

ADVANCED REVIEW

A review of phase change materials and heat enhancement methodologies

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Abstract

Phase change materials (PCMs) are an efficient alternative to store and release heat at a specific range of temperature. Here PCMs and heat enhancement methodologies for PCM storage are reviewed. A short overview of PCMs and their applications is presented in addition to the progress during the last 10 years. Heat enhancement techniques, that is, extended surfaces, multiple and composite PCMs, and encapsulation techniques, are presented along with a statistical overview of studies during 2016–2021. The importance of various fin and storage tank geometries (extended surfaces) is discussed in detail. Advancement in the latest heat enhancement techniques such as use of nano-enhanced PCMs is presented. Recommendations for future research are provided.

This article is categorized under:

Emerging Technologies > Energy Storage
Sustainable Energy > Energy Efficiency

KEYWORDS

fin geometry, heat enhancement, NePCMs, phase change materials

1 | INTRODUCTION

Modern societies heavily rely on energy. Future primary energy consumption may rise by 48% by 2040 (European Commission, 2016). As most of the energy still originates from fossil fuels, the environmental consequences such as global warming will be adverse (Z. Ge et al., 2014). Major efforts and even paradigmatic technology changes will be necessary to reduce the carbon emissions (Sieminski, 2013). Thermal energy, which constitutes the major final energy form, can act as a bridge between the primary and secondary energy sources which is depicted in Figure 1 (Z. Ge et al., 2014; Yongliang et al., 2013). Actually, 90% of the global energy budget relates to heat conversion, transmission, and storage.

Thermal energy storage (TES) systems that store energy by heating or cooling of a storage medium are a useful mean to match demand and supply and also improve the efficiency of the energy processes (Sarbu & Sebarhievici, 2018). Latent heat storage (LHS) employing phase change materials (PCMs) can operate at a constant temperature of charging and discharging and have higher energy density than sensible heat storage (SHS) systems (Crespo et al., 2019). PCMs have a wide temperature range of solidification and melting and hence can be used in many applications such as in spacecraft thermal control, solar engineering, heating, and cooling of buildings (A. Sharma et al., 2009). The choice of PCM for an application is based on its latent heat of fusion, melting temperature, and

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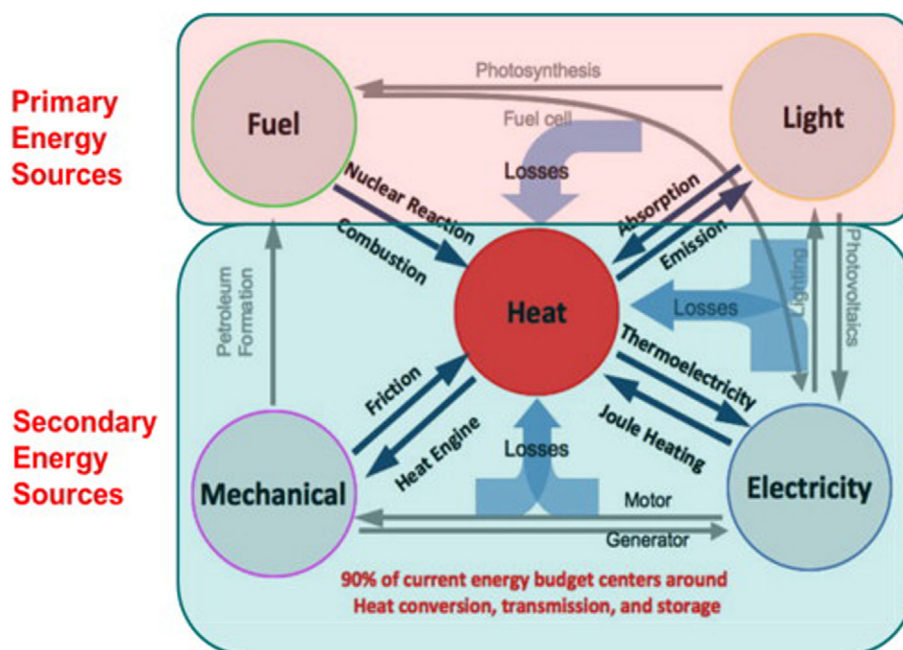


FIGURE 1 Thermal energy at the heart of energy chain. Reprinted with permission from Z. Ge et al. (2014) and Yongliang et al. (2013), Copyright©, Elsevier

thermo-physical properties (Sarbu & Sebarchievici, 2018), but it is hard to find a PCM that has all the requisite properties for an application. One major drawback of PCMs is their low thermal conductivity. Corrosive behavior, thermal instability at high temperatures, phase segregation, and super-cooling of PCMs are other challenges with PCM (P. Tan et al., 2020). New developments could enhance the efficiency of PCMs such as the use of biodegradable PCM, for example, coconut oil and fatty acids, because of their sustainable and nontoxic behavior, and abundance (Andrzejczyk et al., 2021). Hybrid techniques are also used, for example, composite PCMs, extended surfaces, PCM encapsulation, and multiple PCMs having different melting points to enhance the efficiency of TES (Hu et al., 2015). Though several studies have addressed these challenges, enhancement techniques and their recent advancements have been poorly reviewed which is also subject to the present review.

This review will focus on the significance of PCMs in different applications including the enhancement techniques. In Section 2, use of PCMs in different applications will be discussed along with a statistical overview of research work done on PCMs during the last decade (2016–2021). A brief review of the heat transfer enhancement techniques will be discussed in Section 3 including a statistical analysis of work done on different enhancement techniques. Future research recommendations will be proposed in Section 4.

2 | PCMs AND APPLICATIONS

In a LHTES system, storage capacity and operating temperature are primarily determined by PCMs heat of fusion and temperature, respectively. Therefore, it is critical to select a suitable PCM for application desired. Accurate data on thermophysical properties of PCMs such as, melting and solidification temperature, heat capacity, heat of fusion, thermal stability, and volumetric expansion, is also very crucial for LHTES system design. Access to an accurate and up-to-date literature could be a key catalyst in advancement of LHTES system. In respect of temperature, many researchers have reviewed the applications of PCMs on different ranges of temperature, for example, Kasaeian et al. (2017) focused on review of nano-PCMs from 10 to 40°C for heating, cooling, and air-conditioning applications in buildings. Oró et al. (2012) analyzed the applications of PCMs below 20°C while Liu et al. (2012) reviewed TES systems for high-temperature range up to 300°C in concentrated solar thermal power plants. Agyenim et al. (2010) mapped all three aspects of study on PCMs; theoretical, numerical, and experimental studies on different temperature ranges for each application, that is, 0–65°C for domestic cooling and heating, 80–120°C for absorption cooling, and above 150°C for direct steam electricity generation. Du et al. (2018) later reviewed the applications of PCMs for heating, cooling, and electricity generation on four

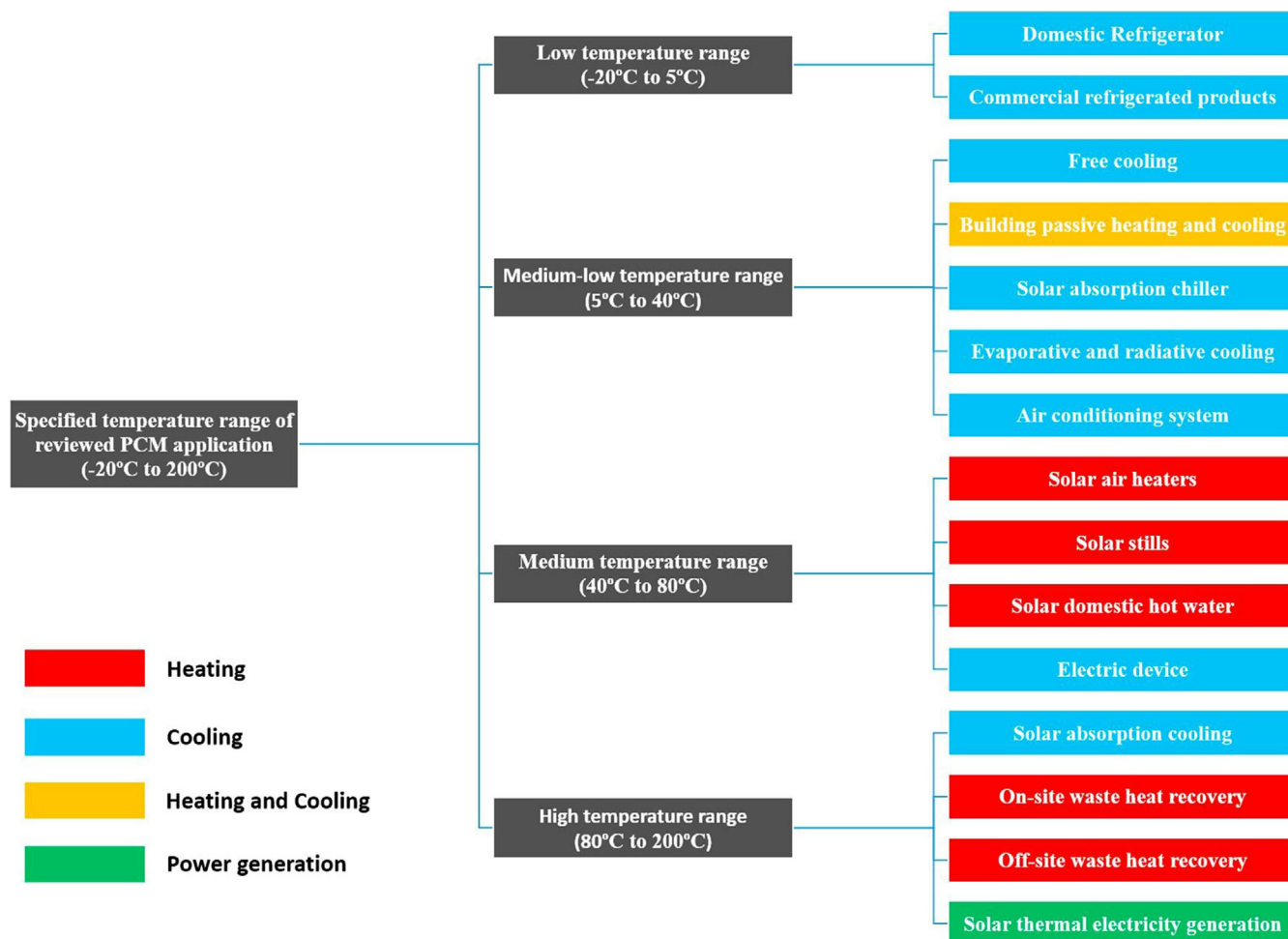


FIGURE 2 Temperature-based review of PCMs applications. Reprinted with permission from Du et al. (2018), Copyright©, Elsevier

temperature scales as shown in Figure 2 (Du et al., 2018). Their study classified -20 to 5°C as low-temperature range for refrigerated products (commercial and domestic), while building passive cooling and heating, solar absorption chiller, radiative cooling as well as evaporative, air conditioning systems, and free cooling applications in the medium low-temperature range 5 – 40°C . Medium temperature range is 40 – 80°C as for the PCMs applications in solar energy like solar stills, solar air heaters, and domestic solar hot water systems, and 80 – 200°C as the high-temperature range for applications of PCMs in solar absorption cooling, solar thermal electricity, offsite, and on-site waste heat recovery.

On the other hand, when considering kinds of PCMs, used in different applications and at different temperature range, literature suggests PCMs such as paraffin, easter, acid facts, and alcohols (Letcher, 2016). In organic PCMs, numerous studies on applications of paraffins available at large temperature range, that is, 5 – 80°C (A. Sharma et al., 2009) have been carried out by many researchers like Manoj Kumar et al. (2020) and Al-Yasiri and Szabó (2021). While non-paraffin organic PCMs' characteristics and applications were also discussed and reviewed, for example, fatty acids by Yuan et al. (2014) and sugar alcohols by del Barrio et al. (2017) and Gunasekara et al. (2016). Inorganic PCMs are widely used in solar applications with high-temperature range. However, freezing at low temperatures and being difficult to deal with at high temperatures is one of the key hindrances to their performance (Sarbu & Sebarchievici, 2018). On the other hand, eutectic PCMs are prepared by combining two or more materials with congruent melting and freezing points. They have high densities and thermal conductivity, and their melting and freezing are mostly observed without segregation. Desired melting point of eutectic PCMs can be acquired using different weight ratios of parent materials (A. Sharma et al., 2009).

Moreover, on the temperature criteria of PCMs, almost all TES systems use PCMs from a defined range of temperature that is suitable to optimize the thermal performance of TES systems in a given application (R. K. Sharma et al., 2015). Table 1 (Punniakodi & Senthil, 2021; Senthil, 2020) and Figure 3 (H. Ge et al., 2013) depict a melting temperature-based classification, depending on the application desired. However, the cheapest and readily available

TABLE 1 Classification of PCMs

Types of PCMs	Melting temperature range (°C)	Commonly used PCMs	Thermal conductivity (W/mK)	Latent heat (J/g)	Density (kg/m ³)	References
Organic	−50 to 200	Paraffin wax, fatty acids, esters, sugar alcohols	0.1–0.3	80–400	600–1500	(Gil et al., 2018; Kabbara et al., 2018; Kenisarin, 2010; Khan & Khan, 2017; Mehling & Cabeza, 2008; Tian & Zhao, 2013; Yagci et al., 2019)
Inorganic	10–900	Salt hydrates, nitrates, chlorides, metallics	0.3–1.0	90–300	700–1600	(Anish et al., 2019; Barreneche et al., 2019; H. Ge et al., 2013; Joybari et al., 2019; Kabbara et al., 2018; Kenisarin, 2010; Khan & Khan, 2017; Mehling & Cabeza, 2008; Raul et al., 2018; Tian & Zhao, 2013; Yagci et al., 2019)
Eutectic	10–600	KNO ₃ –NaNO ₃ , LiNO ₃ –KNO ₃ , MgCl ₂ –KCl–NaCl	0.3–0.7	120–375	600–1450	(Kenisarin, 2010; Z. Li et al., 2020; Mehling & Cabeza, 2008; Senthil, 2020; Tao et al., 2017; Tian & Zhao, 2013)

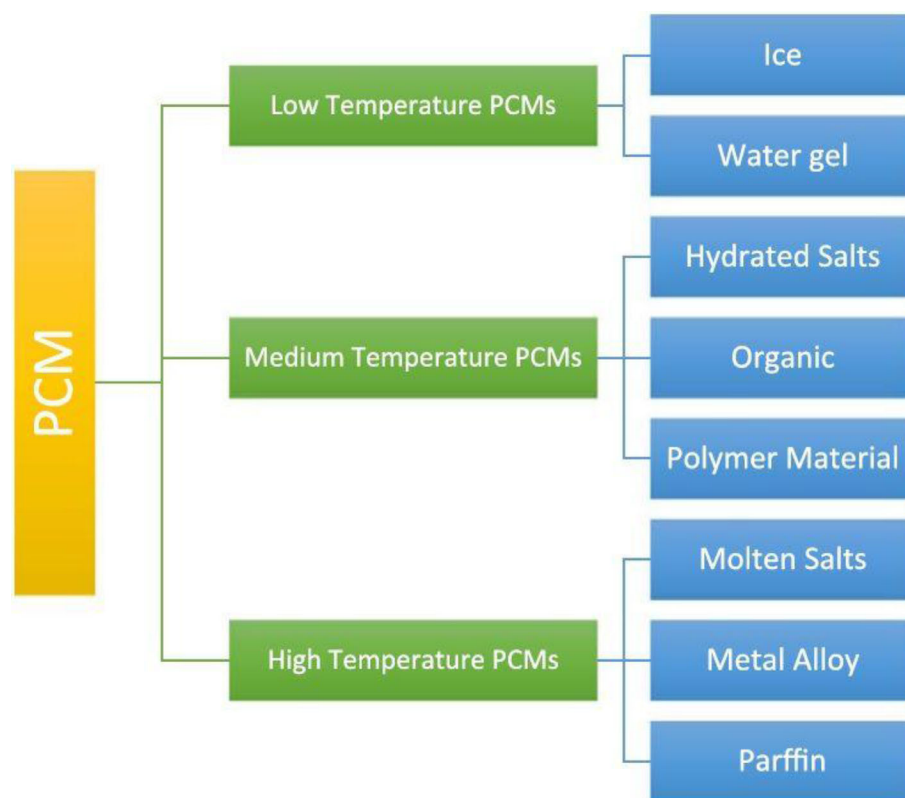


FIGURE 3 Categories of PCM based on melting point. Reprinted with permission from H. Ge et al. (2013), Copyright©, Elsevier

commercially are raw materials like animals and organic fats, for example, coconut oil which is known as biodegradable PCMs. Coconut oil is available in the marketplace as virgin coconut oil and refined coconut oil. Both have a good shelf life (2 years for virgin oil and 5 years for refined one; Jayadas & Nair, 2006). What is more important is that these substances are nontoxic, mostly sustainable, and abundant in nature. It should be stressed that the coconut palm can absorb and use saltwater during growth (Chan & Elevitch, 2006). Kong et al. (2021) investigated the application of biodegradable PCMs on *Lentinus edodes* storage and concluded that biodegradable PCMs enhanced the storage life and

quality of *Lentinus Edodes* as compared to other commercial PCMs. Polylactic acid (PLA) framework-based PCMs has multi-dimensional applications, for example, packaging (Mincheva et al., 2014), biomedical industry (Sabzi et al., 2013) to engineering industries (Deoray & Kandasubramanian, 2017), as an adsorbents in the environmental sector (Matsuzawa et al., 2010), plasticulture (Kasirajan & Ngouajio, 2012), and also as denitrification-assisting materials (Boley et al., 2000). They are used widely because PLA is a versatile aliphatic biodegradable polyester macromolecule and also because of their multitudinous characteristics (Prajapati & Kandasubramanian, 2019) like biodegradability, biocompatibility, nontoxic monomer from renewable sources, good mechanical, optical and physical attributes, and exceptional structural tendency as compared to petro-based polymers (Garlotta, 2019).

Oktaý and Kayaman-Apohan (2021) prepared polyethylene glycol (PEG)/octadecanoyl polyurethane which served as PCM, and it can improve the heat storage capacity of many polymeric materials. Therefore, the prepared bio-based PCMs have considerable potential applications such as temperature control, smart textile, and smart heat storage systems. Qiu et al. (2020) discussed the role of biodegradable PCM and fatty alcohol for controlled release applications like cancer treatment. Entürk et al. (2011) prepared and characterized PEG/cellulose, PEG/agarose, and PEG/chitosan blends as form/stable PCMs for latent heat energy storage. They concluded that prepared shape-stabilized PCM blends had suitable phase change temperatures, latent heat, good thermal reliability, and chemical stability for latent heat energy storage in solar space heating and ventilating applications in buildings.

Biobased PCMs are prepared by using underutilized raw materials, that is, soybean oil, palm oils, coconut oil, and beef tallow. There is yet not much scrutinization done of these, but these are very economical. They have remarkable potential for confinement along with durability in the melting temperature range of -22°C to 77°C for variegated appliances (Kang et al., 2015). However, poor thermal conductivity is a major hindrance to their application. For said reason, Kim and co-workers used different mass fractions of carbon nanotubes and exfoliated graphene nanoplatelets for enhancing the thermal conductivity of biobased PCMs. They recorded a significant percentage of hike about 200%–300% for different mass fractions (S. Yu et al., 2014).

Although, a lot of research is being done up till now to study the different kinds of PCMs for different applications and few of them are discussed above. However, because of remarkable characteristics and significance role of biodegradable PCMs in many applications and existing problems, it is still required to do investigation on reliability and practicability of TES using biodegradable PCMs.

2.1 | Comparative analysis

In the past decade, many researchers studied the PCMs and their role in heat transfer using numerical, experimental, and analytical approaches. We extracted some data from “web of science” (Web of Science, n.d.) to give a simple overview of research work done on PCMs.

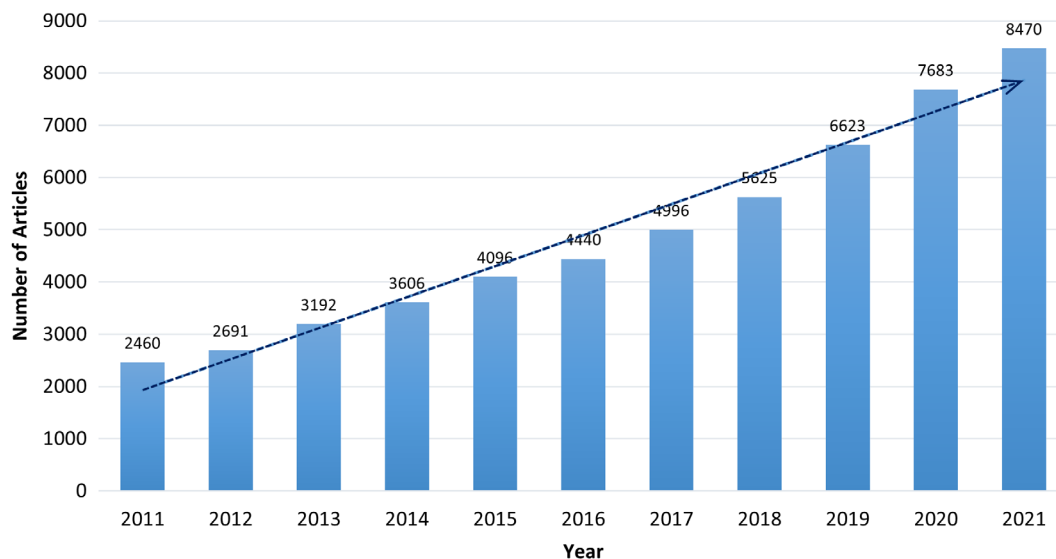


FIGURE 4 Number of articles published on PCMs (2011–2021)

Figure 4 shows the data from yearly publications. This data is extracted from “web of science” using key word “phase change materials.” Trend shown in Figure 4 is a clear indication of researcher’s inclination toward PCMs. Whereas Figures 5 and 6 give us a further insight (year-wise) about each approach in the past decade. Data provided in Figures 5–7 is also taken from “web of science” using key phrases “numerical investigation of phase change materials,” “experimental investigation of phase change materials,” and “analytical study of phase change materials”, for the numerical, experimental, and analytical approaches, respectively.

Figure 5 gives us an overview of yearly publications for each approach while Figure 6 presents the trend of research for each approach throughout the past decade, that is, 2011–2021. It can be seen clearly in Figure 6 that experimental work remains way ahead throughout the decade as compared to numerical and analytical work. Whereas analytical approach was studied more or equal up to 2016 as compared to numerical approach. However, after 2016 researchers inclined more toward numerical investigation than analytical. Figure 7 represents the proportional division of work done to study PCMs using different approaches as validation of Figure 6. Therefore, given data stress on numerical and analytical work parallel to experimental work to get better understanding of PCM.

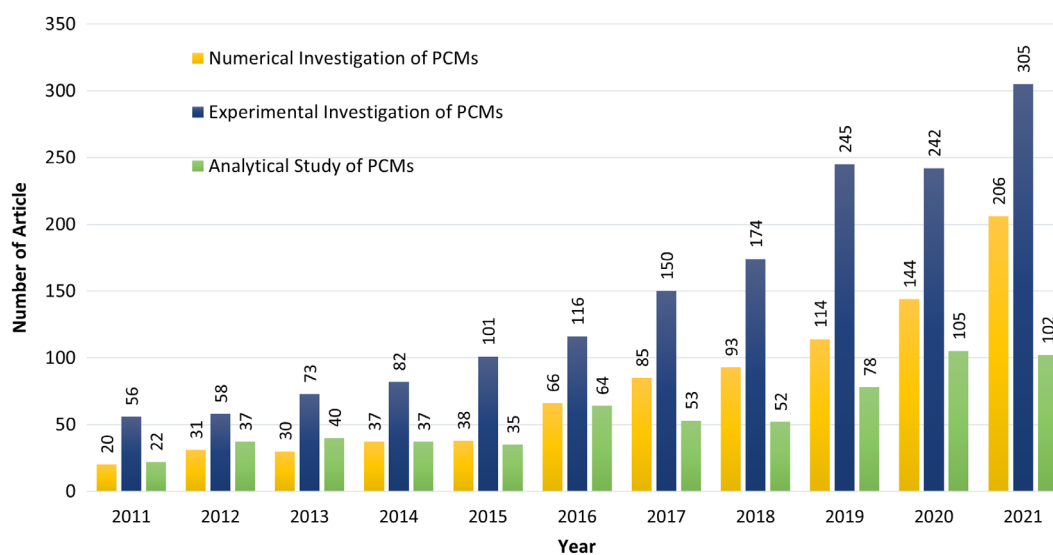


FIGURE 5 Year-wise number of publications of different approaches used to study PCMs (2011–2021)

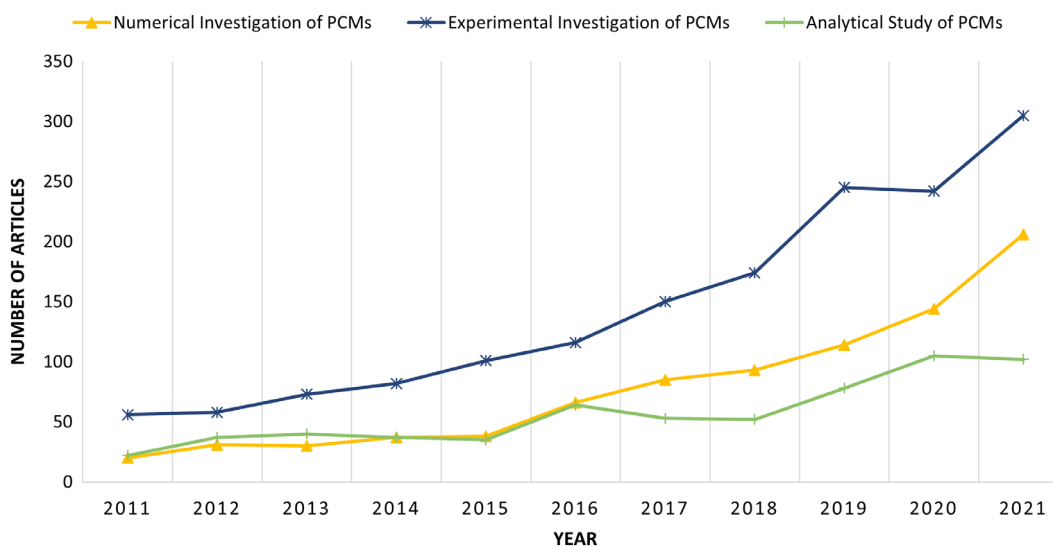


FIGURE 6 Publication trend of different approaches used to study PCMs (2011–2021)

3 | HEAT TRANSFER ENHANCEMENT

Low thermal conductivity is a major reason for poor performance of many PCMs in LHS systems. Heat transfer rate from heat transfer fluid (HTF) to PCMs decreases because of low thermal conductivity, which consequently causes the decrease in energy storage and release capacity. It also increases the melting and solidification process completion time. Many studies have been conducted numerically, analytically, and experimentally to capitalize on the heat enhancement. There are many techniques introduced by researchers to cope with this challenge, namely, composite PCMs, multiple PCMs, extended surface, and encapsulation. All of the above-mentioned techniques are reviewed in this section. However, a new heat enhancement technique based on Nanoparticles (NPs) will also be reviewed as recent advances. Before a short discussion of these techniques, we will discuss a quantitative overview of work done on heat enhancement from 2016 to 2021. This data is also collected from “web of science” (Web of Science, n.d.) using simple key words of heat enhancement techniques i.e., composite PCMs, multiple PCMs, extended surface, encapsulation technique, and nano-enhanced PCMs.

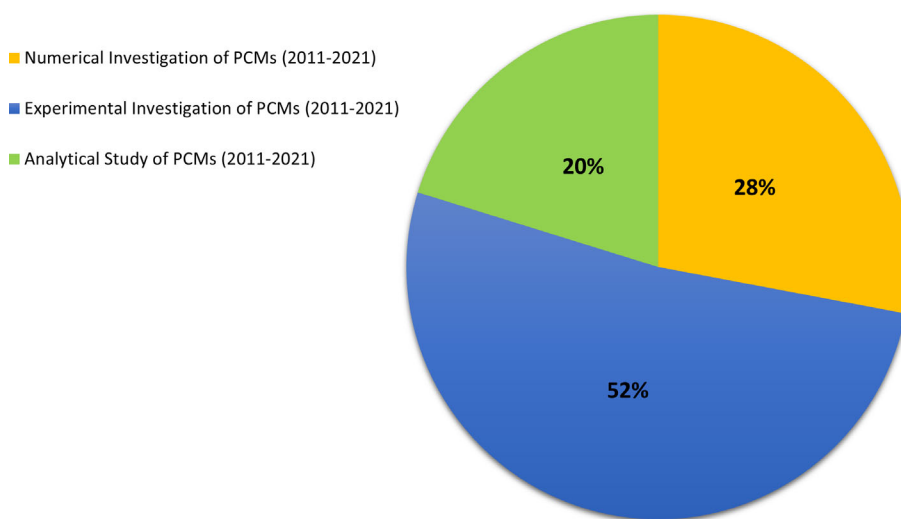


FIGURE 7 Proportional comparison of different approaches to study PCMs (2011–2021)

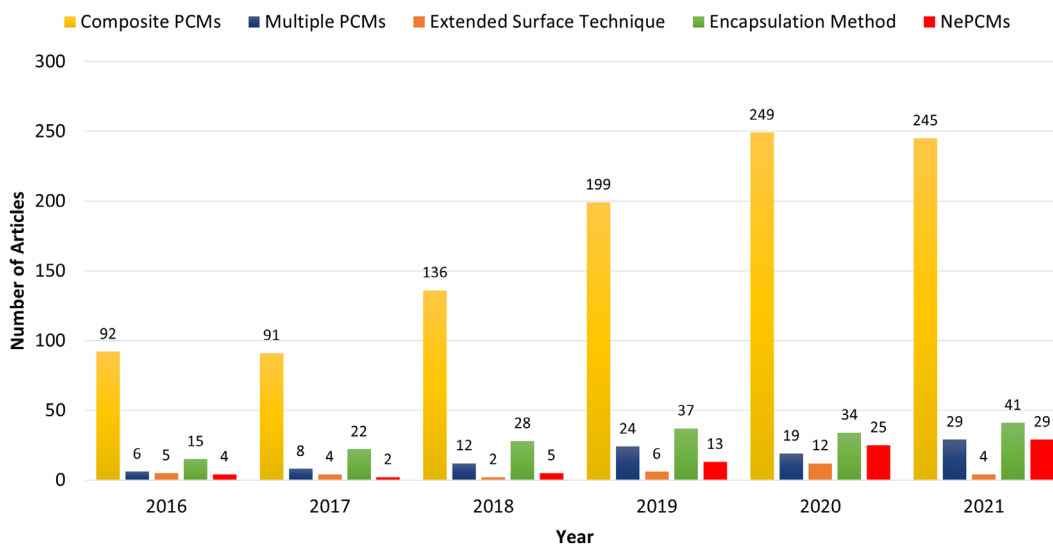


FIGURE 8 Year-wise number of publications of different approaches used to study heat enhancement in PCMs (2016–2021)

Figure 8 simply describes the number of articles published yearly on each technique while Figure 9 shows the trend of work for each scheme from 2016 to 2021. Figure 10 depicts the percentage of work done using each technique from 2016 to 2018. It can be clearly seen that composite PCMs are widely used for heat enhancement and extended surface techniques are given less attention than other techniques. What is more, emergence of nano-enhanced PCMs could be seen from 2019 onward.

3.1 | Composite PCMs

PCMs with low thermal conductivity can be incorporated with materials having high thermal conductivity which helps to get improved phase change behavior. Thermal conductivity enhancement can be done using materials with low-density, for example, carbon fibers and paraffin composites or using porous materials such as graphite or metal foam (aluminum, steel, or copper). Graphite has a thermal conductivity range of 24–470 W/mk (Mehling et al., 2000) which make it very feasible to use.

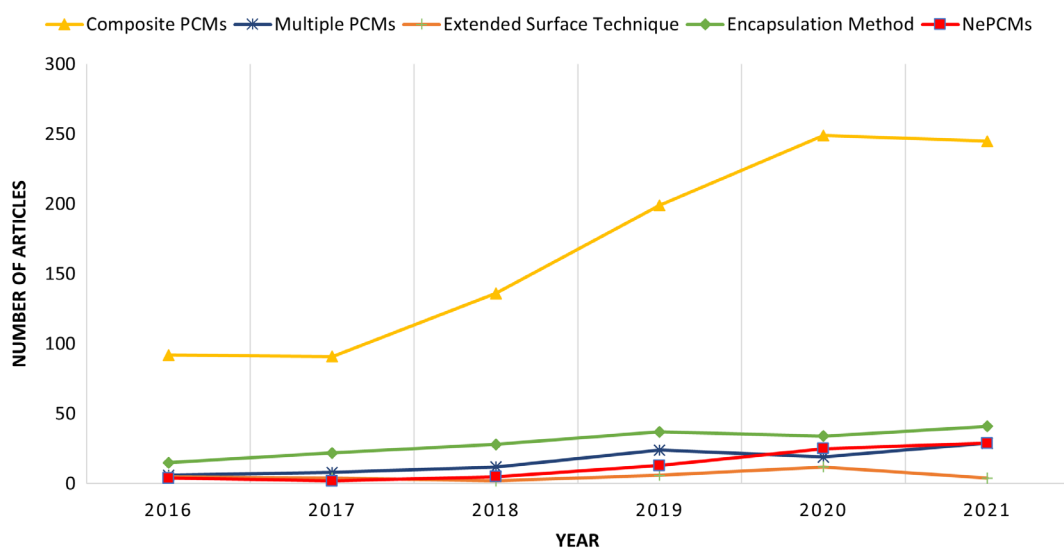


FIGURE 9 Publication trend of different approaches used to study heat enhancement in PCMs (2016–2021)

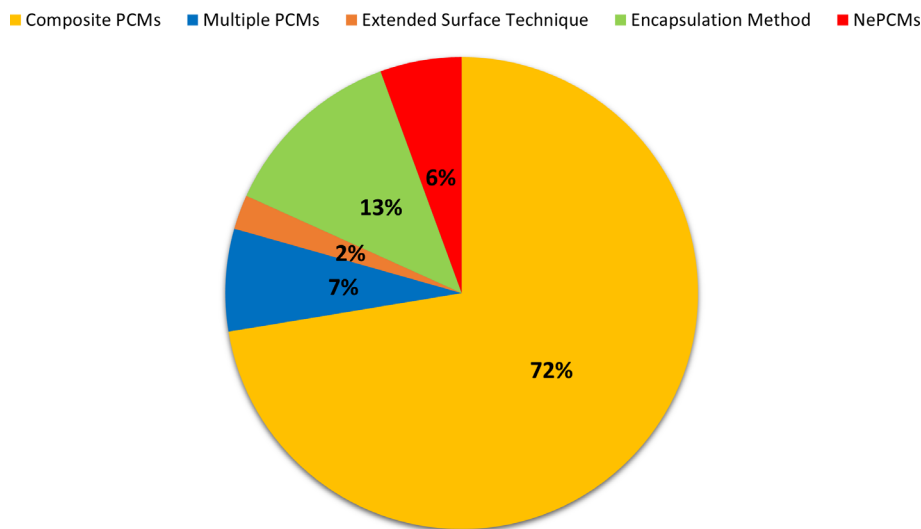


FIGURE 10 Proportional comparison of different approaches to study heat enhancement in PCMs (2016–2021)

Ground-expanded natural graphite flakes, and natural graphite flakes expanded are mostly used in LHS materials (Pincemin et al., 2008). It gives maximum capability of PCMs for energy storage/release and hence it is of great interest. A form-stable PCM has been prepared by Sari and Karaipekli (2009) using palmitic acid (PA) and expandable graphite (EG) composite through vacuum impregnation method. Form-stable composite has 2.5 times higher thermal conductivity than pure palmitic acid and it was concluded that it is more feasible for solar latent heat transfer system applications. The paraffin/graphite composite PCMs (Bilal, Imtiaz Shah, et al., 2022; Py et al., 2001; Rao & Zhang, 2010) can be developed by using feasible mass fraction of graphite and paraffin, they also do not show any chemical attraction to each other. Zhao et al. (2010) did an experimental and a numerical evaluation of heat transfer ability of PCMs installed with metal foams and found that there could be an increase of 3–10 times and 5–20 times in heat transfer rate during melting and solidification process respectively. Stearic acid (SA)/polymethylmethacrylate (PMMA) composite PCM was prepared by Wang et al. (2011) using ultraviolet curing dispersion polymerization for LHTS applications. The composite PCMs technique has a great potential in context of optimum energy storage and release capacity of PCMs.

3.2 | Extended surfaces

Dominance of convection over conduction and then almost disappearance of conductive heat during melting process and opposite in solidification process is well known in literature. A numerical study (Gharebaghi & Sezai, 2007) was done on heat transfer enhancement to study the role of fin configuration, module orientation (horizontal/vertical), and thickness. Results concluded that there was a notable decrease in the required time for melting process for both orientation modules i.e., horizontal, and vertical. Siva et al. (Siva et al., 2010) found that there could be decrease in charging and discharging time if fins are placed inside the spherical or cylindrical encapsulation such that it extended beyond to the center. An experimental study was done by Castell et al. (2008) using external vertical fins to solve the coefficient of natural convection heat transfer. They concluded that heat transfer rate between PCM and HTF has been enhanced significantly because of extended surface of vertical fins. Use of fins with PCMs in electronics is numerically investigated by Bilal, Khan, et al. (2022b), Lacroix and Benmadda (1997), and Nayak et al. (2006) and it is found that the rate of heat transfer is enhanced up to a certain number of fins. Other than number of fins, fins geometry is also effective in heat transfer rate enhancement, such as rod-type fins. Rod-type fins have better output than plate-types because of their ability to keep temperature dissemination better within the PCM. Other than this longitudinal/rectangular (Q. Li et al., 2019), circular/annular (Yang et al., 2017), and pin fins (Abdulateef et al., 2021; Tao & He, 2018) as shown in Figure 11 (Abdulateef et al., 2018b) are widely used configuration.

Longitudinal fins at different angles were numerically investigated by Kazemi et al. (2018). They developed a mathematical model for various forms of PCM heat transfer to investigate the effect of angle of longitudinal fins. It was observed that melting time has been decreased by 62% and 22.5%, when double and triple longitudinal fins were inserted with an angle of 45° and 150° against the case of without fins. Mazhar et al. (2020) used rectangular fins in a novel radially storage unit having cold water (CW) and gray water (GW) corrugated pipes as depicted in Figure 12 (Mazhar et al., 2020b). It was reported that phase change has been completed within 15 min for both processes (melting, freezing) by using fins having pitch of 10 mm. Furthermore, energy efficiency has been enhanced by 72.4% with corrugated pipes in comparison to that of non-finned version. Agyen et al. (Agyenim et al., 2009) examined the efficiency of circular fins, longitudinal fins, and fin-less geometry against the concentric double pipe configuration. It was reported that longitudinal fins showed 20%, and 71% more storage efficiency than circular fins and fin-less geometry, respectively. Zhai et al. (2015) also did an experimental study to observe the effect of different fin geometries on charging rate of PCM by considering the various geometry factors like the number of fins, pitch, and height of fins in given geometries. They observed 58.2% and 200% decrease in charging time for rectangular fin configuration as compared to the circular and fin-less geometries.

A numerical simulation was done by Al-Abidi et al. (2013) to study the effect of external and internal longitudinal fins on PCM charging rate with seven different configurations of TTHX as depicted in Figure 13 (Al-Abidi et al., 2013). It was found that Case-G took about 35% less time than that of the finned tube to achieve complete solidification. They also performed an experimental study (Al-Abidi et al., 2014) to investigate the Case-G as LHS unit. They observed that HTF inlet temperature has more significant impact on melting process than mass flow rate and reported a saving of 58% and 86% of charging time because of the effect of mass flow rate and the HTF inlet temperature respectively.

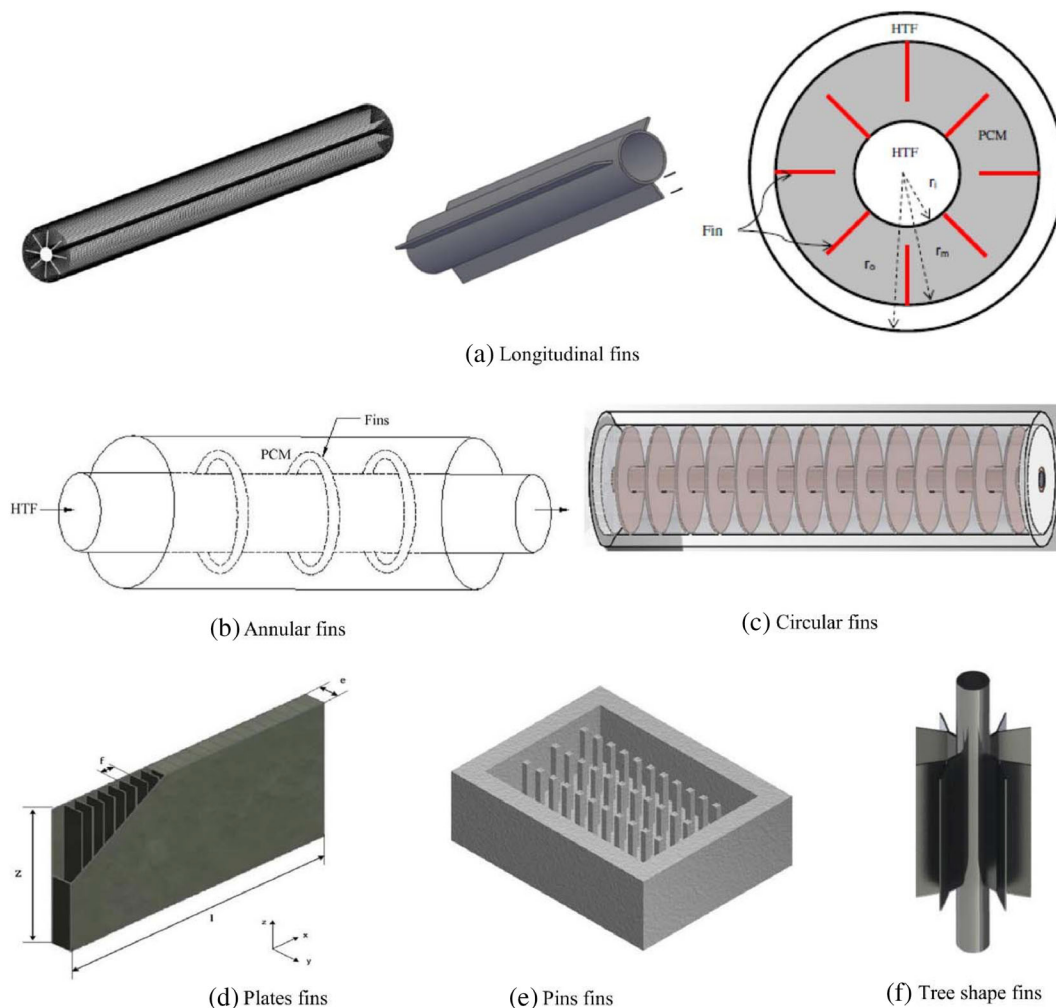


FIGURE 11 Widely used fins configurations. Reprinted with permission from Abdulateef et al. (2018b), Copyright©, Elsevier

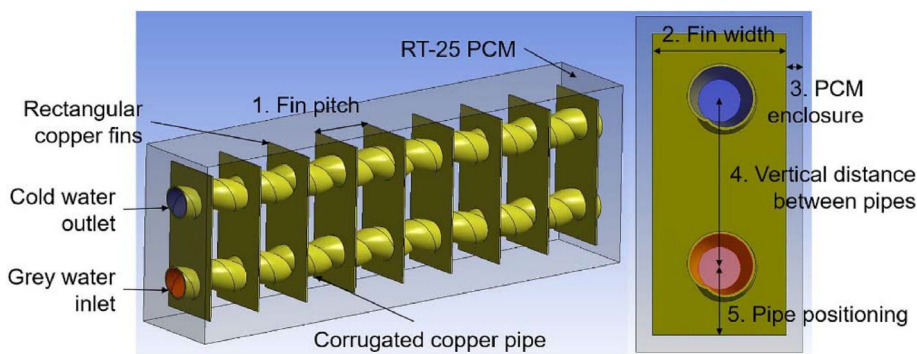


FIGURE 12 Rectangular fin's configuration with corrugated copper pipes. Reprinted with permission from Mazhar et al. (2020b), Copyright©, Elsevier

Three fins configuration in Y-shaped with single and double bifurcation, that is, three-shaped fins, annular-shaped fins, and snowflake-shaped fins described in Figure 14 (Sciacovelli et al., 2015) were numerically investigated by Sciacovelli et al. (2015). It was observed and reported that storage efficiency was improved by 24% with double bifurcation design. Furthermore, it was observed that Y-shaped fins with smaller angles were more effective for longer operating time while for shorter time Y-shaped fins with large angles between branches were more suitable. Another fin-tube

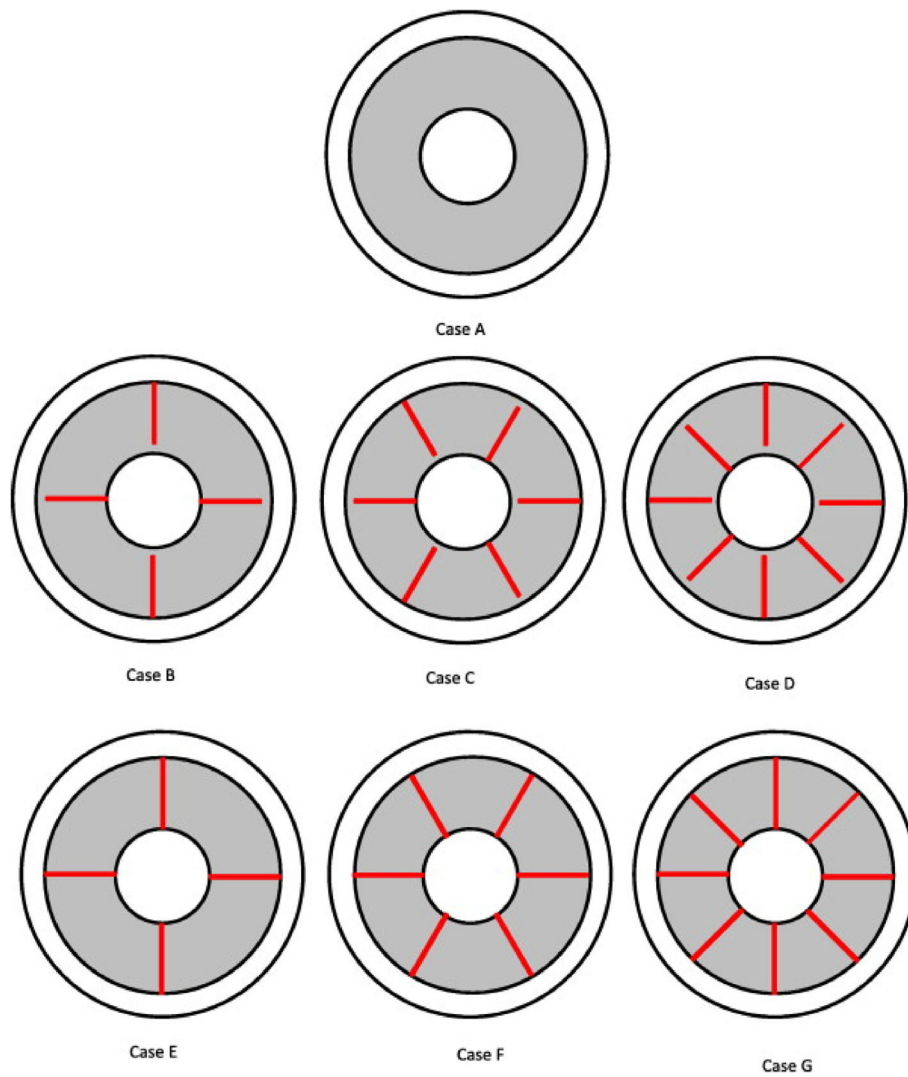


FIGURE 13 Various geometrical cases of TTHX container. Reprinted with permission from Al-Abidi et al. (2013), Copyright©, Elsevier

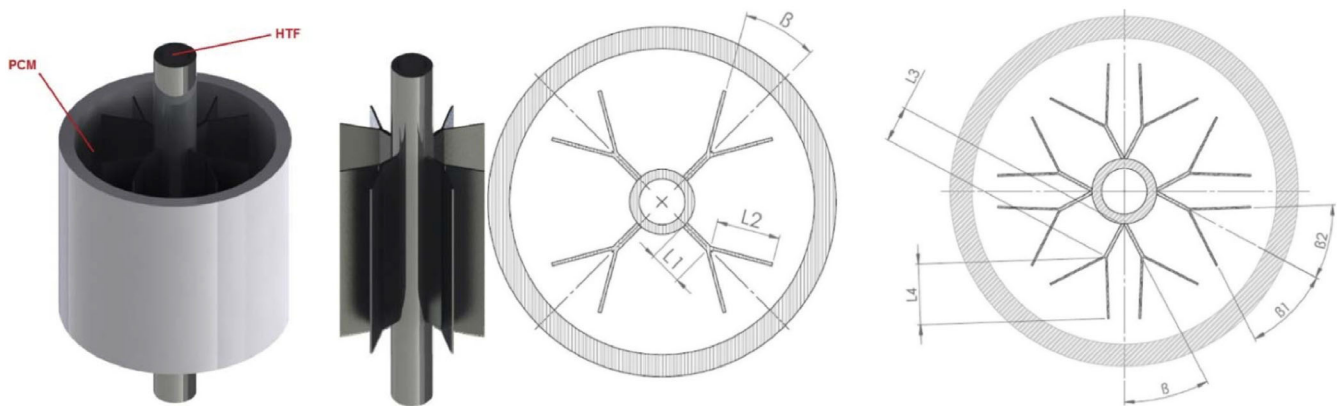


FIGURE 14 Y-shaped fins with single and double bifurcation. Reprinted with permission from Sciacovelli et al. (2015), Copyright©, Elsevier

storage system having HDPE as a PCM was studied numerically and experimentally by Zauner et al. (2016). They concluded that their proposed design has the ability to be used for various applications by introducing some feasible changes to configuration parameters such as fin spacing and thermal conductivity of PCM or mass flow control.

3.2.1 | Significance of thermal storage tank geometries

PCM storage containers are designed to have all fluid pipes and PCMs inside it contrary to conventional heat exchangers which cause the heat transfer and storage simultaneously. Consequently, viable performance of PCMs depends upon the configuration of PCM containers. Geometrical configuration and dimensional parameters of storage container have significant effect on thermal exchange level of storage capacity of PCM (Ismail & Henríquez, 2002). Cylindrical containers (pipe in tube, shell and tube, concentric annulus, and triplex tube), spherical containers, and square/rectangular slab containers are the container geometric configuration as shown in Figure 15 (Zayed et al., 2020), categorized to be used in PCM storage system.

Cylindrical PCM containers: Cylindrical containers have minimum size and high efficiency and considered as most optimal storage systems. There are four configurations of cylindrical container as shown in Figure 15. In the first configuration, as shown in Figure 15a, PCM stored into shell cavity while HTF moves through a single pipe, and it is known as pipe design. In the second configuration, as shown in Figure 15b, PCM occupies the tube and the HTF is propagated parallel to the pipe. Shell and tube design is shown in Figure 15c in which PCM stores into the inner side of shell and

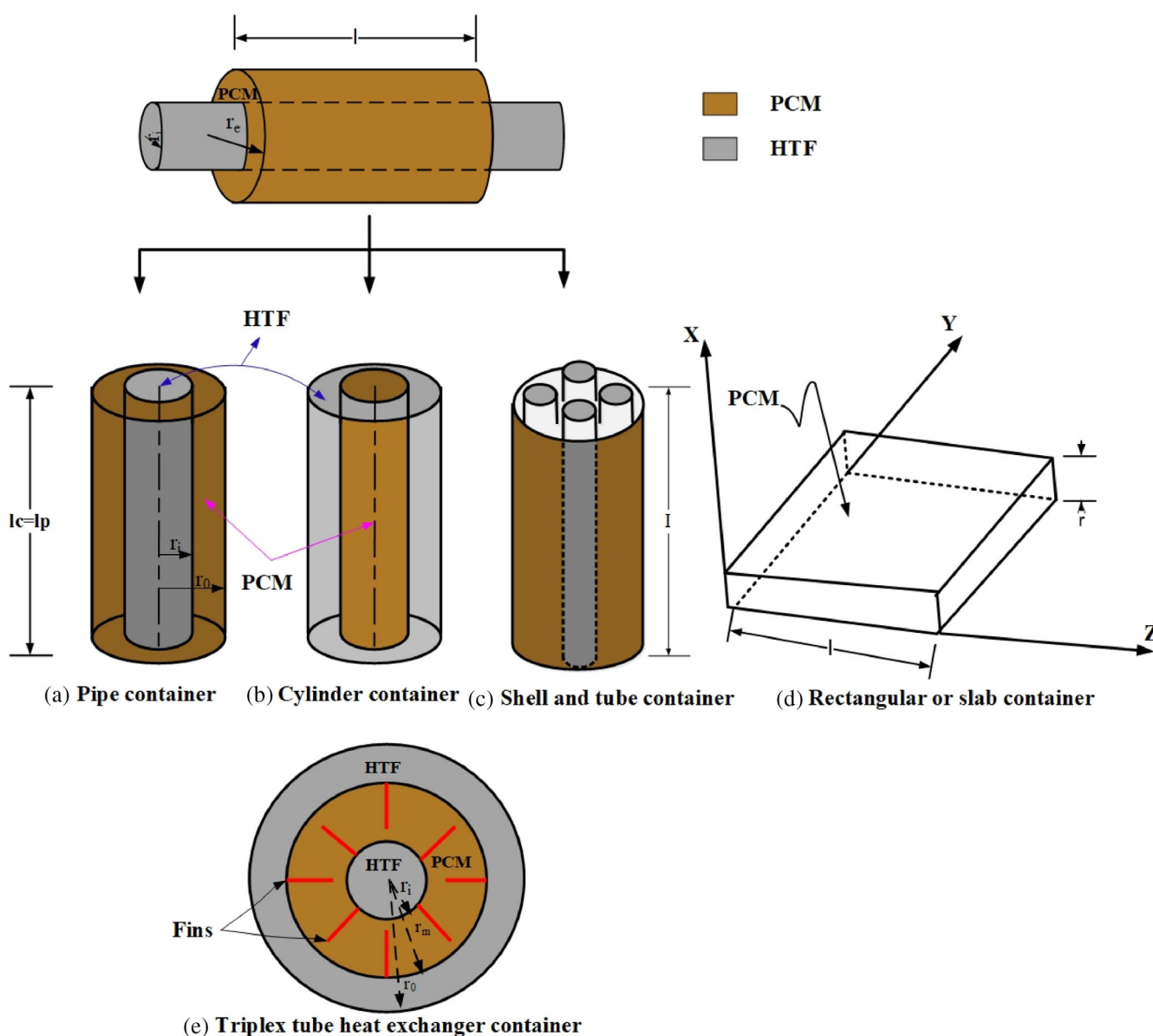


FIGURE 15 Various geometrical configurations of PCM storage containers. Reprinted with permission from Zayed et al. (2020), Copyright©, Elsevier

HTF flows around the other side. Figure 15e depicts the triplex tube heat exchanger (TTHX) having three tubes. PCM is filled in middle tube while inner and outer tubes contain the HTF.

Han et al. (2017) did the numerical investigation on three cylindrical containers namely cylinder, shell and tube, and pipe. He concluded that shell and tube configurations take very less time than others to melt for the same heat transfer surface area and mass of PCM.

Tao et al. (2017) carried out a numerical analysis in high-temperature environment using two cylindrical containers shown in Figure 16 (Tao et al., 2017), under the same operating conditions. They reported that charging rate of 34.4%, and LHS rate of 54.2% can be decreased and increased, respectively, if PCM is applied on tube side. Significance of inclination angle have been studied by Kousha et al. (2017) with different case of horizontal and vertical inclination angle. Horizontal configuration showed better charging abilities while higher heat transfer rate has been observed in vertical configuration. Zayed et al. (2020) reported based on several studies that shell and tube configuration is the most used cylindrical container configuration, and its energy efficiency is more than 70%.

Spherical PCM containers: Usually spherical containers are not considered optimal option because of their volume per unit area yet some researchers did investigate their significance within PCM storage unit. Nazzi Ehms et al. (2018) numerically investigated the discharging rate in spherical container having 98.5% solid PCM with possibility of 1% increase of volume. They investigated container design using different sets of variables and reported that thermal parameters and geometric design of container caused a significant impact on melting rate of PCM. They also validated their results with the numerical and experimental results of Assis et al. (2007) and these results were in a good agreement. Another numerical and exploratory investigation was made by Tan et al. (2009) to examine the melting of PCM

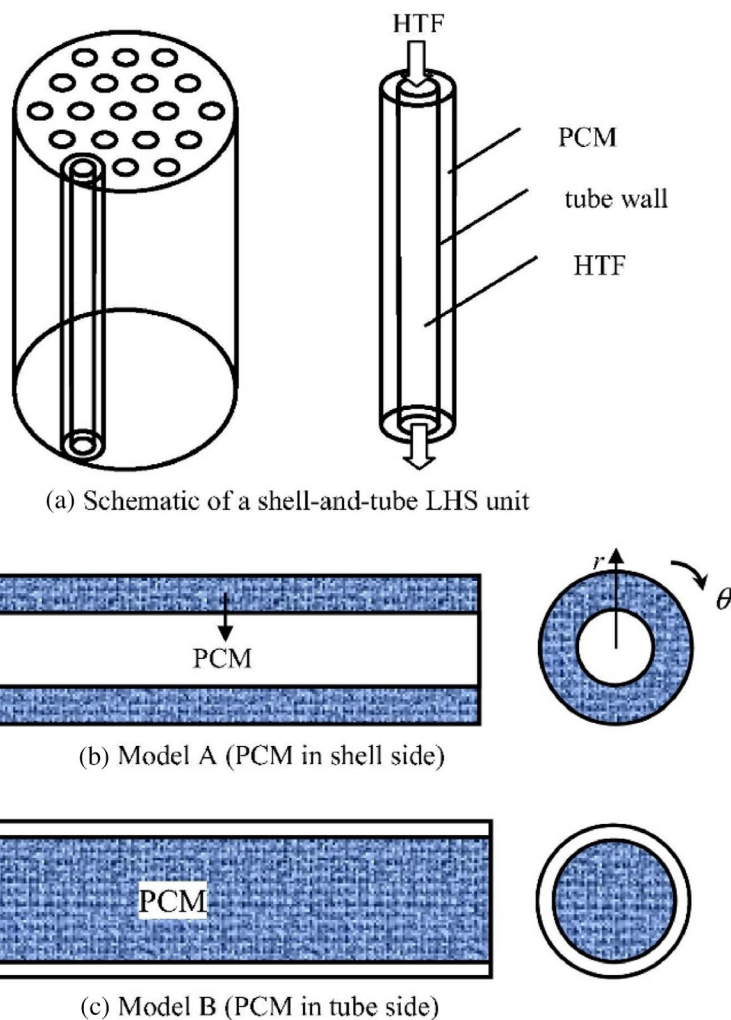


FIGURE 16 Two cylindrical containers. Reprinted with permission from Tao et al. (2017), Copyright©, Elsevier

in a diaphanous spherical crystal shell. They reported that existence of a stable and unstable (thermodynamically) liquid formation close to symmetry axis cause a free convection in spherical capsule.

Unconstrained melting cycle was investigated by Gao et al. (2019) in a spherical container using visualizing experiment. Different factors like diameter of container (20–70 mm), initial temperature (7–22°C), PCM ratio (0.80–0.98), and heating temperature (32–47°C) were part of the investigation. It was reported that change in melting attitude diverse from close contact to floating melting with a marginal improvement. In addition, usual floating melting time decreased after an initial increment and continuous increment have been observed for average melting time.

Slab/rectangular PCM containers: The rectangular PCM containers have been applied in various applications such as power reactors, solar heating/cooling systems, and solar power plants as reported in several studies. Zhao et al. (2018) did an experimental investigation along with numerical simulation to observe the trend of PCM charging using seven tilt angles, that is, 0°, 15°, 30°, 45°, 60°, 75°, and 90°. It was concluded that free convection can cause a considerable improvement in heat transfer of PCM at an inclination of 60° in a rectangular container.

Bashar and Siddiqui (2018) carried out an experimental study to investigate the performance of rectangular containers in melting and heat transfer using nano-composite PCM (NCPCM). Silver, MWCNT, Al₂O₃, and CuO (nanoparticles) were used with Paraffin (PCM) and it is revealed that Silver followed by CuO showed significant and better improvement in heat transfer among all. In addition, different mass fractions of CuO (1, 3, 6, 8, and 10 wt%) were studied with Paraffin (PCM) and it was found that there was 25% improvement in heat transfer with 6% of CuO fraction as compared to pure paraffin. Elbahjaoui and el Qarnia (2017a) accomplished computational modeling based on the enthalpy porosity method to validate the solidification process of nano-enhanced PCMs in a rectangular PCM slab system. The storage unit consisted of different n-octadecane-filled slabs aligned vertically and restricted by rectangular channels as shown in Figure 17 (Elbahjaoui & el Qarnia, 2017a), where water is used as HTF. It was observed that melting and storage efficiency increased while the time required for complete solidification decreased by increasing the concentration and aspect ratio of nano-enhanced PCMs.

3.3 | Multiple PCMs

Use of multiple PCMs can increase the energy efficiency by selecting required number of PCMs and their respective melting temperature (M. Fang & Chen, 2007; Gong & Mujumdar, 1996, 1997). In this technique, descending order of melting points of PCMs were used to arrange them and then a constant temperature difference is sustained during melting process, however, HTF flow decreases in the direction of flow (Jegadheeswaran & Pohekar, 2009). Shaikh and Lafdi (2006) numerically analyzed and explained that use of multiple PCMs enhanced the rate of energy charged significantly as compared to single PCM. Cui et al. (2003) investigated the effect of 3-PCMs and single PCM in solar receiver thermal storage module separately. They concluded that use of multiple PCMs enhanced the energy rate which consequently optimize the receiver performance and reduce the variation of working fluid exit temperature.

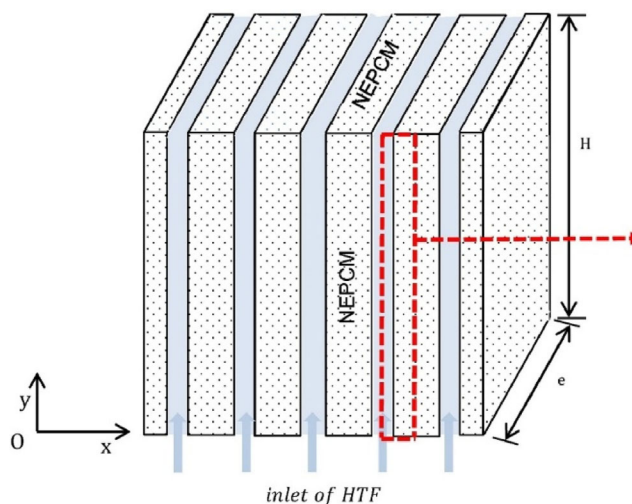


FIGURE 17 Rectangular PCM slabs. Reprinted with permission from Elbahjaoui and el Qarnia (2017a), Copyright©, Elsevier

3.4 | Encapsulation of PCMs

Encapsulation of PCMs is also one of the heat transfer enhancement methods which required micro size PCM particles to be enclosed in a cylinder or sphere. Here, capsule in solid structure is known as shell and PCM inside the capsule is called core. There are mainly two methods of encapsulation of PCMs, one of which is mechanical (or physical) method, for example, spray drying method while the other one is chemical method, for example, interfacial and coacervation methods.

Hawlder et al. (2003) used spray-drying and complex coacervation methods for the preparation of encapsulated paraffin particles to process the encapsulated paraffin-wax. They studied the release and storage of energy and concluded that the microencapsulation had greater energy release and storage ability in the range of 145–240 J/g. Bayés-García et al. (2010) prepared microencapsulated PCMs using different shell formations by agar-agar/Arabic gum (AA/AG) and sterilized gelatine/Arabic gum (SG/AG) methods. It is suggested that microcapsules composed by AA/AG technique possess better capacity to store large amount of thermal energy than microcapsules prepared using SG/AG technique. Polymethylmethacrylate (PMMA) microcapsules having *n*-octacosane as a PCM were investigated by different researchers (Alkan et al., 2009; Sari & Karaipekli, 2009; Sari et al., 2010). Differential scanning calorimetry (DSC) test was used to find the latent heats, melting and freezing temperatures of the microencapsulated octacosane as PCM given as 86.4 J/g, 88.5 J/g, 50.60°C, and 53.20°C, respectively. However, microencapsulated octacosane has good chemical stability and better ability of energy storage and release, but during repeated cycling its performance went down, fluid viscosity increased by macro particles of microencapsulated PCM, and usually pumping also crush these particles. Therefore, it is suggested to use particles in nanoscale between 10 and 140 nm (Lai et al., 2010).

Fang et al. (2008) synthesized the nano-encapsulated PCM with *n*-octadecane as the core and polystyrene as the shell by ultrasonic-assistant miniemulsion in situ polymerization. Where nanocapsules ranged from 100 to 123 nm in size and spherical in shape, nano-encapsulated PCM had very similar phase change temperature as *n*-octadecane which suggested that the nano-encapsulated PCM and *n*-octadecane core also had same kind of thermal properties.

3.5 | Nano-enhanced PCMs

Nanoparticles (NPs) can be used efficiently for heat enhancement in PCMs. NPs can be used as sole enhancement or along with other enhancement techniques, that is, nano-enhanced PCMs with highly conductive porous materials and multiple PCMs, nano-enhanced PCMs with fins, and as well as with heat pipes. NPs helps to increase the overall thermal conductivity without bringing any change in PCM volume. Nano-enhanced PCMs (NePCMs) were first studied by Elgafy and Lafdi (2005). They studied the paraffin wax enhanced with carbon nanofibers using experimental and analytical approaches. Different mass ratios of carbon nanofibers were used to study the temperature profile, and thermophysical properties during solidification. An analytical model was also used to make an effective prediction about thermal conductivity. They found that solidification time decreased by increasing the carbon nanofibers and output power also increased. Experimental and analytical results were in good agreement.

Table 2 summarizes the work done using nano-enhanced PCMs as a sole enhancement and with other above-mentioned techniques from 2016 to 2021. Given data extracted mostly from Tofani and Tiari (2021) and partly (2021) searched by ourselves, which is best to our knowledge. Furthermore, Table 2 includes the NePCMs studied in given temperature range with different mentioned technique along with number of studies done experimentally, numerically, or using both approaches for result validation. It can be seen clearly that most of research done using nano-enhanced PCMs as sole enhancement and all the temperature ranges, that is, low, middle, and high were considered and studied using almost all approaches mentioned above. Cu, CuO, and Al₂O₃ are mostly studied NePCMs. While NePCMs with combined fins were studied only in low range with numerical approach. nano-enhanced PCMs with multiple PCMs were studied only twice from 2016 to 2021. This literature gap was also mentioned by Tofani and Tiari (2021) and we also found only one article after that. So, it means that this technique is still could not find much attention of the researchers and there are lot of opportunities to do some novel work. Besides this technique, nano-enhanced PCMs are still not much studied as it can be concluded from Figures 8–10 and Table 2. Therefore, there is a wide scope of novelty in studying nano-enhanced PCMs not only with multiple PCMs but with other techniques as well.

TABLE 2 Studies on nano-enhanced PCMs (2016–2021)

Method	Temperature range (°C)	NePCMs	Experimental studies	Number of studies	Both	References
NePCMs as a sole enhancement	Low (–14.8 to 85)	Cu, CuO, Al ₂ O ₃ , TiO ₂ , MgO, ZnO, MWCNTs, Graphene, Si ₂ , multi-wall carbon nanotube, CeO ₂ , Ag, Fe ₂ O ₃ , Carbon, Al	16	11	3	(Abdollahzadeh Jamalabadi, 2021; Abdulateef et al., 2021; Algarni et al., 2020; Aqib et al., 2020; Badakhsh et al., 2018; Barreneche et al., 2019; Bashar & Siddiqui, 2018; Dastmalchi & Boyaghchi, 2020; Elbahjaoui & el Qarnia, 2017a, 2017b; Farsani et al., 2017; Ghafari et al., 2021; Ghalambaz et al., 2017; Javadi et al., 2020; Khatibi et al., 2021; Liang & Chen, 2018; Maher et al., 2021; Marcos et al., 2020; Murugan et al., 2018; Nazlı Temel & Yeşim Çiftçi, 2018; Nie et al., 2021; Nitsas & Koronaki, 2020; Pasupathi et al., 2020; Prabhakaran et al., 2019; Santhosh et al., 2020; Song et al., 2019; Thalib et al., 2020; Zaidan & Alhamdo, 2018; Zhou et al., 2016; Zhuang et al., 2021)
	Middle (120–250)	Graphene, COOH-functionalized graphene nanoplatelets (f-GNP), TiO ₂ , CNTs, SiO ₂ , Al ₂ O ₃ , MgO	6	1	1	(Asfattihi et al., 2019; Chieruzzi et al., 2017; Manickam et al., 2008; Mayivelmathan & Valan Arasu, 2020; Saranprabhu & Rajan, 2019; Singh et al., 2021; u Mekrisuh et al., 2021; Vivekananthan & Amirtham, 2019)
	High (306–399.7)	Al ₂ O ₃ , CuO, SiO ₂ , and ZnO	3	0	0	(D. Han et al., 2020; Myers et al., 2016; Xiong et al., 2019)
NePCMs Combined with Fins	Low (0–85)	Cu, CuO, Al ₂ O ₃ , MOS ₂ -TiO ₂ , with fins, branched, and stair fins	0	7	0	(Bondareva et al., 2020; Hajizadeh et al., 2020; Hosseinzadeh et al., 2021; F. Li et al., 2021; Mahdi et al., 2019; Nakhchi et al., 2021; Ren et al., 2019)
NePCMs combined with Heat Pipes	Low (44–57)	Graphite nano-platelets, Cu, CuO, Al ₂ O ₃ , Ag, with horizontal, and finned heat pipes	1	2	0	(Bilal, Khan, et al., 2022a; Koukou et al., 2019; Mahdavi et al., 2019, 2020; Shah et al., 2022)
	High (335–485.85)	Cu, CuO, Al ₂ O ₃ , metal foam with finned heat pipes	0	3	0	(Ren et al., 2018; Tiari, Mahdavi, et al., 2019; Tiari, Rose, & Mahdavi, 2019)
NePCMs combined with Highly conductive porous media	Low (41–62)	Nano-AIN, carbon nanotubes, graphene, Cu, Al, Fe, and Ni, CuO, Al ₂ O ₃ , with graphite, aluminum, and copper foam	2	1	1	(Buonomo et al., 2018; Ma et al., 2020; Senobar et al., 2020; J. Yu et al., 2016)
	Middle (120)	Carbon nanotubes, Al, Ag, graphene NPs, with carbon foams	1	0	0	(Kim et al., 2019; Shahzad et al., 2023)
	High (383.5)	Expanded graphite and SiO ₂ , NPs	1	0	0	(Kim et al., 2019; Q. Yu et al., 2021)
NePCMs with multiple PCMs	Low (51–67)	Al ₂ O ₃ , Cu with multiple PCMs	2	0	0	(Mahdi et al., 2020; Moghaddam & Ganji, 2021)

4 | CONCLUSION

This advance review aims to present a broader overview of PCMs and heat enhancement techniques in LHTES system to the reader. It enabled us to present the following understandings, conclusions, and future research recommendations.

1. This study reviewed the different kinds of PCMs such as organic, inorganic, and eutectic on a wide range of temperature and each one of them has its own limitations. However, recent advancements suggest that the biodegradable PCMs like animals and organic fats, for example, coconut oil emerges as a significant storage medium in LHTES systems. What is more, nontoxic nature of these PCMs addresses the issue of sustainability very well. In addition to that these substances are abundant in nature and thus commercially very cheap.
2. There are numerous studies done on PCMs in the past decade (2011–2021) using analytical, numerical, and experimental approaches. More than half of them are experimental studies which are evidence of that. It is exceedingly difficult to solve PCMs analytically and numerically, because of their complex geometries, nonstandard boundary conditions, and nonlinear phase front interfaces. Hence, numerical investigation required much attention.
3. Statistical data from the past 5 years (2016–2021) endorse the intense use of composite PCMs against other techniques. It is because composite PCMs are considered more viable while other techniques have their drawbacks such as encapsulated enhancement suffering from integrity problems with encapsulation materials. In recent years, NePCMs have also got attention of many researchers. Which could lead to the better prospective of future research rather than intensive use of composite PCMs.
4. Different studies on geometrical configurations such as longitudinal, pin, and circular fins were discussed, and it is found out that rectangular/longitudinal fins are mostly used and have shown better performance than rest of fin geometries. Furthermore, different geometrical configuration parameters such as fin spacing, mass flow control, thermal conductivity, fin location and fin number also significantly impact on heat transfer performance of the storage system. Reducing the fins space considerably reduces the melting time while fin thickness effect the thermal resistance of storage system. It is also concluded from reviewed study that by increasing number of fins at certain limit efficiently helps in the heat enhancement. Furthermore, in addition to the above, applying of extended surface along with enhancing PCM conductivity simultaneously, which is known as “Combined Heat Transfer Enhancement Technique” endorsed for future work.
5. Role of container's geometry in different applications is discussed which conclude that cylindrical configuration among others is widely considered in applications. While the high storage capacity and melting rate of rectangular storage systems make it effective for bulk storage applications. Moreover, in cylindrical design, shell and tube geometry is intensively used and it gives more than 70% energy efficiency. However, from a practical point of view, hexagonal geometry could be recommended for future work. It could be best fit for modular thermal battery applications because of its high packing density
6. This review also focused on recent advancements in heat enhancement such as NePCMs. Their main advantage is that they enhance the overall thermal conductivity without causing any effect on PCM volume and second, these are applicable as a sole enhancement or with any other enhancement technique such as with fins, heat pipes, porous media, and multiple PCMs. Data shows that up till now nano-enhanced PCMs were studied mostly as a sole enhancement in all temperature ranges while CuO, and Al₂O₃ were mostly used as NePCMs. Therefore, the study of various nano-enhanced PCMs such as TiO₂, MgO, ZnO, and MWCNTs, combined with other mentioned techniques, especially with multiple PCMs is recommended for future investigation. Focusing on different temperature ranges (as application desires) and study approaches, that is, numerical and experimental.

AUTHOR CONTRIBUTIONS

Muhammad Saqib: Conceptualization (supporting); data curation (lead); formal analysis (equal); visualization (lead); writing – original draft (lead); writing – review and editing (lead). **Rafal Andrzejczyk:** Conceptualization (lead); formal analysis (equal); supervision (lead); visualization (supporting); writing – original draft (supporting); writing – review and editing (supporting).

CONFLICT OF INTEREST

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this article.



DATA AVAILABILITY STATEMENT

Data sharing is not applicable to this article as no new data was created or analyzed in this study except some statistical data taken from "Web Of Science" which is properly referred.

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