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Abstract

Phase change material (PCM) can be considered as an ideal solution for thermal management challenges. Owing to the large amount of heat energy can be stored or released during the phase change process, PCM widely applied for thermal energy storage (TES), cooling system and thermal comfort purpose. Nevertheless, PCM posting relative low thermal conductivity is the issues that affect its performance. Improvement in thermal performance of PCM are widely studied by former researchers. In this paper, a review on the recent study of heat transfer performance enhancement of PCM is presented. Based on the overview, dispersion of nanoparticles into PCM able to improve the heat transfer performance of PCM but there may also cause little drawback in Latent heat. Lastly, some assumptions and governing equation that applied in the numerical investigation are presented.

Keywords: PCM, heat transfer, nanoparticles, nanofluid

1. Introduction

Phase change material (PCM) play a vital role in thermal management solution due to its superior properties in storing and releasing energy during the phase transition process. PCM are commonly applied as a cooling agent to cool the overheating electronic devices and for thermal comfort purpose [1,2]. Nevertheless, one of the well-known functions of PCM is work a thermal energy storage. Basically, PCM will absorb and store the heat energy from surrounding during the melting process and in contrast release the heat energy back to surrounding during freezing. Thus, PCM are widely used in thermal energy storage system where the heat energy is stored or released based on demand. In Malaysia, most of the energy consumptions are occupied for air conditioning (AC) system in office building since Malaysia’s climate is being hot and humid throughout the year [3]. With the assist of cold thermal energy storage which incorporating with PCM, the high cooling demand during the peak hour can be fulfilled and reduced the burden of the cooling system [4].

Regardless how distinct the nature of PCM, PCM facing a deadly challenge which is the relatively low thermal conductivity of PCM are greatly degraded the thermal performance of PCM in thermal

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energy system. Thus, many methods have been investigated by former researchers to enhance the overall performance of the thermal energy storage system that used PCM as heat transfer medium. In the earlier period, multi PCM was studied to improve the heat transfer performance [5, 6]. After that, insertion of porous metal foam [7-10] and metal matrix [11] into the PCM, addition of fin [12-15] in the thermal energy storage, modification of the shape contact surface between PCM and HTF [16] are been introduced by former authors and followed by the dispersion of nanoparticles into the PCM and nano-encapsulation of PCM [17-19]. Within all the enhancement methods, thermal performance of mixing nanoparticles with the PCM to generate a nano enhanced phase change material (NEPCM) has intensively studied as nanoparticles are a promising additive that has been use in many areas. For examples, nanolubricant, nanocooolant and nanofluid are the products form by addition of nanoparticles as additive and shown a great improvement in heat transfer efficiency.

Nanoparticles can be considered as metal, oxide or carbon tube particles with nano scale that contain higher thermal conductivity [20]. NEPCM is form by dispersion of nanoparticles into the original PCM through two common methods (One-step & Two-Step) [21]. One-step method involves the simultaneously fabrication and dispersing the nanoparticles into the PCM. While the two-step method involves the fabrication of nanoparticles in dry powder form first then followed by the dispersion of nanoparticles into the PCM in subsequent step. Extra steps such as agitation, high-shear mixing, homogenizing, and stirring may require during dispersion in order to achieve a stable NEPCM [22]. In this paper, an overview about the numerical Study on heat Transfer performance enhancement of PCM by dispersing nanoparticles as additive is presented.

2. Enhancement of PCM by Nanoparticles

Khodadadi and Hosseinizadeh [23] were probably the earliest researchers that perform the investigation on enhancing the PCM thought dispersion of nanoparticles in year 2007. Inspired by the report of Mesuda [24] on the improvement of thermal conductivity after dispersed ultra-fine (nanosize) particles in liquids, Khodadadi and Hosseinizadeh conducted an computational study that highlight the potential of using NEPCM in thermal storage applications. By using copper nanoparticles and water as PCM, they studied the freezing of the NEPCM within a differentially-heated square cavity that start with steady state natural convection. From the investigation, they found that as the volume fraction of nanoparticles increases, the solidification time is shorten for a fixed Grashof number. This finding indicates the enhancement of thermal conductivity of the NEPCM in comparison to that of the base PCM. Besides, less energy per unit mass is needed for the freezing of the NEPCM. Thus, Khodadadi and Hosseinizadeh [23] observations concluded that NEPCM possesses great potential for thermal energy storage applications due to its high heat release rate during freezing.

In order to further understanding the NEPCM, Khodadadi and Fan [25] carried out a numerical analysis on the freezing of PCM and nanoparticles composites. The PCM being used in this analysis are water and cyclohexane while the nanoparticles considered are alumina (Al₂O₃), copper (Cu), copper oxide (CuO) and titanium oxide (TiO₂). The analysis is based on a 1-D Stefan problem in a finite slab. The results from the study indicate the suspension of nanoparticles in PCM able to shorten freezing times as high as 11.36 %. Also, as the volume fraction of suspended nanoparticles rises, the thermal conductivity of NEPCM enhances but not too much suspended nanoparticles will give negative effect. Since then, numerous researches are done by other researchers to investigate the possibility of NEPCM in thermal energy storage.

Arasu et al., [26] performed a numerical study to investigate the effect of adding alumina (Al₂O₃) nanoparticles into the paraffin wax that act as PCM in a pipe heat storage system. Both freezing rate and melting rate of paraffin wax ware discovered to be enhanced by dispersion of the nanoparticles.
The freezing rate was fastened by 28.1%, 29.8%, and 33.3% for paraffin wax with 2%, 5%, and 10% Al$_2$O$_3$ whereas melting rate was maximum improved 3.5% for paraffin wax with 2% Al$_2$O$_3$ respectively, as compared to the simple paraffin wax case. Interestingly, this finding indicates the concentration of nanoparticles is an important parameter that required considered in order to enhance the performance of PCM in thermal energy storage at optimum cases. In the same year, Sciacovelli and his co-worker [26] intensively investigated the melting process of pure PCM in a vertical cylindrical shell-and-tube system in order to see the effect of nanoparticles dispersion into the base PCM. A quite similar results obtained from the study where adding 4% volume fraction of copper (Cu) nanoparticles, the melting time of the paraffin wax was reduced by 15% due to the enhancement of heat flux around 16% achieved by the NEPCM.

Unlike the previous researches, instead of doping only one type of nanoparticles into the PCM, Elsayed [27] dispersed of different types of nanoparticles when studying the capability of thermal storage incorporating with neopentyl-glycol (NPG) as PCM. Those nanoparticles involved were Cu, Al, SiO$_2$ and TiO$_2$. Elsayed [27] found that adding SiO$_2$ exhibit highest storage heat capacity (57%) within the NPG compared with Cu nanoparticles in a single nanoparticles system. In binary nanoparticles system (addition of 2 types of nanoparticles), the composite containing (6% SiO$_2$ + 6% Al) enhanced the heat storage at 34% more than the composite containing (6% Al + 6% Cu). Nevertheless, the best performance in heat storage is achieved by the composition (6% Al + 3% SiO$_2$ + 3% TiO$_2$)/NPG in multi nanoparticles system (addition of 3 types of nanoparticles). This numerical investigation had open a new gap for future researchers to study the potential of hybrid NEPCM since dispersion of more than one types of nanoparticles are greatly improved the heat transfer performance of based PCM.

Recently, Kant and his team [28] conducted a heat transfer study on the melting of PCM with graphene nanoparticle in a square cavity. Three common PCMs (Capric Acid, CaCl$_2$·6H$_2$O and n-octadecane) used in thermal energy storage was mixed with graphene nanoparticles with 1%, 3% and 5% volume ratio. The simulation results in their work showed that addition of nanoparticles can improve the thermal conductivity and melting rate of all three PCMs where the melting speed of CaCl$_2$·6H$_2$O was the fastest. However, the presence of graphene nanoparticles had caused the increment of viscosity which may lead to augmentation and hamper the convection heat transfer. A similar findings was found by Sushobhan and Kar [29] in the thermal modeling on melting of NEPCM in square enclosure. Dispersion of copper oxide (CuO) able to improve the thermal conductivity and melting rate of the paraffin (n-octadecane). Higher volume fraction of CuO nanoparticles can shorten the melting time more but excess addition of nanoparticle will cause increase in viscosity that reduced the heat transfer rate.

An intensive study had done by Rabienataj and his colleagues [30] in 2016 to improve the melting and freezing rates of PCM by changing the inner tube shape and adding nanoparticles and fins. Through dispersion of 2% and 4% copper nanoparticles into the n-eicosane as base PCM, the full melting time was decreased by 25% and 46% respectively while the full solidification time was shorten by 9% and 16% subsequently. In addition, the role of adding nanoparticle in the melting of a PCM inside a triplex-tube heat exchanger had been studied comprehensively by Mahdi and Nsofor [31]. They discovered a maximum 17% of melting time can be saved with the presence of 1% volume fraction of nanoparticles. Nonetheless, the above findings were contrary to a study by Tasnim et al., [32]. Tasnim and his team [32] investigated the convection effect on NEPCM (CuO as nanoparticles, cyclohexane as PCM) embedded in porous medium and the scaling analysis showed that thermal conductivity and convection heat transfer inside rectangular cavity are degraded due to additional nano-particles since the melting front indicated that melting time of PCM is prolonged. Table 1 below represents the summary of numerical researches carried out recently by other authors in enhancing PCM thermal properties.
Table 1
Numerical study on enhancement of PCM by Nanoparticles

<table>
<thead>
<tr>
<th>Authors</th>
<th>Nanoparticles</th>
<th>PCM</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al-Jethelah et al., [33]</td>
<td>Aluminium oxide ($\text{Al}_2\text{O}_3$)</td>
<td>Water (H$_2$O)</td>
<td>Adding nanoparticles to base PCM improves the thermal conductivity, melting process, viscosity of the nano-PCM but convection heat transfer degraded by the increased viscosity</td>
</tr>
<tr>
<td>Sahoo et al., [34]</td>
<td>Copper Oxide (CuO)</td>
<td>n-eicosane</td>
<td>The melting rate of NEPCM is increased gradual with addition of nanoparticles from 0 to 5%. The base temperature of heat sink lowered by 4°C which is favorable in electronics application</td>
</tr>
<tr>
<td>Hossain et al., [35]</td>
<td>Copper Oxide (CuO)</td>
<td>Cyclohexane</td>
<td>NEPCM melted faster in lower porosity medium and higher volume fraction of nano-particles. Less energy was required to complete the melting process in higher volume fraction of nano-particles</td>
</tr>
<tr>
<td>Alshaer et al., [36]</td>
<td>Multi Wall Carbon Nano Tubes (MWCNTs)</td>
<td>Paraffin wax (RT65)</td>
<td>Enhancement of thermal conductivity in the carbon foam micro cells owning to the decrement of 11.5% and 7.8% in the module surface temperature with carbon foam porosities lower than 75% and 88% respectively.</td>
</tr>
<tr>
<td>Abdollahzadeh et al., [37]</td>
<td>Copper (Cu)</td>
<td>Water (H$_2$O)</td>
<td>Dispersion of nanoparticle in PCM can shorten the solidification/freezing time but also reduces the energy storage capacity in PCM.</td>
</tr>
<tr>
<td>Jourabian et al., [38]</td>
<td></td>
<td></td>
<td>The melting rate was improved by doping any volume fraction of nanoparticles but enhancement effect decreased in higher volume fraction due to viscosity increased. NEPCM enhanced thermal conductivity but decline latent heat of fusion.</td>
</tr>
<tr>
<td>Darzi et al., [39]</td>
<td></td>
<td></td>
<td>Dispersion of nanoparticles brought enhancement of heat released by 52.7% at 0.04% concentration of Cu nanoparticles in comparison with conventional PCMs. Melting speed also diminished by 75%.</td>
</tr>
<tr>
<td>Sharma et al., [40]</td>
<td></td>
<td></td>
<td>The NEPCM had greater capability to store/release the thermal energy in comparison to the pure PCMs. Increment in nanoparticle dispersion volume fraction caused decrement the solidification time.</td>
</tr>
</tbody>
</table>

3. Assumptions and Governing Equation in Numerical Study

Most of the numerical studies on the heat transfer performance during freezing and melting process of NEPCM are based on enthalphy porosity method. There are some common assumptions that always been made for the numerical study of thermal performance of NEPCM [8, 15, 41, 42].

- The flow of NEPCM in liquid state is considered as an incompressible, unsteady, laminar and Newtonian fluid.
- The liquid NePCM behaves as a continuous medium with thermodynamic equilibrium.
- There are no-slip velocity between the base PCM and solid particles.
- Thermophysical properties of the NEPCM are assumed to be constant.
• The density variation in the buoyancy force term is solved using the Boussinesq approximation. Thus, the formulation for two-dimensional case can be written as follow;

Continuity equation

\[
\frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} = 0, \tag{1}
\]

Momentum equations

\[
\frac{\partial u}{\partial t} + u \frac{\partial u}{\partial x} + v \frac{\partial u}{\partial y} = \frac{1}{\rho_{nf}} \left( - \frac{\partial \rho}{\partial x} + \nu_{nf} \nabla^2 u \right) + S_x, \tag{2}
\]

\[
\frac{\partial v}{\partial t} + u \frac{\partial v}{\partial x} + v \frac{\partial v}{\partial y} = \frac{1}{\rho_{nf}} \left( - \frac{\partial \rho}{\partial y} + \nu_{nf} \nabla^2 v + (\rho \beta_{nf} g (T - T_{ref})) \right) + S_y, \tag{3}
\]

Energy equation

\[
\frac{\partial T}{\partial t} + u \frac{\partial T}{\partial x} + v \frac{\partial T}{\partial y} = \frac{1}{\rho_c p_{nf}} \left( \frac{k_{nf,o} + k_d}{\rho_c p_{nf}} \right) \frac{\partial^2 T}{\partial x^2} + \frac{1}{\rho_c p_{nf}} \left( \frac{k_{nf,o} + k_d}{\rho_c p_{nf}} \right) \frac{\partial^2 T}{\partial y^2} - S_R, \tag{4}
\]

In the above equations, \( t \) is the time, \( u \) and \( v \) are the velocity components respectively in the \( x \) and \( y \) directions, \( \rho \) denotes the pressure, \( T \) is the temperature, \( g \) is the acceleration of gravity and \( S \) represents the source term. In addition, the subscripts \( nf, o, d \) denote nanofluid, stagnant, specific enthalpy and thermal dispersion, respectively.

The density of the nanofluid is written as

\[
\rho_{nf} = (1 - \phi) \rho_f + \phi \rho_s, \tag{5}
\]

Where the subscripts \( f \) and \( s \) denote base fluid and solid, respectively and \( \phi \) represent volume fraction of nanoparticles. Following Brinkman [43], the viscosity of the nanofluid containing a diluted suspension of fine spherical particles can be written as

\[
\nu_{nf} = \frac{\nu_f}{(1 - \phi)^2 \phi_s}, \tag{6}
\]

The heat capacities and the Boussinesq term can be expressed as

\[
(\rho c_p)_{nf} = (1 - \phi)(\rho c_p)_f + \phi (\rho c_p)_s, \tag{7}
\]

\[
(\rho \beta)_{nf} = (1 - \phi)(\rho \beta)_f + \phi (\rho \beta)_s, \tag{8}
\]

The effective thermal conductivity of the nanofluid is given by

\[
k_{eff} = k_{nf,o} + k_d, \tag{9}
\]

where the thermal conductivity of the nanofluid is given as [44]
\[
\frac{k_{nf,0}}{k_f} = \frac{k_s + 2k_f - 2\Phi(k_f - k_s)}{k_s + 2k_f + \Phi(k_f - k_s)}
\]
(10)

and the thermal conductivity enhancement term due to the thermal dispersion is expressed as [45]
\[
k_d = D(\rho c_p)_{nf} \sqrt{u^2 + v^2} \Phi d_p,
\]
(11)

Here, \(D\) is an empirically-determined constant which can be obtained from the work of Wakao and Kaguei [46] and \(d_p\) is the nanoparticle diameter.

The latent heat of the nanofluid is evaluated using
\[
(\rho L_h)_{nf} = (1 - \Phi)(\rho L_h)_f,
\]
(12)

The source terms of the energy equations are expressed as
\[
S_x = \frac{A(1-f)^2}{f^3 + \varepsilon} u,
\]
(13)
\[
S_y = \frac{A(1-f)^2}{f^3 + \varepsilon} v,
\]
(14)
\[
S_h = -\frac{\partial((\rho L_h)_{nf})}{\partial t},
\]
(15)

where \(\frac{A(1-f)^2}{f^3 + \varepsilon}\) cause the gradual change in the velocity from a finite value in the liquid to zero in the solid. Here, \(\varepsilon\) is usually set \(10^{-3}\), a small computational constant used to avoid division by zero. \(A\) is a constant reflecting the morphology of the melting/solidification front. This constant is usually lies in the interval \(10^4-10^7\).

\(H_e\) is the sum of sensible enthalpy, \(h\) is expressed as
\[
h = h_c + \int_{T_c}^{T} C_{p, nf} \, dt
\]
(16)
\[
H_e = h + f L_h
\]
(17)

Here, \(f\) is the liquid fraction during the phase change, which varies between zero for solid and one for liquid and is given by
\[
f = \begin{cases} 
0, & \text{if } T < T_s \frac{T - T_s}{T_l - T_s} \quad \text{if } T_s < T < T_l \\
1, & \text{if } T > T_l
\end{cases}
\]
(18)

where \(T_s\) and \(T_l\) are the solidus and liquids temperature respectively.

4. Conclusions

By referring to the hard works carried out by those former authors, most of the scholars agree that the phase change cycle rate of PCM in thermal energy storage can be enhanced by addition or dispersion of nanoparticles. Increment in the concentration of nanoparticles that mixed with based PCM can further shorten the solidification/ melting time but excess volume fraction may cause a
reversed or negative effect due to occurrence of sedimentation and agglomeration in the NEPCM. Nevertheless, there are also little degradation in latent heat after the doping of nanoparticles in base PCM. Hence, NEPCM can be concluded as a promising material to be selected as functional medium in TES.

In additions, the study on effect of adding multi types nanoparticles or hybrid nanoparticles into the PCM are still poverty. The empirical correlation to determine the optimum condition in order to generate NEPCM with desired properties are insufficient. Thus, further research and development are required to solve those challenges.

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