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State of the art review of thermal energy storage systems using PCM operating with small temperature differences: Focus on Paraffin

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Abstract

Direct solar radiation is considered to be one of the most prospective sources of energy. However, the large utilization of this form of energy is possible only if the effective technology for its storage can be developed with acceptable capital and running costs. Latent heat storage is one of the most efficient ways of storing thermal energy which provides much higher storage density, with a smaller temperature difference between storing and releasing heat. One of potential techniques of storing solar energy is the application of phase change materials (PCMs). There are large numbers of PCMs that melt and solidify at a wide range of temperatures, making them attractive in a number of applications. This paper reviews previous work on latent heat storage and provides an insight to recent efforts of usingPCMs in energy storage. This work summarizes the investigation and analysis of the available thermal energy storage systems incorporating PCMs and also looks at the state of artof thermal energy storage systems, utilizing PCM operating with small temperature differences, such as various Paraffin waxes, which are cheap and have moderate thermal energy storage density but low thermal conductivity and require large surface area.

Keywords: Solar energy, Latent heat storage, PCM,paraffin waxes.

1. Introduction

Energy storageplays important roles in conserving available energy and improving its utilization. Solar energy is available only during the day, and consequently, its application requires efficientthermal energy storage (TES), so that the excess heat collected during sunshine hours may be stored for later use during the night. Therefore, the successful application of solar energy depends to a large extent on the method of energy storage used.

TES is a technology which can reduce the total energy consumption and may involve sensible heat storage (storing of energy by heating or cooling), latent heat storage (by melting or vaporizing or solidifying or liquefying) or a combination of both. The latent heat method of storage has attracted a large number of applications, as will bediscussed in this review paper.

However, practical difficulties usually arise in applying the latent heat method due to thelow thermal conductivity, density change, and stability of properties under extended cycling. During the last studies, many PCMs with a wide range of melting/freezing point have been identified and studied extensively.

Kaygusuz et al. [1] concluded that a comparison between latent and sensible heat storage shows that storage densities is typically 5 to 10 times higher than what can be reached using latent heat storage units. Rathod et al. [2] established that the feasibility of using PCM in the latent heat storage system is based on desirable thermo-physical, kinetic, and chemical properties, in addition to economic criteria. Zalba et al. [2] demonstrated that insufficiently long-term use of PCMs is due to two factors: poor stability of thematerial properties and/or corrosion between the PCM and the container [3].

In this present work, latent heat refers to the latent heat of melting, as other phase changes, such as evaporation, are not practical due to the large volume change associated with it. In accordance with the topic, this paper provides a review of studies dealing with TES using PCMs and classifies different storage concepts of PCMs operating with low temperature.

2. Methods of energy storage

2.1. Energy storage systems

Energy storage (ES) is the storing of some form of energy that can be drawn at a later time to perform some useful operation. A device that stores energy is sometimes called an accumulator.

All forms of energy are potential energy (e.g. chemical or gravitational), kinetic energy, electrical energy or thermal energy, and all these forms of energy could be stored with a suitable method, system or technology. That means that every form of energy has itself an accumulator.

As shown in Figure 1, a large variety of energy storage systems are under development [4].

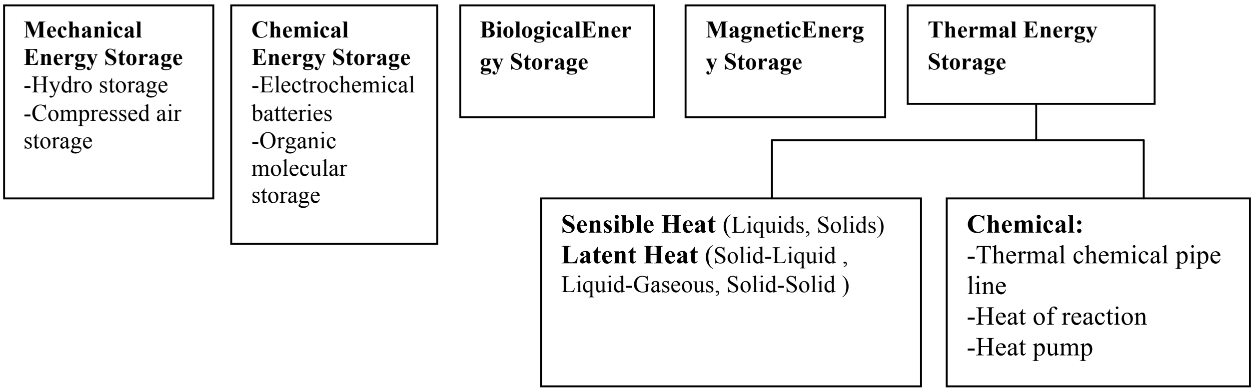

Figure 1: Classification of energy storage systems and different types of thermal storage of solar energy

2.1.1. Mechanical energy storage

Mechanical energy storage systems include gravitational energy storage or pumped hydropower storage (PHPS) and compressed air energy storage (CAES). The PHPS and CAES technologies can be used for large-scale utility energy storage.

2.1.2. Electrical energy storage

Energy storage through batteries is an option for storing the electrical energy. A battery is charged by connecting it to a source of direct electric current and when it is discharged, the stored chemical energy is converted into electrical energy. Potential applications of batteries are utilization of load leveling and storage of electrical energy generated by wind turbine or photovoltaic plants.

2.1.3. Thermal energy storage

As the temperature of a substance increases, its energy also increases. The energy released (or absorbed) by a material as its temperature is reduced (or increased) is called sensible heat. On the other hand, the energy required toconvert a solid material in a liquid material, or a liquid material in a gas (phase change of a material) is called heat of fusion at the melting point(solid to liquid) and heat of vaporization (liquid to gas), respectively.

2.1.4. Thermochemical energy storage

The other category of storing heat is through the use of reversible endothermic chemical reactions. Hasnain et al. [5] reported that, in practical systems, some of the steps may occur simultaneously, and each step can happen morethan once in each storagecycle. Pilkington et al. [6] determined that this kind of storage is a truly attractive option in longer term and could offer relatively low costs.

Thermal energy storage can be stored as a change in internal energy of a material as sensible heat, latent heat and thermo chemical or combination of them. An overview of major technique ofstorage of solar thermal energy is shown inFigure 1.

2.2. Sensible heat storage

Sensible heat storage (SHS) utilizes the heat capacity and the change in temperature of the material during the process of charging and discharging. According to previous mentioned work, water appears to be the best SHS liquid available because it is inexpensive and has a high specific heat. The amount of heat stored **(Q)** depends on the specific heat **(C_P)**, the temperature changes and the amount of storage material as follows:

$$Q= mC_P(T_{env}-T_{mat}) \qquad (1)$$

Sensible heat storage materials are defined as a group of materials which endure no change in phase over the temperature range encountered in the storage process. The amount of thermalenergy stored in a mass of materialcan be expressed as:

$$Q=\rho V C_P \Delta T \qquad (2)$$

Where**Q** is the amount of heat stored [J], **ρ** is the densityof the storage material [kg/L], C_P is the specific heat over the temperature range of operation [J/(kg K)], **V** is the volume of storage materialused (L), and ΔT is the temperature range of operation [°C].

The ability to store sensible thermal energy for a given material depends strongly on the value of the quantity ρC_P, the thermal capacity. For a material to be useful in a TES application, it must be cheap and have good thermal capacity. Another important parameter in sensible TES is the rate at which that heat can be released and extracted. This characteristic is function of the thermal diffusivity**.**

Differential Scanning Calorimetry (DSC) is a thermal analysis technique which is using a calorimeter to measure the heat flow of a PCM sample when heated, cooled or maintained at a constant temperature. DSC is the most used method for determining the *storage capacity* because it's the most common commercial device. Thermal conductivity is obtained by:

$$\lambda = \rho\, C_P\, \alpha \qquad (3)$$

Where **λ** is the thermal conductivity [W/(m K)], **ρ** is the density [kg/m^3], C_P is the specific heat [J/(kg K)] and **α**is the thermal diffusivity [m^2/s].

2.3. Latent heat storage

Latent heat storage (LHS) is based on the heat absorption or release when a storage material undergoes a phase change from solid to liquid or liquid to gas or vice versa. The storage capacity of the LHS system with a PCM is given by:

$$Q= m.L_m \qquad (4)$$

Where L_m (J/Kg) is used to quantify the latent heat (L_{fusion} for L-S phase change, $L_{vaporisation}$ for L-V phase change).

From an energy efficiency point of view, PCM storage systems have the advantage that they operate with small temperature differences between charging and discharging (Figure 2).

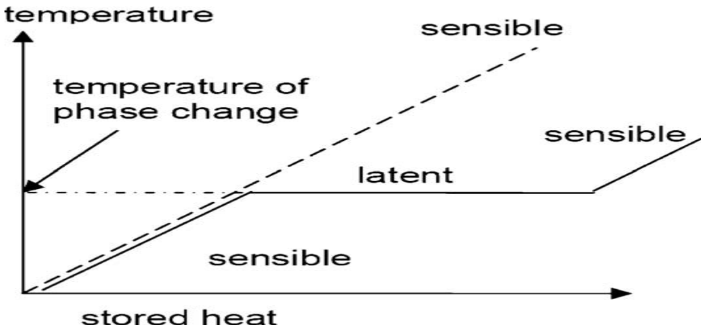

Figure 2: Phase change profile of PCM.

The most interesting phase change to be applied in a thermal storage is the phase change solid–liquid. Figure 3 shows a scheme with the families of materials which could be used as PCM in thermal energy storage systems.

2.4. Storage concept

High temperature storage concepts in solar power plants can be classified as active or passive systems (Figure4).

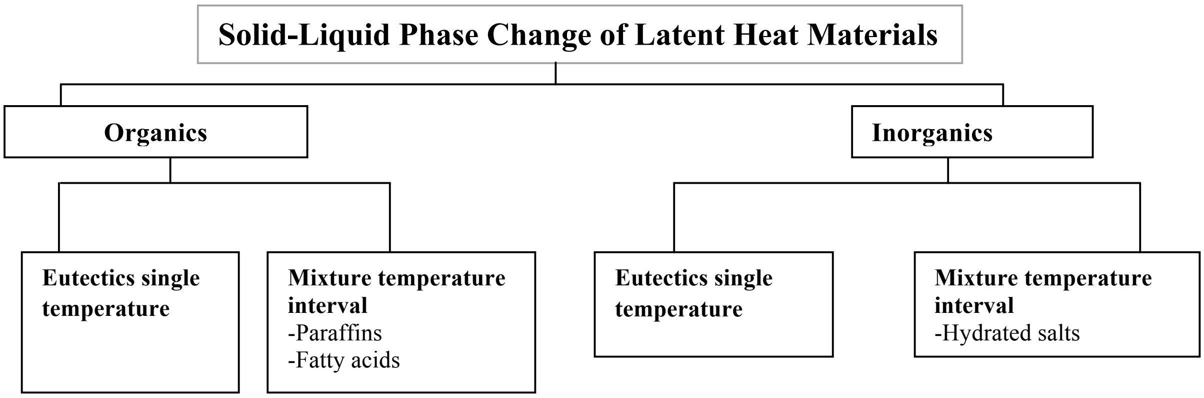

Figure 3: Classification of latent heat materials with solid–liquid phase change.

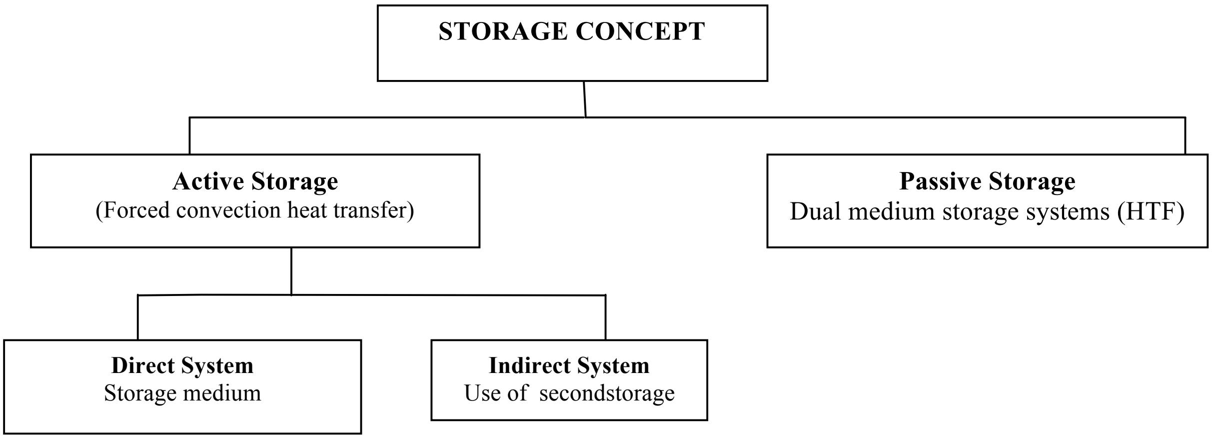

Figure 4: Scheme of different storage systemsclassifications accordingto the storage concept.

2.4.1 Active storage systems

An active storage system is mainly characterized by forced convection heat transfer into the storage material. The storage medium itself circulates through a heat exchanger which can be a solar receiver or a steam generator. Active systems are subdivided into direct and indirect systems. In a direct system, the heat transfer fluid serves also as the storage medium, while in an indirect system, a second medium is used for storing the heat.

2.4.2 Passive storage systems

Passive storage systems are generally dual medium storage systems: the Heat transfer fluid (HTF) passes through the storage only for charging and discharging a solid material. Additionally, the HTF carries energy received from the energy source to the storage medium during charging, and receives energy from the storage when discharging (these systems are also called regenerators).

The main disadvantage ofregenerators is that the HTF temperature decreases during discharging as the storage material cools down.

3. Discussion of PCMs classification and properties

Materials to be used for phase change thermal energy storage must have a large latent heat and high thermal conductivity. They should have a melting temperature lying in the practical range ofoperation, melt congruently with minimum subcooling and be chemically stable, low in cost, nontoxic and non-corrosive.

Materials that have been studied during the last years are hydrated salts, paraffin waxes, fatty acids and eutectics of organic and non-organic compounds. Materials that melt below 15 °C are used for storing coolness in air conditioning applications, while materials that melt above 90 °C are used for absorption refrigeration. All other materials that melt between these two temperatures can be applied in solar heating. These materials represent the class of materials that has been studied most.

Readers who are interested in such information are referred to the papers of Lorsch et al. [7], Lane et al. [8] and Humphries and Griggs [9] who have reported a large number of possible candidates for latent heat storage covering a wide range of temperatures. A classification of PCMs is given, above, in Figure3. Moreover, Table 1 shows a comparison of organic and inorganic materials for heat storage.

Table 1: Comparison of organic and inorganic PCM

Organics	**Inorganics**
Advantages No corrosives , Low or none undercooling Chemical and thermal stability	Greater phase change enthalpy
Disadvantages Lower phase change enthalpy Low thermal conductivity Inflammability	Undercooling Corrosion Phase separation Phase segregation, lack of thermalstability

Investigations showed that, in general, inorganic compounds have almost double volumetric latent heat storage capacity (250–400 kg/dm^3) than the organic compounds (128–200 kg/dm^3). It's found that most organic and inorganic PCMs investigated in the literature are those whose melting temperature is in the range of 30–60°C and latent heat of fusion is in the range of 150–250 kJ/kg.

3.1. Focus onParaffin

Earlier studies have already established the thermos physical properties of the organic paraffin asreported below by Table2.

Table 2: Thermo physical properties of the organic paraffin

Thermophysical properties	**Units**	**Magnitude**
Melting/ solidification T	K	300.7
Latent heat fusion	kJ/kg	206
Thermal conductivity S-L	W/mK	0.18 /0.19
Specific heat S-L	kJ/kgK	1.8 / 2.4
Density	Kg/m^3	789 / 750

Farid et al. [10] established that commercial paraffin waxes, which melt around 55°C, have been studied most. He have similarly employed three commercial waxes having melting temperatures of 44, 53 and 64°C with latent heats of 167, 200 and 210 kJ/kg, respectively, in the same storage unit to improve its performance [11].

The normal paraffin of type C_nH_{2n+2} are the family of saturated hydrocarbons with almost similar properties. Abhat A et al. proved that higher the value of n, the higher is the melting temperature and latent heat of fusion [12].For example, paraffin wax consists of a mixture of mostly straight chain n-alkanes CH_3–(CH_2)–CH_3. The crystallization of the (CH_3)-chain releases a large amount of latent heat. Both the melting point and latent heat of fusion increase with chain length.

Dincer et al. [4] showed that paraffin waxes the most commonly used commercial organic heat storage PCM. It consists of mainly straight chain hydrocarbons having melting temperatures ranging between 23 and 67°C.

Paraffin qualifies as heat of fusion storage materials due to their availability in a large temperature range. But, due to cost consideration, only technical grade paraffin may be used as PCMs in latent heat storage systems. Paraffin is safe, reliable, predictable, less expensive and non-corrosive.

Hadjieva et al. [13] considered three paraffinas samples A, B, and C with hydrocarbon formula $C_{22\cdot2}H_{44.1}$ (melting point 47.1 °C), $C_{23\cdot2}H_{40.4}$ (57.1 °C) and $C_{24\cdot7}H_{51.3}$ (62.6 °C), respectively. They studied the changes in thermo-physical properties after 900 thermal cyclesof operation and observed low enthalpy and broad phase transition range for sample C. Consequently, they concluded that there was no noticeable degradation in the structure of paraffin A and B. However, paraffin of sample C was proposed as an efficient material because it showed highest enthalpy.

Sharma et al. [14] conducted 300 melt/ freeze cyclesof commercial-grade paraffin wax (melting point 53 °C). They analyzed the changes in latent heat of fusion, melting temperature and specific heat using the DSC technique.
Shukla et al. [15] performed thermal cycling tests on three paraffin waxes of different melting temperatures indicated as type A (melting point 58–60 °C), type B (60–62 °C) and type C (54 °C). For type A and type B paraffin, number of cycles of operation performed was 600 while type C was tested for 1500 cycles. The changes in melting point and latent heat with increasing in number of cycles were significant for type A and B. However, type C paraffin wax was found most suitable for latent heat storage purpose on the basis of its stability even after 1500 cycles of operation.
A list of mentionedparaffin is given in Table 3 with a comparison of their melting point and latent heat of fusion. It can be noted that the most studied paraffin has melting temperature in the range of 45 °C to 60 °C. This paraffin was tested for thermal stability up to 1500 thermal cycles. Further, it can also be noted that paraffin does not show regular degradation in its thermal properties after repeated number of thermal cycles.

Table 3: Comparison of melting point and latent heat of thermal cycled paraffin.

Paraffin	**Melting point (°C)**	**Latent heat (J/g)**	**Thermal cycles**	**Reference**
Paraffin ($C_{22.2}H_{44.1}$)	47.1	166	900	Hadjieva et al. [13]
Paraffin ($C_{23.2}H_{48.4}$)	57.1	220	900	Hadjieva et al. [13]
Paraffin wax 53	53	184	300	Sharma et al. [14]
Paraffin wax 54	53.32	184.48	1500	Shukla et al. [15]
Paraffin wax 58–60	58.27	129.8	600	Shukla et al. [15]
Paraffin wax 60–62	57.78	129.7	600	Shukla et al. [15]

3.2. Researches on PCM properties

Thermal energy storage materials must accomplish basic characteristics to be used. Furthermore,Table 4 reports and summarizes the desired PCM properties [3].Based on these characteristics, the appropriate material for a determinate application can be found.

Table 4: Desired PCM properties and main characteristics of energy storage materials.

Properties	**Criteria**	**Observation**
Thermal	Appropriate melting-solidification temperature High latent heat of fusion	High thermal conductivity would assist the charging and discharging of the energy storage.
Physical	High density Less volume change	High density is desirable to allow a smaller size of storage container.
Kinetic	Super cooling resistance Sufficient crystallization	Supercooling has been a worrying aspect of PCM development.
Chemical	Long-term chemical stability No toxicity	PCMs should be non-toxic, nonflammable and non-explosive for safety.
Economics	Cheap / Cost effective and available	Low cost and large-scale availability of the PCM is also very important.

3.2.1. Material properties analysis

The main thermal properties, to study of PCM, for any applications, are the *energy storage capacity and the thermal conductivity*. The energy storage capacity of a PCM, for a given application, is known by the *enthalpy variation* between two temperatures and it involves the total energy (sensible and latent).Several authors have worked in the development of appropriate evaluation methodologies [16– 24].

3.2.2. Recent researches on PCM for performance enhancement

In order to improve the low thermal conductivity of pure PCM, two approaches are possible: the improvement of heat transfer using mass transfer, which is convection (only occurs in the liquid phase), and the improvement of heat transfer through increasing the thermal conductivity (by adding objects with larger thermal conductivity to the pure PCM) [25]. The most common materials added to PCM are graphite, aluminum and butadiene and also employing lessing rings, finned tubes and carbon fibers. In the same way, metallic fins can be used to increase the thermal conductivity of PCMs and supercooling may be suppressed by introducing a nucleating agent or a "cold finger" in the storage material.

Aceves et al. [26] concluded that the development of effective thermal energy storage systems using PCM is increasing the interest, due to the potential improvement in energy efficiency, storing and releasing thermal energy at nearly constant temperature. Alternatively, Do Couto Aktay et al. [27] reported that most PCM have low thermal conductivity**,** and that leads toslow charging and discharging rates.

Similarly, to improve thermal conductivity in PCM storage systems, onepossibility is the use of composite latent heat storage materials(CLHSM) through combining the good thermal conductivity of an additivematerial and the properties of a high latent heat of the PCM. In this direction, both Acem et al. [28] and Tamme et al. [29] established that one of the most common materials added to PCM is thegraphite. According to them, the PCM/graphite composites have a thermal conductivitybetween 5 and 10 W/m K, while PCM have thermalconductivities around 0.2–0.8 W/m K. This value dependson the quantity of graphite imbedded on the PCM.Furthermore, Table 5 reports some ongoing researches to enhance performance of PCM.

Table 5: Summary of some ongoing researches to enhance PCM performance

Properties	Some recent ongoing researches to enhance performance of PCM	References
Thermal conductivity	Wang et al. investigated the thermal conductivity of the paraffin with the dispersion of micron-size graphite flakes (MGMFs) and found improvement of thermal conductivity of the PCM.	[30]
Charge/discharge rate of thermal energy	Arasu et al. studied numerical performance regarding melting and freezing cycle of paraffin embedded with Al_2O_3 and the results showed that the melting ratio increased by 3.5%, 2.3% and 3.5% for paraffin wax with 2%, 5%, and 10% Al_2O_3, respectively. Solidification rate also enhanced by 28.1%, 29.8%, 33% for paraffin wax with the same fraction of Al_2O_3individually than its pure form.	[31]
Heat transfer characteristics	Kalaiselvam et al. minimized solidification time of 60% n-tetradecane and 40% n-hexadecane PCM with the aluminium and alumina nano particles by 12.97% and 4.97%, respectively.	[32]
	Wu et al. minimized the liquefaction and solidification times by 30.3% and 28.2%, respectively of a nano fluid PCM by adding Cu nanoparticle.	[33]

3.2.3. PCM applications

The applications can be divided into two main groups: thermal protection or inertia, andstorage. One difference between these two substantial fields of application relates to the thermalconductivity of the substance. The applications in which PCMs can be applied are vast, ranging from heat and coolness storage in buildings to thermal storage in satellites and protective clothing. The melting point is the most important criterion for selecting a PCM for passive solar applications.

Solar thermal technologies via thermo chemical conversion paths offer the prospect of systems with inherent energy storage for continuous (24 h) generation of electricity. This issue will be increasingly significant as the world moves towards a truly renewable energy based economy.

Conclusion

This paper analyses the information available in the literature regarding low temperature thermal storage, with the main focus on the classification of storage system concepts with PCMs, which are very beneficial for the energy conservation. Most organic PCMs are non-corrosive and chemically stable and have a high latent heat per unit weight and low vapor pressure. Their disadvantages are low thermal conductivity, high changes in volume on phase change and flammability. This review allows us to draw the following conclusions:

- Thermal energy can be stored as sensible heat, latent heat and thermo chemical or combination of these. The most interesting phase change to be applied in a thermal storage is the phase change solid–liquid;
- Earlier studies established that the most important criterion that have limited widespread use of latent heat stores is the number of freeze–melt cycles that the PCMs can endure without any degradation in their properties. Thus, the life duration of PCM depends on thermal, chemical stability and corrosion resistance after number of repeated thermal cycles.
- The most thermal stable PCM should have a negligible change in its latent heat and melting point. Most organic PCMs investigated are paraffin, which have good thermal and chemical stability after number of thermal cycles, but present different problems that must be overcome to be successfully used in any application. Paraffin is safe, reliable, predictable, less expensive and non-corrosive;
- This review paper is focused on paraffin which qualifies as heat of fusion storage materials due to their availability in a large temperature range. But, due to cost consideration, only technical grade paraffin may be used as PCM in latent heat storage systems.

NOMENCLATURE

Q: Energy or heat flow [J]
ρ: Density of the storage material [kg/L]
C_P: Specific heat over the temperature range of operation [J/(kg K)]
V: Volume of storage material used (L)
ΔT: temperature range of operation [°C]
λ: Thermal conductivity [W/(m K)]
α : Thermal diffusivity [m^2/s]
L_m : Latent heat ($L_{fusion}$for L-S phase change, $L_{vaporisation}$for L-V phase change) [J/Kg]

HTF: Heat Transfer Fluid
TES: Thermal Energy Storage
CLHSM: Composite Latent Heat Storage Materials
PHPS: Pumped Hydropower Storage
CAES: Compressed Air Energy Storage
SHS: Sensible Heat Storage
TCR: ThermoChemical Reaction

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