Study of freezing characteristics of water based grapheme Nano-fluid PCM in a spherical capsule

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Abstract. In the present scenario of increasing levels of energy consumption, a lot of research focus is being carried out in optimising thermal energy consumption. The latent heat energy storage system is widely being identified as a viable option which possesses very high potential to optimise thermal energy consumption in Refrigeration and Air-conditioning applications. The efficient functioning of a latent heat energy storage system mainly depends on the phase change material, the phenomenon of subcooling and total freezing time. This paper reports the results of comparative experimental study on the freezing characteristics of water based nano fluid PCM with grapheme nano-particles inside a spherical encapsulation made of different materials. Graphene as a nano-particle possesses large surface area which enhances the heat transfer characteristics of the PCM. The materials used for the spherical encapsulation were high density poly-ethylene (HDPE) polymer and copper metal. Experimental tests are thus carried out on each of these spheres at specific HTF temperatures of the evaporator for a concentration of 0.1 wt% concentration of graphene in the PCM. The experimental results indicated a significantly reduction in total freezing time in the capsule sphere made of copper as compared to the sphere made of HDPE at a fixed HTF temperature for 0.1% graphene. The results also showed the elimination of sub-cooling phenomena for both cases during the charging process.

Keywords: Nucleating agent, subcooling, Solidification time, PCM

1. Introduction

Efficient CTES (cool thermal energy storage) systems are a primary requirement in many industrial sectors such as air –conditioning of buildings, refrigeration systems and other industrial processes, where the peak demand occurs at a particular duration [1-4]. These systems are able to reduce the gap between supply and demand of available energy sources. Thermal energy storage can be divided into two categories. Sensible Heat Thermal Energy Storage (SHTES) involves storing or removing energy through a solid or liquid without phase change. These systems do not have the capacity to store large amounts of energy in comparison to their volume and cannot provide isothermal conditions. Latent Heat Thermal Energy Storage (LHTES) is the process in which the energy is stored or removed under phase change process. The primary advantage of LHTES is its ability to store large energy, constant temperature during charging and discharging process [5, 6]. Among the existing systems, the PCM (phase change material) based CTES systems is popular among the researchers due to exponential increase in the energy consumption in the above mentioned sectors [1-4]. Water is
popularly used as the PCM in the CTES applications due to its higher thermal conductivity ratio between solid to liquid, high latent heat and its abundant availability [2]. In these systems, heat transfer takes place in two stages. First stage is charging. In this stage, refrigerant which is kept at lower temperature removes heat from the HTF and reduces its temperature, this HTF then removes heat from PCM which is encapsulated in spherical balls and freezes it to convert it to solid from liquid. Thus, cold energy is stored. Second stage is discharging. During this process, the flow is opposite. PCM absorbs heat from HTF and converts to liquid, this HTF then absorbs heat from refrigerant so as to do the refrigerating action. Thus, extraction of cold energy take place. However, the sub-cooling of water during freezing is a major problem in the CTES system. This reduces the coefficient of performance of the refrigeration system considerably [5]. The different methods like providing extended surfaces [6-7], dispersing high thermal conductivity materials [8-12] and inserting metal matrix [11] have been reported to reduce the conductive resistance present during freezing process. The disadvantages highlighted in the above methods are overcome with recent developments in the field of nanotechnology [5]. Since thermal conductivity of solids is higher than that of liquids, dispersion of solid particles in a base fluid will tend to increase the heat transport properties [9-10]. However, dispersion of millimetre and micrometre sized particles is prone to sedimentation, clogging, erosion of pipes [8]. Thus, nano fluids are used in the given work to study the freezing characteristics of PCM encapsulated in a spherical capsule.

### Table 1. Abbreviation

| ABBREVIATIONS | MEANING                        |
|---------------|--------------------------------|
| PCM           | Phase Change Material          |
| TES           | Thermal Energy Storage         |
| SHTES         | Sensible Heat Thermal Energy Storage |
| LHTES         | Latent Heat Thermal Energy Storage |
| HTF           | Heat Transfer Fluid            |
| DW            | Deionised Water                |

### Table 2. Properties of Graphene.

| Measurement Method        | Variable Transmission Electronic Microscope (TEM) |
|---------------------------|-----------------------------------------------|
| Thematic class CARBONS    | QGraphene \(^{-}\) - Few Layered Graphene     |
| CAS No                    | -                                             |
| Mean particle size        | 75 nm                                         |
| Specific surface area     | 62 m\(^2\)/gm                                 |
| Crystal Phase             | Flakes of single Layered Carbon Sheets        |
| Morphology                | Platelet and Spherical structure              |
| Physical state            | Solid Dispersion                              |
| Colour                    | Black or dark grey                            |
| Bulk density              | 0.15 gm/cm\(^3\)                              |
| True density              | 2.1 gm/cm\(^3\)                               |
| Electrical conductivity   | Conduction > 10\(^7\) Siemens/m (Along X and Y axis) |
|                           | >90 Siemens/m (Along Z axis)                  |
| Purity wt. %              | 98 %                                          |
| Base Content              | Carbon                                        |
| Source Material           | Argon/Methane/Catalyst                        |
Graphene is an allotrope of carbon with a 2D honeycomb structure [8]. Nano particles have been constructed with an aspect ratio of 7:5. These nano particles have peculiar properties which makes them suitable as an additive to the PCM. They have very high axial strength thermal and electrical conductivity high specific surface area [8]. Some of the properties of graphene are mentioned below in the table 2.

| Property                | Value                                    |
|-------------------------|------------------------------------------|
| Trace Elements Catalyst | Slight Impurities 0.1% Trace catalyst    |
| Additional Content %    | Oxygen 1.5%                               |
| Amorphous carbon %      | Dense impurities 0% Ash 1.5 – 5 wt. %    |
| Average length          | 70 nm                                     |
| Average width           | 50 nm                                     |
| Average thickness       | 9nm                                       |
| Functionalized          | On Demand                                 |
| Thermal conductivity    | >5300 w/m-k (Along X-Y axis)              |
| Tensile Strength        | On Demand                                 |
| Temperature stability   | 3000 degrees                              |
| Dispersion              | Soluble in organic solvents              |
| Aspect Ratio            | 7:5                                       |

Graphene nano particles were used for the preparation of graphene nano fluid with water as a base fluid and sodium dodecyl benzene sulphonate (SDBS) as a surfactant. Nano fluid was prepared using homogeniser to completely disperse the graphene in water to form a stable colloid containing nano particles. Deionised water is used because it prevents coagulation of graphene, which separates graphene from water. Water is used because of its high latent heat, easy availability, low corrosiveness and low cost. The solution is prepared using probe sonicator where the graphene nanoparticle at a concentration of 0.1 wt. % and 0.75% of SDBS is mixed with deionised water. The solution is sonicated for a period of 15 minutes and the required amount of solution is taken for the study.

3. Experimental Setup

The schematic of the experimental apparatus is shown in Fig. 1 which consists of a refrigerator unit, thermally insulated constant temperature bath, spherical capsule made of HDPE and copper, PDTC, data acquisition system (34972A) with necessary temperature sensors for the measurement. The constant temperature bath is made of stainless steel and insulated with PUF which consists of 70% water and 30% ethylene glycol as heat transfer fluid. A refrigeration unit with a capacity of 3 kW were used to maintain the bath temperature by using PDTC (proportionate differential temperature controller). A mechanical stirrer is used to maintain a constant temperature in the bath. Spherical capsule (HDPE) of size 70 mm and copper spherical capsule of size 74 mm is taken for the analysis. One RTD (Pt-100) thermocouple is placed at the centre of each capsule with PCM fill volume of 90% in order to determine the freezing time.
4. Results and Discussion

The temperature history of DI water without graphene nano-particles is presented in Figure 2 to assess degree of sub-cooling. It is observed that the maximum degree of sub-cooling of -3.8°C at HTF temperature of -6°C. The freezing time for 0.1% graphene concentration is shown in Fig.3. It is also observed from the figure that the start of solidification occurred at the same instant for -6°C and -9°C. But for -12°C the freezing initiated at a lesser time. From the Fig.3, it has been observed that the presence of graphene nano-particles completely eliminated the sub-cooling (At HTF = -6°C) as compared to spherical capsule without nucleating agent.
Stability test was performed for 0.1% concentration graphene encapsulated in a HDPE and copper spherical ball and the freezing time was analysed for different cycles as shown in Fig.4. In the first cycle, the solution was prepared and immediately the experiment was started. In the second cycle, the experiment was done with the same solution after two days of preparation. It was observed that Subcooling is observed in second cycle whereas it is absent in first cycle. Time taken for freezing is appreciably higher in second cycle as compared to the first cycle.

The temperature variation of DI water without and with nucleating agent is shown in figs 5,6,7 and 8 at HTF temperatures of -6°C and -9°C.
Figure 5. Temperature variation of 0.1% graphene PCM in HDPE spherical capsule (-6°C).

Figure 6. Temperature variation of 0.1% graphene PCM in Copper spherical capsule (-6°C).
Figure 7. Temperature variation of 0.1% graphene PCM in HDPE spherical capsule (-9°C).

From the Figure 5 to 8, it has been observed that the presence of graphene nanoparticle completely eliminated the degree of sub-cooling at both HTF temperatures. The time taken for freezing in copper capsule is less than the time taken for freezing in HDPE capsule. It is observed that by using copper encapsulation the solidification time is reduced by 56% when compared with HDPE encapsulation at various temperatures such as -6°C and -9°C.

Figure 8. Temperature variation of 0.1% graphene PCM in copper spherical capsule (-9°C).

5. Conclusion
1. By using copper encapsulation the solidification time is reduced by 56% when compared with HDPE encapsulation at various temperatures such as -6°C and -9°C.
2. The stability of higher concentrations of graphene in base fluid is low. The graphene particles sediment after few cycles of charging and discharging. Surfactants may be used along with the base PCM to increase the stability of the graphene nano-particles in the PCM.

3. The degree of super-cooling is reduced by 3.8°C by the addition of nucleating agent in base fluid for HDPE capsule. Sub-cooling is not observed at very low HTF temperatures at both the capsules.

4. The elimination of sub-cooling in water due to the addition of graphene nanoparticle helps us to operate the refrigeration system at a higher temperature.

6. References

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