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Numerical Analysis of Melting of Paraffin Wax with Al₂O₃, ZnO and CuO Nanoparticles in Rectangular Enclosure

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Abstract

A numerical study on variations of thermo-physical properties of Phase Change Material (PCM) due to dispersion of nanoparticles is presented in this article. Dispersed metal oxide nanoparticles in paraffin wax might be a solution to improve latent heat thermal storage performance. Thermo-physical properties such as thermal conductivity and latent heat could be changed for different concentration of dispersed nanoparticle. The paper will focus on numerical investigation of the melting of paraffin wax dispersed with three different metal oxide Alumina $(Al_2O)_3$, Copper Oxide (CuO) and Zinc Oxide (ZnO) that is heated from one side of rectangular enclosure of dimensions of 25 mm × 75 mm. The integrated simulation system ANSYS Workbench 15.0 for the numerical study was used including mesh generation tool ICEM and FLUENT software. In FLUENT, the melting model with Volume Of Fluid (VOF) that includes the physical model to disperse nanoparticles in the PCM and their interactions is applied. During melting process, the enhancement of heat transfer is considered. For each nanoparticle analyzed, three different volume fractions are considered and compared. Dispersed nanoparticles in smaller volumetric fractions show a rise the heat transfer rate. The thermal performances are slightly greater using Al_2O_3 respect both ZnO that CuO nanoparticles.

Keywords: Thermal Storage System; Phase Change Material; Paraffin Wax; Melting Process; Metal Oxide Nanoparticles

1. Introduction

In last years, attention about Thermal Energy Storage (TES) technology is significantly increased for its various benefits in diverse engineering applications. The TES systems to store and release thermal energy can be assembled in to three kinds: sensible heat, latent heat and thermo-chemical. Of the three kinds, the latent heat thermal energy storage technique confirms as a greater engineering opportunity because of its various benefits such as large energy storage for a given volume, uniform energy storage supply, compactness, etc. Phase Change Materials (PCM) during the energy transfer process are used in the latent heat thermal energy storage units.

In thermal energy storage systems, the melting of phase changing materials in the enclosure has significant consideration^{1, 2}. Melting temperature, heat capacity, thermal conductivity and density are crucial properties

to define a material suitable for such applications. Ideally, the required qualities of PCM would be high latent heat of fusion per unit mass, high heat capacity, high density, to be not toxic, not expensive and not corrosive. Numerous PCMs with their properties, advantages and limitations have been comprehensively reported in refs. 3-5Of these, paraffin waxes are low-cost and have modest density of thermal energy storage but low thermal conductivity and, consequently, need vast surface area. A large heat flow for this material can be achieved by increasing the effective thermal conductivity. Nanoparticles added in PCM considerably increase the effective thermal conductivity of the fluid and thus enhance the heat transfer characteristics.3,6-10 In the present work, a numerical investigation of the melting is carried out to estimate the effect on thermal performance of paraffin wax due to the enhancement in thermal conductivity using Al₂O₃, CuO and ZnO nanoparticles. The effect of volumetric fractions

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of three different nanoparticles on the melting performance are presented and discussed. The goal is study of nanostructured materials suitable to implement the efficient thermal storage systems in Concentrated Solar Power. This study involved the authors in the task FP7: "Feasibility study for the synthesis of Nano PCM with attractive properties for using in TES" of STAGE_STE, an Integrated Research Program (IRP) on the topics Concentrating Solar Thermal Energy that engages all major European research institutes¹¹.

2. Physical Model

The geometry used, shown in Figure 1, is a rectangular box of size 25 mm \times 75mm. It contains paraffin wax or paraffin wax dispersed with 1% and 3% by volume of three different nanoparticles $\mathrm{Al_2O_3}$, ZnO and CuO. The initial temperature of the nano PCM is 300 K, the hot wall side is at a constant temperature of 330 K (Tmax) and the cold wall, opposite the hot wall, is at 300 K (Tmin) in order, the other two walls are adiabatic.

Assumptions made:

- The flow is Newtonian, incompressible and laminar;
- The viscous dissipations are negligible;
- The physical properties of PCM are temperature dependent;
- Heat transfer is both conduction and convection controlled;
- The volume variation resulting from the phase change is neglected,
- 2D model is used, neglecting 3D convection. With this hypothesis, the results may be considered almost real because the 3d convection duration is very short¹² compared with the whole melting process.

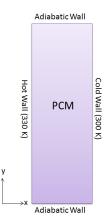


Figure 1. Physical Mode.l

3. Governing Equation

3.1 PCM Storage System

Fluid flow, heat transfer and phase change of the PCM processes with nanoparticles are regarded in the storage system. The governing conservation equations¹³ are as follows.

Continuity equation:

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \vec{U}) = 0 \tag{1}$$

Momentum equation:

$$\partial \Big/ \partial t \Big(\rho \vec{U} \Big) + \nabla . \Big(\rho \vec{U} \vec{U} \Big) = - \nabla . P + \rho \vec{g} + \nabla . \vec{\tau} + \vec{F}$$
 (2)

where P is the static pressure, $\vec{\tau}$ is the stress tensor, and $\rho \vec{g}$ and \vec{F} are the gravitational body force and external body forces, respectively.

Energy equation:

$$\left(\partial(\rho H)\right)/\partial t + \nabla \cdot \left(\rho \vec{U} H\right) = \nabla \cdot \left(K \nabla T\right) + S \tag{3}$$

where H is the enthalpy, T is the temperature, ρ is density, K is the thermal conductivity, \vec{U} is the velocity and S is volumetric heat source term and is equal to zero in the present study. The total enthalpy H of the PCM is computed as the sum of the sensible enthalpy, h and the latent heat, ΔH . The latent heat content, in terms of the latent heat of the PCM, L is:

$$\nabla H = \beta L$$
 (4)

where β is liquid fraction and is defined as:

$$\beta = 0 \qquad \text{if } T < T_{solidus}$$

$$\beta = 1 \qquad \text{if } T > T_{liquidus}$$

$$\beta = \frac{T - T_{solidus}}{T_{liquidus} - T_{solidus}} \qquad \text{if } T_{solidus} < T < T_{liquidus} \qquad (5)$$

The solution for temperature is essentially an iteration between the energy Eq. (3) and the liquid fraction Eq. (5). The enthalpy-porosity technique treats the mushy region (partially solidified region) as a porous medium. The porosity in each cell is set equal to the liquid fraction in that cell. In fully solidified regions, the porosity is equal to zero, which extinguishes the velocities in these regions.

3.2 Thermal Physical Proprieties

The thermo- physical properties of paraffin wax, Al₂O₃ CUO and ZnO nanoparticles¹⁴⁻¹⁶, are listed in Table 1. The

Table 1. Operating Parameters

	Paraffin Wax	Al_2O_3	CuO	ZnO
Density (kg/m³)	$\frac{750}{0.001(T-319.15)+1}$	3600	6510	5606
Specific heat (J/kgK)	2890	765	540	514
Conductivity (W/mk)	0.21 if T <tsolid 0.12 if T>Tliquidus</tsolid 	36	18	23.4
Viscosity (Ns/m²)	$0.001 \exp(-4.25 + \frac{1700}{T})$			
Latent Heat (J/kg)	173400			
Solid Temperature (K)	319			
Liquid Temperature (K)	321			
T ref (K)	298.15			
dnp(nm)		59	29	50

difference in the solidus and liquids temperatures defines the transition from solid to liquid phases during the melting of PCM. The density, specific heat capacity and latent heat of the nano PCM are defined as follows¹⁷:

$$\rho_{npcm} = \varphi \rho_{np} + (1 - \varphi) \rho_{pcm} \tag{6}$$

$$C\rho_{npcm} = \frac{\varphi(\rho C_p)_{np} + (1 - \varphi)(\rho C_p)_{pcm}}{\rho_{npcm}}$$
 (7)

$$L_{npcm} = \frac{\left(1 - \varphi\right) \left(\rho L\right)_{pcm}}{\rho_{npcm}} \tag{8}$$

where ϕ is volumetric fraction of nanoparticle. The dynamic viscosity and thermal conductivity of the nano PCM are given by the following¹⁸:

$$\mu_{npcm} = 0.983e^{(12.958\varphi)} \tag{9}$$

The effective thermal conductivity of the nano PCM, which includes the effects of particle size, particle volume fraction and temperature dependence as well as properties of the base PCM and the particle subject to Brownian motion, is given by:

$$K_{npcm} = \frac{K_{np} + 2K_{pcm} - 2(K_{pcm} - K_{np})\varphi}{K_{np} + 2K_{pcm} + 2(K_{pcm} - K_{np})\varphi} K_{pcm} + 5 \times 10^4 \beta_k \varsigma \varphi \rho_{pcm} C_{p_{pcm}} \sqrt{\frac{BT}{\rho_{npd_{np}}}}$$
(10)

where:

B is Boltzmann constant, 1.381×10-23 J/K

$$\beta_k = 8.4407 * (100\varphi)^{-1.07304}$$
 (11)

$$f(T,\varphi) = \left(2.8217 \times 10^{(-2)} \varphi + 3.917 \times 10^{(-3)T/T_{ref}}\right) + \left(-0.669 \times 10^{(-2)} \varphi - 3.91123 \times 10^{(-3)}\right)$$
(12)

where T_{ref} is the reference temperature. The first part of Eq. (10) is obtained directly from the Maxwell model while the second part accounts for Brownian motion, which causes the temperature dependence of the effective thermal conductivity. Note that there is a correction factor ς in the Brownian motion term, since there should be no Brownian motion in the solid phase. Its value is defined as the same as for liquid fraction, β in Eq. (5).

4. Boundary and Test Conditions

The boundary and test conditions (Table 2) are prescribed as follows:

- Hot wall T = Tmax
- Cold wall T = Tmin
- Adiabatic walls (Knpcm Δ T) = 0
- Initial condition Ti = Tmin

5. Computational Methodology

For the numerical study, the integrated simulation system ANSYS Workbench 15.0 is used. The platform includes mesh generation tool ICEM and FLUENT software.

Table 2. Test Conditions

Melting	%(volume)	Time(s)	
Pcm = Paraffin Wax	-	500s, 1000s.	
$Pcm + Al_2O_3$	1%,3%	500s, 1000s.	
Pcm +CuO	1%,3%	500s,1000s	
Pcm +ZnO	1%,3%	500s, 1000s.	

Order to reduce the computational time, first, a fine structured mesh near the boundary layer and an increasingly coarser mesh in the rest of the domain is generated, and then the mesh is exported into FLUENT for solving the governing equations.

To investigate both about dispersed nanoparticles in the PCM that about their interactions, in FLUENT, the melting model together to volume of fluid (VOF) model are applied. For modeling the melting process, the enthalpy-porosity technique is used. In this technique, the melt interface is not tracked explicitly. The liquid fraction indicating the fraction of the cell volume that is in liquid form is computed at each iteration, based on an enthalpy balance. The mushy zone is the region where the porosity increases from 0 to 1 as the PCM melts.

To account for temperature dependence, the input parameters of PCM and of nanoparticles were defined using different user- defined functions (UDF) written in C++ language. The PRESSURE BASED method with the FIRST ORDER UPWIND differencing scheme are used for solving the momentum and energy equations, whereas the PRESTO scheme is adopted for the pressure correction. The under-relaxation factors for the velocity components, pressure correction and thermal energy are 0.5, 0.3 and 1 respectively.

Grid dependence test showed that the maximum difference of the PCM temperature at an identical time is within 0.01% between using 4000 cells and 4800 cells with a time step of 0.1 s. After mesh independence study, considering both accuracy and computing time, 4400 cells with a time step of 0.1 s are used in the computations.

6. Results and Discussion

Transient two-dimensional numerical simulations are implemented at operative conditions listed in Table 2. The material used was the paraffin wax dispersed with three different metals oxide Al2O3, CuO and ZnO. For all used nanoparticles, three different volumetric nanoparticle concentrations are performed during melting process. The simulation process ends after 1000 seconds. Aim was examining the performances of nanoparticles suspended in the PCM respect to:

- Thermo-physical properties
- Heat transfer rate

Finally, considering numerical results, for every type of metal oxide dispersed in PCM, were analyzed limitations and advantages

6.1 Thermo-Physical Properties

Figures 2, 3 and 4 show the thermo-physical properties of nano PCM. Essentially, thermal conductivity and dynamic viscosity of paraffin wax dispersed with 1% and 3%, by volume of nanoparticles ${\rm Al_2O_3}$, ZnO and CuO are plotted as a function of temperature and volumetric concentration.

From Figures 2(left), 3(left) and 4(left), it is clear that the thermal conductivity of nano PCM is greater than the simple PCM. Hence, nano PCM has higher heat transfer rate compared to the same mass of simple PCM. Nonetheless, viscosity of nano PCM increases with the increase in the volumetric concentration of nanoparticles, as shown in Figure 2(right), 3(right), 4(right).

In figures 2(left), 3(left), 4(left) it can observe that the thermal conductivity enhancement of the nanoparticles dispersed in paraffin can be seen markedly augmented with increasing temperature, (range 330K–360 K). This event, typically observed for the nanofluids, is due to the increased Brownian motion of nanoparticles in the base fluid having considerably reduced viscosity following a rise in temperature. More, with increasing temperature, the relative increase in the dynamic viscosity for the nanoparticle in paraffin dispersion compared with that for the pure paraffin appears slightly promoted. Moreover,

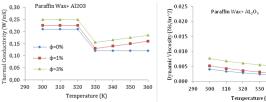


Figure 2. Thermo-physical properties of nanoPCM comprising paraffin wax and Al₂O₃ for (left) Thermal Conductivity and (right) Dynamic Viscosity for volumetric concentration of nanoparticle 0%, 1% and 3%.

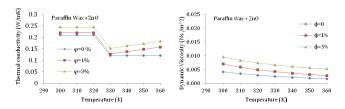


Figure 3. Thermo-physical properties of nanoPCM comprising paraffin wax and ZnO for (left) Thermal conductivity and (right) Dynamic Viscosity for volumetric concentration of nanoparticle 0%, 1% and 3%.

for two used volumetric concentrations during melting, the viscosity is greater for CuO compared with ZnO and Al_2O_3 as shown in Figure 5. In the end, the variation in thermal conductivity and dynamic viscosity of nano PCM with temperature and volume fraction agree well with the experimental and numerical results reported in 12,19,20 .

6.2 Heat Transfer Performance

The melting rate of Al₂O₃, ZnO and CuO nanoparticles enhanced paraffin for two volumetric concentrations 1%, and 3% wax is examined. In Figures 6, 7, 8 is shown the

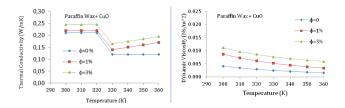


Figure 4. Thermo-physical properties of nanoPCM comprising paraffin wax and CuO for (left) thermal conductivity and (right) viscosity for volumetric concentration of nanoparticle 0%, 1% and 3%.

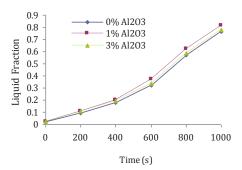


Figure 5. Dynamic Viscosity Comparison of nanoparticles of Al₂O₃, ZnO and CuO at 1 %(left)) and 3 %(right) by volume concentration.

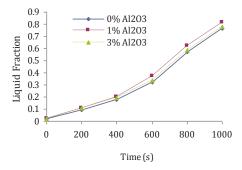


Figure 6. Melting processes of paraffin wax and Al_2O_3 at nanoparticle concentration of 0%, 1% and 3%.

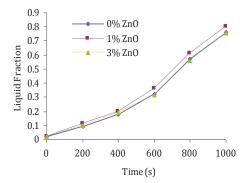


Figure 7. Melting processes paraffin wax and ZnO at nanoparticle concentration of 0%, 1% e 3%.

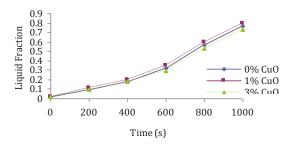


Figure 8. Melting processes of paraffin wax and CuO at nanoparticle concentration of 0%, 1% and 3%.

time evolution of melting of paraffin wax without and with nanoparticles.

Adding nanoparticles in paraffin, the heat transfer performance is planned to improve; this is in fact true for low nanoparticle concentration of 1%, as can be inferred from Figures 6, 7, 8, for all considered nanoparticles. In order, at volumetric concentrations of 1% compared to that for pure paraffin wax, it can observe that $\mathrm{Al_2O_3}$ is the nanoPCM faster to melt followed by ZnO and then CuO. This justifies the small improvement in the thermal conductivity of paraffin with $\mathrm{Al_2O_3}$ nanoparticles.

When the volumetric concentration of nano PCM is increased at 3%, the time required for melting is longer than that for pure and low concentration (1%) of nano PCM. This is consequence to the fact that adding nano PCM increases viscosity as the volumetric concentration increased. (see figure 3 right, 4 right, 5 right).

In the melting process, the natural convection controls the heat transfer rate, as higher is dynamic viscosity then lower is the liquid fraction and consequently slower is the melting process. In Figures 9 and 10 dynamic viscosity versus liquid fraction for Al₂O₃, ZnO and CuO nano PCM at 1% and 3% volumetric concentration is shown

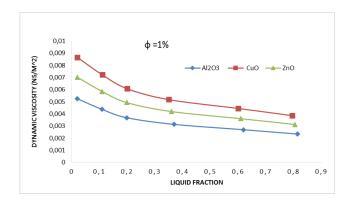


Figure 9. Dynamic Viscosity Vs liquid fraction of Al2O3, ZnO, and CuO nanoPCM at 1% volumetric concentration.

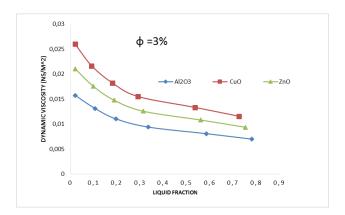


Figure 10. Dynamic Discosity Vs liquid fraction of Al2O3, ZnO, CuO nanoPCM at 3% volumetric concentration.

confirming that higher is dynamic viscosity lower is the liquid fraction.

The melting rate for Al_2O_3 is somewhat slower for nanoparticle concentration of 3 %, the longer melting time is observed for CuO nanoparticle, while the melting time for ZnO is longer of AL_2O_3 and slower of CuO.

In particular, the melting time increases more for CuO nanoparticle concentration of 3%. There are not important differences on heat transfer rate at first 400 s because the heat transfer is controlled by conduction mode. Again PCM melted, the dominant mechanism shifts to natural convection where the viscosity effect is greater. This is further mirrored by lower heat transfer rate for higher nanoparticle concentration due to viscosity increase at time higher than 400s.

In Table 3, we present the liquid fraction for a melting period of 1000 s for all test cases and we confirm again that the advantages are greater for ${\rm Al_2O_3}$ compared to ZnO and CuO and the overall performance of melting

Table 3. Liquid Fraction for a melting period of 1000 s

Pure paraffin wax	Paraffin wax with 1% AL2O3	Paraffin wax with 3% AL2O3
0.765	0.813	0.780
Pure paraffin wax	Paraffin wax with 1% ZnO	Paraffin wax with 3% ZnO
0.765	0.803	0.752
Pure paraffin wax	Paraffin wax with 1% CuO	Paraffin wax with 3% CuO
0.765	0.794	0.725

process is better for lower concentration of nanoparticles. It is because the increase in the dynamic viscosity with Al_2O_3 is lower at volumetric concentration of 1% (Figures. 2right, 3right, 4right) than ZnO and CuO nanoparticles. Moreover, compared to that of CuO and ZnO the thermal conductivity of Al_2O_3 is greater (Table 1). Intuitively, dispersing great amount of nanoparticles dispersed in PCM improve the thermal conductivity. However, one must take into account that consequently increases, also the viscosity. This effect reduces the latent heat for PCM and, can reduce the stability of the nano PCM as consequence of agglomeration and sedimentation phenomena.

In melting processes, thus the selection of proper nanoparticles and its concentration is essential to improve the heat transfer performance of PCM

7. Conclusion

In this paper, a numerical study on variations of thermophysical properties of phase change material (PCM) due to dispersion of nanoparticles is presented. We focused on investigation of the melting of paraffin wax dispersed with three different metal oxide Al₂O₃, CuO and ZnO that is heated from one side of rectangular enclosure of dimensions of 25 mm×75 mm. The integrated simulation system ANSYS Workbench 15.0 for the numerical study was used including mesh generation tool ICEM and FLUENT software

Aim was examining effects of nanoparticles suspended in the PCM respect to:

- 1. Thermo-physical properties
- 2. Heat transfer rate
- 1. For all nano PCM considered at 1% and 3% volumetric concentration, results confirm that:

- Thermal conductivity of nano PCM is greater than the simple PCM.
- Dynamic viscosity of nano PCM increases with the increase in the volumetric concentration of nanoparticles.
- The viscosity is greater for CuO compared with ZnO and Al₂O₃ for two used volumetric concentrations during melting.

The variation in thermal conductivity and dynamic viscosity of nano PCM with temperature and volume fraction agree well with the experimental reported in literature.

- 2. The effect of volumetric concentration of the nanoparticles on the melting performance was examined and compared between with and without enhancement of nanoparticles
 - The melting rate decreases with the increase in the volumetric composition of adding nanoparticles.
 - The thermal performance of paraffin wax is enhanced only marginally with the dispersion of Al2O3, CuO and ZnO nanoparticles. The overall performance of melting process of paraffin wax is better for lower concentration of nanoparticles.
 - At volumetric concentrations of 1% Al2O3, ZnO and then CuO follow the nanoPCM faster to melt.
 - The melting rate for Al2O3 is somewhat slower for nanoparticle concentration of 3 %, the longer melting time is observed for CuO nanoparticle, while the melting time for ZnO is longer of Al2O3 and slower of CuO.
 - In particular, the melting time increases more for CuO nanoparticle concentration of 3%.

Based on this study, it can be concluded that dispersed metal oxide nanoparticles in paraffin wax to enhanced only marginally latent heat thermal storage performance. Although phase change material due to dispersion of nanoparticles have great potential for demanding thermal energy storage applications, the selection of proper nanoparticles and its concentration is essential to improve the heat transfer performance of PCM.

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