

Evaluations of Multi Walled Carbon Nanotubes-Paraffin Wax Compositions for Thermal Energy Storage Systems

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Abstract - One of the potential techniques of storing solar energy is the application of phase change materials (PCMs). Phase change material (PCM) composites for latent thermal energy storage were made by mixing the PCM (paraffin wax) loaded with multi walled carbon Nanotubes (MWCNTs) in liquid PCM with a mass fraction of 3 wt%. The effect of MWCNTs on thermal behaviors of the PCM composites was evaluated. As a result, the charging efficiency of the PCM composites increased with increasing the MWCNTs content. Among the three types of the PCM materials, nanocomposites (PW+MWCNTs) were observed to have relative enhancement up to 20% at 3 wt% MWCNTs content.

Key Words: Thermal energy storage (TES), Phase change materials (PCMs), Carbon Nanotubes (CNTs), Heat transfer fluid (HTF).

1. INTRODUCTION

The most abundance source of energy to be found on the planet is solar energy. This energy can be stored as thermal energy or electricity, but thermal energy storage is considered the more economical method. Solar thermal energy finds its simplest application in the form of solar water heating, which in itself has enormous potential [1]. Energy is the strength of all human actions on the earth. The rate of fossil fuels increases day by day in nature due to the increasing demand for energy where the fossil fuels in reserve are decreasing. Energy is the backbone of human activities. There is strong relationship between energy and economic development of any country. Scientists all over the world are in search of new and renewable energy sources to minimize the mismatch between the supply and demand of energy [2]. Therefore we are concentrating Renewable energy sources these energies are eco-friendly and less pollution in nature than the fossil fuels. Renewable energies are solar energy, wind energy, bio energy, geothermal energy, tidal energy, and hydro-energy.

All these energy sources are very high cost except solar energy. Solar energy is one of the most important sources of the renewable energy. Energy storage is not only reducing the difference between supply and demand but also improves the performance, efficiency and reliability of energy systems and plays an important role in conserving the energy. The energy in the form of solar radiation is obtained from the sun then these energies can be stored in the thermal energy storage system. The thermal Energy is a primary subject in examine for most recent 20 years. Thermal Energy can be put away as an adjustable in the

inward vitality of specific materials as sensible heat, latent heat or both

1.1 Thermal Energy Storage

Thermal energy storage can be stored as a change in internal energy of a material as sensible heat, latent heat and thermochemical or combination of these thermal energy storage systems are temporary storage of thermal energy at high or low temperatures [3]. These systems reduce the mismatch between supply and demand of energy. They also play very important role in energy conservation. These systems are used in the sectors like air conditioning, concentrated solar power plant, co-generation, waste to heat recovery, district heating & cool food and textile industries.

Advantages of Thermal Energy Storage

- Dynamic balancing between energy demand and availability.
- Conservation of primary fuels
- Reduce the equipment size and the initial cost.
- More effective and efficient utilization of equipment.
- Utilization of waste heat recovery
- Maintenance of environmental quality
- Greater flexibility in operation
- Economical energy consumption
- Thermal protection and control of electronic components
- Heating and cooling of buildings and
- Hot water preparation.

1.2 Phase Change Materials (PCMs)

The Phase change materials (PCM) are the Latent heat storage materials. The thermal energy exchange happens when a material changes from solid to liquid, or liquid to solid PCM to be used as energy storage material must possess high Thermal conductivity, large latent heat of fusion, thermal cycling stability, high Sensible Heat Capacity and low cost. Unlike conventional (sensible) storage materials, PCM absorbs and release heat at a nearly constant temperature [3].

1.2.1 Paraffin Wax

Paraffin are one of the significantly used TES materials because of its potential properties such as non corrosive, chemical stability, high latent heat of fusion and

negligible super cooling [4]. Paraffin is a saturated n-alkane aliphatic hydrocarbon. They are represented by a general formula $(CH_3-(CH_2)_n-CH_3)$. Paraffin waxes the mainly used commercial organic heat storage PCM. It consists of mainly straight chain hydrocarbons that have melting temperatures from 23 °C to 67 °C.

Table 1: Thermophysical properties of paraffin wax

Properties	Specifications	Units
Thermal conductivity in solid state	0.346	W/m K
Thermal conductivity in liquid state	0.167	W/m K
Density in solid state	916	kg/m ³
Density in liquid state	790	kg/m ³
Specific Heat capacity in solid state	2.9	kJ/kg K
Specific Heat capacity in liquid state	2.14	kJ/kg K
Heat of Fusion	173	kJ/kg
Melting temperature	55	°C

1.2.2 Fatty Acid

General formula for all the fatty acid is given by $CH_3-(CH_2)_n-COOH$. Fatty acids (FA) have the same characteristics as paraffins and have high values of latent heat of fusion compared to paraffins [3]. Fatty acids have the ability of many cycling of melting and freezing with no super cooling, and they are characterized by sharper phase temperature than technical grade paraffins. The major drawback of fatty acids is their high cost that is 2–2.5 times greater than that of the technical grade paraffins.

Table 2: Thermophysical properties of fatty acid

Properties	Specifications	Units
Thermal conductivity in solid state	0.27	W/m K
Thermal conductivity in liquid state	0.162	W/m K
Density in solid state	860	kg/m ³
Density in liquid state	833	kg/m ³
Specific Heat capacity in solid state	0.73	kJ/kg K
Specific Heat capacity in liquid state	0.67	kJ/kg K
Heat of Fusion	210	kJ/kg
Melting temperature	60	°C

1.3 Introduction to Carbon Nanotubes

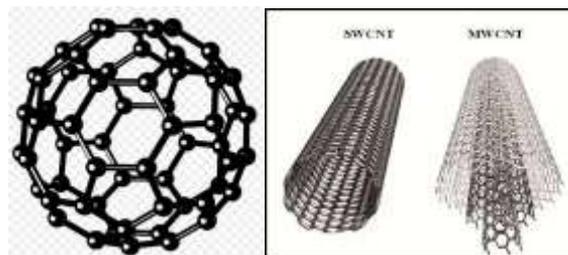


Fig.1.3 Structure of CNTs

A Carbon Nanotubes (CNTs) is a type of very attractive material for many unique properties because of its nanometer size tubular structure. Extremely high thermal conductivity is theoretically predicted for CNTs, due to large phonon mean free path in strong carbon bond network of CNT walls. Carbon nanotubes are fullerene related structure and it can be classified as two types one is grapheme cylinder called Single-wall carbon nanotubes (SWCNTs). a number of concentric cylinders called Multiwalled carbon nanotubes (MWCNTs) [5] and it is shown by the Fig.1.3.

1.3.1 Multi walled Carbon Nanotubes



Fig.1.3.1 MWCNTs

“Multiwall Carbon Nanotubes (MWCNTs) are allotropes of carbon with molecular structures that are tubular in shape, Having Overlap of Multiple tubular tube, diameters on the order of a few nanometers and lengths that can be as much as several millimeters”.

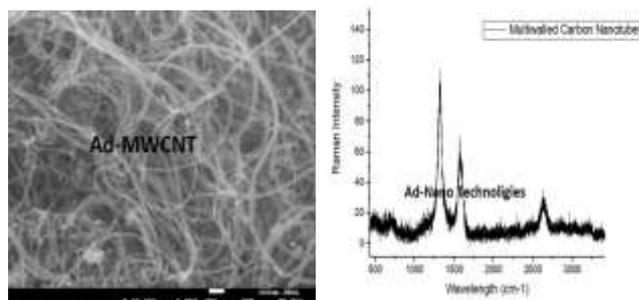


Fig.1.3.2:SEM Image and wave length of MWCNTs

Multi walled Carbon Nanotubes have been selected for this particular research work because Multiwalled carbon nanotubes have high thermal conductivity, do not react with most base fluids, and are relatively inexpensive when compared to single walled carbon nanotubes. Multiwalled carbon nanotubes have been found to increase the thermal conductivity of the base fluid when they were homogeneously dispersed in it. Also while carbon nanotubes have a higher aspect ratio due to their cylindrical structure, they are expected to give better thermal conductivity

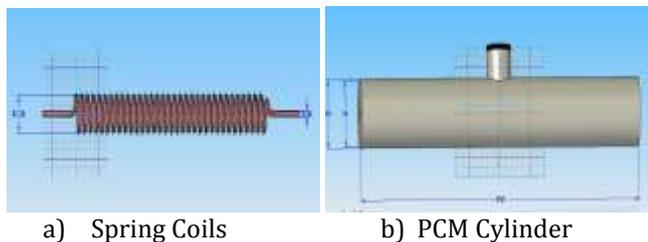
improvement than their spherical counterparts. Hence Multiwalled carbon nanotubes were chosen for our work.

Table 3: Thermophysical properties of MWCNTs

Carbon Nano Tube	Description
Type	Multiwall Carbon Nanotubes
Colour	Black
Purity	>99%
Average Diameter	10-15 Nm
Average Length	5µm
Amorphous Carbon	1%
Surface Area	400 m ² /g
Thermal Conductivity	3000 W/m K
Electrical Conductivity	10 ⁸ S/m

2. METHODOLOGY

In this project design and developed a PCM cylinder based on shell and tube heat exchanger are used. In that cylinder water flows through the spherical coil which is made up of copper material. The nanocomposites are filled in PCM which is made up of stainless steel. The inlet and outlet temperatures of HTF and PCM cylinder are measured by thermocouple is mounted on PCM cylinder.



Selection of suitable heat exchanger: A tube in shell type heat exchanger is the simplest choice of heat exchanger. Incorporation of phase change material is also easy in this type of exchanger. The phase change material is incorporated in the outer shell of the heat exchanger and the heat transfer fluid (HTF), which is water in this case, flows from the inner tube.

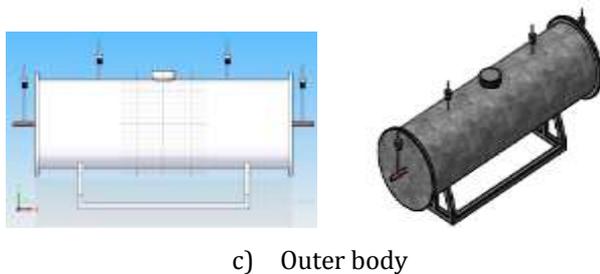


Fig 2: Design of PCM cylinder with different parts

2.1 Materials

Selection of a suitable phase change materials is very important and is the fundamental requirement of this

project. The paraffin wax and fatty acid have high latent heat capacity of 173 kJ/kg and 210 kJ/kg. The phase transition temperature of the wax and fatty acid is 55 °C and 60 °C. The change in volume from solid to liquid of PCMs is negligible. The wax is chemically stable and does not affect any component of the heat exchanger. In this work, the multi walled carbon nanotubes are chosen because the thermal conductivity is very high (1000 W/mK) compared to PCM materials and also cost is low compared to single walled carbon nanotubes. These CNTs have diameter in the range from 10-50 nm and length is 5 micro meters. The specifications of the paraffin wax, fatty acid and Multi walled carbon nanotubes (MWCNTs) as shown in the table1, 2 & 3.

2.2 Preparation of Nanocomposite[PW/MWCNTs]

The Nanofluid preparation technique followed for all types of MWCNTs was similar. The Nanofluid preparation technique discussed below involves 10-50 nm diameter sized particles with length is 5 µm and hot oven magnetic stirrer time of 30 minutes. The temperature of hot oven ranges from 50-85 °C. Carbon nanofluid preparation involves dispersing carbon nanotubes in a base fluid paraffin wax. To disperse carbon nanotubes in PW, some kind of dispersant or surfactant is needed, since carbon nanotubes are non-polar and do not have any affinity towards polar substances like water. In this particular case, Sodium lauryl sulphate is used as the surfactant.

2.2.1 Procedure for the dispersion of CNTs in the base fluid

Initially the paraffin wax is taken in to a small piece, and then take 1000 ml of beaker properly wash it after that the small pieces of paraffin wax is added. The beaker is placed in hot oven with temperature is maintained at 70-80 °C. The wax should be melted until; the paraffin wax is converted in liquid wax .the measured amount of carbon Nano powders is added to liquid paraffin wax. The mixture is stirred for 30 minutes using a magnetic stirrer. This process usually takes about 20-30 minutes to complete.



a) Beaker with paraffin wax b) Melted liquified paraffin wax



c) Carbon Nano powder



d) Stirring process



e) Final liquified NC

Fig 3: Preparations of Nanocomposite (PW+3%MWCNTs)

2.3 Working of the TES systems

The working of the system starts with filling of water in the cold HTF storage tank. Once this tank is full the water is uplifted to the HTF hot/cold source tank by switching the pump on. When water overflows the pump is switched off and heat is supplied to the water by switching on the electric heaters. Once water at required temperature is available in the HTF hot/cold source tank the appropriate valves are open and allow the hot water to flows through the heat exchanger of the targeted PCM cylinders.

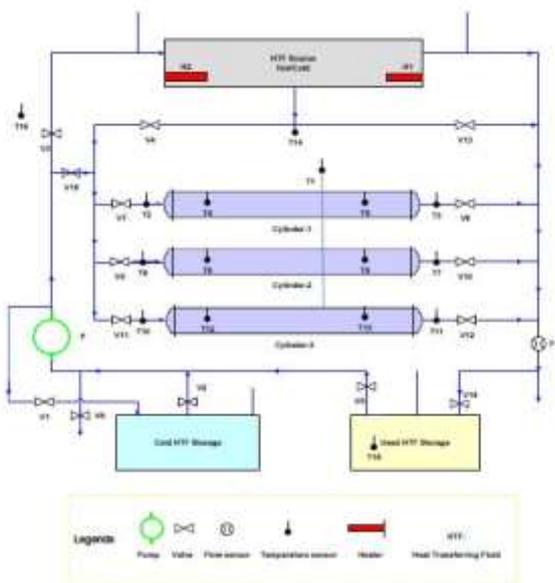


Figure-4: Thermal energy storage system

The hot water gives heat to the PCM by the process of convection and conduction on its way of flow from one end to other of the heat exchangers. This stage in which the PCMs accrued energy is known as charging stage. After giving heat to PCM the water get accumulated into the used

HTF storage tank. Hot water keeps flowing continuously through the heat exchanger till the PCM charged fully. Once the PCM stored energy up to the maximum level the hot water is stopped by closing the appropriate valves. With the stop of flow of hot water the charging stage of the system gets completed. After completing the charging stage the remaining hot water in the HTF hot/cold source tank drains out to the used HTF storage tank by unlocking the drain valve. To cool the HTF hot/cold source tank some cold water can also be pass through it from the cold HTF tank by using the pump.

The 2nd step of the experiment is extraction of heat from the PCM. This step is also known as discharging of PCM. To discharge the PCM cold water is sent through the heat exchanger of the targeted PCM cylinder from the same HTF hot/cold source tank. The cold water can also be sent from the cold HTF tank directly by using the pump. The direct option is use only when high flow rate of water is required. The cold water, while flows from one end to the other of the heat exchangers absorb heat from the PCM. After absorbing heat the water get accumulated in the used HTF storage tank. There is a control unit in the system. All required meters and control knots are fitted in this unit. From this unit the user can take the values of different parameters such as water flow rate, temperature at different condition of the system.

3. RESULTS AND DISCUSSIONS

3.1 Charging Period

During the charging period, the hot HTF is made to flow through the pipe from source tank to the PCM cylinder. The fluid inlet temperature is varied between 89 °C to 95 °C. In PCM cylinders the hot water flows through the spherical coil. The PCM absorbs the energy in the form of heat from the HTF. Initially, due to the temperature gradient, sensible heat is transferred through conduction mode of heat transfer from the HTF to solid PCM. As on the temperature of the solid PCM increase, melting temperature of PCM also increases.

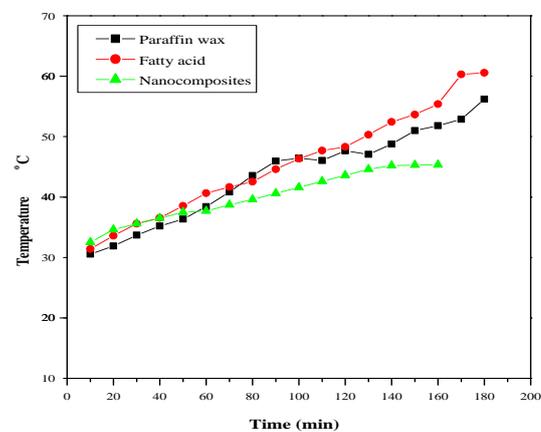


Figure -5: Variations of PCM temperature with time during charging period

Where temperature measurements are carried out at different mass flow rates of water ranging from 0.078 kg/min to 1.5 kg/min for the same fluid inlet temperature. The melting temperature of the pure Paraffin wax, fatty acid and nanocomposites (PW + 3% of MWCNTs) are 55 °C, 60 °C and 47.7 °C respectively. During melting process, the PCM temperature near the HTF pipe increases first due to the temperature gradient between the HTF and solid PCM. As the PCM reaches nearer to the HTF pipe is completely melted (after 2 h), a thin layer of molten PCM is formed between tube wall and softened PCM. The temperature of the paraffin increases slowly until it reaches the melting temperature. It should also be noted that in paraffin, phase transition does not occur isothermally, but it occurs over a certain range of temperatures, which is called the phase transition range.

3.2 Storing Period

Once charging process is completed, the storing period is started immediately. Figure-6 shows that variations of PCM temperature with time during storing period. In storing period the PCM materials such as paraffin wax, fatty acid and nanocomposite with melting temperature 55 °C, 60 °C and 47.7 °C. It is observed that the temperature of the phase change materials is constant with respect to time. Once the melting temperature is reached, then the PCM stores amount of energy in the form of latent heat. The storing efficiency of the pure PW, FA and NC is 94.7%, 97.2% and 99.93% respectively [6-10]. The storing efficiency of the Nanocomposite is very high compared to base materials because there is no heat loss occurs in this period and also the time consumption of this period is very low therefore the storing efficiency is high.

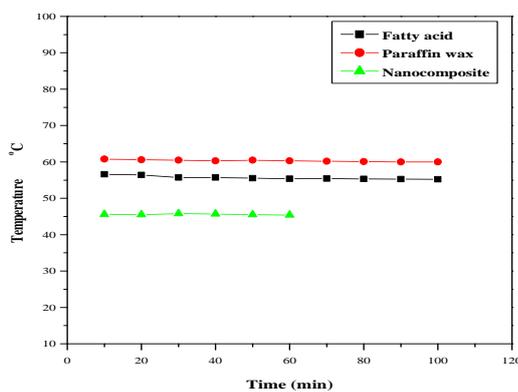


Figure -6: Variations of PCM temperature with time during storing period

3.2 Discharging Period

After the storing process is completed, the discharging process is started immediately by passing cold HTF. During the discharging or solidification process, the PCM in the annulus is in liquid phases. As the cold HTF passes through the HTF pipe, melted PCM is start to solidify and release the heat. Hence the temperature of the HTF is increased at the outlet of the experiment section.

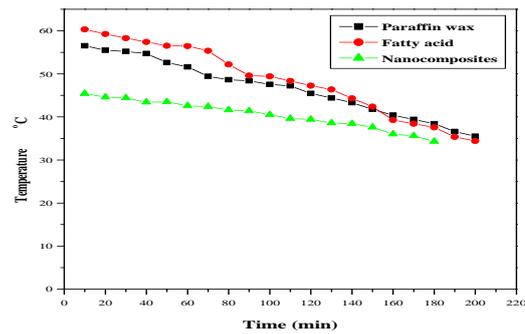


Figure -7: Variations of PCM temperature with time during discharging period

Figure -7 shows the variation of PCM temperature with time during discharging period (solidification). At the phase transition range, PCM starts to solidify by releasing the energy. It is observed that the temperature of the PCM is reduced rapidly near the HTF pipe until it reaches an onset solidification temperature of the PCM (about 60 °C). In discharging period, 98%, efficiency of the paraffin wax is obtained by keeping mass flow rate 1.2 kg/min, 98.7% efficiency of fatty acid is obtained by keeping mass flow rate 1.5 kg/min similarly nanocomposite is 99.85% with mass flow rate 0.0118 1.2 kg/min [8-9]. It must be noted that the total solidification time required is higher than the melting time. When the CNTs were added to PW, then the time consumption for discharging period reduced from 200 mins to 180 mins, because the thermal conductivity of the nanocomposite is very high compared to base material.

3.3 Variations of Outlet Water Temperature with Time during Discharging Period

Figure-8 shows the variations of outlet water temperature with time. During discharging period, initially the PCM material is in liquid state when the cold water is passed to the liquid stage of the material then the loss of heat takes place. The cold HTF absorbs the heat from the melted PCM and flow outside of the PCM cylinder then the outlet water temperature is high. This process is continued until the PCM comes to original stage (solid state). Here inlet water temperature is 25.5 °C and outlet water temperature is varied with respect to time.

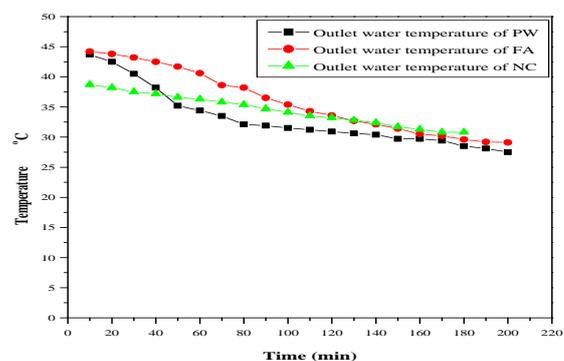


Figure -8: Variations of outlet water temperature with time during discharging period

3.4 Variations of Thermal Conductivity with Different Mass Fractions

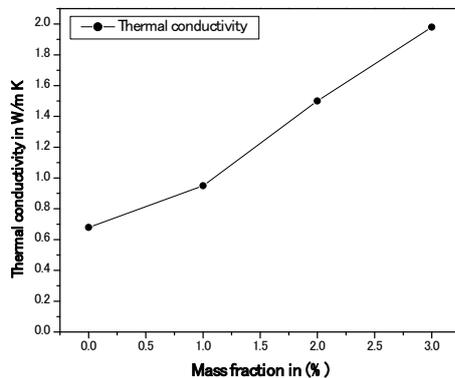


Figure -9: Variations of Thermal conductivity with different mass fractions

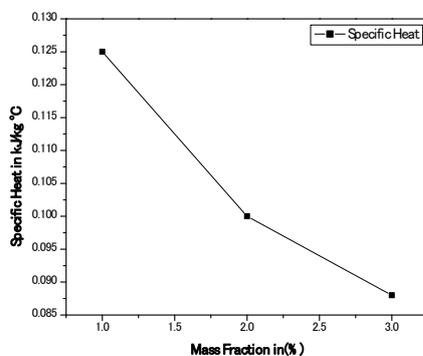


Figure -10: Variations of Specific heat with different mass fractions

By observing the figure-9, due to increasing the mass fractions of the nanoparticles, the thermal conductivity is also increases with temperature. Therefore the thermal conductivity of the nanocomposite is increased by addition of MWCNTs. The thermal conductivity of the pure paraffin wax is 0.764 W/m °C at temperature 35.5 °C and by the addition of CNTs in paraffin wax, the TC is increased to 0.955, 1.52 and 2.03 W/m °C with temperature 43.5°C, 48.5 °C and 55 °C at 1%, 2% and 3% of mass fraction. While increasing the mass fraction, thermal conductivity increases but specific heat decreases as shown in Fig-10, due to agglomeration of carbon nanoparticles because, the agglomeration of nanoparticles reduces the potential enhancement of thermal properties in nanocomposite, due to the restriction of interfacial area. Therefore; the main challenge in production of nanocomposite includes the achievement of small nanoparticles and good dispersion of nanoparticles. The nanoparticles tend to agglomerate due to the attraction between nanoparticles such as Vander Waals forces and chemical bonds or the strong reduction in surface separation as filler size decreases. Hence 3% mass fractions of carbon nanotubes were suitable in this project.

3.5 Efficiency of the Paraffin wax (PW), Fatty acid (FA) and Nanocomposite (NC)

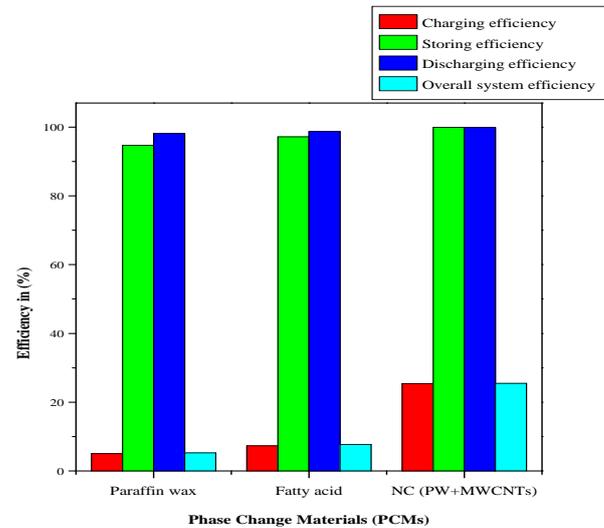


Figure -11: Efficiency of the Paraffin wax (PW), Fatty acid (FA) and Nanocomposite (NC)

Figure-11 shows the efficiency of the paraffin wax, fatty acid and Nanocomposite. In storing period the pure paraffin wax, fatty acid and nanocomposite of 94.69%, 97.21%, 99.93% efficiency is obtained. By observing the figure-11, the nanocomposite storing efficiency is high compared to paraffin wax and fatty acid, because the thermal conductivity of MWCNTs is very high (3000 W/m K) compared to paraffin wax (0.346 W/m K). And also overall system efficiency of that material is like paraffin wax is 5%, fatty acid is 7.37% and nanocomposite is 25.42%. Therefore by adding the nanocarbon tubes (MWCNTs) in PCMs the thermal energy storage system efficiency was increased.

4. CONCLUSIONS

- In this present work, the thermal conductivity of the paraffins as PCM was efficiently improved by adding the MWCNTs.
- The charging efficiency of the paraffin was increased by 20%, by the addition of MWCNT, respectively, at a mass fraction of 3 %. Because the thermal conductivity of the multi walled carbon tube is high compared to base material However, the latent heat of the composites was decreased.
- Higher the thermal conductivity of the material gives the higher heat transfer rate.
- During discharging period (Solidification process), the time required is higher than that of charging period (melting process) time.
- Convection is important during the melting process, while the conduction mode of heat transfer is considerable for the solidification process.
- The thermal conductivity is measured using steady state thermal conductivity composite wall for the following weight fraction of 1%, 2%, 3% and pure paraffin wax, by the addition of MWCNTs to paraffin

wax there is an increase of thermal conductivity but 3wt% is higher thermal conductivity compared to other mass fraction with further increasing the concentrations of MWCNTs, the specific heat values were decreased. This decrease could be explained on the basis of agglomeration of MWCNTs. When the MWCNTs agglomerate, the total surface area decreases.

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