Nano Enhanced Phase Change Material Paraffin wax with $Ti0_2$ for Thermal Energy Storage Application

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Abstract - *In past few decades usage of phase change materials (PCMs) in thermal energy storage is considered to be an effective way of absorbing and releasing thermal energy. The storage of thermal energy is a major area at present advanced research. In thermal energy storage the PCM are used to store the thermal energy. Due to the low thermal conductivity of PCM's, nano particles are introduced to improve the thermal performance of base PCM. In present work, thermo physical properties of the paraffin wax used as a PCM (58˚C -60˚C) with* Tio_2 *(nanoparticles) were analyzed. The effect of dispersion of nanoparticle in base PCM increase the thermal conductivity of the paraffin wax. In this experiment the thermal storage capacity of paraffin wax and the combined thermal storage capacity of paraffin wax with titanium dioxide (nano PCM) are compared in a shell and tube heat exchanger. The results shows that there is an improved performance in the thermal storage capacity using nanoPCM (paraffin wax with Tio2) than using paraffin wax as PCM.*

1. INTRODUCTION

Energy demands in the commercial, industrial, and utility sectors vary on daily, weekly, and seasonal bases. These demands can be linked with the help of thermal energy storage (TES) systems that operate synergistically. The use of TES for thermal applications such as space and water heating, cooling, air-conditioning, and so on has recently received much attention. A variety of TES techniques have developed over the past three or seven decades as industrial countries have become highly electrified. Such TES systems have an enormous potential to make the use of thermal energy equipment more effective and for facilitating large-scale energy substitutions from an economic perspective. In general, a coordinated set of actions in several sectors of the energy system is needed if the potential benefits of thermal storage are to be fully realized.

TES deals with the storage of energy by cooling, heating, melting, solidifying, or vaporizing a material; the thermal energy becomes available when the process is reversed. Storage by causing a material to raise or lower in temperature is called sensible heat storage; its effectiveness depends on the specific heat of the storage material and, if volume is important, on its density. Storage by phase change (the change from solid to liquid or from liquid to vapor with no change in temperature) is a mode of TES known as latent heat storage. Sensible storage systems commonly use rocks, ground, or water as the storage medium, and the thermal energy is stored by increasing the storage-medium temperature. Latent heat storage systems store energy in phase change materials (PCMs), with the thermal energy stored when the material changes phase, usually from a solid to a liquid. The specific heat of solidification/fusion or vaporization and the temperature at which the phase change occurs are of design importance. Both sensible and latent TES also may occur in the same storage material.

Latent heat thermal energy storage technique has proved to be a better engineering option primarily due to its advantage of providing higher energy storage density with the smaller temperature difference between storage and retrieval. Thermal energy can be stored in the form of sensible heat in which the energy is stored by raising the temperature of the storage material solid or liquid. Rock or water is the best example. Meanwhile thermal energy can be stored as latent heat in which energy is stored when a substance changes from one phase to another by either melting or freezing. The temperature of the substance remains same during phase change. In order to increase the effective thermal conductivity usually highly conducting materials are added to the paraffin wax. Titanium dioxide nano particle is mixed with phase change material and experimental analysis has been carried out to investigate the performance improvement due to the addition of nano titanium(Tio2) particles in paraffin wax in a shell and tube heat exchanger by both the cyclic as well as individual charging and discharging.

1.1 Phase Change Materials

When a material melts or vaporizes, it absorbs heat; when it changes to a solid (crystallizes) or to a liquid (condenses), it releases this heat. This phase change is used for storing thermal energy in PCMs. Also, the PCM has been subjected to speed up the life cycling equivalent to 10 years of performance with no loss of capacity. With the physical equilibrium of the PCM established after the first few cycles, the phase change appears to be stable and the TES capacity constant indefinitely, or at least as long as the life of cooler equipment used to freeze the PCM. Latent TES in the temperature range 0–135 ◦C is of interest for a variety of

The melting and freezing characteristics of PCMs, and their ability to undergo thermal cycling, and their compatibility with construction materials is essential for assessing the short and long-term performance of a latent TES. Using two different measurement techniques (e.g., differential scanning calorimetry and thermal analysis), the melting and freezing behavior of PCMs can be determined. Thermal cycling and corrosion behavior are also of importance in the appropriate choice of materials as they damge the life of a latent heat storage.

1.2 Characteristics and Thermo physical Properties of PCMs

Thermo physical properties of paraffin's generally change monotonously as a function of melting temperature, homogeneous mixtures can be readily prepared. However, properties of mixtures cannot be calculated from simple interpolation of properties of pure components, and therefore experimental characterization is required. Paraffin's generally have higher specific heats in both the solid and liquid states than salt hydrates. When the conductivity is high, the heat transfer for a given design will be more efficient .The density of a PCM is important, because it affects its storage effectiveness per unit volume. Salt hydrates are generally denser than paraffin's, but are slightly more effective on a per volume basis, despite a slightly lower heat of fusion. The rate of crystallization of a salt hydrate can below, and can become the limiting factor in the rate of heat storage and restitution. Crystallization is generally more quicker for paraffin's, and heat-transfer mechanisms are then the limiting factors. In addition, paraffins exhibit little or no supercooling, which is frequent and often significant in magnitude with salt hydrates. Paraffins have very low vapor pressures, which leads to low long-term loss of material and flammability. Salt hydrates have significantly higher vapor pressures, which induce water loss and progressive changes of thermal behaviour. The vapor pressure of salt hydrates increases with the degree of hydration, and salt hydrates exhibit variable chemical stability and can be subject to long term degradation by oxidization, hydrolysis, thermal decomposition, and other reactions. Some salt hydrates are very corrosive in the presence of water. Paraffins are very stable and unreactive, but slow oxidization may occur when they are exposed to air at elevated temperatures over extended periods. Paraffins are not corrosive Latent TES using PCMs provides an effective way to store thermal energy from a range of sources, high storage capacity, and heat recovery at almost constant temperatures.

2. Paraffin wax as PCM:

Paraffin are selected due to their availability, inexpensive nature and melt at different temperatures relating to their carbon chain length with the general formula CnH2n+2. They are chemically stable, their volume increase upon melting is in the order of 8% of their volume. Paraffin are safe and non-reactive. They do not react with most common chemical agents. They are economical, having a high heat of fusion, a low vapour pressure in the melt, exhibit negligible super cooling and no phase segregation, and are chemically stable and inert. Commercially available paraffin's from Rubi herm RT21 and RT27 were investigated.

Melting temperature of the PCM	50-75°C
Latent heat of fusion	220 kg/m3
Density of the PCM (liquid phase)	735 kg/m3
Density of the PCM (solid phase)	825 kg/m3
Specific heat of the PCM (solid phase)	2.78 kJ/kgk
Specific heat of the PCM (liquid phase)	2.43 kJ/kgk
Thermal conductivity	0.64 w/mK

Table -1: Thermo physical properties of paraffin wax

2.1 Dispersion of high conductivity particles in the PCM

Using graphite made composite PCMs has been proven as efficient and successful way in enhancing the performance of LHTS systems. However, graphite composites can be prepared only through various mechanical/chemical processes like heat treatment, drying, mixing, grinding/compression, etc., which are time and energy consuming processes. The porosity of graphite is very crucial in deciding the effectiveness of the composites. If graphite of small mean pore size is used, then there may be decrease in latent heat value as small mean pore size hinders the molecular motion and thus very difficult to impregnate the porous media with the PCM. On the other hand, increasing pore size reduces the capillary force resulting in leakage of liquid PCM.

2.2 Use of high conductivity and low density materials

Due to relatively high density, the metal particles/metal structures may settle on the bottom surface of the container and add considerable weight to the system. Besides, all metal particles are not compatible with all PCMs. For example, with paraffin, Titanium dioxide is compatible, whereas copper and nickel are not compatible. Similarly, Titanium dioxide and copper are not compatible with some salt hydrates. Hence, there has been a search for low-density high conductivity additives, which should be compatible with all PCMs. Since the densities of carbon fibers are relatively lower than those of metals and the thermal conductivities are almost equal to that of Titanium dioxide and copper, these can be better alternatives to improve the thermal performance of LHTS systems. Moreover, carbon fibers possess high corrosive resistance and hence compatible with most of the PCMs. In a cylindrical capsule, carbon fibers were added in the PCM in two ways. In the first case fibers were randomly distributed, where as in the second case brush type fibers were used. The two cases of distribution of carbon fibers in cylindrical capsule can be seen in fig below. The effective thermal conductivity with brush type was found to be five times higher than that with random type. This is because in brush type the fibers were distributed uniformly in such a way all the fibers were arranged in perpendicular direction, which was the heat flow direction. For lower mass fraction of fibers, the randomly distributed arrangement could not present higher melting rate than that with pure paraffin, even though the effective thermal conductivity of former is greater than that of latter. This is due to the loss in natural convection in case of randomly distributed arrangement. On the other hand, the loss in natural convection could not affect the higher melting rate in case of brush type. This shows that the fibers should be arranged in such a way that they are oriented in the direction of heat flow. They could achieve 20% and 10% higher solidification rate and melting rate respectively with 3% mass fraction carbon brush type fibers as compared to those with pure PCM. Mathematical modeling of LHTS systems employing performance improvement techniques.

Phase change problems are examples of what are closely referred to as moving boundary problems and their study presents one of the most exciting and challenging areas of current applied mathematical research. The existence of a moving boundary generally means that the problem does not admit a simple closed form analytical solution and accordingly much research has focused on approximate solution techniques. In general, phase change problems involve a transient, non-linear phenomenon with a moving liquid–solid interface whose position is unknown a priori and also flow problems associated with HTF.

In addition, the two phases of PCM may have different properties and configuration of the LHTS unit may differ with the applications. Substantial number of numerical based studies on LHTS units employing enhancement techniques and on their performance measurement is available in the literature. The numerical formulations widely implemented so far are enthalpy method and effective heat capacity method. In the enthalpy method, the enthalpy which is a function of temperature is considered as a dependent variable along with temperature. Thus the enthalpy based conduction equation is valid for both solid and liquid phases. Besides, it is valid for solid–liquid interface. Therefore, there is no need to track the interface which makes this formulation attractive. In the effective heat capacity method, the heat capacity of the PCM during phase change process (effective heat capacity) is introduced. The effective heat capacity is directly proportional to the stored/released energy during the phase change and the specific heat. Therefore, with effective heat capacity it is also possible to describe the non-isothermal phase change in the PCM. For the details of these two formulations, readers are referred to for enthalpy method and for effective heat capacity method. Besides these two formulations there is another method called alternate thermal resistance method. The numerical studies on LHTS units employing performance improvement technique have mainly focused on evaluation of melting/solidification time, heat transfer rate and amount of energy stored/retrieved in comparison with those of system without enhancement techniques.

3 NANOPARTICLES

3.1 Introduction of nanotechnology

Nanotechnology deals with nanometer scale of natural and artificial structures, i.e. in the range from 1 μm down to . one nanometer, 1 nm=10-9 m, Generally nanotechnology deals with structures sized between 1 to100 nm.

3.2 Nanotechnology

Improvement of convective heat transfer and thermal conductivity of liquids was earlier made possible by mixing micron sized particles with a base fluid. A very small amount of nanoparticles, when dispersed uniformly and suspended stably in base fluids, can provide impressive improvements in the thermal properties of base fluids. Nanofluids, which are a colloidal mixture of nano particles (1-100 nm) and a base liquid (nanoparticle fluid suspension). Nano particles often possess unexpected optical properties and as they are small enough to confine their electrons and produce quantum effects. For example gold nanoparticles appear deep-red to black in solution. Nanoparticles of yellow gold and grey silicon are red in color. Gold nanoparticles melt at much lower temperature (250 ˚C for 2.5 nm size) than the gold slabs (1089 ˚C). Absorption of solar radiation is much higher in materials composed of nanoparticles than it is in thin films of continuous seeds of material for example, thermal conductivity of copper at room temperature is about 500 times greater than that of water and about 2800 times greater than that of engine oil. Nanotechnology, a particle is defined as a small object that behaves as a whole unit in terms of its transport and properties.

Nano particles are the particles of size between 1 nm to 100 nm. It is further classified according to size in terms of diameter, fine particles cover a range between 100 and 2500 nm, while ultrafine particles, on the other hand, are sized between 1 and 100 nm. Similar to ultrafine particles, nanoparticles are sized between 1 and 100 nm. Nanoparticles may or may not exhibit size related properties that differ significantly from those observed I fine particles or bulk materials. Nanoparticles are the simplest form of structures with sizes in the nm range. In principle any collection of atoms bonded together with a structural radius of < 100 nm can be considered a nano particles.

Specific heat capacity of Tio2	692 kJ/kg K
Thermal conductivity of Tio2	25 W/mK
Density of Tio2	3000 kg/m3
Diameter of Tio2	10-30 nm
Weight of Tio2	25g

Table-2 thermo physical properties of nanoparticle Tio_2

3.3 Calculation of volumetric concentration of Tio2 nanoparticle

Volumetric concentration = weight/density

= 25/3000

Volumetric concentration = 0.833%

3.4 Preparation methods of nano PCM

Initially, Tio2 nanoparticle of 30g are divided approximately 6 g each needed for the addition to the paraffin wax of 1.37 kg. Then the paraffin wax of 250g is filled in a small tank. The tank with paraffin wax immersed in another tank in which the water is maintained at 78 ˚C. By the convection process the heat from the hot water is transferred to the paraffin wax material. As the temperature increase, the paraffin wax starts changing its phase from the normal. Once the paraffin wax increases above 45 ˚C, Tio2 nanoparticles of 6 g are added to the paraffin wax of 250 g, before its melting temperature. After preparing it, the tank with nano PCM is cooled by water at 35 ˚C to get nano PCM in solid phase the same procedure is repeated for the remaining nanoparticles which is further added to the annulus side of concentric tube heat exchanger

4. EXPERIMENTATION

4.1 Methodology

To improve the effective thermal conductivity of the system, the copper tube is formed in coil form. 12 number of coil are used with the distance of 5 cm between the coils. 2 mm thick circular fin has been fitted with spiral coil. The inner tube is made of copper. The outer tube is made of mild steel. The outside of the outer pipe was insulated with 2 mm thick asbestos rope to reduce the heat loss during charging and discharging process of the PCM. The outer tube inner side was filled with 1.374 kg commercial grade paraffin wax being used as latent heat storage media. Type T-copper constantan thermocouples were used for measuring the inlet and outlet temperature of heat transfer fluid (HTF) and the PCM temperature at two locations in the PCM tank. A two tank system are used form maintaining a constant pressure head for inlet water to maintain nearly constant flow rate. Heaters with thermocouple were also provided in the water tanks for constant inlet water temperature during charging mode. Flowing hot water through inner tube started the energy charging test, and the stored energy was extracted by passing cold water in the inner tube. The temperature of water at inlet and outlet of the heat exchanger at four axial locations were measured simultaneously at an interval of 15 min.

4.2 Charging Process-Heat Stored

The temperature distribution of HTF and the PCM in the TES tank for different mass flow rates are recorded during charging and discharging processes. The cumulative heat stored and system efficiency of process is studied in detail during the charging process. The first experiment was conducted with flow rate 6 lt/hr and the inlet temperature of the hot water was kept 78˚C and the atmospheric temperature is 29˚C. During the charging process, the HTF is circulated through the TES tank continuously. Initially, temperature of PCM is 29˚C and as HTF exchanges its heat energy to PCM, the PCM gets heated up to melting temperature (storing the energy as sensible heat). Later heat is stored as latent heat once the PCM melts and becomes liquid. The energy is then stored as sensible heat in liquid PCM. The temperature of PCM and HTF are recorded at interval of 15 min. the charging process is continued until the PCM temperature reaches maximum temperature. The graph represented hot water outlet temperature (HTF) and mean PCM temperature with respect to the time. Like that the flow rate changed to 15 lt/hr, the inlet temperature of hot water was kept at 78˚C and the atmospheric temperature is 290C. During the charging process the HTF is circulated through the TES tank continuously. The temperature of the PCM and HTF are recorded at intervals of 15 min. the charging process is continued until the PCM temperature reaches maximum temperature. The charging process has been completed for PCM with two mass flow rates (6 lt/hr, 15 lt/hr). After that, I have taken the charging process was conducted with flow rate 6 lt/hr, 15 lt/hr for nanoPCM and the inlet temperature of the hot water was kept 78˚C and the atmospheric temperature is 29˚C. During the charging process, the HTF is circulated through the TES tank continuously. Initially the temperature of the nano PCM is 29˚C and as the HTF exchanges its heat energy to nano PCM. The nanoPCM gets heated up to melting temperature (storing the energy as sensible heat). Later heat is stored as latent heat once the nanoPCM melts and becomes liquid. The energy is then stored as sensible heat in liquid nanoPCM. The temperature of nanoPCM and HTF are recorded at intervals of 15 min. The charging process is continued until the nanoPCM temperature reaches maximum temperature.

4.3 Discharging Process – heat released

At the beginning of the solidification period the temperature of the paraffin wax decreased rapidly by transferring the sensible heat stored to the cooling water. During this period, the temperature of the paraffin wax is high, and the paraffin wax is in liquid state. This is mainly because heat transfer inside the molten paraffin wax is by natural convection and the temperature gap between PCM tube and the cooling water is large.

Then the paraffin wax adjacent to the PCM tube begins to freeze and discharge its latent heat. Hence we find that the PCM releases its sensible heat very rapidly and, then a longer time is needed to transfer the latent heat during the phase change. Since the paraffin wax is basically in a liquid state, the major portion of heat dissipated from the PCM is its latent heat. However towards the final period of solidification, the amount of latent heat transfer to the heat transfer fluid is becoming smaller and smaller, and the heat dissipation from the PCM is again mainly the sensible heat of the solid paraffin wax.

The discharging process the first experiment was conducted with flow rate 6lt/hr and the inlet temperature of the cold water kept at the atmospheric temperature is 29˚C. During the discharging process the cold water is circulated through the TES tank continuously. Now that heat energy stored in PCM is transferred to the cold water, so the cold water temperature is increased. The temperature of the PCM and cold water outlet temperature are recorded at intervals of 15 min.

The discharging process is continued until the PCM temperature reduced to atmospheric temperature. The graph represented the values of cold water outlet temperature (HTF) and PCM temperature respect with time. Like that the flow rate changed to 15 lt/hr the inlet temperature of cold water kept at the atmospheric temperature is 290C. The temperature of the PCM and cold water outlet temperature (HTF) are recorded at intervals of 15 min. The discharging process of nano PCM was conducted with flow rate 6 lt/hr and the inlet temperature of the cold water kept at the atmospheric temperature is 290C. During the discharging process the cold water is circulated through the TES tank continuously. Now the heat energy stored in nano PCM is transferred to the cold water, so the cold water temperature is increased. Temperature of the nano PCM and cold water temperature (HTF) are recorded at intervals of 15 min. The discharging process is continued until the nano PCM temperature reduced to atmospheric temperature. The graph represented the values of cold water outlet temperature (HTF) and nano PCM temperature respect with time. Like that the flow rate changed to 15 lt/hr the inlet temperature of cold water kept at the atmospheric temperature is 29˚C. The temperature of the PCM and cold water outlet temperature (HTF) are recorded at intervals of 15 min.

4.4 CALCULATION

4.4.1 Loading calculation of PCM

VPCM = [(π/4) x (0.06)2] x 0.06 = 1.169 x10-3 m3

Vcopper tube = [(π/4) x (0.006)2] x 1.7 = 4.806 x 10-5 m3
MPCM = (VPCM - Vcopper tube) x ρPCM

= (1.169 x10-3 - 4.806 x 10-5) x 818

MPCM =1.3480 kg

4.4.2 Performance During Charging Process

In charging process, the HTF entered LHSS at high temperature.

It cause melting of PCM,

Heat stored QS = MW * CpW *(T hi –T ho) * t

Heat available QA = MW * CpW *(T hi –T ci) *t

Charging Efficiency Ƞ = (QS /QA) * 100

4.4.3 Performance during Discharging Process

In discharge process, the HTF entered at low temperature to the LHSS. It cause solidification of PCM.

Heat Released QR = MW x CpW x (T co –T ci) x t

Heat available QA = m pcm x Cp pcm x (T pcm – T ci) + (m pcm x L pcm)

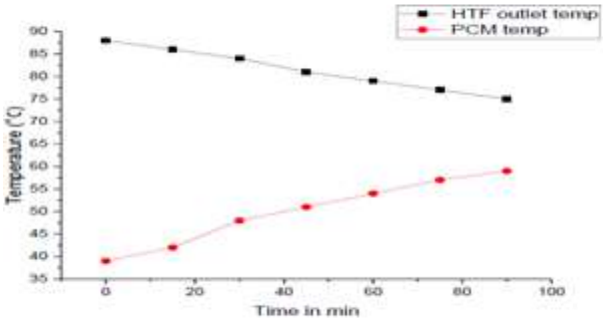
Charging Efficiency Ƞ = (QR /QA) * 100

5. RESULT AND DISCUSSION

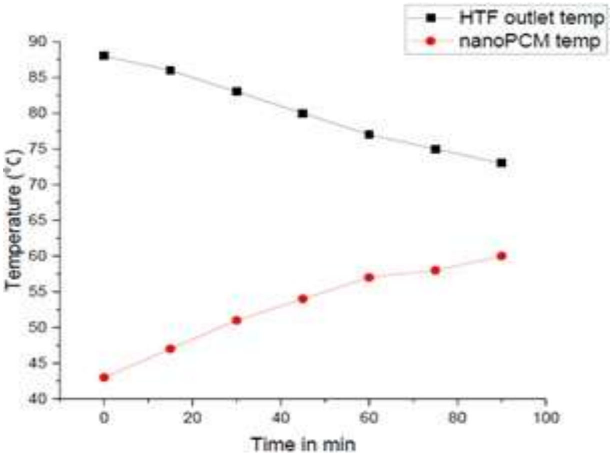
Thus the experimental analysis on the latent heat thermal energy storage system has been done using Tio2 nanoparticle. The effect of 0.833% volumetric concentration of nanoparticles on the melting and solidification performance is examined and compared between nanoPCM and pure paraffin wax. The reading were tabulated for PCM as well as nanoPCM. From the experimental results, it is found that the use of nanoparticles with paraffin wax reduces the melting and solidification time. It is also observed that there is almost 50% reduction in charging time and discharging time of the PCM for a volume concentration of 0.833%.

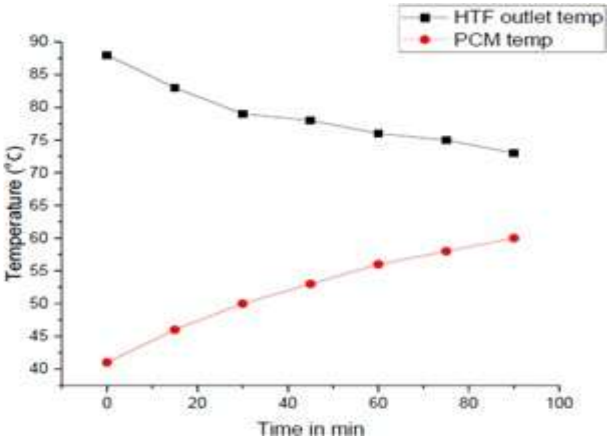
6. GRAPHICAL REPRESENTATION

6.1 Charging process for PCM (6L/hr, 15L/hr)



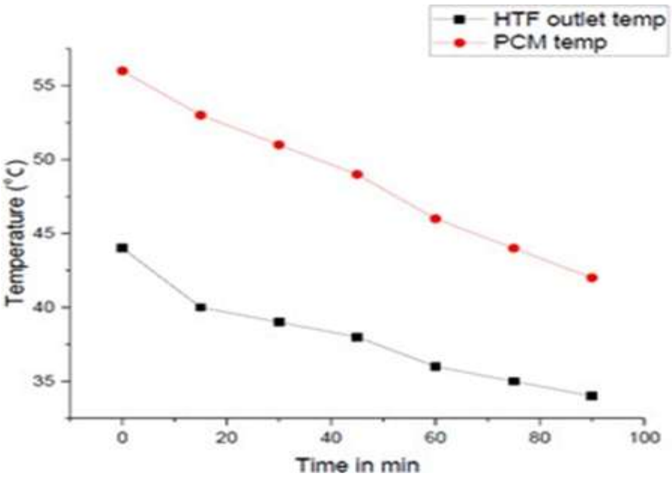
Variation of PCM mean temperature and HTF outlet temperature with time during charging mode with average flow rate of 5L/hr



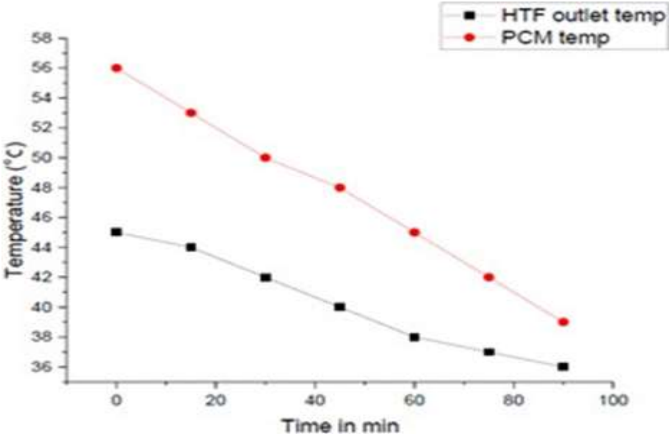


Variation of PCM mean temperature and HTF outlet temperature with time during charging mode with average flow rate of 15L/hr

6.2 Discharging process for PCM (5L, 15L/hr)

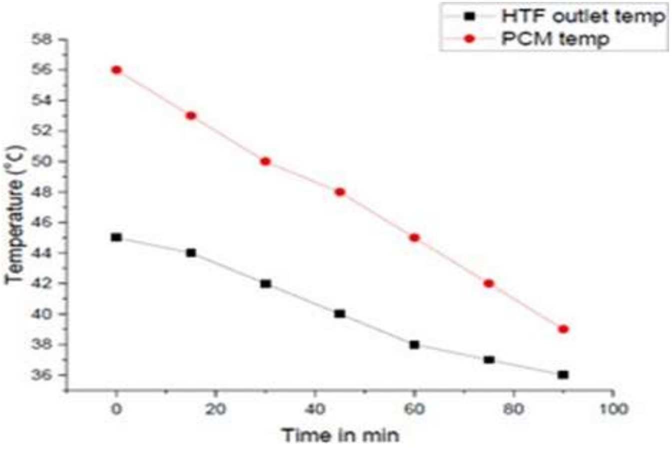


Variation of PCM mean temperature and HTF outlet temperature with time during discharging mode with average flow rate of 6L/hr

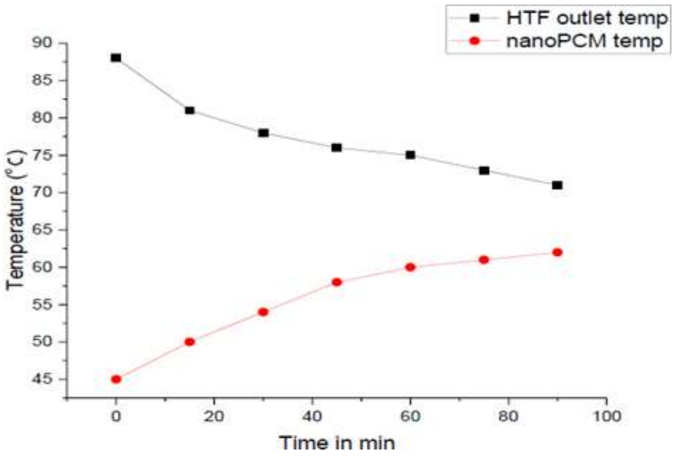


Variation of PCM mean temperature and HTF outlet temperature with time during discharging mode with average flow rate of 15L/hr

6.3 Charging process for nano PCM (6L/hr, 15L/hr)

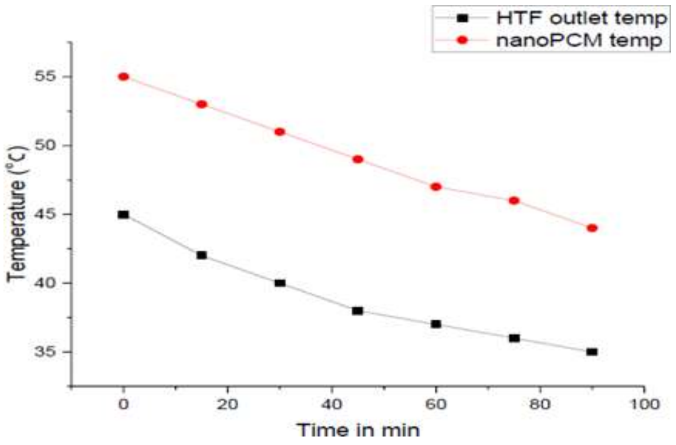


Variation of nano PCM mean temperature and HTF outlet temperature with time during charging mode with average flow rate of 6L/hr

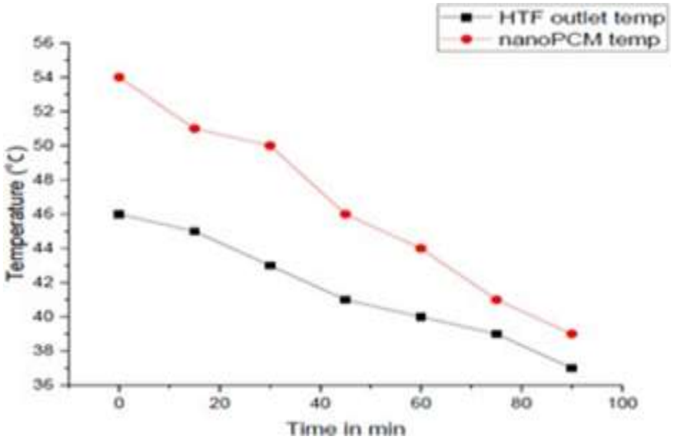


Variation of Nano PCM mean temperature and HTF outlet temperature with time during charging mode with average flow rate of 15L/hr

6.4 Discharging process for nano PCM (6L, 15L/hr)

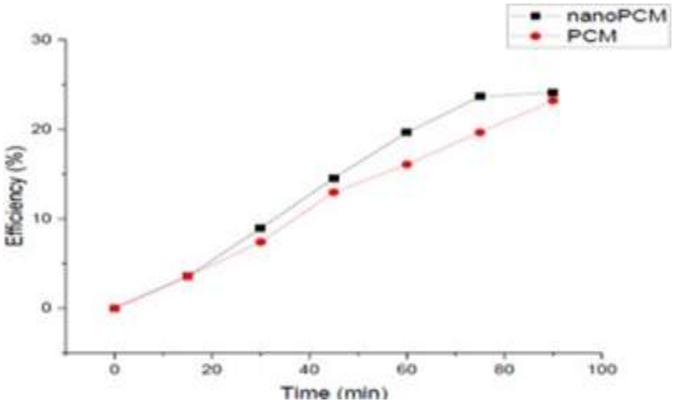


Variation of nano PCM mean temperature and HTF outlet temperature with time during discharging mode with average flow rate of 5L/hr

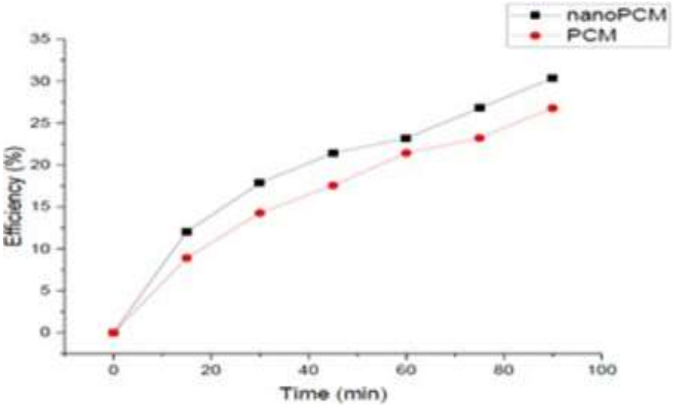


Variation of nano PCM mean temperature and HTF outlet temperature with time during discharging mode with average flow rate of 15L/hr

6.5 Charging process for PCM vs nano PCM (6L/hr, 15L/hr)

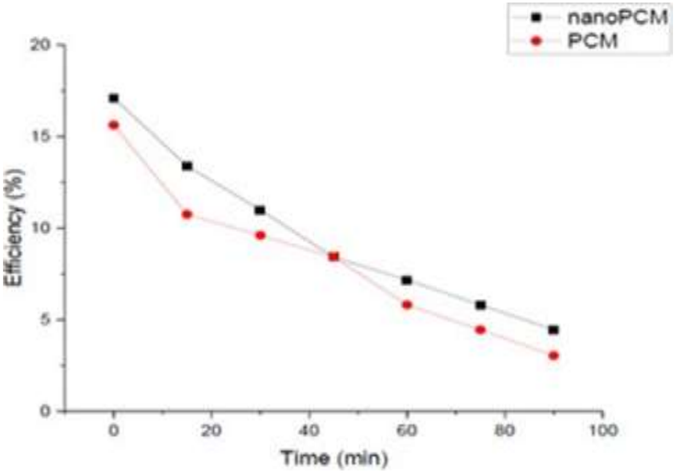


Charging process for Time vs Efficiency of PCM & nanoPCM with for 6L/hr

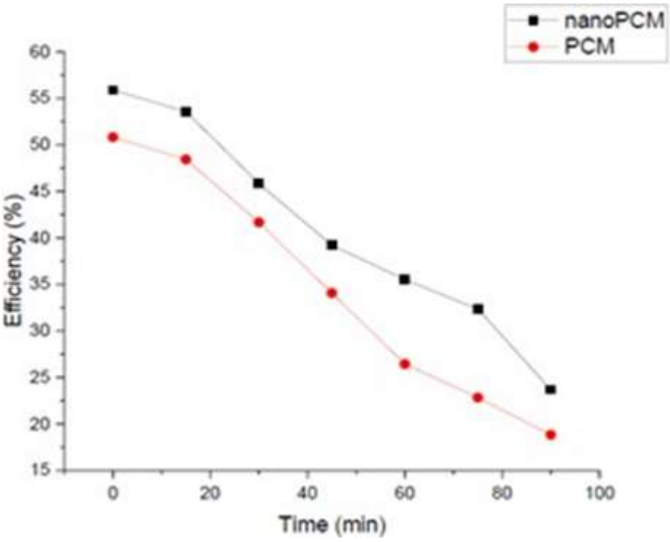


Charging process for Time vs Efficiency of PCM & nano PCM with for 15L/hr

6.5 Discharging process for PCM vs nano PCM (5L/hr,15L/hr



Discharging process for Time vs Efficiency of PCM & nanoPCM with for 6L/hr



Discharging process for Time vs Efficiency of PCM & nano PCM with for 15L/hr

7. CONCLUSION

In this work, the experimental analysis has been carried out to study the performance enhancement of paraffin wax with nano Titanium (TiO_2) particles in comparison with simple paraffin wax in a shell and tube heat exchanger in latent heat thermal energy storage system. It is concluded that the usage of TiO_2 nanoparticle with paraffin wax reduces the melting and solidification time by 50% as compared to that of paraffin wax. It was found that the use of TiO_2 with paraffin wax enhance the charging efficiency by 6% to that of the pure paraffin wax. It was also found that the use of TiO_2 with paraffin wax enhance the discharging efficiency by 4% as compared to that of the pure paraffin wax.

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