Using Nanoparticles for Enhance Thermal Conductivity of Latent Heat Thermal Energy Storage

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ABSTRACT

Phase change materials (PCMs) such as paraffin wax can be used to store or release large amount of energy at certain temperature at which their solid-liquid phase changes occurs. Paraffin wax that used in latent heat thermal energy storage (LHTES) has low thermal conductivity. In this study, the thermal conductivity of paraffin wax has been enhanced by adding different mass concentration (1wt.%, 3wt.%, 5wt.%) of (TiO_2) nano-particles with about (10nm) diameter. It is found that the phase change temperature varies with adding (TiO_2) nanoparticles in to the paraffin wax. The thermal conductivity of the composites is found to decrease with increasing temperature. The increase in thermal conductivity has been found to increase by about (10%) at nanoparticles loading (5wt.% and 15°C).

Key words: phase change materials (PCM), LHTES, thermal conductivity, TiO_2.

استخدم جزيئات نانوية لتحسين الموصلية الحرارية لخزين من الطاقة الحرارية الكامنة

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الخلاصة

المواد متغيرة الطور(PCM) مثل شمع البرافين يستطيع خزن او تحرير كمية كبيرة من الطاقة عند درجة حرارة تغير الطور من الصلب الى السائل. لذلك يستخدم شمع البرافين في خزن الطاقة الحرارية كطاقة كامنة الا انه يمتلك موصلية حرارية واطئة. وقد تم في هذه الدراسة تحسين الموصلية الحرارية لشمع البرافين بأضافة نسب كتلية مختلفة (% .5wt. %,3wt 1 wt.%) من الجزيئات النانوية (TiO$_2$) اوكسيد التيتانيوم . وقد وجد ان درجة حرارة تغير الطور تتغير مع اضافة (TiO$_2$) الى شمع البافين. كما لوحظ ان الموصلية الحرارية للمركبات تقل بزيادة درجة الحرارة وان الموصلية الحرارية تزداد مع زيادة النسبة الكتلية لجزيئات النانو (TiO$_2$) وبنسبة (10%) عند (5wt.% و 15°C).

الكلمات الرئيسية: المواد متغيرة الطور ، خزن الطاقة الحرارية كطاقة كامنة،الموصلية الحرارية، اوكسيد التيتانيوم.

1. INTRODUCTION

Thermal energy can be stored when a change in internal energy of a material as sensible and latent heat. And it will be important energy management with emphasis on efficient use and conversation of the waste heat and solar energy .Energy storage plays important role in conserving the over demand of energy. **,Abhat, 1983.** gave a useful classification of the substances used for thermal energy storage as shown in **Fig.1**.

In sensible heat storage, thermal energy is stored based on the specific heat capacity of the material. Here the temperature of the material varies and does not undergo any phase transformation during charging or discharging cycles, for example: water, copper, cast iron **,Garg, and Prakach, 2002.** And in latent heat storage system the process of storing and retrieving the thermal energy is based on the latent heat of fusion, where storage medium undergoes a phase transformation. The heat stored during the phase change process of the material is called latent heat. As the source temperature increases the chemical bonds of the material breaks up which leads to the transformation from one phase to other, **,Sharma, et al., 2009.** Here the temperature is almost constant with less temperature swing. Latent heat storage materials can be classified based on temperature, phase transition and compounds used to: Organic PCMs and inorganic PCMs. A phase change material PCM which contains carbon atom is known as organic PCM, so phase change materials PCMs is a kind of very important latent heat energy storage materials with the general chemical formula (C_nH_{2n+2}) are categorized under paraffin, where the heat of fusion and melting point increases with the increasing value of carbon atom number, **,Abhat, 1980.** Paraffin having 5 to 15 carbon atoms is liquid at room temperature, and those with more carbon atoms are waxy solid. PCMs have wide applications in many fields, such as refrigeration and air-conditioning systems, solar energy systems, heating and cooling of building. It has attracted great interest in recent years , **,Qinbo He, et al., 2012.** Few of the advantages of using organic PCM are no tendency to segregate, chemically stable, high heat of fusion, no tendency of sub-cooling and compatible with all containers except plastic at high temperature. Some of the demerits are low thermal conductivity, sometime flammable and mildly corrosive, **,Garg, and Prakach, 2002.**

Many researchers have carried out similar studies for the heat transfer performance of nanofluids. For example, **,Lee and Choi, 1996.** have tried to use nanofluids and miniature heat exchangers constitute efficient cooling system. In recent years, nanofluids have been employed to enhance the heat transfer in PCMs for energy storage, due to its desirable properties of high thermal conductivity. **,Xie HQ, et al., 2002.** revealed that the thermal conductivity of Al_2O_3 nanofluid was higher than that of the base fluid and increased with increasing nanoparticle concentration level. The enhanced thermal conductivity ratio decreases with an increase in PH value, from (PH 2.0 to PH 11.5). They also found that the thermal conductivity of nanofluids varied with particle size and the optimal particle size for thermal conductivity enhancement was (60nm). **,Khodadadi and Hosseinizadeh, 2007.** studied the phase change process of Cu-H_2O nanofluids by using numerical simulation method. The nanofluids shows the preferable thermal energy storage characteristic, the heat release rate is high than that of pure water. **,Wu et al., 2009.** investigated the thermal properties of (Al_2O_3-H_2O) nanofluid   they concluded that the supercooling degree was reduced by 70.9% with suspending 0.2 wt.% Al_2O_3 nanoparticles in water. **,Ho and Gao, 2009.** studied the effective thermophysical properties, such as latent   heat of fusion, density, dynamic viscosity and thermal conductivity of n-octadecane PCM embedded with Al_2O_3 nanoparticles with the composition of 5%

and 10%. Prepared by emulsifying alumina by means of non-ionic surfactant. The change in the values of melting temperature, freezing temperature and latent heat of fusion is given in **Table 1.**

,Shin and Banerjee, 2011. studied the high-temperature silica-nanofluids for soler thermal storage application, the specific heat capacity of the nanofluid was enhanced by (14.5%). ,**Qinbo He, et al., 2012.** investigated the thermal properties of TiO_2 nanoparticles in saturated $BaCL_2$ aqueous solution, they concluded that the thermal conductivities of nanofluids PCMs is enhanced by (12.76%) at (-5^oC) with volume fraction (1.13%).

,Parameshwaran, et al., 2013. investigated the performance of organic ester by incorporating silver nanoparticles in terms of latent heat capacity, thermal conductivity, and heat storage and release capabilities. Report shows, latent heat capacities decreased by (7.88%) in freezing and (8.91%) in melting whereas thermal conductivity of composite PCMs increased from (0.284 to 0.765 W/m.K). **,Alhamdo, et al., 2013.** study thermal conductivity enhancement of paraffin and natural waxes composites by employing four different high conductivity additives in filtrated within waxes. It is found that for copper network (CN) composite with (6%) additives, the charging and discharging time decreased by (26.4%) and (30.3%) respectively, than that of pure wax and the thermal conductivity enhanced by (2.57) times than of pure wax.

The aim of this   work is to present a method to enhance the thermal conductivity of paraffin wax as PCM by adding different mass concentration of nanoparticle (TiO_2).

2. THEORETICAL FORMULATION

Generally paraffin based PCMs have low thermal conductivity, during the discharge the thermal energy from liquid PCM is released and a layer of solid PCM develops on the container wall. Thermal resistance of this layer increases with increasing thickness, thus diminishing heat transfer rate **,Sharma, and Sagara, 2005.** To overcome this problem has been added nanoparticle   (TiO_2) into the PCM, due to its bigger specific surface area and surface energy its small size. The experimental temperature records have been used in theoretical formulation. The following assumptions and boundary conditions were used in the modeling:

1. The study case is transient state because the temperature is changing over the time.
2. The inlet of the test section defined as velocity inlet with velocity magnitude of 7m/sec and constant temperature for the heat transfer fluid of 76^oC (during charging) and 12^oC (during discharging).
3. The outlet portion of the test section was considered outflow boundary. This is intended to use with incompressible flow.

Fig. 2 shows a physical representation of the numerical model. The governing conservation equations are as follows **,Alhamdo, et al., 2013.**

❖ Continuity equation: $\nabla \vec{u} = 0$ (1)
❖ Momentum equation:

$$\rho_{wf} \cdot \frac{\partial u}{\partial t} = -\nabla P + \mu \nabla^2 \vec{u}$$ (2)

Where P: Pressure gradient with velocity fluid (N/m^2).

❖ Energy equation:
The enthalpy of a material is **,Alhamdo, et al., 2013.**

$$H = H_{sensible} + H_{latent} \tag{3}$$

$$\&\ \ H_{sensible} = H_{ref} + \int_{T_{ref}}^{T} C_p dT \tag{4}$$

Where: H_{ref} = Reference enthalpy, kJ/kg.
   T_{ref} = Reference temperature, ^oC.

The latent heat content can be written by latent heat of the material and L:

$$H_{latent} = \beta . L \tag{5}$$

Where β: Liquid fraction can be defined as:
$\beta = 0$ if $T \leq T_{solidus}$
$\beta = 1$ if $T \geq T_{liquidus}$

$$\beta = (T - T_{solidus})/(T_{liquidus} - T_{solidus})\qquad if\ T_{solidus} < T < T_{liquidus} \tag{6}$$

The energy equation is written as **,Alhamdo, et al., 2013.**

$$\frac{\partial}{\partial t}(\rho H) + \nabla . (\rho \vec{u} H) = \nabla . (K \nabla T) + S \tag{7}$$

Where S: Dissipation function. This function includes the energy transformed into heat due to the fluid shear stress.

The thermal conductivity is an important property of PCMs because the rate of energy storage or release is highly depended on the thermal conductivity of materials. PCMs are used for thermal energy storage in environments with temperature variation. Therefore, it is important to know the thermal conductivity of the PCMs in both solid and liquid states of the temperature range of interest. Many theoretical works had carried out to estimate the thermal conductivities of the composite. The equation used to calculate the thermal conductivities of the composite is, **,Bhattachary, et al., 2004.**

$$k_C = \varphi_v * k_P + (1 - \varphi_v) * k_f \tag{8}$$

Where k_C , k_P and k_f are thermal conductivities of the composite, nanoparticle and the matrix respectively. The relationship between volume fraction φ_v and weight fraction φ_w is **,Bhattachary, et al., 2004.**

$$\varphi_v = (m_P * \rho_c)/(m_c * \rho_p) = \varphi_w * (\rho_c/\rho_p) \tag{9}$$

The mass fraction associated with volume fraction of the samples is shown in **Table 2. Table 3.** shows the properties of nanoparticle (TiO_2) and PCM.

3. EXPERIMENTAL TEST RIG

Fig. 3 shows the experimental test rig. Experimental test rig consists of the components required as shown schematically in **Fig. 4** such as, the flow unit which contain refrigerated air operates by a three phase electric motor, the heating unit which contain three electrical helical heaters (600 Watt, each) used for heating the test section and the duct section which has a square section (15x15) cm^2 with a length of (210 cm) the test section placed at the last (60cm) of the duct. (120) spherical capsules filled with (25g) of PCM have been packed inside the test section. The test rig insulated by using a layer of glass wool.

4. MEASUREMENT INSTRUMENT

Temperature and air velocity were measured by measuring devices. Thermocouples of (T type) were used to measure the temperatures of PCM and air at five different locations along the axial direction in the test section and recorded by using digital thermometers. Five special spherical capsules having thermocouples are locate at the center line of the test section at axial location of (X/L = 0, 0.25, 0.5, 0.75 and 1). Thermal camera (Ti32) was used to measure the surface temperature of the test capsules, as shown in **Fig.5**. A digital vane-type anemometer was used to measure the average air velocity at the inlet and outlet of the section. The measurement test is carried out at A/C laboratory in Mech. Eng. Dept. /College of Engineering/AL-Mustansiriya University.

5. RESULTS AND DISCUSSION

In the present study, the improvement of thermal conductivity of PCM for thermal storage, the result of charging and discharging process also presented here.

Fig. 6 shows photograph images, thermal images of PCM and changes in thermo- physical properties with respect to different weight% of nanoparticle TiO_2 at 60°C and after 15 minute, also it shows three dimensional images and the temperature distribution. It can be noted, the melting process occurs faster with increasing mass fraction of nanoparticles TiO_2 compared to that of pure paraffin because of the high surface energy with so small size to nanoparticles

Fig.s 7, 8 and 9 show the temperature distribution of the PCM along the axial direction of the test section at (X/L=0, 0.25, 0.5, 0.75 and 1) with flow rate of (7m/s). It can be observed for charging process, at (X/L = 0) the PCM melt faster than the other locations because it absorb most the energy carried by the heat transfer fluid, where the flow over the capsules mentioned along the test section, this energy decreased gradually until the last PCM capsules in the end section have less energy to melt. The heat transfer processes between the PCM and heat transfer fluid enhanced and become more active by (11.5%) in the adding mass fraction (5 wt. %) of nanoparticle TiO_2, because the thermal resistance becomes smaller.

In discharge process a reveres process take place to release the energy absorbed. It can be noted that the first capsules solidify faster than the others, and the solidification occur faster than the melting, due to low thermal resistance of liquid PCM. The adding different mass fraction of nanoparticle TiO_2 in PCM enhanced the heat transfer process between PCM and heat transfer fluid.

Fig. 10 shows the temperature distribution of the PCM with different weight fraction of nanoparticle (TiO_2) during charging and discharging processes. It can be noted, nanoparticle (TiO_2) was added into PCM to improve thermal storage performance. Thermal storage (charging) and

release rate (discharging) were increased by (0.95) times and (1.5) times respectively at (50°C), as compared with the PCM without nanoparticle (TiO$_2$).

   Fig. 11 shows the latent heat at different mass fraction of TiO$_2$ nanoparticle. As can be seen the latent heat of fusion of composite PCMs decreases with increasing mass fraction by (4%). The decrease can be attributed to two reasons: The first is that the nanoparticle specific heat is lower than the PCM specific heat which decreases the overalls thermal absorptance of the composite PCM. The second reason is that the nanoparticles change the molecular arrangement of the PCM crystals which affects on the ability to melt which eventually affect the latent heat of fusion. Hence the thermal property of system is affected **,Cai et al., 2008.**

   Fig. 12 shows depicts the enhanced thermal conductivity (K) as a function of mass fraction of nanoparticles TiO$_2$ at three test temperatures. It seen that thermal conductivity decreases by (0.17%) with increasing temperature, but it increases with increasing loading of the nanoparticles TiO$_2$. When the mass fraction is (5 wt. %) and temperature is (15°C) thermal conductivity is increased to (10%). However, the enhancement of thermal conductivity may be due to the dynamic viscosity.

6. CONCLUSIONS

   In the present work, the following conclusions have been found:
   1. The heat transfer process has been found to enhance by (11.4%) with adding mass fraction of (5 wt. %) nanoparticle TiO$_2$.
   2. The solidification is found to occur faster than the melting due to low thermal resistance.
   3. Thermal storage and release rate were found to increase by about (0.95) and (1.5) respectively times at (50°C) as compared with the PCM without nanoparticles loading.
   4. Increasing of nanoparticle TiO$_2$ concentration leads to a decrease in PCM latent heat of fusion by (4%), but with significant increase in composite PCM thermal conductivity.
   5. Thermal conductivity decreases with increasing temperature by (0.17%), on the other hand, it increases with increasing of nanoparticle TiO$_2$ loading by (10 %) at mass fraction (5 wt.%) and temperature is (15°C).

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NOMENCLATURE

Cp= specific heat at constant pressure, kJ/kg.^{o}C.

D= diameter of capsule, m.

H= specific enthalpy, kJ/kg.

K=thermal conductivity, W/m.^{o}C.

L= length of test section, m.

M=mass, kg.

U= velocity, m/s.

GREEK SYMBOLS

∇= gradient, dimensionless.

μ=dynamic viscosity, N.s/m^{2}.

φ_v=particle volume fraction, %vol.

φ_w= particle weight fraction, %wt.

Table 1. Variation in melting, freezing temperatures and latent heat of fusion as a function of different weight % of Al_2O_3 nanoparticle, **,Ho and Gao, 2009.**

Mass fraction of nanoparticles (wt.%).	Melting temperature (^{o}C)	Freezing temperature (^{o}C)	latent heat of fusion (kJ/kg)
0	26.5	25.1	243.1
5	26	25	225.6
10	26.3	25.3	212.3

Table 2. The wt. % associated with vol. % of the nanoparticle sample at 20^0C.

wt.%	vol.%
1	2.57
3	2.68
5	2.798

Table 3. The properties of nanoparticle TiO_2 and PCM.

	Density (kg/m^3)	Thermal conductivity (W/m.K)	Specific heat (J/kg.K)	Melting temperature (^{0}C)
TiO2 (dp=10 nm)	4230	8.4	710	---
PCM (paraffin wax)	785	0.214	2871	62-68
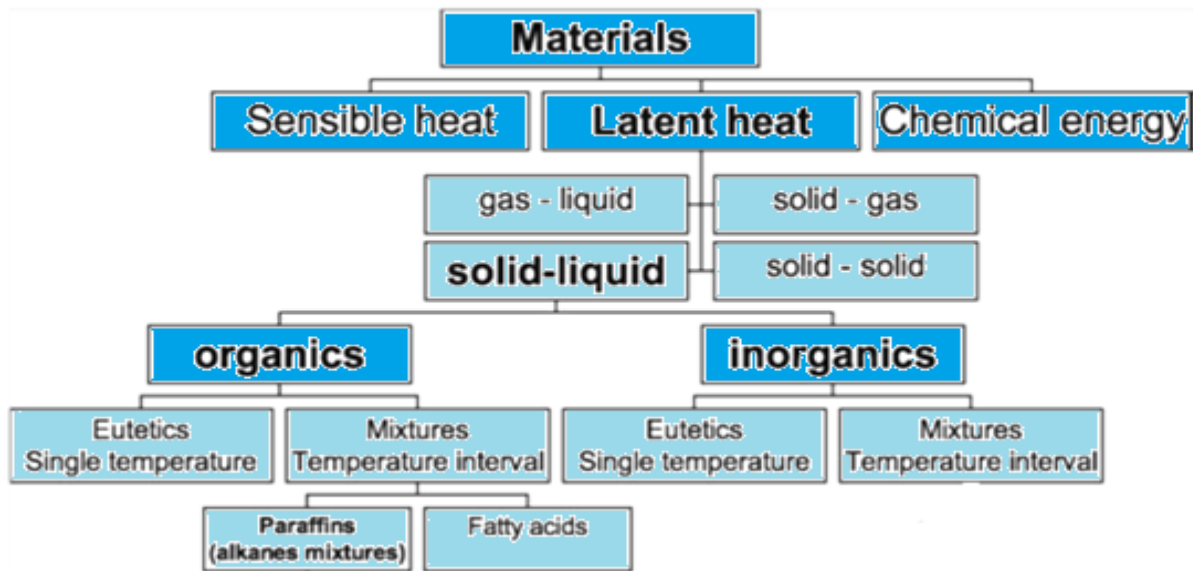
Figure. 1 Classification of energy storage materials, **,Abhat, 1983.**
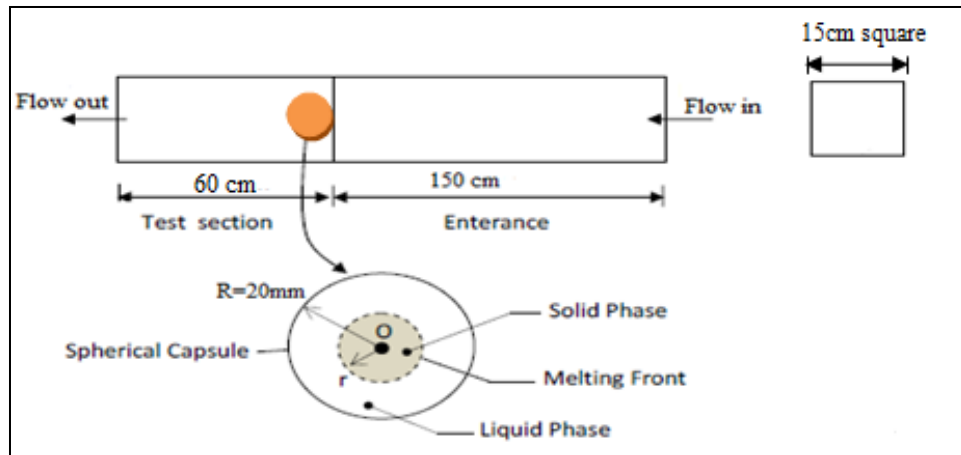
Figure. 2 Schematic diagram of the numerical model.
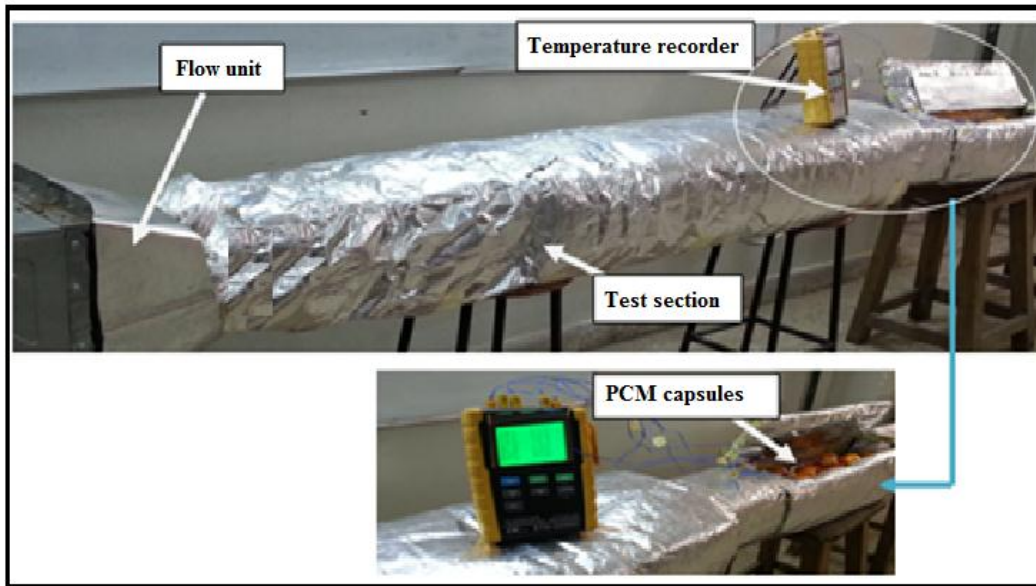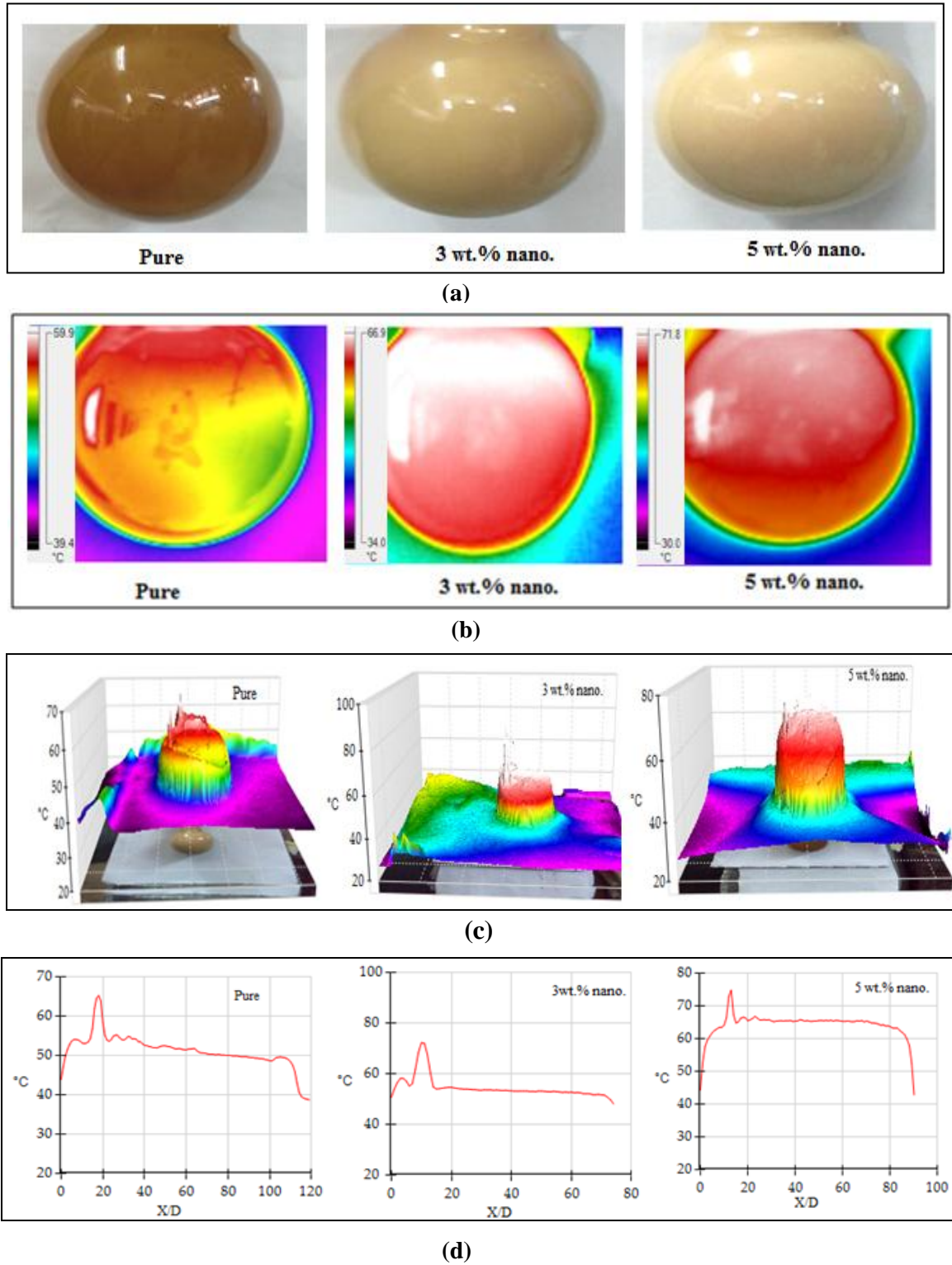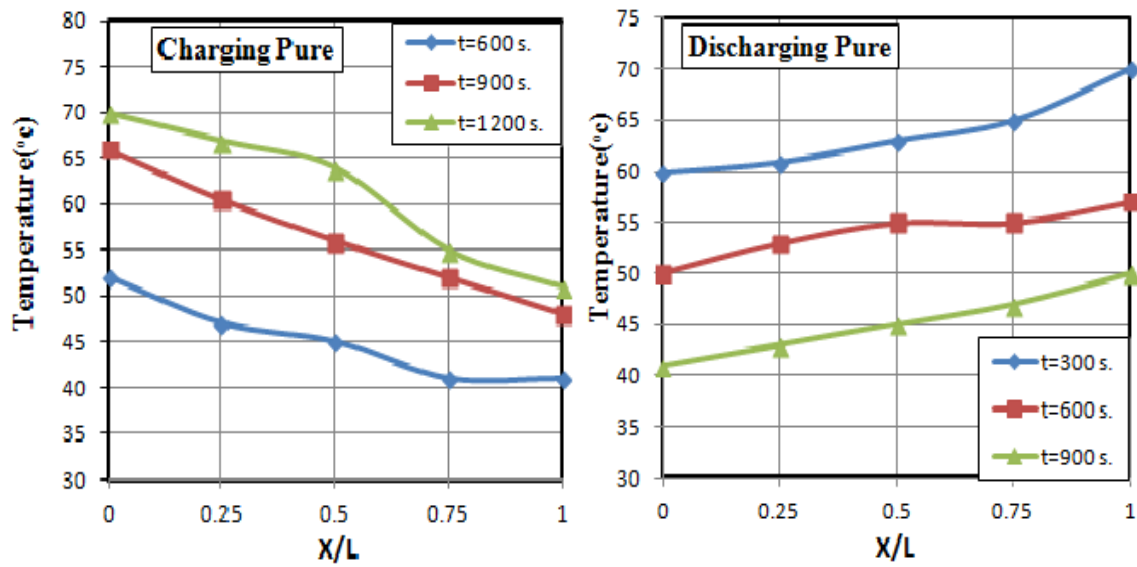
Figure. 3 Experimental test rig.
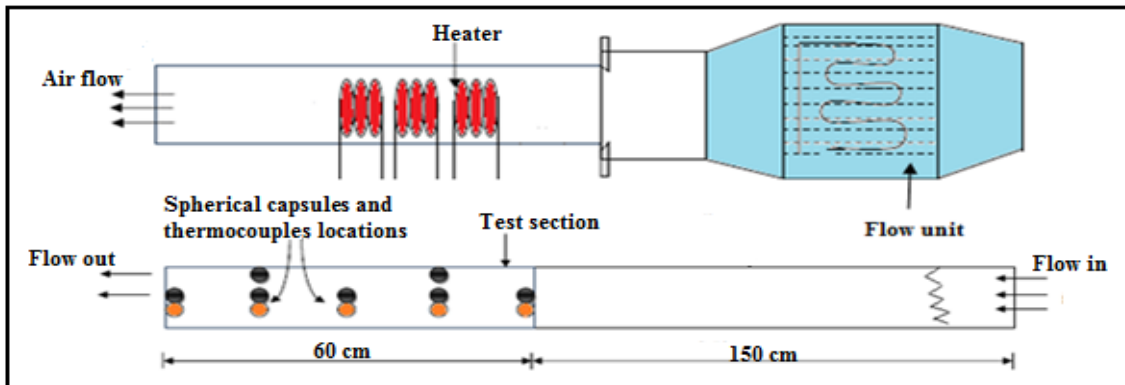

Figure. 4 Schematic diagram of the experimental apparatus.

**Figure. 5** Thermal camera.

(a)

(b)

(c)

(d)

Figure. 6 (a) Photograph images (b) Thermal images of PCM at different weight% of nanoparticle TiO_2 at $60^{o}C$ and after15 minute, (c) 3-Dimantion images and (d) Temperature distribution.
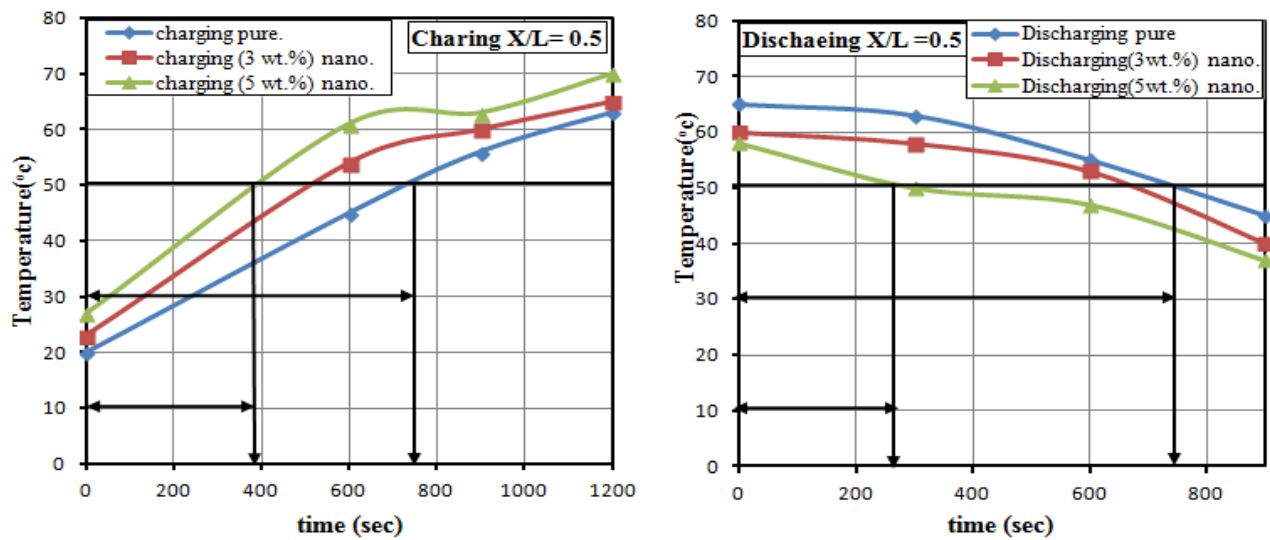
Figure. 7 Distribution the temperature of PCM along the axial direction of the test section during charging and discharging processes.
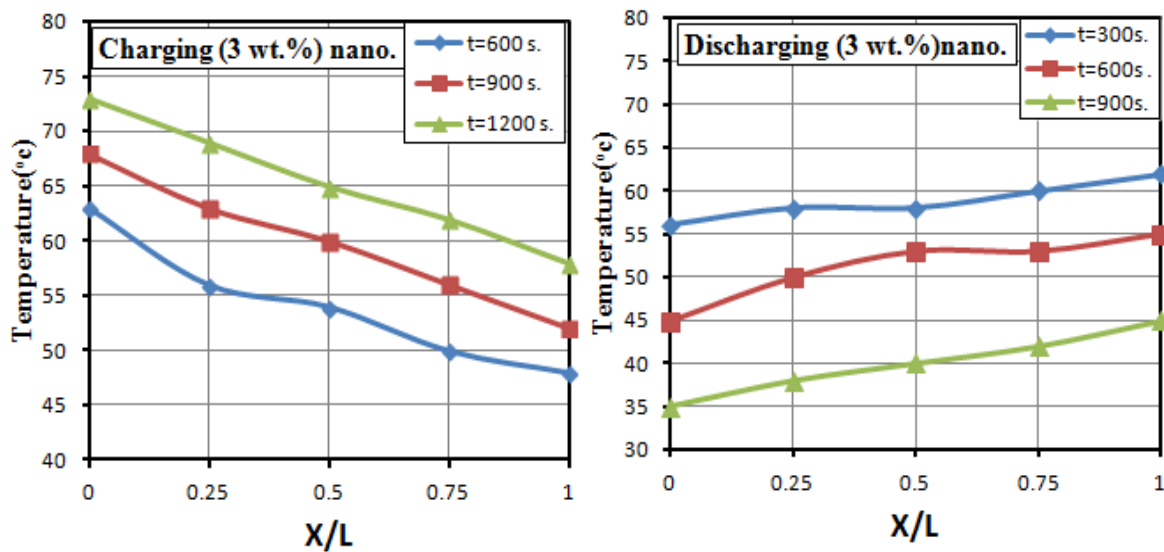

Figure. 8 Distribution the temperature of PCM with (3 wt. %) nano. along the axial direction of the test section during charging and discharging processes.
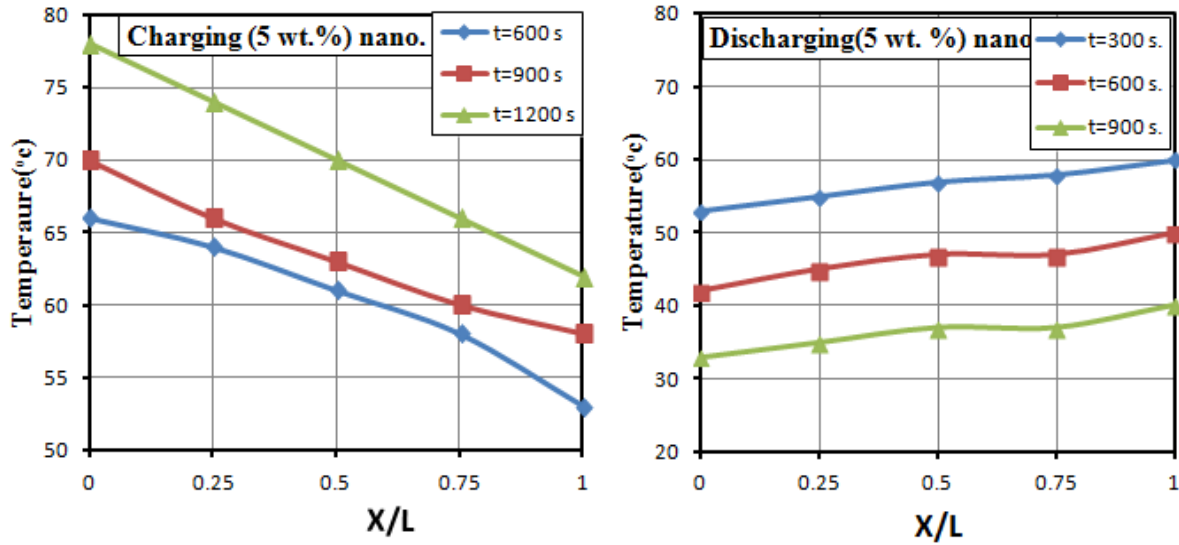
Figure. 9 Distribution the temperature of PCM with (5 wt. %) nano. along the axial direction of the test section during charging and discharging processes.

Figure. 10 Distribution the temperature of PCM with different weight fraction of nanoparticles along the axial direction of the test section during charging and discharging processes at X/L of (0.5).
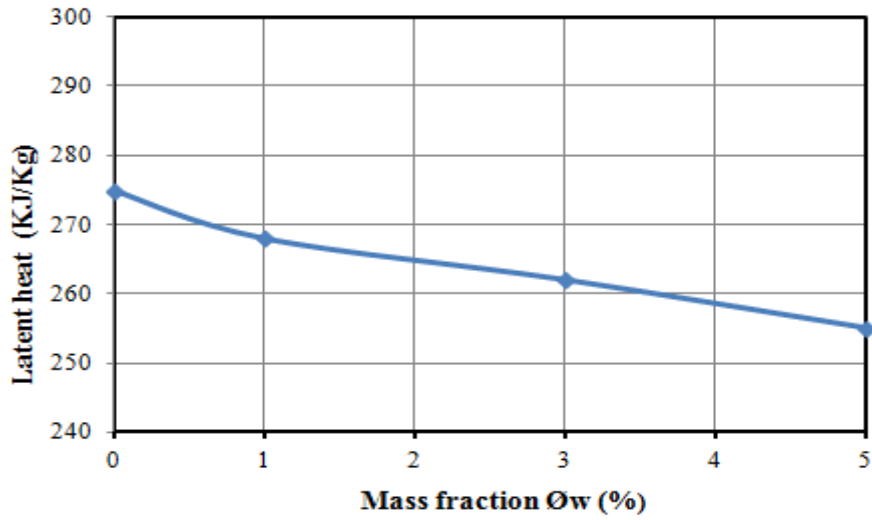
Figure. 11 Effect mass fraction of nanoparticles on the latent heat of fusion of composite PCMs.
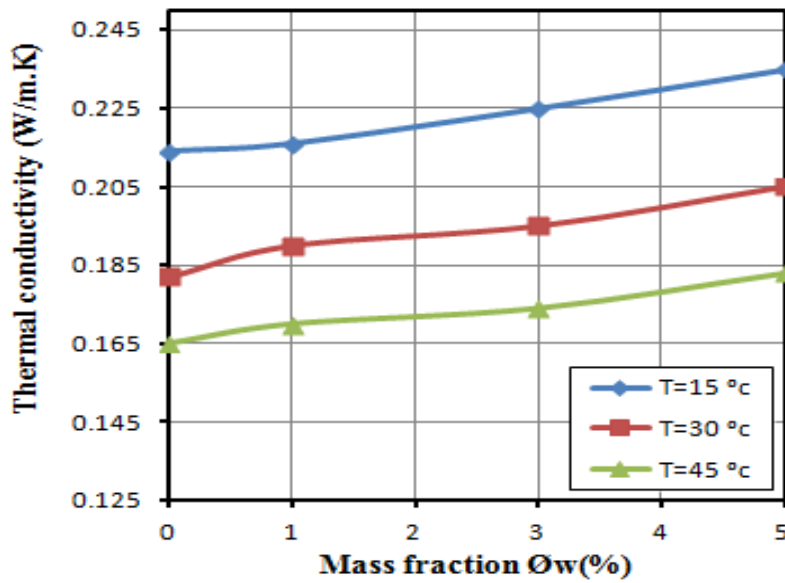
Figure. 12 Effect mass fraction of nanoparticles on the thermal conductivity at different temperatures.