CHAPTER 2

LITERATURE REVIEW

The present section is classified into three sections based on various PCMs-based TES systems, a technique to enhance the thermal performance of TES systems, and the application of TES systems in multiple fields with various PCMs. A thorough literature review has been conducted based on the topics connected to the current research work.

2.1. Mechanism of PCMs based TES system

One of the most efficient energy storage methods is the thermal energy storage system. TES system stored or released thermal energy in phase change materials during the melting or solidification process. According to the classification of PCMs, researchers worked on organic, inorganic, and eutectic PCMs-based TES systems. Organic PCMs such as paraffin wax and fatty acids are most suiTable for latent heat storage purposes based on their stability in melting temperature and latent heat of fusion.

(Hasan and Sayigh, 1994) were studied myristic acid, palmitic acid, and stearic acid-based TES systems. It observed a 10% reduction in the heat of fusion after 450 thermal cycles and 10% volumetric expansion from room temperature to 80^{o}C. (Gasanaliev and Gamataeva, 2000) examined the heat-accumulating properties of melts (HAM). It generalized that melts are the most popular heat accumulators due to the heat capacity of solid/liquid or the latent heat of fusion and chemical reactions as thermal heat storage. Ionic compounds, alkali and alkaline-earth metal fluorides, chlorides, carbonates, and sulfates have the best thermal properties based on the accumulation of high-potential thermal energy. However, salt eutectics use the most energy due to melting enthalpy. But, given the high cost of the HAM, the main disadvantage of this type of material is the high cost of collected energy.

(Shukla et al., 2008) thermal cycle tests checked the thermal stability of some organic and inorganic PCMs in the TES systems. The heat of fusion and the melting temperature of PCMs were investigated through DSC. They observed that selected inorganic (Sodium hydroxide, Di-sodium borate, Ferric nitrate, Barium hydroxide) were less useful in heat storage systems due to higher deviation in thermal stability after a few thermal cycles. However, the inorganic PCMs, i.e., paraffin wax with a melting temperature of 54°C and latent heat of 184kJ/kg, were the most useful PCM in the TES system. After the 1500th thermal cycle, it has been revealed that there is a minor variation in latent heat (up to 18kJ/kg) and melting temperature (up to 3°C). Erythritol has a high energy density, posing a potential PCM for storing thermal energy at higher temperatures. (Putri et al.,2016) coconut oil as a PCM and found that the latent phase of coconut oil, which is linked to the solid-liquid phase transition, has the most significant heat absorption capacity. (Irsyad and Harmen, 2016) worked on a coconut oil PCM-based TES system. It observed with an air velocity of 1-1.5 m/s and a temperature of 30-33°C, heat transfer by forced convection on the PCM container surface can lower the ambient temperature by 0.82- 1.29°C. (Sharma et al., 2016) studied experimentally on organic PCMs thermal and chemical reliability for 1500 thermal cycles. During thermal cycles, the DSC and FT-IR tests were conducted for thermal stability and chemical stability. From the DSC test, the charging temperature and latent heat of fusion of organic PCMs very gradually after specific thermal cycles. Fatty acid organic PCMs show more minor variation in melting temperature and latent heat of fusion than paraffin wax. Also, the FT-IR spectra test confirmed that the chemical compositional and the functional groups were not altered. All experimental results show that organic PCMs possess good thermal reliability in melting temperature, the latent heat of fusion, and chemical stability during thermal cycle testing. (Aydın and Toprakçı, 2021) observed that suberic acid PCMs had melting enthalpy higher than 195kJ/kg with single-phase change also, no supercooling and insignificant changes in thermal properties 1000^{th} after thermal cycling.

Some researchers worked on the TES systems with inorganic PCMs. They found significant problems in inorganic PCMs-based TES systems such as under-cooling, phase separation, less compatibility with vessel materials, and corrosion effects were also seen in systems. Table B.1 shows the finding of the inorganic PCM-based TES system.

To improve the properties of inorganic PCMs, people worked on eutectic PCMs. Eutectic PCMs are the combination of two or more PCMs. (Hadjieva et al., 1992) found no significant changes in thermo-physical properties after 900 thermal cycles of operation by the composition of $C_{22}.2H_{44}$, $C_{23}.2H_{40}$, and $C_{24}.7H_{51}$ in weight ratio 1:4:3. Results revealed that the structure of the paraffin tested shows no signs of deterioration during thermal cycling. (Bajnóczy et al., 2007) observed the heat capacity of two grade phase change material (211.4 and 166.6 mol $CaCl_2$/1000 mol H_2O) based TES system. The temperature interval accumulation and theoretical storage capacity of two grade PCM-based TES systems were extended by 60^oC-12^oC and 374kJ/dm^3. This TES system was used to store solar energy, and the stored energy will be used to warm the water input of the home hot water delivery system. (Cabeza et al., 2005) informed that anti-corrosion properties are one of the aspects before selecting PCMs in any application. Due to the lack of commercial PCMs between melting temperatures from 5^oC to 29^oC, $CaCl_2.6H_2O$ and $MgCl_2.6H_2O$ mixed in 2:1wt% and obtained a new PCM with a melting temperature around 23^oC. This eutectic PCM conducted a corrosion test over five different materials such as aluminum, brass, copper, steel, and stainless steel. They investigated the maximum corrosion rate obtained in aluminum and steel metals. The eutectic PCM was recommended only for brass, copper, and stainless steel.

(Liu et al., 2015) were compared carbonate salts (Na_2CO_3, K_2CO_3, and Li_2CO_3) and chloride salts (NaCl, $MgCl_2$, and KCl) based on eutectic PCMs, and the results revealed that the degrees of supercooling of carbonate salts are much higher than that of chloride salts. The demerits of sub-cooling in chloride PCMs are almost non-existent. One carbonate PCM and chloride PCM were recommended as potential latent heat storage materials. (Jiang et al.,2016) were observed that the composition of Na_2CO_3–NaCl by 59.45:40.55 weight ratio, the improved melting-freezing temperature, melting-solidifying latent heat, and were 637.0°C - 626.9°C and 283.3J/g - 252.8J/g, respectively. Also, the specific heat was enhanced from 0.96J/g-K to 1.3J/g-K between temperature variations of 100°C to 450°C. Using the Temperature-History approach, (Gunasekara et al., 2016) studied the properties of some selected polyols, Erythritol, Xylitol, and Polyethylene glycol (PEG) 10,000. Erythritol showed variable melting temperatures during different cycles and posed a subcooling of 18.5ºC. Thermodynamic characteristics of Xylitol would alter between 0 and 113ºC. After a few heating/cooling cycles, the oxidation process is also visible in Xylitol and Erythritol. Whereas there was no subcooling, no glass transition, and thermally triggered oxidation in PEG 10,000. In contrast, PEG 10,000 has a significantly simpler phase change, predicting greater longevity in a genuine TES system. However, the reduced enthalpy of fusion and hysteresis it exhibits must be taken into account when evaluating it as a PCM. (Jiang et al., 2017) also worked on the composition of Na_2CO_3–$Li_2CO_3$by 58:42 weight ratio. It has founded that the melting/solidification of the eutectic Na_2CO_3-Li_2CO_3 salt was 498.3 0.1°C/483.9 0.1°C, respectively—also, the fusion heat is 330.8 ± 0.6 J/g, while the solidification heat is 329.2 ± 0.3 J/g. According to the thermal decomposition, the investigation found that the eutectic molten salt has good thermal stability in a CO_2 environment without weight loss at temperatures up to 600°C.

(Liu and Yang, 2017) had studied the composition of $Na_2CO_3 \cdot 10H_2O$ and $Na_2HPO_4 \cdot 12H_2O$ by 40:60 weight ratio and found phase change temperature, supercooling degree, and latent heat are 27.3°C, 3.6°C, and 220.2J/g, respectively. Furthermore, SEM and XRD studies show that in the eutectic hydrated salt, $Na_2CO_3 10H_2O$ and $Na_2HPO_4 12H_2O$ interact, resulting in crystal morphological changes. In terms of phase change temperature, results reveal that the eutectic hydrate salt is a good PCM for comfort applications in buildings. (Liu and Yang, 2017) also studied the composition of $Na_2SO_4 \cdot 10H_2O$ and $Na_2HPO_4 \cdot 12H_2O$ by 25:75 weight ratio and obtained the supercooling degree eutectic hydrated salt was 7.8°C. The melting temperature of eutectic hydrated salt was 31.2 °C, and the latent heat was 280.1 J/g. In terms of application, phase separation, supercooling, and poor thermal conductivity of hydrated salts, PCMs are critical drawbacks of the TES system. (Li et al., 2017) attempted to address these issues by including additives and a supporting matrix. In this study, Sodium acetate trihydrate (SAT) was used as PCM in the TES system for domestic hot water storage and building heating. The phase separation and supercooling, i.e., the overcoming selected PCMs, were reduced by adding nucleating and thickening agents (i.e., disodium hydrogen phosphate dodecahydrate and Carboxyl methylcellulose, respectively). However, the low thermal conductivity was improved by copper form-based modified PCM. They found that the modified SAT has good thermal stability, and its supercooling degree is lower than 3°C after 20 cycling tests. The latent heat of fusion and melting temperature of the modified SAT were obtained at 258J/g and 57–58°C, respectively. The charging and discharging time were reduced by 40% due to improved thermal conductivity (11 times higher than pure SAT) in copper foam/SAT composite PCM.

(Kumar et al., 2017) used a binary composition of 1-Dodecanol, lauric acid, myristic acid, and palmitic acid to create novel eutectic fatty acid PCMs. DSC test reported that the fusion's melting temperature and heat for lauric acid - dodecanol, myristic acid - dodecanol, and palmitic acid - dodecanol binary composites were 17, 18.43 20.08ºC and 175.3, 180.8, 191kJ/kg, respectively. This research shows that by mixing two or more fatty acid PCMs, new eutectic fatty acid PCMs with low melting temperatures could be formed. These studies sparked the concept of designing and developing accepTable melting temperatures and a large latent heat of fusion for use in various latent heat thermal energy storage systems. (Shen et al., 2017) worked on lauric acid/modified sepiolite composite, were prepared vacuum impregnation method. They investigated that the corresponding latent heats of the composite PCMs were 125.2J/g at 42.5°C melting temperatures and 113.9J/g at 41.3°C freezing temperatures, respectively. The higher latent heat could be attributed to the modified sepiolite's better microstructure. For the composite PCMs, thermal conductivity (0.59 W/mk) was also higher than lauric acid. The composite PCMs, on the other hand, showed chemical and thermal stability after 200 thermal cycle testing. (Gunasekara et al., 2017) studied on the fatty acids linoleic, palmitic, oleic, margaric, and stearic, at 84.51, 33.05, 1327.23, 5.76, 89.48, and 1540.03 in µg/ml oil, were considered to be present in olive oil. It concluded that erythritol could be a cost-effective and long-lasting PCM for low-temperature heating applications. Due to their very glassy properties, glycerol or erythritol-glycerol blends are doubtful as PCMs. Olive oil possesses appealing phase change temperatures and enthalpies. Thus, it can function as a long-term PCM for cooling applications after being refined into a more appropriate composition. Furthermore, a simplified cost analysis of high-purity erythritol manufacturing with glycerol shows potential cost savings of up to 130-1820 times lower than current laboratory-grade pricing.

The composition of myristic acid and stearic acid with a 30:70 weight ratio (Atinafu et al., 2018) investigated the new value of phase change enthalpy and the melting temperature 187.54kJ/kg and 49.83°C, respectively. However, Mesoporous N-doped carbons in the myristic acid and stearic acid composite materials increased the thermal conductivity, energy storage density, and shape stability due to porous carbons' interfacial contact area, intermolecular interaction between porous carbons and PCM. As a result, applying these simple methodologies will open up new possibilities for designing shape-stabilized composite PCMs.(Kahwaji and White, 2018) also predicted the thermo-physical properties of eutectic fatty acid PCMs using a computational technique. Decanoic – tetradecanoic acids and dodecanoic – tetradecanoic acids are the composite materials. Decanoic - tetradecanoic acids (with a mass fraction of 0.82 of decanoic) have melting temperatures and heat of fusion of 24.9^{o}C and 155J/g, respectively. The melting temperature and fusion heat of dodecanoic–tetradecanoic acids (with a mass fraction of 0.71 dodecanoic) were 33.9^{o}C and 182J/g, respectively. Decanoic, dodecanoic, and tetradecanoic fatty PCMs have melting temperatures of 31.6^{o}C, 44^{o}C, and 54.4^{o}C, respectively. As a result, the required operating temperature of a fatty acid PCMs-based TES system may be obtained by adding fatty acid PCMs of varying melting temperatures. (Karim et al., 2018) investigated high melting temperature-based metal and metal alloy PCM for the TES system. They demonstrated that metal alloys (based on Cu, Al, Mg, and Si) posed high thermal conductivity, one of the critical advantages of PCMs. It may reduce the heat exchanger area, which directly impacts the final cost of a heat exchanger. The composition of lauric acid - myristyl alcohol with 40:60 weight ratios (Chinnasamy and Appukuttan, 2019) investigated that up to 1000th thermal cycles, the composite PCM was sTable . Also, after the 1000th thermal cycle, the variation in the melting point and corresponding latent heat were in an accepTable range. Furthermore, the thermogravimetric findings indicated that created eutectic PCM degrades at 165°C, higher than the application temperature. The results of corrosion tests using building materials including Cu, Al, and stainless steel were also seen, along with the essential advice for employing it in real-time applications. The unique eutectic PCM produced has a lot of promise for use in interior thermal comfort applications.

These are the literature survey that has been done for organic, inorganic, and eutectic PCMs-based TES system.

2.2. Technique to enhance the thermal performance of the TES system

Thermal energy storage and thermal energy devices could benefit from phase change materials. However, their charging and discharging rates are retarded by their low thermal conductivity. From the literature survey, it has been observed that the significant weakness of PCM is the thermo-physical properties of PCMs. Researchers are working on additives-based PCM with better thermal properties, including faster charging and discharging times, reduced supercooling issues, and improved latent heat. Also, people found several good techniques to overcome the problem of PCM based TES systems:

2.2.1. Foam-based PCMs in the TES system

The impacts of metal foams on heat transfer enhancement in Phase Change Materials were computationally studied by (Tian and Zhao, 2011) using a 2D and non-equilibrium heat transfer model. Experimental evidence also backed up the numerical results. Here is a piece of rectangular copper foam embedded in paraffin wax RT58. It was observed that utilizing metal foams in PCM enhances heat conduction rate due to high thermal conductivities. Heat conduction and natural convection are considered during phase transition, although natural convection is inhibited due to the increased flow resistance in metal foams. When comparing samples with metal foams embedded in PCM to samples with pure PCM, it was discovered that the inclusion of metal foams might significantly improve PCM heat transfer performance (10 times) by successfully transmitting heat from the metal skeleton to the PCM. The simulation findings also showed that metal foams with smaller pore sizes and porosities perform better in heat transmission than larger ones.

(Karthik et al., 2015) prepared graphite foam-based erythritol as a sTable composite phase change material by applying an incipient wetness impregnation method. In this method, graphite form was added with melted erythritol, and after infiltration, the foam piece was removed and allowed to cool down. The excess erythritol was removed. The thermal conductivity of the composite form was improved by five-time than pure erythritol, which reduced the charging and discharging times of the TES system as XRD analysis found long-term stability at 120^{o}C for one month. Also, from the DSC experiment, the subcooling behavior of erythritol was reduced. They concluded that the melting temperature and enthalpy are not affected by adding the graphite matrix to the erythritol. Overall, the erythritol–graphite foam composite PCM could be considered a reliable material for various TES applications.

(Cheiw et al., 2017) applied void spaces of air in phase change material to enhance the thermal storage capacity of the TES system. It compared two models, with a 20% air space and without air space in a constant PCM volume. The thermal image taken with the thermal camera increases faster than without air void space in the PCM-based TES system. It indicates that the void space exhibited properties similar to a sensible heat storage system rather than the latent heat storage of system constant temperature features. Also, because of the reduced surface to surface contact between the PCM and the heat source, the heat storage capacity of a PCM-based TES system was reduced. (Zheng et al., 2018) used copper foam to enhance the thermal performance of the paraffin. The total melting time of the copper foam composite PCM (CPCM) was 20.5% less than that of pure paraffin. The CPCM heated at the top melted the slowest and attained the most incredible temperature differential in the three heating conditions, indicating that natural convection impacted the CPCM melting process. (Wu et al., 2019) studied castor oil-based polyurethane-acrylate oligomer (COPUA) foam-based palmitic acid (P.A.) and obtained a 141.2J/g value of phase change enthalpy. Diatomite foam-based capric acid PCM was studied by (Liu et al. 2020) and found the improved value of melting point and latent heat of fusion were 34.9^{o}C and 89.2J/g, respectively. (Tiari and Mahdav, 2020) improved the entire charging process from 2860 s to 880 s using Copper foam-based potassium nitrate (KNO_3).

2.2.2. Nano additives based PCMs in TES system

By mixing nanoparticles with high heat conductivity in the PCM, the rate of discharging and charging of the LHS can be increased. This technology improves the energy storage of systems' effective thermal conductivity and reduces the charging and discharging times. When making the nano-enhanced PCM, homogeneous dispersion and prolonged stability of the nanoparticles, and low or no aggregation of the nanoparticles in the PCMs should all be considered. The single-step and two-step are two methods for the preparation of the NEPCM. Nanomaterials are produced and dispersed continuously based on PCM in the one-step method.

In contrast, nanomaterials are prepared first and then dispersed into the base PCMs in the two-step method. Nanoparticles are first produced in dried powder form employing multiple chemical and mechanical procedures such as the sol-gel method, ball milling technology, and chemical reduction in the two-step method. The generated nanoparticle powder was then mixed with the base PCM. Several techniques such as high shear mixing, ultrasonic bath, and magnetic stirring are adopted to ensure that the particles are evenly dispersed. Table B.2 shows the finding of researchers by applying nano additives in PCM-based TES systems.

Also, using a single wall or multiwall carbon nanotubes (SWCNT/MWCNT) in the PCM improved the thermal physical properties of the PCM, which improved the thermal performance of the TES system. Researchers' findings using SWCNT/MWCNT in a PCM-based TES system are shown in Table B.3.

According to the findings, the thermo-physical properties increased at nano additives' constant volume fraction/mass fraction.

2.2.3. Improvement in TES system design

This section includes data and conclusions about TES shape, operating settings, heat transfer improvement designs, and experimental setups often used by other researchers. With the improvement in the design of the TES system, the thermal performance has been enhanced. Fins or extended surfaces, microencapsulation of PCM, and position and type of shell of TES system play essential roles in improving thermal performance. Also, packed bed and tube bundles arrangement-based TES systems are used in several applications.

(Choi and Kim, 1994) have done a comparative study on heat-transfer characteristics of circular finned-and unfinned-tube TES systems. Results revealed that the volume of melted PCM in the 5-finned-tube system is 25% greater than in the unfinned-tube system. (Sari and Kaygusuz, 2001) used a container filled with stearic acid as a TES system and a tube as a heat exchanger. Stearic acid is a valuable PCM for energy storage in various applications because of its appropriate melting point and fusion heat. Temperature sensor points were positioned radially and axially. The temperature of heated water (74–81ºC) circulated in a tube at a mass flow rate of 1.2–6.0kg/min to transfer heat to the PCM container, and the temperature was measured every 5 minutes.

After melting, low-temperature water (34-45.5^{o}C) was pumped through the tube at a mass flow rate of 1.2–6.0 kg/min to transfer heat from the PCM container. It calculated the charging and discharging times and the heat transfer rate from water to PCM and PCM to water. The behavior of stearic acid in phase transition was studied independently in two locations in the PCM container: horizontal and vertical. In addition to conduction and forced convection heat transfer, natural convection was shown to significantly impact heat transfer from the tube to the container at the melting layer section. In addition, when the heat exchanger tube is horizontal, the PCM has more effective and consistent phase change properties than when it is vertical. (Jilani et al., 2002) were numerically studied the ratio of the length and diameter of the TES system and found that at the ratio of 0.1, the radial temperature distribution in the TES system is maximum. A theoretical study has been done on several fin parameters, such as fin spacing and fin diameter in the finned tube TES system (Erek et al., 2005). They conclude that the stored energy was increased with increasing fin radius and decreasing fin space. (Agyenim et al., 2009) were done a comparative study on the thermal performance of circular finned and longitudinal finned-based TES systems. Results revealed that the longitudinal finned system achieved the best thermal performance than the circular finned-based TES system with insignificant subcooling during discharge. (Al-Abidi et al., 2013) worked on internal and external fin heat transfer enhancement techniques for TES systems in triplex tube heat exchangers. It found that the melting time of the PCM decreases by using triplex tube heat exchangers with internal and external fins and the increment length and thickness of fins. (Zhao and Tan, 2015) were optimized the fin height in a finned-based TES system. They concluded that the system effectiveness was generally 0.5 higher than without a finned-based TES system. (Yuan et al., 2016) studied the installation angle of fins. It observed that melting characteristics of TES system optimum at 0^o of installation angle of fins. (Seddegh et al.,

2016) were compared to the thermal behavior of a horizontal and vertical shell-and-tube TES system. They found that heat transfer effectiveness in the vertical unit is almost constant during the entire charging process, but it is not seen in the horizontal unit. (Xiong et al., 2017) done a comparative study on U-tube and single tube-based TES systems. The U-tube system reduced the total charging time by 25% with the same heat transfer area and boundary conditions. (Alshara, 2018) has done a numerical study on the diameter ratio of concentric tube type TES system. The small diameter ratio is best at a constant PCM volume because it gives a faster melting rate for PCM. (Seddegh et al. 2018) studied the heat transfer between cylindrical and conical vertical shell-and-tube TES systems. Results revealed that the conical system could store thermal energy much 12% faster than the cylindrical system at the same operating condition. (Park et al., 2019) researched the flexible elliptical PCM container-based TES system and investigated that at an axis ratio (A.R.) range of 0.05–0.20, the enhancement rate was increased by 1.1–2.7 times of the TES system. (Demirkıran and Cetkin, 2021) Compared eccentric two tubes with rectangular shells and concentric tubes with circular shells. They found the melting time and sensible energy in eccentric two tubes with the rectangular surface decreased compared to the concentric tubes with the circular shell.

The application bases, researchers were studied on tube bundles arrangement type TES system. There is two tubes arrangement: inline and staggered tube bundles. Table B.4 shows the finding of the tube bundles arrangement type TES system.

2.3. Mythology of TES system in waste heat recovery

Techniques for converting waste energy (from power plants, IC engines, chemical, and industrial sectors) into useable energy are essential for meeting energy demand. (Mangarella et al., 2017) observed that the fluctuating temperature of flue gases and corrosion due to high temperature reduced the efficiency of the plant. It proposed a solution that increases total energy efficiency using a PCM-based refractory brick. It allowed the additional superheaters in the combustion chamber to raise the temperature of the superheated steam without causing corrosion. Furthermore, the study emphasizes the life cycle assessment of methodology capacity as a tool for comprehensively evaluating plant environmental performance. Table B.5 shows the application of the TES system in waste heat recovery.

Researchers have integrated the TES systems with an IC engine to recover waste heat with strong stability during large thermal cycles and suiTable working temperature ranges of organic PCMs. A heat exchanger-based TES system with spherical PCM (paraffin) capsules was designed and fabricated (Subramanian et al., 2004). The system was coupled to a 3.5kW capacity of the IC engine, and its performance was evaluated. It has been revealed that 15% of the fuel energy was stored in the TES system. They concluded the total stored energy at a full load of an engine of the system was 3060kJ at 85ºC and 60% of the total stored energy stored in the PCM. (Pandiyarajan et al., 2011) tested the thermal performance of a shell and finned tube heat exchanger with cylindrical paraffin wax PCM capsules type TES system integrated with 7.5kW capacity of IC engine at exhaust gas side. At castor oil as heat transfer fluid with 86ºC rise of temperature, the total energy stored in the TES system was 19,500 kJ, with 67.2% energy stored in PCM. They found that the charging efficiency and saving percentage increase as the load increases. Also, it suggested the application of stored energy, as improved emission, wind shielded clearing and warm-up performance, cabin heating, and fuel economy in automobile vehicles.

(Gopal et al., 2010) coupled exhaust heat exchanger with 10.3kW rated four-stroke diesel engine. The exhaust heat exchanger consists of a horizontal and elliptical shape heater core wounded by a copper tube across the length. For additional increment in heat surface, lathe scrap was used. Water acts as a heat transfer fluid, extracting waste heat from the engine's exhaust gas. The results showed that fuel's total energy and chemical availability were saved by 6.13% and 0.47%, respectively. Also, the energy and exergy efficiency of the integrated system varied between 3.19% to 34.15% and 0.25% to 27.41%, respectively, at 0-85% of engine load. (Pandiyarajan et al., 2010) recovered nearly 10% to 15% of the total heat by using a heat exchanger having 99% effectiveness. It has extracted maximum heat of around 3.6kW. They found that charging rate and efficiency varied from 245 to 85min. and 98.13% to 99.34%, respectively. (Raja et al., 2014) was designed and manufactured a thermal energy storage (TES) tank with paraffin and ethylene glycol as phase change material (PCM). It looked into how waste heat from diesel engine exhaust may be recovered using a heat recovery system that included a compact shell and tube heat exchanger. Castor oil is employed as a heat transfer fluid (HTF) on the tube side to remove heat from the exhaust gas. Those (paraffin wax/E.G.) two-phase change materials are used to evaluate the cascading technique of heat recovery. Heat is recovered during phase shift material's endothermic and exothermic processes. This cascaded thermal storage system recovers around 14 percent of waste heat from diesel engine exhaust.

(Kiran and Reddy, 2015) designed and fabricated a TES system integrated with a 50kW capacity diesel engine. The exhaust gas flow pipe was inserted in the cylindrical tank-type TES system, and the gas pipe was fixed at both ends. PCM (paraffin wax/stearic acid) was filled into the gap between the outer cylindrical tank and the exhaust gas flow pipe. Also, fins were located at the gas flow pipe surface to increase the heat transfer rate in PCM. It evaluated the performance parameters such as charging and discharging time, the effect of water flow rate, energy saved, and percentage of energy saved. It observed that percentage of energy saved through stearic acid is 6% higher than paraffin wax. The conserved energy was utilized to heat 250 liters of water from 36 to 43 degrees Celsius at a flow rate of 2 liters per minute. (Rajagopal and Natarajan, 2015) Revealed that 6 to 7% of the energy in exhaust heat may be captured and stored in the TES tank. However, the heat extraction rate may be enhanced by applying forced circulation and increasing the mass of water circulation.It's also been recommended that increasing the surface area of contact of the heat recovery heat exchanger and adequately insulating the thermal storage tank will improve the percentage of heat recovered and charging efficiency. The shell and tube heat exchanger and thermal energy storage system used in the study featured paraffin phase change material (Prabhu and Asokan, 2015) with a diesel engine system to extract heat from the exhaust gas. Under various loading conditions, the performance of the heat exchanger and thermal storage tank was evaluated. About 86.45kJ/kg of heat energy is extracted from the heat exchanger at full load, and 0.54kW of heat energy is conserved. However, a 7% of fuel power is stored as heat in the storage system, and the water may be used for suiTable applications that are available at a reasonable temperature.

(Park et al., 2017) focused on waste heat recovery through engine cooling. They built a heat storage system filled with stearic acid as PCM. This proposed PCM-based heat storage system recovered 30% of the heat energy lost through the coolant. They observed that the heat storage system was charged at 95ºC and 70ºC, and the time of the coolant to warm up was decreased by 27.9% and 18.3%, respectively. It also found that fuel consumption was reduced by 18.1% and 27.1% at 95ºC and 70ºC temperatures in the heat storage system. For LHTES applications, three pure fatty acids (capric, myristic, and palmitic acids), as well as two fatty acid-based eutectic combinations (capric/myristic acids, capric/palmitic acids), were completely described by (Duquesne et al., 2021). The tested fatty acids and mixtures have relatively low thermal conductivities but are slightly higher than those of paraffin. Also, the energy storage was between 34.15kWh/m^3 and 49.93kWh/m^3, similar to paraffin waxes commonly used in storage systems.

2.4. Highlights

Based on the literature review, organic PCMs such as paraffin wax, lauric acid, stearic acid, and others were found to be the most suited for latent heat storage due to their melting temperature and latent heat of fusion stability. Undercooling and phase separation are two significant issues with inorganic hydrated PCMs. In addition, the thermal capacity of pure salts quickly degraded from its base value. On the other hand, under-cooling cannot be removed; it can only be minimized as much as possible to prepare eutectic PCMs. In the case of metal PCM, there is a lack of information on the metallurgical implications of melting and solidifying these materials during thermal cycling at high temperatures. The key factors to consider are vapor pressure, undercooling, corrosion, segregation, changes in composition and microstructure, thermal characteristics, and unwanted reactions. Most metal alloys require heat treatment to achieve the correct microstructure.

Furthermore, significant volume fluctuations during melting can encourage the creation of voids during solidification. There may be unfavorable reactions with the container, coil, and pipes if the metal is in liquid form. To overcome of heat transfer rate, extended surfaces such as the attachment of fins increase the effective thermal conductivity and decrease the charging and discharging periods of the energy storage system. For space heating purposes, the heat transfer rate from the TES system was improved by implementing tube bundles arrangements. The PCMs used in TES systems have poor thermal conductivity by default. Still, they can reach a high thermal conductivity benefit by adding nanoparticles, single wall and multiwall carbon nanotubes, and preparation of foam-based PCMs. TES systems are applicable in various applications like the solar water heater, solar cooker, greenhouse, waste heat recovery, transportation of medicines and blood, cooling of electronic instruments and electrical engines, air-conditioning in houses/buildings, and thermal protection of food, beverages, coffee, wine, milk products.

2.5. Research gap

Based on the above concluding observations, the research gaps are identified. To overcome it, additional research is required:

- A little work has been done on organic PCMs and nano-additives in the TES system.
- Also, a little work has been done on MWCNT based organic PCMs type TES system.
- Furthermore, little work has been done on integrating the TES system with the IC engine.
- A little work has been done on tube bundles-type TES systems.
- A little work has been done on applications of TES in-cabin heating and overcoming the cold start problem of vehicles.

To bridge these gaps, research is needed on various organic PCM-based TES systems integrated with IC engines for space heating applications. An experimental study is required on the compatibility of nanoparticles in organic PCMs for enhancement in the thermal performance in the TES system. Also, research requires the design and implementation of tube bundles-type TES systems. The next chapter deals with energy and exergy comparison of the TES system with the mass fraction of organic PCMs such as capric acid, lauric acid, paraffin wax, and stearic acid integrated with the IC engine.

2.6. The objective of the present work

The principal objective of the present research deals with the comparative study of various organic PCMs by the mass fraction in TES integrated with IC engine exhaust. The comparative analysis for the thermal performance of TES combined with IC engine with different vol. fractions of nano additives in organic PCMs. Also, it deals with the comparative study of thermo-physical properties of MWCNT-based organic PCMs based on the T-history method. Furthermore, theoretical and experimental analysis for in-line and staggered tube arrangement types TES system and their comparisons. Lastly, the evaluation of performance parameters using this in-line and staggered tube arrangement classifies the TES system for cabin heating purposes.

2.7. Structure of the Thesis

The present thesis has been broadly classified into seven chapters. **Chapter-1** deals with waste heat recovery through phase change material (PCM) based thermal energy storage (TES) systems in IC engine exhaust, concept and classification of TES systems, application of TES systems, idea and type of PCMs, and nano-enhanced PCMs, and selection criteria of PCMs/NEPCMs. The objectives of the research and the structure of the thesis are also presented. Also, **Chapter 2** presents an extensive review of the literature in the field of TES systems with various PCMs, the technique to enhance the thermal performance of TES systems, and the application of TES systems in space heating. At the end of the chapter, the highlights from the literature review and specific objectives of the present research are also summarized. However, in **Chapter 3**, the thermal performance comparisons of the TES system integrated with the IC engine based on energy and exergy analysis by variation of mass fraction in organic PCMs (capric acid, lauric acid, paraffin wax, and stearic acid) have been discussed.

Furthermore, in **Chapter 4,** PCMs/NEPCMs characteristics, comparative studies for the thermophysical properties of pure PCMs, and various nano additives-based PCMs have been investigated. The evaluation of optimum mass fraction and compatibility of nano additives in PCMs have been discussed. Furthermore, in this chapter, comparisons of the thermal performance of TESwith various nano additives-based PCMs have been addressed at the end of the chapter. **Chapter 5** deals with the thermophysical properties and thermal performance analysis of the MWCNT-based organic PCMs TES system using the T-History method. In **Chapter 6,** a tube bundles-based TES system has been designed and fabricated for ambient air heating. Furthermore, the thermal performance of tube bundles-based TES system integrated with IC engine has been discussed, which results in in-cabin heating by the variation of air velocity with various nano additives-based PCMs thermal energy storage. Lastly, in **Chapter 7,** the conclusion phase summarises the findings drawn from the present research work. Also, the scope for future work has been included at the end of this chapter.