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Advances in the Study of Phase Change Materials and Ne-PCMs for the Storage of Energy Applications

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Abstract

Phase change materials with nanoparticles that are used to store passive latent heat are proving of utmost importance to the present technology, because of their usage in wide applications right from domestic applications to space technologies. It is attracting the focus of all researchers because energy saving that to renewable energy saving such as solar energy is the biggest demand of the twenty-second century. As fossil fuel storage is getting depleted and is harming the environment, energy demand is increasing, and focusing on renewable energy storage becomes an important task in every application. The present paper focuses on various applications and recent trends of the phase change material. Later the properties of Phase Change materials are being studied. Though the PCMs are proving to be the best option as compared to other energy-saving options such as using solar concentrators, or using fins, solely using pure PCMs is not giving satisfactory results. Hence to improve the thermal properties of PCMs research is being done on the characterization of PCM through the addition of nanoparticles. This article aims at the various combinations and options of PCM and nanoparticles for different applications which give the best result.

Keywords: *PCM, Ne-PCM, Synthesis of PCM, Solar energy*

1.0 Introduction

In the twenty-first century, energy demand is more but the supply is less. Worldwide accepted fact is that sources of non-renewable energy sources such as fossil fuels, natural gases, and petroleum are depleting over time hence to reduce the demand and supply gap between the energy sources modern era demands some solutions for energy storage. Scientists are focusing on the different ways to store energy, especially renewable energy such as solar energy, geothermal energy, wind energy, etc. Moreover, storage of thermal energy has become a very important area of research. But as we know renewable energy sources are not continuous but are intermittent. The research area demands storing renewable energy when available in ample. Therefore, thermal energy storage system plays a vital role in modern-day technology.

Phase Change Material (PCM) has many advantages in the above context such as high latent heat, non-flammable, and being readily available at a low cost. Phase change materials are also known as latent heat storage materials. When any material changes its phase from solid to liquid or liquid vapor energy gets stored in the form of latent heat per unit mass and it is readily available to use when liquid is frozen or vapor is condensed. PCMs have high heat capacity, boiling point, and latent heat many of them are corrosion resistant. Only the disadvantage is the thermal conductivity of the PCMs is low. There are many methods to improvise the properties of these materials such as insertion of nanoparticles, encapsulation, and usage of heat pipes or metal foams. Here in the present paper, the method of insertion of nanoparticles is reviewed as it is found to be a more significant method than others.

If we speak about the applications of PCMs, these can be used in most of the technologies present these days. Right from day to day needs such as domestic appliances (water heater, solar cooker, air conditioners, etc.), buildings, industries to space technologies, medical sciences, and transport systems. PCMs, come in a wide range variety.

2.0 Research Trends in the Applications of Phase Change Materials

As discussed, earlier PCMs are used in many applications. There are few applications where directly PCM can be used. But maximum of the time improvisation of the property is needed. Nanoparticulated PCM, encapsulated PCM, or composited PCM can be used in a variety of applications with increased efficiency without any disadvantage. Now let us see one by one how these PCMs help in a wide variety of applications.

2.1 Building Applications

Based on different latitudes and the earth's rotation human beings have to face different weather conditions. Therefore, building applications refer to space heating, space cooling, water heating, etc. Harald Mehling et al. studied performances of energy saving through PCMs. While used in building applications PCMs can be used passively or actively. When used passively it can be used directly into materials or components used for construction. Being integrated as part of the building materials along with PCM serve the best temperature control system. If temperature crosses the phase change temperature transfers the heat to the building material and thereby it cools the surrounding till the PCM melts. Contrarily if the temperature drops below the phase change temperature it takes from the building material and ultimately heats the surrounding. Another passive mode of storage of release of heat through PCM is used with the building components. This is a rather more flexible method to control the temperature. In actively used methods extra components are added such as fans, pumps, etc. Another such building application where PCMs can be best used is in-floor heating or cooling the ceiling.

2.2 Space Technologies

One more application where PCM technology is used widely in space technology. In space, lots of constraints are there. While designing the components in space ships or shuttles, researchers must consider these constraints. Mohammad Y. Tharwan et al. focused on how the usage of phase change materials helps in space to store the energy and use it whenever required. The major constraint in space equipment is the availability of space. Whatever equipment or technology scientists want to use there has to fit in a small space. Secondly, sources of energy available are very limited and hence storage of energy plays a vital role in such cases. Lots of work has been carried out in these fields scientists have carried out the performances experimentally as well as numerically. One such case study was carried out by Cyril Reuben Raj, S. Suresh, et al. where they experimented with PCM (Hexamethylene Di-isocyanate Polyethylene Glycol-6000 based Form-Stable Phase Change Material) in the heat sink. Eventually, it is used in various equipment, especially electronic equipment. They investigated experimentally as well as numerically using governing equations for conduction and convection. In one more study scholar, Mohammad Ghalambaz et al. studied the effect of phase change material as a heat sink. They investigated PCM in the form of metal foam which is supposed to be one more method to improve the properties of the material. They verified this numerically using FEM. The equation of energy in PCM-metal foam was open was

$$(\rho C_{\mathrm{p}})_{\mathrm{m}} = k_{\mathrm{m}}(\frac{\partial^2 T}{\partial x^2} + \frac{\partial^2 y}{\partial y^2}) - \rho_{\mathrm{l}} h_{\mathrm{sf.m}} \frac{\partial \emptyset(T)}{\partial t}$$

The research gap identified here in this area is that very limited materials can be used in space equipment due to limitations such as specific gravity working on the material, density, etc. Hence scientists have to focus more on the characterization of these limited materials.

2.3 Domestic Application

When it comes to storage of heat domestic applications are also the area of focus for the researchers. As a substitute for LPG or it may be for electricity also people started using renewable energy sources specifically solar energy for their day-to-day needs. Equipment like flat plate collectors, water heaters, and cookers are widely used in many houses. The two very important properties of PCMs make them unique to use in a maximum of the applications, viz. at a particular temperature phase change occurs and this phase-transfer involves energy transition. Abed Mourad et al. studied the applications of PCM for domestic uses such as a solar collector. Scholars also studied the practical limitations in usage and their challenges.

One such important domestic application is the solar water heater. Not only during rainy days or winter days, there is a necessity to store the solar energy for the usage during the night also. Hence again here latent heat can be stored through PCM and can be used when solar energy is not available. Especially for polar or cold regions such as European countries this application using PCM plays a vital role. Greg Wheatley et al. studied exactly this area of application. They observed that not only one PCM but a combination of PCMs can be used in different ratios, hence they focused in the paper that still lots of work has to be done on the different ratios and combinations of PCMs. Some improvements can also be done in designing the instruments itself such as PCM tubes and fin design or design and development of water tank. This is validated numerically, experimentally, or analytically. Not only a water heater but the same principle can be used for solar cookers also. Performance characteristics and design of solar box cooker using encapsulated PCM were studied by Avnish Kumar et al. They carried out this experiment in Uttarakhand state of India where maximum time temperature is very low and storage of solar energy is of absolute necessity. They also did some economic and feasibility analyses. They found that using PCM can save the energy about 2.21MJ energy/meal. This in turn was saving the fuel. If the instrument itself is changed to suit for PCM application, this can save the amount of energy that is being wasted. Mohammad Houcine Dhaou et al. studied the working of the solar water heaters using paraffin wax as PCM and then adding copper particles as nanoparticles. Here apart from casual testing (experimental or numerical), they also did an uncertainty test. There can be two factors due to which uncertainty can happen. One is a systematic error caused due to miss calibration or the instrument itself and the second one is a random error.

A numerical investigation was made on metal foam PCM by Jasim M Mahdi et al. These results were studied for domestic air heater application. Whereas the heater was simultaneously and consecutively charging and discharging. This is another application using PCM where results showed the favorable conditions, through experiments.

2.4 Miscellaneous Applications

Today's research trend also demands energy saving in other fields such as food storage, vehicles, industries, etc. X.M. Ren studied the effect of PCM on array systems on vehicles for cooling. Apart from normal vehicles here, the author studied the application of hypersonic vehicles. As we all are aware that these hypersonic vehicles are used for military purposes but the excessive thermal load may cause a malfunction in the other parts of the equipment. To reduce this thermal load multilayer thermal coating is used. And as a part of one insulating layer erythritol PCM is used which absorbs the excess heat generated and stores it. Investigations were confirmed with numerical validations. This is possible due to high latent heat, high specific heat capacity, and correct phase transition temperature of the material. Now coming to food storage applications, as we discussed earlier just like vehicles power connection is missing sometimes while storing the food especially while transporting. Therefore, energy storage becomes important in the case of food. PCM helps to overcome this problem.

3.0 Types of TES System

To avoid the wastage of excessive energy, Thermal Energy Storage (TES) system technology has been adapted. To avoid the gap between the supply and demand of renewable energy sources, this idea is developed Ex. The most commonly used renewable energy source is solar energy. But this energy is unavailable during the rainy season and night time. In peak hours it is available in bulk to such an extent that only a few per cent of energy is used and the remaining is wasted. So, the concept behind a thermal energy storage system is that the excess amount of energy that is available during the daytime can be stored and used during the night time, rainy season, or any other time when it is needed. Thermal energy can be stored by the following methods,

3.1 Sensible Heat Storage

When the temperature increases of any substance in any phase whether it is solid or liquid energy is stored. Studies show that thermal energy storage depends on the specific heat of the substance and temperature change during discharging and charging. Sensible heat energy storage solely depends upon thermal heat capacity and thermal diffusivity these factors. They decide the energy density and energy release rate. But the disadvantage in storing thermal energy through sensible heat is the quantity of the material required is more and hence the volume will be more. Secondly, energy cannot be stored or released at a specific temperature but can be stored or released within a range of temperatures.

3.2 Latent Heat Storage

Latent heat of storage is also called the latent heat of fusion or enthalpy of fusion. It occurs when any substance undergoes phase transformation. This transformation may be solid-liquid, liquid-gas, and vice versa. Because of this technique, these materials are called phase change materials. The parameters on which the latent heat storage system is designed are latent heat of fusion and the coefficient of thermal expansion. As we all know latent heat storage is an isothermal process. So it allows more energy to be stored, almost 5-14 times than a sensible heat storage system working under the same range of temperature. In this method, we see that all the disadvantages of sensible heat storage are overcome while giving more efficiency.

3.3 Thermochemical Energy Storage System

When any chemical reaction takes place energy is released (exothermic) or absorbed (endothermic). Energy can be stored during this process. In this process actually what happens is energy will be released or absorbed during the formation or breaking of molecular bonds within the material. So, the energy storage or release depends upon reaction heat, the amount of the material, and at the time what is the extent of that reaction. Control the kinetics of the reaction sometimes becomes a very complex process. This is the disadvantage of a thermochemical storage system.

4.0 Properties of Phase Change Material

Phase change material is commonly known as latent heat storage material. As the name suggests while the transformation of phase whether from solid to liquid, liquid to vapor, or vice versa materials store energy i.e., latent heat. As discussed, earlier energy storage has become a vitally important thing due to the reduction in conventional energy systems. Phase change materials are preferred because of their following properties:

Physical properties

a. They have high density.
b. During the phase change, they have a very low volume change.
c. They work on low vapor pressure.
d. phase equilibrium is favourable.

Thermal properties

a. While getting desired range temperature of phase change can be easily Matched.
b. It has high phase transformation latent heat present per unit volume.
c. Specific heat content is high.

Thermal properties

a. Supercooling effect is nil.
b. Adequate crystallization rate.
c. Abundant nucleation rate.

Chemical properties

a. Chemical stability lasts long.
b. Many of them are compatible with maximum materials.
c. It shows anti-corrosion properties for materials.
d. Non-explosive, non-toxic and non-flammable.
e. Reversible melting or freezing cycle.

Economic

a. Available at low cost.
b. Can be used for large-scale applications.
c. Economically feasible.

It can be classified based on its chemical nature, phase transition, shape stabilization encapsulation, and temperature of the application.

Now according to the applications, the selection of a suitable PCM is a big task. Hence to study the thermal properties of the material becomes of utmost importance. The properties which are very important for this process are melting point, boiling point, heat capacity, thermal conductivity, density, etc. There are different methods to study the thermal properties of the material. Let us see that one by one: -

4.1 Differential Scanning Calorimetry (DSC) method

This method is used to measure the heat capacity of the material. It is the method of calorimetry. Here heat flow difference between the reference sample and the sample to be tested. During constant cooling and heating heat flow is measured. Heating is done by heating the furnace electrically while cooling is done by liquid nitrogen or compression cooling. Therefore, a reference sample has to be selected such that its thermal capacity is within the test temperature range. The heat transferred the difference between the atmosphere and test sample and the reference sample and atmosphere.

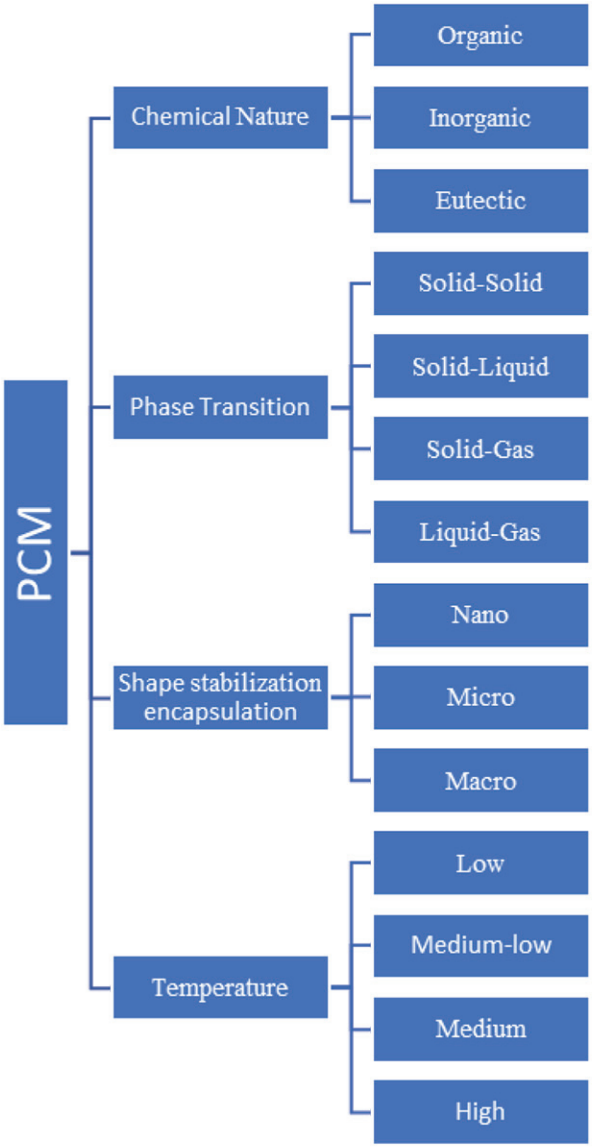

Figure 1: Classification of PCM

4.2 T-History Method

This method can be used for measuring the conductivity of the material. The conductivity of the PCMs whose phase change has a clear interface between its two phases can be measured easily with this method. Along with conductivity melting point specific heat, the heat of fusion, degree of supercooling, etc. can also be determined. However, all the properties cannot be measured simultaneously. Specially conductivity and specific heat. Moreover, no experimental set up is available for the T-history method. It is the analytical method through which all the parameters can be measured. Ylenia Cascone and Marco Perino focused on all these measuring methods along with the advantages and disadvantages of these methods. They also studied the feasibility of these methods. They observed that though the tests are under controlled boundary conditions, all the material properties are evaluated at normal room temperature and hence the dependency of the thermal properties on the temperature is not calculated by all the above methods. This is calculated by the temperature segment method.

4.3 Temperature Segment Method

The advantage of this method is if specific heat is not known priorly other properties such as heat capacity, thermal conductivity, and thermal diffusivity can be calculated simultaneously. The advantage of this method lies in that the segments of temperature are directly proportional to the number of variables in the optimized problems. Researchers have proposed a process based on the measurement of the temperature distribution subjected to Dirichlet boundary conditions or Neumann boundary conditions.

4.4 Inverse Method

Looking at the advantages and disadvantages of the above methods, scholars have proposed the inverse method. In this method, thermophysical parameters obtained from the experiments are matched with the theoretical i.e., numerical ones. Scholars used the (λ+μ) Evaluation Strategy. It was then validated by the Rosenbrock function. Algorithms estimated were found to be stochastic optimistic algorithms.

Table 1 describes the thermos-physical properties of a few organic materials. Based on the above studies and test procedure it is found that merely using the PCMs is not sufficient, except in a few applications. We can see that it is important to improvise the thermal properties of PCM. Especially the conductivity and because of this system's efficiency decreases. There are different methods to improve the properties of PCM such as introducing nanoparticles, encapsulated PCMs, and composite PCMs. In this paper, we will be focusing on nano-enhanced PCMs.

5.0 Introduction to Nanotechnology

It is clear from the above studies that mere usage of PCMs will not achieve the desired results. PCMs have better thermal properties like latent heat storage capacity, specific heat, etc. but simultaneously it has

Table 1: Thermo-physical properties of some organic PCMs

Compound	K(W/m K)	T (°C)	Cp (kJ/kg K)	ρ(kg/m^3)	H (kJ/kg)
Paraffin C15-C16	-	8	2.2(s)	-	153
Paraffin C16-C18	-	20-22	-	-	152
Paraffin C13-C14	0.21	22-24	2.1	790 (l)900(s)	189
Paraffine C20-C33	0.21	48-50	2.1	769(l)912(s)	189
Paraffin C22-C45	0.21	58-60	2.1	795(IC)920(s)	189
Paraffin C23-C45	0.21	62-64	-	0.915	189
Paraffin C21-C50	0.21	66-68	-	830(l)930(s)	189
Paraffin wax	0.167(l)	64	-	790(l)	173.6
	0.346(s)			916(s)	266.0
Paraffin blend (n=14-16)	-	5-6	-	783(s)	152
Paraffin blend (n=15-16)	-	8	-	751.6	147-153
Paraffin blend (n=16-18)	-	20-22	-	-	152
Decane	-	-29.65	-	726(l)	202
Undecane	-	-25.6	-	737(l)	177
Dodecane	-	-9.6	-	745(l)	216
Tridecane	-	-5.4	2.21(l)	753(l)	196
Tetra decane+Octadecane	-	-4.02 to 2.1	-	-	227.52
Octadecane+heneicosane	-	25.8-26	-	-	193.93
Octadecane+docosane	-	25.5-27	-	-	203.80
Naphthalene	0.132(l)0.341(s)	80	2.8	976(l)1145(s)	147.7
Capric	0.149(l)	32	-		
	0.153(l)	31.5			
Undecylic	-	28.4	-		
Vinyl stearate	-	27-29	-		
Undecylenic	-	24.6	-		
Dimethyl sebacate	-	21	-		
Butyl stearate	-	19	-		
Caprylic	0.149(l)	16	-		
	0.148(l)	16.5			
Isopropyl stearate	-	14-18	-		
Pelorganic	-	12.3	-		
Propyl Palmitate	-	10	-		
Caproic	-	-3	-		
Butyric	-	-5.6	-		
Enanthic	-	-7.4			

low conductivity and, in some cases, melting and boiling points. Hence to overcome the disadvantages of PCMs and to enhance the properties of the PCMs various methods are incorporated such as using metal foams, encapsulated PCMs, composites, using extended fins, or using nanoparticles. Depending upon the applications and required thermophysical properties procedure can be selected.

Here in this review paper, we will be concentrating on the procedure of introduction of nanoparticles in PCMs. There are many combinations of PCMs and nano-particles scholars have researched earlier. Many of them used analytical methods to investigate the results still in some cases experimental set ups are not available to do the investigations. Many combinations can also be done with the same PCM but different concentrations of nanoparticles. For example, Muhammad Aquib et al. used paraffin wax, an organic PCM, and added MWCNT in 2 wt%, 4 wt%, and 6 wt%. They found that using only PCM highest temperature attended was 61.53ºC after 90mins. But for the above concentrations of alumina temperatures attended were 62.65ºC for 2%, 63ºC for 4%, and 64ºC for 6%. Now if we see the case of MWCNT maximum temperatures attended by the composite was 68ºC at 2%, 69.86ºC at 4%, and 70.55ºC at 6% of MWCNT. It can be easily seen that there is almost a 9º-10ºC difference in using only PCM and nonenhanced PCM. Therefore, scholars who used the combination of this PCM and nanoparticle have concluded that paraffin wax with 6% wt of MWCNT gives the best results. as compared to other samples.

In investigating this they experimented with the combinations. Magnetic stirring is the method (at 900 rpm, 80ºC, for 2.5 hr) used for combining PCM and nanoparticles. Degasification was done in Sonicator (at moderate frequency, for 2 hr). However practical usage in various applications is not yet cleared. In another study, Raja Elarem et al. studied the combination of paraffin wax as PCM and Cu as nanoparticles with two concentrations of mass (1% and 2%). For investigating the results, they used a numerical method instead of experimentation. They used FLUENT software to carry out the CFD. A study was carried out for Evacuated Tube Solar Collector (ETSC). They concluded that the addition of Cu not only increased the outlet temperature of the tube by 2K but also found that the flow rate which causes a mass of PCM to melt was 0.003 kg/s. Validation experimentally can be the next step to get a better result. Now in another study copper porous material is used as PCM with two different porosity values (98% and 95%) and Al_2O_3 is used as a nanoparticle. Here they carried out the study with 9 different cases. Shu-Bo Chen et al. considered the following cases pure PCM, nanoparticles and pure PCM, pure PCM and nanoparticles, pure PCM with two different porosities, and finally pure PCM with porosity and nanoparticles. Initially, they investigated it numerically and then validated it experimentally. Investigations show that the addition of nanoparticles with high volume fractions gives better melting performance by saving the time up to 184s as compared to pure PCM. Further addition of porous medium improved melting point even more. But porosity with 95% showed the best result reducing melting process time up to 93% than 98% porosity case.

F.A. Essa et al. investigated solar still, which is again a very important application and which needs energy to be stored. This study was carried out to study the development of the tubular solar still having rotating drums, and performance. Instead of adding nanoparticles' to PCM, they coated the rotating drum with copper oxide as nanoparticle-containing paraffin wax as PCM. They experimented to investigate the results. It is found that nanoparticles coating inside the drum gave productivity up to 6650 mL/m^2 per day as compared to 2800mL/m^2 per day. The comparison was also done with the results of the experiment using a parabolic solar concentrator to save solar energy. Comparison concluded that by both the methods energy is stored but productivity improvement using solar parabolic concentrator was 195% while that of using PCM was 218%. The thermal efficiency was also 34% for solar concentrators whereas it was 63.8% for PCM at 0.3 rpm. Even economically the later one proved to be the best.

One more such study is carried out where nanoparticles-embedded PCM is used in water to store thermal energy. Its development and characterization were studied by Xiyao Zhang et al. Scholars used n-hexadecane as PCM and silicon dioxide particles are used as nanoparticles to enhance the properties. Preparation of the PCM and nanoparticles emulsion is dome by the phase inversion temperature method. Later water was slowly added to the emulsifier. These are mixed with magnetic stirring. Then the analysis was done for the emulsion droplets and thermal analysis was done for the composite. They observed that the emulsified fluid behaved as a Newtonian fluid with a low viscosity. The strength of this particular study was found to be the application specification. They specifically studied this for air conditioning systems where the combination is used in chillers. Observing that using this PCM-nano emulsified in water composite increases the efficiency of the chiller. Due to this, it can be concluded that in the application where the energy utilization is more, after using the particular combination energy is getting saved and hence the efficiency of the system is more.

In another very interesting case study, Soroush Ebadi et al. used bio base PCM-nano combination used cylindrical TES. Here in this study coconut oil is used as PCM while copper oxide is used as a nanoparticle. They studied geometry and the insertion effects of the nanoparticles. Initially, they studied energy storage experimentally and then they validated it numerically. They used MATLAB software for the current study. They aimed to study the height of the PCM, hot-wall temperature, and the effect of the weight fraction of copper oxide on the melting of the material. They calculated PCM's thermos-physical found Al_2O_3 and those to be enhanced after the addition of nanoparticles.

Jasim M. Mahdi et al. studied different ways to store the energy for one single application. They carried out an experiment with pure PCM, metal foam, extended fins, and nano-enhanced PCMs to store the thermal energy in a heat exchanger triple-tube. Nanoparticles of aluminium trioxide are used to improve the properties of PCM RT82. They validated it with CFD analysis. Not only with one combination but they studied nano-enhanced PCM with two combinations of nanoparticles present in 1%wt and nanoparticles present in 2% wt. Finally, they concluded that nano-enhanced PCM is not an efficient solution for that particular applicational properties, and PCM does not show any considerable effect in storing the energy. On the other hand, fin insertion proved to be the best option in the particular application to save energy.

Impact on rotating, surface, as well as area expansion, were studied during nanofluid convection by Kaouther Ghachem et al. They studied this during the convection of nanofluid. PCM stuffed bed introduced cylinder was used. Al_2O_3 – TiO_2 are these binary particles we used in ethylene-glycol in a 40% combination. Full phase transposition time is estimated using ANFIS. They observed that the phase transition process was 60% faster after using nanoparticles.

6.0 Conclusions

This paper gives an exhaustive review of past examinations connected with the assessment of how PCMs are very important for every application in the twenty-second century. It focuses on the recent trends and applications of PCMs. Moreover, it studies the thermophysical properties of PCMs and different methods to calculate the properties. After studying different papers, it is concluded in this write-up that merely using pure PCMs will not complete the requirement as it has some drawbacks such as low conductivity, melting point, the temperature range in which it works, etc. Hence to overcome this, scholars have suggested different methods to overcome the disadvantages of PCMs. One such method is introduced to nanoparticles into the PCM. In the present study different combinations of PCMs and nanoparticles are studied and summarised. Not only single PCM and single nanoparticles but different combinations with different volume percentages are focused on. After the addition of nanoparticles, it is concluded that –

- By adding a little number of nanoparticles (1% by wt – 6% by wt.) thermal properties of PCMs increase tremendously.
- These are easily available.
- This technology proved to be the best as compared to other energy storage technologies.
- Economically feasible.
- One composite can be used for many applications.

Focusing on the above parameters it can be stated that non-enhanced PCM will prove to be an altogether different technology in present as well as in the future.

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