CHAPTER 1

INTRODUCTION

1.1. General Background

Energy is essential to a country's social, economic, industrial, and innovative evolution. Although power has existed in numerous forms since the beginning of life, humankind has only recently discovered and modified its end-use applications. The rapid industrial and economic expansion in emerging countries has raised the energy in recent years. The primary issue for the engineering community is to narrow the gap between global energy demand and supply, which can be limited by using conventional (fossil fuel) power plants. However, after 1973, the non-conventional energy supplies oil crisis, rising energy prices, and rising carbon dioxide emissions. Generally, the non-conventional energy method is non-uniform, time-dependent, and expensive initial cost. TES systems based on PCMs are the real value - add to energy efficiency. Phase Change Materials (PCMs) can store and release enormous energy in a relatively small space. Maintaining a consistent temperature during the melting-solidification process has a wide range of technical applications. It may be utilized in several household and industrial applications as a waste heat recovery system. Thermochemical processes, sensible heat, and latent heat are all ways to store thermal energy. In energy-saving technologies, phase transition materials have become significant for energy storage. Furthermore, the use of TES systems results in a 30–50% reduction in energy usage.

1.2. Motivation for the Research

The automotive sector has led to a surge in recent years. In the last decade, the production of motor vehicles globally was 1,09,21,58,316 units (data provided by the International Organization of Motor Vehicle Manufacturers (OICA)). In terms of energy distribution, only around 35% of total fuel energy is converted into mechanical work in cars, utilized to drive the vehicle. However, the coolant in the engine cooling system absorbs 30% of the total energy input, and the exhaust fumes absorb another 35% (Fig.1.1). It represents that much fuel has been burned, and much CO_2 has been released into the atmosphere in the previous ten years. The thermal energy storage (TES) systems using PCMs/NEPCMs, which play a significant role in converting available energy and a green technology alternative, may optimize the energy lost in exhaust gases.

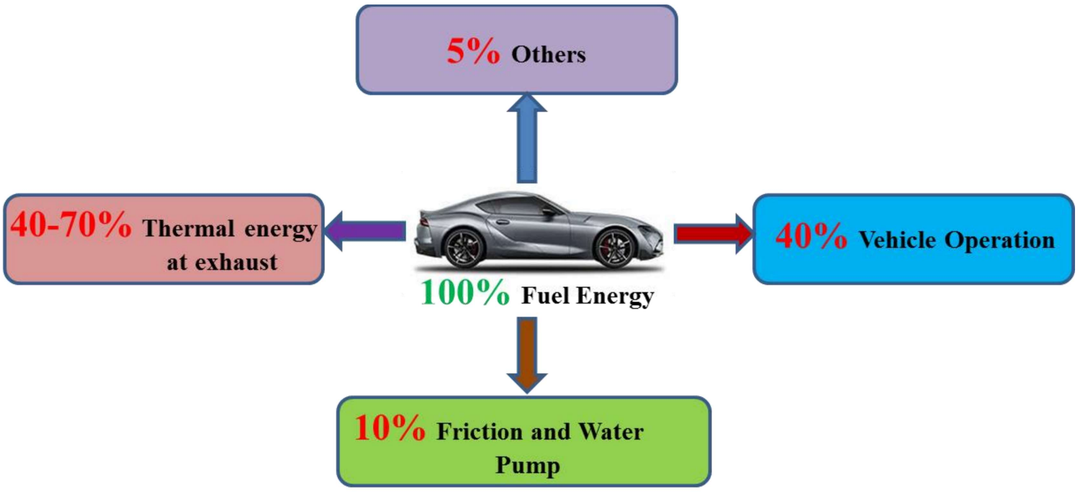

Fig.1.1. An internal combustion engine's typical energy distribution (Tie and Tan, 2013)

1.3. Thermal Energy Storage (TES) and its importance

Thermal energy storage (TES) is a technique for storing thermal energy by heating or cooling a storage medium, which may be used for heating, cooling, or power generation later. The heat is stored as sensible heat, latent heat of fusion (solid-liquid phase transition), or latent heat of evaporation in the storage medium (liquid-gas phase change).

The three major thermal energy storage system components are the storage medium, energy transfer mechanism, and control system. Thermal Energy Storage systems promise to improve the efficiency of energy conversion equipment and allow large-scale fuel replacements in the global economy. The TES systems enhance the efficiency of the relationship between energy supply and consumption, increasing the dependability and performance of energy systems. Using the TES in an energy system can reduce device size, improve economics, lower investment and operating costs, and less pollution of the environment, such as less carbon dioxide (CO_2) emissions.

1.3.1. Classification of Energy Storage

There are three types of thermal energy storage technologies: sensible heat storage (SHS), latent heat storage (LHS), and thermochemical storage.

1.3.1.1. Sensible Heat Storage (SHS)

The most frequent method for heat storage is sensible heat storage (SHS). It is the most basic and straightforward sort of heat storage technology. The heat exchanged by a system that does not change its phase but changes the temperature of a storage medium is known as sensible heat, and temperature changes in a linear relationship with the amount of heat stored. The heat transfer rate is affected by the material's specific heat capacity. The most commonly used storage materials in SHS are metals, ceramics, rocks, water, and oil.

1.3.1.2. Latent heat storage (LHS)

In this method, heat storage is the latent heat of materials. The heat exchanged by a system does not change the temperature of the storage medium but does change the phase (solid-liquid/liquid-gas) of the material in the system. The most frequently used for this purpose are organic PCM, such as waxes, fatty acids, and salts based on inorganic PCM. The heat transfer rate is affected by the thermal physical properties of the PCM.

1.3.1.3. Thermo Chemical Energy Storage (TCES)

TCES (thermochemical energy storage) has high energy density, exergetic efficiency, and operating temperature. A reversible chemical reaction is used to achieve thermochemical energy storage. Potential chemical energy is stored in the chemical bonds of the molecules participating in the charge/discharge cycle. High reaction enthalpy, quick reaction kinetics, high thermal conductivity, and strong cycle stability are desirable characteristics in thermochemical energy storage materials. Further, the thermal energy storage chart classification is shown in Fig.1.2.

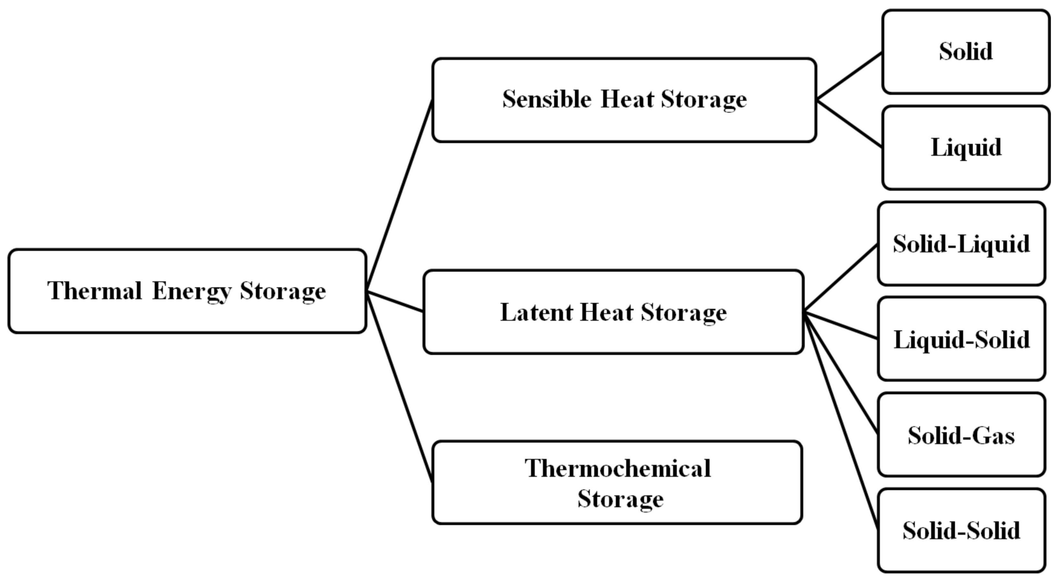

Fig.1.2. Classification chart of thermal energy storage (Faraj et al., 2020)

1.3.2. Application of various thermal energy storage

Potential applications of thermal energy storage are given as follows:

- Solar cooking and power plants.
- Air-Conditioning in houses/buildings.
- Cooling of electronic instruments and electrical engines.

- Transportation of medicines and blood.
- The human body is cooling under bulky clothing or costumes.
- Waste heat recovery.
- Off-peak power utilization: Heating hot water and Cooling.
- Heat pump systems.
- Smoothing exothermic temperature peaks in chemical reactions.
- Spacecraft thermal systems.
- Thermal comfort in vehicles.
- Thermal protection for food, beverages, coffee, wine, and milk products.
- Textiles are used in clothing.

1.4. Phase Change Materials (PCMs)

Phase change materials (PCMs) are those materials that can store or release large amounts of energy during the solid to liquid or liquid to solid phase change process. The phase change from solid to liquid is known as melting, and the phase change from liquid to solid is known as solidification. Phase change materials can store and release energy under isothermal conditions during melting and solidification. A wide range of Phase change materials have been found; such as paraffin waxes and non-paraffin organic PCMs, salt hydrates inorganic PCMs, and compounds organic-inorganic PCMs. Generally, the phase change materials used in latent heat thermal energy storage (LHTES)have several heating and cooling application requirements.

1.4.1. Merits of PCMs

The uses of PCM in TES systems have fruitful merits as follows:

- Chemically and thermally sTable in repeaTable operations.

- More minor changes in specific volume (up to 10%) during the phase change process.
- Availability of PCMs in the desired operating melting temperature.
- Non-toxic, non-flammable, and non-explosive.
- Fast nucleation, growth, and dissociation of a sTable nucleus during freezing/melting processes for a constant temperature.
- High latent heat of fusion.
- No degradation was found after a large number of freeze/melt cycles.
- Economic in rate and also readily available.

1.4.2. Demerits of PCMs

Also, there are some demerits of PCM based TES systems as follows:

- Subcooling (generally in inorganic PCMs).
- Low solid/liquid thermal conductivity.
- Corrosion (generally in inorganic PCMs).

1.5. Classification of PCMs

1.5.1. Organic Materials

Organic PCMs are based on pure paraffin, waxes, fatty acids, sugars, sugar alcohols, and carboxylic acid. The organic PCMs are more chemically sTable than inorganic PCMs.

1.5.1.1. Paraffin and Waxes

Primarily, studies have been done on paraffin and paraffin waxes as a PCM. It was applicable in various fields due to its availability over a wide range of melting temperatures, low or no sub-cooling problem, and non-corrosive. But the paraffin and paraffin waxes are generally flammable, having low latent heat and thermal conductivity.

Pure paraffin is formulated by C_nH_{2n+2} and is also known as n-alkanes. Paraffin wax is a combination of n-alkanes (>75 wt %) and other hydrocarbon molecules (<25 wt%). This combining technique allows the wax to be adjusted to a specific melting range while extending the phase transition breadth.

1.5.1.2. Fatty Acids

Fatty acids also have similar properties as paraffin (highly chemical sTable , low thermal conductivity, low latent heat, and significant melting range). The fatty acid is formulated by $CH_3(CH_2)_{(n-2)}COOH$. The source of fatty acids PCMs are vegeTable s and animal oil. Saturated fatty acids have minimal volume changes during the phase transition and little or no super-cooling during freezing. In addition, the fatty acids are mildly corrosive and more expansive than other PCMs. Blends of fatty acids and paraffin provide altered melting temperatures but at the cost of high latent heat loss. Alcohols, esters, and other fatty acid-containing compounds were investigated and shown to have a higher latent heat than their primary material.

1.5.1.3. Sugars and Sugar Alcohols

Sugars and sugar alcohols are high-temperature-based organic PCMs. Polyalcohol is another name for it. From the literature review, high-temperature PCMs are less applicable in the TES system. But the majority of sugars and sugar alcohols in the temperature range between 90ºC -200ºC are equally imported as paraffin and fatty acid organic PCMs in the TES system. Among sugar alcohols material, erythritol has attracted the most attention in the TES system due to its melting temperature and high latent heat. Many sugar alcohols, including erythritol, have been demonstrated to have a significantly higher degree of super-cooling than lower temperature organics, with re-solidification occurring at temperatures much below the melting point. Because of supercooling, these materials experience the usual 10–15% volume expansion on melting as organic materials face, and degradation has been observed at high temperatures.

1.5.1.4. Other Organic PCMs

In addition, some other materials such as carboxylic acid, clathrate hydrates, polymers, ketones, phenols, amines, and other organic materials with high volumetric latent heat values at temperatures up to 160ºC. There isn't a lot of information about TES with these PCMs. Some organic phase change materials with their thermophysical properties have been listed in Table A.1.

1.5.2. Inorganic Materials

1.5.2.1. Salt Hydrates

Salt hydrates, which are salt and water solutions that form a crystalline solid, are classified as inorganic materials. $M_xN_yH_2O$ is the formula for salt hydrates, where M denotes the salt molecule, and N represents the number of water molecules in a solid solution with the salt. The value of latent heat and thermal conductivity is higher in the case of salt hydrates-based PCMs than paraffin wax and other organic PCMs but relatively more costly. In addition, latent heat reduces over repeated phase change process, and many salt hydrates have been shown to exhibit significant supercooling. Both of these issues can be alleviated by adding additional material to the PCM mixture, such as excess water to minimize phase segregation, nucleating agents to reduce supercooling, and thickening agents to improve long-term phase change stability.

1.5.2.2. Fused/Molten salt-based PCMs

Molten salts depend on their primary state. These materials are limited as PCMs in TES systems due to high application temperatures, the corrosive character of molten salts, and observed melting expansions for various salts ranging from 1% to 30%.

Furthermore, molten salts' density and heat conductivity are significantly higher than most organic materials.

1.5.2.3. Metal-based PCMs

Metals and metal alloys, which have a high storage density per volume and a significantly more excellent heat conductivity, have received less attention. Vapour pressure, undercooling, corrosion, segregation, changes in composition and microstructure, changes in thermal characteristics, and unwanted reactions are disadvantages of metals-based PCMs. Furthermore, some inorganic PCMs with their thermo-physical properties have been listed in Table A.2.

1.5.3. Eutectics Materials

A eutectic mixture of two or more PCMs at a particular proportion, each of which melts and freezes congruently during crystallization, creating a combination of the component crystals. Inorganic eutectics and organic eutectics are the two types of eutectics. Eutectics can be utilized for excellent and passive solar storage with low or medium-temperature applications and solar collectors, depending on their melting point. Some eutectics PCMs with their thermophysical properties have been listed in Table A.3.

1.6. Nano-enhanced phase change materials (NEPCMs)

The product created by mixing nanoparticles with PCM is called nanoparticle-enhanced phase change materials (NEPCMs). Nanoparticles are added as an additive to improve the thermal characteristics. Nanoparticles are classified as organics, inorganics, and hybrid, as shown in Fig.1.3.In thermal energy storage, the addition of nanoparticles to PCM has shown significant potential. Different chemical and mechanical techniques, such as the sol-gel method, ball milling, and chemical reduction, create nanoparticles in dry powder form. The resulting nanoparticle powder is next combined with the base PCM.

Several techniques such as high shear mixing, ultrasonic bath, and magnetic stirring ensure that the particles are evenly dispersed.

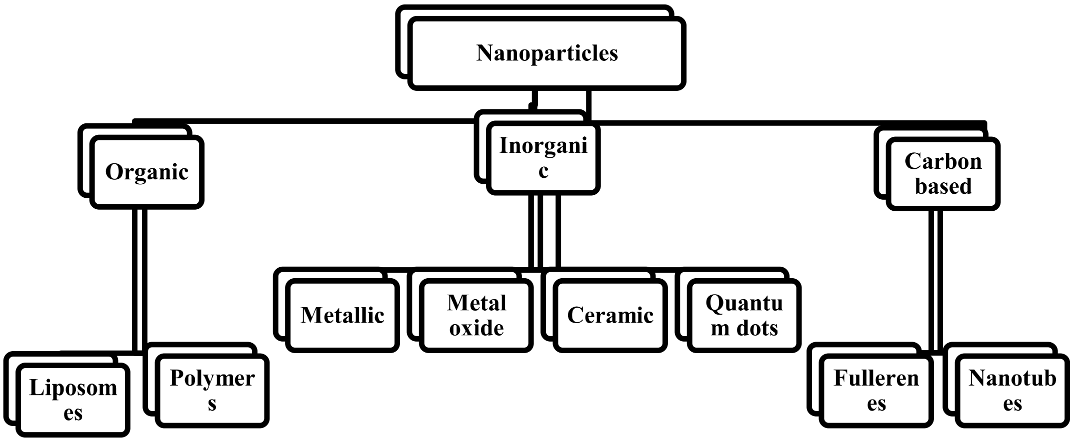

Fig.1.3. Classification chart of Nanoparticles (Bhatia and Saurabh,2016)

1.7. Classification of NEPCMs

Nano-enhanced phase change materials can be classified into organics and inorganics. Organic nano-enhanced phase change materials are also called polymer nanocomposites. Table A.4 lists a few published research articles on investigating the thermal behavior of NEPCMs using certain types of nanoparticles.

1.8. Classification of PCMs/ NEPCMs based on temperature

1.8.1. Low temperature PCMs/NEPCMs

The melting temperature range below 100°C is classified as low-temperature PCMs/NEPCMs. The paraffin and salt hydrates, a few clathrate hydrates, and other organics-based PCMs/NEPCMs are included in this group. However, the thermophysical properties of low-temperature PCMs are low. The combination of poor conductivity and low volumetric latent heat increases the size of the energy storage container and the difficulty of distributing heat across a greater volume, which might explain some less than the system performance of previous TES systems utilizing these materials. But after the addition of nanoparticles in PCMs, the melting temperature reduces from the original value due to enhancement in thermal conductivity. For vehicle applications, these are the best suiTable materials.

1.8.2. Medium temperature PCMs/NEPCMs

PCMs/NEPCMs with melting temperatures ranging from 100ºC to 200ºC are categorised as medium temperature PCMs/NEPCMs. The highest temperature paraffin, fatty acids, salt hydrates, sugar, sugar alcohol, and carboxylic acid-based PCMs are found. Sugar alcohol-based PCMs/NEPCMs showed the highest specific latent heat, high density, and highest specific latent heat in this temperature range. These materials are useful in mechanical EHR applications and electronic and thermoelectric devices.

1.8.3. High temperature PCMs/ NEPCMs

High-temperature PCMs/NEPCMs are defined as PCMs/NEPCMs having melting temperatures of more than 200ºC. Molten salts, metals, and metal alloys are found in this temperature range. Due to the high density, latent volumetric heats rise dramatically in this temperature range. These materials are highly useful in thermoelectric exhaust heat recovery applications, the TES systems for organic Rankine-based WHR systems, TEG, and catalytic converter WHR systems.

1.9. Selection criteria of PCMs/NEPCMs

The following qualities will be assessed while selecting the PCMs/NEPCMs for waste heat recovery via the TES system:

- The melting temperature is within the required working temperature range.
- Modest volume changes on phase transformation and slight vapor pressure at working temperatures are used to alleviate the confinement challenge.
- A high nucleation rate is used to avoid liquid phase supercooling.
- Thermal conductivity, density, and specific heat should be high.
- There is no deterioration after a significant number of freeze/melt cycles.

- Freeze/melt cycle that is entirely reversible.
- Materials should be non-flammable, non-toxic, non-explosive, and non-corrosiveness.
- Low in cost and readily available.

PCMs should be safe, eco-friendly, economical, durable, and do not have a limited working temperature range, according to the following selection criteria. PCMs that are non-corrosive can be stored in any sort of medium. PCMs with high thermophysical properties can store and release energy frequently. These parameters could meet the present research's desire for waste heat recovery via a TES system based on PCMs.