EFFECT OF CARBON NANO COMPOSITES ON MELTING BEHAVIOR IN LATENT HEAT THERMAL ENERGY STORAGE SYSTEM

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ABSTRACT
In the present work, we numerically investigate the melting phenomena of carbon based nanocomposites in vertically oriented shell-tube latent heat thermal energy storage system. Organic alkane n-eicosane was considered as the phase change material and carbon allotropes as the nano fillers to enhance the thermal conductivity of n-alkane. The effect of different carbon allotropes like nanodiamond (spherical), single-walled carbon nanotubes (one-dimensional) and graphene nanoplatelets (two-dimensional) were considered. Thermal conductivity of nanocomposites was modeled using effective medium based formulation taking the interfacial thermal boundary resistance between nanomaterial and the surrounding host matrix into account. Numerical results show that spherical nano inclusions do not enhance the melting rate due to limited enhancement in the thermal conductivity of nanocomposites. However, the inclusion of one-dimensional and two-dimensional nanostructures shorten the melting time by ~ 15 % and ~ 25 % respectively at 1 vol. % loading as a result of higher thermal conductivity enhancement.

INTRODUCTION
Solar energy is one of the most promising sources of renewable energy resources. Due to the intermittent nature of sunlight, storage of excess thermal energy is of vital importance to match the energy demand and supply. Thermal energy storage (TES) system is popular one among the various storage systems. Generally, TES is classified into two types - latent heat thermal energy storage (LHTES) and sensible heat thermal energy storage (SHTES). Higher storage density as well as isothermal nature during phase transition make LHTES more suitable than SHTES. On the other hand, lower thermal conductivity of phase change materials (PCM) is a concern which limit the energy storage and discharge rates. Therefore, higher thermal conductive PCM are necessary for the advancement of the LHTES systems.

Vyshak et al. [1] numerically investigated the melting behavior of PCM in cylindrical, rectangular and cylindrical shell-tube configuration for a constant PCM volume and heat transfer surface area. It was shown that cylindrical shell-tube configuration showed better performance among these configurations. Esen et al.[2] proposed two different cylindrical shell-tube configurations and calculated the melting behavior of these systems numerically. In their calculations, PCM was placed on the shell side and the heat transfer fluid (HTF) was allowed to flow inside the tube and vice versa. It was reported that the placing of PCM in the shell side resulted in less melting time compared to the other configuration. Ettouney et al.[3] suggested importance of HTF flow direction experimentally in vertical shell tube heat storage system. It was found that upward flow of HTF intensified the natural convection inside the PCM. Further impact of different operational parameters like mass flow rate of HTF, inlet HTF temperature on thermal performance of shell-tube heat storage system was performed experimentally and numerically by several authors [4-6]. Several researchers have performed numerical and experimental results to optimize the geometrical configuration of the TES system and understand the effect of operational parameters. However, the thermal conductivity of PCM used to store and release energy is in the order of 0.2 - 0.5 W m¹ K¹ which results in the reduced heat transfer performance of LHTES systems.

The commonly adopted techniques to enhance the thermal conductivity of PCM is to include a high thermal conductive material in the PCM matrix [7-9] and incorporation of fins on the heat exchanger wall [10-13]. Mettawee et al.[14] investigated the thermal performance of LHTES system with aluminum powder based PCM. Due to increment of thermal conductivity of PCM, 60% melting time reduction was achieved. Zhang et al. [15] experimentally investigated the melting behaviour of expanded graphite/paraffin composites and reported a 68 % reduction in melting time. Carbon based allotropes possess exceptionally high thermal conductivity compared to other metallic and metal oxide based nanoparticles. Especially, recent experimental measurements of thermal conductivity of carbon nanotubes and graphene show excellent thermal conductivity in the range of 3000 – 5000 W m¹ K¹ [16, 17]. Hence, it is natural to anticipate that the development of nano composites with carbon additives will yield promising enhancement at limited loading compared to other structures. Recent experiments on nanoparticle based suspensions show that the thermal conductivity enhancement is significantly limited and can be predicted using effective medium theory. Carbon nanotubes and graphene show significantly higher thermal conductivity enhancement compared to nanoparticles due to their large aspect ratio and higher thermal conductivity. However, despite the high intrinsic thermal conductivity
of carbon nanostructures, the effective thermal conductivity enhancement is limited due to the presence of high interfacial thermal resistance between nanostructure and the surrounding PCM matrix [18 - 21]. Sciacovelli et al. [22] numerically investigated the influence of copper nanoparticles in vertically oriented shell-tube LHTES system. They showed a 15% reduction in melting time compared to that of pure paraffin at 4 vol. % loading of copper nanoparticles. However, in their numerical calculations the interfacial thermal resistance between the nanoparticle and the surrounding PCM was not taken into account while calculating the effective thermal conductivity using Maxwell’s model. Das et al. [23] numerically investigated the effect of heat transfer fluid temperature and the graphene concentration on the melting characteristics of n-eicosane based nanocomposites in shell-tube LHTES systems. It was shown that the melting time decreases with increasing the loading of graphene nanoplatelets and also increasing temperature of heat transfer fluid. In their numerical calculations, effective thermal conductivity of nanocomposites was calculated using effective medium theory considering the role of interfacial thermal resistance and effective viscosity was estimated using the Kreiger - Dougherty approach.

In this work, we systematically investigate the effect of carbon nanomaterial dimensionality on the melting characteristics of PCM in LHTES systems. To enhance the thermal conductivity of PCM, high conductive carbon nanomaterials of different dimensionality namely nano-diamond (spherical), single-walled carbon nanotubes (SWCNT, 1-dimensional) and graphene nanoplatelets (GnP, 2-dimensional) are considered. For a constant HTF temperature and constant loading of the nanomaterial, we show that the inclusion of 1 vol. % GnP and 1 vol. % SWCNT show ~ 25 % and ~ 15 % reduction in melting time compared to that of pure PCM. On the other hand, inclusion of nano-diamond does not show any appreciable decrease in the melting time due to limited enhancement in the thermal conductivity.

### 1. Modeling

#### 1.1 System description

For the numerical calculations, we have made use of a vertically oriented cylindrical single shell-tube LHTES system which is used by Akgun et al. [5] for their experiments. Figure 1 shows the 3 dimensional schematic of the computational model which is created based on the dimensions reported in the Ref [5]. Shell and tube is situated concentrically in the system. Water is used as HTF. HTF flows through the inner tube of the system at constant temperature. PCM is placed in annular gap between tube wall and shell wall. Shell wall and tube wall are considered as steel and high conductive copper material. For melting purpose, initially, PCM is at ambient temperature \(T_s\) in solid phase. Hot inlet HTF flows inside the tube at constant temperature \(T_{htf}\) that is higher than PCM melting temperature \(T_m\). The melting process is continued until solid phase of PCM transforms into liquid phase, thus latent heat stores into PCM.

![Figure 1. 3D view of the geometry of LHTES system. The direction of HTF fluid flow is indicated in red.](image)

#### 1.2 Governing Equations:

In this section, we show the governing equations and the mathematical formulations adopted to model the melting characteristics of the nanocomposites. The governing equation are shown below:

- **Continuity equation:**
  \[
  \frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \vec{V}) = 0
  \]

- **Momentum equation:**
  \[
  \rho \frac{\partial \vec{V}}{\partial t} + \rho (\vec{V} \cdot \nabla) \vec{V} = -\nabla P + \mu \nabla^2 \vec{V} + \rho \alpha (T - T_{ref}) \vec{a} + \vec{S}
  \]

- **Energy equation:**
  \[
  \frac{\partial \rho H}{\partial t} + \nabla \cdot (\rho \vec{V} H) = \nabla \cdot (K_{pcm} \nabla T)
  \]

where \(\rho\) is the PCM density, \(\vec{V}\) is the velocity vector of PCM, \(P\) is the pressure, \(\alpha\) thermal expansion coefficient, \(\mu\) is the dynamic viscosity of PCM. To model the density variations in the liquid which drives the natural convection phenomena, Boussinesq approximation is used. Similarly, we have limited our calculations to turbulent flow conditions in the heat transfer fluid side. To model the turbulent flow in HTF inside the tube, the standard k-epsilon model is used.

In this work, we made use of enthalpy-porosity approach to model the solid-liquid phase change problem. Mushy zone is treated as porous medium and the porosity in each element is considered as liquid fraction at that element. Here, solid-liquid interface is not tracked.
adopted to solve the governing equation

\[ S = -A_{\text{mushy}} \frac{(1 - \Delta)^2}{(\Delta^3 + \varepsilon)} V \]

(4)

\( \Delta \) is defined as liquid fraction that means fraction of solid-liquid quantity present in PCM and it depends on temperature of PCM

\[ \begin{align*}
\Delta &= 0 & \text{if } & T < T_{\text{solidus}} \\
\Delta &= 1 & \text{if } & T > T_{\text{liquidus}} \\
\Delta &= \frac{T - T_{\text{solidus}}}{T_{\text{liquidus}} - T_{\text{solidus}}} & \text{if } & T_{\text{solidus}} < T < T_{\text{liquidus}}
\end{align*} \]

(5)

\( \varepsilon \) is a small number (approximately \( 10^{-3} \)) which helps to prevent division by zero. \( A_{\text{mushy}} \) is the mushy zone constant, which indicates the magnitude of damping in momentum equation. In present work, \( A_{\text{mushy}} \) is considered as \( 10^2 \) which shows good agreement with experimental results of Akgun et al. [5].

\[ H = H_{\text{ref}} + \Delta L + \int_{T_{\text{ref}}}^{T} c_p \, dT \]

(6)

where \( H \) is the enthalpy of PCM that is sum of sensible heat and latent heat \( L \). \( H_{\text{ref}} \) is the reference enthalpy at reference temperature, \( K_{\text{pcm}} \) is the thermal conductivity of PCM.

The thermophysical properties of nanocomposites based PCM is calculated based on the formulations shown below. All thermal properties like density, specific heat, latent heat, thermal expansion coefficient were calculated following equations [22, 23]:

\[ \rho = (1 - \varphi) \rho_{\text{pcm}} + \varphi \rho_p \]

(7)

\[ \rho c_p = (1 - \varphi) (\rho c_p)_{\text{pcm}} + \varphi (\rho c_p)_p \]

(8)

\[ \rho L = (1 - \varphi) (\rho L)_{\text{pcm}} + \varphi (\rho L)_p \]

(9)

\[ \rho \alpha = (1 - \varphi) (\rho \alpha)_{\text{pcm}} + \varphi (\rho \alpha)_p \]

(10)

where \( \varphi \) is the volume fraction of nanomaterial, subscripts \( \text{pcm} \) and \( p \) indicate properties of pure PCM and nanomaterial.

The effective dynamic viscosity is evaluated using Krieger-Dougherty [24] modified model for spherical and ellipsoidal particles as shown in the following equation:

\[ \mu = \mu_{\text{pcm}} \left(1 - \frac{\varphi}{\varphi_{\text{max}}} \right)^{-A \varphi_{\text{max}}} \]

(11)

\( \varphi_{\text{max}} \) and \( A \) are maximum packing factor and intrinsic viscosity that are influenced by nanomaterial’s shape. The values of maximum packing factor used in the model calculations for spherical, 1-dimensional and 2-dimensional materials are 0.632, 0.268 and 0.382 respectively [24, 25]. Similarly, the intrinsic viscosity used for spherical, 1-dimensional and 2-dimensional materials are 2.5, 9.25 and 9.87 respectively [26].

The effective thermal conductivity of nanocomposites based PCM is calculated based on effective medium theory considering the role of thermal boundary resistance into account [27]. The detailed equations are described in Ref 27. For model calculations, the aspect ratio of spherical particles, SWCNT and GnP were considered to be currently (diameter 10 nm), 10 (length 1 µm and diameter 1 nm) and \( 10^3 \) (length 1 µm and thickness 1 nm) respectively. The thermal boundary resistance between the nanomaterials and surrounding PCM is \( ~10^{-8} \text{ m}^2 \text{K W}^{-1} \) based on the existing literature results [18-21, 28-30].

1.3 Boundary and initial conditions

(i) Outer wall of shell is considered as adiabatic i.e \( q_{\text{wall}} = 0 \).

(ii) no slip boundary between HTF and HTF tube is considered.

(iii) Ambient pressure at outlet of HTF is considered.

(iv) Inlet HTF temperature and HTF velocity for all cases are taken constant that are \( T_{\text{htf}} = 60^\circ \text{C} \) and \( m_{\text{inlet}} = 9.2 \text{ kg/min} \).

(v) Initial temperature of PCM is \( T_i = 20^\circ \text{C} \) and PCM is considered as motionless solid.

The heat transfer fluid considered in this study is water. For numerical calculations water is considered as Newtonian and incompressible fluid. Furthermore, in liquid and solid phase of PCM, all thermophysical properties are considered to be constant. We have also assumed that the volume changes during phase change of the PCM to be negligible and the effect of voids is not taken into consideration. Also, the nanomaterials are considered to be homogeneously distributed in the PCM to utilize effective medium formulations.

1.4 Numerical approach

In this work, to minimize the computational time and cost, 2-dimensional (2D) axi-symmetric model on X-Y plane is analyzed. We made use of commercial software FLUENT to perform the melting calculations. Finite volume technique is adopted to solve the governing differential equations. SIMPLE algorithm has been applied to solve pressure and velocity coupling, second order upwind scheme and PRESTO have been used for the discretization of energy, momentum, turbulence and pressure correction. Second order implicit time integration is adopted in this work. 0.2 s time steps size has been adopted for calculation as it is found to obtain time step independency. For meshing evaluation, 23600 quadrilateral cells are sufficient to obtain grid independency. The relative residual of all variables like mass, velocity and energy is less than \( 10^{-3} \) for each time step to satisfy the convergence criteria.
2. Result and discussion:

2.1 Melting behavior of pure PCM

Melting behavior of pure PCM (case 1) inside the shell after absorbing heat from hot HTF is illustrated in figure 2. First contour of the figure at t = 300 s shows that the melt front thickness along the tube length is very small except at upper region of the tube due to conduction dominance. In second contour as time increases, melting front reaches at shell wall in upper region due to natural convection effect. Still melting front thickness at lower region is small because of lower conductivity of PCM. It is observed that conduction and convection plays simultaneously a significant role for melting progression at this time. Later, at t = 7200 s, it is seen that convection dominates the melting front progression. Last contour indicates the initiation of solid shrinking.

Figure 2: Liquid fraction contour for pure PCM at different time intervals with 60 °C HTF inlet temperature

Further effect of buoyancy driven natural convection is more visible through the streamlines in figure 3. Initially, small dense liquid from lower region moves toward the upward direction and forms small recirculation zone in the upper region. As time increases, the mean temperature of the liquid PCM increases which increases the recirculation of PCM due to convection dominance. Such increases recirculation enhances the melting rate due to heat transfer increment from the hot HTF tube wall to the liquid PCM. Temperature contours are shown in figure 4. First contour at t = 300 s shows diffusion dominated melting behavior along the shell diameter. Later, effect of buoyancy driven convection prevails over the liquid PCM, that forms temperature gradient along the tube length also. Melting rate is improved and after completion of melting, sensible heat is stored in PCM, its temperature is raised to inlet HTF temperature because of adiabatic nature of the shell wall.

Figure 3: Streamline contours for pure PCM at different time intervals

Figure 4: Temperature contour for pure PCM at different time intervals

2.2 Effect of carbon nanocomposites

To enhance the thermal performance of LHTES system, we study the effect of carbon based nano materials inclusions in this section. The influence of spherical, one dimensional and two – dimensional inclusions for a fixed volume percent loading (1 vol. %) is illustrated in this section.

Figure 5: Liquid fraction for different nanocomposites at inlet HTF of 60 °C

Figure 5 shows the melting front movement of 1 vol. % nanocomposites in comparison with pure PCM at t = 4800 s and t = 7200 s. It can be seen from figure 5 that the melt front propagation of 1 vol. % nano diamond based nanocomposites is almost similar to that of original PCM. This behavior is attributed to the limited increase in
the thermal conductivity of PCM which is consistent with the results of Sciacovelli et al [22]. Figure 5 also shows the rapid melt front propagation for SWCNT and GnP based nanocomposites compared to the pure PCM. Despite the presence of thermal boundary resistance, the enhancement in thermal conductivity is higher for ellipsoidal particles which causes this trend. It can be seen that GnP based nanocomposites show superior performance compared to other nanomaterials due to a high thermal conductivity enhancement predominantly attributed to its high aspect ratio and planar structure.

Figure 6 shows the average liquid fraction results of pure PCM in comparison with the carbon nanocomposites. It can be seen from the figure that the pure PCM takes nearly 225 minutes to completely melt when the inlet HTF temperature is 60 °C. Similar trend was seen for the case of 1 vol. % ND based composites due to the limited increase in thermal conductivity. For the case of 1 vol. % ND nanocomposites, melting rate is reduced to 222 minutes which is insignificant. However, for the case of 1 vol. % SWCNT and 1 vol. % GnP melting time reduces to 191 and 168 minutes respectively. Though the latent heat of these nanocomposites decreases marginally ~ 2.5 % the utilization of GnP based nanocomposites can still be beneficial considering the significant reduction in melting rate due to the high thermal conductivity enhancement.

Figure 7 shows the average temperature profile for different nanocomposites investigated in this work. ND based nanocomposites temperature profile almost overlaps with pure PCM due to limited thermal conductivity enhancement which is consistent with the average liquid fraction results. Further SWCNT and GnP based nanocomposites show a higher rate of temperature rising due to higher thermal conductivity of nanocomposites.

Further, average heat flux is illustrated for pure PCM and all nanocomposites in figure 8. Initially conduction dominated heat flow from HTF pipe to PCM which is indicated by the higher heat flux. GnP shows maximum heat flow due to higher thermal conductivity which is followed by SWCNT nanocomposites. ND composites do not show any promising improvement. Further with increase in time the average heat flux starts to decrease rapidly after 30 min.

Figure 7: Average temperature profile for different nanocomposites at inlet HTF of 60 °C

Figure 6: Liquid fraction for different nanocomposites at inlet HTF of 60 °C

Figure 8: Average heat flux for different nanocomposites at inlet HTF of 60 °C

Conclusions

This paper numerically investigates the thermal performance of vertical LHTES system with different carbon based nanocomposites for constant inlet HTF temperature and mass flow rate conditions. The role of varying geometry of carbon nanomaterials in enhancing the thermal conductivity and its impact on the system level performance is investigated. In this context, the effect of 1 vol. % of spherical (nano diamond), 1-dimensional (single-walled carbon nanotube) and 2-dimensional (graphene) is considered as the nano inclusion to enhance the thermal conductivity of the PCM. Effective thermal conductivity of such nanocomposites is modeled theoretically based on effective medium theory considering the role of thermal boundary resistance between the nanomaterial and the surrounding PCM.

Numerical results show that the inclusion of 1 vol. % nanodiamond increases the melting rate only by ~1.5 % due to limited increase in thermal conductivity which is compensated by the increase in fluid viscosity. The inclusion of 1 vol. % SWCNT and 1 vol. % GnP decreases the melting time by ~ 15 % and ~ 25 % respectively due to higher thermal conductivity enhancement. The results show that despite the high thermal conductivity of all the nanostructures considered, maximum improvement in the thermal performance of the LHTES system is obtained for the case of 2-D nanomaterial inclusions. The present numerical calculations show that one must be careful in
selecting the dimensionality of the nanomaterial to enhance the thermal conductivity of the pure PCM.

References
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