

Characterization Study of Phase Change Materials Destined for Thermal Energy Storage Systems: A Review

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Introduction

Storage of solar energy is an important issue as solar radiation is a time-dependent energy source, i.e. has an intermittent character. Thus, the energy source and the heating demands of the systems do not match. Solar thermal energy can be stored as sensible heat (water and rock), latent heat (water/ice and salt hydrates), heat of reaction, or combination of these. Parameters including storage period required, economic viability or operating conditions are effective on selection of these methods [1].

The use of solar energy in drying is becoming an important and viable alternative since it decreases consumption of conventional energy, and improves production efficiency. Solar drying helps to overcome the inherent disadvantage of open sun drying i.e. it protects the product from unpredicted rain, wind-borne dirt and dust, Infestation by insects, rodents etc... Using a solar dryer, the drying time can be shortened by about 65% compared to the open sun drying because the efficiency of dryer is higher, and its payback period ranges from 2~4 years depending on the rate of utilization [2].

Drying is an essential process in the preservation of agricultural products. Food products, especially fruits and vegetables require hot air in the temperature range of 45-60 °C for safe drying. Drying under controlled conditions of temperature and humidity helps the agricultural food products to dry reasonably rapidly to a safe moisture content and to ensure a superior quality of the product [3].

PCM take advantage of latent heat that can be stored or released from a material over a narrow temperature range. PCM possesses the ability to change their state with a certain temperature range. These materials absorb energy during the heating process as phase change takes place and release energy to the environment in the phase change range during a reverse cooling process. Basically, there are three methods of storing thermal energy: sensible, latent and thermo-chemical heat or cold storage [4].

By 1990, only about 12 companies, mainly in the USA, were engaged in the manufacture of heat storage products. Manufactured heat storage modules in the form of polyethylene tubes and polyolefin balls used calcium chloride hexahydrate, sodium sulphate decahydrate, paraffin etc., as PCMs. Only storage devices built on the basis of $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ had a guaranteed service period of 10 years, while for others this period was between 1 and 2 years.

At present, the main supply companies in the market of phase change heat and cold storage materials include Cristopia (France), TEAP Energy (Australia), Rubitherm GmbH (Germany), EPS Ltd. (UK), PCM Thermal Solutions (USA), Climator (Sweden) and Mitsubishi Chemical (Japan). A wide range of heat and cold storage materials is produced by EPS Ltd [5].

Application of PCM in solar collectors

Y. Rabin et al [6], used the salt-hydrate as a phase change material in an integrated solar collector storage system (Fig. 1). The salt-hydrate is used to store solar energy and to heat the cold water which is passing through a heat exchanger located in a layer of stationary heat transfer liquid. The quantity of the used salt-hydrate is 13.4 kg, composed of an eutectic mixture (in wt%) of: 48.0 CaCl₂, 4.5 KCl, 0.4 NaCl and 47.1 H₂O, with the addition of 1 wt% BaCl₂·2H₂O as a nucleating agent. This PCM has a phase transition temperature interval of 27-29°C a latent heat of 164.5 kJ/kg, solid and liquid densities of 1610 and 1490 kg/m³, and solid and liquid thermal conductivities of 0.6 and 0.5 W/mk, respectively. They found that the phase transition temperature interval and the thickness of the salt-hydrate PCM layer are important design parameters of the ICS-PCM system. The PCM stored the solar energy at 28°C in the winter. Theoretical study on the effects of the transition phase change temperature (in the range 15-35°C) and the thickness of the PCM layer (in the range 20-100 mm) showed that for the phase transition at 20°C-which is suitable for heating greenhouses-the PCM thickness for energy collection has to be 30-65 mm.

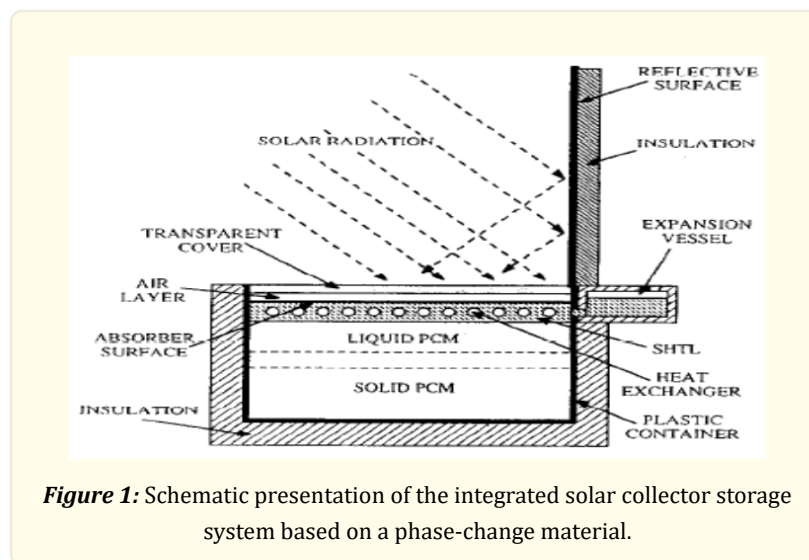


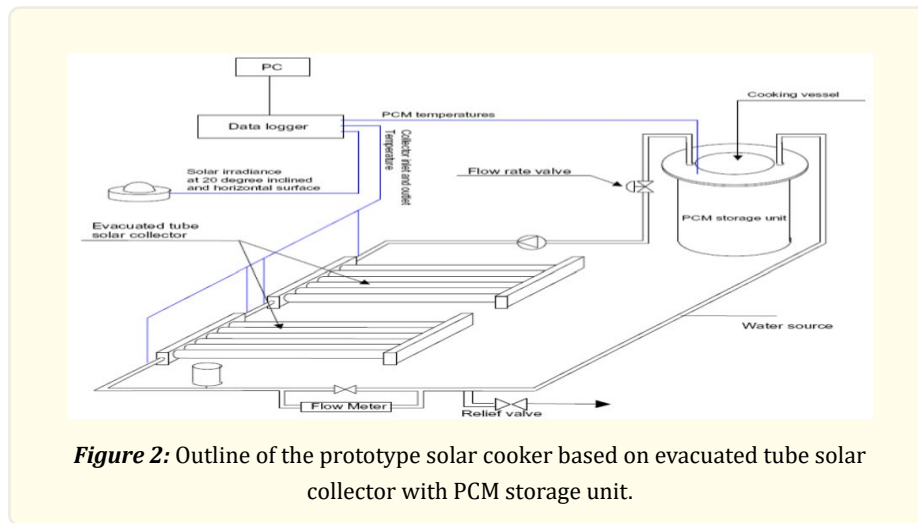
Figure 1: Schematic presentation of the integrated solar collector storage system based on a phase-change material.

S. D.Sharma et al [7], studied the thermal performance of a solar cooker based on an evacuated tube solar collector with a PCM storage unit (Fig. 2). Solar energy is stored in the PCM storage unit during sunshine hours and is utilized for cooking in late evening/night time. Commercial grade erythritol (C₄H₁₀O₄) was used as a latent heat storage material. The used PCM have the following thermophysical properties: 118°C is the melting temperature with high heat of fusion 339kJ/kg, its low cost (US\$5/kg) and large-scale availability in the Japanese market. The other properties are: Specific heat (kJ/kg C) 1.38 at (20 C) and 2.76 at (140 C), density (kg/dm³) 1.48 at (20 C) and 1.30 at (140 C), heat conductivity (W/m K) 2.64 at (20C) and 1.17 at (140C).

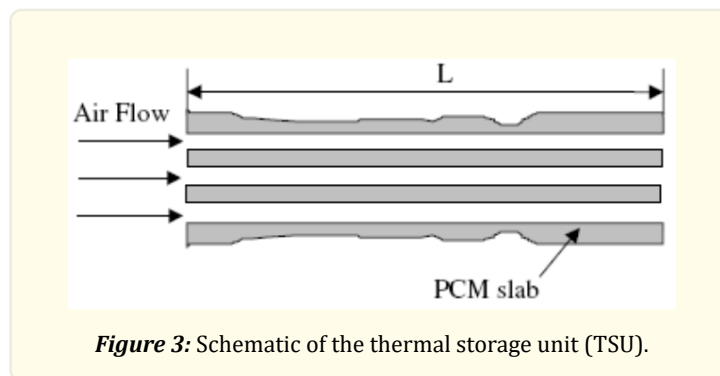
It was found that night cooking using PCM heat storage faster than noon cooking. The choice of the material is based on the melting temperature, the latent heat of fusion, density and other considerations such as toxicity, corrosiveness and cost. They found that The PCM did not melt in January (winter) in Japan. In summer, PCM temperatures reached more than 110 C at the time of evening cooking. cooking experiments showed that the PCM storage unit is able to store an adequate amount of heat for noon and evening cooking and is also capable to keep PCM temperatures (near 75C) until the next morning.

W. Saman et al [8], studied the thermal performance of PCM thermal storage unit for a roof integrated solar heating system (Fig. 3). The unit consists of several layers of phase change material (PCM) slabs with a melting temperature of 29°C. The used PCM is (CaCl₂·6H₂O), it has the following thermophysical properties: melting temperature = 29C, densities: $\rho_{\text{solid}} = 1710\text{kg/m}^3$, $\rho_{\text{liquid}} = 1500\text{kg/m}^3$, thermal conductivities: $k_{\text{solid}} = 1.09\text{W/mK}$, $k_{\text{liquid}} = 0.54\text{W/mK}$. The total mass of PCM is 600kg. For melting the PCM

initial temperature was 20°C whilst for freezing the PCM initial temperature was 40°C.



It was found that a higher inlet air temperature increases the heat transfer rates and shortens the melting time. Conversely, during freezing, a lower inlet air temperature increases the heat transfer rates and shortens the freezing time. Likewise, a higher air flow rate increases the heat transfer rate and shortens the melting time but increases the outlet air temperature. For freezing, a higher air flow rate increases the heat transfer rate and shortens the freezing time but reduces the outlet air temperature.



Mohammad Dashtban et al [9], studied the thermal analysis of a weir-type cascade solar still integrated with PCM storage (Fig. 4). The used quantity of PCM is 18kg (2cm thickness) beneath the absorber plate. Paraffin wax is chosen as PCM because of its medium storage, safety, reliability, uniform melting and moderate cost. Some thermophysical properties of paraffin wax are: melting temperature 56°C, specific heat of solid/liquid (kJ/kg °C) 2.95/2.51, density of solid/liquid (kg/m³) 818/760, thermal conductivity of solid/liquid (W/m °C) 0.24/0.24, heat of fusion 226 kJ/kg).

It is noted that the max reached temperature without PCM of water, glass and absorber is 58, 53 and 65°C respectively which demonstrate the choice of the PCM with 56°C melting temperature. The results showed that the productivity of the still with PCM was theoretically 31% higher than that of without PCM. The daily productivity was theoretically found to be 6.7 and 5.1 kg/m²day, for the still with and without PCM, respectively.

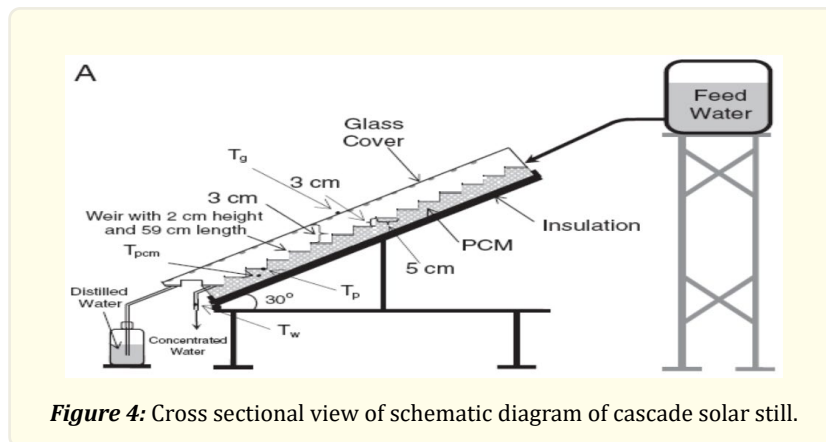


Figure 4: Cross sectional view of schematic diagram of cascade solar still.

Mounia chaabane e al [10], studied Thermal performance of integrated collector storage solar water heater (ICSSWH) with phase change materials (PCM). They used two kind of PCM myristic acid and RT42-graphite with three radiuses ($R = 0.2$ m, $R = 0.25$ m and $R = 0.3$ m) of this PCM layer. Thermophysical properties of the two PCM are presented below:

PCM	ρ (kg/m ³)	C_p (J/kg k)	K_s (W/m k)	K_l (W/m k)	ΔH (kJ/kg)	T_m (K)
Myristic acid	1000	3670	0.17	0.19	189	327
RT42-graphite	789	1570	5	5	139.7	316

Regarding the night operating of this solar system, it is found that the LHSU is more effective for both PCMs as it allows lower thermal losses and better heat preservation. It was observed that the maximum temperature of water without integration of PCM was 328K at 13H00 which justify the choice of the PCM which have the melting temperature of 327K. the results showed that water temperature with Myristic acid as PCM equal to 327K, while it was found 316K in the case of using RT42-grafite and this is due to the higher melting temperature of Myristic.

The study of the effect of PCM radius shows that higher temperature is obtained for lower radius, but the temperature difference between the two extreme values of the PCM radius does not exceed 1C unlike the night thermal losses where the optimum case corresponds to the highest radius.

Y.Q. Li et al [11], studied the numerical analysis and parameters optimization of shell-and-tube heat storage unit using three phase change materials as shown in the table below.

Thermo-physical properties and compositions of PCM1, PCM2 and PCM3 [25].

Composition (wt, %)	PCM1	PCM2	PCM3
	$K_2CO_3(51) - 49Na_2CO_3$	$Li_2CO_3(20) - 60Na_2CO_3 - 20K_2CO_3$	$Li_2CO_3(32) - 35K_2CO_3 - 33Na_2CO_3$
ρ_f (kg m ⁻³)	2400	2380	2310
k_f (W m K ⁻¹)	1.73	1.83	2.02
C_p (J kg ⁻¹ K ⁻¹)	1670 (solid) 1560 (liquid)	1590 (solid) 1880 (liquid)	1670 (solid) 1630 (liquid)
T_m (K)	983	823	670
ΔH (KJ kg ⁻¹)	163	283	275

It was found that:

- Among PCM1, PCM2 and PCM3, melting rate both x, r directions of PCM3 is the fastest, and that of PCM1 is the slowest.
- Namely, among PCM1, PCM2 and PCM3, PCM1 firstly begins to melt and PCM3 lastly begins to melt. However, PCM3 finishes firstly melting process and PCM1 finishes lastly melting process.
- The melting times of PCM1, PCM2 and PCM3 decrease with increase in inlet temperatures of the air. Namely, the higher inlet temperature of the air, the smaller melting times are needed. Moreover, decreasing degree of the melting times are different, decreasing degree of the melting time of PCM1 is the biggest and that of PCM3 is the smallest.
- However, most PCMs have low thermal conductivity ranging from 0.1 to 0.6W/mK, as a result, leading to slow charging and discharging rates, hence heat transfer enhancement techniques are necessary for most LHTES applications.

Salwa Bouadila et al [12], studied the enhancement of latent heat storage in a rectangular cavity: Solar water heater case study (Fig. 5). This system takes the form of two rectangular cavities incorporating behind the absorber of a flat plat solar collector. The PCM used is Paraffin and its thermophysical properties are: melting point 56.3°C, heat of fusion 189Kj/Kg, thermal conductivity 0.21W/m°C, specific heat liquid/solid 3.89/2.94 Kj/kg°C and density liquid/solid 0.74/0.86Kg/m³.

It is found that the outlet temperature of the collector under clear sky conditions, increases gradually at the beginning and attains a maximum value of 75 °C. The lower PCM temperature inside the cavities of the solar collector was recorded in the morning with an average value around 18 C, increasing with the insulation to a maximum value of 57 C at 12:30, which corresponds to the melting point of the paraffin. The PCM temperature starts to decrease at the afternoon, the average temperature at 16:00 was about 50 C and at midnight it was about 35 C which is suitable for domestic use.

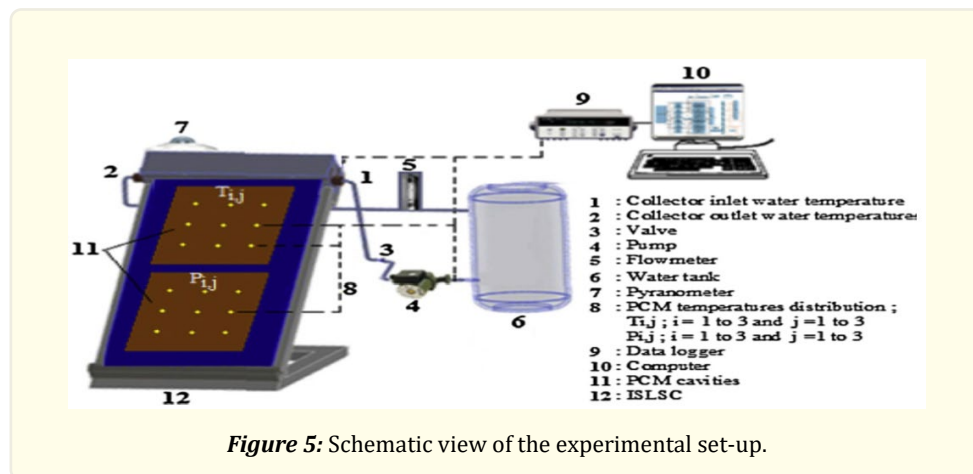


Figure 5: Schematic view of the experimental set-up.

Yasin Varol et al [13], studied the forecasting of thermal energy storage performance of phase change material in a solar collector using soft computing techniques (Fig. 6). Sodium carbonate decahydrate (Na₂CO₃·10H₂O) is used as phase change material (PCM), its thermophysical properties are: melting point 306K, heat of fusion 267Kj/Kg, and density 1.44g/m³. The experience was investigated during March 23, 2003, and collector efficiency was compared with those of convectonal system including no PCM. PCM was placed to bottom of the collector.

It was found that the efficiency of collector increases due to presence of the PCM. Using of PCM enhances the performance of solar collectors such as collector efficiency and useful energy although the experiments were performed during March. The used PCM is suitable for this application.

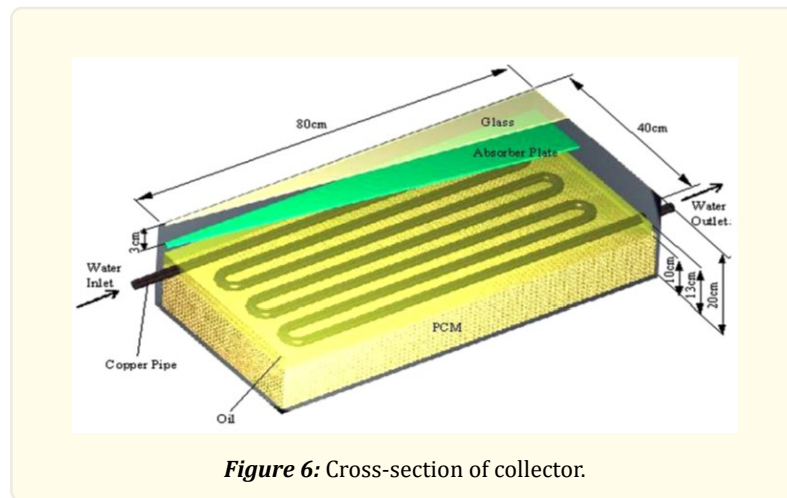


Figure 6: Cross-section of collector.

S. O. Enibe [14], studied the performance of a natural circulation solar air heating system with phase change material energy storage (Fig. 7). The PCM is prepared in modules, with the modules equispaced across the absorber plate. The experience was performed in Nigeria over the ambient temperature range of 19-41 °C, and a daily global irradiation range of 4.919.9 MJ/m². The used PCM is Paraffin with thermophysical properties: melting point 58-60°C, heat of fusion 214.4KJ/Kg, thermal conductivity 0.2W/mK, specific heat 900J/kgK, viscosity 1.07*10⁻⁶ Kg/ms and density liquid/solid 775/850 Kg/m³. Experimental day-time performance data on the system was obtained for 14 different days in May and June at Nsukka, usually between the hours of 6:30 and 18:30 local time.

The results show that the system is suitable for use as a solar cabinet crop dryer for aromatic herbs, medicinal plants and other crops, which do not require direct exposure to sunlight.

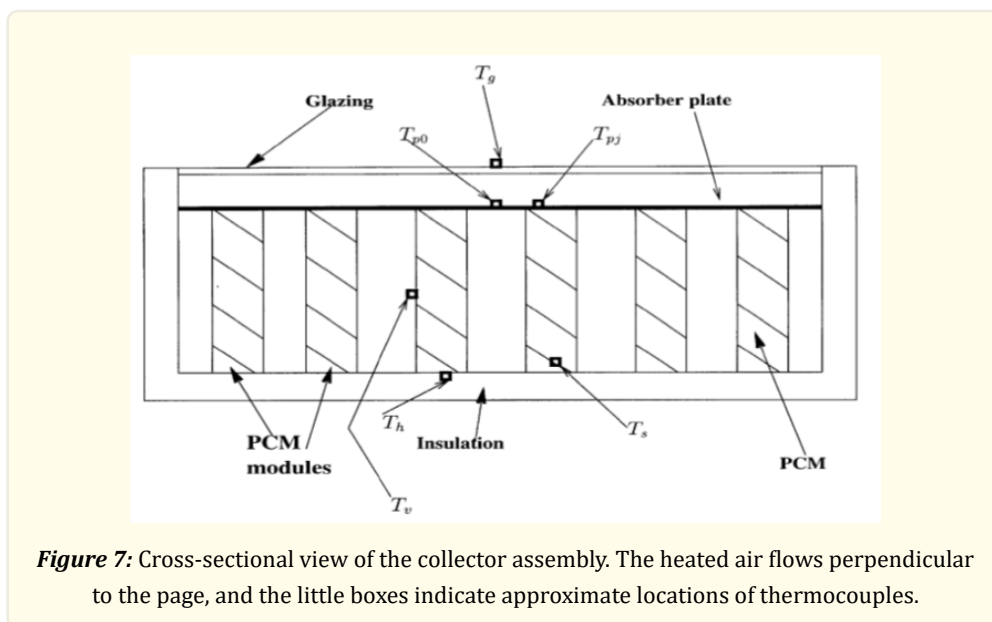


Figure 7: Cross-sectional view of the collector assembly. The heated air flows perpendicular to the page, and the little boxes indicate approximate locations of thermocouples.

Benli H et al [15], investigated five designs (corrugated, reverse corrugated, trapeze, reverse trapeze, and flat) of solar air collectors. They used $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ as the PCM with a melting temperature of 29°C . They concluded that the proposed solar air collectors and the selected PCM system created a $6\text{-}9^\circ\text{C}$ temperature difference between the inside and the outside the greenhouse.

Application of PCM in solar dryers

Gülsah Çakmak and Cengiz Yıldız [16], studied The drying kinetics of seeded grape in solar dryer with PCM-based solar integrated collector (Fig. 8). The system consists of drying room and solar collector with phase change material used to perform drying after sunset. During day hours, solar energy was collected in the PCM with the help of collector. After the sunset, the air sent with the help of fan was passed through the surface where PCM was located, and so the stored energy was utilized. Thereby, even after the sunset, drying process continued using the collector where PCM was located. Calcium chloride hegzahidrat as PCM was placed to the lower section of the collector. It has been determined that drying time shortens as drying air velocity increases and the drying process has occurred in decreasing drying period. The obtained results show that the proposed system can be used for drying the other fruits and vegetable by increasing the quality of food values.

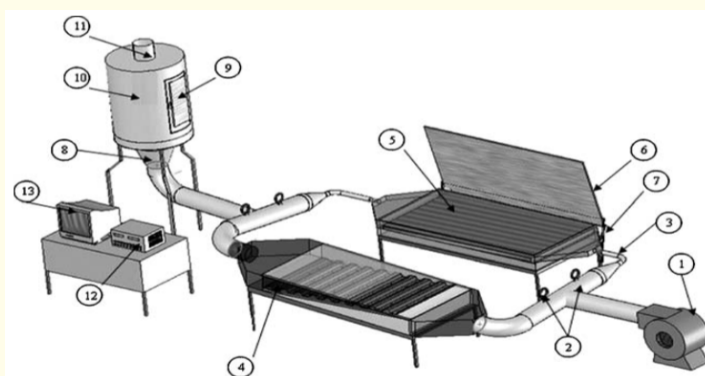


Figure 8: Schematic view of manufactured experimental set-up. (1) Fan, (2) valves, (3) connection pipe, (4) expanded-surface solar air collector, (5) collector with PCM, (6) adjustable mirror, (7) adjustable collector tripod, (8) diffuser, (9) observation glass, (10) drying room, (11) air exit chimney, (12) datalogger and (13) PC.

Alejandro Reyes et al [17], studied Mushrooms dehydration in a hybrid-solar dryer, using a phase change material. The used PCM is paraffin wax, its properties are: fusion temperature $56\text{-}58^\circ\text{C}$, fusion heat $200\text{-}220\text{KJ/Kg}$, thermal conductivity solid/liquid $0.4/0.15\text{ W/m}^\circ\text{C}$ and density solid/liquid $861/778\text{ Kg/m}^3$. At the outlet of the drying chamber the air was recycled (70% or 80%) and the air temperature was adjusted to 60°C . At the outlet of the solar panel the air temperature rose up to 30°C above the ambient temperature, depending on solar radiation level. The system consists of solar panel, solar energy accumulator and drying chamber. The solar energy accumulator contained 14 kg of paraffin wax (PCM) distributed in 100 copper pipes (inner diameter of 14 mm) with external aluminum fins that favor heat transfer to the drying air:

The obtained results showed that using of PCM improve the global thermal efficiency of the system and that the thermal efficiency could be further increased by augmenting the paraffin wax mass in the accumulator:

Dilip Jain et al [18], studied the performance of indirect through pass natural convective solar crop dryer with phase change thermal energy storage (Fig. 9). The dryer consists of flat plate solar collector, packed bed phase change energy storage, drying plenum with crop trays and natural ventilation system. The paraffin wax is used as phase change material (PCM) which was placed below the

drying chamber that consisted of 48 numbers of cylindrical tubes. The phase change material stores the thermal energy during sun shine hours and releases the latent and sensible heat after sunset, thus dryer is effectively operative for next 5-6 h. The results showed that the temperature in drying chamber was observed 6 C higher than the ambient temperature after sunshine hours till the mid night during the month of June at Jodhpur.

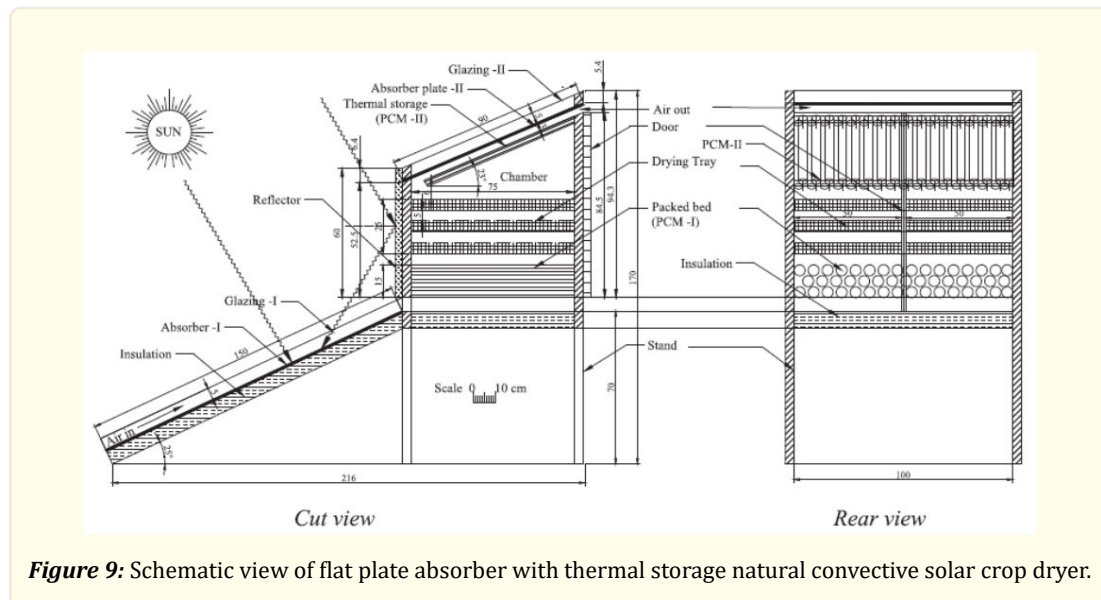


Figure 9: Schematic view of flat plate absorber with thermal storage natural convective solar crop dryer.

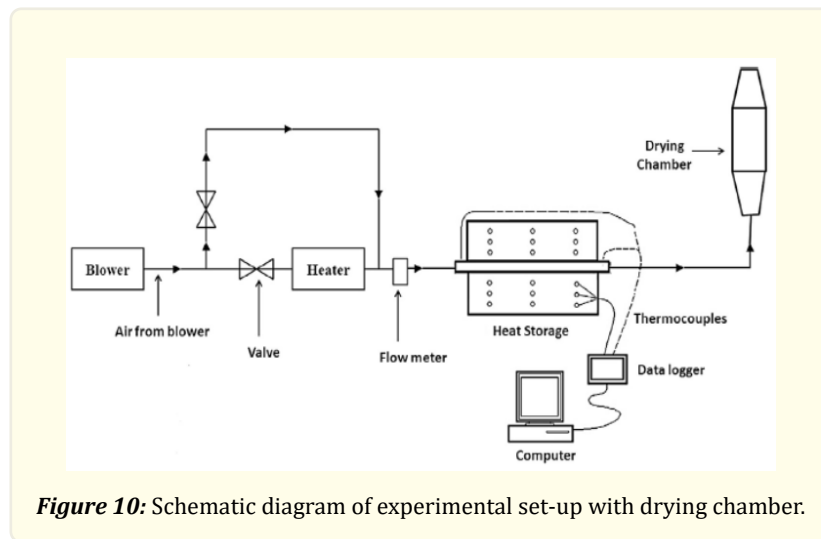
S. M. Shalaby et al [19], reviewed the previous works on solar drying systems which implemented the phase change material as an energy storage medium. It was found that the latent heat storage provides much higher storage density than sensible heat storage, with a smaller temperature difference between storing and releasing heat. The phase change materials provide constant and moderate temperature which is needed for drying most agriculture crops sufficiently. The solar dryer with a PCM reduces the heat losses and improves the efficiency of the system.

Lalit M. Bal et al [3], reviewed Solar dryer with thermal energy storage systems for drying agricultural food products. It was found that solar energy storage can reduce the time between energy supply and energy demand, thereby playing a vital role in energy conservation. With the storage unit, agricultural food materials can be dried at late evening, while late evening drying was not possible with a normal solar dryer.

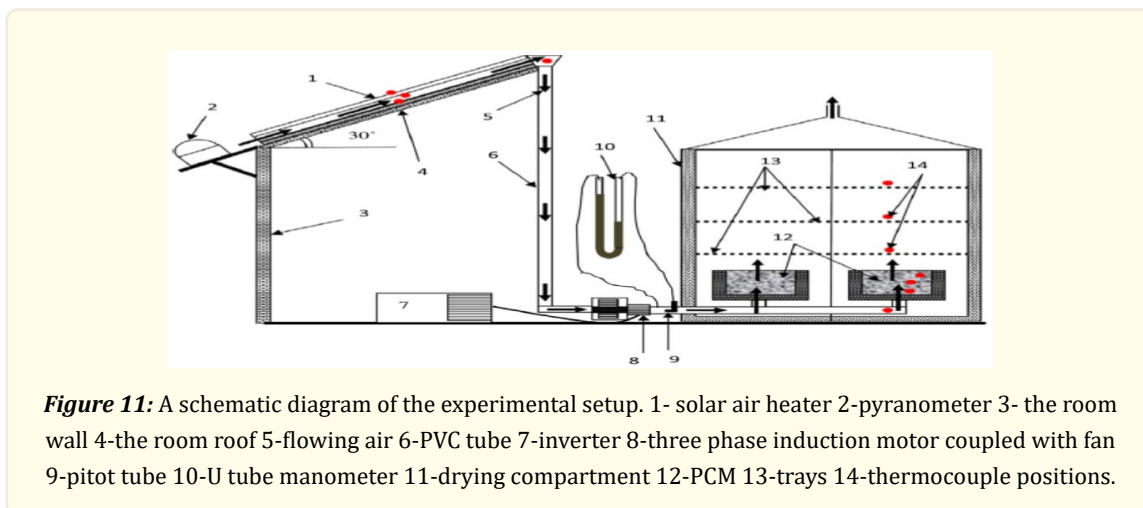
The effect of latent heat storage has two main advantages:

- (i) It is possible to store large amounts of heat with only small temperature changes and therefore to have a high storage density.
- (ii) Because the change of phase at a constant temperature takes some time to complete, it becomes possible to smooth temperature variations.

Ashish Agarwal et al [20], made an experimental investigation of shell and tube latent heat storage for solar dryer using paraffin wax as heat storage material (Fig. 10). The shell and tube type latent heat storage (LHS) has been designed for solar dryer and paraffin wax is used as heat storage material. The heat exchanger system is placed horizontally and liquid PCM is filled in the heat exchanger. Experimental results show that the LHS is suitable to supply the hot air for drying of food product during non sunshine hours or when the intensity of solar energy is very low.



S.M. Shalaby et al [21], made an experimental investigation of a novel indirect solar dryer implementing PCM as energy storage medium (Fig. 11). The system consists of two identical solar air heaters, drying compartment, PCM storage units and a blower. Two plastic cylindrical containers with a height of 0.3 m and inner radii of 0.15 m were filled with PCM (paraffin wax of melting temperature 49 C) to be used as heat storage units. It is found that after using the PCM, the temperature of the drying air is higher than ambient temperature by 2.5-7.5 C after sunset for five hours at least.



M. Ayadi et al [22], studied the simulation and performance of a solar air collector and a storage system for a drying unit (Fig. 12). The system consists of solar collector, storage unit and drying room. The gravel of specific heat 0.99 kJ/kg K and a density of 2702 kg/m³ is used as the storage material. The gravel has been disposed inside the storage unit. The study of the storage system during the day of 19 September gave a storage temperature difference ΔT of 10 C and an average drying temperature of about 35.3°C.

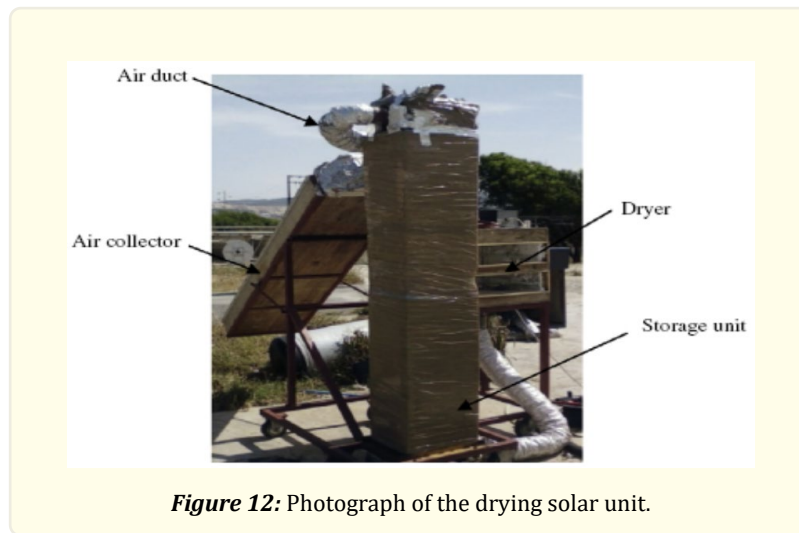


Figure 12: Photograph of the drying solar unit.

Sari Farah Dina et al [23], Studied the effectiveness of continuous solar dryer integrated with desiccant thermal storage for drying cocoa beans (Fig. 13). The system consists of drying chamber and solar collector. The PCM is disposed inside the drying chamber below the agro alimentary products. The results revealed that during sunshine hours, the maximum temperature within the drying chamber varied from 40 C to 54 C. In average, it was 9-12 C higher than ambient temperature. The solar dryer integrated with desiccant thermal storage makes drying using solar energy more effective in term of drying time and specific energy consumption.

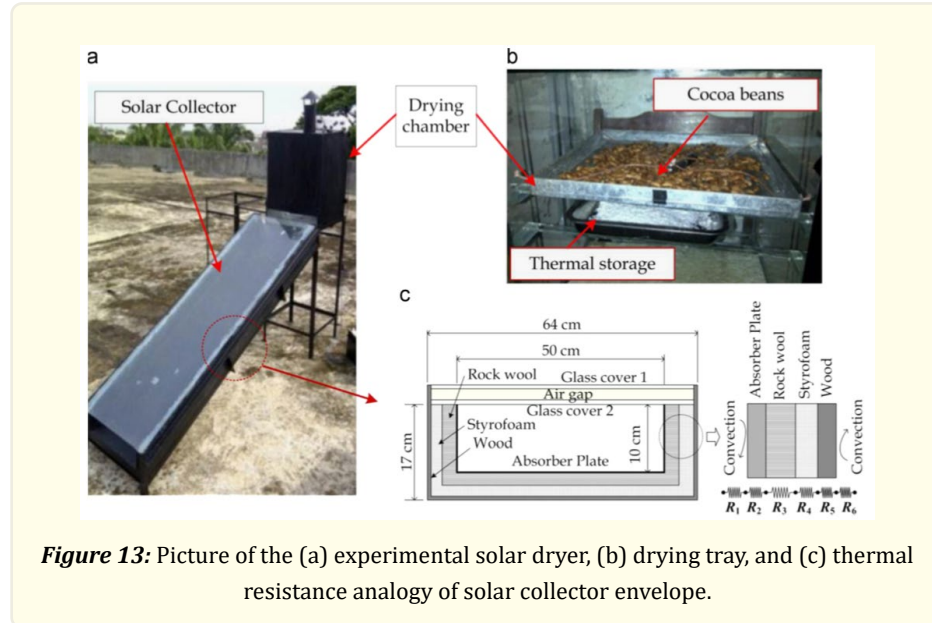


Figure 13: Picture of the (a) experimental solar dryer, (b) drying tray, and (c) thermal resistance analogy of solar collector envelope.

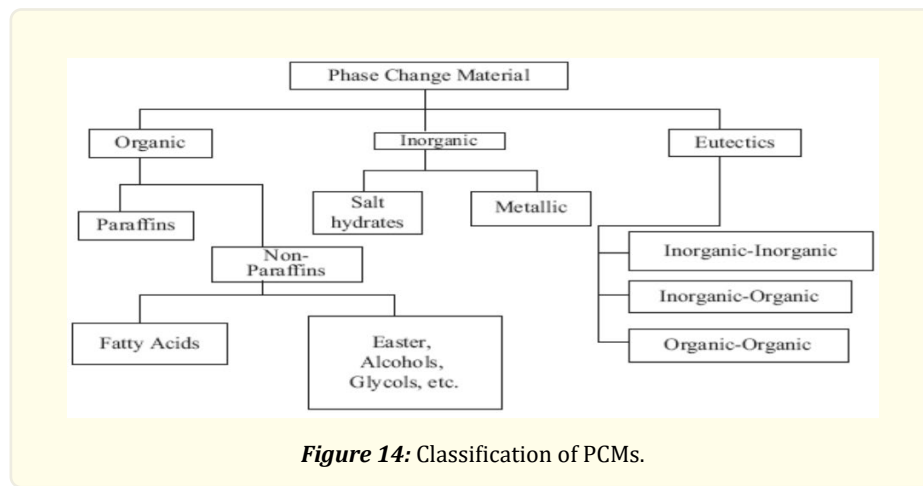
Definition of phase change materials

PCM are materials that accumulate energy when changing from solid to liquid state (melting heat), and turns it over when changing from liquid to solid state (solidification heat). Phase change heat exhibits a high heat density and a minimum temperature variation during fusion and solidification periods [17].

A phase change material is a solid which stores energy by melting upon the application of heat. The melting temperature may be fixed or vary over a small range. The stored energy is recovered upon solidification of the liquid [14].

Classification of phase change materials

During the last four decades many phase change materials, with a wide range of melting/freezing point, have been identified and studied extensively. These materials include organic (e.g., paraffins, fatty acids), inorganic (e.g., salt hydrates, metallic) and eutectics (e.g., mixture of organic and/or inorganic materials). A classification of PCMs for solid-liquid phase transformation is given in Fig. 14. Each group of PCMs with their properties, advantages and limitations have been comprehensively reported in various literatures [24].



The most used and important PCMs

The most important PCMs include Glauber’s salt, calcium chloride hexahydrate, sodium thiosulfate penthydrate, sodium carbonate decahydrate, fatty acid, and paraffin waxes. These applications are listed in Zalba et al [25]. Both fatty acids and paraffins are cheap, readily available, and melt at different temperatures.

Target application areas for some studied PCMs [26].

Temperature range (C)	PCMs studied/melting temperature (C)	Target application area (rationale behind selection of PCM)
0–65 C	-- Paraffins (-3 to 64), water/ice/0, stearic acid/41–43, n-octadecane/27.7	-Storage for domestic heating/cooling. Passive storage in bio-climatic building/architecture. Thermal storage of solar energy. Application in off-peak electricity for cooling and heating. Protection of electrical devices.
80–120 C	-Erythritol/117.7; RT100 (99); MgCl ₂ -6H ₂ O (116.7)	-Storage for the hot-side of LiBr/H ₂ O absorption cooling system with generator temperature requirements of less than 120 C
>150	-NaNO ₃ /310, KNO ₃ /330 NaOH/318, KOH/380 ZnCl ₂ /280	- Storage for solar power plants based on parabolic trough collectors and direct steam generation.

Desirable properties of phase change materials

Murat Kenisarin et al [5], determined the most desirable properties for choosing the best phase change material and which are listed below:

- A high value of the heat of fusion and specific heat per unit volume and weight,
- A melting point which matches the application,
- A low vapor pressure (0.1 bar) at the operational temperature,
- A chemical stability and non-corrosiveness,
- A PCM should not be hazardous, highly inflammable or poisonous,
- A PCM should have a reproducible crystallisation without degradation,
- A PCM should have a small supercooling degree and high rate of crystal growth,
- A PCM should have a small volume variation during solidification,
- A high thermal conductivity,
- A PCM should be of abundant supply and at a low cost.

The main criteria that govern the selection of phase change heat storage materials are given by Abhat. A [27]:

1. Possess a melting point in the desired operating temperature range (temperature range of application).
2. Possess high latent heat of fusion per unit mass, so that a smaller amount of material stores a given amount of energy.
3. High specific heat to provide additional significant sensible heat storage effects.
4. High thermal conductivity, so that the temperature gradients for charging and discharging the storage material are small.
5. Small volume changes during phase transition, so that a simple container and heat exchanger geometry can be used.
6. Exhibit little or no subcooling during freezing.
7. Possess chemical stability, no chemical decomposition and corrosion resistance to construction materials.
8. Contain non-poisonous, non-flammable and non-explosive elements/compounds.
9. Available in large quantities at low cost.

It is desirable to select the thermal energy storage based on the following criteria: cost, efficiency, environmental impact, life cycle cost, safety, and the required space [28].

Lalit M. Bal et al [5], found that the PCM to be used in the design of thermal-storage systems should possess desirable thermophysical, kinetics and chemical properties which are as follows:

Thermal properties

- Suitable phase-transition temperature (melting temperature) in the desired operating temperature range.
- High sensitive heat capacity and latent heat of fusion per unit volume to minimize the physical size of the heat storage container.
- High specific heat to provide for additional significant sensible heat storage.
- High thermal conductivity of both solid and liquid phases to assist the charging and discharging of energy of the storage systems.

Physical properties

- High density, so that a smaller container volume holds the material.
- Small volume changes on phase transformation.
- Low vapor pressure at operating temperatures to reduce the containment problem.
- Congruent melting (phase stability) of the phase change material for a constant storage capacity of the material with each freezing/melting cycle.

Kinetic properties

- High nucleation rate to avoid super cooling of the liquid phase.
- High rate of crystal growth, so that the system can meet demands of heat recovery from the storage system.

Chemical properties

- Long-term chemical stability.
- Complete reversible freeze/melt cycle.
- No degradation after a large number of freeze/melt cycle.
- Compatibility (non-corrosiveness) with materials of construction.
- Non-toxic, non-flammable and non-explosive materials for safety.

Applications of PCMs in thermal energy storage systems

Murat Kenisarin et al [5], listed the different applications of PCM in thermal energy storage systems:

- Cooling of heat and electrical engines
- Cooling: use of off-peak rates
- Cooling: food, wine, milk products (absorbing peaks in demand), greenhouses
- Heating and hot water: using off-peak rates
- Medical applications: transportation of blood, operating tables, hot-cold therapies
- Passive storage in bio-climatic building/architecture (HDPE, paraffin)
- Safety: temperature level maintenance in rooms with computers or electrical/electronic appliances
- Smoothing exothermic temperature peaks in chemical reactions
- Solar power plants
- Thermal comfort in vehicles
- Thermal protection of electronic devices (integrated in the appliance)
- Thermal protection of food: transport, hotel trade, ice-cream, etc.
- Thermal storage of solar energy.

Recent investigations on PCMs

It is found that most organic and inorganic PCMs investigated in the literature are those whose melting temperature is in the range of 30-60C and latent heat of fusion is in the range of 150-250 kJ/kg. The most eutectic PCMs studied in literature has the melting point in the range of 20-60C and latent heat of fusion is in the range of 125-200kJ/kg [24].

Organic materials

Most organic PCMs investigated are paraffins and fatty acids. It is found that paraffins have good thermal and chemical stability after number of the thermal cycles. The fatty acids studied widely are stearic, lauric, myristic, capric and palmitic acid. Most of the fatty acids used as PCMs are industrial grade.

Inorganic materials

The inorganic materials have not been investigated as heat storage materials to the same extent as the organic ones have.

Heat storage material	Transition temperature (°C)	Melting range (°C)	Heat of fusion including transition heat (kJ/kg)	Sensible heat solid/liquid (kJ/kg °C)	Heat conductivity (W/mK)	Density solid/liquid (kg/l)
Suntech P116 Paraffin wax		43–56	266	2.95/2.51	0.24/0.24	0.818/0.760
Unicere 55 Paraffin		52.5–53.7	182–189			
Paraffin 44		44	167			
Paraffin 53		53	200			
Paraffin 64		64	210			
Paraffin 56 (Russia)		56 ± 2	72–86		0.75 (25 °C)	1.06
Paraffin 57 (Russia)		57 ± 2	98		0.7	
Paraffin 63 (Russia)		63 ± 2	60			
Paraffin natural wax 79 (Russia)		79 ± 2	80		0.63	1.20
Paraffin natural wax 84 (Russia)		84 ± 2	85		0.72	1.20
Paraffin natural wax 106 (Russia)		106 ± 2	80		0.65	1.20
Paraffin wax 53 (commercial grade)		53	184	2.05		
Paraffin 53	35.4	53	164	2.13 (30 °C)/ 2.62 (70 °C)	0.28 (30 °C)/ 0.19 (70 °C)	0.978 (30 °C)/ 0.795 (70 °C)
RT 60 Rubitherm paraffin		58–60	214	0.93	0.2	0.850/0.775

Table 1: Thermo-physical properties of some commercial paraffin and paraffin waxes [5].

Heat storage composition	Type of composition	Melting point (°C)	Heat of fusion (kJ/kg)	Sensible heat solid/liquid (kJ/kg °C)	Heat conductivity (W/mK)	Density solid/liquid (kg/l)
Acetamide (commercial grade)	Chemical compound	82	263	1.94		1.159/0.998
Acetanilide (commercial grade)	Chemical compound	118.9	222	2.00		
Erythrol (food additive grade)	Chemical compound	118	339.8	1.38 (20 °C)/2.76 (140 °C)	2.64 (20 °C)/1.17 (140 °C)	1.48 (20 °C)/1.30 (140 °C)
Erythritol (commercial grade of Mitsubishi Chemical Co.)		116 ± 2	338 ± 7			
Trimethylolethane (62.5 wt%)+ water (37 wt%)—(PCM30)	Mixture	29.8	218	2.75 (10 °C)/3.58 (50 °C)	0.65 (22 °C)/0.21 (56 °C)	1.12 (10 °C)/1.09 (56 °C)
Trimethylolethane (38.5 wt%)+ water (31.5 wt%)+ urea (30 wt%)—(PCM13)	Mixture	14.4	160	4.22 (0 °C)/3.09 (30 °C)	0.66 (5 °C)/0.37 (38 °C)	1.17 (0 °C)/1.14 (30 °C)
Mn(NO ₃) ₂ · 6H ₂ O + MnCl ₂ · 4H ₂ O (4.0 wt%)	Mixture	15–25	125.9	2.34 (4.4 °C) 2.78 (13.7 °C)		1.795 (5 °C)/1.728 (40 °C)
Mg(NO ₃) ₂ · 6H ₂ O	Chemical compound	89.3–89.9	167–175	1.84/2.51	0.57 (120 °C)	
Mg(NO ₃) ₂ · 6H ₂ O + MgCl ₂ · 6H ₂ O (7.0 wt%)	Mixture	77.2–77.9	150.7–152.4	3.72 (50 °C)		

Table 2: Thermo-physical properties of some organic and inorganic materials [5].

Nagano et al [29], discovered that manganese nitrate hexahydrate could be used as the basis for the development of a new heat storage composition. The melting range for this material varies from 7.7 to 25.3 °C and its heat of fusion is 125.9 kJ/kg. It was observed that salt has a significant degree of supercooling. They also examined the influence of introducing various additives to change the melting temperature, the heat of fusion and the degree of supercooling. For example, they discovered that adding manganese chloride tetrahydrate into Mn(NO₃)₂ · 6H₂O in quantities of up to 10% in weight did not change the heat of fusion value.

Material	Melting point (°C)	Heat of fusion (kJ/kg)	Density (kg/l) (at 20 °C)	Cost (US\$/kg)
Erythritol	120	339.8	1.45	5.0
D-mannitol	166–168	316.4	1.52	6.7–7.5
Galactitol	188–189	351.8	1.47	—
Xylitol	93–94.5	263.3	1.52	6.7–8.3
D-sorbitol	96.7–97.7	185.0	1.50	1.1

Table 3: Thermo-physical properties of some inorganic materials.

It can be seen that erythritol have a specific feature is its high-density value. It should be noted that there is also a 10% change in erythritol's volume during the solid-to-liquid transition and therefore the storage vessel and heat exchanges need to be designed to take this into account [30].

Eutectic PCM

A eutectic PCM is a combination of two or more compounds which are either organic, inorganic or both. In the last decade, many researchers have shown significant interest in new eutectic type PCMs instead of pure compounds. It is observed that the most of the organic and inorganic eutectics which are proposed as PCMs are made from fatty acids and salt hydrates, respectively [24].

Problems and disadvantage of phase change materials

It is concluded that most of the phase change problems have been carried out at temperature ranges between 8C and 60 °C suitable for domestic heating applications.

The major disadvantage, as reported by many researchers has been the low thermal conductivities possessed by many PCMs, leading to low charging and discharging rates (especially for the organic based materials). The development of a latent heat thermal energy storage system therefore involves the understanding of heat transfers/exchanges in the PCMs when they undergo solid-to-liquid phase transition in the required operating temperature range, the design of the container for holding the PCM and formulation of the phase change problem [26].

The natural paraffins are a mixture of pure alkanes which have quite a wide range of the phase change temperature. These paraffins also have low heat conductivity and therefore the choice of those which can be used for practical solar applications is very limited. The common shortcoming of many potential phase change heat storage materials is their low heat conductivity. This is between 0.15 and 0.3 W/(mK) for organic materials and between 0.4 and 0.7 W/(mK) for salt hydrates.

At present, the cost of PCMs is quite high. For example, paraffin products of Rubitherm GmbH cost 2900-3500 h/ton and the price for a salt hydrate product is 9000-11,000 Australian dollars/ton [5].

Heat transfer in PCMs and enhancement techniques

Several studies have been conducted to study heat transfer enhancement techniques in phase change materials (PCMs) and include finned tubes of different configurations, bubble agitation, insertion of a metal matrix into the PCM, using PCM dispersed with high conductivity particles, micro-encapsulation of the PCM or shell and tube (multitubes).

To ensure long-term thermal performance of any PCM system, the size and shape of the PCM container must correspond to the melting time of the PCM and the daily insulation at a given location, if the source of energy is a solar collector. PCMs are typically placed in long thin heat pipes, cylindrical containers or rectangular containers [26].

None of the heat storage products which are commercially available on the market have heat transfer enhancement capabilities which would improve performance of low temperature devices. The means for enhancement of heat transfer in heat storage devices with a PCM are the use of fins and Lessing rings from various materials and carbon fibers [5].

In additions, various heat transfer enhancement techniques for paraffin as a PCM thermal storage medium were studied, such as those using fins, pin fins and lessing rings [31].

Despite the fact that paraffin wax is cheap and has moderate thermal energy storage density, its main drawback is the poor thermal conductivity. One of the effective ways of increasing paraffin wax thermal conductivity is to add some material of high thermal conductivity such as carbon fibers, graphite and metal foams that will be discussed as follows,

Fukai et al [32] used carbon fibers as a high thermal conductivity material. They investigated two different enhancement techniques. The first technique uses oriented fibers randomly, while the other is using a fiber brush. The carbon fibers essentially enhance the effective thermal conductivity of fibers/paraffin composites. The authors concluded that the random type and the fibers' length have little effect on the effective thermal conductivity of the PCM. However, the fiber brush increases the effective thermal conductivities to the maximum expected values.

Zhong et al [33], implemented mesosphere pitch based graphite foams (GFs) to increase the thermal diffusivity of paraffin wax. The thermal diffusivity of the Paraffin-GF can be enhanced 190, 270, 500, and 570 times as compared with that of pure paraffin wax. The key factors of such improvement are pore-size and thickness of ligaments of the foam. Small pore size and thicker ligament in the GF improves the composite thermal diffusivity, While, large pore-size and thinner ligament increases the composite latent heat.

Results of studies from Morrison and Abdel-Khalik [34] and Ghoneim [35], show that to store the same amount of energy from a unit collector area, rock (sensible heat storage material) requires more than seven times the storage mass of Paraffin 116 Wax (P116-Wax), five times the storage mass of medicinal paraffin and more than eight times the storage mass of Na₂SO₄-10H₂O.

PCM proposed in our application

Paraffin wax RT41: fusion temperature 45°C, latent heat 125KJ/Kg, thermal conductivity solid/liquid 0.2 W/mK and density solid/liquid 0.88/0.76 Kg/l, specific heat solid/liquid 1.8/2.4 KJ/kg°C.

P116 paraffin wax: fusion temperature 43-56°C, fusion heat 266KJ/Kg, specific heat solid/liquid 2.95/2.51 KJ/kg°C, thermal conductivity 0.24 W/mk and density solid/liquid 0.818/0.760 Kg/l [5].

Paraffin 53, its properties are: fusion temperature 53°C, fusion heat 164 KJ/Kg, specific heat solid/liquid 2.13/2.62 KJ/kg°C, thermal conductivity solid/liquid 0.28/0.19 W/mK and density solid/liquid 0.978/0.795 Kg/l [5].

Paraffin wax: melting temperature 56°C, specific heat of solid/liquid (kJ/kg °C) 2.95/2.51, density of solid/liquid (kg/m³) 818/760, thermal conductivity of solid/liquid (W/m °C) 0.24/0.24, heat of fusion 226 kJ/kg) [9].

Paraffin wax: melting point 56.3°C, heat of fusion 189Kj/Kg, thermal conductivity 0.21W/m°C, specific heat liquid/solid 3.89/2.94 KJ/kg°C and density liquid/solid 0.74/0.86Kg/m³.

Salt-hydrate: melting temperature 27-29°C a latent heat of 164.5 kJ/kg, solid and liquid densities of 1610 and 1490 kg/m³, and solid and liquid thermal conductivities of 0.6 and 0.5 W/mK, respectively [6].

Conclusion

Some natural substances, such as salt hydrates, paraffin and paraffin waxes, fatty acids and other compounds, have the required high latent heat of fusion in the temperature range from 0 to 150 °C and these materials could be used for solar applications, though have certain shortcomings. The main limitation of salt hydrates is their chemical instability when they are heated, as at elevated temperatures they degrade, losing some water content every heating cycle.

The ideal phase change material to be used for latent heat storage system must meet following requirements: high sensitive heat capacity and heat of fusion; stable composition; high density and heat conductivity; chemical inert; non-toxic and non-inflammable; reasonable and inexpensive.

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