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Performance Enhancement of Cold Thermal Energy Storage System using Nanofluid Phase Change Materials: A Review



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ARTICLE INFO	ABSTRACT		
Article history: Received 24 October 2017 Received in revised form 4 February 2018 Accepted 23 February 2018 Available online 28 April 2018	Cold thermal energy storage (CTES) plays a vital role in many industrial applications such as central air-conditioning in the large buildings, high powered electronic cooling applications, waste heat recovery, food processing, and restoring the electrical power imbalance between daytime need and night-time abundance. In addition, CTES system incorporating phase change materials (PCM) is proved as a viable option for achieving high energy efficiency by many systems. Due to the significance of this issue, many studies has been conducted on the applications of PCM in CTES system. The main aim of this article is to provide a comprehensive review, which summarizes recent research progress on PCM-CTES and an overview of numerical and experimental studies on the heat transfer performance of different base fluid of PCMs. This article also discusses several factors affecting the thermal conductivity of PCMs, such as nanoparticle enhanced PCMs, shape of encapsulated PCM materials, solid volume fraction and particle size. Observation and findings from past studies are discussed in detail. Recommendations based on research results, advantages and drawbacks of PCM-CTES are made for future research directions.		
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1. Introduction

Nowadays, township buildings are undergoing careful and detailed development by town planners. At the same time, building centralised air conditioning (AC) system such as District Cooling Plant, to serve the development of vicinity area has gained much consideration owing to its economic scale. According to Saidur [1], AC system is the biggest energy consumer of a building for temperate country like Malaysia, accounting 57% energy usage as shown in Fig. 1. Therefore, to reduce energy usage, cold thermal energy storage (CTES) is becoming viable in large centralised AC systems as latent energy storage.

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Fig. 1. Energy usage of office building (%)

CTES plays a vital role in many industrial applications such as central air-conditioning in large buildings, high powered electronic cooling applications, waste heat recovery, food processing, to restore the electrical power imbalance between daytime need and night-time abundance.

CTES stores cool energy via ice making during night time or off-peak period which is considered as unoccupied time since chiller is not required to cool down the temperature. On the other hand, it releases cool energy via ice melting to support the main chilling equipment during day time whereby it is considered as peak period since cooling is mainly needed for thermal comfort [2-5]. The maximum demand charge during daytime is minimised considerably while the installed capacity of chilling equipment could be reduced to half. The cooling load demand from peak hour is shifted to off-peak hour, making use of energy generated inefficiently by grid or power plant during night time to store ice [6, 7] and hence, benefitting from lower electricity tariff rate and lower operating cost.

Figure 2 is an illustration of estimated current cooling load demand profile from a typical development in city centre. The latent energy stored during charging at night time is released at day time for use. Note that the chiller is producing about 18,000RT as base load consistently during day time, far less from the peak load demand at an approximate of 29,500RT. The balance of 11,500RT (29,500RT – 18,000RT) will be topped from the ice melting, stored during night time. Hence, the electricity required during daytime is only equivalent to electrical energy of chiller plant to produce 18,000RT load and the balance of load demand has been shifted to night time.

The common type of CTES is ice on coil and ice ball system. For ice on coil, normally described as shell and tube construction, the coil is surrounded by heat transfer fluid (HTF) in a tank [8]. The outer surface of coil is in contact with the phase change material (PCM) where the cooling energy is transmitted from the coil at freezing point temperature, 0° C during charging/icing and release back to the coil during discharging/melting process. For ice ball system, water and nucleating agent are filled in an encapsulated ball nodule, called ice ball. There are plenty amount of ice balls as PCM loaded in tank and immersed in HTF [9, 10].

In early days, mixture of water and ethylene glycol of 25% concentration (EG25) is added in many applications. The purpose is to lower the freezing point of HTF so that it remains as flowing fluid at temperature below freezing point (0° C to -12° C) to circulate for heat transfer. This is for enabling charging and discharging process, mainly via convection to store or release cold energy. However, when EG25 is added, the average thermal conductivity of HTF is lowered [11]. As the specific heat capacity of the fluid is decreased, more circulating fluid is required to carry heat thus more pumping energy is needed to deliver higher flow rate. Therefore, improving the HTF thermal conductivity will enhance the CTES efficiency. One of the solutions is introducing foreign element of



higher heat carrier capacity and thermal conductivity, known as nanoparticles which could improve the overall performance of HTF [12-14].



Fig. 2. Estimated cooling load of typical mixed development per day

Recently, there have been few studies on the nanofluids performance CTES. For example, Qunzhi *et al.*, [15] has observed that thermal response for water medium is slow due to its low thermal conductivity. By adding nanoparticles into water, the amount of cool energy stored increases. Meanwhile, Muhd Mustafizur Rahman [16] has conducted investigation on the fluid flow interaction during phase change process. The rate at which melting and solidification takes place with the influence of Grashof, Stefan and Prandtl is recorded.

It was also discovered by He *et al.* [17] that suspending a small amount of nanoparticles (1.13% by volume) in aqueous solution, the thermal conductivities of nanoparticle enhanced PCM was enhanced by 12.76% @ -5° C and supercooling degree was reduced by 84.92%. Zhang *et al.* [18] used bio-organic nanofluid palmatic-stearic acid expanded graphite (PA-SA/EG) in their experiment, discovering good thermal stability and high thermal conductivities.

Teng [19] conducted experiments showing that combination of chitosan and nanoparticles to certain weightage has actually improved the thermal response and lower peak temperature for equivalent heat transfer. Chitosan is used to suspend the nanoparticles to achieve an even heat transfer in steel tank. However, putting too much chitosan will decrease the thermal conductivity of nanoparticles. He also pointed out that nanoparticles are favourable due to its nanoscale size as adding other additives in miliscale or microscale in size will cause blockage in piping thus increasing freezing temperature and reducing latent heat stored.

In a study by Wang *et al.*, [20], they found that by using Cu-H₂O nanofluid, supercooling degree can be reduced and shorter freezing time was observed during cold storage process. Meanwhile, Ali *et al.*, [21] conducted numerical investigation by lattice Boltzman method demonstrated that introducing nanoparticles leads to enhancement of thermal conductivity of conventional PCMs. Hence, there are many researches being performed for improving the thermal conductivity and overall efficiency of CTES. Most of the researches are conducted experimentally and statistically. This poses a challenge on the real time application at large scale as the application of nanofluid blend with EG at large scale is rare. Therefore, it is paramount to study the thermal properties of



nanoparticles suspended in EG and the effect of its volume fraction, temperature, size and heat transfer [22].

The research on CTES requires further exploration though numerous studies, have been conducted. Therefore, this paper aims to give a comprehensive review, which summarizes recent research progress on PCM-CTES and an overview of numerical and experimental studies on the heat transfer performance of different base fluid of PCMs. This article also discusses several factors affecting thermal conductivity of PCM, such as nanoparticles enhanced PCM, shape of encapsulated PCM materials, solid volume fraction and particle size.

2. Phase Change Material (PCM) for CTES

2.1 PCM as Latent Heat Energy Storage

CTES stores latent energy for use at a later time. Fig. 3 below, shows typical schematics of chiller plant with CTES. Sharma *et al.*, [23] concurred that latent energy stores about 5-14 times higher in intensity compared to sensible heat and this make it an attraction to researchers. This claim was similarly reported by Safari *et al.*, [24] in their comprehensive review article. The amount of latent energy stored is determined as [25]:

$$Q = \int_{Ti}^{Tm} mC_p dT + ma_m \Delta h_m + \int_{Tm}^{Tf} mC_p dT$$
(1)

- where Q : total energy
 - Cp : specific heat
 - *h* : enthalpy
 - Ti : initial temperature
 - Tm : melting temperature
 - Tf : freezing temperature



Fig. 3. Typical schematics of chilling equipment with CTES





Fig. 4. Typical CTES with tank and ice nodules as PCM

Fig. 4 illustrates the typical district cooling centre with CTES system to serve several office towers. This CTES contain tanks with ice nodules as PCM. PCM are used as latent heat storage materials in CTES. Fig. 5 shows the basic working principle of PCM and its energy level with respect to temperature. It changes phase from solid to liquid thru melting process or from liquid to solid via freezing process. During the phase change from liquid to solid, it stores energy. Conversely, it releases latent heat energy during melting. Fig. 6 shows the cycle of storing and releasing of latent heat from liquid to solid and vice-versa. With PCM, large amount of heat can be absorbed during melting (cold energy is released) and the cold energy supplied by the chilled water system is stored during solidification process.



2.2 Classification of PCM

Currently, water is widely used as the PCM in the CTES applications owing to its higher thermal conductivity, high latent heat, superior storage density and its abundant availability compared to any other PCM. However, supercooling of water during solidification is a major problem in CTES. Water does not solidify immediately upon cooling below the freezing temperature, but start crystallization only after a temperature well below the melting temperature is reached. With high



degree of supercooling, the rate of nucleation is very slow which results in long freezing time. In refrigeration system, big supercooling degree will cause the evaporating temperature of refrigerator lower and reduce the refrigeration efficiency.

PCM can be classified into organic, inorganic and eutectic based on their compositions as shown in Fig 7. Zalba *et al.*, [26] has made classification and stated that suitable PCM is essential to fit the requirement of the system.



Fig.6. Solid-liquid-solid phase change cycle

Phase Change Material

Organic		Inorganic		Eutectic
1. Paraffin	1.	Salt Hydrate	1.	Organic
2. Non-paraffin	2.	Metallic	2.	Inorganic-Inorganic
			3.	Inorganic-Organic

Fig. 7. Classification of PCM

Organic material such as glycerine and vinyl stearate is divided into paraffin and non-paraffin type. It can absorb or release large amount of latent heat due to the nature of the long carbon chain. Having high chemical stability, the paraffin PCM can be used repeatedly and is non-corrosive and non-sub cooling. However, organic PCMs major drawback is that it has low thermal conductivity. Organic non-paraffin PCM is similar to paraffin PCM but is relatively corrosive, more expensive and highly flammable [22].

Inorganic PCM has higher latent heat per unit mass due to its higher density [25]. It has higher heat conductivity (approximately 0.5W/m°C), less flammable, high toxicity, corrosive and cheaper compared to organic PCM. Salt hydrate is formed by mixing water based with inorganic salts such as calcium chloride hexahydrate, CaCl₂.6H₂O. However, the salt hydrate PCM is prone to sub-cooling and phase separation. The metallic inorganic PCM contains metal alloy component, exhibit higher heat fusion per unit volume and thermal conductivity. On the other hand, it shows low heat fusion per weight and low specific heat capacity as well as vapour pressure [27].



Eutectic PCM is the combination of two or more organic or inorganic component. Segregation is unlikely as both organic and inorganic change phase simultaneously [25]. Ice ball nodule is an example that is using eutectic PCM in CTES. Chemical properties are engineered for enhancing stability without decomposition, preventing corrosion, less-toxic, non-flammable and non-explosive [27].

2.3 Selection of PCM

The suitable PCM should be selected for particular energy storage application. A PCM is considered satisfactory when the phase change cycle repeats itself in consistent, posting desirable properties [25] as shown in Table 1.

	Table 1		
	General properties of PCM		
•	Thermal properties	•	Physical properties
0	Suitable phase change temperature	0	High density
0	High specific heat	0	No or little sub-cooling during freezing
0	High latent heat	0	Low vapour pressure
0	High thermal conductivity	0	Small volume change
0	Long term thermal stability		
•	Chemical properties	•	Kinetic properties
0	Prolonged chemical stability	0	No super-cooling
0	Compatible with capsule material	0	Sufficient crystallization rate
0	Non-toxic, non-flammable, non-explosive		
•	Economic properties		
0	Abundant, available		
0	Inexpensive		

2.4 Base Fluid Type

The common HTF used is mixture of ethylene glycol at 25% (EG25) concentration by volume in water (75:25), lowering the freezing point from 0° C to -12° C. Hussein *et al.*, [28] stated that thermal conductivity of pure water of 0.05655W/mK is being suppressed when using EG. As the concentration of EG in water become higher, the freezing point could drop lower, at the expense of poorer thermal conductivity. As the temperature -12° C is good enough for the application of CTES, EG25 is used as the base mixture that having the highest thermal conductivity at 0.4565W/mK compared to other concentration of EG.

3. Nanofluid and it's Thermal Conductivity

Lately, in the breakthrough of nanotechnology, many researchers have explored the role of nanoparticles to improve existing application in electrical, mechanical and thermal properties [13, 29-32]. According to Pinto and Flavio [33], thermal conductivity of nanofluid is influenced by the following properties:



- i. Nanoparticle size
- ii. Nanoparticle volume fraction
- iii. Thermal conductivity of basefluid
- iv. Thermal conductivity of nanoparticle
- v. Temperature of nanofluid

Nanoparticle size contributes greatly to the thermal conductivity enhancement. Few reports have shown that thermal conductivity increases with incorporation of smaller size of nanoparticles. Angayarkanni and John [34] and Tawfik [35] both have compiled the findings that by decreasing the nanoparticles size, thermal conductivity increases. However, this relation is not the case as both researchers also found out that decrease on nanoparticles size will also lead to decrease in thermal conductivity. Tawfik has pointed out that it was due to increased phonon scattering effect.

Meanwhile, Angayarkanni and John findings on reported value of effective thermal conductivity shown that gross optimum nanoparticle size should not be larger than 50nm. Vanaki *et al.*, [36] has found out that the nanoparticles shape will affect greatly on the performance of heat transfer. Highest heat transfer enhancement is observed using platelet shape, followed by cylindrical, brick, blade and last spherical shape.

Consequently, the volume fraction or concentration of nanoparticles, most researchers have found that increasing concentration will increase thermal conductivity enhancement. To a certain extent, as the concentration increases, the viscosity of the nanofluid also increases and pressure drop become a predominant factor negating the overall heat transfer performance. This was testified by Sommers and Kirk [37] experimentally. The pressure drop is more prominent at lower flow rates. However, Li and Yimin [38] had contradict observations. They cited that under the same Reynolds number, the dilution or increased concentration will not cause significant pressure drop and hence will not penalise the pumping energy.

Vanaki *et al.*, [36] has also suggested that performance evaluation criterion (PEC) to be used in quantifying the overall optimum performance of heat transfer for nanoparticles. According to the researchers, the physical shape of the channel such as different phase shift and different wavy amplitude will also affect the manner of heat transfer performance.

 $\theta = 0^{\circ}$ phase shift promotes better heat transfer against all Reynolds number. Meanwhile, phase shift of $\theta = 30^{\circ}$ bears the highest PEC at Re=6000. Hence, this condition develops into the optimum heat transfer. Similarly to wavy amplitude scenario, higher amplitude of 1.5mm has higher heat transfer enhancement, but this is negated by the higher Reynolds number due to higher friction factor. Hence, lower amplitude of 0.5mm has highest PEC, and better overall heat transfer.

Carbon oxide (CuO) is a metal oxide nanoparticles that have been a general choice for researchers due to its natural higher conductivity in both thermal and electrical properties. Based on the data collected by Angayarkanni and John [34] on enhancement of different nanofluids, Cu/CuO is expected to produce high percentage of enhancement.

4. CTES System with Nanofluid

The unacceptable low thermal conductivity of conventional PCM is a primary limitation in enhancing the charging and discharging rate of heat flux. Also low thermal conductivity would increase the time required for completing the melting and solidification processes, decrease the energy storage capacity and yield difficulty in retrieving the stored energy.

For more than a century time, vast efforts have been made to improve the thermal conductivity of PCMs such as extended surface and fins, microencapsulation, bubble agitation, metal ring and metal matrix insertion, inserting porous media, dispersion of high conductivity particles, etc.



4.1 PCM Particles Suspension in Flow

Many studies have examined the use of microencapsulated phase change materials (MEPCM) particles (PCM suspension) to enhance the performance of liquid-cooled heat sink. For example, Ho and his co-workers [39] compared the laminar forced convective cooling effectiveness by applying Al_2O_3 -water nanofluid and MEPCM through a horizontal cylinder heated with constant heat flux. Both PCM suspension and nanofluid of 2-10 wt.% and volume flowrate of 25-240cm³/min were set in their experimental study. However, low efficiency was obtained (0.87 to 1.03) due to high friction factor and pressure drop penalty for both functional fluids. In another attempt, Ho *et al.*, [40] considered a hybrid water-based suspension of Al_2O_3 nanoparticles and MEPCM particle through the same circular tube. The hybrid suspension showed inferior efficacy to that of pure PCM suspension and pure nanofluid. Meanwhile, the problem of high pressure drop due to increased viscosity was remain unsolved. The hybrid suspension of alumina nanoparticles and MEPCM particles in minichannel heat sink has been considered by Ho *et al.*, [41]. The heat sink was fabricated by copper with hydraulic diameter of 1.2mm. Their experimental results indicated that with the hybrid suspension, the highest enhancement of average heat transfer coefficient (56%) can be achieved at laminar flow condition.

4.2 Nanoparticles Enhanced PCM (NEPCM)

In CTES, the aim of NEPCM is to improve the thermal performance by dispersing the nanoparticles into the HTF or PCM itself. PCM with nanoparticles tends to increase the rate of solidification and melting of PCM, while HTF enhanced with nanoparticles shows increase in thermal conductivity. In one of the earliest research, Zeng *et al.* [42] measured the thermal conductivity enhancement of nanofluid organic phase change material (Ag nanoparticles dispersed in 1-tetradecanol (TD)) and found that the thermal conductivity of the suspension was enhanced as the volume fraction of nanoparticles increased. Experimental studies by Wu *et al.* [43] have shown that the total freezing time of Al_2O_3 - H_2O nanofluid with SDBS surfactant could be reduced by 20.5% with only 0.2wt.% of Al_2O_3 nanoparticles.

Motivated by previous studies of Ryu *et al.*, [44], Liu and his co-workers [45] experimentally investigated the thermal conductivity and phase change performance of TiO_2 nanoparticles in saturated BaCl₂ aqueous solution at pH 8. The nanoparticles volume fraction was varied from 0.167 to 1.13%. They observed that the thermal conductivity was increased up to 15.65% as the nanoparticle volume fraction was increased to 1.13% at 15°C. The total melting time was also reduced around 40% with this type of NEPCM.

Solidification time for the 60% n-tetradecane: 40% n-hexadecane PCM dispersed with alumina and aluminium nanoparticles was investigated by Kalaiselvam *et al.*, [46]. The results indicated that the size of nanoparticles has significantly influenced the energy storage and heat release rate. With 0.07vol.% of nanoparticles, the solidification time was reduced by 12.97%. In a comprehensive study by Manila et al [47], different types of nanoparticles (silica, alumina, titania and hybrid silicaalumina) were mixed with base salt mixture (Na_nO₃-kNO₃) at three weight fractions 0.5,1.0, 1.5wt.% respectively. Interestingly, the measured specific heat was deviated from the theoretical model that suggesting a greater interaction between nanoparticles and the salt.

Using two-step method, Harikrishnan *et al.*, [48] prepared water-glycerol based nanofluid containing CuO nanoparticles for thermal energy storage system. The proportion of water-glycerol was set at 80:20 (by weight) and the mass fraction of nanoparticles were 0.1, 0.3, 0.5, 0.8 and 1.0wt.%. Maximum enhancement of thermal conductivity of 40.24% was obtained at 1.0wt.% of



CuO indicating that the composite PCM can be an efficient candidate for CTES. In conjunction to understand the thermal energy storage characteristics of Cu-H₂O nanofluid as a new PCM, Wang et al [20] monitored the freezing process of the nanofluids using infrared imaging instrument and high speed color digital camera. They confirmed the previous findings by Khodadadi and Hosseinizadeh [49] that the freezing time can be reduced at higher concentration of nanofluids. Dispersing copper oxide into conventional PCM was proposed by Chandrasekaran et al [50]. In that paper, two-step preparation method was employed with nanoparticle weight fraction of 0.1% and size of 37-59nm. With addition of nanoparticles, the thermal transport properties were enhanced and yield reduced in solidification time by more than 30%.

In a different study, Luo and his co-workers [51] considered erythritol and nano-titania as PCM and nano additive respectively as a new potential of NEPCM. They reported that the triethanolamine (TEA) can act as an effective dispersant due to its specific chemical properties. Furthermore, they found that the total heat storage capacity was enhanced by 8%. In an interesting study by Mo *et al.* [52], they dispersed 0.1-0.4wt.% of titania particles in aqueous ethylene glycol (EG) solutions at different EG volume concentration (12%, 22% and 34%). Due to hydrophilic nature of titania particles, the growth rate of water crystal was found higher at high EG fraction. As a result, for the nanofluid with 34% of EG, the phase change temperature was observed decreased by 1.3° C.

The presence of nanoparticles in PCM not only enhance the thermal properties but also increase the contact surface and act as nucleating agent for solidification process which will increase the growing rate of grows layer. This was proved by Ahmed et al [53] during their experimental works to study the performance of water based Al_2O_3 nanoparticle PCM on cool storage system. The results were in good agreement with Wu *et al.*, [43] indicating charging time reduced by 20% in 0.08wt.% of Al_2O_3 .

In 2012, for the first time, He *et al.* [17] developed a new type of phase change material (PCM) by suspending a small amount of TiO_2 nanoparticles in saturated $BaCl_2$ aqueous solution. With the addition of nanoparticles in PCM (0.167 to 1.13vol.%), the latent heat and specific heat were slightly increased. At the highest volume fraction, the thermal conductivity of nanofluid PCM was enhanced by 12.76% and the supercooling degree was reduced by 84.92%. Harikrishnan and Kalaiselvam [54] prepared CuO-oleic acid nanofluid as a new phase change material and found that by adding 2 wt.% of CuO nanoparticles in oleic acid, the complete solidification time and melting time can be saved by 27.67% and 28.57% respectively.

Brian *et al.*, [55] monitored the stability of CNT enhanced distilled water as a PCM by means of electrical conductivity test. In a similar research, Kumaresan *et al.* [56] investigated the thermal conductivity enhancement and degree of supercooling of a new phase change material (MWCNT in liquid paraffin). Based on their experimental results, the NEPCM showed 40-45% enhancement of thermal conductivity as compared to base PCM. In addition, higher reduction in degree of supercooling was obtained at lower concentration of MWCNT than that of higher concentration. Hence it is important to find the optimal value of volume fraction of MWCNT which are to be added in the base PCM.

In another study, He *et al.*, [57] prepared TiO_2-H_2O nanofluid and found that by adding 2.4wt.% TiO_2 nanoparticles into deionized water, the supercooling degree was reduced by 100% and the total freezing time was reduced by 33.33%. Experimental studies were performed by Wu *et al.*, [58] on the heat transfer rate of Cu, Al and C/Cu nanoparticles in melting paraffin. They observed that the 1wt.% of Cu suspended in melting paraffin not only enhance the thermal conductivity, but also reduce the heating and cooling time by 30.3% and 28.2%, respectively.



Attia *et al.*, [59] has conducted an experiment with nanoparticles that applied PCM contained in a spherical capsules and another experiment with nanoparticles dispersed in the HTF of EG25 solution. As for PCM, the nanoparticles of Al_2O_3 with different concentration of 0.0%, 0.5%, 1.0%, 1.5% and 2.0% act as nucleation agent, enhancing crystallisation process of PCM to become ice at faster rate compared to pure water. As the concentration of nanoparticles become higher, the crystallisation effect increases. Since the time for complete charging decreases. The charging time also decrease with respect to rise of HTF flow rate or lowering of HTF temperature. The result of this experiment is in agreement with the findings by few other researchers [20, 60, 61]. However, it was also observed by Attia *et al.*, [59] that once ice layer form in the inner wall of spherical capsules, thermal conductivity reduces, increasing charging time as the concentration of nano-fluid increases. This was found out to be true by Myers [62] that viscosity increases with addition of nanoparticles. Flow rate reduces in a high viscosity area that acts as insulating layers, hence the discharging rates.

For dispersion of nanoparticles in HTF, nanoparticles with concentration of 0.00%, 0.25%, 0.50%, 0.75% and 1.00% are added to enhance the overall fluid thermal conductivity. As the concentration of nanoparticles increase, Altohamy *et al.*, [59] observed that the charging time decrease due to improvement on thermal conductivity. The heat flux at external surface of capsule also increases. The findings by Hussein *et al.*, [28] concurred with Altohamy et al report. Nevertheless, it was also found that the complete charging or discharging time taken for NEPCM is still shorter and more effective compared to HTF enhanced with nanoparticles as the nanoparticles concentration increase.

4.3 CNT Nanoparticles in PCM

Reporting on the use of CNTs nanofluid in thermal energy storage applications, it is found to be limited. Dispersed CNT in phase change material (PCM) to increase its thermal efficiency has been tried by few researchers. For example, Aitor Zabalegui *et al.*, [63] observed that addition of carbon nanotubes dispersed in paraffin wax could affect latent heat capacity. The particle with smaller diameter will show higher degree of latent heat reduction. Pau Gimenez-Gavarrell *et al.*, [64] has attempted to use different synthesis method and sonication time in preparing the CNT suspended ionic liquid based material. However, it was found out that no substantial change in latent heat and melting temperature.

Instead of nodule, Chougule *et al.*, [65] used MCNT/water heat pipe charged with PCM for his test. Paraffin and water were tested at different fan speed and heating powers. The result shows that the CNT with higher volume fraction of 3% was heated up faster. The use of paraffin in cooling module with heat pipe was found to be saving fan energy compared to water.

Kumaresan *et al.*, [56] attempted an experiment by dispersing multiwalled carbon nanotubes (MWCNT) with volume fraction of 0.15%, 0.30%, 0.45% and 0.60% in water with sodiums dodecvl benzene sulfonate (SDBS) surfactant. Thermal conductivity was enhanced with reduction in degrees of supercooling as MWCNT concentration was increased.

Kumaresan *et al.*, [60] pursued the same experiment using NEPCM encapsulated in spherical container, surrounded with HTF temperature at -9 $^{\circ}$ C and -12 $^{\circ}$ C. It was observed that the solidification time of NEPCM with MWCNT reduced by 14.0% and 20.1% respectively. It showed that cooling rate is lower when HTF temperature is higher at -9 $^{\circ}$ C. It was also reported that solidification time for pure water PCM at HTF -12 $^{\circ}$ C matches with the NEPCM of 0.60% MWCNT by volume fraction at HTF -9 $^{\circ}$ C. This is due to presence of MWCNT that advances the solidification process. Hence, saving the chiller compression energy around 6%-9%.



Chandrasekaran with his researcher comrades [66] further continue the above experiment to study the solidification behaviour of NEPCM with MWCNT. Addition of SDBS surfactant has a negligible effect during liquid sensible cooling region and the degree of subcooling. The freezing took place at the minutes of 25th – 30th from the start. During the first 25% of solidification time about 50% of PCM was solidified, followed by the 25% of PCM in the next 25% of time. The remaining of 50% solidification time was required to freeze the last part of PCM. This was similar with NEPCM as well. Hence, the short charging and discharging of CTES is efficient as the first 25% of time considering 50% of energy could be stored or released.

4.3.1 Graphene Nanoparticles in PCM

Another rare nanoparticle, graphite based has shown exceptional stability when dispersed in phase change emulsion containing 30wt% of OP10E. Wang *et al.*, [67] found that the addition of graphite nanoparticles of 2 wt.% has no effect on latent heat but exhibits remarkably enhancement by 88.9% to 0.578W/mK, whilst reduces degrees of supercooling from 9.9 °C to almost 0.0 °C. Liu *et al.*, [68, 69] has caught attention by posing experimental result on effect of graphene oxide nanosheets with ultrasonic oscillation. Graphene oxide nanosheets is a two-dimensional material compare to CNT which worth studies. With graphene oxide nanosheet, the supercooling degrees reduced to 69.1% with nucleation forming earlier by 90.7%. Basing on heterogeneous nucleation theory, Yudong Liu et al founded that nucleation can only grow on the top or bottom surface of nanosheet when the nanosheet size D comply with the formula $D.\Delta T >= 4.2X10^{-8}$.

The nucleation is also additionally enhanced by ultrasound oscillation, interpreted as cavitation effect. The cavitation effect causes bubbles to develop and collapse rapidly. Hence, energy changes as nanosheets move and collide with each other with ease at frequent manner.

Liu *et al.*, [68] further refined the research and experiment via levitation of ultrasonic wave to avoid contamination from container walls or other external objects. It was found that the supercooling degrees of deionized water reduced by 59.79% and it gradually weakened as the cooling temperature decreases. Hence, difference between nanofluid and deionized water was reducing. Guided by Wenzel's wetting model, the authors also deduce few mathematical model to explain the nucleation rate of graphene oxide nanofluid.

Sathishkumar *et al.*, [66] carried out an investigation on the solidification behaviour of water dispersed grapheme nanoplatelets (GNP) in a spherical container. The mass concentration of GNP being tested in PCM were 0.3%, 0.6%, 0.9% and 1.2%, corresponding to $324m^2$, $648m^2$, $972m^2$ and $1296m^2$. About 15% of improvement in thermal conductivity were recorded using 0.3 wt.% and as much as 42% enhancement with 0.6 wt.%. However, only 7%-10% enrichment was noticed on 0.9 wt.% and 1.2 wt.% respectivley, showing that the enhancement is nonlinear. Solidification time is observed reduced by 22.5% and 64.77% respectively under HTF bath temperature from -9 °C, to -15 °C. This trend is seen as potential in reducing energy consumption of chiller with CTES system. For first 42% of total solidification time, 34% volume in PCM solidified. With 0.3 wt.%, 0.6 wt.%, 0.9 wt.% and 1.2 wt.%, solidification percentage is reducing at 41.8%, 41.1%, 36.8% and 35.2% respectively.

In another experiment, Sathiskumar and his team [70] have recorded that solidification time reduction of 24% for GNP PCM with 0.6 wt.% at -12 °C, concurred with earlier experiment. However, the only 9.5% thermal conductivity enhancement were achieved compared to experiment conducted in [28]. The thickness of graphene nanopowder, GNP used in the experiment [28] is about 60nm in EG30 bath fluid while the latter GNP thickness was 120nm in EG40 bath fluid. Both GNP were obtained from the same source, Cheap Tubes USA. Hence, with the drop in thermal



conductivity enhancement, it could be attributed to lesser exposed surface area of GNP with higher EG concentration in the latter experiment.

4.4 Numerical Study of NEPCM

Many of previous numerical studies on heat transfer enhancement during solidification/melting of NEPCM have been conducted using enthalphy porosity technique. Considering NEPCM as continuous media, Newtonian, incompressible and in thermal equilibrium, the formulation for two-dimensional case can be written as follow;

Continuity equation

$$\frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} = 0,$$
(2)

Momentum equations

$$\frac{\partial u}{\partial t} + u \frac{\partial u}{\partial x} + v \frac{\partial u}{\partial y} = \frac{1}{\rho_{nf}} \left(-\frac{\partial P}{\partial x} + \mu_{nf} \nabla^2 u \right) + S_x, \tag{3}$$

$$\frac{\partial v}{\partial t} + u \frac{\partial v}{\partial x} + v \frac{\partial v}{\partial y} = \frac{1}{\rho_{nf}} \left(-\frac{\partial P}{\partial y} + \mu_{nf} \nabla^2 v + (\rho \beta)_{nf} g(T - T_{ref}) \right) + S_y, \tag{4}$$

Energy equation

$$\frac{\partial T}{\partial t} + u \frac{\partial T}{\partial x} + v \frac{\partial T}{\partial y} = \frac{\partial}{\partial x} \left[\frac{(k_{nf,o} + k_d)}{(\rho c_p)_{nf}} \frac{\partial T}{\partial x} \right] + \frac{\partial}{\partial y} \left[\frac{(k_{nf,o} + k_d)}{(\rho c_p)_{nf}} \frac{\partial T}{\partial y} \right] - S_h, \tag{5}$$

Note that the formulations were modelled by Boussinesq approximation to account for the thermal buoyancy.

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

The density of the nanofluid is written as

$$\rho_{nf} = (1 - \emptyset)\rho_f + \emptyset\rho_s,\tag{6}$$

where the subscripts f and s denote base fluid and solid, respectively. Following Brinkman [71], the viscosity of the nanofluid containing a diluted suspension of fine spherical particles can be written as

$$\mu_{nf} = \frac{\mu_f}{(1-\emptyset)^{2.5}},\tag{7}$$

The heat capacities and the Bousinesq term can be expressed as

$$(\rho c_p)_{nf} = (1 - \emptyset)(\rho c_p)_f + \emptyset(\rho c_p)_{s'}$$
(8)

$$(\rho\beta)_{nf} = (1 - \emptyset)(\rho\beta)_f + \emptyset(\rho\beta)_s,\tag{9}$$



The effective thermal conductivity of the nanofluid is given by

$$k_{eff} = k_{nf,o} + k_d,\tag{10}$$

where the thermal conductivity of the nanofluid is given as [72]

$$\frac{k_{nf,o}}{k_f} = \frac{k_s + 2k_f - 2\phi(k_f - k_s)}{k_s + 2k_f + \phi(k_f - k_s)},\tag{11}$$

and the thermal conductivity enhancement term due to the thermal dispersion is expressed as [73]

$$k_d = D(\rho c_p)_{nf} \sqrt{u^2 + v^2} \emptyset d_p, \tag{12}$$

Here, *D* is an empirically-determined constant which can be obtained from the work of Wakao and Kaguei [74] and d_p is the nanoparticle diameter.

The latent heat of the nanofluid is evaluated using

$$(\rho L_h)_{nf} = (1 - \emptyset)(\rho L_h)_f, \tag{13}$$

The source terms of the momentum and energy equations are expressed as

$$S_x = \frac{A(1-f)^2}{f^3 + \varepsilon} u, \tag{14}$$

$$S_y = \frac{A(1-f)^2}{f^3 + \varepsilon} v,$$
 (15)

$$S_h = -\frac{\partial [(\rho L f)_{nf}]}{\partial t},\tag{16}$$

where $\frac{A(1-f)^2}{f^3+\varepsilon}$ cause the gradual change in the velocity from a finite value in the liquid to zero in the solid. Here, ε is usually set 10⁻³, a small computational constant used to avoid division by zero. **A** is a constant reflecting the morphology of the melting/solidification front. This constant is usually lies in the interval 10⁴-10⁷.

The total enthalpy, H_e is the sum of sensible enthalpy, h as

$$h = h_c + \int_{T_c}^T \quad C_{p,nf} dt \tag{17}$$

$$H_e = h + fL_h \tag{18}$$

Here, f is the liquid fraction during the phase change, which varies between zero for solid and one for liquid and is given by

$$f = \{0, if T < T_s \ \frac{T - T_s}{T_l - T_s}, \ if T_s < T < T_l \ 1, if T > T_l$$
(19)

where T_s and T_l are the solidus and liquids temperature respectively.



Khodadi *et al.*, [49] were probably the first group who numerically investigated the thermal conductivity of copper nanoparticles enhanced PCM. Since then, numerous research have been presented to investigate the solid-liquid phase change process in thermal energy storage. Sebti *et al.*, [75] studied the effect of Cu nanoparticles dispersed in pure fluid on heat transfer characteristics during melting process in a square cavity. Their data indicated that the melting time was reduced with the presence of nanoparticles. In addition, the size of cavity played a significant effect on the heat transfer rate. Zabalegui *et al.*, [63] extended their previous research [76] on the effect of particle size on the amount energy stored by nanofluid. A finite element numerical model was developed to determine the transient process of nanofluid phase change in an annular storage container. Interestingly, they found that the nanoscale inclusion degrade the storage performance when compared to microscale particles.

The solidification of phase change materials in isosceles trapezoidal cavity was investigated by Sharma *et al.*, [77] using commercial CFD package ANSYS Fluent. They noted that the heat transfer performance of Cu/water PCM was enhanced with the use of trapezoidal cavity when compared to a square cavity. Further, at constant temperature (10°C) and 10 vol.% of Cu nanoparticles, increasing the inclination angle of side walls has reduced the solidification time of NEPCM. A detailed numerical procedure of predicting the effect of embedding nanoparticle in PCM to improve the thermal energy storage performance was given by Sushobhan and Kar [78]. They investigated the melting of n-octadecane PCM dispersed with various volume fraction of CuO nanoparticle in a square cavity. The results showed the melting time was reduced for higher concentration of nanoparticle. However, too much of nanoparticles could reduce the heat transfer rate due to increase in the viscosity and hence decrease the flow velocity. The solidification of Cu-water nanofluid inside a vertical enclosure with wavy surface, wide range of nanoparticle volume fraction and different Grashof numbers has been tried by Abdollahzadeh and Esmaeilpour [79]. Surface waviness was found to compensate the reduction of energy storage capacity due to the addition of nanoparticles.

To see the effect of Brownian motion on freezing of PCM containing copper nanoparticles, Jamalabadi and Park [80] modified the thermal conductivity equation as follow

$$\frac{k_{nf}}{k_f} = \frac{k_s + 2k_f - 2\phi(k_f - k_s)}{k_s + 2k_f + \phi(k_f - k_s)} [1 + A(Re_p)^m Pr^{0.333}\phi],$$
(20)

where Re_p is the particle Reynolds number based on Brownian velocity, which can be defined as

$$Re_p = \frac{1}{v_f} \sqrt{\frac{18k_B T}{\pi \rho_p d_p}},\tag{21}$$

The Prandtl number for base fluid, Pr is defined as

$$Pr = \frac{C_{p,f}\mu_f}{k_f},\tag{22}$$

In the study, A and m in the above equation were set 40000 and 2.75 respectively, and the particle size of 10nm to give Reynolds number of 1.87×10^{-2} . They found that with the inclusion on Brownian effect, the rate of phase change process increased and yields decrement in total solidification time. In 2011, Corcione [81] proposed empirical models for the expression of viscosity and thermal conductivity as follow

$$\frac{\mu_{eff}}{\mu_l} = \frac{1}{1 - 34.87 (\frac{d_{np}}{d_f})^{-0.3} \phi^{1.03}},$$

$$\frac{\lambda_{eff}}{\lambda_l} = 1 + 4.4Re^{0.4}Pr^{0.66}(\frac{T}{T_l})^{10}(\frac{\lambda_{np}}{\lambda_f})^{0.03}\phi^{0.66}$$

Table 2

Numerical Study on enhancement of NEPCM

Authors	Nanoparticles	PCM	Remarks
Al-Jethelah <i>et al.,</i> [85]	Aluminum oxide(Al ₂ O ₃₎	Water (H ₂ O)	Addition of Al nanoparticles to base PCM improves the thermal conductivity, melting process, viscosity of the nano-PCM but convection heat transfer degraded as the viscosity increased
Sahoo <i>et al.,</i> [86]	Copper Oxide (CuO)	n-eicosane	Dispersion of nanoparticles from 0 to 5%. Causes the melting rate of NEPCM is increased gradually. The base temperature of heat sink lowered by 4°C which is favorable in electronics application
Bechiri <i>et al.,</i> [87]	NaNO ₃ as NEPC	M	Dispersion of nanoparticles within PCM accelerates the phase change cycles and the melting time of NEPCM diminished as volume fraction of nanoparticles increases
Hossain <i>et al.,</i> [88]	Copper Oxide (CuO)	Cyclohexane	NEPCM melted faster in lower porosity medium and higher volume fraction of nano-particles. Less energy was required to complete the melting process in higher volume fraction of nano-particles
Alshaer <i>et al.,</i> [89]	Multi Wall Carbon Nano Tubes (MWCNTs)	Paraffin wax (RT65)	Enhancement of thermal conductivity in the carbon foam micro cells owning to the decrement of 11.5% and 7.8% in the module surface temperature with carbon foam porosities lower than 75% and 88% respectively.
Nabavitabatabayi <i>et al.,</i> [90]	Copper (Cu), Aluminum oxide(Al2O3)	PCM(not mentioned)	The complete solidification time of NEPCM was saved by 60% (103 min to 64 min) and more power demand was shifted compared to off-peak periods pure PCM.
Abdollahzadeh <i>et</i> <i>al.,</i> [79]	Copper (Cu)	Water (H_2O)	Dispersion of nanoparticle in PCM can shorten the solidification/freezing time but also reduces the energy storage capacity in PCM.
Jourabian <i>et al.,</i> [91]			Doping of nanoparticles improves the melting rate of PCM but enhancement effect decreased in higher volume fraction due to viscosity increased. NEPCM enhanced thermal conductivity but decline latent heat of fusion.
Sharma <i>et al.,</i> [77]			The NEPCM had greater capability to store/release the thermal energy in comparison to the pure PCMs. Increment in nanoparticle dispersion volume fraction caused decrement the solidification time.
Sciacovelli <i>et al.,</i> [92]	Copper (Cu)	Paraffinic wax	4% of Cu nanoparticles can saved of melting time. Besides, melting time shorten by 7% when mass flow rate of heat transfer fluid was doubled.
Dhaidan <i>et al.,</i> [93, 94]	Copper Oxide (CuO)	Paraffin (n- octadecane)	Addition of nanoparticles expedited the melting rate of NEPCM. Lower concentration of nanoparticles has higher energy storage capacity and melting rate as agglomeration and sedimentation effect is smaller.

The models were found good agreement in determining the properties of metal oxide nanofluids such as Al_2O_3 , Cuo and TiO₂ nanoparticles dispersed in water, ethylene glycol and propylene, when compared to the experimental works by Ho and Gao [82] and Motahar et al., [83].

Akademia Baru

(23)

(24)



Madruga and Mischlich [84] believed that this was due the inclusion of important features of nanoparticles such as size, temperature and properties of base fluid to the models. In a recent work by Madruga and Mischlich, they investigated the melting of n-octadecane in half a disk with dispersed small amount of Al_2O_3 nanoparticles. They compared the obtained transport coefficient using the conventional Maxwell Garnett model for thermal conductivity and Brinkmann model for viscosity, and the empirical correlations proposed by Corcione [81]. The results demonstrated that Maxwell Garnett/Brinkmann model overestimated the rate of heat transfer for most of the ranges of nanoparticles concentration, size and temperature. The summary of some numerical studies on improvement of PCM by dispersion of nanoparticles was represented in Table 2.

5. Conclusion

Recent research progress on PCM-CTES and an overview of numerical and experimental studies on the heat transfer performance PCM-CTES have been discussed on this paper. The paper also reported several factors affecting thermal conductivity of PCM, such as nanoparticles enhanced PCM, shape of encapsulated PCM materials, solid volume fraction and particle size.

Thermal conductivity is always an important parameter which guarantees the use of nanofluid as PCM for CTES. Meanwhile, more recent studies have confirmed the possibility of using hybrid nanofluid for heat transfer enhancement. Even though few reports can be seen in the literature, there is a need for more experimental research to ensure maximum performance when using hybrid nanofluid in thermal energy storage system. At the same time, there are still some problems and challenges regarding the mechanisms of heat transfer enhancement using nanoparticles enhanced PCM. The research on PCM-CTES has gained significant attention due to its capability to restore the electrical power imbalance between daytime need and night time abundance efficiently. However, the application of nanoparticles enhanced PCM for cold thermal energy storage system is still at its initial stage and needs further development.

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