaluated before their selection for a particular application.

Thus, the thermal stability test of PCMs should be performed prior to its actual applications. The previous literature addresses preparation, leakage, thermal conductivity and thermal storage properties of PCMs exhaustively. However, the reports on the thermal stability and/or

reliability of PCMs are found to be relatively inadequate. Till now, two major review papers are found in the literatures which emphasize the importance of thermal stability. Rathod and Banerjee [5] presents lists of PCMs for which thermal cycling test was carried out by different researchers and reported in the literature. Ferrer et al. [12] also presents a list of different PCMs undergone thermal cycling test. They also focus on the methodologies used by the different researchers, along with the equipment used and the analytical conditions in which the tests were carried out. Thus a lucid review of different low temperature PCMs for which thermal stability tests were carried out and reported in the literature is presented here.

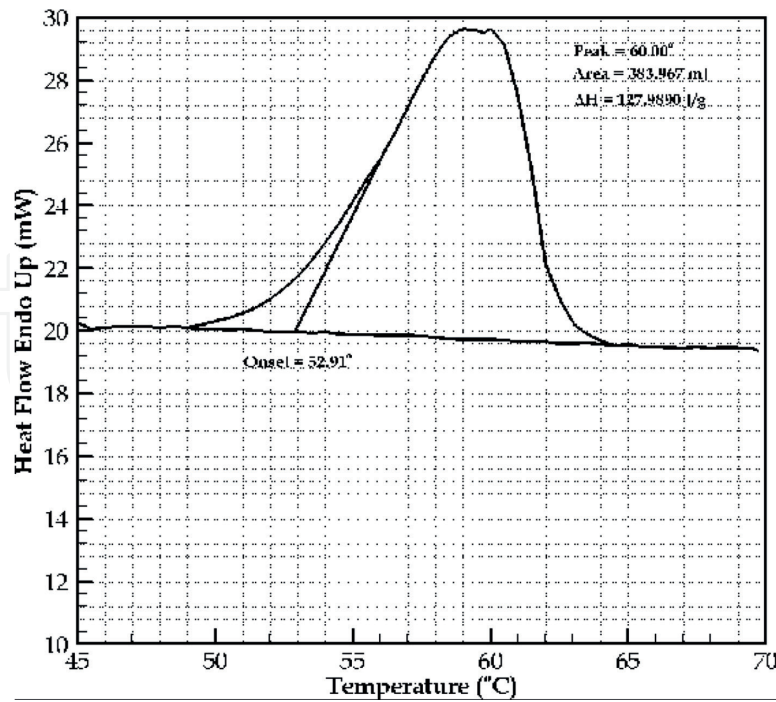
#### 4.1. Thermal stability test

A LHSU integrated with solar thermal systems undergo at least one melt/freeze thermal cycle a day, also known as normal cycle. This thermal cycle test can be established using different equipment like thermostatic chamber/bath, thermal bath, electric hot plate, constant temperature oven, etc. Other more specific equipment for thermal cycle test is thermal cyler which is most commonly used in biomedical applications [12]. Such thermal cycle tests carried out under controlled conditions in the laboratory are also known as accelerated thermal cycle tests [13, 14]. A small quantity sample of tested PCM is withdrawn after each specified number of thermal cycles for measuring the thermo-physical properties i.e. melting point and latent heat of fusion of the PCM.

The differential scanning calorimeter (DSC) is widely used in the laboratory to measure the melting temperature and heat of fusion of PCM. DSC works on a thermo-analytical principle. In this technique, the difference in the amount of heat required to raise the temperature of a sample and a reference is obtained as a function of temperature. During this process, it is required to maintain nearly the same temperature of the sample and reference. The heat capacity over the range of temperatures of a reference sample should be well-defined in prior. The alumina ( $\text{Al}_2\text{O}_3$ ) is most recommended reference material for DSC analysis of PCM [9].

During DSC analysis, heat is supplied to both the sample and reference material. The heat is provided in such a manner that the temperature of the sample and reference material is maintained constant. When the sample undergoes a physical transformation such as phase transitions, more or less amount of heat will be required by the sample than the reference material for maintaining the same temperature. The requirement of less or more heat flow to the sample depends on whether the process is exothermic or endothermic [15–17]. By observing the difference in heat flow between the sample and reference, the amount of heat absorbed or released during such transitions is established by DSC. A plot between heat flow and temperature, known as DSC curve, is then drawn. Latent heat of fusion is calculated using the area under the peak of that curve. The phase transition temperature is taken as the onset obtained by line fitting of the rising part of the peak. The phase transition range is calculated between onset temperature and temperature corresponding to the peak of the curve. This range is commonly known as the “mushy zone” during which the PCM first softens and then melts. In this way the melting point and latent heat of fusion can be obtained with the use of DSC. The observed changes in these properties after a number of repeated thermal cycles can establish the stability of the PCM.





**Figure 3.** DSC measurement of the latent heat of fusion and the melting temperature of paraffin [18].

**Figure 3** shows the DSC curve for a sample PCM, i.e. paraffin wax. The obtained temperature range of paraffin is 52.9–60.0°C. As area under the curve is 383.967 mJ and mass of sample is 3 mg, latent heat of fusion is 127.989 J/g. In order to analyze the changes in latent heat of fusion and phase transition temperature, a relative percentage difference is obtained after every specified thermal cycle, i.e. 50th or 100th. The relative percentage difference (RPD) of any property  $i$  of the PCM at any number of cycles  $n$  and the 0th cycle may be defined as [19]:

$$RPD = \frac{X_{n,i} - X_{0,i}}{X_{0,i}} \times 100(\%) \quad (1)$$

where  $X_{n,i}$  denotes to the values of onset and peak temperatures and the latent heat of the PCM after  $n$  cycles and  $X_{0,i}$  are the values of these quantities at 0th cycle. A critical review is carried out for thermal stability of different group of PCM with number of thermal cycles.

## 5. Thermal stability of PCM: a review

The thermal stability test carried out by various researchers on different groups of PCMs is discussed in this section.

### 5.1. Organic PCMs

This class of materials covers the wide range of melting temperature, i.e. between 0°C and about 200°C. The most of organic PCMs are not stable at higher temperatures because of the

covalent bonds. In most cases, the density of organic PCM is lesser than that of inorganic materials, i.e., less than  $10^3 \text{ kg/m}^3$  [10]. Therefore, organic materials usually have smaller latent heat of fusion per volume than inorganic materials. Merits and demerits of the organic PCMs are as follows [5, 8].

#### Merits

- Available in large temperature range
- High latent heat of fusion
- Less supercooling (also called self-nucleation)
- Melt and freeze repeatedly without phase segregation
- Congruent phase transition process
- High thermal stability
- Non-corrosive

#### Demerits

- Lower thermal conductivity inherently
- Lower density of material
- Least compatible with plastic containments
- Combustible
- Costly

Organic PCMs are further divided in the group of paraffins and non-paraffins.

##### 5.1.1. Paraffins

The natural paraffins are a mixture of pure alkanes, which have quite a wide range of the phase change temperature. The chemical formula of normal paraffins is  $C_n H_{2n+2}$ . They are straight chain saturated hydrocarbons with melting temperature range from 23 to 67°C. The chemical structure of paraffins is as shown in the **Figure 4**.

Paraffin wax is the most commonly used commercial organic heat storage PCM. Their volume increase upon melting is in the order of 10 vol.%. However, it is less critical because paraffins build up smaller forces upon expansion as they are softer. Paraffins are insoluble in water. They do not react with most common chemical reagents [10]. Many researchers have reported that paraffins are favorable because they are with the high heat of fusion, less supercooling and stable behavior. Paraffins are comparatively less costly and widely available. These PCMs are ecologically harmless and non-toxic [27, 28]. A list of paraffins studied by different researchers for stability test is given in **Table 2**. It can be observed that majority



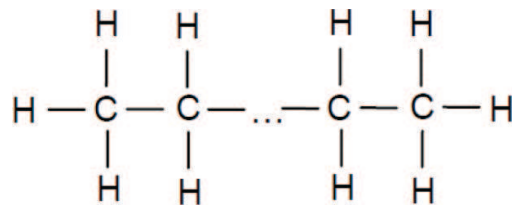


Figure 4. Chemical structure of paraffins.

Sr. no.	PCMs	Thermal cycles	Reference
1.	Paraffin (70 wt%) + Polypropylene (30 wt%)	3000	Alkan et al. [20]
2.	Paraffin (C <sub>22.2</sub> H <sub>44.1</sub> ) (technical grade)	900	Hadjieva et al. [21]
3.	Paraffin (C <sub>23.2</sub> H <sub>48.4</sub> ) (technical grade)	900	Hadjieva et al. [21]
4.	Paraffin wax 53 (commercial grade)	300	Sharma et al. [14]
		1500	Sharma et al. [22]
		1000	Silakhori et al. [23]
5.	Paraffin wax 54	1500	Shukla et al. [24]
6.	Paraffin wax 58–60	600	Shukla et al. [24]
7.	Paraffin wax 60–62	600	Shukla et al. [24]
8.	n-heptadecane/Poly methyl methacrylate (C <sub>17</sub> H <sub>36</sub> )	5000	Sari et al. [25]
9.	n-eicosane (C20)	1000	Karaipekli et al. [26]

Table 2. Thermal cycled paraffins.

of paraffins which is tested for thermal cycles are with melting temperature in the range of 45–60°C. Further, it noticed from the literature that paraffins do not degrade in their thermal properties even after number of thermal cycles.

5.1.2. Non-paraffins

Non-paraffins are the most studied and favorable PCMs for the researchers. These organic materials can be further categorized in subgroups of fatty acids and other non-paraffin organics (i.e., esters, alcohol, glycols, etc.). Due to the availability in suitable phase change temperature and high heat of fusion, fatty acids are the most potential PCM among all non-paraffins. A fatty acid is characterized by the formula CH<sub>3</sub>(CH<sub>2</sub>)<sub>2n</sub>COOH. The chemical structure of fatty acid is shown in Figure 5. Fatty acids are easily producible from common vegetable and animal oils and thus provide an assurance of continuous supply despite the shortage of fuel sources [29–33]. The fatty acids are thermally stable after repeated melting/freezing cycles because they consist of only one component there cannot be phase separation. Table 3 provides a list of non-paraffins studied for thermal stability.

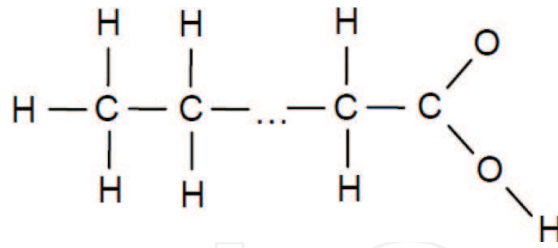


Figure 5. Chemical structure of fatty acid.

## 5.2. Thermal stability of inorganic PCMs

Inorganic materials are also available in a wide range of temperature. Inorganic materials usually have similar latent heat of fusion per mass compared to organic materials. However, latent heat of fusion per volume is higher due to their high density. Merits and demerits of the inorganic PCMs are as follows [5, 8].

### Merits

- High volumetric latent heat storage capacity
- Sharp melting point
- Low vapor pressure in the melt state
- High thermal conductivity
- Relatively low volume change
- Noncorrosive, nonreactive and nonflammable
- Better compatibility with the conventional construction materials
- Low cost and readily available

### Demerits

- Supercooling
- Low degree of nucleation
- Dehydration occurs during the phase change process
- Compatibility with some building materials is limited
- Corrosive with some metals
- Slightly toxic in nature

The family of inorganic materials includes salt hydrates and metallic PCMs.

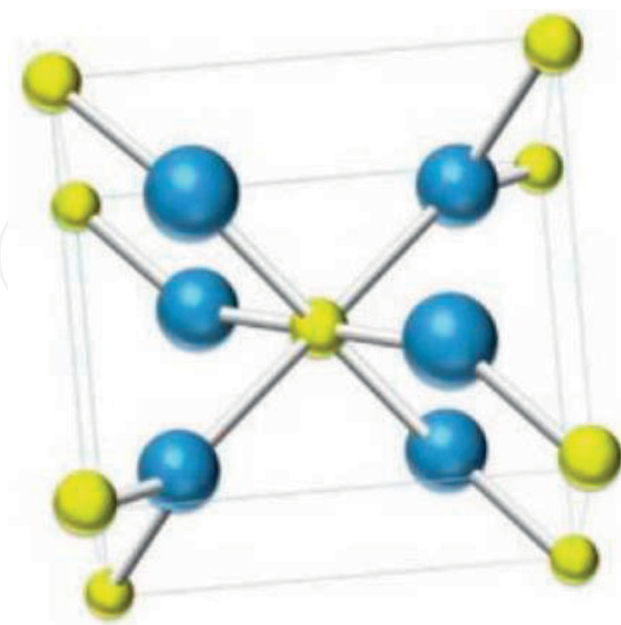
Sr. no.	PCM	Thermal cycles	Reference
1.	Acetamide (CH <sub>3</sub> CONH <sub>2</sub> )	300 1500	Sharma et al. [14] Sharma et al. [22]
2.	Acetanilide (C <sub>8</sub> H <sub>9</sub> NO)	500	El-Sebaei et al. [34]
3.	Benzamide	1000	Dheep and Shreekumar [35]
4.	Capric acid (55 wt%) + Expanded perlite (45 wt%)	5000	Sari and Karaipekli [31]
5.	Erythritol	1000	Shukla et al. [24]
6.	Lauric acid (C <sub>11</sub> H <sub>23</sub> COOH)	120 1200 910	Abhat and Malatidis [36] Sari [37] Sari and Kaygusuz [30]
7.	Methyl palmitate	50	Nikolic et al. [38]
8.	Methyl stearate	50	Nikolic et al. [38]
9.	Myristic acid (C <sub>13</sub> H <sub>27</sub> COOH)	450 1200 910	Hasan and Sayigh [39] Sari [37] Sari and Kaygusuz [30]
10.	Palmitic acid (C <sub>15</sub> H <sub>31</sub> COOH)	120 450 1200 910	Abhat and Malatidis [36] Hasan [40] Sari [37] Sari and Kaygusuz [30]
11.	Palmitic acid (80 wt%) + Expanded graphite (20 wt%)	3000	Sari and Karaipekli [32]
12.	Palmitic acid-TiO <sub>2</sub> composite	1500	Sharma et al. [41]
13.	Stearic acid (C <sub>17</sub> H <sub>35</sub> COOH)	450 300 1200 910 1500	Hasan [42] Sharma et al. [14] Sari [37] Sari and Kaygusuz [30] Sharma et al. [22]
14.	Sebacic acid	1000	Dheep and Shreekumar [35]
15.	Urea	50	Sharma et al. [43]
16.	D-mannitol 99%	50	Sole et al. [44]
17.	Myo-inositol 98%	100	Sole et al. [44]
18.	Galactitol 97%	50	Sole et al. [44]

**Table 3.** Thermal cycled non-paraffins.

### 5.2.1. Salt hydrates

The oldest group of PCMs is salt hydrates. Salt hydrates are alloys of members of the inorganic salt family (oxides, carbonates, sulfates, and nitrates) with water molecules with a specific ratio. The chemical formula for salt hydrates is  $AB \cdot nH_2O$  (salt compound). The salt hydrates show a three dimensional structure which is open enough to absorb and adjust water molecules inside the crystal lattice. **Figure 6** shows the crystal lattice of calcium chloride, which easily attracts  $H_2O$  molecules and forms calcium chloride hexahydrate.

The bonds are usually hydrogen bonds. The location and orientation of water molecules are well-defined in the structure. These types of PCMs have sharp transitions at the melt point, higher latent heats, smaller density change and have higher thermal conductivities than the organics. They have higher densities than the organics. Though these advantages, wide spread utilization are limited due to some negative attributes. The most significant issue with salt hydrates is their chemical instability. As salt hydrates consist of salt and water, there is a tendency to separate it into different phases. They lose some water content after every heating cycle. During the melting of salt hydrates dehydrated salts tend to settle out. It is called phase separation. The problem of phase separation can be eliminated to a certain extent with the use of gelled or thickened mixtures. High degree of supercooling is another major problem. They do not start to crystallize at the specified freezing point. The problem of supercooling can be eliminated with the use of suitable nucleating agents to start the crystal growth in the storage media. Regarding the compatibility with other materials, salts can be corrosive to metals. Their safety differs strongly between different salts. The volume change of salt hydrates is up to 10 vol.%. They have high thermal conductivity and low cost. Furthermore, some salts are chemically aggressive towards structural materials. Due to sharp melting point, higher



**Figure 6.** Crystal lattice of calcium chloride [10].

thermal conductivity, low cost and abundant in nature, salt hydrates have potential for heat storage applications [28]. However, less consideration has given by the researchers due to the major issues of it i.e. phase separation and supercooling. A list of salt hydrates tested by various researchers for stability along with their melting point and latent heat of fusion is shown in **Table 4**.

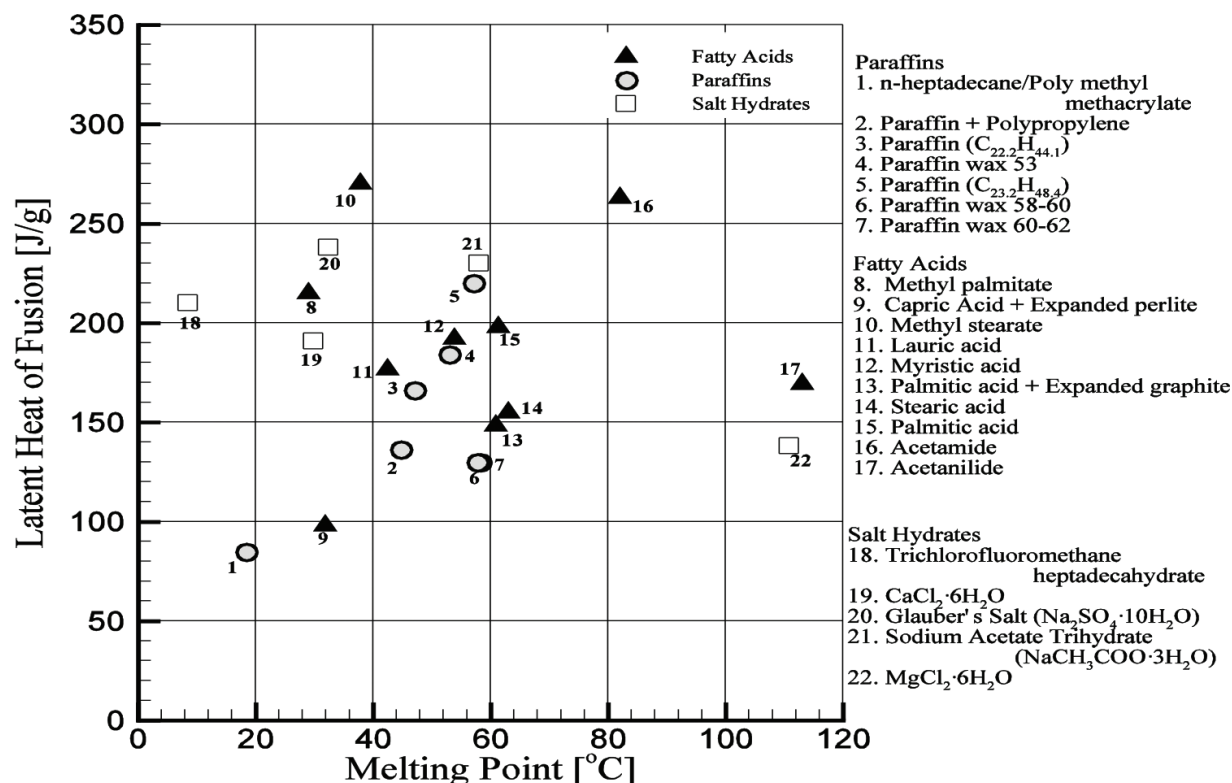
The latent heat of fusion of paraffins, fatty acids and salt hydrates whose melting temperatures are within 0–120°C is observed in **Figure 7**. It is noted that the melting temperature range of almost all PCMs is 20–60°C except acetamide, acetanilide, trichlorofluoromethane heptadecahydrate,  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ . Further, it is observed that the latent heat of fusion of these PCMs are in the range of 120–225 kJ/kg.

5.2.2. Metal alloy PCMs

This group consists of the low melting metals and metal alloys. This category of PCMs is the most underused of all the common PCM categories, perhaps due to the low latent heat and weight penalties. However, despite this, the metals exhibit the potential in certain applications where the compactness is important. This is due to the fact that it has high heat of fusion per unit volume. The metals that can be used in low temperature applications are cesium, gallium, indium, tin and bismuth, while the metals for high temperature applications include zinc, magnesium, aluminum and their alloys [10]. The researchers are attracted to these PCMs at some extend because of higher thermal conductivities and high

Sr. no.	PCMs	Thermal cycles	Reference
1.	Calcium chloride hexahydrate ( $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ )	1000	Kimura and Kai [45]
		1000	Fellchenfeld et al. [46]
		5650	Porisini [47]
		1000	Tyagi et al. [48]
2.	Glauber's salt ( $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ )	320	Marks [49]
		5650	Porisini [47]
3.	Magnesium chloride hexahydrate ( $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ )	500	El-Sebaili et al. [34]
		1000	El-Sebaili et al. [19]
4.	$\text{Na}_2\text{SO}_4 \cdot n\text{H}_2\text{O}$	1000	Ting et al. [50]
5.	$\text{Na}_2\text{SO}_4 \cdot 1/2\text{NaCl} \cdot 10\text{H}_2\text{O}$	5650	Porisini [47]
6.	$\text{NaOH} \cdot 3.5\text{H}_2\text{O}$	5650	Porisini [47]
7.	Sodium acetate trihydrate ( $\text{NaCH}_3\text{COO} \cdot 3\text{H}_2\text{O}$ )	500	Wada et al. [51]
		100	Kimura and Kai [52]
8.	Trichlorofluoromethane heptadecahydrate ( $\text{CCl}_3\text{F} \cdot 17\text{H}_2\text{O}$ )	100	Kimura and Kai [53]

**Table 4.** Thermal cycled salt hydrates.



**Figure 7.** Latent heat of fusion of paraffins, fatty acids and salt hydrates undergoing a phase transition within the temperature range 0–120°C [5].

physical and chemical stability. Sun et al. [54] established the thermal stability and corrosion characteristics of the PCM, i.e. Al–34% Mg–6% Zn alloy. The melting temperature is 454°C and latent heat of fusion is 314.4 kJ/kg. Thermal stability test was carried out for 1000 thermal cycles. The change in melting temperature of this alloy was observed in the range of 3.06–5.3°C after 1000 thermal cycles. The latent heat of fusion is also decreased only 10.98% after 1000 thermal cycles.

Sr. no.	PCM	Thermal cycles	Reference
1.	$CaCl_2 \cdot 6H_2O$ (80 mol%) + $CaBr_2 \cdot 6H_2O$ (20 mol%)	1000	Kimura and Kai [56]
2.	$CaCl_2 \cdot 6H_2O$ (93 wt%) + $Ca(NO_3)_2 \cdot 4H_2O$ (5 wt%) + $Mg(NO_3)_2 \cdot 6H_2O$ (2 wt%)	1000	Kimura and Kai [56]
3.	$CaCl_2 \cdot 6H_2O$ (96 wt%) + $KNO_3$ (2 wt%) + $KBr$ (2 wt%)	1000	Kimura and Kai [56]
4.	$CaCl_2 \cdot 6H_2O$ (96 wt%) + $NH_4NO_3$ (2 wt%) + $NH_4Br$ (2 wt%)	1000	Kimura and Kai [56]
5.	$NaCH_3COO \cdot 3H_2O$ (90 wt%) + $NaBr \cdot 2H_2O$ (10 wt%)	1000	Kimura and Kai [52]
6.	$NaCH_3COO \cdot 3H_2O$ (85 wt%) + $NaHCOO \cdot 3H_2O$ (15 wt%)	1000	Kimura and Kai [52]
7.	$Mg(NO_3)_2 \cdot 6H_2O$ (93 wt%) + $MgCl_2 \cdot 6H_2O$ (7 wt%)	1000	Nagano et al. [57]

**Table 5.** Thermal cycled inorganic eutectics.



Sr. no.	PCM	Thermal cycles	Reference
1.	Ammonium alum ( $\text{NH}_4\text{Al}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ )(15%) + ammonium nitrate ( $\text{NH}_4\text{NO}_3$ )(85%)	1100	Jotshi et al. [58]
2.	Butyl stearate (49 wt%) + Butyl palmitate (48 wt%) + Other (3 wt%)	100	Feldman et al. [59]
3.	Capric acid (65 mol%) + Lauric acid (35 mol%)	120	Dimaano and Escoto [60]
		360	Shilei et al. [61]
4.	Capric acid (73.5 wt%) + Myristic acid (26.5 wt%)	5000	Karaipekli et al. [62]
5.	Capric acid (83 wt%) + Stearic acid (17 wt%)	5000	Karaipekli et al. [63]
6.	Caprylic acid (70 wt%) + 1-dodecanol (30 wt%)	120	Zuo et al. [64]
7.	Lauric acid (66 wt%) + Myristic acid (34 wt%)	1460	Sari [65]
8.	Lauric acid (69 wt%) + Palmitic acid (31 wt%)	1460	Sari [37]
9.	Lauric acid (75.5 wt%) + Stearic acid (24.5 wt%) +	360	Sari et al. [66]
10.	Lauric acid (77.05 wt%) + Palmitic acid (22.95 wt%)	100	Zhang et al. [29]
11.	Methyl stearate (86 wt%) + Methyl palmitate (14 wt%)	50	Nikolic et al. [38]
12.	Methyl stearate (91 wt%) + Cetyl palmitate (9 wt%)	50	Nikolic et al. [38]
13.	Methyl stearate (91 wt%) + Cetyl stearate (9 wt%)	50	Nikolic et al. [38]
14.	Myristic acid (58 wt%) + Palmitic acid (42 wt%)	360	Sari et al. [66]
15.	Myristic acid (64 wt%) + Stearic acid (36 wt%)	1460	Sari [65]
16.	Myristic acid + Glycerol	1000	Sari et al. [67]
17.	Palmitic acid (64.2 wt%) + Stearic acid (35.8 wt%)	360	Sari et al. [66]
18.	Palmitic acid + Glycerol	1000	Sari et al. [67]
19.	Stearic acid + Glycerol	1000	Sari et al. [67]
20.	Tetradodecanol (53.60 wt%) + Lauric acid (46.40 wt%)	1000	Jingyu et al. [68]
21.	Tetradodecanol (71.84 wt%) + Myristic acid (28.16 wt%)	1000	Jingyu et al. [68]

Table 6. Thermal cycled organic eutectics.

5.3. Thermal stability of eutectics

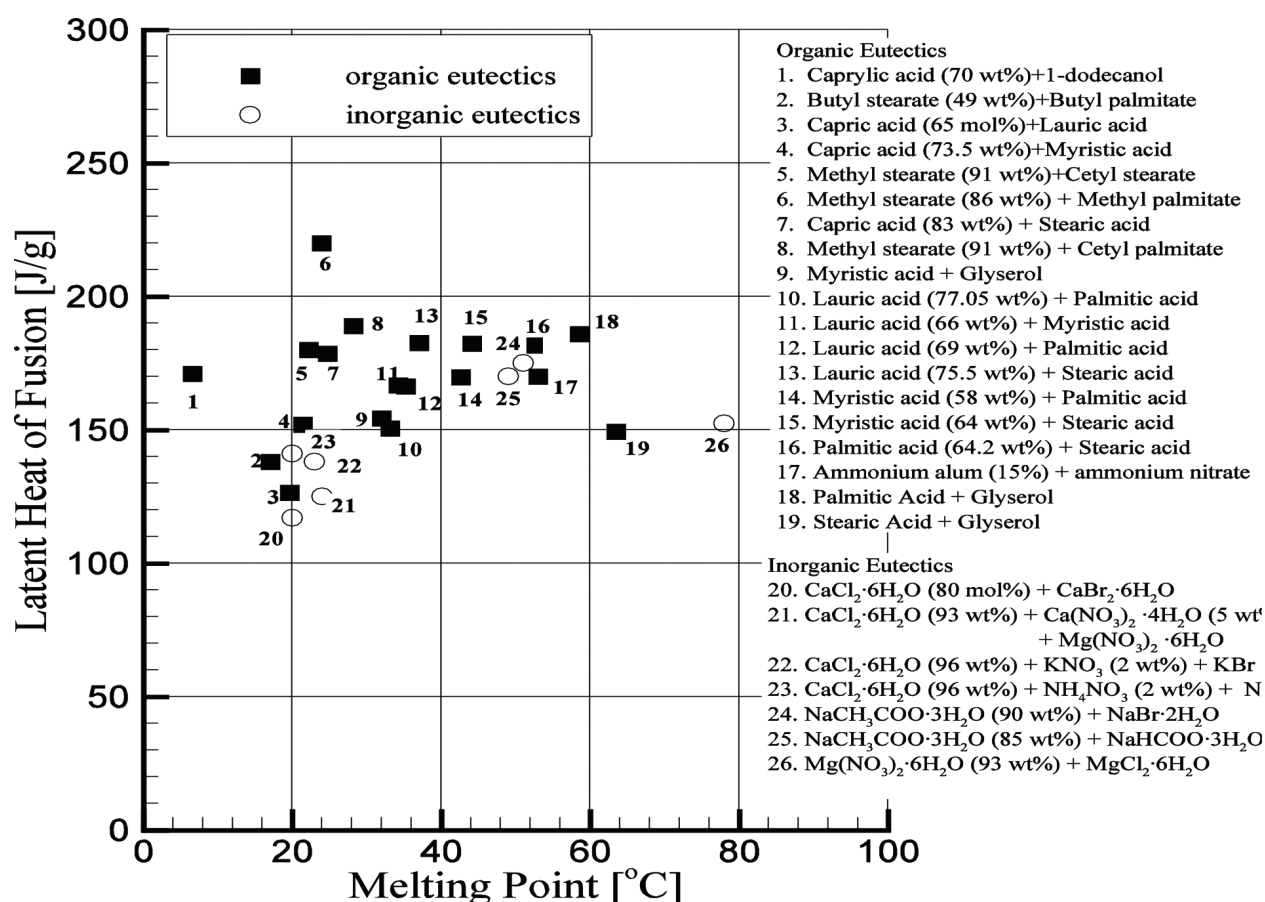
A eutectic is a congruent composition of two or more components, each of which melts and freezes as a single compound. The eutectic PCM can be a mixture of two or more compounds of either organic materials, inorganic materials or both. The mixture of these compound forms

a crystal during crystallization. They melt and freeze to an intimate mixture of crystals simultaneously without separation [55]. The primary issue with these compounds is the cost. They are two or three times costlier than organic or inorganic PCMs.

Myriad eutectics can be produced for any preferred melting point for thermal energy storage systems. However, only limited data are available on their thermo-physical properties of these eutectics as the use of these materials is very new to thermal storage applications. Some of the inorganic and organic eutectics which were produced and studied for thermal stability by earlier investigators are listed in **Tables 5** and **6** respectively.

It can be noted that the most developed eutectics proposed as PCM were tailored from fatty acids and salt hydrates respectively. The recent research is more focused to organic eutectics, considering the phase separation and super cooling issues of the salt hydrates. It is observed that the thermal stability test was carried out for most of the eutectics for at least 1000 thermal cycles.

**Figure 8** shows the latent heat of fusion of eutectics having melting temperature within a temperature range of 0–80°C. The most of the organic eutectics have melting point and latent heat of fusion are in the range of 20–60°C and 150–200 kJ/kg respectively. Also, the inorganic eutectics developed from calcium chloride hexahydrate has melting point near 20°C and latent heat of fusion below 150 kJ/kg. It can be noted that the eutectic developed from methyl stearate and methyl palmitate has higher latent heat of fusion out of all eutectics.



**Figure 8.** Latent heat of fusion per unit mass of eutectics undergoing a phase transition within the temperature range 0–100°C [5].

The equipment used to carry out thermal cycle test for different sample of PCMs are thermostatic chamber, thermal bath, electric hot plate, thermal box with heater and cooler, two thermostatic bath, etc. Most researchers have used have used thermostatic chamber setup to cycle the sample. However, there are vast varieties of equipments through which thermal cycle test will be carried out. There is no standard rule or format for selection of the equipment to conduct thermal cycles. The selection of the equipment is based on its availability, cost and rapidity of thermal cycles required.

## 6. Concluding remarks

It is required to make sure thermal stability of PCM after repeated number of thermal cycles for long term performance of latent heat energy storage unit. The PCM is most thermally stable and reliable, if the change in its thermo-physical properties, especially latent heat and melting point PCM is negligible after repeated number of thermal cycles. The following conclusions are drawn from the analysis of literature related to thermal stability of PCMs.

1. The differential scanning calorimetry (DSC) technique is the most common method to measure thermal properties of PCM i.e. melting point and latent heat of fusion. It is also noted that baring a few exception, no measurements were performed to establish the temperature dependent properties like specific heat, thermal conductivity etc. of PCMs. The thermal stability with respect to these temperature dependence parameters should also be observed after repeated number of thermal cycles.
2. It is found that most studied PCMs are those whose melting temperature and latent heat of fusion are in the range of 40–60°C and 150–225 kJ/kg respectively. However, most of the salt hydrates analyzed by the researchers has melting point near 20–30°C.
3. Paraffins are perhaps the most popular type of PCM as they are available in wide range of phase transition temperature. As paraffin melts more slowly over a wide range of temperatures, it is preferable to speak of a melt range instead of melting temperature. Fatty acids are prospective PCMs as they are produced from common vegetable and animal oils which ensure continuous supply even during shortage of fuel sources. The most analyzed fatty acids are stearic acid, lauric acid, myristic acid, capric acid and palmitic acid. It is also observed that organic PCM have better thermal stability after number of thermal cycles.
4. The major issues with the salt hydrates are phase separation and subcooling. In most cases phase separation can be overcome using a gelling additive. In order to suppress subcooling, a suitable nucleating material has to be added to the PCM to ensure that the solid phase is formed with little subcooling.
5. Many researchers focus on development of new eutectic type PCMs in spite of pure compounds since last decade. It is also observed here that almost all eutectic PCMs analyzed for thermal cycling test are made from fatty acids which give the melting temperature range and latent heat of fusion between 20 and 60°C and 150–200 kJ/kg respectively.

## Author details

Manish K. Rathod

Address all correspondence to: mkr@med.svnit.ac.in

Department of Mechanical Engineering, Sardar Vallabhbhai National Institute of Technology (SV NIT), Surat, Gujarat, India

## References

- [1] Dincer I, Rosen MA. Thermal Energy Storage Systems and Applications. 2nd ed. United Kingdom: John Wiley and Sons Ltd; 2002
- [2] Kaygusuz K. The viability of thermal energy storage. *Energy Sources*. 1999;**21**:745-755
- [3] Farid MM, Khudhair AM, Siddique AK, Sari A. A review on phase change energy storage: Materials and applications. *Energy Conversion and Management*. 2004;**45**:1597-1615
- [4] Sharma A, Tyagi V, Chen CR, Buddhi D. Review on thermal energy storage with phase change materials and applications. *Renewable and Sustainable Energy Reviews*. 2009; **13**(2):318-345
- [5] Rathod MK, Banerjee J. Thermal stability of phase change materials used in latent heat energy storage systems: A review. *Renewable and Sustainable Energy Reviews*. 2013; **18**:246-258
- [6] Telkes M, Raymond E. Storing solar heat in chemicals—A report on the Dover house. *Heat Vent*. 1949;**46**(11):80-86
- [7] Abhat A. Low temperature latent heat thermal energy storage: Heat storage materials. *Solar Energy*. 1983;**30**(4):313-331
- [8] Kalaiselvam, Parameshwaran. Thermal Energy Storage Technologies for Sustainability. Elsevier Inc; 2014
- [9] Cabeza LF. Advances in Thermal Energy Storage Systems: Methods and Applications. Woodhead Publishing Series in Energy: Number 66. Elsevier Inc; 2015
- [10] Fleischer AS. Thermal energy storage using phase change materials. In: SpringerBriefs in Thermal Engineering and Applied Science. 2015
- [11] Kenisarin M, Mahkamov K. Solar energy storage using phase change material. *Renewable and Sustainable Energy Reviews*. 2007;**11**(9):1913-1965
- [12] Ferrer G, Sole A, Barreneche C, Martorell I, Cabeza LF. Review on the methodology used in thermal stability characterization of phase change materials. *Renewable and Sustainable Energy Reviews*. 2015;**50**:665-685

- [13] Buddhi D, Sawhney RL. In: Proceedings on Thermal Energy Storage and Energy Conversion; 1994
- [14] Sharma SD, Buddhi D, Sawhney RL. Accelerated thermal cycle test of latent heat storage materials. *Solar Energy*. 1999;**66**(6):483-490
- [15] Dean JA. *The Analytical Chemistry Handbook*. New York: McGraw Hill, Inc; 1995. pp. 15.1-15.5
- [16] Pungor EA. *Practical Guide to Instrumental Analysis*. Boca Raton, Florida; 1995. pp. 181-191
- [17] Skoog DA, Holler FJ, Timothy N. *Principles of Instrumental Analysis*. 5th ed. New York; 1998. pp. 805-808
- [18] Rathod MK, Banerjee J, Chaudhari VN. Thermal reliability of stearic acid as phase change material used in latent heat storage. In: *International Conference on Advances and Trends in Engineering Materials and their Applications*; Montreal, Canada; 2011
- [19] El-Sebaai AA, Al-Heniti S, Al-Ghamdi AA, Al-Marzouki F. One thousand thermal cycles of magnesium chloride hexahydrate as a promising PCM for indoor solar cooking. *Energy Conversion and Management*. 2011;**52**:1771-1777
- [20] Alkan C, Kaya K, Sari A. Preparation, thermal properties and thermal reliability of form-stable paraffin/polypropylene composite for thermal energy storage. *Journal of Polymers and the Environment*. 2009;**17**:254-258
- [21] Hadjieva M, St K, Argirov J. Thermophysical properties of some paraffins applicable to thermal energy storage. *Solar Energy Materials and Solar Cells*. 1992;**27**:181-187
- [22] Sharma A, Sharma SD, Buddhi D. Accelerated thermal cycle test of acetamide, stearic acid and paraffin wax for solar thermal latent heat storage applications. *Energy Conversion and Management*. 2002;**43**:1923-1930
- [23] Silakhori M, Naghavi MS, Metselaar HSC, Mahlia TMI, Fauzi H, Mehrali M. Accelerated thermal cycling test of microencapsulated paraffin wax/polyaniline made by simple preparation method for solar thermal energy storage. *Materials*. 2013;**6**:1608-1620
- [24] Shukla A, Buddhi D, Sawhney RL. Thermal cycling test of few selected inorganic and organic phase change materials. *Renewable Energy*. 2008;**33**:2606-2614
- [25] Sari A, Eroglu R, Biçer A, Karaipekli A. Synthesis and thermal energy storage properties of erythritol tetrastearate and erythritol tetrapalmitate. *Chemical Engineering and Technology*. 2011;**34**(1):87-92
- [26] Karaipekli A, Bicer A, Sari A, Tyagi VV. Thermal characteristics of expanded perlite/paraffin composite phase change material with enhanced thermal conductivity using carbon nanotubes. *Energy Conversion and Management*. 2017;**134**:373-381
- [27] Hasnain S. Review on sustainable thermal energy storage technologies. Part I: Heat storage materials and techniques. *Energy Conversion and Management*. 1999;**39**:1127-1138



- [28] Zalba B, Marin JM, Cabeza LF, Mehling H. Review on thermal energy storage with phase change: Materials, heat transfer analysis and applications. *Applied Thermal Engineering*. 2003;**23**:251-283
- [29] Zhang JJ, Zhang JL, He SM, Wu KZ, Liu XD. Thermal studies on the solid-liquid phase transition in binary systems of fatty acids. *Thermochimica Acta*. 2001;**369**:157-160
- [30] Sari A, Kaygusuz K. Some fatty acids used for latent heat storage: Thermal stability and corrosion of metals with respect to thermal cycling. *Renewable Energy*. 2003;**28**:939-948
- [31] Sari A, Karaipekli A. Preparation, thermal properties and thermal reliability of capric acid/expanded perlite composite for thermal energy storage. *Materials Chemistry and Physics*. 2008;**109**:459-464
- [32] Sari A, Karaipekli A. Preparation, thermal properties and thermal reliability of palmitic acid/expanded graphite composite as form-stable PCM for thermal energy storage. *Solar Energy Materials and Cells*. 2009;**93**:571-576
- [33] Zalba B, Marin JM, Cabeza LF, Mehling H. Free-cooling of buildings with phase change materials. *International Journal of Refrigeration*. 2003;**27**:839-849
- [34] El-Sebaai AA, Al-Amir S, Al-Marzouki FM, Faidah AS, Al-Ghamdi AA, Al-Heniti S. Fast thermal cycling of acetanilide and magnesium chloride hexahydrate for indoor solar cooking. *Energy Conversion and Management*. 2009;**50**:3104-3111
- [35] Dheep GR, Shreekumar A. Influence of accelerated thermal charging and discharging cycles on thermo-physical properties of organic phase change materials for solar thermal energy storage applications. *Energy Conversion and Management*. 2015;**105**:13-19
- [36] Abhat A, Malatidis NA. Determination of properties of heat of fusion storage materials for low temperature applications. In: 1st IEA Conference on New Energy Conservation Technologies and their Commercialisation; Berlin, FRG: Springer; 1981
- [37] Sari A. Thermal reliability test of some fatty acids as PCMs used for solar thermal latent heat storage applications. *Energy Conversion and Management*. 2005;**44**:2277-2287
- [38] Nikolic R, Marinovic-Cincovic M, Gadzuric S, Zsigrai JJ. New materials for solar thermal storage solid/liquid transitions in fatty acid esters. *Solar Energy Materials & Solar Cells*. 2003;**79**:285-292
- [39] Hasan A, Sayigh AA. Some fatty acids as phase-change thermal energy storage materials. *Renewable Energy*. 1994;**4**(1):69-76
- [40] Hasan A. Phase change material energy storage system employing palmitic acid. *Solar Energy*. 1994;**52**(2):143-154
- [41] Sharma RK, Ganesh P, Tyagi VV, Metselaar HSC, Sandaran SC. Thermal properties and heat storage analysis of palmitic acid-TiO<sub>2</sub> composite as nano-enhanced organic phase change material (NEOPCM). *Applied Thermal Engineering*. 2016;**99**:1254-1262
- [42] Hasan A. Thermal energy storage system with stearic acid as phase change material. *Energy Conversion and Management*. 1994;**35**(10):843-856



- [43] Sharma A, Sharma SD, Buddhi D, Sawhney RL. Thermal cycle test of urea for latent heat storage applications. *International Journal of Energy Resources*. 2001;**25**:465-468
- [44] Solé A, Neumann H, Niedermaier S, Martorell I, Schossig P, Cabeza LF. Stability of sugar alcohols as PCM for thermal energy storage. *Solar Energy Materials & Solar Cells*. 2014;**126**:125-134
- [45] Kimura H, Kai J. Phase change stability of  $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ . *Solar Energy*. 1984;**33**(1):49-55
- [46] Fellchenfeld H, Sarig S. Calcium chloride hexahydrate: A phase-changing material for energy storage. *Industrial and Engineering Chemistry Product Research and Development*. 1985;**24**:130-133
- [47] Porosini FC. Salt hydrates used for latent heat storage: Corrosion of metals and reliability of thermal performance. *Solar Energy*. 1988;**41**:193-197
- [48] Tyagi VV, Buddhi D. Thermal cycle testing of calcium chloride hexahydrate as a possible PCM for latent heat storage. *Solar Energy Materials & Solar Cells*. 2008;**92**(8):891-899
- [49] Marks S. An investigation of the thermal energy storage capacity of Glauber's salt with respect to thermal cycling. *Solar Energy*. 1980;**25**:225-258
- [50] Ting KC, Giannakakos PN, Gilbert SG. Durability of latent heat storage tube-sheets. *Solar Energy*. 1987;**39**(2):79-85
- [51] Wada T, Yamamoto R, Matsuo Y. Heat storage capacity of sodium acetate trihydrate during thermal cycling. *Solar Energy*. 1984;**33**(3/4):373-375
- [52] Kimura H, Kai J. Phase change stability of sodium acetate trihydrate and its mixtures. *Solar Energy*. 1985;**35**(6):527-534
- [53] Kimura H, Kai J. Feasibility of trichlorofluoromethane ( $\text{CCl}_3\text{F}$ , R11) heptadecahydrate as a heat storage material. *Energy Conversion and Management*. 1985;**25**(2):179-186
- [54] Sun JQ, Zhang RY, Liu ZP, Lu GH. Thermal reliability test of Al-34%Mg-6%Zn alloy as latent heat storage material and corrosion of metal with respect to thermal cycling. *Energy Conversion and Management*. 2007;**48**(2):619-624
- [55] Lane GA. Phase change thermal storage materials. In: Guyer C, editor. *Hand Book of Thermal Design*. McGraw Hill Book Co; 1981
- [56] Kimura H, Kai J. Mixture of calcium chloride hexahydrate with some salt hydrates or anhydrous salts as latent heat storage materials. *Energy Conversion and Management*. 1988;**28**(3):197-200
- [57] Nagano K, Ogawa K, Mochida T, Hayashi K, Ogoshi H. Thermal characteristics of magnesium nitrate hexahydrate and magnesium chloride hexahydrate mixture as a phase change material for effective utilization of urban waste heat. *Applied Thermal Engineering*. 2004;**24**(2-3):221-232
- [58] Jotshi CK. Thermal storage in ammonium alum/ammonium nitrate eutectic for solar space heating applications. *Solar Energy Engineering*. 1998;**120**:20-24

- [59] Feldman D, Banu D, Hawes D, Ghanbari E. Obtaining an energy storing building material by direct incorporation of an organic phase change material in gypsum board. *Solar Energy Materials*. 1991;**22**:231-242
- [60] Dimaano M, Escoto A. Preliminary assessment of a mixture of capric acid and lauric acids for low-temperature thermal energy storage. *Energy*. 1998;**23**:421-427
- [61] Shilei L, Neng Z, Guohui F. Eutectic mixture of capric acid and lauric acid applied in building wallboards for heat energy storage. *Energy and Buildings*. 2006;**38**:708-711
- [62] Karaipekli A, Sari A. Capric-myristic acid/expanded perlite composite as form-stable phase change material for latent heat thermal energy storage. *Renewable Energy*. 2008;**33**:2599-2605
- [63] Karaipekli A, Sari A, Kaygusuz K. Thermal properties and thermal reliability of capric acid/stearic acid mixture for latent heat thermal energy storage. *Energy Sources, Part A: Recovery, Utilization, and Environmental Effects*. 2009;**31**:199-207
- [64] Zuo J, Li W, Weng L. Thermal performance of caprylic acid/ 1-dodecanol eutectic mixture as phase change material (PCM). *Energy and Buildings*. 2011;**43**:207-210
- [65] Sari A. Eutectic mixtures of some fatty acids for low temperature solar heating applications: Thermal properties and thermal reliability. *Applied Thermal Engineering*. 2005;**25**: 2100-2107
- [66] Sari A, Sari H, Onal A. Thermal properties and thermal reliability of eutectic mixtures of some fatty acids as latent heat storage materials. *Energy Conversion and Management*. 2004;**45**:365-376
- [67] Sari A, Bicer A, Karaipekli A, Alkan C, Karadag A. Synthesis, thermal energy storage properties and thermal reliability of some fatty acid esters with glycerol as novel solid-liquid phase change materials. *Solar Energy Materials & Solar Cells*. 2010;**94**:1711-1715
- [68] Jingyu H, Shilei L, Xiangfei K, Shangbao L, Yiran I. Form stable phase change material based on eutectic mixture of tetradecanol and fatty acids for building energy storage: Preparation and performance analysis. *Materials*. 2013;**6**:4758-4775

