Experimental and numerical investigations of nano-additives enhanced paraffin in a shell-and-tube heat exchanger: a comparative study

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1 Abstract

2 The impact of metal oxides, metal nitrides and carbon allotropes based nano-additives on thermal conductivity and thermal storage performance of paraffin based latent heat storage 3 (LHS) system is experimentally and numerically investigated. Aluminium oxide (Al₂O₃), 4 5 aluminium nitride (AIN) and graphene nano-platelets (GnP) based nano-PCM samples are prepared with ultrasonic emulsification technique. Thermal performance enhancements of 6 7 nano-PCM samples are investigated by conducting a series of charging and discharging 8 experiments in shell-and-tube heat exchanger at various operating conditions. Moreover, a 9 numerical model is developed to account for an impact of varying operating temperature, nano-additives particle size and volume fraction on the effective thermal conductivity and 10 dynamic viscosity of nano-PCM. The numerical model is simulated to investigate the 11 influence of effective thermal conductivity and dynamic viscosity on heat transfer and 12 13 temperature distribution, phase transition rate and total enthalpy of the system. It is noticed 14 that the charging rates for Al₂O₃, AIN and GnP based nano-PCM samples are significantly enhanced by 28.01%, 36.47% and 44.57% as compared to pure paraffin, respectively. 15 Likewise, the discharging rates are augmented by 14.63%, 34.95% and 41.46%, 16 17 respectively. However, the addition of nano-additives compromises the overall thermal storage capacity and augments the effective dynamic viscosity which has adverse impact on 18 natural convection. Therefore, an optimum volume fraction of nano-additives is determined 19 20 by conducting experimental examinations on Al₂O₃ based nano-PCM samples with volume 21 fraction of 1%, 3% and 5%, at varied operating conditions. It is observed that by increasing 22 volume fraction from 1% to 3%, the charging and discharging rates are significantly 23 enhanced. However, an insignificant enhancement is noticed with further increase in volume fraction from 3% to 5%. Therefore, the optimum volume fraction of 3% is established. 24 Furthermore, GnP based nano-PCM samples have demonstrated higher potential for 25 thermal performance enhancement of LHS system and respective utilisation in practical 26 27 applications.

28 Keywords

29 Thermal energy storage, Latent heat storage, Phase change materials, Thermal conductivity

30 enhancement, Nano-PCM, Shell-and-tube heat exchanger

Nomenclature

C_p	specific heat capacity at constant pressure (kJ / kg. K)	ρ	density (kg / m ³)
d	diameter (m)	δ_{VF}	volume fraction of nano-additives
F	buoyant force term (N / m ³)	μ	dynamic viscosity (kg / m. s)
g	gravitational acceleration (m / s ²)	arphi	fraction of nano-PCM
k	thermal conductivity (W / m. K)	ω	mushy zone constant
k_B	Boltzmann constant	Subscript	ts
L	latent heat capacity (kJ / kg)	S	solidus phase
M_W	molecular weight	l	liquidus phase
N_A	Avogadro number	рс	phase change
Pr	Prandtl number	пр	nano-additives
р	pressure (N / m ²)	рст	base material
q	heat source term (W / m ³)	прст	nano-PCM
Re	Reynolds number	Acronym	S
S	momentum sink term	AI_2O_3	aluminium oxide
Т	temperature of nano-PCM (°C)	AIN	aluminium nitride
t	time (s)	GnP	graphene nano-platelets
u	velocity (m / s)	HTF	heat transfer fluid
Greel	K	LHS	latent heat storage
α	small constant value	PCM	phase change material
β	thermal expansion coefficient (1 / °C)	TES	thermal energy storage

33 1. Introduction

The rapid increase in energy demands to meet world economic developments have 34 escalated dependency on fossil fuels. The energy and fuel crisis along with environmental 35 pollutions and climate change due to extensive usage of fossil fuels to meet industrial and 36 37 domestic energy demands have raised serious challenges [1, 2]. To mitigate such serious concerns, the development in functional technologies for renewable energy sources or heat 38 39 recovery systems is imperative to minimise the gap between energy demand and supply. 40 Thermal energy storage (TES) is considered as a decisive technique to store excess thermal energy and utilise it at times to balance energy demand and supply. Latent heat storage 41 (LHS) approach is more attractive category of TES system due to its higher thermal storage 42 capacity and ability to an almost isothermal energy capture and release [3, 4]. LHS system 43 44 employs phase change materials (PCM) to store and release thermal energy during phase 45 change. LHS systems are integrated with numerous practical applications ranging from solar power plants, waste heat recovery systems, buildings temperature control systems, heating 46 and air conditioning systems, energy balancing and peak shaving management systems, 47 48 agricultural processing and drying [5-10]. However, due to low thermal conductivity of PCM, 49 the charging and discharging rates of LHS systems are significantly affected, which hinders the widespread practical employability of LHS systems [11, 12]. Therefore, researchers have 50 proposed several techniques to improve overall thermal performance of LHS systems which 51 are: container geometrical orientation, addition of extended surfaces, incorporation of 52 53 thermal conductive additives and encapsulation techniques [13-18].

Shell-and-tube heat exchanger based LHS systems are extensively studied in previous 54 55 literature due to their better heat transfer performance, minimal thermal losses, design simplicity and easier integration to practical applications. Similarly, extended surfaces are 56 57 widely adopted for thermal performance enhancement due to their better thermo-physical stability and cost effectiveness. Rathod and Banerjee [19] experimentally investigated the 58 59 augmentation in charging and discharging rate of stearic acid in shell-and-tube heat 60 exchanger without and with three longitudinal fins. It was informed that the inclusion of 61 longitudinal fins reduced the charging and discharging time by 24.52% and 43.6% as compared to no fins configuration. Likewise, Rabienataj Darzi et al. [20] numerically 62 examined the enhancement in charging and discharging rate of n-eicosane in shell-and-tube 63 heat exchanger with and without longitudinal fins. It was reported that with an increase in 64 number of longitudinal fins from 4 to 20, the melting and solidification rate was enhanced by 65 39-82% and 28-85% as compared to no fins configuration, respectively. Similarly, the phase 66 transition rate and thermal storage capacity of paraffin is numerically examined in a novel 67 68 geometrical orientation of shell-and-tube heat exchanger with longitudinal fins in [21]. It was discussed that the geometry and material of longitudinal fins had profound impact on 69 charging rate of paraffin. It was reported that with an increase in fins length from 12.7 mm to 70 38.10 mm, the heat transfer was augmented and thus the melting rate was improved by 71 72 57.32%. Likewise, it was argued that charging rate and thermal storage capacity was improved by 68.8% and 18.06% as the inlet temperature was increased from 50 - 70 °C. 73 Furthermore, this novel design was then developed and connected to flat plate solar 74 75 collector to conduct experimental studies on charging and discharging cycles [22, 23]. It was 76 noticed that as compared to shell-and-tube heat exchanger without extended fins 77 orientations, the proposed design had displayed relatively higher charging/discharging rate, accumulative thermal energy charge/discharge and mean charge/discharge power. Besides 78

the extended surfaces technique, the inclusion of thermal conductive additives technique is largely acknowledged as an alternate solution to enhance thermal performance with relatively smaller increase in weight of the system.

Venkitaraj et al. [24] examined the influence of aluminium oxide (Al_2O_3) nano-particles on 82 83 thermal performance of pentaerythritol. It was deduced that with an increase in mass fraction of Al₂O₃ from 0.1% to 1%, the effective thermal conductivity was increased from 18.11% to 84 85 51.79% as compared to pure pentaerythritol. Moreover, the specific heat capacity and latent heat was reported to be decreased from 1.65% to 5.25% and from 1.45% to 4.60%, 86 respectively. Similarly, Tang et al. [25] investigated the thermal performance enhancement 87 of myristic acid with inclusion of Al₂O₃ and graphite nano-particles. It was reported that with 88 an increase in mass fraction from 4% - 12%, the thermal conductivity was improved from 89 90 0.283 - 0.397 W/m.K for Al₂O₃ and 0.323 - 0.451 W/m.K for graphite based PCM 91 composite. However, the latent heat capacity was recorded to be reduced from 122.87 -92 109.45 kJ/kg for Al₂O₃ and 112.35 – 88.00 kJ/kg for graphite based composite. Harikrishnan et al. [26] experimented the improvement in thermal conductivity of lauric acid and stearic 93 94 acid (LA/SA) mixture as base material with dispersion of 1 wt% of TiO₂, ZnO and CuO nano-95 particles. It was discussed that the thermal conductivity of LA/SA composite was improved by 34.85%, 46.97% and 62.12%, respectively. 96

97 Shi et al. [27] reported that thermal conductivity of paraffin was augmented by 10 times with 98 inclusion of 10 wt% of exfoliated graphite nano-platelets. Likewise, Yu et al. [28] inspected 99 the enhancement in thermal performance of paraffin wax with inclusion of short and long multi-walled carbon nanotubes (MWCNT), carbon nanofibers and graphene nano-platelets 100 (GnP). It was discussed that GnP based paraffin composite had elaborated relatively higher 101 thermal conductivity. Likewise, the dynamic viscosity was reported to be increased to 800 102 mPa.s for short/long MWCNT, 40 mPa.s for carbon nanofibers and 11.5 mPa.s for GnP 103 based paraffin composites as compared to 5.892 mPa.s for paraffin wax. Likewise, Fan et al. 104 105 [29] informed that the thermal conductivity of paraffin is improved by 164% with inclusion of 5 106 wt.% of GnP. Also, Yuan et al. [30] studied the impact of GnP and expanded graphite 107 additives on thermal behaviour of palmitic-stearic acid mixture. It was observed that the thermal conductivity of composites was improved by 2.7 and 15.8 times as compared to 108 base material. However, the latent heat capacity was reduced by 20.90% and 25.17%, 109 respectively. 110

111 Wang et al. [31] conducted experimental analysis on thermal performance enhancement of polyethylene glycol with aluminium nitride (AIN). It was informed that with an increase in 112 concentration from 5% - 30%, the thermal conductivity of composite was significantly 113 improved from 0.3847 - 0.7661 W/m.K. It was also noticed that inclusion of AIN nano-114 particles had an insignificant impact on phase transition temperature. Zhang et al. [32] 115 conducted thermal enhancement test on polymethyl methacrylate, polyethylene glycol and 116 117 AIN nano-particles composite. The concentration of AIN nano-particles was ranged from 5 -30 wt%. It was noticed that thermal conductivity was improved by 7.9% - 53.8%. 118 respectively. However, the latent heat capacity was reduced from 168.5 kJ/kg for 119 120 polyethylene glycol to 102.5 - 79.2 kJ/kg, respectively. Likewise, Fang et al. [33] reported that the thermal conductivity of paraffin wax was increased from 0.4 - 0.53 W/m.K by 121 inclusion of 10 wt% of boron nitride. Similarly, Yang et al. [34] performed experimental 122 investigation on paraffin and Si₃N₄ based composite. It was reported that thermal 123

124 conductivity was significantly enhanced by a fraction of 47% for 10 wt% composite.
 125 However, the latent heat capacity was observed to be reduced from 186.59 – 113.63 kJ/kg.

Arasu and Mujumdar [35] simulated Al_2O_3 nano-particles dispersed in paraffin wax in a 126 square container. It was noticed that as the concentration of nano-additives increased, the 127 128 dynamic viscosity was augmented which diminishes the impact of increased effective thermal conductivity on melting rate. Therefore, it was concluded that a smaller 129 concentration of nano-additives should be adopted for thermal performance enhancement. 130 131 Likewise, Mahdi and Nsofor [36] performed numerical examination of Al₂O₃ nano-particles based paraffin in a triplex-tube. It was reported that the solidification time was reduced from 132 8 - 20% as the volumetric concentration was increased from 3 - 8%, respectively. Moreover, 133 Meng and Zhang [37] conducted experimental and numerical investigations on copper foam 134 based paraffin in a rectangular tube in tank orientation. It was discussed that the charging 135 and discharging power was significantly influenced by inlet temperature and flow rate of heat 136 137 transfer fluid (HTF). Das et al. [38] conducted numerical simulation on n-eicosane and GnP composite in a vertical single tube in shell heat exchanger. It was concluded that for 138 volumetric concentration of 2%, the melting time was shortened by 41% and 37% for inlet 139 temperature of 60 °C and 70 °C, respectively. 140

141 It can be observed from previous literature that nano-additives based thermal performance 142 enhancement can significantly improve the effective thermal conductivity of nano-PCM; 143 however it will also augment the effective dynamic viscosity and reduce the overall thermal storage capacity. Also, it is noted that the inclusion of metal oxides, metal nitrides and 144 carbon allotropes have presented excellent improvement in thermal conductivity, however 145 the literature lacks a comparatively analysis of these three nano-additives families. It is also 146 identified that the literature lacks an experimental and numerical examination of thermal 147 performance enhancement of nano-PCM in an actual shell-and-tube heat exchanger. 148 Moreover, it is perceived from the literature that the variation in dynamic viscosity with 149 temperature and particle size of nano-additives had not been considered in previous 150 151 numerical studies [35-38], which had certainly produced erroneous results.

This article is focused on the experimental and numerical investigations of metal oxides, 152 metal nitrides and carbon allotropes based thermal performance enhancement of paraffin in 153 a shell-and-tube heat exchanger. Thermal behaviour of nano-PCM samples are examined 154 by conducting a series of charging and discharging cycles in shell-and-tube heat exchanger 155 156 at various operating conditions. Moreover, this article proposes a numerical model that incorporates the operating temperature, particle size and volumetric concentration of nano-157 additives while calculating the effective thermal conductivity and dynamic viscosity of nano-158 PCM. The experimental and numerical studies are focused on identifying the impact of 159 varying effective thermal conductivity and dynamic viscosity of nano-PCM on temperature 160 distribution, liquid fraction, charging/discharging rate and overall enthalpy of the system. The 161 experimental and numerical results discuss the significant enhancement achieved by the 162 three types of nano-additives and identify an optimum volume concentration value to achieve 163 an appropriate thermal performance. 164

- 166 2. Experimental
- 167
- 168 2.1 Materials and Nano-PCM samples preparation

In this article, paraffin (RT44HC) is selected as base material for all experimental tests. In order to enhance thermal conductivity of paraffin, three nano-additives are selected which are aluminium oxide (Al₂O₃), aluminium nitride (AlN) and graphene nano-platelets (GnP). The details about materials suppliers and their specifications are listed in **Table 1**. Likewise, the thermo-physical properties of pure paraffin and nano-additives provided by materials suppliers are listed in **Table 2**. The materials are used as received from the dealers without any additional purification.

Table 1

List of dealers and specifications of materials used in this study

Materials	Dealers	Particle size	Purity
Paraffin (RT44HC)	Rubitherm Technologies GmbH		99.9%
Al ₂ O ₃	EPRUI Nanoparticles and Microspheres Co. Ltd	30 - 60 nm	99.9%
AIN	Sigma-Aldrich Co. Ltd	<100 nm	99%
GnP	Ionic Liquids Technologies GmbH	6 - 8 nm	99.5%

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The preparation of nano-PCM sample is accomplished by adopting ultrasonic emulsification technique, as shown in **Fig. 1**. In first step, the calculated amount of nano-additive is added to pre-melted base PCM and the suspension is formed by strong agitation using magnetic stirrer for 1 hr. In second step, to achieve complete dispersion of nano-additives in base PCM, the sample is subjected to intensive ultrasonication for 2 hr. In both steps, the temperature of sample is maintained at 60 °C to ensure that the base PCM remains in liquid state. In final step, the nano-PCM sample is poured into the shell of heat exchanger.



184 185

186 Fig. 1 Schematic illustration of nano-PCM sample preparation and loading in heat exchanger

In order to investigate the impact of various nano-additives, a sample for each nano-additive with volume fraction of 1% is prepared. Moreover, three samples of Al_2O_3 based nano-PCM are prepared with volume fraction of 1%, 3% and 5% to examine the influence of increasing volume fraction on thermal performance, as shown in **Table 3**. Prior to investigating nano-PCM in heat exchanger, a sample of pure paraffin is examined to provide a baseline for comparison. 193 The current study is focused on investigating thermal behaviour of nano-PCM samples of three different nano-additives materials with particle size ranging from 6 nm to 100 nm, as 194 listed in **Table 1**. As reported in literature [18, 28, 39], an increase in operating temperature 195 and reduction in particle size could improve the probability and frequency of particles 196 collisions with base material and could increase interfacial surface area, which would result 197 in formation of a quasi-convection state. Therefore, the thermal performance of nano-PCM 198 samples with smaller particle diameter and higher operating temperature would be relatively 199 200 higher as compared to larger particle and lower operating temperature. However, the impact 201 of varying particle sizes of same material on thermal performance of nano-PCM samples are not investigated in this article. 202

Table 2

Thermo-physical properties of pure paraffin and nano-additives

Properties	Paraffin	Al ₂ O ₃	AIN	GnP
Density (kg/m ³)	800 (solid)	3500	3300	400
	700 (liquid)			
Thermal conductivity (W/m.K)	0.2 (solid)	36	180	3000
	0.2 (liquid)			
Specific heat capacity (kJ/kg. K)	2.0	0.765	0.74	0.643
Latent heat of fusion (kJ/kg)	255	-	-	-
Phase change temperature (°C)	41-44	-	-	-

203

Table 3

Experimental tests of various nano-PCM samples

Sample	Nano-	Volume	Mass of nano-		Mass of paraffin	
	additives	fraction	additives added		added	
А	AI_2O_3	1%	10.61	(g)	207.88	(g)
В	Al ₂ O ₃	3%	32.47	(g)	203.51	(g)
С	Al ₂ O ₃	5%	55.26	(g)	198.95	(g)
D	AIN	1%	10	(g)	207.88	(g)
E	GnP	1%	1.21	(g)	207.88	(g)

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205 2.2 Experimental setup

To investigate thermal behaviour of nano-PCM samples in a heat exchanger, an experimental setup is developed as shown in **Fig. 2**. The devised system includes water tank with electric heater, shell-and-tube heat exchanger, centrifugal pump, manual flow control valves, connections to municipal water and a versatile data acquisition system (VDAS) with computer.



211

212 Fig. 2 Schematic illustration of experimental setup

The electric heater in water tank is governed by digital temperature controller to ensure 213 214 constant temperature of HTF during charging cycles. Likewise, centrifugal pump is operated to direct high temperature HTF from water tank to shell-and-tube heat exchanger. The shell 215 of heat exchanger is made of acrylic plastic and the outer diameter, length and thickness of 216 shell are 60 mm, 185 mm and 5 mm, respectively. Similarly, the bundle of seven tubes is 217 made of stainless steel, with outer diameter and thickness of 6 mm and 1 mm, respectively. 218 219 Moreover, the shell-and-tube heat exchanger is insulated with 50 mm thick glass wool to reduce thermal losses. The insulation layer can be untied to conduct visual inspection of 220 221 phase transition process. The shell of heat exchanger is filled with nano-PCM sample and 222 water as HTF is directed to circulate in the tubes.

In order to record transient temperature response of nano-PCM to charging/discharging 223 224 cycles, four K-type thermocouples are installed within nano-PCM in the shell. As illustrated in Fig. 3 (A), two zones are selected to investigate temperature distribution in nano-PCM. The 225 selected zones are sections close to inlet and outlet regions with a horizontal distance of 23 226 mm from shell boundaries (both left and right side). Two thermocouples are installed at each 227 228 zone, at a vertical distance of ± 24 mm from central tube, as shown in Fig. 3 (B). Likewise, 229 two K-type thermocouples are attached to stainless steel tube at inlet and outlet to register temperature data of HTF. Manual operated flow control valve (turbine flow meter) is installed 230 at hot/cold circuit each to adjust and record the desired volume flow rate during 231 charging/discharging cycles. The accuracy values of K-type thermocouples, digital 232 temperature controller for electric heater and turbine flow meter are ± 1.5 °C, 0.5% and 3% 233 of the reading, respectively. To register temperature and flow rate data in computer, VDAS is 234 operated to transfer data from sensors to computer. VDAS software is used to register 235 temperature and flow rate reading at time step of 5 s. 236



- **Fig. 3** Physical model of shell-and-tube heat exchanger with (A) description of dimensions and (B)
- 238 vertical positioning of thermocouples at both zone A and B.

239 2.3 Experimental procedure

240 During charging cycles, the low temperature municipal water is initially circulated through the tubes of heat exchanger to provide a good baseline for all charging cycles with initial 241 temperature of 15 °C. The desired temperature is set in digital temperature controller for 242 electric heater to increase temperature of water in tank. Upon reaching the desired 243 temperature, the centrifugal pump is switched on to circulate high temperature HTF through 244 the tubes of heat exchanger. The manual operated flow control valve is adjusted to specific 245 volume flow rate value. In this study, the charging cycles are conducted at three inlet 246 temperatures of 47, 52 and 57 °C and four volume flow rates of 1.5, 2.0, 2.5 and 3.0 l/min for 247 each nano-PCM sample. HTF transfers thermal energy to nano-PCM in heat exchanger and 248 the low temperature HTF at outlet of heat exchanger is directed back to water tank to repeat 249 the cycle. Charging cycle is completed once all thermocouples register temperature value 250 251 higher than melting temperature of PCM.

252 Prior to conducting discharging cycle, the inlet temperature of HTF is increased to maintain a 253 uniform initial temperature of 50 °C for all discharging cycles. The discharging cycle is 254 started by directing low temperature municipal water to extract thermal energy from nano-PCM. The discharging cycles are examined by regulating flow control valve to a specific flow 255 rate value of 1.5, 2.0, 2.5 and 3.0 l/min. Due to thermal energy discharge to low temperature 256 HTF, the solidification of nano-PCM begins. Discharging cycle is completed once the 257 temperature gradient between inlet temperature and all thermocouples in shell is less than 2 258 259 °C.

- 260 3. Numerical Model
- 261 3.1 Mathematical formulation and governing equations

The physical model for numerical investigations is illustrated in Fig. 3. In order to simplify numerical model and shorten simulation time, the following assumptions are made:

- a) The acrylic plastic shell is neglected and the outer boundary is considered as adiabaticby ignoring convective heat losses to surrounding.
- b) The thickness of stainless steel tubes is neglected due to the fact that stainless steelpossesses comparatively higher thermal conductivity to nano-PCM.
- c) The liquid phase of nano-PCM is considered as incompressible Newtonian fluid and the
 change in density with temperature complies with the Boussinesq approximation.
- d) The volumetric expansion of nano-PCM is neglected and natural convection is assumedto be laminar.
- e) The computational domain of nano-PCM is considered to be at uniform initial
 temperature. Likewise, the inlet temperature and flow rate of HTF are assumed to be
 constant.

Based on above assumptions, a numerical model is formulated considering the governing
equations of continuity, momentum and energy to investigate thermal performance of
various nano-PCM samples in the computational domain of shell-and-tube heat exchanger.
The governing equations are discussed as follow:

279 Continuity equation:

$$\frac{\partial \rho_{npcm}}{\partial t} + \nabla . \left(\rho_{npcm} \boldsymbol{u} \right) = 0 \tag{1}$$

280 Momentum equation:

$$\frac{\partial(\rho_{npcm}\boldsymbol{u})}{\partial t} + \nabla . \left(\rho_{npcm}\boldsymbol{u}\boldsymbol{u}\right) = -\nabla p_{npcm} + \nabla . \left(\mu_{npcm}\nabla \boldsymbol{u}\right) + \boldsymbol{F} + \boldsymbol{S}$$
(2)

281 Energy equation:

$$\frac{\partial (\rho_{npcm} C_p T_{npcm})}{\partial t} + \nabla . \left(\rho_{npcm} C_p T_{npcm} \boldsymbol{u} \right) = \nabla . \left(k_{npcm} \nabla T_{npcm} \right) + q$$
(3)

In Eq. (2), *F* represents buoyant force term which is responsible for upward rise of lower density and higher temperature molecules of nano-PCM. Buoyant forces control the natural convection in nano-PCM and it can be approximated by using Boussinesq approximation [40]:

$$\boldsymbol{F} = \rho_{npcm} \mathbf{g} \beta \left(T_{npcm} - T_{pc} \right) \tag{4}$$

Likewise, *S* in Eq. (2) defines momentum sink term which can be estimated by employing KozenyCarman equation, which is derived from Darcy law for porous medium [41]. This term is applied to equate for porosity in mushy zone, as follow:

$$S = \frac{\omega(1-\varphi)^2}{(\varphi^3 + \alpha)} \boldsymbol{u}$$
(5)

where ω is the mushy zone constant, which illustrates an approximate magnitude of damping in governing equation of momentum. In this study, the mushy zone constant value is set to 10⁶, which presents good agreement between numerical and experimental results. Likewise, α denotes a small constant value equal to 10⁻⁴ and is used to prevent division by zero at liquid fraction $\varphi = 0$. The range of liquid fraction with respect to temperature is defined as follow:

$$\varphi = \begin{cases} 0 & T_{npcm} < T_s \\ \frac{T_{npcm} - T_s}{T_l - T_s} & T_s \le T_{npcm} \le T_l \\ 1 & T_{npcm} > T_l \end{cases}$$
(6)

where s and I are the indices for solidus and liquidus phase of nano-PCM. The effective specific heat capacity in Eq. (3) is calculated by differentiating specific enthalpy with respect to temperature:

$$C_{p} = \frac{1}{\rho} \left(\varphi_{s} \rho_{npcm,s} C_{p,npcm,s} + \varphi_{l} \rho_{npcm,l} C_{p,npcm,l} \right) + L_{npcm} \frac{\partial}{\partial T} \left[\frac{\left(\varphi_{l} \rho_{npcm,l} - \varphi_{s} \rho_{npcm,s} \right)}{2\rho_{npcm}} \right]$$
(7)

The right hand side of Eq. (7) represents that specific heat capacity is the summation of sensible and latent portion of heat. Likewise, the thermo-physical properties of nano-PCM are estimated based on theoretical equations for mixture of two components, as follow [42]:

$$\rho_{npcm} = \delta_{VF} \rho_{np} + (1 - \delta_{VF}) \rho_{pcm} \tag{8}$$

$$C_{p,npcm} = \frac{\delta_{VF}\rho_{np}C_{p,np} + (1 - \delta_{VF})\rho_{pcm}C_{p,pcm}}{\rho_{npcm}}$$
(9)

$$L_{npcm} = \frac{(1 - \delta_{VF})\rho_{pcm}L_{pcm}}{\rho_{npcm}}$$
(10)

where δ_{VF} represents the volume fraction of nano-additives. Moreover, the effective dynamic 301 viscosity and effective thermal conductivity of nano-PCM samples are evaluated by 302 implementing the semi-empirical models proposed by Corcione [43] as given in Eq. (11) and 303 Eq. (14), respectively. These propose models by Corcione, on contrary to earlier standard 304 models and theories proposed by Einstein [44] and others [45-48] for estimating the effective 305 dynamic viscosity and Maxwell [49] and others [50-52] for approximating the effective 306 thermal conductivity, account for particle size of nano-additives, volume fraction and 307 operating temperature. Therefore, these earlier standard models fail to predict an accurate 308 309 increase in dynamic viscosity and thermal conductivity of nano-PCM due to the fact that 310 these standard models are developed for larger particle size nano-additives and these models only depend on shape and volume fraction of nano-additives. 311

312 The effective dynamic viscosity is estimated as follow [43]:

$$\mu_{npcm} = \frac{\mu_{pcm}}{1 - 34.87 (d_{np}/d_{pcm})^{-0.3} \delta_{VF}^{1.03}}$$
(11)

where μ_{pcm} , d_{pcm} and d_{np} represents the dynamic viscosity of pure paraffin, equivalent diameter of pure paraffin and diameter of nano-additives, respectively. The dynamic viscosity [53] and equivalent diameter of pure paraffin [43] are determined as follow:

$$\mu_{pcm} = 0.001 exp \left(-4.25 + \frac{1790}{T_{pcm}} \right) \tag{12}$$

$$d_{pcm} = 0.1 \left(\frac{_{6M_W}}{_{\pi N_A \rho_{pcm,o}}}\right)^{1/3}$$
(13)

- 316 where M_W , N_A and $\rho_{pcm,o}$ are the molecular weight of pure paraffin, Avogadro number and
- density of pure paraffin at $T_{pcm} = 20$ °C, respectively.
- 318 Similarly, the effective thermal conductivity is evaluated from the following equation [43]:

$$k_{npcm} = k_{pcm} \left(1 + 4.4Re^{0.4} Pr^{0.66} \left(\frac{T_{npcm}}{T_{pc}} \right)^{10} \left(\frac{k_{np}}{k_{pcm}} \right)^{0.03} \delta_{VF}^{0.66} \right)$$
(14)

where Re and Pr represent the Reynolds number of nano-additives and Prandtl number of pure paraffin, respectively. Re and Pr can be calculated using the following relations [43]:

$$Re = \frac{2\rho_{pcm}k_B T_{npcm}}{\pi\mu_{pcm}^2 d_{np}} \tag{15}$$

$$Pr = \frac{\mu_{pcm}C_{p,pcm}}{k_{pcm}} \tag{16}$$

Using Eq. (11) and Eq. (14), the effective dynamic viscosity and thermal conductivity of 321 nano-PCM are computed for volume fraction of 1%, 2%, 3%, 4% and 5% of Al₂O₃, AIN and 322 323 GnP nano-additives, as presented in Fig. 4 and Fig. 5, respectively. It can be noticed that in 324 all cases, the dynamic viscosity of nano-PCM as compared to pure paraffin is enhanced with 325 an increase in volume fraction of nano-additives. However, the enhancement in effective dynamic viscosity of GnP based nano-PCM is more significant as compared to Al₂O₃ and 326 AIN based nano-PCM. This is due to the fact that the effective dynamic viscosity is highly 327 influenced by the particle size and shape of nano-additives. Moreover, a higher dynamic 328 viscosity can have an adverse impact on natural convection. 329

Likewise, the enhancements in thermal conductivity of nano-PCM due to varied volume fraction concentration of nano-additives are illustrated against temperature in **Fig. 5**. It can be observed that GnP based nano-PCM samples have shown significantly higher thermal conductivity due to their smaller particle size and higher thermal conductivity as compared to Al₂O₃ and AlN.



Fig. 4 Effective dynamic viscosity of nano-PCM samples with varied volume fractions and nanoadditives (A) Al₂O₃, (B) AlN and (C) GnP.



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Fig. 5 Effective thermal conductivity of nano-PCM samples with varied volume fractions and nanoadditives (A) Al₂O₃, (B) AlN and (C) GnP.

341 3.2 Initial and boundary conditions

During melting process, the initial temperature of nano-PCM is set to 15 °C which is less than phase change temperature, as shown in **Table 2**. Therefore, the initial temperature ensures that entire mass of nano-PCM is in complete solid state. Likewise, the HTF tubes
 are set to a constant inlet temperature of 52 °C for the complete charging cycle.

346 3.3 Computational procedure and model validation

The geometrical orientation and dimensions of shell-and-tube heat exchanger provided in 347 Fig. 3 are adopted for the computational model. The governing equations are discretised by 348 implementing finite volume method. PISO algorithm is employed to solve the pressure-349 velocity coupling. PRESTO and second order upwind schemes are adopted for spatial 350 discretisation of pressure, momentum and energy equations, respectively. The relative 351 residuals values for the convergence criteria of continuity, velocity and energy equations are 352 set to 10⁻⁶, respectively. The time step and mesh size independency study are conducted on 353 nano-PCM sample A (see Table 3) to ensure accuracy of numerical results, as presented in 354 Table 4. As a result, the time step of 1 s and mesh size of 27420 are selected for all nano-355 PCM samples in this study. In order to validate the computational model with experimental 356 results, the transient temperature profiles for three nano-PCM samples are acquired from 357 numerical and experimental procedures for conducting charging cycles at constant inlet 358 temperature of 52 °C, which are compared and plotted in Fig. 6. The set of three samples 359 include pure paraffin, Al₂O₃ and GnP based nano-PCM samples with 1% volume fraction, 360 respectively. The mean absolute percentage error between numerical and experimental 361 results for pure paraffin and nano-PCM samples are computed to be 2.87%, 2.53% and 362 363 2.75%, respectively.

Table 4

Mesh size and time stepping independency conducted on sample A (Al ₂ O ₃ – 1% VF)						
Case	Inlet	Mesh element	Time step	Total melting	Percent error	
	temperature (°C)	size	(s)	time (min)	(%)	
1	52	6930	1	98	6.81	
II	52	27420	1	91.75	-	
	52	43585	1	91.5	0.27	
IV	52	27420	0.1	91.25	0.54	
V	52	27420	0.5	91.5	0.27	





- 367 4. Results and discussions
- 368 4.1 Thermal performance of pure paraffin

In order to understand the thermal performance of nano-PCM samples in shell-and-tube
 heat exchanger, a sample of pure paraffin is initially examined to develop a good baseline
 for comparison.

372 4.1.1 Experimental

Pure paraffin sample is melted and poured in the shell of heat exchanger. In order to study the transient thermal response of pure paraffin to various inlet temperatures and volume flow rates of HTF, the data is registered from all four k-type thermocouples installed at zone A and B, as presented in **Fig. 3**. The temperature distribution in both vertical and horizontal positions in shell is examined at three inlet temperatures of 47, 52 and 57 °C. Likewise, the impact of varying flow rate of HTF is studied at four values of 1.5, 2.0, 2.5 and 3.0 l/min.

379 The melting behaviour of pure paraffin at various temperatures is presented in Fig. 7. It can 380 be noticed that the linear rise from initial temperature to about 40 °C represents sensible heat and it is dominated by conduction heat transfer. The sensible heat capacity is rapidly 381 stored due to small specific heat capacity of paraffin. Afterwards, a steady and gradual rise 382 is observed, which represents the latent portion of heat storage. During this phase, the 383 384 higher latent heat capacity is gradually stored as the temperature rises from 41 °C to 44 °C. Consequently, the phase transformation of solid paraffin to mushy and then to liquid state 385 occurs. After completion of latent portion of heat storage, a relatively quicker increase in 386 temperature is observed which again represent the sensible heat storage in liquid phase of 387 388 paraffin.

Moreover, it can be observed from **Fig. 7** that phase transition at top position is quicker as 389 compared to bottom position. The reason behind is that conduction dominates the heat 390 391 transfer at initial stages and after phase transition; the amount of liquid paraffin increases which results into upward rise against the gravity and thus it makes natural convection as 392 dominant mode of heat transfer. Due to upward rise of high temperature molecules, the 393 394 phase transition is relatively higher at top position as compared to bottom position. The 395 natural convection is highly influenced by density and dynamic viscosity. Moreover, it can be noticed that with an increase in inlet temperature of HTF, the temperature gradient for heat 396 transfer increases which results in relatively higher melting/charging rate of paraffin. Also, 397 due to small volume capacity of shell-and-tube heat exchanger, the varying volume flow rate 398 of HTF has insignificant influence on phase transition rate. It is noticed that with an increase 399 in volume flow rate from 1.5 to 3.0 l/min, an almost identical transient temperature response 400 is recorded with a relative standard deviation of 0.43%. 401



402 **Fig. 7** Transient temperature response of pure paraffin to experimental charging cycles at varied inlet 403 temperatures of 47, 52 and 57 °C and constant volume flow rate of 1.5 l/min.

404 4.1.2 Numerical

405 In numerical simulation, the melting/charging cycles of pure paraffin sample are investigated at three constant inlet temperatures of 47, 52 and 57 °C. As presented in Fig. 8, the left side 406 of plots indicates liquid fraction and the right side demonstrates temperature contours of 407 pure paraffin in shell of heat exchanger. It can be observed that as liquid fraction around the 408 409 HTF tubes increases, the buoyant forces enable liquid particles to rise above and thus, it 410 results in comparatively higher melting rate at top position of shell. Likewise, the temperature contours demonstrate a relatively higher temperature of paraffin at top position as compared 411 to bottom position. Moreover, it is noticed that with an increase in inlet temperature, the 412 melting rate is significantly improved, as shown in Fig. 8. It is observed that with an increase 413 414 in inlet temperature from 47 to 52 and 57 °C, the total melting time is reduced by a fraction of 415 56.96% and 72.60%, respectively. Furthermore, the sensible portion of heat storage in liquid

the phase is increased with an increase in inlet temperature, which enhances the overall thermal

energy storage of LHS system. It is noticed that with an increase in inlet temperature from 47
to 52 and 57 °C, the overall enthalpy of LHS system is upgraded from 299 to 309 and 319
kJ/kg, respectively.



- Fig. 8 Liquid fraction and temperature contours of pure paraffin at various inlet temperatures of 47, 52
 and 57 °C.
- 423 4.2 Thermal performance of nano-PCM samples
- 424 After understanding the thermal behaviour of pure paraffin in shell-and-tube heat exchanger,
 425 the experimental and numerical examination of nano-PCM samples are conducted.
- 426 4.2.1 Experimental
- As discussed in section 2.1, ultrasonic emulsification technique is adopted to prepare various nano-PCM samples and shell-and-tube heat exchanger is utilised to investigate thermal behaviour of the nano-PCM samples. Thermal conductivity of paraffin improves with an inclusion of nano-additives and thus, the total charging time can be significantly reduced. However, as illustrated in **Fig. 4**, an increase in volume fraction of nano-additives also augments the dynamic viscosity, which has an adverse impact on natural convection and therefore the thermal performance can be affected.

To begin with experimental investigations, the repeatability and reliability study of nano-PCM samples are conducted to examine the consistency of experimental results. For instance, **Fig. 9** represents the transient temperature profiles acquired while charging Al_2O_3 based nano-PCM sample with 1% volume fraction at constant inlet temperature of 52 °C. The mean statistical standard deviation between the transient temperature profiles for three charging cycles is computed to be 0.138.



440

441 **Fig. 9** Repeatability study of Al₂O₃ based nano-PCM sample with 1% volume fraction while 442 conducting experimental charging cycles at constant inlet temperature of 52 °C.

Following to repeatability tests, three Al₂O₃ based nano-PCM samples are developed with volume fraction of 1, 3 and 5%. Nano-PCM sample in liquid phase is poured into the shell of heat exchanger and the experimental investigations are conducted at three varied inlet temperatures of 47, 52 and 57 °C. The transient temperature profiles for these three Al₂O₃ based nano-PCM samples are recorded by thermocouple installed at bottom position at zone B and are plotted against pure paraffin in **Fig. 10**.

It can be noticed that at constant inlet temperature of 47 °C, the melting/charging time at 449 bottom position is significantly reduced by a fraction 33.75%, 55.41% and 56.25% for Al₂O₃ 450 451 based nano-PCM samples with volume fraction of 1, 3 and 5% as compared to pure paraffin, respectively. Likewise, at constant inlet temperature of 52 °C, the charging time is 452 considerably decreased by a fraction of 35.92%, 48.80% and 56.37%, respectively. 453 Similarly, in case of constant inlet temperature of 57 °C, the charging time is lessened by a 454 fraction of 11.36%, 21.71% and 24.74% for Al₂O₃ based nano-PCM samples as compared to 455 pure paraffin, respectively. It can be noticed that for all three varied inlet temperatures, the 456 melting/charging time is significantly reduced by incorporating Al₂O₃ based nano-additives to 457 paraffin. However, with an increase in volume fraction from 3% to 5%, just a slight increment 458 in thermal performance is observed which is due to adverse effects of higher dynamic 459 viscosity on natural convection. Therefore, it can be deduced that an optimum volume 460 fraction is essential to be identified for an appropriate enhancement in thermal performance. 461

462 Subsequently, the nano-PCM samples based on 1% volume fraction of Al₂O₃, AlN and GnP 463 are prepared and experimentally investigated for thermal performance in shell-and-tube heat 464 exchanger at three varied inlet temperatures of 47, 52 and 57 °C. In order to identify the 465 thermal performance enhancement due to inclusion of same volume fraction of varied nano-466 additives in paraffin, the transient temperature profiles are recorded from thermocouples 467 installed at top and bottom positions at zone A, as presented in **Fig. 11**.

468 It can be observed that at constant inlet temperature of 47 °C, the total melting time at top position for 1% volume fraction of Al₂O₃, AlN and GnP based nano-PCM samples are 469 reduced by a fraction of 9.04%, 18.74% and 37.85% as compared to pure paraffin, 470 471 respectively. Similarly, the total melting time at bottom position is reduced by a fraction of 33.75%, 35.90% and 62.56%, respectively. Moreover, at inlet temperature of 52 °C, the 472 melting time at top position is decreased by 6.42%, 27.27% and 57.22%, respectively. 473 Likewise, at bottom position, the melting time is lessened by 32.70%, 36.40% and 38.07%, 474 475 respectively. Furthermore, at inlet temperature of 57 °C, the total melting time is decreased by a fraction of 19.04%, 28.57% and 49.78% at top position and 28.01%, 36.47% and 476 477 44.57% at bottom position, respectively. It can be perceived from experimental results that nano-additives material plays a significant role in enhancing thermal performance of paraffin. 478 479 For instance, it is noticed that thermal performance enhancement for GnP based nano-PCM 480 sample is relatively higher than Al_2O_3 and AIN based nano-PCM samples due to relatively higher thermal conductivity and smaller particle size of GnP nano-additives. 481

Furthermore, similar to pure paraffin, the variations in volume flow rate of HTF from 1 to 3
I/min have presented an insignificant enhancement in charging rate of nano-PCM samples.
This is due to small volumetric capacity of shell-and-tube heat exchanger and consequently,
the tubes in shell are at same temperature throughout its length.



Fig. 10 Transient thermal performance of Al₂O₃ based nano-PCM samples with volume fraction of
1%, 3% and 5% during experimental charging cycles at various inlet temperatures of 47, 52 and 57 °C
and at constant volume flow rate of 1.5 l/min.



491 Fig. 11 Transient temperature plots attained from experimental charging cycles of 1% volume fraction
 492 of Al₂O₃, AlN and GnP based nano-PCM samples at varied inlet temperatures of 47, 52 and 57 °C
 493 and at constant volume flow rate of 1.5 l/min.

494 4.2.2 Numerical

In this section, the numerical simulations of charging cycles of nano-PCM samples based on Al₂O₃, AlN and GnP nano-additives with volume fraction of 1%, 2%, 3%, 4% and 5% are conducted at constant inlet temperature of 52 °C, respectively. As illustrated in **Fig. 12**, the left sides of plots represent total enthalpy of nano-PCM based LHS system and the right sides demonstrate temperature contours. The plots are attained from simulation results at 30 mins of charging cycle.

It is observed that temperature contours for Al₂O₃, AIN and GnP based nano-PCM samples 501 with varied volume fraction represent a small variation in temperature. This is contrary to the 502 fact that GnP based nano-PCM possess higher effective thermal conductivity, as shown in 503 Fig. 4. The reason behind is that GnP based nano-PCM also have relatively higher dynamic 504 viscosity which limits the influence of buoyant forces and natural convection on temperature 505 distribution and melting rate. Therefore, the temperature contours are indicating just a slight 506 507 variation. However, it can be noticed from enthalpy plots that GnP based nano-PCM samples possess significantly higher enthalpy as compared to Al₂O₃ and AlN based nano-508 PCM samples for all respective volume fraction cases. This is due to the fact that Al₂O₃ and 509 AIN nano-additives have relatively higher density and particle size which considerably 510 511 reduces the overall thermal capacity and enthalpy of the system.

For control volume, the thermal storage capacity is reduced for nano-PCM as compared to 512 pure paraffin because nano-additives occupy certain volume. Therefore, the total enthalpy is 513 reduced for nano-PCM samples. As illustrated in Fig. 13, the total enthalpy of nano-PCM 514 samples reduces with an increase in volume fraction of nano-additives as compared to pure 515 paraffin (309 kJ/kg). It is recorded that with an inclusion of 1% volume fraction of Al₂O₃, AIN 516 and GnP nano-additives, the total enthalpy of system is reduced by a fraction of 4.75%, 517 518 4.46% and 0.55%, respectively. Likewise, in case of 5% volume fraction of nano-additives, 519 the total enthalpy is decreased by a fraction of 20.58%, 19.64% and 2.88%, respectively. It is noted that due to smaller density and particle size, the GnP based nano-PCM samples have 520 illustrated higher thermal storage capacity as compared to Al₂O₃ and AlN based nano-PCM. 521 Moreover, Al₂O₃ and AIN based nano-PCM have presented higher charging rate as 522 compared to pure paraffin, however the increase in weight and reduction in thermal storage 523 capacity can minimise their utilisation in widespread practical applications. 524



Fig. 12 Total enthalpy and temperature contours of Al₂O₃, AlN and GnP based nano-PCM samples with varied volume fractions attained after 30 mins of charging at constant inlet temperature of 52 °C.



531



533 4.3 Thermal performance of pure paraffin and nano-PCM during discharging cycles

After charging cycles, the thermal performance of various samples of nano-PCM in shelland-tube heat exchanger are experimentally investigated during discharging cycles. Municipal water is directed through the tubes of heat exchanger to extract thermal energy from nano-PCM. In discharging cycles, the inlet temperatures for all cases are set constant to 15 °C.

Due to higher temperature gradient generated between HTF in tubes and nano-PCM in 539 shell, the sensible portion of thermal energy is rapidly transferred to HTF. As a result, the 540 temperature of nano-PCM is almost linearly declined to about 44 °C. After this stage, the 541 discharge of latent portion of thermal energy starts. Due to higher latent heat capacity, the 542 decrease in temperature from 44 to 41 °C is relatively slow and steady. During this period, 543 the liquid phase nano-PCM transforms to mushy and then to solid phase. As the latent 544 545 portion of thermal energy discharges, a rapid decline in temperature is observed which 546 represents sensible portion of thermal energy discharge in solid phase.

Initially, the influence of varying volume fraction of nano-additives on thermal performance 547 during discharging cycle is examined and plotted against pure paraffin in Fig. 14. It can be 548 noticed that with inclusion of Al₂O₃ nano-additives, the thermal conductivity is enhanced and 549 therefore, the discharging time is significantly reduced. It is observed that the time required 550 551 to discharge latent portion of thermal energy at bottom position at zone A is reduced by a fraction of 28.45%, 39.05% and 39.52% for Al₂O₃ based nano-PCM samples with volume 552 fraction of 1%, 3% and 5% as compared to pure paraffin, respectively. Moreover, it can be 553 noticed that similar to charging cycles, an increase in volume fraction from 3% to 5% has an 554 555 insignificant impact on phase transition rate of Al₂O₃ based nano-PCM.

Furthermore, in order to examine the impact of varying nano-additives material on thermal performance, the discharging cycles are experimentally investigated for 1% volume fraction of Al₂O₃, AlN and GnP based nano-PCM. The temperature data for nano-PCM samples registered by thermocouple installed at bottom at zone B are plotted against pure paraffin in **Fig. 15**. It can be noticed that the discharging time of latent portion of thermal energy is decreased by 14.63%, 34.95% and 41.46% for Al₂O₃, AIN and GnP based nano-PCM as compared to pure paraffin, respectively. It can be perceived that due to higher thermal conductivity of GnP and AIN nano-additives, the discharge rate is significantly higher.



564

Fig. 14 Transient temperature profiles attained during experimental discharging cycles of pure paraffin and Al₂O₃ nano-PCM samples of various volume fractions 1%, 3% and 5%. The inlet temperature of HTF is set to 15 °C for all cases.



Fig. 15 Transient temperature plots acquired during experimental discharging cycles of pure paraffin and nano-PCM samples of 1% volume fraction of Al₂O₃, AlN and GnP. The inlet temperature is kept constant to 15 °C for all cases.

572 5. Conclusions

573 In this article, experimental and numerical studies are conducted to identify the impact of metal oxides, metal nitrides and carbon allotropes based nano-additives on thermal 574 performance enhancement of paraffin based LHS system. Ultrasonic emulsification 575 576 technique is adopted to prepare Al₂O₃, AIN and GnP based nano-PCM samples with varied volume fractions. Thermal behaviour of nano-PCM samples are investigated in shell-and-577 tube heat exchanger by conducting series of charging and discharging cycles at various 578 579 operating conditions. Meanwhile, a numerical model is developed and simulated to help understand and predict the effect of improved thermal conductivity and dynamic viscosity of 580 nano-PCM samples on heat transfer mechanism, temperature distribution and overall 581 enthalpy of the LHS system. The numerical model accounts for operating temperature, 582 particle size and volume fraction of nano-additives while computing the effective thermal 583 conductivity and dynamic viscosity of nano-PCM samples. Based on experimental and 584 585 numerical investigations, the following conclusions are derived:

- It is observed that as the liquid fraction around the tubes increases during charging 586 cycles, an upward rise of high temperature molecules due to buoyant forces enable 587 natural convection to dominate the heat transfer in top position. Therefore, the melting 588 rate is higher at top position as compared to bottom position of the shell-and-tube heat 589 exchanger based LHS system. Likewise, it is noticed that with an increase in inlet 590 temperature of HTF from 47 to 52 and 57 °C, the phase transition rate is significantly 591 592 improved by a fraction of 56.96% and 72.60%, respectively. Moreover, the overall 593 thermal enthalpy of the system is also improved with an increase in inlet temperature.
- It is deduced that the effective thermal conductivity and dynamic viscosity of paraffin is 595 significantly enhanced with inclusion of nano-additives. Likewise, the particle size, 596 597 volume fraction and operating temperature significantly influence the effective thermal conductivity and dynamic viscosity. The experimental and numerical results indicated 598 that the thermal performance is improved for all nano-PCM samples. However, GnP 599 600 based nano-PCM samples have illustrated relatively higher effective thermal conductivity and dynamic viscosity due to their smaller particle size and higher thermal 601 602 conductivity as compared to Al_2O_3 and AIN. It is observed that while charging at inlet 603 temperature of 47 °C, the charging time for Al₂O₃, AIN and GnP based nano-PCM samples is significantly reduced by 33.75%, 35.90% and 62.56% as compared to pure 604 paraffin. Likewise, for inlet temperature of 52 °C, the charging time is decreased by 605 32.70%, 36.40% and 38.07%, respectively. Similarly, for inlet temperature of 57 °C, the 606 charging time is reduced by 28.01%, 36.47% and 44.57%, respectively. Moreover, the 607 discharging time is also decreased by a fraction of 14.63%, 34.95% and 41.46%, 608 respectively. Therefore, it is concluded that all three nano-additives have presented 609 610 significant improvement in charging/discharging rate. However, GnP based nano-PCM 611 samples have illustrated relatively better thermal performance.
- 612

594

An optimum volume fraction of nano-additives is critical for an ideal enhancement in thermal performance of LHS system. Al₂O₃ based nano-PCM samples with varying volume fractions of 1%, 3% and 5% are investigated at inlet temperature of 47, 52 and 57 °C. In case of inlet temperature of 47 °C, the charging time of Al₂O₃ based nano-PCM samples is significantly reduced by a fraction of 33.75%, 55.41% and 56.25% as

618 compared to pure paraffin. Likewise, in case of inlet temperature of 52 °C, the charging 619 time is decreased by 35.92%, 48.80% and 56.37%, respectively. Also, in case of inlet temperature of 57 °C, the charging time is lessened by 11.36%, 21.71% and 24.74%, 620 respectively. Furthermore, the discharging time is also reduced by a fraction 28.45%, 621 39.05% and 39.52%, respectively. It can be observed that Al₂O₃ based nano-PCM 622 samples have illustrated higher charging and discharging rate. However for all 623 charging/discharging cycles, a minimal enhancement in charging/discharging rate is 624 625 noticed as the volume fraction of Al₂O₃ is increased from 3% to 5%. Therefore, the 626 optimum volume fraction for Al₂O₃ based nano-PCM samples is identified as 3%.

627

628 The inclusion of nano-additives captures certain volume and as a result, it reduces the • overall thermal storage capacity of LHS system. It is noticed that with an addition of 629 5% volume fraction of Al₂O₃, AIN and GnP nano-additives, the total enthalpy of LHS 630 system is reduced by 20.58%, 19.64% and 2.88% as compared to pure paraffin. It is 631 noticed that GnP based nano-PCM samples have indicated a slight reduction in 632 thermal storage capacity as compared to Al_2O_3 and AIN based nano-PCM samples. 633 Due to significant reduction in thermal storage capacity and an increase in overall 634 635 weight of the LHS system, the employability of Al₂O₃ and AlN based nano-PCM 636 samples in large scale practical applications is limited.

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